PHYSICAL SCIENCES
(Physics & Chemistry)

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CHAPTER-1

PHYSICAL WORLD

1.1 WHAT IS PHYSICS?

Humans have always been curious about the world around them. The night sky with its bright celestial objects has fascinated humans since time immemorial. The regular repetitions of the day and night, the annual cycle of seasons, the eclipses, the tides, the volcanoes, the rainbow have always been a source of wonder. The world has an astonishing variety of materials and a bewildering diversity of life and behaviour. The inquiring and imaginative human mind has responded to the wonder and awe of nature in different ways. One kind of response from the earliest times has been to observe the physical environment carefully, look for any meaningful patterns and relations in natural phenomena, and build and use new tools to interact with nature. This human endeavour led, in course of time, to modern science and technology.

The word **Science** originates from the Latin verb *Scientia* meaning 'to know'. The Sanskrit word *Vijnan* and the Arabic word *Ilm* convey similar meaning, namely 'knowledge'. Science, in a broad sense, is as old as human species. The early civilisations of Egypt, India, China, Greece, Mesopotamia and many others made vital contributions to its progress. From the sixteenth century onwards, great strides were made in science in Europe. By the middle of the twentieth century, science had become a truly international enterprise, with many cultures and countries contributing to its rapid growth.

.What is Science and what is the so-called **Scientific Method**? Science is a systematic attempt to understand natural phenomena in as much detail and depth as possible, and use the knowledge so gained to predict, modify and control phenomena. Science is exploring, experimenting and predicting from what we see around us. The curiosity to learn about the world, unravelling the secrets of nature is the first step towards the discovery of science. The scientific method involves several interconnected steps: Systematic observations, controlled experiments, qualitative and Quantitative reasoning, mathematical modelling, prediction and verification or falsification of theories. Speculation and conjecture also have a place in science; but ultimately, a scientific theory, to be acceptable, must be verified by relevant observations or experiments. There is much philosophical debate about the nature and method of science that we need not discuss here.

The interplay of theory and observation (or experiment) is basic to the progress of science. Science is ever dynamic. There is no ‘final’ theory in science and no unquestioned authority among scientists. As observations improve in detail and precision or experiments yield new results, theories must account for them, if necessary, by introducing modifications. Sometimes the modifications may not be drastic and may lie within the framework of existing theory. For example, when Johannes Kepler (1571-1630) examined the extensive data on planetary motion collected by Tycho Brahe (1546-1601), the planetary circular orbits in heliocentric theory (sun at the centre of the solar system) imagined by Nicolas Copernicus (1473–1543) had to be replaced by elliptical orbits to fit the data better. Occasionally, however, the existing theory is simply unable to explain new observations. This causes a major upheaval in science. In the beginning of the twentieth century, it was realized that Newtonian mechanics, till then a very successful theory, could not explain some of the most basic features of atomic phenomena. Similarly, the then accepted wave picture of light failed to explain the photoelectric effect properly. This led to the development of a radically new theory (*Quantum Mechanics*) to deal with atomic and molecular phenomena.

Just as a new experiment may suggest an alternative theoretical model, a theoretical advance may suggest what to look for in some experiments. The result of experiment of scattering of alpha particles by gold foil, in 1911 by Ernest Rutherford (1871–1937) established the nuclear model of the atom, which then became the basis of the quantum theory of hydrogen atom given in 1913 by Niels Bohr (1885–1962). On the other hand, the concept of antiparticle was first introduced theoretically by Paul Dirac (1902–1984) in 1930 and confirmed two years later by the experimental discovery of positron (antielectron) by Carl Anderson.

Its Sanskrit equivalent is *Bhautiki* that is used to refer to the study of the physical world. A precise definition of this discipline is neither possible nor necessary. We can broadly describe physics as a study of the basic laws of nature and their manifestation in different natural phenomena. The scope of physics is described briefly in the next section. Here we remark on two principal thrusts in physics: **unification** and **reduction**.

In Physics, we attempt to explain diverse physical phenomena ***in terms of a few concepts and laws***. The effort is to see the physical world as manifestation of some universal laws in different domains and conditions. For example, the same law of gravitation (given by Newton) describes the fall of an apple to the ground, the motion of the moon around the earth and the motion of planets around the sun. Similarly, the basic laws of electromagnetism

(Maxwell's equations) govern all electric and magnetic phenomena. The attempts to unify fundamental forces of nature (section 1.4) reflect this same quest for unification.

A related effort is to derive the properties of a bigger, more complex, system from the properties and interactions of its constituent simpler parts. This approach is called **reductionism** and is at the heart of physics. For example, the subject of thermodynamics, developed in the nineteenth century, deals with bulk systems in terms of macroscopic quantities such as temperature, internal energy, entropy, etc. Subsequently, the subjects of kinetic theory and statistical mechanics interpreted these quantities in terms of the properties of the molecular constituents of the bulk system. In particular, the temperature was seen to be related to the average kinetic energy of molecules of the system.

1.2 SCOPE AND EXCITEMENT OF PHYSICS

We can get some idea of the scope of physics by looking at its various sub-disciplines. Basically, there are two domains of interest: macroscopic and microscopic. The macroscopic domain includes phenomena at the laboratory, terrestrial and astronomical scales. The microscopic domain includes atomic, molecular and nuclearphenomena*. **Classical Physics** deals mainly with macroscopic phenomena and includes subjects like **Mechanics**, **Electrodynamics, Optics** and **Thermodynamics**. Mechanics founded on Newton's laws of motion and the law of gravitation is concerned with the motion (or equilibrium) of particles, rigid and deformable bodies, and general systems of particles. The propulsion of a rocket by a jet of ejecting gases, propagation of water waves or sound waves in air, the equilibrium of a bent rod under a load, etc., are problems of mechanics. Electrodynamics deals with electric and magnetic phenomena associated with charged and magnetic bodies. Its basic laws were given by Coulomb, Oersted, Ampere and Faraday, and encapsulated by Maxwell in his famous set of equations. The motion of a current-carrying conductor in a magnetic field, the response of a circuit to an ac voltage (signal), the working of an antenna, the propagation of radio waves in the ionosphere, etc., are problems of electrodynamics. Optics deals with the phenomena involving light.

* *Recently, the domain intermediate between the macroscopic and the microscopic (the so-called mesoscopic physics), dealing with a few tens or hundreds of atoms, has emerged as an exciting field of research.*

The working of telescopes and microscopes, colours exhibited by thin films, etc., are topics in optics. Thermodynamics, in contrast to mechanics, does not deal with the motion of bodies as a whole. Rather, it deals with systems in macroscopic equilibrium and is concerned with changes in internal energy, temperature, entropy, etc., of the system through external work and transfer of heat. The efficiency of heat engines and refrigerators, the direction of a physical or chemical process, etc., are problems of interest in thermodynamics.

The microscopic domain of physics deals with the constitution and structure of matter at the minute scales of atoms and nuclei (and even lower scales of length) and their interaction with different probes such as electrons, photons and other elementary particles. Classical physics is inadequate to handle this domain and Quantum Theory is currently accepted as the proper framework for explaining microscopic phenomena. Overall, the edifice of physics is beautiful and imposing and you will appreciate it more as you pursue the subject. You can now see that the scope of physics is truly vast. It covers a tremendous range of magnitude of physical quantities like length, mass, time, energy, etc. At one end, it studies phenomena at the very small scale of length (10^{-14} m or even less) involving electrons, protons, etc.; at the other end, it deals with astronomical phenomena at the scale of galaxies or even the entire universe whose extent is of the order of 10^{26} m. The two length scales differ by a factor of 10^{40} or even more. The range of time scales can be obtained by dividing the length scales by the speed of light: 10^{-22} s to 10^{18} s. The range of masses goes from, say, 10^{-30} kg (mass of an electron) to 10^{55} kg (mass of known observable universe). Terrestrial phenomena lie somewhere in the middle of this range.

Physics is exciting in many ways. To some people the excitement comes from the elegance and universality of its basic theories, from the fact that a few basic concepts and laws can explain phenomena covering a large range of magnitude of physical quantities. To some others, the challenge in carrying out imaginative new experiments to unlock the secrets of nature, to verify or refute theories, is thrilling. Applied physics is equally demanding. Application and exploitation of physical laws to make useful devices is the most interesting and exciting part and requires great ingenuity and persistence of effort.

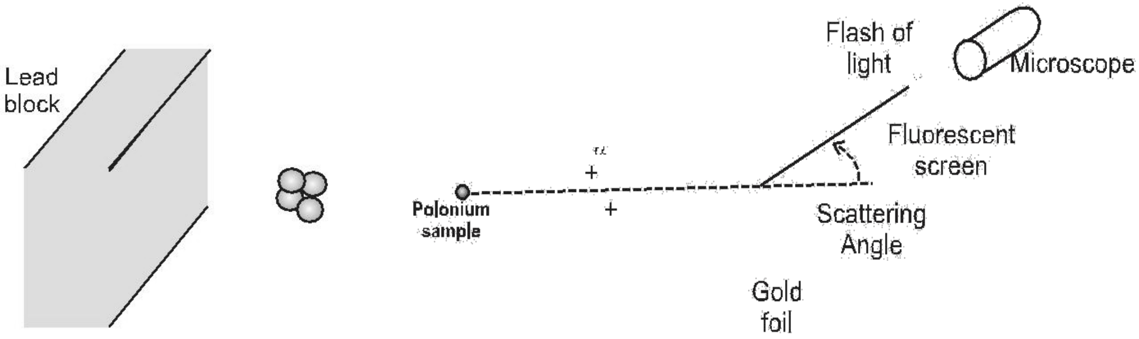


Fig. 1.1 *Theory and experiment go hand in hand in physics and help each other's progress. The alpha scattering experiments of Rutherford gave the nuclear model of the atom.*

What lies behind the phenomenal progress of physics in the last few centuries? Great progress usually accompanies changes in our basic perceptions. First, it was realized that for scientific progress, only qualitative thinking, though no doubt important, is not enough. Quantitative measurement is central to the growth of science, especially physics, because the laws of nature happen to be expressible in precise mathematical equations. The second most important insight was that the basic laws of physics are universal — the same laws apply in widely different contexts. Lastly, the strategy of approximation turned out to be very successful. Most observed phenomena in daily life are rather complicated manifestations of the basic laws. Scientists recognized the importance of extracting the essential features of a phenomenon from its less significant aspects. It is not practical to take into account all the complexities of a phenomenon in one go. A good strategy is to focus first on the essential features, discover the basic principles and then introduce corrections to build a more refined theory of the phenomenon. For example, a stone and a feather dropped from the same height do not reach the ground at the same time. The reason is that the essential aspect of the phenomenon, namely free fall under gravity, is complicated by the presence of air resistance. To get the law of free fall under gravity, it is better to create a situation where in the air resistance is negligible. We can, for example, let the stone and the feather fall through a long evacuated tube. In that case, the two objects will fall almost at the same rate, giving the basic law that acceleration due to gravity is independent of the mass of the object. With the basic law thus found, we can go back to the feather, introduce corrections due to air resistance, modify the existing theory and try to build a more realistic theory of objects falling to the earth under gravity.

Hypothesis, axioms and models

One should not think that everything can be proved with physics and mathematics. All physics, and also mathematics, is based on assumptions, each of which is variously called a hypothesis or axiom or postulate, etc.

For example, the universal law of gravitation proposed by Newton is an assumption or hypothesis, which he proposed out of his ingenuity. Before him, there were several observations, experiments and data, on the motion of planets around the sun, motion of the moon around the earth, pendulums, bodies falling towards the earth etc. Each of these required a separate explanation, which was more or less qualitative. What the universal law of gravitation says is that, *if we assume* that any two bodies in the universe attract each other with a force proportional to the product of their masses and inversely proportional to the square of the distance between them, then we can explain all these observations in one stroke. It not only explains these phenomena, it also allows us to predict the results of future experiments.

A hypothesis is a supposition without assuming that it is true. It would not be fair to ask anybody to prove the universal law of gravitation, because it cannot be proved. It can be verified and substantiated by experiments and observations.

An axiom is a self-evident truth while a model is a theory proposed to explain observed phenomena. But you need not worry at this stage about the nuances in using these words. For example, next year you will learn about Bohr’s model of hydrogen atom, in which Bohr assumed that an electron in the hydrogen atom follows certain rules (postulates). Why did he do that? There was a large amount of spectroscopic data before him which no other theory could explain. So Bohr said that if we assume that an atom behaves in such a manner, we can explain all these things at once.

Einstein’s special theory of relativity is also based on two postulates, the constancy of the speed of electromagnetic radiation and the validity of physical laws in all inertial frame of reference. It would not be wise to ask somebody to prove that the speed of light in vacuum is constant, independent of the source or observer.

In mathematics too, we need axioms and hypotheses at every stage. Euclid’s statement that parallel lines never meet, is a hypothesis. This means that if we assume this statement, we can explain several properties of straight lines and two or three dimensional figures made out of them. But if you don’t assume it, you are free to use a different axiom and get a new geometry, as has indeed happened in the past few centuries and decades.

1.3 PHYSICS, TECHNOLOGY AND SOCIETY

The connection between physics, technology and society can be seen in many examples. The discipline of thermodynamics arose from the need to understand and improve the working of heat engines. The steam engine, as we know, is inseparable from the Industrial Revolution in England in the eighteenth century, which had great impact on the course of human civilization. Sometimes technology gives rise to new physics; at other times physics generates new technology. An example of the latter is the wireless communication technology that followed the discovery of the basic laws of electricity and magnetism in the nineteenth century. The applications of physics are not always easy to foresee. As late as 1933, the great physicist Ernest Rutherford had dismissed the possibility of tapping energy from atoms. But only a few years later, in 1938, Hahn and Meitner discovered the phenomenon of neutron-induced fission of uranium, which would serve as the basis of nuclear power reactors and nuclear weapons. Yet another important example of physics giving rise to technology is the silicon ‘chip’ that triggered the computer revolution in the last three decades of the twentieth century.

A most significant area to which physics has and will contribute is the development of alternative energy resources. The fossil fuels of the planet are dwindling fast and there is an urgent need to discover new and affordable sources of energy. Considerable progress has already been made in this direction (for example, in conversion of solar energy, geothermal energy, etc., into electricity), but much more is still to be accomplished.

Table1.1 lists some of the great physicists, their major contribution and the country of origin. You will appreciate from this table the multi-cultural, international character of the scientific endeavour. Table 1.2 lists some important technologies and the principles of physics they are based on. Obviously, these tables are not exhaustive. We urge you to try to add many names and items to these tables with the help of your teachers, good books and websites on science. You will find that this exercise is very educative and also great fun. And, assuredly, it will never end. The progress of science is unstoppable!

Physics is the study of nature and natural phenomena. Physicists try to discover the rules that are operating in nature, on the basis of observations, experimentation and analysis. Physics deals with certain basic rules/laws governing the natural world. What is the nature of physical laws? We shall now discuss the nature of fundamental forces and the laws that govern the diverse phenomena of the physical world.

Table 1.1 Some physicists from different countries of the world and their major contributions

Name	Major contribution/discovery	Country of Origin
Archimedes	Principle of buoyancy; Principle of the lever	Greece
Galileo Galilei	Law of inertia	Italy
Christiaan Huygens	Wave theory of light	Holland
Isaac Newton	Universal law of gravitation; Laws of motion; Reflecting telescope	U.K.
Michael Faraday	Laws of electromagnetic induction	U.K.
James Clerk Maxwell	Electromagnetic theory; Light-an electromagnetic wave	U.K.
Heinrich Rudolf Hertz	Generation of electromagnetic waves	Germany
J.C. Bose	Ultra short radio waves	India
W.K. Roentgen	X-rays	Germany
J.J. Thomson	Electron	U.K.
Marie Sklodowska Curie	Discovery of radium and polonium; Studies on natural radioactivity	Poland
Albert Einstein	Explanation of photoelectric effect; Theory of relativity	Germany
Victor Francis Hess	Cosmic radiation	Austria
R.A. Millikan	Measurement of electronic charge	U.S.A.
Ernest Rutherford	Nuclear model of atom	New Zealand
Niels Bohr	Quantum model of hydrogen atom	Denmark
C.V. Raman	Inelastic scattering of light by molecules	India
Louis Victor de Borglie	Wave nature of matter	France
M.N. Saha	Thermal ionisation	India
S.N. Bose	Quantum statistics	India
Wolfgang Pauli	Exclusion principle	Austria
Enrico Fermi	Controlled nuclear fission	Italy
Werner Heisenberg	Quantum mechanics; Uncertainty principle	Germany
Paul Dirac	Relativistic theory of electron; Quantum statistics	U.K.
Edwin Hubble	Expanding universe	U.S.A.
Ernest Orlando Lawrence	Cyclotron	U.S.A.
James Chadwick	Neutron	U.K.
Hideki Yukawa	Theory of nuclear forces	Japan
Homi Jehangir Bhabha	Cascade process of cosmic radiation	India
Lev Davidovich Landau	Theory of condensed matter; Liquid helium	Russia
S. Chandrasekhar	Chandrasekhar limit, structure and evolution of stars	India
John Bardeen	Transistors; Theory of super conductivity	U.S.A.
C.H. Townes	Maser; Laser	U.S.A.
Abdus Salam	Unification of weak and electromagnetic interactions	Pakistan

1.4 FUNDAMENTAL FORCES IN NATURE*

We all have an intuitive notion of force. In our experience, force is needed to push, carry or throw objects, deform or break them. We also experience the impact of forces on us, like when a moving object hits us or we are in a merry-go-round. Going from this intuitive notion to the proper scientific concept of force is not a trivial matter. Early thinkers like Aristotle had wrong ideas about it.

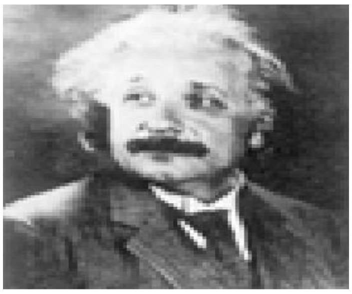
The correct notion of force was arrived at by Isaac Newton in his famous laws of motion. He also gave an explicit form for the force for gravitational attraction between two bodies. We shall learn these matters in subsequent chapters In the macroscopic world, besides the gravitational force, we encounter several kinds of forces: muscular force, contact forces between bodies, friction (which is also a contact force parallel to the surfaces in contact), the forces exerted by compressed or elongated springs and taut strings and ropes (tension), the force of buoyancy and viscous force when solids are in contact with fluids, the force due to pressure of a fluid, the force due to surface tension of a liquid, and so on There are also forces involving charged and magnetic bodies. In the microscopic domain again, we have electric and magnetic forces, nuclear forces involving protons and neutrons, interatomic and intermolecular forces, etc. We shall get familiar with some of these forces in later parts of this course. A great insight of the twentieth century physics is that these different forces occurring in different contexts actually arise from only a small number of fundamental forces in nature. For example, the elastic spring force arises due to the net attraction/repulsion between the neighbouring atoms of the spring when the spring is elongated / compressed. This net attraction/repulsion can be traced to the (unbalanced) sum of electric forces between the charged constituents of the atoms.

* *Sections 1.4 and 1.5 contain several ideas that you may not grasp fully in your first reading. However, we advise you to read them carefully to develop a feel for some basic aspects of physics. These are some of the areas which continue to occupy the physicists today.*

Table 1.2 Link between technology and physics

Technology	**Scientific principle(s)**
Steam engine	Laws of thermodynamics
Nuclear reactor	Controlled nuclear fission
Radio and Television	Generation, propagation and detection of electromagnetic waves
Computers	Digital logic
Lasers	Light amplification by stimulated emission of radiation
Production of ultra high magnetic fields	Superconductivity
Rocket propulsion	Newton's laws of motion
Electric generator	Faraday's laws of electromagnetic induction
Hydroelectric power	Conversion of gravitational potential energy into electrical energy
Aeroplane	Bernoulli's principle in fluid dynamics
Particle accelerators	Motion of charged particles in electromagnetic fields
Sonar	Reflection of ultrasonic waves
Optical fibres	Total internal reflection of light
Non-reflecting coatings	Thin film optical interference
Electron microscope	Wave nature of electrons
Photocell	Photoelectric effect
Fusion test reactor (Tokamak)	Magnetic confinement of plasma
Giant Metrewave Radio Telescope (GMRT)	Detection of cosmic radio waves
Bose-Einstein condensate	Trapping and cooling of atoms by laser beams and magnetic fields.

In principle, this means that the laws for 'derived' forces (such as spring force, friction) are not independent of the laws of fundamental forces in nature. The origin of these derived forces is, however, very complex. At the present stage of our understanding, we know of four fundamental forces in nature, which are described in brief here:



Albert Einstein (1879-1955), born in Ulm, Germany in 1879, is universally regarded as one of the greatest physicists of all time. His astonishing scientific career began with the publication of three path-breaking papers in 1905. In the first paper, he introduced the notion of light quanta (now called photons) and used it to explain the features of photoelectric effect that the classical wave theory of radiation could not account for. In the second paper, he developed a theory of Brownian motion that was confirmed experimentally a few years later and provided a convincing evidence of the atomic picture of matter. The third paper gave birth to the special theory of relativity that made Einstein a legend in his own life time. In the next decade, he explored the consequences of his new theory which included, among other things, the mass-energy equivalence enshrined in his famous equation $E = mc^2$. He also created the general version of relativity (The General Theory of Relativity), which is the modern theory of gravitation. Some of Einstein's most significant later contributions are: the notion of stimulated emission introduced in an alternative derivation of Planck's blackbody radiation law, static model of the universe which started modern cosmology, quantum statistics of a gas of massive bosons, and a critical analysis of the foundations of quantum mechanics. The year 2005 was declared as International Year of Physics, in recognition of Einstein's monumental contribution to physics, in year 1905, describing revolutionary scientific ideas that have since influenced all of modern physics.

1.4.1 Gravitational Force

The gravitational force is the force of mutual attraction between any two objects by virtue of their masses. It is a universal force. Every object experiences this force due to every other object in the universe. All objects on the earth, for example, experience the force of gravity due to the earth. In particular, gravity governs the motion of the moon and artificial satellites around the earth, motion of the earth and planets around the sun, and, of course, the motion of bodies falling to the earth. It plays a key role in the large-scale phenomena of the universe, such as formation and evolution of stars, galaxies and galactic clusters.

1.4.2 Electromagnetic Force

Electromagnetic force is the force between charged particles. In the simpler case when charges are at rest, the force is given by Coulomb’s law: attractive for unlike charges and repulsive for like charges. Charges in motion produce magnetic effects and a magnetic field gives rise to a force on a moving charge. Electric and magnetic effects are, in general, inseparable – hence the name electromagnetic force. Like the gravitational force, electromagnetic force acts over large distances and does not need any intervening medium. It is enormously strong compared to gravity.

The electric force between two protons, for example, is 10^{36} times the gravitational force between them, for any fixed distance.

Matter, as we know, consists of elementary charged constituents like electrons and protons. Since the electromagnetic force is so much stronger than the gravitational force, it dominates all phenomena at atomic and molecular scales. (The other two forces, as we shall see, operate only at nuclear scales.) Thus it is mainly the electromagnetic force that governs the structure of atoms and molecules, the dynamics of chemical reactions and the mechanical, thermal and other properties of materials. It underlies the macroscopic forces like ‘tension’, ‘friction’, ‘normal force’, ‘spring force’, etc.

Gravity is always attractive, while electromagnetic force can be attractive or repulsive. Another way of putting it is that mass comes only in one variety (there is no negative mass), but charge comes in two varieties : positive and negative charge. This is what makes all the difference. Matter is mostly electrically neutral (net charge is zero). Thus, electric force is largely zero and gravitational force dominates terrestrial phenomena. Electric force manifests itself in atmosphere where the atoms are ionised and that leads to lightning.

If we reflect a little, the enormous strength of the electromagnetic force compared to gravity is evident in our daily life. When we hold a book in our hand, we are balancing the gravitational force on the book due to the huge mass of the earth by the ‘normal force’ provided by our hand. The latter is nothing but the net electromagnetic force between the charged constituents of our hand and the book, at the surface in contact. If electromagnetic force were not intrinsically so much stronger than gravity, the hand of the strongest man would crumble under the weight of a feather! Indeed, to be consistent, in that circumstance, we ourselves would crumble under our own weight?

1.4.3 Strong Nuclear Force

The strong nuclear force binds protons and neutrons in a nucleus. It is evident that without some attractive force, a nucleus will be unstable due to the electric repulsion between its protons. This attractive force cannot be gravitational since force of gravity is negligible compared to the electric force. A new basic force must, therefore, be invoked. The strong nuclear force is the strongest of all fundamental forces, about 100 times the electromagnetic force in strength. It is charge-independent and acts equally between a proton and a proton, a neutron and a neutron, and a proton and a neutron. Its range is, however, extremely small, of about nuclear dimensions (10^{-15}m). It is responsible for the stability of nuclei. The electron, it must be noted, does not experience this force. Recent developments have, however, indicated that protons and neutrons are built out of still more elementary constituents called quarks.

1.4.4 Weak Nuclear Force

The weak nuclear force appears only in certain nuclear processes such as the β-decay of a nucleus. In β-decay, the nucleus emits an electron and an uncharged particle called neutrino. The weak nuclear force is not as weak as the gravitational force, but much weaker than the strong nuclear and electromagnetic forces. The range of weak nuclear force is exceedingly small, of the order of 10^{-16} m.

1.4.5 Towards Unification of Forces

We remarked in section 1.1 that unification is a basic quest in physics. Great advances in physics often amount to unification of different theories and domains. Newton unified terrestrial and celestial domains under a common law of gravitation. The experimental discoveries of Oersted and Faraday showed that electric and magnetic phenomena are in general inseparable. Maxwell unified electromagnetism and optics with the discovery that light is an electromagnetic wave. Einstein attempted to unify gravity and electromagnetism but could not succeed in this venture. But this did not deter physicists from zealously pursuing the goal of unification of forces.

Recent decades have seen much progress on this front. The electromagnetic and the weak nuclear force have now been unified and are seen as aspects of a single ‘electro-weak’ force. What this unification actually means cannot be explained here. Attempts have been (and are being) made to unify the electro-weak and the strong force and even to unify the gravitational force with the rest of the fundamental forces. Many of these ideas are still speculative and inconclusive. Table 1.4 summarises some of the milestones in the progress towards unification of forces in nature.

Satyendranadh Bose (1894-1974)

Satyendranath Bose, born in Calcutta in 1894, is among the great Indian physicists who made a fundamental contribution to the advance of science in the twentieth century. An outstanding student throughout, Bose started his career in 1916 as a lecturer in physics in Calcutta University; five years later he joined Dacca University.

Here in 1924, in a brilliant flash of insight, Bose gave a new derivation of Planck's law, treating radiation as a gas of photons and employing new statistical methods of counting of photon states. He wrote a short paper on the subject and sent it to Einstein who immediately recognised its great significance, translated it in German and forwarded it for publication. Einstein then applied the same method to a gas of molecules.

The key new conceptual ingredient in Bose's work was that the particles were regarded as indistinguishable, a radical departure from the assumption that underlies the classical Maxwell-Boltzmann statistics. It was soon realised that the new Bose-Einstein statistics was applicable to particles with integers spins, and a new quantum statistics (Fermi-Dirac statistics) was needed for particles with half integers spins satisfying Pauli's exclusion principle. Particles with integers spins are now known as bosons in honour of Bose.

An important consequence of Bose-Einstein statistics is that a gas of molecules below a certain temperature will undergo a phase transition to a state where a large fraction of atoms populate the same lowest energy state. Some seventy years were to pass before the pioneering ideas of Bose, developed further by Einstein, were dramatically confirmed in the observation of a new state of matter in a dilute gas of ultra cold alkali atoms - the Bose-Eintein condensate.

1.5 NATURE OF PHYSICAL LAWS

Physicists explore the universe. Their investigations, based on scientific processes, range from particles that are smaller than atoms in size to stars that are very far away. In addition to finding the facts by observation and experimentation, physicists attempt to discover the laws that summarise (often as mathematical equations) these facts.

In any physical phenomenon governed by different forces, several quantities may change with time. A remarkable fact is that some special physical quantities, however, remain constant in time. They are the conserved quantities of nature. Understanding these conservation principles is very important to describe the observed phenomena quantitatively.

For motion under an external conservative force, the total mechanical energy i.e. the sum of kinetic and potential energy of a body is a constant. The familiar example is the free fall of an object under gravity. Both the kinetic energy of the object and its potential energy change continuously with time, but the sum remains fixed.

Table 1.4 Progress in unification of different forces/domains in nature

Name of the physicist	Year	Achievement in unification
Issac Newton	1687	Unified celestial and terrestrial mechanics; showed that the same laws of motion and the law of gravitation apply to both the domains
Han Christian Oersted Miechael Faraday	1820 1830	Showed that electric and magnetic phenomena are inseparable aspects of a unified domain: electromagnetism
James Clerk Maxwell	1873	Unified electricity, magnetism and optics; showed that light is an electromagnetic wave
Sheldon Glashow, Abdus Salam, Sreven Weinberg	1979	Showed that the ‘weak’ nuclear force and the electromagnetic force could be viewed as different aspects of a single electro-weak force
Carlo Rubia, Simon Vander Meer	1984	Verified ecperimentally the predictions of the theory of electro-weak force

If the object is released from rest, the initial potential energy is completely converted into the kinetic energy of the object just before it hits the ground. This law restricted for a conservative force should not be confused with the general law of conservation of energy of an isolated system (which is the basis of the First Law of Thermodynamics).

The concept of energy is central to physics and the expressions for energy can be written for every physical system. When all forms of energy e.g., heat, mechanical energy, electrical energy etc., are counted, it turns out that energy is conserved. The general law of conservation of energy is true for all forces and for any kind of transformation between different forms of energy. In the falling object example, if you include the effect of air resistance during the fall and see the situation after the object hits the ground and stays there, the total mechanical energy is obviously not conserved. The general law of energy conservation, however, is still applicable. The initial potential energy of the stone gets transformed into other forms of energy: heat and sound. (Ultimately, sound after it is absorbed becomes heat.) The total energy of the system (stone plus the surroundings) remains unchanged.

The law of conservation of energy is thought to be valid across all domains of nature, from the microscopic to the macroscopic. It is routinely applied in the analysis of atomic, nuclear and elementary particle processes. At the other end, all kinds of violent phenomena occur in the universe all the time. Yet the total energy of the universe (the most ideal isolated system possible!) is believed to remain unchanged.

Until the advent of Einstein’s theory of relativity, the law of conservation of mass was regarded as another basic conservation law of nature, since matter was thought to be indestructible. It was (and still is) an important principle used, for example, in the analysis of chemical reactions. A chemical reaction is basically a rearrangement of atoms among different molecules. If the total binding energy of the reacting molecules is less than the total binding energy of the product molecules, the difference appears as heat and the reaction is exothermic. The opposite is true for energy absorbing (endothermic) reactions. However, since the atoms are merely rearranged but not destroyed, the total mass of the reactants is the same as the total mass of the products in a chemical reaction. The changes in the binding energy are too small to be measured as changes in mass.

According to Einstein’s theory, mass m is equivalent to energy E given by the relation $E= mc^2$, where c is speed of light in vacuum. In a nuclear process mass gets converted to energy (or vice-versa). This is the energy which is released in a nuclear power generation and nuclear explosions. Energy is a scalar quantity. But all conserved quantities are not necessarily scalars. The total linear momentum and the total angular momentum (both vectors) of an isolated system are also conserved quantities. These laws can be derived from Newton’s laws of motion in mechanics. But their validity goes beyond mechanics. They are the basic conservation laws of nature in all domains, even in those where Newton’s laws may not be valid.

Sir C.V. Raman (1888-1970)

Chandrashekhara Venkata Raman was born on 07 Nov 1888 in Thiruvanaikkaval. He finished his schooling by the age of eleven. He graduated from Presidency College, Madras. After finishing his education he joined financial services of the Indian Government.

While in Kolkata, he started working on his area of interest at Indian Asso-ciation for Cultivation of Science founded by Dr. Mahendra Lal Sirkar, during his evening hours. His area of interest included vibrations, variety of musical instru-ments, ultrasonics, diffraction and so on.

In 1917 he was offered Professorship at Calcutta University. In 1924 he was elected ‘Fellow’ of the Royal Society of London and received Nobel prize in Physics in 1930 for his discovery, now known as Raman Effect.

The **Raman Effect** deals with scattering of light by molecules of a medium when they are excited to vibrational energy levels. This work opened totally new avenues for research for years to come.

He spent his later years at Bangalore, first at Indian Institute of Science and then at Raman Re-search Institute. His work has inspired generation of young students.

Besides their great simplicity and generality, the conservation laws of nature are very useful in practice too. It often happens that we cannot solve the full dynamics of a complex problem involving different particles and forces. The conservation laws can still provide useful results. For example, we may not know the complicated forces that act during a collision of two automobiles; yet momentum conservation law enables us to bypass the complications and predict or rule out possible outcomes of the collision. In nuclear and elementary particle phenomena also, the conservation laws are important tools of analysis. Indeed, using the conservation laws of energy and momentum for β-decay, Wolfgang Pauli

(1900-1958) correctly predicted in 1931 the existence of a new particle (now called neutrino) emitted in β-decay along with the electron.

Conservation laws have a deep connection with symmetries of nature that you will explore in more advanced courses in physics. For example, an important observation is that the laws of nature do not change with time! If you perform an experiment in your laboratory today and repeat the same experiment (on the same objects under identical conditions) after a year, the results are bound to be the same. It turns out that this symmetry of nature with respect to translation (i.e. displacement) in time is equivalent to the law of conservation of energy. Likewise, space is homogeneous and there is no (intrinsically) preferred location in the universe. To put it more clearly, the laws of nature are the same everywhere in the universe. (Caution: the phenomena may differ from place to place because of differing conditions at different locations. For example, the acceleration due to gravity at the moon is one-sixth that at the earth, but the law of gravitation is the same both on the moon and the earth.)

This symmetry of the laws of nature with respect to translation in space gives rise to conservation of linear momentum. In the same way isotropy of space (no intrinsically preferred direction in space) underlies the law of conservation of angular momentum*****. The conservation laws of charge and other attributes of elementary particles can also be related to certain abstract symmetries. Symmetries of space and time and other abstract symmetries play a central role in modern theories of fundamental forces in nature.

Conservation laws in physics

Conservation of energy, momentum, angular momentum, charge, etc are considered to be fundamental laws in physics. At this moment, there are many such conservation laws. Apart from the above four, there are others which mostly deal with quantities which have been introduced in nuclear and particle physics. Some of the conserved quantities are called spin, baryon number, strangeness, hypercharge, etc, but you need not worry about them.

A conservation law is a hypothesis, based on observations and experiments. It is important to remember that a conservation law cannot be proved. It can be verified, or disproved, by experiments. An experiment whose result is in conformity with the law verifies or substantiates the law; it does not prove the law. On the other hand, a single experiment whose result goes against the law is enough to disprove it.

It would be wrong to ask somebody to prove the law of conservation of energy. This law is an outcome of our experience over several centuries, and it has been found to be valid in all experiments, in mechanics, thermodynamics, electromagnetism, optics, atomic and nuclear physics, or any other area.

Some students feel that they can prove the conservation of mechanical energy from a body falling under gravity, by adding the kinetic and potential energies at a point and showing that it turns out to be constant. As pointed out above, this is only a verification of the law, not its proof.

SUMMARY

1. Physics deals with the study of the basic laws of nature and their manifestation in different phenomena. The basic laws of physics are universal and apply in widely different contexts and conditions.
2. The scope of physics is wide, covering a tremendous range of magnitude of physical quantities.
3. Physics and technology are related to each other. Sometimes technology gives rise to new physics; at other times physics generates new technology. Both have direct impact on society.
4. There are four fundamental forces in nature that govern the diverse phenomena of the macroscopic and the microscopic world. These are the ‘gravitational force’, the ‘electromagnetic force’, the ‘strong nuclear force’, and the ‘weak nuclear force’. Unification of different forces/domains in nature is a basic quest in physics.
5. The physical quantities that remain unchanged in a process are called conserved quantities. Some of the general conservation laws in nature include the laws of conservation of mass, energy, linear momentum, angular momentum, charge, parity, etc. Some conservation laws are true for one fundamental force but not for the other.
6. Conservation laws have a deep connection with symmetries of nature. Symmetries of space and time, and other types of symmetries play a central role in modern theories of fundamental forces in nature.

CHAPTER TWO

UNITS AND MEASUREMENT

2.1 INTRODUCTION

Measurement of any physical quantity involves comparison with a certain basic, arbitrarily chosen, internationally accepted reference standard called **unit**. The result of a measurement of a physical quantity is expressed by a number (or numerical measure) accompanied by a unit. Although the number of physical quantities appears to be very large, we need only a limited number of units for expressing all the physical quantities, since they are inter-related with one another. The units for the fundamental or base quantities are called **fundamental** or **base units**. The units of all other physical quantities can be expressed as combinations of the base units. Such units obtained for the derived quantities are called **derived units**. A complete set of these units, both the base units and derived units, is known as the **system of units**.

2.2 THE INTERNATIONAL SYSTEM OF UNITS

In earlier time scientists of different countries were using different systems of units for measurement. Three such systems, the CGS, the FPS (or British) system and the MKS system were in use extensively till recently.

The base units for length, mass and time in these systems were as follows:

- In CGS system they were centimeter, gram and second respectively.
- In FPS system they were foot, pound and second respectively.
- In MKS system they were metre, kilogram and second respectively.

The system of units which is at present internationally accepted for measurement is the ***Système International d’ Unites*** (French for International System of Units), abbreviated as SI. The SI, with standard scheme of symbols, units and abbreviations, was developed and recommended by General Conference on Weights and Measures in 1971 for International usage in scientific, technical, industrial and commercial work. Because SI units used decimal system, conversions within the system are quite simple and convenient. We shall follow the SI units in this book.

In SI, there are seven base units as given in Table 2.1. Besides the seven base units, there are two more units that are defined for (a) plane angle dθ as the ratio of length of arc ds to the radius r and (b) solid angle dΩ as the ratio of the intercepted area dA of the spherical surface, described about the apex O as the centre, to the square of its radius r, as shown in Fig. 2.1(a) and (b) respectively. The unit for plane angle is radian with the symbol rad and the unit for the solid angle is steradian with the symbol sr. Both these are dimensionless quantities.

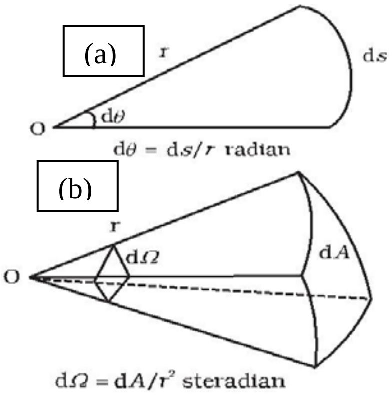


Fig. 2.1 *Description of (a) plane angle dθ and (b) Solid angle dΩ*

Base quantity	**SI Units**		
	Name	**Symbol**	**Definition**
Length	metre	m	The metre is the length of the path travelled by light in vacuum during a time interval of 1/299,792,458 of a second. (1983)
Mass	kilogram	kg	The kilogram is equal to the mass of the international prototype of the kilogram (a platinum-iridium alloy cylinder) kept at international Bureau of Weights and Measures, at Sevres, near Paris, France. (1889)
Time	second	s	The second is the duration of 9,192,631,770 periods of the radiation corresponding to the transition between the two Hyperfine levels of the ground state of the cesium-133 atom. (1967)
Electric current	ampere	A	The ampere is that constant current which, if maintained in two straight parallel conductors of infinite length, of negligible circular cross-section, and placed 1 metre apart in vacuum, would produce between these conductors a force equal to 2×10^{-7} Newton per metre of length. (1948)
Thermo dynamic Temperature	Kelvin	K	The Kelvin, is the fraction 1/273.16 of the thermodynamic Temperature of the triple point of water. (1967)
Amount of substance	Mole	mol	The mole is the amount of substance of a system, which contains as many elementary entities as there are atoms in 0.012 Kilogram of carbon - 12. (1971)
Luminous intensity	candela	cd	The candela is the luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency 540×10^{12} hertz and that has a radiant intensity in that direction of 1/683 watt per steradian. (1979)

* The values mentioned here need not be remembered or asked in a test. They are given here only to indicate the extent of accuracy to which they are measured. With progress in technology, the measuring techniques get improved leading to measurements with greater precision. The definitions of base units are revised to keep up with this progress.

Table 2.2 some units retained for general use (Though outside SI)

Name	Symbol	Value in SI Unit
Minute	min	60 s
Hour	h	60 min=3600 s
Day	d	24 h = 86400 s
Year	y	36.25 d =3.156 x 10^7 s
Degree	^{c}	1^c=($\pi/180$) rad
Litre	l	1 dm^3=10^{-3} m^3
Tonne	t	10^3 kg
Carat	c	200 mg
Bar	bar	0.1 MPa =10^5 Pa
Curie	ci	3.7 x 10^{10} s^{-1}
Roentgen	r	2.58 x 10-4 C/kg
Quintal	q	100 kg
Barn	b	100 fm^2 = 10^{-25} m^2
Arc	a	1 dam^2=10^2 m^2
Hectare	ha	1 hm^2=10^4 m^2
Standard atmospheric pressure	atm	101325 Pa = 1.013 x 105 Pa

Note that when mole is used, the elementary entities must be specified. These entities may be atoms, molecules, ions, electrons, other particles or specified groups of such particles.

We employ units for some physical quantities that can be derived from the seven base units (Appendix A 6). Some derived units in terms of the SI base units are given in (Appendix A 6.1). Some SI derived units are given special names (Appendix A 6.2) and some derived SI units make use of these units with special names and the seven base units (Appendix A 6.3). These are given in Appendix A 6.2 and A 6.3 for your ready reference. Other units retained for general use are given in Table 2.2.

Common SI prefixes and symbols for multiples and sub-multiples are given in Appendix A2. General guidelines for using symbols for physical quantities, chemical elements and nuclides are given in Appendix A7 and those for SI units and some other units are given in Appendix A8 for your guidance and ready reference.

2.3 MEASUREMENT OF LENGTH

You are already familiar with some direct methods for the measurement of length. For example, a metre scale is used for lengths from 10^{-3} m to 10^{2} m. A vernier callipers is used for lengths to an accuracy of 10^{-4} m. A screw gauge and a spherometer can be used to measure lengths as less as to 10^{-5} m. To measure lengths beyond these ranges, we make use of some special indirect methods.

2.3.1 Measurement of Large Distances

Large distances such as the distance of a planet or a star from the earth cannot be measured directly with a metre scale. An important method in such cases is the **parallax method**.

When you hold a pencil in front of you against some specific point on the background (a wall) and look at the pencil first through your left eye A (closing the right eye) and then look at the pencil through your right eye B (closing the left eye), you would notice that the position of the pencil seems to change with respect to the point on the wall. This is called **parallax**. The distance between the two points of observation is called the **basis**. In this example, the basis is the distance between the eyes.

To measure the distance D of a far away planet S by the parallax method, we observe it from two different positions (observatories) A and B on the Earth, separated by distance AB = b at the same time as shown in Fig. 2.2. We measure the angle between the two directions along which the planet is viewed at these two points. The ∠ASB in Fig. 2.2 represented by symbol θ is called the **parallax angle** or **parallactic angle**.

As the planet is very far away, $\frac{b}{d} \ll$ therefore, θ is very small. Then we approximately take AB as an arc of length b of a circle with centre at S and he distance D as the radius AS = BS so that AB=b= Dθ where θ is in radians.

$$D = \frac{b}{\theta} \tag{2.1}$$

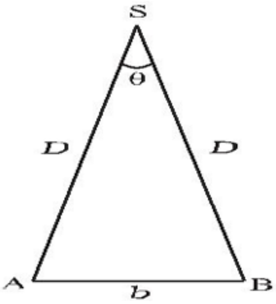


Fig. 2.2 *Parallax method.*

determined *D*, we can employ a similar method to determine the size or angular diameter of the planet. If *d* is the diameter of the planet and α the angular size of the planet (the angle subtended by *d* at the earth), we have

$$\alpha = d/D \tag{2.2}$$

The angle α can be measured from the same location on the earth. It is the angle between the two directions when two diametrically opposite points of the planet are viewed through the telescope. Since *D* is known, the diameter *d* of the planet can be determined using Eq. (2.2).

Example 2.1 Calculate the angle of (a) 1^0 (degree) (b) $1'$ (minute of arc or arcmin) and (c) $1''$ (second of arc or arc) in radians. Use $360^0=2\pi$ rad, $1^0=60'$ and $1' = 60\ ''$

Answer (a) We have $360^0 = 2\pi$ rad

$1^0 = (\pi /180)$ rad $= 1.745\times10^{-2}$ rad

(b) $1^0 = 60' = 1.745\times10^{-2}$ rad

$1' = 2.908\times10^{-4}$ rad **;** 2.91×10^{-4} rad

(c) $1' = 60'' = 2.908\times10^{-4}$ rad

$1'' = 4.847\times10^{-4}$ rad **;** 4.85×10^{-6} rad

Example 2.2 A man wishes to estimate the distance of a nearby tower from him. He stands at a point A in front of the tower C and spots a very distant object O in line with AC. He then walks perpendicular to AC up to B, a distance of 100 m, and looks at O and C again. Since O is very distant, the direction BO is practically the same as AO; but he finds the line of sight of C shifted from the original line of sight by an angle θ = 400 (θ is known as 'parallax') estimate the distance of the tower C from his original position A.

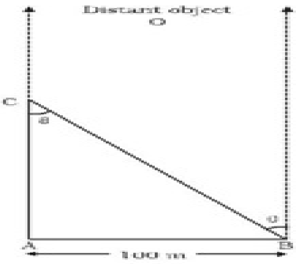


Fig. 2.3

Answer: We have, parallax angle $\theta = 40^0$

From Fig. 2.3, AB = AC tan θ

AC = AB/tanθ = 100 m/tan 40^0

= 100m/0.8391 = 119 m

Example 2.3 The moon is observed from two diametrically opposite points A and B on Earth. The angle θ subtended at the moon by the two directions of observation is 1^o 54′. Given the diameter of the Earth to be about 1.276 □10^7 m, compute the distance of the moon from the Earth.

Answer: We have θ **=** 1° $54'$ = $114'$

= (114 x 60)″ x ($4.85 x 10^{-6}$) rad

= 3.32×10^{-2} rad

since 1″ = 4.85×10^{-6} *rad*. Also

b = AB =1.276×10^7 m

Hence from Eq. (2.1), we have the earth-moon distance,

D= b/θ

$$= \frac{1.276 \text{ x } 10^7}{3.32 \text{ x } 10^{-2}} = 3.58 \text{ x } 10^8 \text{ m}$$

Example 2.4 The Sun’s angular diameter is measured to be 1920″. The distance D of the Sun from the Earth is 1.496×10^{11} m. What is the diameter of the Sun?

Answer Sun’s angular diameter α = 1920"

= $1920 \times 4.85 \times 10^{-6}$ rad

= 9.31×10^{-3} rad

Sun’s diameter d = αD

= ($9.31 \times 10^{-3)}$ × ($1.496 \times 10^{11)}$ m

= 1.39×10^{9} m.

2.3.2 Estimation of Very Small Distances: Size of a Molecule

To measure a very small size like that of a molecule (10^{-8} m to 10^{-10} m), we have to adopt special methods. We cannot use a screw gauge or similar instruments. Even a microscope has certain limitations. An optical microscope uses visible light to 'look' at the system under investigation. As light has wave like features, the resolution to which an optical microscope can be used is the wavelength of light (A detailed explanation can be found in the Class XII Physics textbook). For visible light the range of wavelengths is from about 4000 Å to 7000 Å (1 angstrom = 1 Å = 10^{-10} m). Hence an optical microscope cannot resolve particles with sizes smaller than this. Instead of visible light, we can use an electron beam. Electron beams can be focused by properly designed electric and magnetic fields. The resolution of such an electron microscope is limited finally by the fact that electrons can also behave as waves! (You will learn more about this in class XII). The wavelength of an electron can be as small as a fraction of an angstrom. Such electron microscopes with a resolution of 0.6 Å have been built. They can almost resolve atoms and molecules in a material. In recent times, tunneling microscopy has been developed in which again the limit of resolution is better than an angstrom. It is possible to estimate the sizes of molecules.

A simple method for estimating the molecular size of oleic acid is given below. Oleic acid is a soapy liquid with large molecular size of the order of 10^{-9} m.

The idea is to first form mono-molecular layer of oleic acid on water surface. We dissolve 1 cm^3 of oleic acid in alcohol to make a solution of 20 cm^3. Then we take 1 cm^3. Of this solution and dilute it to 20 cm^3, using alcohol. So, the concentration of the solution is equal to $(\frac{1}{20\ x\ 20})$ cm^3 of oleic acid/cm^3 of solution.

Volume of n drops of solution = nV cm^3

Amount of oleic acid in this solution = $nV \frac{1}{20 \times 20}$ cm^3

This solution of oleic acid spreads very fast on the surface of water and forms a very thin layer of thickness t. If this spreads to form a film of area A cm^2, then the thickness of the film

$$t = \frac{volume\ of\ the\ film}{Area\ of\ the\ film}$$

Or, $$t = \frac{nV}{20\ x\ 20\ A}\ cm \qquad (2.3)$$

If we assume that the film has mono-molecular thickness, then this becomes the size or diameter of a molecule of oleic acid. The value of this thickness comes out to be of the order of 10^{-9} m.

Example 2.5 If the size of a nucleus (in the range of 10^{-15} to 10^{-14} m) is scaled up to the tip of a sharp pin, what roughly is the size of an atom ? Assume tip of the pin to be in the range 10^{-5}m to 10^{-4}m.

Answer The size of a nucleus is in the range of 10^{-15} m and 10^{-14} m. The tip of a sharp pin is taken to be in the range of 10^{-5} m and 10^{-4} m. Thus we are scaling up by a factor of 10^{10}. An atom roughly of size 10^{-10} m will be scaled up to a size of 1 m. Thus a nucleus in an atom is as small in size as the tip of a sharp pin placed at the centre of a sphere of radius about a metre long.

2.3.3 Range of Lengths

The sizes of the objects we come across in the universe vary over a very wide range. These may vary from the size of the order of 10^{-14} m of the tiny nucleus of an atom to the size of the order of 10^{26} m of the extent of the observable universe. Table 2.3 gives the range and order of lengths and sizes of some of these objects.

We also use certain special length units for short and large lengths. These are

1 fermi = 1 f = 10^{-15} m

1 angstrom = 1 Å = 10^{-10} m

1 astronomical unit = 1 AU (average distance of the Sun from the Earth)

= 1.496×10^{11} m

1 light year = 1 ly = 9.46×10^{15} m

(distance that light travels with velocity of 3×10^{8} m s^{-1} in 1 year)

1 parsec = 3.08×10^{16} m (Parsec is the distance at which average radius of earth's orbit subtends an angle of 1 arc second)

2.4 MEASUREMENT OF MASS

Mass is a basic property of matter. It does not depend on the temperature, pressure or location of the object in space. The SI unit of mass is kilogram (kg). The prototypes of the International standard kilogram supplied by the International Bureau of Weights and Measures (BIPM) are available in many other laboratories of different countries. In India, this is available at the National Physical Laboratory (NPL), New Delhi.

While dealing with atoms and molecules, the kilogram is an inconvenient unit. In this case, there is an important standard unit of mass, called the **unified atomic mass unit** (u), which has been established for expressing the mass of atoms as

1 unified atomic mass unit = 1u

= (1/12) of the mass of an atom of carbon-12 isotope $\left({}^{12}{}_{6}\,\mathrm{C}\right)$

including the mass of electrons

= 1.66 × 10^{-27} kg

Mass of commonly available objects can be determined by a common balance like the one used in a grocery shop. Large masses in the universe like planets, stars, etc., based on Newton's law of gravitation can be measured by using gravitational method (See Chapter 8). For measurement of small masses of atomic/sub-atomic particles etc., we make use of mass spectrograph in which radius of the trajectory is proportional to the mass of a charged particle moving in uniform electric and magnetic field.

2.4.1 Range of Masses

The masses of the objects, we come across in the universe, vary over a very wide range. These may vary from tiny mass of the order of 10^{-30} kg of an electron to the huge mass of about 10^{55} kg of the known universe. Table 2.4 gives the range and order of the typical masses of various objects.

Table 2.3 Range and order of lengths

Size of object or distance	Length (m)
Size of a proton	10^{-15}
Size of a atomic nucleus	10^{-14}
Size of hydrogen atom	10^{-10}
Length of typical virus	10^{-8}
Wavelength of light	10^{-7}
Thickness of a paper	10^{-1}
Height of the Mount Everest above sea level	10^{4}
Radius of the Earth	10^{7}
Distance of Moon from the Earth	10^{8}
Distance of the Sun from the Earth	10^{11}
Distance of Pluto from the Sun	10^{18}
Size of our galaxy	10^{21}
Distance of Andromeda galaxy	10^{22}
Distance of the boundary of observable universe	10^{26}

Table 2.4 Range and order of masses

Object	Mass (kg)
Electron	10^{-30}
Proton	10^{-27}
Uranium atom	10^{-25}
Red blood cell	10^{-13}
Dust particle	10^{-9}
Rain drop	10^{-6}
Mosquito	10^{-5}
Grape	10^{-3}
Huamn	10^{2}
Automobile	10^{3}
Boeing 747 aircraft	10^{8}
Moon	10^{23}
Earth	10^{25}
Sun	10^{30}
Milky way galaxy	10^{41}
Observable Universe	10^{55}

2.5 MEASUREMENT OF TIME

To measure any time interval we need a clock. We now use an **atomic standard of time**, which is based on the periodic vibrations produced in a cesium atom. This is the basis of the **cesium clock**, sometimes called **atomic clock**, used in the national standards. Such standards are available in many laboratories. In the cesium atomic clock, the second is taken as the time needed for 9,192,631,770 vibrations of the radiation corresponding to the transition between the two hyperfine levels of the ground state of cesium-133 atom. The vibrations of the cesium atom regulate the rate of this cesium atomic clock just as the vibrations of a balance wheel regulate an ordinary wristwatch or the vibrations of a small quartz crystal regulate a quartz wristwatch.

The cesium atomic clocks are very accurate. In principle they provide portable standard. The national standard of time interval ‘second’ as well as the frequency is maintained through four cesium atomic clocks. A cesium atomic clock is used at the National Physical Laboratory (NPL), New Delhi to maintain the Indian standard of time.

In our country, the NPL has the responsibility of maintenance and improvement of physical standards, including that of time, frequency, etc. Note that the Indian Standard Time (IST) is linked to this set of atomic clocks. The efficient cesium atomic clocks are so accurate that they impart the uncertainty in time realisation as $\pm 1 \times 10^{-13}$, i.e. 1 part in 10^{13}.

This implies that the uncertainty gained over time by such a device is less than 1 part in 10^{13}; they lose or gain no more than 3 μs in one year. In view of the tremendous accuracy in time measurement, the SI unit of length has been expressed in terms the path length light travels in certain interval of time (1/299, 792, 458 of a second) (Table 2.1).

The time intervals of events that we come across in the universe vary over a very wide range. Table 2.5 gives the range and order of some typical time intervals.

You may notice that there is an interesting coincidence between the numbers appearing in Tables 2.3 and 2.5. Note that the ratio of the longest and shortest lengths of objects in our universe is about 10^{41}. Interestingly enough, the ratio of the longest and shortest time intervals associated with the events and objects in our universe is also about 10^{41}. This number, 10^{41} comes up again in Table 2.4, which lists typical masses of objects. The ratio of the largest and smallest masses of the objects in our universe is about $(10^{41})^2$. Is this a curious coincidence between these large numbers purely accidental?

2.6 ACCURACY, PRECISION OF INSTRUMENTS AND ERRORS IN MEASUREMENT

Measurement is the foundation of all experimental science and technology. The result of every measurement by any measuring instrument contains some uncertainty. This uncertainty is called **error**. Every calculated quantity which is based on measured values, also has an error. We shall distinguish between two terms: **accuracy** and **precision**. The accuracy of a measurement is a measure of how close the measured value is to the true value of the quantity. Precision tells us to what resolution or limit the quantity is measured.

Table 2.5 Range and order of time intervals

Event	Time intervals
Life-span of most unstable particle	10^{-24}
Time required for light to cross a nuclear distance	10^{-22}
Period of X-rays	10^{-19}
Period of atomic vibrations	10^{-15}
Period of light wave	10^{-15}
Life time of an excited state of an atom	10^{-8}
Period of radio wave	10^{-6}
Period of a sound wave	10^{-3}
Wink of eye	10^{-1}
Time between successive human heart beats	10^{0}
Travel time for light from moon to the Earth	10^{0}
Travel time for light from Sun to the Earth	10^{2}
Time period of a satellite	10^{4}
Rotation period of the Earth	10^{5}

Rotation and revolution periods of the moon	10^{6}
Revolution period of the earth	10^{7}
Travel time for light from nearest star	10^{8}
Average human life-span	10^{9}
Age of Egyptian pyramids	10^{11}
Time since dinosaurs became extinct	10^{15}
Age of the Universe	10^{17}

The accuracy in measurement may depend on several factors, including the limit or the resolution of the measuring instrument. For example, suppose the true value of a certain length is near 3.678 cm. In one experiment, using a measuring instrument of resolution 0.1 cm, the measured value is found to be 3.5 cm, while in another experiment using a measuring device of greater resolution, say 0.01 cm, the length is determined to be 3.38 cm. The first measurement has more accuracy (because it is closer to the true value) but less precision (its resolution is only 0.1 cm), while the second measurement is less accurate but more precise. Thus every measurement is approximate due to errors in measurement. In general, the errors in measurement can be broadly classified as (a) systematic errors and (b) random errors.

Systematic errors

The **systematic errors** are those errors that tend to be in one direction, either positive or negative. Some of the sources of systematic errors are :

(a) Instrumental errors that arise from the errors due to imperfect design or calibration of the measuring instrument, zero error in the instrument, etc. For example, the temperature graduations of a thermometer may be inadequately calibrated (it may read 104 °C at the boiling point of water at STP whereas it should read 100 °C); in a vernier callipers the zero mark of vernier scale may not coincide with the zero mark of the main scale, or simply an ordinary metre scale may be worn off at one end.

(b) Imperfection in experimental technique or procedure To determine the temperature

(c) Personal errors that arise due to an individual's bias, lack of proper setting of the apparatus or individual's carelessness in taking observations without observing proper precautions, etc. For example, if you, by habit, always hold your head a bit too far to the right while reading the position of a needle on the scale, you will introduce an error due to parallax.

Systematic errors can be minimised by improving experimental techniques, selecting better instruments and removing personal bias as far as possible. For a given set-up, these errors may be estimated to a certain extent and the necessary corrections may be applied to the readings.

Random errors

The random errors are those errors, which occur irregularly and hence are random with respect to sign and size. These can arise due to random and unpredictable fluctuations in experimental conditions (e.g. unpredictable fluctuations in temperature, voltage supply, mechanical vibrations of experimental set-ups, etc), personal (unbiased) errors by the observer taking readings, etc. For example, when the same person repeats the same observation, it is very likely that he may get different readings everytime.

Least count error

The smallest value that can be measured by the measuring instrument is called its least count. All the readings or measured values are good only up to this value.

The least count error is the error associated with the resolution of the instrument. For example, a vernier callipers has the least count as 0.01 cm; a spherometer may have a least count of 0.001 cm. Least count error belongs to the category of random errors but within a limited size; it occurs with both systematic and random errors. If we use a metre scale for measurement of length, it may have graduations at 1 mm division scale spacing or interval.

Using instruments of higher precision, improving experimental techniques, etc., we can reduce the least count error. Repeating the observations several times and taking the arithmetic mean of all the observations, the mean value would be very close to the true value of the measured quantity.

Absolute Error, Relative Error and Percentage Error

(a) Suppose the values obtained in several measurements are a_1, a_2, a_3...., a_n. The arithmetic mean of these values is taken as the best possible value of the quantity under the given conditions of measurement as:

$$a_{mean} = (a_1+a_2+a_3+...+a_n)/\text{n}$$

(2.4)

or ,

$$a_{mean} = \sum_{i=1}^{n} \frac{a_i}{n} \tag{2.5}$$

This is because, as explained earlier, it is reasonable to suppose that individual measurements are as likely to overestimate as to underestimate the true value of the quantity

The magnitude of the difference between the true value of the quantity and the individual measurement value is called the absolute error of the measurement. This is denoted by $|a|$. In absence of any other method of knowing true value, we considered arithmatic mean as the true value. Then the errors in the individual measurement values are

$$a1 = {}^{a}mean - {}^{a}1,$$

$$^{a}2 = {}^{a}mean - {}^{a}2,$$

....

....

$$^{a}\,n = {}^{a}mean - {}^{a}n$$

The *a* calculated above may be positive in certain cases and negative in some other cases. But absolute error | *a*| will always be positive.

(b) The arithmetic mean of all the *absolute errors* is taken as the *final* or *mean absolute error* of the value of the physical quantity *a*. It is represented by a_{mean}.

Thus,

$$a_{mean} = (|\, a_1|+|\, a_2\, |+|\, a_3\, |+\ldots|\, a_n\,)/n|$$

(2.6)

$$= \sum_{i=1}^{N} |a_i|/n \qquad (2.7)$$

If we do a single measurement, the value we

get may be in the range $a_{mean} \pm {}^{a}mean$

i.e. $a = a_{mean} \pm a_{mean}$

$$a_{mean} - \Delta a_{mean} \leq a \leq a_{mean} + \Delta a_{mean} \qquad (2.8)$$

This implies that any measurement of the physical quantity *a* is likely to lie between

$$(a_{mean} + \Delta a_{mean})\ and (a_{mean} - \Delta a_{mean})$$

Instead of the absolute error, we often use the **relative error** or the **percentage error** (δ*a*). ***The* relative error is the ratio of the mean absolute error *a***

relative error is the ratio of the mean absolute error a_{mean} to the mean value a_{mean} of the quantity measured.

$$\text{Relative error} = a_{mean}/a_{mean} \qquad (2.9)$$

When the relative error is expressed in per cent, it is called the **percentage error** (δ*a*). Thus,

Percentage error

$$\delta a = (a_{mean}/a_{mean}) \times 100\% \qquad (2.10)$$

Let us now consider an example.

Example 2.6 Two clocks are being tested against a standard clock located in a national laboratory. At 12:00:00 noon by the standard clock, the readings of the two clocks are:

	Clock 1	**Clock 2**
Monday	12:00:05	10:15:06
Tuesday	12:01:15	10:14:59
Wednesday	11:59:08	10:15:18
Thursday	12:01:50	10:15:07
Friday	11:59:15	10:14:53
Saturday	12:01:30	10:15:24
Sunday	12:01:19	10:15:11

If you are doing an experiment that requires precision time interval measurements, which of the two clocks will you prefer ?

Answer The range of variation over the seven days of observations is 162 s for clock 1, and 31 s for clock 2. The average reading of clock 1 is much closer to the standard time than the average reading of clock 2. The important point is that a clock's zero error is not as significant for precision work as its variation, because a 'zero-error' can always be easily corrected. Hence clock 2 is to be preferred to clock 1.

Example 2.7 We measure the period of oscillation of a simple pendulum. In successive measurements, the readings turn out to be 2.63 s, 2.56 s, 2.42 s, 2.71s and 2.80 s. Calculate the absolute errors, relative error or percentage error.

Answer The mean period of oscillation of the pendulum

$$T = \left(\frac{2.63 + 2.56 + 2.42 + 2.71 + 2.80}{5}\right) s$$

$$= \frac{13.12}{5}\ s$$

$= 2.624$ s

$= 2.62$ s

As the periods are measured to a resolution of 0.01 s, all times are to the second decimal; it is proper to put this mean period also to the second decimal.

The errors in the measurements are

$$2.63\ \text{s} - 2.62\ \text{s} = 0.01\ \text{s}$$

$$2.56\ \text{s} - 2.62\ \text{s} = -0.06\ \text{s}$$

$$2.42\ \text{s} - 2.62\ \text{s} = -0.20\ \text{s}$$

$$2.71\text{s} - 2.62\ \text{s} = 0.09\ \text{s}$$

$$2.80\ \text{s} - 2.62\text{s} = 0.18\ \text{s}$$

Note that the errors have the same units as the quantity to be measured.

The arithmetic mean of all the absolute errors (for arithmetic mean, we take only the magnitudes) is

$$T_{mean} = [(0.01+ 0.06+0.20+0.09+0.18)\text{s}]/5$$

$$= 0.54\ \text{s}/5$$

$$= 0.11\ \text{s}$$

That means, the period of oscillation of the simple pendulum is (2.62 ± 0.11) s i.e. it lies between (2.62 + 0.11) s and (2.62 – 0.11) s or between 2.73 s and 2.51 s. As the arithmetic mean of all the absolute errors is 0.11 s, there is already an error in the tenth of a second. Hence there is no point in giving the period to a hundredth. A more correct way will be to write

$$T = 2.6 \pm 0.1\ \text{s}$$

Note that the last numeral 6 is unreliable, since it may be anything between 5 and 7. We indicate this by saying that the measurement has two significant figures. In this case, the two significant figures are 2, which is reliable and 6, which has an error associated with it. You will learn more about the significant figures in section 2.7.

For this example, the relative error or the percentage error is

$$\delta a = \frac{0.1}{2.6} X\ 100 = 4\%$$

density is the ratio of the mass to the volume of the substance. If we have errors in the measurement of mass and of the sizes or dimensions, we must know what the error will be in the density of the substance. To make such estimates, we should learn how errors combine in various mathematical operations. For this, we use the following procedure.

2.6.2 Combination of Errors

If we do an experiment involving several measurements, we must know how the errors in all the measurements combine. For example,

How will you measure the length of a line?

What a naïve question, at this stage, you might say! But what if it is not a straight line? Draw a zigzag line in your copy, or on the blackboard. Well, not too difficult again. You might take a thread, place it along the line, open up the thread, and measure its length.

Now imagine that you want to measure the length of a national highway, a river, the railway track between two stations, or the boundary between two states or two nations. If you take a string of length 1 metre or 100 metre, keep it along the line, shift its position every time, the arithmetic of man-hours of labour and expenses on the project is not commensurate with the outcome. Moreover, errors are bound to occur in this enormous task. There is an interesting fact about this. France and Belgium share a common international boundary, whose length mentioned in the official documents of the two countries differs substantially!

Go one step beyond and imagine the coastline where land meets sea. Roads and rivers have fairly mild bends as compared to a coastline. Even so, all documents, including our school books, contain information on the length of the coastline of Gujarat or Andhra Pradesh, or the common boundary between two states, etc. Railway tickets come with the distance between stations printed on them. We have ‘milestones’ all along the roads indicating the distances to various towns. So, how is it done?

One has to decide how much error one can tolerate and optimise cost-effectiveness. If you want smaller errors, it will involve high technology and high costs. Suffice it to say that it requires fairly advanced level of physics, mathematics, engineering and technology. It belongs to the areas of fractals, which has lately become popular in theoretical physics. Even then one doesn’t know how much to rely on the figure that props up, as is clear from the story of France and Belgium. Incidentally, this story of the France-Belgium discrepancy appears on the first page of an advanced Physics book on the subject of fractals and chaos!

(a) Error of a sum or a difference

Suppose two physical quantities *A* and *B* have Measured values $A \pm \mathrm{A}$, $B \pm \mathrm{B}$ respectively Where A and B are their absolute errors. We Wish to find the error Z in the sum $Z = A + B$.

We have by addition, $Z \pm \Delta \mathrm{Z} = (A \pm \Delta A) + (B \pm \Delta B)$.

The maximum possible error in $Z\ \Delta Z = \Delta A + \Delta B$

For the difference $Z = A - B$, we have $Z \pm \Delta Z = (A \pm \Delta A) - (B \pm \Delta B)$

$$= (A - B) \pm \Delta A \pm \Delta B$$

Or, $\pm \Delta Z = \pm \Delta \mathrm{A} \pm \Delta B$

The maximum value of the error Z is again $\Delta A + \Delta B$.

Hence the rule: When two quantities are added or subtracted, the absolute error in the final result is the sum of the absolute errors in the individual quantities.

Example 2.8 The temperatures of two bodies measured by a thermometer are $t_1 = 20\ ^0\mathrm{C} \pm 0.5\ ^0\mathrm{C}$ and $t_2 = 50\ ^0\mathrm{C} \pm 0.5\ ^0\mathrm{C}$. Calculate the temperature difference and the error theirin.

Answer $t' = t_2 - t_1 = (50\ ^0\mathrm{C} \pm 0.5\ ^0\mathrm{C}) - (20^0\mathrm{C} \pm 0.5\ ^0\mathrm{C})$ $t' = 30\ ^0\ \mathrm{C} \pm 1\ ^0\mathrm{C}$

(b) Error of a product or a quotient

Suppose $Z = AB$ and the measured values of *A* and *B* are $A \pm \Delta A$ and $B \pm \Delta B$. Then

$$Z \pm \Delta Z = (A \pm \Delta A)(B \pm \Delta B)$$

$= AB \pm B\Delta A \pm A\Delta B \pm \Delta A\Delta B$. Dividing LHS by *Z* and RHS by *AB* we have,

$$1 \pm (\Delta Z/Z) = 1 \pm (\Delta A/A) \pm (\Delta B/B) \pm (\Delta A/A)(\Delta B/B).$$

Since *A* and *B* are small, we shall ignore their product.

Hence the maximum relative error

$$\Delta Z/Z = (\Delta \mathrm{A}/\mathrm{A}) + (\Delta \mathrm{B}/\mathrm{B}).$$

You can easily verify that this is true for division also.

Hence the rule: When two quantities are multiplied or divided, the relative error in the result is the sum of the relative errors in the multipliers.

Example 2.9 The resistance $R = V/I$ where $V = (100 \pm 5)$V and $I = (10 \pm 0.2)$A. Find the percentage error in R.

Answer The percentage error in V is 5% and in I it is 2%. The total error in R would therefore be

5% + 2% = 7%.

Example 2.10 Two resistors of resistances $R_1 = 100 \pm 3$ ohm and $R_2 = 200 \pm 4$ ohm are connected (a) in series, (b) in parallel. Find the equivalent resistance of the (a) series combination, (b) parallel combination. Use for (a) the relation $R = R_1 + R_2$, and for (b) $\frac{1}{R'} = \frac{1}{R_1} + \frac{1}{R_2}$

Answer (a) The equivalent resistance of series combination

$$R = R_1 + R_2 = (100 \pm 3) \text{ ohm} + (200 \pm 4) \text{ ohm}$$

$$= 300 \pm 7 \text{ ohm}.$$

(a) The equivalent resistance of parallel combination

$$R' = \frac{R_1 \ R_2}{R_1 + R_2} = \frac{200}{3} = 66.7 \ ohm$$

Then, from

$$\frac{1}{R'} = \frac{1}{R_1} + \frac{1}{R_2}$$

We get $\frac{\Delta R'}{R'^2} = \frac{\Delta R_1}{R_1^2} + \frac{\Delta R_2}{R_2^2}$

$$R' = (R')^2 \frac{\Delta R_1}{R_1^2} + (R')^2 \frac{\Delta R_2}{R_2^2}$$

$$= (66.7/100)^2 \times 3 + (66.7/200)^2 \times 4 = 1.8$$

Then, $R' = 66.7 \pm 1.8$ ohm

(Here, ΔR is expressed as 1.8 instead of 2 to keep in confirmity with the rules of significant figures.)

(c) Error in case of a measured quantity raised to a power

Suppose $Z = A^2$, Then,

$\Delta Z/Z = (\Delta A/A) + (\Delta A/A) = 2 (\Delta A/A)$. Hence, the relative error in A^2 is two times the error in A. In general, if $Z = A^p B^q/C^r$ Then, $\Delta Z/Z = p (\Delta A/A) + q (\Delta B/B) + r (\Delta C/C)$.

Hence the rule : **The relative error in a physical quantity raised to the power k is the k times the relative error in the individual quantity.**

Example 2.11 Find the relative error in Z, if $Z = A^4B^{1/3}/CD^{3/2}$

Answer The relative error in Z is Z/Z =

$4(A/A) +(1/3) (B/B) + (C/C) + (3/2) (D/D)$.

Example 2.12 The period of oscillation of a simple pendulum is $T = 2\pi\sqrt{l/g}$ Measured value of L is 20.0 cm known to 1 mm accuracy and time for 100 oscillations of the pendulum is found to be 90 s using a wrist watch of 1 s resolution. What is the accuracy in the determination of g?

Answer $g = 4\pi^2L/T^2$

Here T = $\frac{t}{n}$ and $\Delta t = \frac{\Delta t}{n}$. Therefore, $\frac{\Delta T}{T} = \frac{\Delta t}{t}$.

The errors in both L and t are the least count errors. Therefore,

$(\Delta g/g) = (\Delta L/L) + 2(\Delta T/T)$

$$\frac{0.1}{20.0} + 2\frac{1}{90} = 0.032$$

Thus, the percentage error in g is

$100(\Delta g/g) = (\Delta L/L) + 2 \times 100 (\Delta T/T) = 3\%$

2.7 SIGNIFICANT FIGURES

As discussed above, every measurement involves errors. Thus, the result of measurement should be reported in a way that indicates the precision of measurement. Normally, the reported result of measurement is a number that includes all digits in the number that are known reliably plus the first digit that is uncertain. The reliable digits plus the first uncertain digit are known as **significant digits** or **significant figures**.

If we say the period of oscillation of a simple pendulum is 1.62 s, the digits 1 and 6 are reliable and certain, while the digit 2 is uncertain. Thus, the measured value has three significant figures. The length of an object reported after measurement to be 287.5 cm has four significant figures, the digits 2, 8, 7 are certain while the digit 5 is uncertain. Clearly, reporting the result of measurement that includes more digits than the significant digits is superfluous and also misleading since it would give a wrong idea about the precision of measurement.

The rules for determining the number of significant figures can be understood from the following examples. Significant figures indicate, as already mentioned, the precision of measurement which depends on the least count of the measuring instrument. **A choice of change of different units does not change the number of significant digits or figures in a measurement.** This important remark makes most of the following observations clear:

(1) For example, the length 2.308 cm has four significant figures. But in different units, the same value can be written as 0.02308 m or 23.08 mm or 23080 μm.

All these numbers have the same number of significant figures (digits 2, 3, 0, 8), namely four. This shows that the location of decimal point is of no consequence in determining the number of significant figures.

The example gives the following rules:

- **All the non-zero digits are significant.**
- **All the zeros between two non-zero digits are significant, no matter where the decimal point is, if at all.**
- **If the number is less than 1, the zero(s) on the right of decimal point but to the left of the first non-zero digit are not significant.** [In $\underline{0}.\underline{00}$ 2308, the underlined zeroes are not significant].
- **The terminal or trailing zero(s) in a number without a decimal point are not significant.**
- **The trailing zero(s) in a number with a decimal point are significant.** [The numbers 3.500 or 0.06900 have four significant figures each.] [Thus 123 m = 12300 cm = 123000 mm has *three* significant figures, the trailing zero(s) being not significant.] However, you can also see the next observation.

(2) There can be some confusion regarding the trailing zero(s). Suppose a length is reported to be 4.700 m. It is evident that the zeroes here are meant to convey the precision of measurement and are, therefore, significant. [If these were not, it would be superfluous to write them explicitly, the reported measurement would have been simply 4.7 m]. Now suppose we

change units, then 4.700 m = 470.0 cm = 4700 mm = 0.004700 km.

Since the last number has trailing zero(s) in a number with no decimal, we would conclude erroneously from observation (1) above that the number has *two* significant figures, while in fact, it has four significant figures and a mere change of units cannot change the number of significant figures

(3) **To remove such ambiguities in determining the number of significant figures, the best way is to report every measurement in scientific notation (in the power of 10).** In this notation, every number is expressed as $a \times 10^b$, where a is a number between 1 and 10, and b is any positive or negative exponent (or power) of 10. In order to get an approximate idea of the number, we may round off the number a to 1 (for $a \leq 5$) and to 10 (for $5 < a \leq 10$). Then the number can be expressed approximately as 10^b in which the exponent (or power) b of 10 is called **order of magnitude** of the physical quantity. When only an estimate is required, the quantity is of the order of 10^b. For example, the diameter of the earth (1.28×10^7m) is of the order of 10^7m with the order of magnitude 7. The diameter of hydrogen atom (1.06×10^{-10}m) is of the order of 10^{-10}m, with the order of magnitude –10. Thus, the diameter of the earth is 17 orders of magnitude larger than the hydrogen atom.

It is often customary to write the decimal after the first digit. Now the confusion mentioned in (a) above disappears :

$$4.700 \text{ m} = 4.700 \times 10^2 \text{ cm}$$

$$= 4.700 \times 10^3 \text{ mm} = 4.700 \times 10^{-3} \text{ km}$$

The power of 10 is irrelevant to the determination of significant figures. However, all Zeroes appearing in the base number in the scientific notation are significant. Each number in this case has *four* significant figures.

Thus, in the scientific notation, no confusion arises about the trailing zero(s) in the base number a. They are always significant.

(4) The scientific notation is ideal for reporting measurement. But if this is not adopted, we use the rules adopted in the preceding example:

- **For a number greater than 1, without any decimal, the trailing zero(s) are not significant.**
- **For a number with a decimal, the trailing zero(s) are significant.**

(5) The digit 0 conventionally put on the left of a decimal for a number less than 1 (like 0.1250) is never significant. However, the zeroes at the end of such number are significant in a measurement.

(6) The multiplying or dividing factors which are neither rounded numbers nor numbers representing measured values are exact and have infinite number of significant digits. For example in $r = d/2$ or $s = 2\pi r$, the factor 2 is an exact number and it can be written as 2.0, 2.00 or 2.0000 as required. Similarly, in $T= t/n$, n is an exact number

2.71 Rules for Arithmetic Operations with Significant Figures

The result of a calculation involving approximate measured values of quantities (i.e. values with limited number of significant figures) must reflect the uncertainties in the original measured values. It cannot be more accurate than the original measured values themselves on which the result is based. In general, the final result should not have more significant figures than the original data from which it was obtained. Thus, if mass of an object is measured to be, say, 4.237 g (four significant figures) and its volume is measured to be 2.51 cm^3, then its density, by mere arithmetic division, is 1.68804780876 g/cm^3 upto 11 decimal places. It would be clearly absurd and irrelevant to record the calculated value of density to such a precision when the measurements on which the value is based, have much less precision. The following rules for arithmetic operations with significant figures ensure that the final result of a calculation is shown with the precision that is consistent with the precision of the input measured values:

(1) **In multiplication or division, the final result should retain as many significant figures as are there in the original number with the least significant figures.**

Thus, in the example above, density should be reported to *three* significant figures.

Density = $\frac{4.237\ g}{2.51\ cm^3}$ = 1.69 cm^{-3}

Similarly, if the speed of light is given as 3.00×10^8 m s^{-1} (*three* significant figures) and one year (1y = 365.25 d) has 3.1557×10^7 s (*five* significant figures), the light year is 9.47×10^{15} m (*three* significant figures).

(2) **In addition or subtraction, the final result should retain as many decimal places as are there in the number with the least decimal places.**

For example, the sum of the numbers 436.32 g, 227.2 g and 0.301 g by mere arithmetic addition, is 663.821 g. But the least precise measurement (227.2 g) is correct to only one decimal place. The final result should, therefore, be rounded off to 663.8 g.

Similarly, the difference in length can be expressed as:

$0.307 \text{ m} - 0.304 \text{ m} = 0.003 \text{ m} = 3 \times 10^{-3} \text{ m}$.

Note that we should not use the *rule* (1) applicable for multiplication and division and write 664 g as the result in the example of **addition** and 3.00×10^{-3} m in the example of **subtraction**. They do not convey the precision of measurement properly. For addition and subtraction, the rule is in terms of decimal places.

2.7.2 Rounding off the Uncertain Digits

The result of computation with approximate numbers, which contain more than one uncertain digit, should be rounded off. The rules for rounding off numbers to the appropriate significant figures are obvious in most cases. A number $2.74\underline{6}$ rounded off to three significant figures is 2.75, while the number 2.743 would be 2.74. The *rule* by convention is that the **preceding digit is raised by 1 if the insignificant digit to be dropped (the underlined digit in this case) is more than 5, and is left unchanged if the latter is less than 5**. But what if the number is $2.74\underline{5}$ in which the insignificant digit is 5. Here, the convention is that **if the preceding digit is even, the insignificant digit is simply dropped and, if it is odd, the preceding digit is raised by** 1. Then, the number $2.74\underline{5}$ rounded off to three significant figures becomes 2.74. On the other hand, the number $2.73\underline{5}$ rounded off to three significant figures becomes 2.74 since the preceding digit is odd.

In any involved or complex multi-step calculation, you should retain, in intermediate steps, one digit more than the significant digits and round off to proper significant figures at the end of the calculation. Similarly, a number known to be within many significant figures, such as in $2.99792458 \cdot 10^8$ m/s for the speed of light in vacuum, is rounded off to an approximate value $3 \cdot 10^8$ m/s , which is often employed in computations. Finally, remember that exact numbers that appear in formulae like $T = 2\pi\sqrt{l/g}$ have a large (infinite) number of significant figures. The value of π = 3.1415926.... is known to a large number of significant figures. You may take the value as 3.142 or 3.14 for π, with limited number of significant figures as required in specific cases.

Example 2.13 Each side of a cube is measured to be 7.203 m. What are the total surface area and the volume of the cube to appropriate significant figures?

Answer The number of significant figures in the measured length is 4. The calculated area and the volume should therefore be rounded off to 4 significant figures.

Surface area of the cube = $6(7.203)^2$ m^2

$= 311.299254$ m^2

$= 311.3$ m^2

Volume of the cube = $(7.203)^3$ m^3

$= 373.714754$ m^3

$= 373.7$ m^3

Example 2.14 5.74 g of a substance occupies 1.2 cm^3. Express its density by keeping the significant figures in view.

Answer There are 3 significant figures in the measured mass whereas there are only 2 significant figures in the measured volume. Hence the density should be expressed to only 2 significant figures.

$$\text{Density} = \frac{5.74}{1.2}\ \text{g cm}^{-3} = 4.8\ \text{g cm}^{-3}$$

2.72 Rules for Determining the Uncertainty in the Results of Arithmatic Calculations

The rules for determining the uncertainty or error in the number/measured quantity in arithmetic operations can be understood from the following examples.

(1) If the length and breadth of a thin rectangular sheet are measured, using a metre scale as 16.2 cm and, 10.1 cm respectively, there are three significant figures in each measurement. It means that the length l may be written as

$$l = 16.2 \pm 0.1 \text{ cm}$$

$$= 16.2 \text{ cm} \pm 0.6\ \%.$$

Similarly, the breadth b may be written as

$$b = 10.1 \pm 0.1 \text{ cm}$$

$$= 10.1 \text{ cm} \pm 1\ \%$$

Then, the error of the product of two (or more) experimental values, using the combination of errors rule, will be

$lb = 163.62\ \text{cm}^2 \pm 1.6\%$

$= 163.62 \pm 2.6\ \text{cm}^2$

This leads us to quote the final result as

$lb = 164 \pm 3\ \text{cm}^2$

Here 3 cm^2 is the uncertainty or error in the estimation of area of rectangular sheet.

(2) **If a set of experimental data is specified to n significant figures, a result obtained by combining the data will also be valid to n significant figures.**

However, if data are subtracted, the number of significant figures can be reduced. For example, 12.9 g – 7.06 g, both specified to three significant figures, cannot properly be evaluated as 5.84 g but only as 5.8 g, as uncertainties in subtraction or addition combine in a different fashion (smallest number of decimal places rather than the number of significant figures in any of the number added or subtracted).

(3) **The relative error of a value of number specified to significant figures depends not only on n but also on the number itself.**

For example, the accuracy in measurement of mass 1.02 g is ± 0.01 g whereas another measurement 9.89 g is also accurate to ± 0.01 g. The relative error in 1.02 g is

$= (\pm 0.01/1.02) \times 100\ \%$

$= \pm 1\%$

Similarly, the relative error in 9.89 g is

$= (\pm 0.01/9.89) \times 100\ \%$

$= \pm 0.1\ \%$

Finally, remember that **intermediate results in a multi-step computation should be calculated to one more significant figure in every measurement than the number of digits in the least precise measurement.**

These should be justified by the data and then the arithmetic operations may be carried out; otherwise rounding errors can build up. For example, the reciprocal of 9.58, calculated (after rounding off) to the same number of significant figures (three) is 0.104, but the reciprocal of 0.104

calculated to three significant figures is 9.62. However, if we had written 1/9.58 = 0.1044 and then taken the reciprocal to three significant figures, we would have retrieved the original value of 9.58.

This example justifies the idea to retain one more extra digit (than the number of digits in the least precise measurement) in intermediate steps of the complex multi-step calculations in order to avoid additional errors in the process of rounding off the numbers.

2.8 DIMENSIONS OF PHYSICAL QUANTITIES

The nature of a physical quantity is described by its dimensions. All the physical quantities represented by derived units can be expressed in terms of some combination of seven fundamental or base quantities. We shall call these base quantities as the seven dimensions of the physical world, which are denoted with square brackets [ ]. Thus, length has the dimension [L], mass [M], time [T], electric current [A], thermodynamic temperature [K], luminous intensity [cd], and amount of substance [mol].

The dimensions of a physical quantity are the powers (or exponents) to which the base quantities are raised to represent that quantity. Note that using the square brackets [ ] round a quantity means that we are dealing with '**the dimensions of**' the quantity.

In mechanics, all the physical quantities can be written in terms of the dimensions [L], [M] and [T]. For example, the volume occupied by an object is expressed as the product of length, breadth and height, or three lengths. Hence the dimensions of volume are $[L] \times [L] \times [L] = [L]^3 = [L^3]$. As the volume is independent of mass and time, it is said to possess zero dimension in mass $[M^\circ]$, zero dimension in time $[T^\circ]$ and three dimensions in length.

Similarly, force, as the product of mass and acceleration, can be expressed as Force = mass × acceleration = mass × (length)/$(\text{time})^2$

The dimensions of force are $[M][L]/[T]^2 = [MLT^{-2}]$. Thus, the force has one dimension in mass, one dimension in length, and –2 dimensions in time. The dimensions in all other base quantities are zero.

Note that in this type of representation, the magnitudes are not considered. It is the quality of the type of the physical quantity that enters. Thus, a change in velocity, initial velocity, average velocity, final velocity, and speed are all equivalent in this context. Since all these quantities can be expressed as length/time, their dimensions are $[L]/[T]$ or $[L\,T^{-1}]$.

2.9 DIMENSIONAL FORMULAE AND DIMENSIONAL EQUATIONS

The expression which shows how and which of the base quantities represent the dimensions of a physical quantity is called the *dimensional formula* of the given physical quantity. For example, the dimensional formula of the volume is $[M^{\circ} L^3 T^{\circ}]$, and that of speed or velocity is $[M^{\circ} L T^{-1}]$. Similarly, $[M^{\circ} L T^{-2}]$ is the dimensional formula of acceleration and $[M L^{-3} T^{\circ}]$ that of mass density.

An equation obtained by equating a physical quantity with its dimensional formula is called the **dimensional equation** of the physical quantity.

Thus, the dimensional equations are the equations, which represent the dimensions of a physical quantity in terms of the base quantities. For example, the dimensional equations of volume $[V]$, speed $[v]$, force $[F]$ and mass density $[\rho]$ may be expressed as

$$[V] = [M^0 L^3 T^0]$$

$$[v] = [M^0 L T^{-1}]$$

$$[F] = [M L T^{-2}]$$

$$[\rho] = [M L^{-3} T^0]$$

The dimensional equation can be obtained from the equation representing the relations between the physical quantities. The dimensional formulae of a large number and wide variety of physical quantities, derived from the equations representing the relationships among other physical quantities and expressed in terms of base quantities are given in Appendix 9 for your guidance and ready reference.

2.10 DIMENSIONAL ANALYSIS AND ITS APPLICATIONS

The recognition of concepts of dimensions, which guide the description of physical behaviour is of basic importance as only those physical quantities can be added or subtracted which have the same dimensions. A thorough understanding of dimensional analysis helps us in deducing certain relations among different physical quantities and checking the derivation, accuracy and dimensional consistency or homogeneity of various mathematical expressions. When magnitudes of two or more physical quantities are multiplied, their units should be treated in the same manner as ordinary algebraic symbols. We can cancel identical units in the numerator and denominator. The same is true for dimensions of a physical quantity. Similarly, physical quantities represented by symbols on both sides of a mathematical equation must have the same dimensions.

2.10.1 Checking the Dimensional Consistency of Equations

The magnitudes of physical quantities may be added together or subtracted from one another only if they have the same dimensions. In other words, we can add or subtract similar physical quantities. Thus, velocity cannot be added to force, or an electric current cannot be subtracted from the thermodynamic temperature. This simple principle called **the principle of homogeneity of dimensions** in an equation is extremely useful in checking the correctness of an equation. If the dimensions of all the terms are not same, the equation is wrong. Hence, if we derive an expression for the length (or distance) of an object, regardless of the symbols appearing in the original mathematical relation, when all the individual dimensions are simplified, the remaining dimension must be that of length. Similarly, if we derive an equation of speed, the dimensions on both the sides of equation, when simplified, must be of length/ time, or $[\mathrm{L\ T^{-1}}]$.

Dimensions are customarily used as a preliminary test of the consistency of an equation, when there is some doubt about the correctness of the equation. However, the dimensional consistency does not guarantee correct equations. It is uncertain to the extent of dimensionless quantities or functions. The arguments of special functions, such as the trigonometric, logarithmic and exponential functions must be dimensionless. A pure number, ratio of similar physical quantities, such as angle as the ratio (length/length), refractive index as the ratio (speed of light in vacuum/speed of light in medium) etc., has no dimensions.

Now we can test the dimensional consistency or homogeneity of the equation

$$x = x_0 + v_0\, t + (1/2)\, a\, t^2$$

for the distance x travelled by a particle or body in time t which starts from the position x_0 with an initial velocity v_0 at time $t = 0$ and has uniform acceleration a along the direction of motion. The dimensions of each term may be written as $[x] = [\mathrm{L}]$

$$[x_0\,] = [\mathrm{L}]$$

$$[v_0\, t] = [\mathrm{L\ T^{-1}}]\,[\mathrm{T}] = [\mathrm{L}]$$

$$[(1/2)\, a\, t^2] = [\mathrm{L\ T^{-2}}]\,[\mathrm{T^2}] = [\mathrm{L}]$$

As each term on the right hand side of this equation has the same dimension, namely that of length, which is same as the dimension of left hand side of the equation, hence this equation is a dimensionally correct equation.

It may be noted that a test of consistency of dimensions tells us no more and no less than a test of consistency of units, but has the advantage that we need not commit ourselves to a particular choice of units, and we need not worry about conversions among multiples and submultiples of the units. It may be borne in mind that **if an equation fails this consistency test, it is proved wrong, but if it passes, it is not proved right. Thus, a dimensionally correct equation need not be actually an exact (correct) equation, but a dimensionally wrong (incorrect) or inconsistent equation must be wrong**.

Example 2.15 Let us consider an equation $\frac{1}{2}$ mv^2 = mgh, where *m* is the mass of the body, *v* its velocity, *g* is the acceleration due to gravity and *h* is the height. Check whether this equation is dimensionally correct.

Answer The dimensions of LHS are

$$[M]\,[L\,T^{-1}\,]^2 = [M]\,[\,L^2\,T^{-2}]$$

$$= [M\,L^2\,T^{-2}]$$

The dimensions of RHS are

$$[M][LT^{-2}]\,[L] = [M][L^2T^{-2}]$$

$$= [M\,L^2\,T^{-2}]$$

The dimensions of LHS and RHS are the same and hence the equation is dimensionally correct.

Example 2.16 The SI unit of energy is J = kg m^2 s^{-2}; that of speed *v* is m s^{-1} and of acceleration *a* is m s^{-2}. Which of the formulae for kinetic energy (*K*) given below can you rule out on the basis of dimensional arguments (*m* stands for the mass of the body):

(a) $K = m^2 v^3$

(b) $K = (1/2)mv^2$

(c) $K = ma$

(d) $K = (3/16)mv^2$

(e) $K = (1/2)mv^2 + ma$

Answer Every correct formula or equation must have the same dimensions on both sides of the equation. Also, only quantities with the same physical dimensions can be added or subtracted. The dimensions of the quantity on the right side are [M^2 L^3 T^{-3}] for (a); [M L^2 T^{-2}] for (b) and (d); [M L T^{-2}] for (c). The quantity on the right side of (e) has no proper dimensions since two quantities of different dimensions have been added. Since the kinetic energy *K* has the dimensions of [M L^2 T^{-2}], formulas (a), (c) and (e) are ruled out. Note that dimensional arguments cannot tell which of the two, (b) or (d), is the correct formula. For this, one must turn to the actual definition of kinetic energy (see Chapter 6). The correct formula for kinetic energy is given by (b).

2.10.2 Deducing Relation among the Physical Quantities

The method of dimensions can sometimes be used to deduce relation among the physical quantities. For this we should know the dependence of the physical quantity on other quantities (upto three physical quantities or linearly independent variables) and consider it as a product type of the dependence. Let us take an example

Example 2.17 Consider a simple pendulum, having a bob attached to a string, that oscillates under the action of the force of gravity. Suppose that the period of oscillation of the simple pendulum depends on its length (*l*), mass of the bob (*m*) and acceleration due to gravity (*g*). Derive the expression for its time period using method of dimensions.

Answer The dependence of time period *T* on the quantities *l*, *g* and *m* as a product may be written as :

$$T = k\, l^x g^y m^z$$

where k is dimensionless constant and *x*, *y* and *z* are the exponents.

By considering dimensions on both sides, we have

$$[L^o M^o T^1] = [L^1][L^1 T^{-2}]^y [M^1]^z$$

$$= L^{x+y} T^{-2y} M^z$$

On equating the dimensions on both sides, we have

$x + y = 0$; $-2y = 1$; and $z = 0$

So that $x = 1, y = -1, z = 0$ 2 2

Then, $T = k\, l^{1/2} g^{-1/2}$

$T = k\sqrt{l/g}$

Note that value of constant k cannot be obtained by the method of dimensions. Here it does not matter if some number multiplies the right side of this formula, because that does not affect its dimensions

Actually, $k = 2\pi \sqrt{l/g}$

Dimensional analysis is very useful in deducing relations among the interdependent physical quantities. However, dimensionless constants cannot be obtained by this method. The method of dimensions can only test the dimensional validity, but not the exact relationship between physical quantities in any equation. It does not distinguish between the physical quantities having same dimensions.

SUMMARY

1. Physics is a quantitative science, based on measurement of physical quantities. Certain physical quantities have been chosen as fundamental or base quantities (such as length, mass, time, electric current, thermodynamic temperature, amount of substance, and luminous intensity).
2. Each base quantity is defined in terms of a certain basic, arbitrarily chosen but properly standardised reference standard called unit (such as metre, kilogram, second, ampere, kelvin, mole and candela). The units for the fundamental or base quantities are called fundamental or base units.
3. Other physical quantities, derived from the base quantities, can be expressed as a combination of the base units and are called derived units. A complete set of units, both fundamental and derived, is called a system of units.
4. The International System of Units (SI) based on seven base units is at present internationally accepted unit system and is widely used throughout the world.
5. The SI units are used in all physical measurements, for both the base quantities and the derived quantities obtained from them. Certain derived units are expressed by means of SI units with special names (such as joule, newton, watt, etc).
6. The SI units have well defined and internationally accepted unit symbols (such as m for metre, kg for kilogram, s for second, A for ampere, N for newton etc.).
7. Physical measurements are usually expressed for small and large quantities in scientific notation, with powers of 10. Scientific notation and the prefixes are used to simplify measurement notation and numerical computation, giving indication to the precision of the numbers.
8. Certain general rules and guidelines must be followed for using notations for physical quantities and standard symbols for SI units, some other units and SI prefixes for expressing properly the physical quantities and measurements.
9. In computing any physical quantity, the units for derived quantities involved in the relationship(s) are treated as though they were algebraic quantities till the desired units are

obtained.

10. Direct and indirect methods can be used for the measurement of physical quantities. In measured quantities, while expressing the result, the accuracy and precision of measuring instruments along with errors in measurements should be taken into account.

11. In measured and computed quantities proper significant figures only should be retained. Rules for determining the number of significant figures, carrying out arithmetic operations with them, and ‘rounding off ‘ the uncertain digits must be followed.
12. The dimensions of base quantities and combination of these dimensions describe the nature of physical quantities. Dimensional analysis can be used to check the dimensional consistency of equations, deducing relations among the physical quantities, etc. A dimensionally consistent equation need not be actually an exact (correct) equation, but a dimensionally wrong or inconsistent equation must be wrong.

CHAPTER THREE

MOTION IN A STRAIGHT LINE

3.1 INTRODUCTION

Motion is common to everything in the universe. We walk, run and ride a bicycle. Even when we are sleeping, air moves into and out of our lungs and blood flows in arteries and veins. We see leaves falling from trees and water flowing down a dam. Automobiles and planes carry people from one place to the other. The earth rotates once every twenty-four hours and revolves round the sun once in a year. The sun itself is in motion in the Milky Way, which is again moving within its local group of galaxies.

Motion is change in position of an object with time. How does the position change with time? In this chapter, we shall learn how to describe motion. For this, we develop the concepts of velocity and acceleration. We shall confine ourselves to the study of motion of objects along a straight line, also known as **rectilinear motion**. For the case of rectilinear motion with uniform acceleration, a set of simple equations can be obtained. Finally, to understand the relative nature of motion, we introduce the concept of relative velocity.

In our discussions, we shall treat the objects in motion as point objects. This approximation is valid so far as the size of the object is much smaller than the distance it moves in a reasonable duration of time. In a good number of situations in real-life, the size of objects can be neglected and they can be considered as point-like objects without much error.

In **Kinematics**, we study ways to describe motion without going into the causes of motion. What causes motion described in this chapter and the next chapter forms the subject matter of Chapter 5.

3.2 POSITION, PATH LENGTH AND DISPLACEMENT

Earlier you learnt that motion is change in position of an object with time. In order to specify position, we need to use a reference point and a set of axes. It is convenient to choose a rectangular coordinate system consisting of three mutually perpendicular axes, labelled X-, Y-, and Z- axes. The point of intersection of these three axes is called origin (O) and serves as the **reference point**. The coordinates (x, y. z) of an object describe the position of the object with respect to this coordinate system. To measure time, we position a clock in this system. This coordinate system along with a clock constitutes a **frame of reference**.

If one or more coordinates of an object change with time, we say that the object is in motion. Otherwise, the object is said to be at rest with respect to this frame of reference. The choice of a set of axes in a frame of reference depends upon the situation. For example, for describing motion in one dimension, we need only one axis. To describe motion in two/three dimensions, we need a set of two/ three axes. Description of an event depends on the frame of reference chosen for the description. For example, when you say that a car is moving on a road, you are describing the car with respect to a frame of reference attached to you or to the ground. But with respect to a frame of reference attached with a person sitting in the car, the car is at rest.

To describe motion along a straight line, we can choose an axis, say *X*-axis, so that it coincides with the path of the object. We then measure the position of the object with reference to a conveniently chosen origin, say O, as shown in Fig. 3.1. Positions to the right of O are taken as positive and to the left of O, as negative. Following this convention, the position coordinates of point P and Q in Fig. 3.1 are +360 m and +240 m. Similarly, the position coordinate of point R is –120 m.

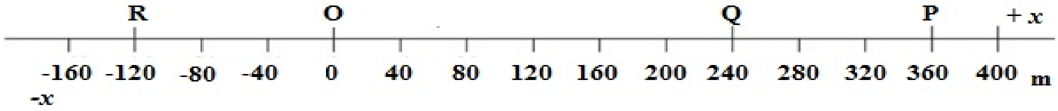


Fig. 3.1 *x-axis, origin and positions of a car at different times.*

Path length

Consider the motion of a car along a straight line. We choose the *x*-axis such that it coincides with the path of the car's motion and origin of the axis as the point from where the car started moving, i.e. the car was at $x = 0$ at $t = 0$ (Fig. 3.1). Let P, Q and R represent the positions of the car at different instants of time. Consider two cases of motion. In the first case, the car moves from O to P. Then the distance moved by the car is OP = +360 m. **This distance is called the path length** traversed by the car**.** In the second case, the car moves from O to P and then moves back from P to Q. During this course of motion, the path length traversed is OP + PQ = + 360 m (+120 m) = + 480 m. Path length is a scalar quantity — a quantity that has a magnitude only and no direction (see Chapter 4).

Displacement

It is useful to define another quantity displacement as the hange in position. Let x_1 and x_2 be the positions an object at time t_1 and t. Then its displacement, denoted by Δx, in time $\Delta t = (t_2 - t_1)$, is given by the difference between the final and initial positions:

$\Delta x = x_2 - x_1$ (We use the Greek letter delta (Δ) to denote a change in a quantity.)

If $x_2 > x_1$, Δx is positive; and if $x_2 < x_1$, Δx is negative.

Displacement has both magnitude and direction. Such quantities are represented by vectors. You will read about vectors in the next chapter. Presently, we are dealing with motion along a straight line (also called **rectilinear motion**) only. In one-dimensional motion, there are *only two* directions (backward and forward, upward and downward) in which an object can move, and these two directions can easily be specified by + and – signs. For example, displacement of the car in moving from O to P is:

$$\Delta x = = (+360 \text{ m}) - 0 \text{ m} = +360 \text{ m}$$

The displacement has a magnitude of 360 m and is directed in the positive x direction as indicated by the + sign. Similarly, the displacement of the car from P to Q is 240 m – 360 m = – 120 m. The negative sign indicates the direction of displacement. Thus, it is not necessary to use vector notation for discussing motion of objects in one-dimension.

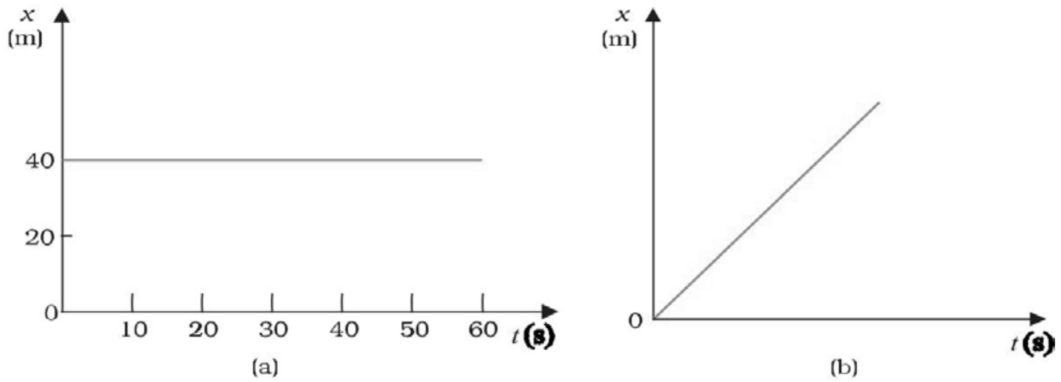
The magnitude of displacement may or may not be equal to the path length traversed by an object.

For example, for motion of the car from O to P, the path length is +360 m and the displacement is +360 m. In this case, the magnitude of displacement (360 m) is equal to the path length (360 m). But consider the motion of the car from O to P and back to Q. In this case, the path length = (+360 m) + (+120 m) = + 480 m. However, the displacement = (+240 m) – (0 m) = + 240 m. Thus, the magnitude of displacement (240 m) is not equal to the path length (480 m).

The magnitude of the displacement for a course of motion may be zero but the corresponding path length is **not zero**. For example, if the car starts from O, goes to P and then returns to O, the final position coincides with the initial position and the displacement is zero. However, the path length of this journey is OP + PO = 360 m + 360 m = 720 m.

Motion of an object can be represented by a position-time graph as you have already learnt about it. Such a graph is a powerful tool to represent and analyse different aspects of motion of an object. For motion along a straight line, say *X*-axis, only *x*-coordinate varies with time and we have an *x*-*t* graph. Let us first consider the simple case in which an object is stationary, e.g. a car standing still at $x = 40$ m. The position-time graph is a straight line parallel to the time axis, as shown in Fig. 3.2(a).

If an object moving along the straight line covers equal distances in equal intervals of time, it is said to be in **uniform motion** along a straight line. Fig. 3.2(b) shows the position-time graph of such a motion.



(a) (b)

Fig. 3.2 *Position-time graph of (a) stationary object, and (b) an object in uniform motion.*

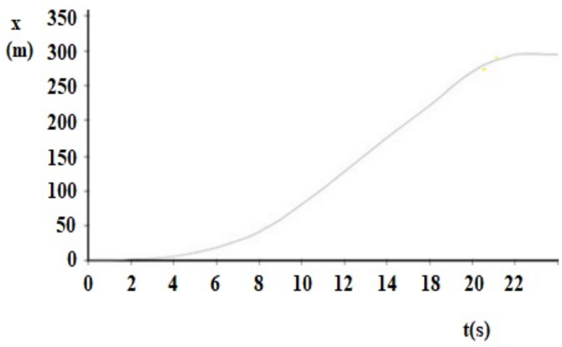


Fig. 3.3 *Position-time graph of a car.*

Now, let us consider the motion of a car that starts from rest at time $t = 0$ s from the origin O and picks up speed till $t = 10$ s and thereafter moves with uniform speed till $t = 18$ s. Then the brakes are applied and the car stops at $t = 20$ s and $x = 296$ m. The position-time graph for this case is shown in Fig. 3.3. We shall refer to this graph in our discussion in the following sections.

3.3 AVERAGE VELOCITY AND AVERAGE SPEED

When an object is in motion, its position changes with time. But how fast is the position changing with time and in what direction? To describe this, we define the quantity **average velocity**. Average velocity is defined as the change in position or displacement (*x*) divided by the time intervals (*t*), in which the displacement occurs:

$$\bar{v} = \frac{x_2 - x_1}{t_2 - t_1} = \frac{\Delta x}{\Delta t} \tag{3.1}$$

where x_2 and x_1 are the positions of the object at time t_2 and t_1, respectively. Here the bar over the symbol for velocity is a standard notation used to indicate an average quantity. The SI unit for velocity is m/s or ms^{-1}, although km h^{-1} is used in many everyday applications.

Like displacement, average velocity is also a vector quantity. But as explained earlier, for motion in a straight line, the directional aspect of the vector can be taken care of by + and – signs and we do not have to use the vector notation for velocity in this chapter.

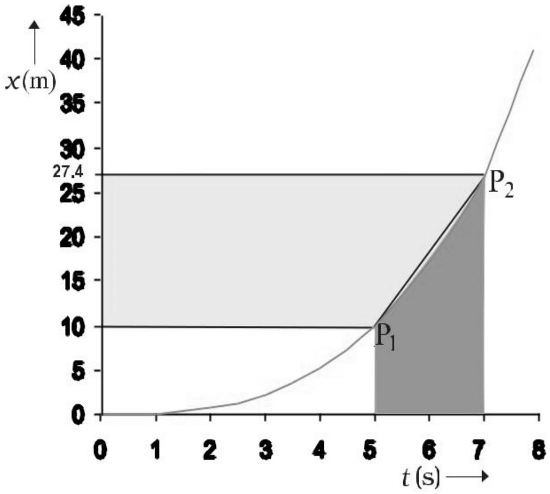


Fig. 3.4 *The average velocity is the slope of line* P_1P_2

Consider the motion of the car in Fig. 3.3. The portion of the *x*-*t* graph between *t* = 0 s and *t* = 8 s is blown up and shown in Fig. 3.4. As seen from the plot, the average velocity of the car between time *t* = 5 s and *t* = 7s is:

$$\bar{v} = \frac{x_2 - x_1}{t_2 - t_1} = \frac{(27.4 - 10.0)m}{(7-5)s} = 8.7 \text{ ms}^{-1}$$

Geometrically, this is the slope of the straight line P_1P_2 connecting the initial position P_1 to the final position P_2 as shown in Fig. 3.4. The average velocity can be positive or negative depending upon the sign of the displacement. It is zero if the displacement is zero. Fig. 3.5 shows the *x-t* graphs for an object, moving with positive velocity (Fig. 3.5a), moving with negative velocity (Fig. 3.5b) and at rest (Fig. 3.5c).

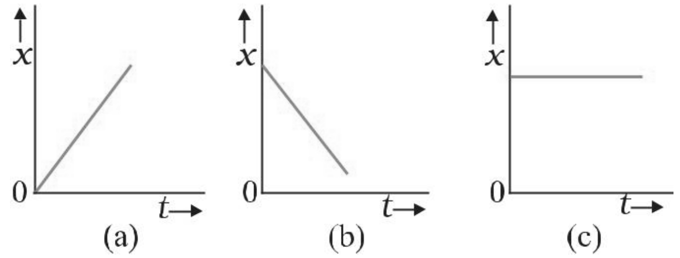


Fig. 3.5 *Position-time graph for an object (a) moving with positive velocity, (b) moving with negative velocity, and (c) at rest.*

Average velocity as defined above involves only the displacement of the object. We have seen earlier that the magnitude of displacement may be different from the actual path length. To describe the rate of motion over the actual path, we introduce another quantity called **average velocity.**

Average speed is defined as the total path length travelled divided by the total time interval during which the motion has taken place:

$$\text{Average speed} = \frac{Total\ Path\ length}{Total\ Time\ interval} \tag{3.2}$$

Average speed has obviously the same unit (ms^{-1}) as that of velocity. But it does not tell us in what direction an object is moving. Thus, it is always positive (in contrast to the average velocity which can be positive or negative). If the motion of an object is along a straight line and in the **same direction**, the magnitude of displacement is equal to the total path length. In that case, the magnitude of average velocity is equal to the average speed. . This is not always the case, as you will see in the following example.

Example 3.1 A car is moving along a straight line, say OP in Fig. 3.1. It moves from O to P in 18 s and returns from P to Q in 6.0 s. What are the average velocity and average speed of the car in going (a) from O to P? and (b) from O to P and back to Q?

Answer (a) Average velocity = $\frac{Displacement}{time\ interval}$

$$\bar{v} = \frac{+360\ m}{18\ s} + 20\ ms^{-1}$$

$$\text{Average speed} = \frac{Path\ length}{Time\ interval} = \frac{360\ m}{18\ s} = 20\ ms^{-1}$$

Thus, in this case the average speed is equal to the magnitude of the average velocity.

(b) In this case,

Average velocity = $\frac{Displacement}{time\ interval}$

$$= \frac{+\ 240\ m}{(18+6.0)s} = 10\ ms^{-1}$$

Average speed = $\frac{Path\ length}{Time\ interval} = \frac{OP+PQ}{\Delta t}$

$$= \frac{(360+120)m}{24\ s} = 20\ ms^{-1}$$

Thus, in this case the average speed is *not* equal to the magnitude of the average velocity. This happens because the motion here involves change in direction so that the path length is greater than the magnitude of displacement. This shows that **speed is, in general, greater than the magnitude of the velocity.**

If the car in Example 3.1 moves from O to P and comes back to O in the same time interval, average speed is 20 m/s but the average velocity is zero!

3.4 INSTANTANEOUS VELOCITY AND SPEED

The average velocity tells us how fast an object has been moving over a given time interval but does not tell us how fast it moves at different instants of time during that interval. For this, we define **instantaneous velocity** or simply velocity *v* at an instant *t*.

The velocity at an instant is defined as the limit of the average velocity as the time interval *t* becomes infinitesimally small. In other words,

$$v = \lim_{\Delta t \to 0} \Delta x/\Delta t \tag{3.3a}$$

$$= dx/dt \tag{3.3b}$$

where the symbol $\lim_{\Delta t \to 0}$ stands for the operation of taking limit as *t*0 of the quantity on its right. In the language of calculus, the quantity on the right hand side of Eq. (3.3a) is the differential coefficient of *x* with respect to *t* and is denoted by dx/dt (see Appendix 3.1). It is the rate of change of position with respect to time, at that instant.

We can use Eq. (3.3a) for obtaining the value of velocity at an instant either **graphically** or **numerically**. Suppose that we want to obtain graphically the value of velocity at time $t = 4$ s (point P) for the motion of the car represented in Fig. 3.3. The figure has been redrawn in Fig. 3.6 choosing different scales to facilitate the calculation.

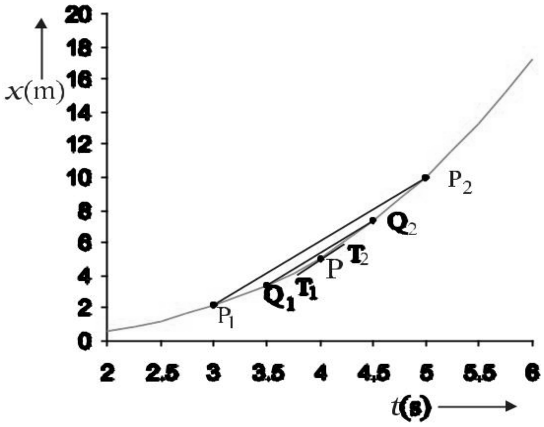


Fig. 3.6 *Determining velocity from position-time graph. Velocity at $t = 4$ s is the slope of the tangent to the graph at that instant.*

Let us take $t = 2$ s centred at $t = 4$ s. Then, by the definition of the average velocity, the slope of line P_1P_2 (Fig. 3.6) gives the value of average velocity over the interval 3 s to 5 s. Now, we decrease the value of t from 2 s to 1 s. Then line P_1P_2 becomes Q_1Q_2 and its slope gives the value of the average velocity over the interval 3.5 s to 4.5 s. In the limit $t \rightarrow 0$, the line P_1P_2 becomes tangent to the position-time curve at the point P and the velocity at $t = 4$ s is given by the slope of the tangent at that point. **It is difficult to show this process graphically. But if we use numerical method to obtain the value of the velocity, the meaning of the limiting process becomes clear**.

For the graph shown in Fig. 3.6, $x = 0.08\, t^3$. Table 3.1 gives the value of $x/\ t$ calculated for t equal to 2.0 s, 1.0 s, 0.5s, 0.1 s and 0.01 s centred at $t = 4.0$ s. The second and third columns give the value of $t_1 = \left(t - \frac{\Delta t}{2}\right)$ and $\left(\mathrm{t} + \frac{\Delta \mathrm{t}}{2}\right)$ and the fourth and fifth columns give the corresponding values of x, i.e. $x(t_1) = 0.08\, t_1^3$ and $x(t_2) = 0.08\, t_2^3$. The sixth column lists the difference $x = x(t_2) - x(t_1)$ and the last column gives the ratio of x and t, i.e. the average velocity corresponding to the value of Δt listed in the first column.

We see from Table 3.1 that as we decrease the value of Δt from 2.0 s to 0.010 s, the value of the average velocity approaches the limiting value 3.84 m s^{-1} which is the value of velocity at $t = 4.0$ s, i.e. the value of dx/dt at t= 4.0 s. In this manner, we can calculate velocity at each instant for motion of the car shown in Fig. 3.3. For this case, the variation of velocity with time is found to be as shown in Fig. 3.7.

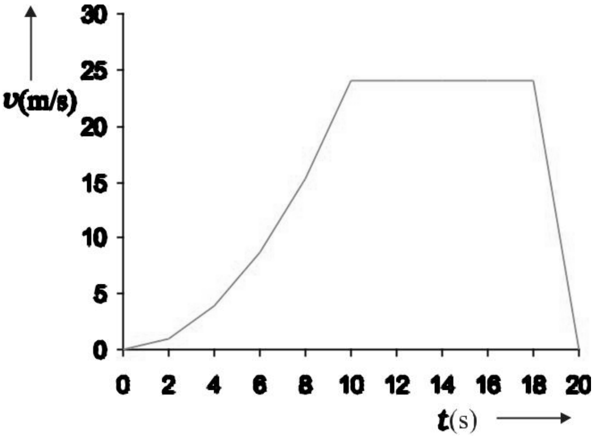


Fig. 3.7 *Velocity–time graph corresponding to motion shown in Fig. 3.3.*

The graphical method for the determination of the instantaneous velocity is always not a convenient method. For this, we must carefully plot the position–time graph and calculate the value of average velocity as *t* becomes smaller and smaller. It is easier to calculate the value of velocity at different instants if we have data of positions at different instants or exact expression for the position as a function of time. Then, we calculate x/ t from the data for decreasing the value of t and find the limiting value as we have done in Table 3.1 or use differential calculus for the given expression and caclculate dx/dt at different instants as done in the following example.

Table 3.1 Limiting value of $\Delta x/\Delta t$ at t=4s

Δt (s)	**t_1(s)**	**t_2(s)**	**xt_1 (m)**	**xt_2(m)**	**Δx(m)**	**$\Delta x/\Delta t$ (ms^{-1})**
2.0	3.0	5.0	2.16	10.0	7.84	3.92
1.0	3.5	4.5	3.43	7.29	3.86	3.86
0.5	3.75	4.25	4.21875	6.14125	1.9225	3.845
0.1	3.95	4.05	4.93039	5.31441	0.38402	3.8402
0.01	3.995	4.005	5.100824	5.139224	0.0384	3.8400

Example 3.2 The position of an object moving along x-axis given by $x = a + bt^2$ where a = 8.5 m, b = 2.5 ms^{-2} and t is measured in seconds. What is the average velocity between t = 2.0s and t = 4.0 s?

Answer In notation of differential calculus, the velocity is

$$v = \frac{dx}{dt} = \frac{d}{dt}(a + bt^2) = 2bt = 5.0\, t\, ms^{-1}$$

At t = 0 S, $v = 0\ ms^{-1}$ and t = 2.0 s, $v = 10\ ms^{-1}$

Average velocity = $\frac{x\,(4.0) - x\,(2.0)}{4.0 - 2.0}$

$= \frac{a + 16b - a - 4b}{2.0} = 6.0 \text{ x } b$

= 6.0 2.5 = ms^{-1}

This led to the concept of acceleration as the rate of change of velocity with time.

The average acceleration a over ā time interval is defined as the change of velocity divided by the time interval:

$$\bar{a} = \frac{v_2 - v_1}{t_2 - t_1} = \frac{\Delta v}{\Delta t} \qquad (3.4)$$

Where v_2 and v_1 are the instantaneous velocities or simply velocities at time t_2 and t_1.

It is the average change of velocity per unit time. The SI unit of acceleration is ms^{-2}.

On a plot of velocity versus time, the average acceleration is the slope of the straight line connecting the points corresponding to (v_2, t_2) and (v_1, t_1). The average acceleration for velocity-time graph shown in Fig. 3.7 for different time intervals 0 s - 10 s, 10 s – 18 s, and 18 s – 20 s are:

0 s- 10 s $\bar{a} = \frac{(24-0)ms^{-1}}{(10-0)s} = 2.4\ ms^{-2}$

10 s – 18 s $\bar{a} = \frac{(24-24)ms^{-1}}{(18-10)s} = 0\ ms^{-2}$

18 s – 20s $\bar{a} = \frac{(0-24)ms^{-1}}{(20-18)s} = -12\ ms^{-2}$

From Fig. 3.7, we note that during the period *t* =10 s to 18 s the velocity is constant. Between period *t* =18 s to *t* = 20 s, it is uniformly decreasing and during the period *t* = 0 s to *t* = 10 s, it is increasing. **Note that for uniform motion, velocity is the same as the average velocity at all instants**.

Instantaneous speed or simply speed is the magnitude of velocity. For example, a velocity of + 24.0 m s^{-1} and a velocity of 24.0 m s^{-1} both have an associated speed of 24.0 m s^{-1}. It should be noted that though average speed over a finite interval of time is greater or equal to the magnitude of the average velocity, instantaneous speed at an instant is equal to the magnitude of the instantaneous velocity at that instant. Why so?

3.5 ACCELERATION

The velocity of an object, in general, changes during its course of motion. How to describe this change? Should it be described as the rate of change in velocity **with distance** or **with time**? This was a problem even in Galileo's time. It was first thought that this change could be described by the rate of change of velocity with distance. But, through his studies of motion of freely falling objects and motion of objects on an inclined plane, Galileo concluded that the rate of change of velocity with time is a constant of motion for all objects in free fall. On the other hand, the change in velocity with distance is not constant – it decreases with the increasing distance of fall.

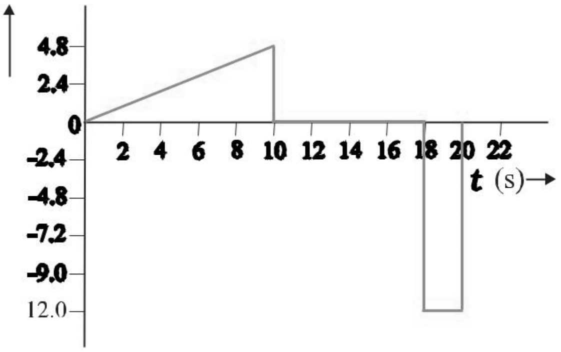


Fig.3.8 *Acceleration as a function of time for motion represented in Fig. 3.3.*

Instantaneous acceleration is defined in the same way as the instantaneous velocity:

$$a = \lim_{\Delta t \to \infty} \left(\frac{\Delta v}{\Delta t}\right) = \frac{dv}{dt} \qquad (3.5)$$

The acceleration at an instant is the slope of the tangent to the *v*–*t* curve at that instant. For the *v*–*t* curve shown in Fig. 3.7, we can obtain acceleration at every instant of time. The resulting *a* – *t* curve is shown in Fig. 3.8. We see that the acceleration is non uniform over the period 0 s to 10 s. It is zero between 10 s and 18 s and is constant with value –12 m s^{-2} between 18 s and 20 s. When the acceleration is uniform, obviously, it equals the average acceleration over that period.

Since velocity is a quantity having both magnitude and direction, a change in velocity may involve either or both of these factors. Acceleration, therefore, may result from a change in speed (magnitude), a change in direction or changes in both. Like velocity, acceleration can also be positive, negative or zero. Position-time graphs for motion with positive, negative and zero acceleration are shown in Figs. 3.9 (a), (b) and (c), respectively. Note that the graph curves upward for positive acceleration; downward for negative acceleration and it is a straight line for zero acceleration. As an exercise, identify in Fig. 3.3, the regions of the curve that correspond to these three cases.

Although acceleration can vary with time, our study in this chapter will be restricted to motion with constant acceleration. In this case, the average acceleration equals the constant value of acceleration during the interval. If the velocity of an object is *v* at *t* = 0 and *v* at time *t*,

we have

$$\bar{a} = \frac{v - v_0}{t - 0} \text{ or, } v = v_0 + at \tag{3.6}$$

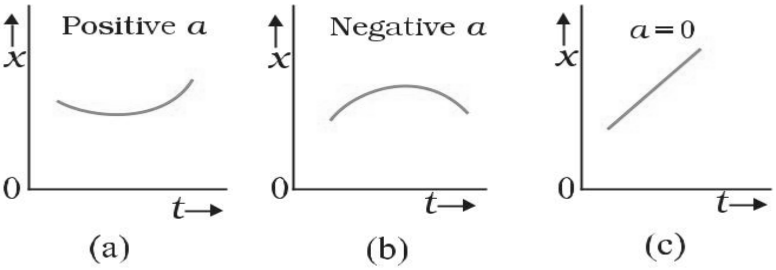


Fig. 3.9 Position-time graph for motion with (a) positive acceleration; (b) negative acceleration, and (c) zero acceleration

Let us see how velocity-time graph looks like for some simple cases. Fig. 3.10 shows velocity-time graph for motion with constant acceleration for the following cases:

(a) An object is moving in a positive direction with a positive acceleration, for example the motion of the car in Fig. 3.3 between

t = 0 s and t = 10 s

t = 0 s and t = 10 s.

(b) An object is moving in positive direction with a negative acceleration, for example, motion of the car in Fig 3.3 between *t* = 18 s and 20 s.

(c) An object is moving in negative direction with a negative acceleration, for example the motion of a car moving from O in Fig. 3.1 in negative *x*-direction with increasing speed.

(d) An object is moving in positive direction till time t_1, and then turns back with the same negative acceleration, for example the motion of a car from point O to point Q in Fig. 3.1 till time t_1 with decreasing speed and turning back and moving with the same negative acceleration.

An interesting feature of a velocity-time graph for any moving object is that **the area under the curve represents the displacement over a given time interval**. A general proof of this statement requires use of calculus.

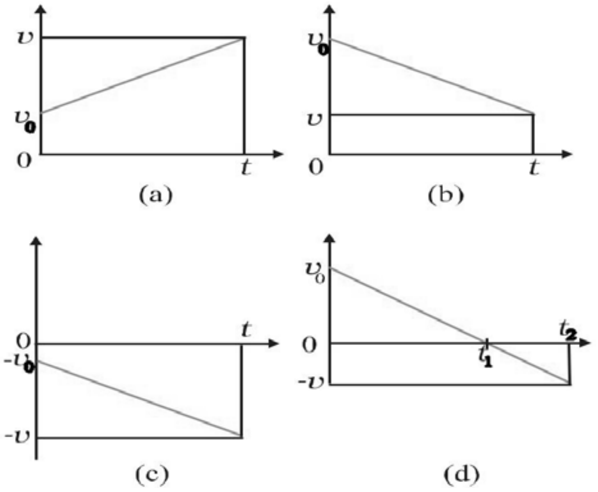


Fig. 3.10 *Velocity–time graph for motions with constant acceleration. (a) Motion in positive direction with positive acceleration (b) Motion in positive direction with negative acceleration, (c) Motion in negative direction with negative acceleration, (d) Motion of an object with negative acceleration that changes direction at time t1. Between times 0 to t1, its moves in positive x - direction and between t1 and t2 it moves in the opposite direction*

We can, however see that it is true for the simple case of an object moving with constant velocity u. Its velocity-time graph is as shown in Fig. 3.11.

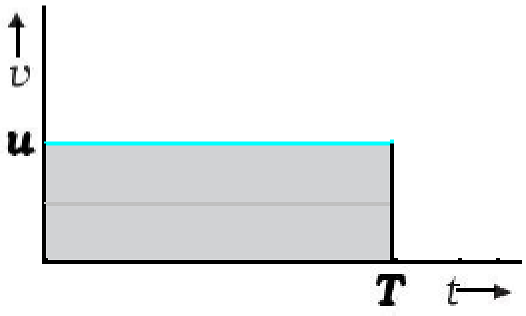


Fig. 3.11 *Area under v–t curve equals displacement of the object over a given time interval.*

The v-t curve is a straight line parallel to the time axis and the area under it between $t = 0$ and $t = T$ is the area of the rectangle of height u and base T. Therefore, area = $u \times T = uT$ which is the displacement in this time interval. How come in this case an area is equal to a distance? Think! Note the dimensions of quantities on the two coordinate axes, and you will arrive at the answer.

Note that the x-t, v-t, and a-t graphs shown in several figures in this chapter have sharp kinks at some points implying that the functions are not differentiable at these points. In any realistic situation, the functions will be differentiable at all points and the graphs will be smooth.

What this means physically is that acceleration and velocity cannot change values abruptly at an instant. Changes are always continuous.

3.6 KINEMATICEQUATIONS FOR UNIFORMLY ACCELERATED MOTION

For uniformly accelerated motion, we can derive some simple equations that relate displacement (x), time taken (t), initial velocity (v_0), final velocity (v) and acceleration (a). Equation (3.6) already obtained gives a relation between final and initial velocities v and v_0 of an object moving with uniform acceleration a:

$$v = v_0 + at \tag{3.6}$$

This relation is graphically represented in Fig. 3.12.

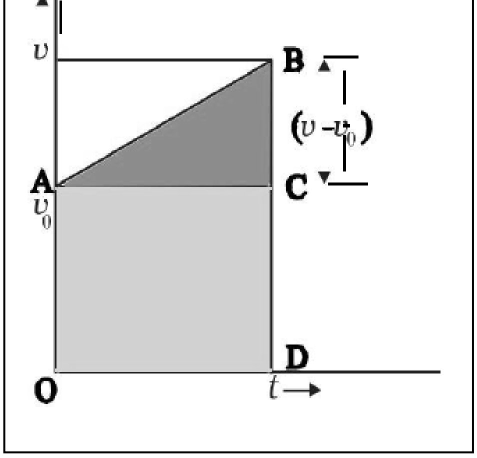


Fig. 3.12 *Area under v-t curve for an object with uniform acceleration.*

The area under this curve is:

Area between instants 0 and *t* = Area of triangle ABC + Area of rectangle OACD

$$=\frac{1}{2}\,(v-v_0)t=(v-v)_0\,t$$

As explained in the previous section, the area under *v-t* curve represents the displacement. Therefore, the displacement *x* of the object is:

$$x=\frac{1}{2}(v-v_0)t+v_0t \qquad (3.7)$$

But $v\text{-}v_0 = at$

Therefore $$x=\frac{1}{2}at^2+v_0t$$

Or $$x=v_0t+\frac{1}{2}at^2 \qquad (3.8)$$

Equation (3.7) can also be written as

$$x=\ \frac{v+v_0}{2}\ t=\bar{v}t \qquad (3.9a)$$

where, $\bar{v}=\ \frac{v+v_0}{2}$ (constant acceleration only) (3.9b)

Equations (3.9a) and (3.9b) mean that the object has undergone displacement *x* with an average velocity equal to the arithmetic average of the initial and final velocities.

From Eq. (3.6), $t = (v - v_0)/a$. Substituting this in Eq. (3.9a), we get

$$\bar{x}=\left(\frac{v+v_0}{2}\right)\left(\frac{v-v_0}{a}\right)=\frac{v^2-{v_0}^2}{a}$$

$$v^2=v_0^2+\ 2ax \qquad (3.10)$$

This equation can also be obtained by substituting the value of t from Eq. (3.6) into Eq. (3.8). Thus, we have obtained three important equations:

$$v = v_0 + at$$

$$x = v_0 t + \frac{1}{2} at^2$$

$$v^2 = v_0^2 + 2ax \qquad (3.11a)$$

Connecting five quantities v_0, v, a, t and x. These are kinematic equations of rectilinear motion for constant acceleration.

The set of Eq. (3.11a) were obtained by assuming that at $t = 0$, the position of the particle, x is 0. We can obtain a more general equation if we take the position coordinate at $t = 0$ as non-zero, say x_0. Then Eqs. (3.11a) are modified (replacing x by $x - x_0$) to :

$$v = v_0 + at$$

$$x = x_0 + v_0 t + \frac{1}{2} at^2 \qquad (3.11b)$$

$$v^2 = v_0^2 + 2a(x - x_0) \qquad (3.11c)$$

Example 3.3 Obtain equations of motion for constant acceleration using method of calculus.

Answer By definition

$$a = \frac{dv}{dt}$$

$$dv = a\, dt$$

Integrating both sides

$$\int_{v_0}^{v} dv = \int_0^t a\, dt$$

$$= a \int_0^t dt$$

$$v = v_0 + at$$

Further, $v = \frac{dx}{dt}$

$$dx = v\, dt$$

Integrating both sides

$$\int_{x_0}^{x} dx = \int_0^t v\, dt$$

$$= \int_0^t (v_0 + at)dt$$

$$x - x_o = v_0 t + \frac{1}{2}\, at^2$$

$$x = x_o\ +\ v_0 t + \frac{1}{2}\, at^2$$

We can write

$$a = \frac{dv}{dt} = \frac{dv}{dx}\,\frac{dx}{dt} = v\ \frac{dv}{dx}$$

or $v\ dv = a\ dx$

Integrating both sides,

$$\int_{v_0}^{v} v\ dv = \int_{x_0}^{x} a\ dx$$

$$\frac{v^2 - v_0^2}{2} = a\ (x - x_0)$$

$$v^2 = v_0^2 + 2a\ (x - x_0)$$

The advantage of this method is that it can be used for motion with non-uniform acceleration also.

Now, we shall use these equations to some important cases.

Example 3.4 A ball is thrown vertically upwards with a velocity of 20 m s^{-1} from the top of a multi storey building. The height of the point from where the ball is thrown is 25.0 m from the ground. (a) How high will the ball rise? and (b) how long will it be before the ball hits the ground? Take g = 10 m s^{-2}.

Answer (a) Let us take the y-axis in the vertically upward direction with zero at the ground, as shown in Fig. 3.13.

Now v_o = + 20 m s^{-1},

$a = -g = -10$ m s^{-2}, $v = 0$ m s^{-1}

If the ball rises to height y from the point of launch, then using the equation

$$v^2 = v_0^2 + 2\,a\,(y - y_0)$$

we get

$$0 = (20)^2 + 2(-10)(y - y_0)$$

Solving, we get, $(y - y_0) = 20$ m.

(a) We can solve this part of the problem in two ways.

(b) Note carefully the methods used.

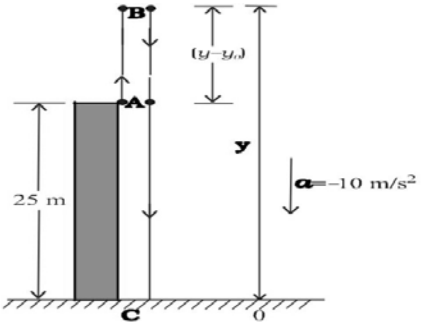


Fig. 3.13

FIRST METHOD: In the first method, we split the path in two parts : the upward motion (A to B) and the downward motion (B to C) and calculate the corresponding time taken t_1 and t_2. Since the velocity at B is zero.

we have :

$$v = v_o + at$$

$$0 = 20 - 10\, t_1$$

$$\text{Or, } t_1 = 2\text{s}$$

This is the time in going from *A* to *B*. From *B*, or the point of the maximum height, the ball falls freely under the acceleration due to gravity. The ball is moving in negative *y* direction. We use equation

$$= y_0 + v_0 t + \frac{1}{2} at^2$$

We have, $y_0 = 45$ m, $y = 0$, $v_0 = 0$, $a = -g = -10$ m s^{-2} $0 = 45 + (½)(-10)\, t_2^2$

Solving, we get $t_2 = 3$s

Therefore, the total time taken by the ball before it hits the ground = $t_1 + t_2 = 2$ s + 3 s = 5 s.

SECOND METHOD: The total time taken can also be calculated by noting the coordinates of initial and final positions of the ball with respect to the origin chosen and using equation

$$y = y_0 + v_0 t + \frac{1}{2} at^2$$

Now $y_0 = 25$, $y = 0$ m

$v_0 = 20$ ms^{-1}, a= -10 ms^{-2}, t=?

$$0 = 25 + 20\, t + (½)(-10)\, t^2$$

Or, $5t^2 - 20t - 25 = 0$

Solving this quadratic equation for t, we get

$$t = 5\text{s}$$

Note that the second method is better since we do not have to worry about the path of the motion as the motion is under constant acceleration.

Example 3.5 **Free-fall: Discuss** the motion of an object under free fall. Neglect air resistance.

Answer An object released near the surface of the Earth is accelerated downward under the influence of the force of gravity. The magnitude of acceleration due to gravity is represented by ***g***. If air resistance is neglected, the object is said to be in **free fall**. If the height through which the object falls is small compared to the earth's radius, g can be taken to be constant, equal to 9.8 m s^{-2}. Free fall is thus a case of motion with uniform acceleration.

We assume that the motion is in y-direction, more correctly in $-y$-direction because we choose upward direction as positive. Since the acceleration due to gravity is always downward, it is in the negative direction and we have

$$a = -g = -9.8 \text{ m s}^{-2}$$

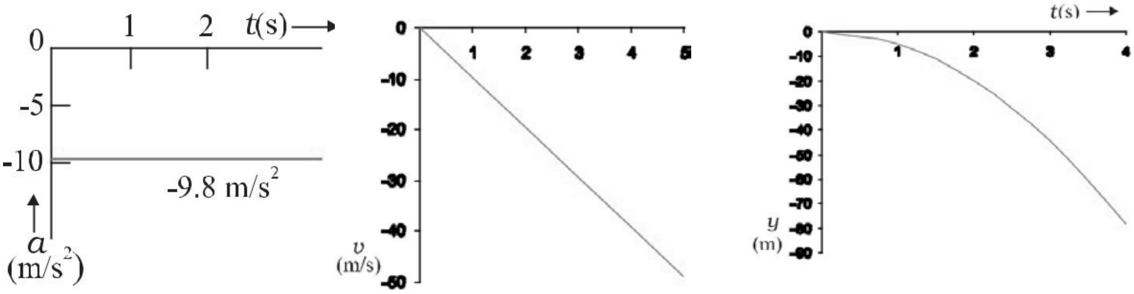
The object is released from rest at $y = 0$. Therefore, $v_0 = 0$ and the equations of motion become:

$$v = 0 - g\,t = -9.8\,t \qquad \text{m s}^{-1}$$

$$y = 0 - \tfrac{1}{2}\,g\,t^2 = -4.9\,t^2 \qquad \text{m}$$

$$v^2 = 0 - 2\,g\,y = -19.6\,y \qquad \text{m}^2\,\text{s}^{-2}$$

These equations give the velocity and the distance travelled as a function of time and also the variation of velocity with distance. The variation of acceleration, velocity and distance, with time has been plotted in Fig. 3.14(a), (b) and (c).



(a) **(b)** **(c)**

Fig. 3.14 *Motion of an object under free fall. (a)Variation of acceleration with time. (b) Variation of velocity with time.(c) Variation of distance with time*

Example 3.6 **Galileo's law of odd numbers** :*"The distances traversed, during equal intervals of time, by a body falling from rest, stand to one another in the same ratio as the odd numbers beginning with unity* [*namely,* 1: 3: 5: 7…...]." Prove it.

Answer Let us divide the time interval of motion of an object under free fall into many equal intervals τ and find out the distances traversed during successive intervals of time. Since initial velocity is zero, we have

$$y = -\frac{1}{2}\,gt^2$$

Using this equation, we can calculate the position of the object after different time intervals, 0, τ, 2 τ , 3 τ … which are given in second column of Table 3.2. If we take (–1/ 2) $g\,\tau^2$ as y_0 — the position coordinate after first time interval τ , then third column gives the positions in the unit of y_o. The fourth column gives the distances traversed in successive τ s. We find that the distances are in the simple ratio 1: 3: 5: 7: 9: 11… as shown in the last column. This law was established by Galileo Galilei (1564-1642) who was the first to make quantitative studies of free fall.

Table 3.2

t	**y**	**y in terms of y_0**	**Distance traversed in successive intervals**	**Ratio of distance traversed**
0	0	0		
T	$-(1/2)\ g\ \tau^2$	y_0	y_0	1
2 τ	$-4(1/2)\ g\ \tau^2$	4 y_0	3 y_0	3
3 τ	$-9(1/2)\ g\ \tau^2$	9 y_0	5 y_0	5
4 τ	$-16(1/2)\ g\ \tau^2$	16 y_0	7 y_0	7
5 τ	$-25(1/2)\ g\ \tau^2$	25 y_0	9 y_0	9

$6\,\tau$	$-36(1/2)\,g\,\tau^2$	$36\,y_0$	$11\,y_0$	11

***Example 3.7* Stopping distance of vehicles:** When brakes are applied to a moving vehicle, the distance it travels before stopping is called stopping distance. It is an important factor for road safety and depends on the initial velocity (v_0) and the braking capacity, or deceleration, $-a$ that is caused by the braking. Derive an expression for stopping distance of a vehicle in terms of v_o and a.

Answer Let the distance travelled by the vehicle before it stops be d_s. Then, using equation of motion $v^2 = v_o^2 + 2\,ax$, and noting that $v = 0$, we have the stopping distance

Thus, the stopping distance is proportional to the square of the initial velocity. Doubling the initial velocity increases the stopping distance by a factor of 4 (for the same deceleration).

For the car of a particular make, the braking distance was found to be 10 m, 20 m, 34 m and 50 m corresponding to velocities of 11, 15, 20 and 25 m/s which are nearly consistent with the above formula.

Stopping distance is an important factor considered in setting speed limits, for example, in school zones.

***Example 3.8* Reaction time :**When a situation demands our immediate action, it takes some time before we really respond. Reaction time is the time a person takes to observe, think and act. For example, if a person is driving and suddenly a boy appears on the road, then the time elapsed before he slams the brakes of the car is the reaction time. Reaction time depends on complexity of the situation and on an individual.

You can measure your reaction time by a simple experiment. Take a ruler and ask your friend to drop it vertically through the gap between your thumb and forefinger (Fig. 3.15). After you catch it, find the distance d travelled by the ruler. In a particular case, d was found to be 21.0 cm. Estimate reaction time.

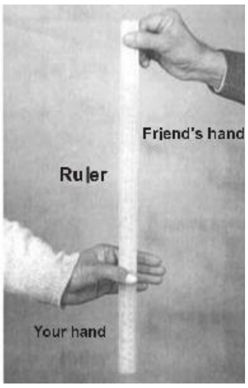


***Fig. 3.15** Measuring the reaction time.*

Answer The ruler drops under free fall.

Therefore, $v_o = 0$, and $g = -9.8 \text{ m s}^{-2}$.

The distance travelled d and the reaction time t_r are related by

$$d = -\frac{1}{2} g t_r^2$$

$$\text{or } t_r = \sqrt{\left(\frac{2d}{g}\right)} \text{ s}$$

Given $d = 21.0$ cm and $g = 9.8 \text{ m s}^{-2}$the reaction time is

$$t_r = \sqrt{\frac{2 \text{ x } 0.21}{9.8}} \text{s} = 0.2 \text{ s.}$$

3.7 RELATIVE VELOCITY

You must be familiar with the experience of travelling in a train and being overtaken by another train moving in the same direction as you are. While that train must be travelling faster than you to be able to pass you, it does seem slower to you than it would be to someone standing on the ground and watching both the trains. In case both the trains have the same velocity with respect to the ground, then to you the other train would seem to be not moving at all. To understand such observations, we now introduce the concept of relative velocity.

Consider two objects A and B moving uniformly with average velocities v_A and v_B in one dimension, say along x-axis. (Unless otherwise specified, the velocities mentioned in this chapter are measured with reference to the ground). If x_A (0) and x_B (0) are positions of objects A and B, respectively at time $t = 0$, their positions $x_A(t)$ and $x_B(t)$ at time t are given by:

$$x_A(t) = x_A(0) + v_A t \qquad (3.12a)$$

$$x_B(t) = x_B(0) + v_B t \qquad (3.12b)$$

Then, the displacement from object A to object B is given by

$$x_{BA}(t) = x_B(t) - x_A(t)$$

$$= [x_B(0) - x_A(0)] + (v_B - v_A)t. \qquad (3.13)$$

Equation (3.13) is easily interpreted. It tells us that as seen from object *A*, object *B* has a velocity $v_B - v_A$ because the displacement from *A* to *B* changes steadily by the amount $v_B - v_A$ ineach unit of time. We say that the velocity of object *B relative to object A* is $v_B - v_A$:

$$\mathrm{v_{BA}} = \mathrm{v_B} - \mathrm{v_A} \qquad (3.14a)$$

Similarly, velocity of object A relative to object B is:

$$\mathrm{v_{AB}} = \mathrm{v_A} - \mathrm{v_B} \qquad (3.14b)$$

This shows: $v_{BA} = -v_{AB}$

(3.14c)

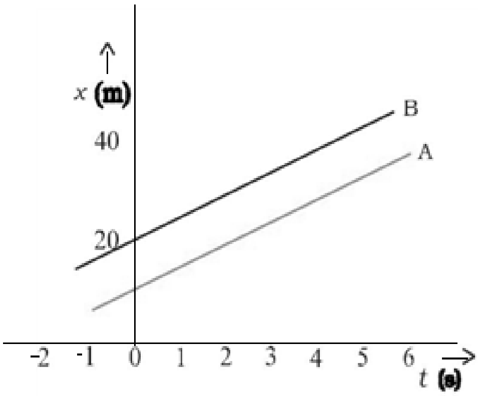


Fig. 3.16 *Position-time graphs of two objects with equal velocities*

Now we consider some special cases :

(a) If $v_B = v_A$, $v_B - v_A = 0$. Then, from Eq. (3.13), $x_B(t) - x_A(t) = x_B(0) - x_A(0)$. Therefore, the two objects stay at a constant distance $(x_B(0) - x_A(0))$ apart, and their position–time graphs are straight lines parallel to each other as shown in Fig. 3.16. The relative velocity v_{AB} or v_{BA} is zero in this case.

(b) If $v_A > v_B$, $v_B - v_A$ is negative. One graph is steeper For example, suppose $v_A = 20\ ms^{-1}$ and $x_A(0) = 10$ m and $v_B = 10\ ms^{-1}$ and $x_B(0) = 40$ m; then the time at which they meet is t = 3s (Fig. 3.17). At this instant they are both at a position $x_A(t) = x_B(t) = 70$ m. Thus, object A overtakes object B at this time. In this case, v_{BA}= 10 ms^{-1} – 20 ms^{-1}= – 10 m s^{-1}= $-v_{AB}$

(c) Suppose v_A and v_B are of opposite signs. For example, if in the above example object A is moving with 20 ms^{-1} starting at and object B is moving with – 10 ms^{-1} starting at $x_B(0)$ = 40 m, (Fig. 3.18). The velocity of B relative to A, v_{BA} = [–10 – (20)] ms^{-1} = –30 ms^{-1} case, the magnitude of v_{BA} or v_{AB}(=30 ms^{-1}) is greater than the magnitude of velocity of A or that of B. If the objects under consideration are two trains, then for a person sitting on either of the two, the other train seems to go very fast.

Note that Eq. (3.14) are valid even if v_A and v_B represent instantaneous velocities.

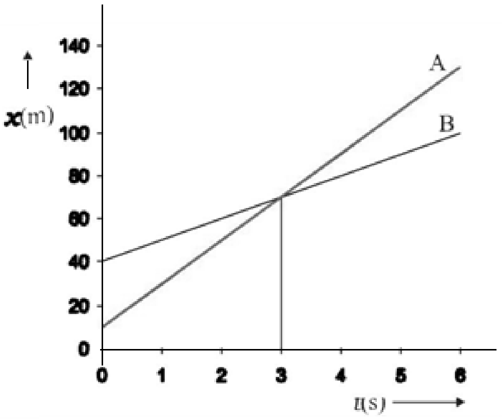


Fig. 3.17 Position-time graphs of two objects with unequal velocities, showing the time of meeting

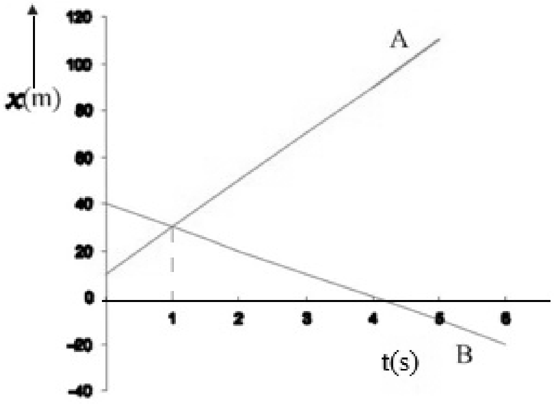


Fig. 3.18 *Position-Time graphs of two objects with velocities in opposite directions, showing the time of meeting*

Example 3.9 Two parallel rail tracks run north-south. Train A moves north with a speed of 54 kmh^{-1}, and train B moves south with a speed of 90 kmh-1. What is the (a) velocity of b with respect to A?, (b) velocity of ground with respect to B ? (c) velocity of a monkey running on the roof of the A against its motion (with a velocity of 18 kmh^{-1} with respect to the train A) as observed by a man standing on the ground?

Answer Choose the positive direction of x-axis to be from south to north.

Then,

$v_A = +54\ \text{kmh}^{-1} = 15\ \text{ms}^{-1}$

$v_B = -90\ \text{kmh}^{-1} = -25\ \text{ms}^{-1}$

Relative velocity of B with respect to A = $v_B - v_A = -40\ \text{m s}^{-1}$,

i.e. the train B appears to A to move with a speed of40 ms^{-1} from north to south.

Relative velocity of ground with respect to B= $0 - v_B = 25\ \text{ms}^{-1}$.

In (c), let the velocity of the monkey with respect to ground be v_M.

Relative velocity of the monkey with respect to *A*,

$$v_{MA} = v_M - v_A = -18\ \text{km h}^{-1} = -5\ \text{ms}^{-1}.$$

Therefore, $v_M = (15 - 5)\ \text{m s}^{-1} = 10\ \text{m s}^{-1}$.

SUMMARY

1. An object is said to be in *motion* if its position changes with time. The position of the object can be specified with reference to a conveniently chosen origin. For motion in a straight line, position to the right of the origin is taken as positive and to the left as negative.
2. *Path length* is defined as the total length of the path traversed by an object.
3. *Displacement* is the change in position: $x = x_2 - x_1$. Path length is greater or equal to the magnitude of the displacement between the same points.

4. An object is said to be in *uniform motion* in a straight line if its displacement is equal in equal intervals of time. Otherwise, the motion is said to be *non-uniform.*

5. *Average velocity* is the displacement divided by the time interval in which the displacement occurs :

$$\bar{v} = \frac{\Delta x}{\Delta t}$$

On an *x-t* graph, the average velocity over a time interval is the slope of the line connecting the initial and final positions corresponding to that interval.

6. *Average Speed* is the ratio of total path length traversed and the corresponding time interval. The average speed of an object is greater or equal to the magnitude of the average velocity over a given time interval.

7. *Instantaneous velocity* or simply velocity is defined as the limit of the average velocity as the time interval *t* becomes infinitesimally small:

$$v = \lim_{\Delta t \to 0} \bar{v} = \lim_{\Delta t \to 0} \frac{\Delta x}{\Delta t} = \frac{dx}{dt}$$

The velocity at a particular instant is equal to the slope of the tangent drawn on position-time graph at that instant.

8. *Average acceleration* is the change in velocity divided by the time interval during which the change occurs :

$$\bar{a} = \frac{\Delta v}{\Delta t}$$

9. *Instantaneous acceleration* is defined as the limit of the average acceleration as the time interval *t* goes to zero :

$$v = \lim_{\Delta t \to 0} \bar{a} = \lim_{\Delta t \to 0} \frac{\Delta v}{\Delta t} = \frac{dv}{dt}$$

The acceleration of an object at a particular time is the slope of the velocity-time graph at that instant of time. For uniform motion, acceleration is zero and the *x-t* graph is a straight line inclined to the time axis and the *v-t* graph is a straight line parallel to the time axis. For motion with uniform acceleration, *x-t* graph is a parabola while the *v-t* graph is a straight line inclined to the time axis.

10. The area under the velocity-time curve between times t_1 and t_2 is equal to the displacement of the object during that interval of time.

11. For objects in uniformly accelerated rectilinear motion, the five quantities, displacement x, time taken t, initial velocity v_0, final velocity v and acceleration a are related by a set of simple equations called *kinematic equations of motion*

$$v = v_0 + at$$

$$x = v_0 t + \frac{1}{2} at^2$$

$$v^2 = v_o^2 + 2ax$$

if the position of the object at time $t = 0$ is 0. If the particle starts at $x = x_0$, x in above equations is replaced by $(x - x_0)$.

CHAPTER FOUR

MOTION IN A PLANE

4.1 INTRODUCTION

In the last chapter we developed the concepts of position, displacement, velocity and acceleration that are needed to describe the motion of an object along a straight line. We found that the directional aspect of these quantities can be taken care of by + and – signs, as in one dimension only two directions are possible. But in order to describe motion of an object in two dimensions (a plane) or three dimensions (space), we need to use vectors to describe the above-mentioned physical quantities. Therefore, it is first necessary to learn the language of vectors. What is a vector?. How to add, subtract and multiply vectors?. What is the result of multiplying a vector by a real number?. We shall learn this to enable us to use vectors for defining velocity and acceleration in a plane. We then discuss motion of an object in a plane. As a simple case of motion in a plane, we shall discuss motion with constant acceleration and treat in detail the projectile motion. Circular motion is a familiar class of motion that has a special significance in daily-life situations. We shall discuss uniform circular motion in some detail.

The equations developed in this chapter for motion in a plane can be easily extended to the case of three dimensions.

4.2 SCALARS AND VECTORS

In physics, we can classify quantities as scalars or vectors. Basically, the difference is that a **direction** is associated with a vector but not with a scalar. A scalar quantity is a quantity with magnitude only. It is specified completely by a single number, along with the proper unit. Examples are: the distance between two points, mass of an object, the temperature of a body and the time at which a certain event happened. The rules for combining scalars are the rules of ordinary algebra. Scalars can be added, subtracted, multiplied and divided just as the ordinary numbers*. For example, if the length and breadth of a rectangle are 1.0 m and 0.5 m respectively, then its perimeter is the sum of the lengths of the four sides, 1.0 m + 0.5 m +1.0 m + 0.5 m = 3.0 m. The length of each side is a scalar and the perimeter is also a scalar. Take another example: the maximum and minimum temperatures on a particular day are 35.6 °C and 24.2 °C respectively. Then, the difference between the two temperatures is 11.4 °C. Similarly, if a uniform solid cube of aluminium of side 10 cm has a mass of 2.7 kg, then its volume is 10^{-3} m^3 (a scalar) and its density is 2.7 x 10^3 kg m^{-3} (a scalar).

A vector quantity is a quantity that has both a magnitude and a direction and obeys the triangle law of addition or equivalently the parallelogram law of addition. So, a vector is specified by giving its magnitude by a number and its direction. Some physical quantities that are represented by vectors are displacement, velocity, acceleration and force.

To represent a vector, we use a bold face type in this book. Thus, a velocity vector can be represented by a symbol v. Since bold face is difficult to produce, when written by hand, a vector is often represented A by an arrow placed Ā over a letter, say v. Thus, both v and v represent the velocity vector. The magnitude of a vector is often called its absolute value, indicated by |v| = v. Thus, a vector is represented by a bold face, e.g. by A, a, p, q, r, ... x, y, with respective magnitudes denoted by lightface A, a, p, q, r, ... x, y.

4.2.1 Position and Displacement Vectors

To describe the position of an object moving in a plane, we need to choose a convenient point, say O as origin. Let P and P′ be the positions of the object at time t and t′, respectively [Fig. 4.1(a)]. We join O and P by a straight line. Then, OP is the position vector of the object at time t. An arrow is marked at the head of this line. It is represented by a symbol r, i.e. OP = r. Point P′ is represented by another position vector, OP′ denoted by r′. The length of the vector r represents the magnitude of the vector and its direction is the direction in which P lies as seen from O.

If the object moves from P to P′, the vector PP′ (with tail at P and tip at P′) is called the displacement vector corresponding to motion from point P (at time t) to point P′ (at time t′).

It is important to note that displacement vector is the straight line joining the initial and final positions and does not depend on the actual path undertaken by the object between the two positions.

* *Addition and subtraction of scalars make sense only for quantities with same units. However, you can multiply and divide scalars of different units.*

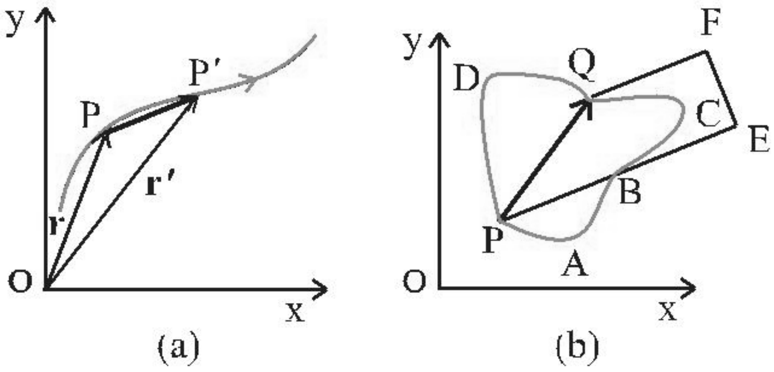


Fig. 4.1 (a) Position and displacement vectors. (b) Displacement vector PQ and different courses of motion.

It is important to note that displacement vector is the straight line joining the initial and final positions and does not depend on the actual path undertaken by the object between the two positions. For example, in *Fig. 4.1b*, given the initial and final positions as P and Q, the displacement vector is the same PQ for different paths of journey say PABCQ, PDQ, and PBEFQ. Therefore, the magnitude of displacement is either less or equal to the path length of an object between two points. This fact was emphasised in the previous chapter also while discussing motion along a straight line.

4.2.2 Equality of Vectors

Two vectors A and B are said to be equal if, and only if, they have the same magnitude and the same direction.**

Figure 4.2(a) shows two equal vectors A and B. We can easily check their equality. Shift B parallel to itself until its tail Q coincides with that of A, i.e. Q coincides with O. Then, since their tips S and P also coincide, the two vectors are said to be equal. In general, equality is indicated as **A** = **B**.

*** In our study, vectors do not have fixed locations. So displacing a vector parallel to itself leaves the vector unchanged. Such vectors are called f*ree vectors. *However, in some physical applications, location or line of application of a vector is important. Such vectors are called* localized vectors.

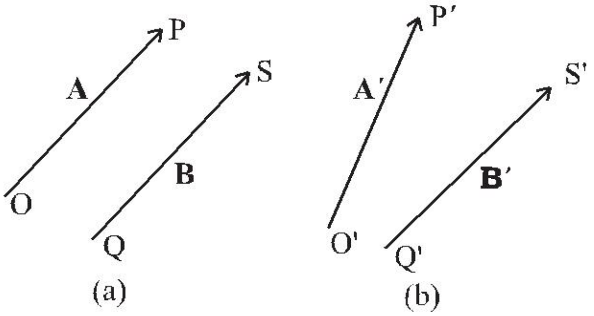


Fig. 4.2 *(a) Two equal vectors **A** and **B**. (b) Two vectors **A′** and **B′** are unequal though they are of the same length.*

Note that in Fig. 4.2(b), vectors A′ and B′ have the same magnitude but they are not equal because they have different directions. Even if we shift B′ parallel to itself so that its tail Q′ coincides with the tail O′ of A′, the tip S′ of B′ does not coincide with the tip P′ of A′.

4.3 MULTIPLICATION OF VECTORS BY REAL NUMBERS

Multiplying a vector A with a positive number λ gives a vector whose magnitude is changed by the factor λ but the direction is the same as that of A:

$$\lambda \mathbf{A} = \lambda \quad \mathbf{A} \text{ if } \lambda > 0.$$

For example, if **A** is multiplied by 2, the resultant vector 2**A** is in the same direction as **A** and has a magnitude twice of |**A**| as shown in Fig. 4.3(a).

Multiplying a given vector **A** by negative numbers, say –1 and –1.5, gives vectors as shown in Fig 4.3(b).

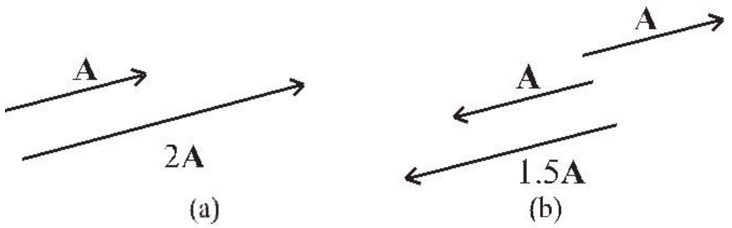


Fig. 4.3 *(a) Vector A and the resultant vector after multiplying A by a positive number 2 (b) Vector A and resultant vectors after multiplying it by a negative number -1 and -1.5.*

The factor **λ** by which a vector **A** is multiplied could be a scalar having its own physical dimension. Then, the dimension of **λA** is the product of the dimensions of **λ** and **A**. For example, if we multiply a constant velocity vector by duration (of time), we get a displacement vector.

4.4 ADDITION AND SUBTRACTION OF VECTORS — GRAPHICAL METHOD

As mentioned in section 4.2, vectors, by definition, obey the triangle law or equivalently, the parallelogram law of addition. We shall now describe this law of addition using the graphical method. Let us consider two vectors A and B that lie in a plane as shown in Fig. 4.4(a). The lengths of the line segments representing these vectors are proportional to the magnitude of the vectors. To find the sum A + B, we place vector B so that its tail is at the head of the vector A, as in Fig. 4.4(b). Then, we join the tail of A to the head of B. This line OQ represents a vector R, that is, the sum of the vectors A and B. Since, in this procedure of vector addition, vectors are arranged head to tail, this graphical method is called the head-to-tail method.

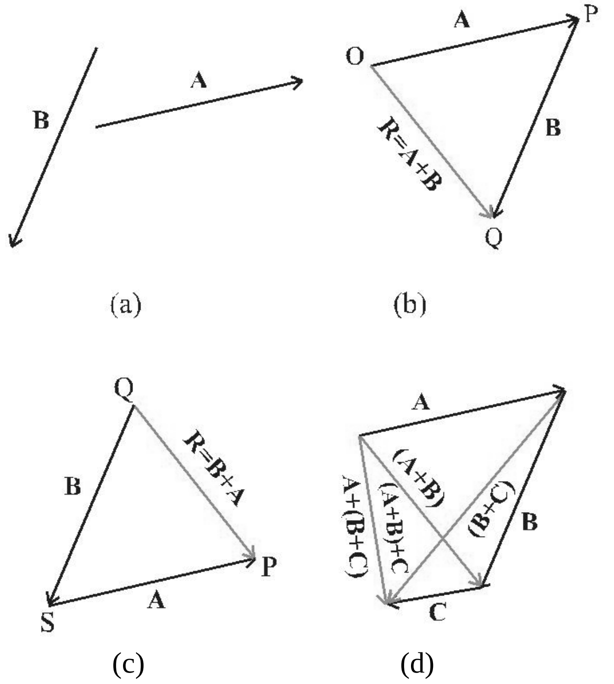


Fig. 4.4 (a) Vectors A and B. (b) Vectors A and B added graphically. (c) Vectors B and A added graphically. (d) Illustrating the associative law of vector addition.

The two vectors and their resultant form three sides of a triangle, so this method is also known as **triangle method of vector addition**. If we find the resultant of **B** + **A** as in

Fig. 4.4(c), the same vector **R** is obtained. Thus, vector addition is **commutative**:

$$\mathbf{A} + \mathbf{B} = \mathbf{B} + \mathbf{A} \tag{4.1}$$

The addition of vectors also obeys the associative law as illustrated in Fig. 4.4(d). The result of adding vectors A and B first and then adding vector C is the same as the result of adding B and C first and then adding vector A :

$$(\mathbf{A} + \mathbf{B}) + \mathbf{C} = \mathbf{A} + (\mathbf{B} + \mathbf{C}) \tag{4.2}$$

What is the result of adding two equal and opposite vectors?

Consider two vectors A and – A shown in Fig. 4.3(b). Their sum is A + (–A). Since the magnitudes of the two vectors are the same, but the directions are opposite, the resultant vector has zero magnitude and is represented by 0 called a null vector or a zero vector:

$$\mathbf{A} - \mathbf{A} = 0 \qquad |\mathbf{0}| = 0 \tag{4.3}$$

Since the magnitude of a null vector is zero, its direction cannot be specified. The null vector also results when we multiply a vector A by the number zero. The main properties of 0 are:

$$\begin{aligned} A + 0 &= A \\ \lambda\, 0 &= 0 \\ 0\, A &= 0 \end{aligned} \tag{4.4}$$

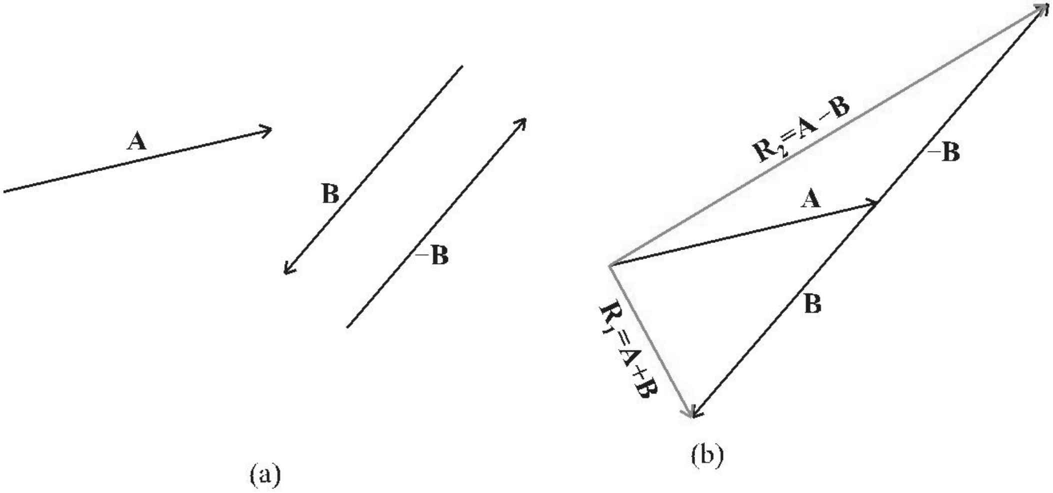


Fig. 4.5 (a) *Two vectors* **A** *and* **B**, **–B** *is also shown.* (b) *Subtracting vector* **B** *from vector* **A***–the result Is* $\mathbf{R}_2$. *For comparison, addition of vectors* **A** *and* **B**, *i.e.* $\mathbf{R}_1$ *is also shown*

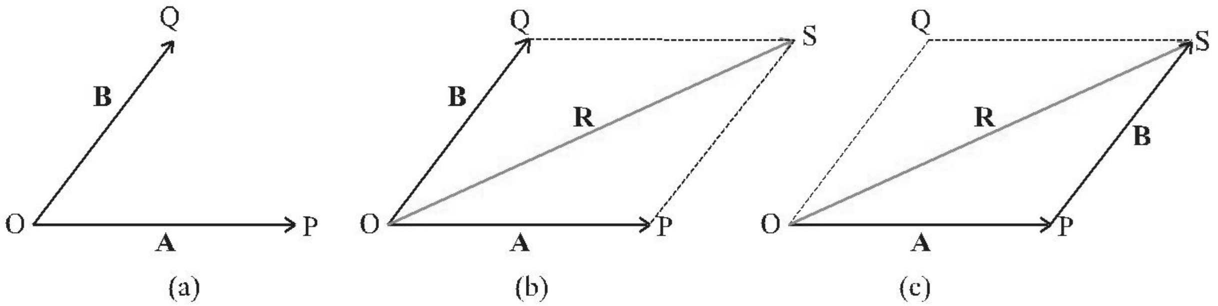


Fig. 4.6 (a) *Two vectors* **A** *and* **B** *with their tails brought to a common origin.* (b) *The sum* **A** + **B** *obtained using the parallelogram method.* (c) *The parallelogram method of vector addition is equivalent to the triangle method.*

Example 4.1 Rain is falling vertically with a speed of 35 m s^{-1}. Winds start blowing after sometime with a speed of 12 m s^{-1} in east to west direction. In which direction should a boy waiting at a bus stop hold his umbrella?

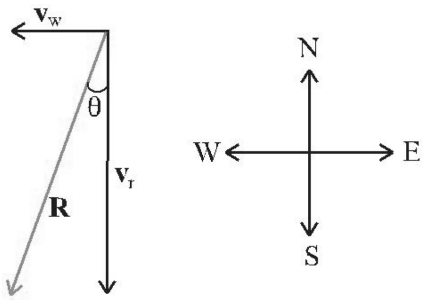


Fig. 4.7

Answer: The velocity of the rain and the wind are represented by the vectors $\mathbf{v_r}$ and $\mathbf{v_w}$ in Fig. 4.7 and are in the direction specified by the problem. Using the rule of vector addition, we see that the resultant of $\mathbf{v_r}$ and $\mathbf{v_w}$ is **R** as shown in the figure. The magnitude of **R** is

R = $\sqrt{v_r^2 + v_w^2} = \sqrt{35^2 + 12^2}\, ms^{-1} = 37 ms^{-1}$

The direction θ that R makes with the vertical is given by

$$\text{Tan}\, \theta = \frac{v_w}{v_r} = \frac{12}{35} = 0.343$$

$$\theta = Tan^{-1}(0.343) = 19°$$

Therefore, the boy should hold his umbrella in the vertical plane at an angle of about 19° with the vertical towards the east.

4.5 RESOLUTION OF VECTORS

Let a and b be any two non-zero vectors in a plane with different directions and let A be another vector in the same plane (Fig. 4.8). A can be expressed as a sum of two vectors – one obtained by multiplying a by a real number and the other obtained by multiplying b by another real number. To see this, let O and P be the tail and head of the vector A. Then, through O, draw a straight line parallel to a, and through P, a straight line parallel to b. Let them intersect at Q. Then, we have

$$A = OP = OQ + QP \qquad (4.6)$$

But since OQ is parallel to a, and QP is parallel to b, we can write:

$$OQ = \lambda a, \text{ and } QP = \mu\, b \qquad (4.7)$$

where λ and μ are real numbers

$$\text{Therefore, } A = \lambda a + \mu b \qquad (4.8)$$

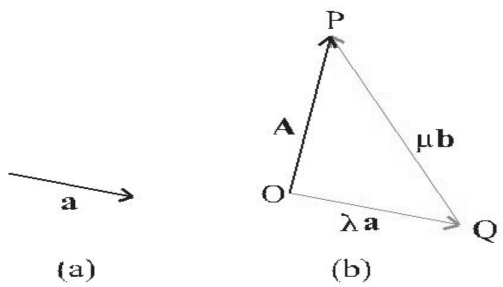


Fig. 4.8 (a) *Two non-co linear vectors* **a** *and* **b**. (b) *Resolving a vector* **A** *in terms of vectors* **a** *and* **b**.

We say that A has been resolved into two component vectors λa and μb along a and b respectively. Using this method one can resolve a given vector into two component vectors along a set of two vectors – all the three lie in the same plane.

It is convenient to resolve a general vector along the axes of a rectangular coordinate system using vectors of unit magnitude. These are called unit vectors that we discuss now.

Unit vectors: A unit vector is a vector of unit magnitude and points in a particular direction. It has no dimension and unit. It is used to specify direction only. Unit vectors along the x-, y-and z-axes of a rectangular coordinate system are denoted by $\hat{i}, \hat{j}$ and $\hat{k}$, respectively as shown in Fig. 4.9 (a).

Since these are unit vectors, we have

$$|\hat{\mathbf{i}}| = |\hat{\mathbf{j}}| = \left|\hat{\mathbf{k}}\right| = 1 \qquad (4.9)$$

These unit vectors are perpendicular to each other. In this text, they are printed in bold face with a cap (^) to distinguish them from other vectors. Since we are dealing with motion in two dimensions in this chapter, we require use of only two unit vectors. If we multiply a unit vector, say **n** by a scalar, the result is a vector **λ** = λ**n** . In general, a vector **A** can be written as

$$\mathbf{A} = |A|\, \mathbf{n} \tag{4.10}$$

where **n** is a unit vector along **A**.

We can now resolve a vector A in terms of component vectors that lie along unit vectors î and ĵ. Consider a vector A that lies in xy plane as shown in Fig. 4.9(b). We draw lines from the head of A perpendicular to the coordinate axes as in Fig. 4.9(b), and get vectors $\mathbf{A_1}$ and $\mathbf{A_2}$ such that $\mathbf{A_1} + \mathbf{A_2} = \mathbf{A}$. Since $\mathbf{A_1}$ is parallel to $\hat{\boldsymbol{\imath}}$**.**

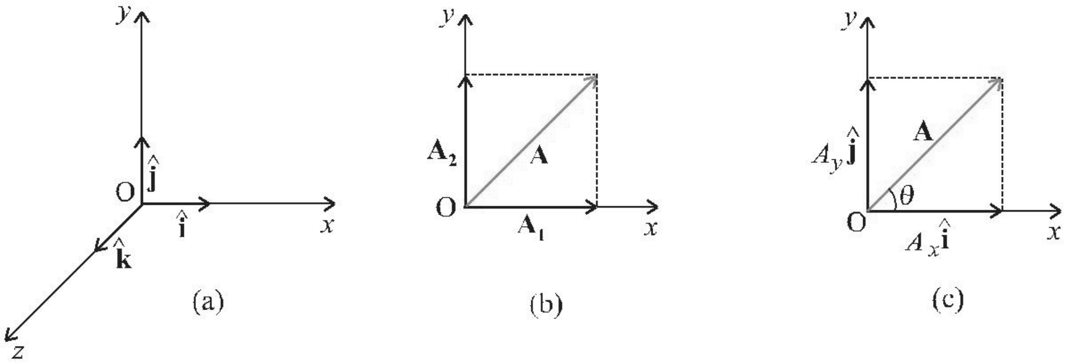


Fig. 4.9 (a) *Unit vectors $\hat{\imath}, \hat{\jmath}$ and $\hat{k}$ lie along the x-, y-, and z-axes.* (b) *A vector* **A** *is resolved into its components* $\mathbf{A_1}$ *and* $\mathbf{A_2}$ *along x-, and y- axes.* (c) $\mathbf{A_1}$ *and* $\mathbf{A_2}$ *expressed in terms of* $\hat{\imath}$ *and* $\hat{\jmath}$.

So far we have considered a vector lying in an *x*-*y* plane. The same procedure can be used to resolve a general vector A into three components along *x*-, *y*-, and z-axes in three dimensions. If α, β, and γ are the angles* between A and the *x*-, *y*-, and *z*-axes, respectively Fig. 4.9(d), we have

$$A_x = A\cos\alpha, A_y = \cos\beta, A_z = \cos\gamma \tag{4.16a}$$

In general we have

$$\mathbf{A} = A_x\hat{\imath} + A_y\hat{\jmath} + A_z\hat{k} \tag{4.16b}$$

---

* *Note that angles α, β and γ are angles in space. They are between pairs of lines, which are not coplanar*

The magnitude of vector A is

$$A = \sqrt{A_x^2 + A_y^2 + A_z^2} \qquad (4.16c)$$

A position vector **r** can be expressed as

$$R = x\hat{\imath} + y\hat{\jmath} + z\hat{k} \qquad (4.17)$$

where x, y, and z are the components of **r** along x-, y-, z-axes, respectively.

4.6 VECTOR ADDITION – ANALYTICAL METHOD

Although the graphical method of adding vectors helps us in visualising the vectors and the resultant vector, it is sometimes tedious and has limited accuracy. It is much easier to add vectors by combining their respective components. Consider two vectors **A** and **B** in x-y plane with components A_x, A_y and B_x, B_y:

$$\mathbf{A} = A_x\hat{\imath} + A_y\hat{\jmath} \qquad (4.18)$$

$$\mathbf{B} = B_x\,\hat{\imath} + B_y\,\hat{\jmath}$$

Let **R** be their sum. We have

$$\mathbf{R} = \mathbf{A} + \mathbf{B}$$

$$= (A_x\hat{\imath} + A_y\hat{\jmath}) + (B_x\hat{\imath} + B_y\hat{\jmath}) \qquad (4.19a)$$

Since vectors obey the commutative and associative laws, we can arrange and regroup the vectors in Eq. (4.19a) as convenient to us:

$$\mathbf{R} = (A_x+B_x)\hat{\imath} + (A_y+B_y)\hat{\jmath} \qquad (4.19b)$$

Since $\mathbf{R} = R_x\hat{\imath} + R_y\hat{\jmath}$ (4.20)

we have, $R_x = A_x+B_x$, $R_y = A_y+B_y$ (4.21)

Thus, each component of the resultant vector **R** is the sum of the corresponding components of **A** and **B**.

In three dimensions, we have

$$\mathbf{A} = A_x\,\hat{\imath} + A_y\,\hat{\jmath} + A_z\,\hat{k}$$

$$\mathbf{B} = B_x\,\hat{\imath} + B_y\,\hat{\jmath} + B_z\,\hat{k}$$

$$\mathbf{R} = \mathbf{A} + \mathbf{B} = R_x\hat{\imath} + R_y\hat{\jmath} + R_z\,\hat{k}$$

With $R_x = A_x + B_x$

$R_y = A_y + B_y$

$R_z = A_z + B_z$ (4.22)

This method can be extended to addition and subtraction of any number of vectors. For example, if vectors **a**, **b** and **c** are given as

$$A = a_x\hat{i} + a_y\hat{j} + a_z\hat{k} \quad (4.23a)$$

$$B = b_x\hat{i} + b_y\hat{j} + b_z\hat{k}$$

$$C = c_x\hat{i} + c_y\hat{j} + c_z\hat{k}$$

then, a vector **T** = **a** + **b** – **c** has components :

$$T_x = a_x + b_x - c_x$$

$$T_y = a_y + b_y - c_y$$

(4.23b)

$$T_z = a_z + b_z - c_z$$

Example 4.2 Find the magnitude and direction of the resultant of two vectors **A** and **B** in terms of their magnitudes and angle θ between them.

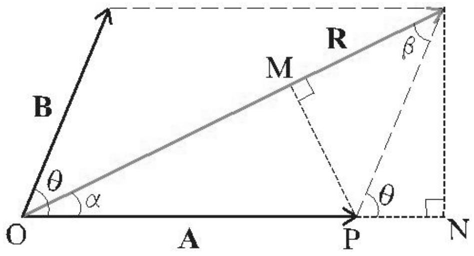


Fig. 4.10

Answer Let **OP** and **OQ** represent the two vectors **A** and **B** making an angle θ (Fig. 4.10). Then, using the parallelogram method of vector addition, **OS** represents the resultant vector **R**:

$$\mathbf{R} = \mathbf{A} + \mathbf{B}$$

SN is normal to OP and PM is normal to OS. From the geometry of the figure,

$$OS^2 = ON^2 + SN^2$$

But $ON = OP + PN = A + B\cos\theta$

$$SN = B\sin\theta$$

$$OS^2 = (A + B\cos\theta)^2 + (B\sin\theta)^2$$

or, $R^2 = A^2 + B^2 + 2AB\cos\theta$

$$R = \sqrt{A^2 + B^2 + 2AB\,cos\theta} \quad (4.24a)$$

In OSN $SN = OS\sin\alpha = R\sin\alpha$, and

In PSN $SN = PS \sin\theta = B \sin\theta$

Therefore $R \sin\alpha = B \sin\theta$

$$\frac{R}{\sin\theta} = \frac{B}{\sin\alpha} \tag{4.24b}$$

Similarly PM = $A \sin\alpha = B \sin\beta$

$$\frac{A}{\sin\beta} = \frac{B}{\sin\alpha} \tag{4.24c}$$

Combining Eqs. (4.24b) and (4.24c), we get

$$\frac{R}{\sin\theta} = \frac{A}{\sin\beta} = \frac{B}{\sin\alpha} \tag{4.24d}$$

Using Eq. (4.24d), we get:

$$\sin\alpha = \frac{B}{R}\sin\theta \tag{4.24e}$$

where R is given by Eq. (4.24a)

$$\tan\alpha = \frac{SN}{OP+PN} = \frac{B\sin\theta}{A+B\cos\theta} \tag{4.24f}$$

Equation (4.24a) gives the magnitude of the resultant and Eqs. (4.24e) and (4.24f) its direction. Equation (4.24a) is known as the **Law of cosines** and Eq. (4.24d) as the **Law of sines**.

Example 4.3 A motorboat is racing towards north at 25 km/h and the water current in that region is 10 km/h in the direction of 60° east of south. Find the resultant velocity of the boat.

Answer The vector $\mathbf{v_b}$ representing the velocity of the motorboat and the vector $\mathbf{v_c}$ representing the water current are shown in Fig. 4.11 in directions specified by the problem. Using the parallelogram method of addition, the resultant **R** is obtained in the direction shown in the figure.

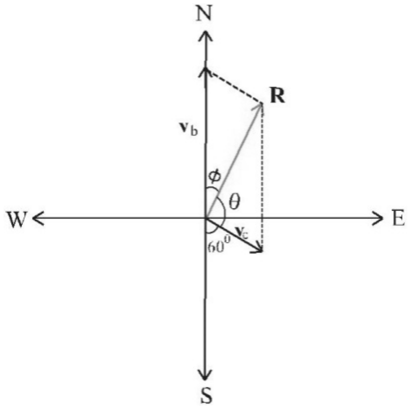


Fig. 4.11

We can obtain the magnitude of **R** using the Law of cosine:

$$R = \sqrt{v_b^2 + v_c^2 + 2v_b v_c \, cos \, 120°}$$

$$= \sqrt{25^2 + 10^2 + 2x25x10 \left(-\frac{1}{2}\right)} \cong 22 \text{ km/h}$$

To obtain the direction, we apply the Law of sines

$$\frac{R}{\sin\theta} = \frac{v_c}{\sin\emptyset} \; or, sin \, \emptyset = \frac{v_c}{R} \, sin\theta$$

$$= \frac{10 \, x \sin 120°}{21.8} = \frac{10\sqrt{3}}{2 \, x \, 21.8} \cong 0.397$$

$$\emptyset = 23.4°$$

4.7 MOTION IN A PLANE

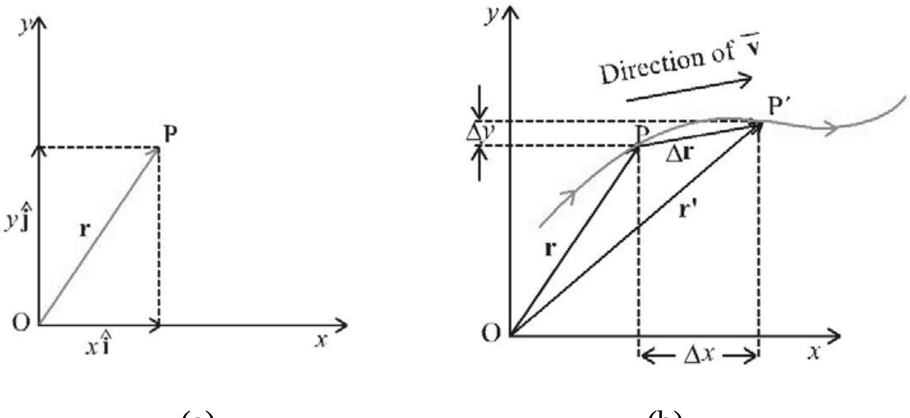
In this section we shall see how to describe motion in two dimensions using vectors

4.7.1 Position Vector and Displacement

The position vector **r** of a particle P located in a plane with reference to the origin of an *x*-*y* reference frame (Fig. 4.12) is given by

$$\mathbf{r} = x\,\hat{\imath} + y\,\hat{\jmath}$$

where *x* and *y* are components of **r** along *x*-, and *y*- axes or simply they are the coordinates of the object.



(a) (b)

Fig. 4.12 (a) *Position vector* **r**. (b) *Displacement* **r** *and average velocity* **v** *of a particle.*

Suppose a particle moves along the curve shown by the thick line and is at P at time t and P′ at time t′ [Fig. 4.12(b)]. Then, the displacement is:

$$\Delta \mathbf{r} = \mathbf{r}' - \mathbf{r} \tag{4.25}$$

and is directed from P to P′.

We can write Eq. (4.25) in a component form:

$$\Delta r = (x'\hat{\imath} + y'\hat{\jmath}) - (x\hat{\imath} + y\hat{\jmath}) = \hat{\imath}\Delta x + \hat{\jmath}\Delta y$$

Where $\Delta x = x' - x, \Delta y = y' - y$ (4.26)

Velocity

The average velocity $\bar{\boldsymbol{v}}$ of an object is the ratio of the displacement and the corresponding time interval:

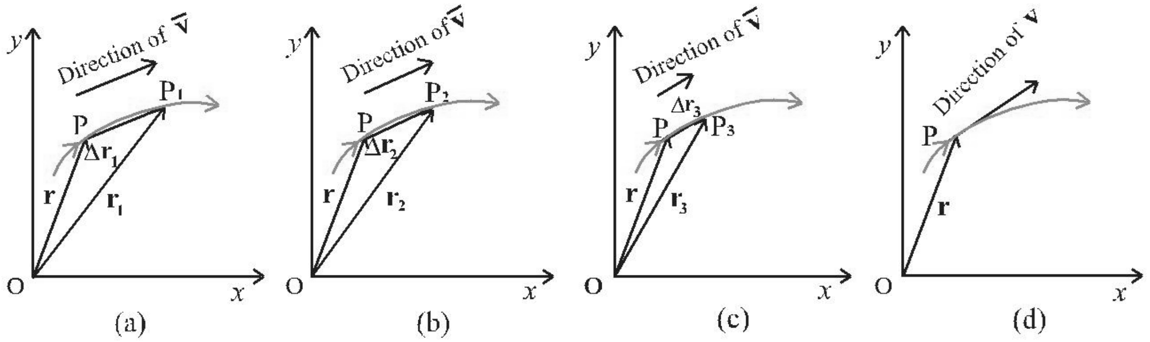
$$\bar{v} = \frac{\Delta r}{\Delta t} = \frac{\Delta x\hat{\imath} + \Delta y\hat{\jmath}}{\Delta t} = \hat{\imath}\,\frac{\Delta x}{\Delta t} + \hat{\jmath}\,\frac{\Delta y}{\Delta t} \tag{4.27}$$

Or, $\bar{v} = \bar{v}_x\hat{\imath} + \bar{v}\hat{\jmath}$

Since $\bar{v} = \frac{\Delta r}{\Delta t}$, the direction of the average velocity is the same as that of $\Delta\mathbf{r}$ (Fig. 4.12). The **velocity** (instantaneous velocity) is given by the limiting value of the average velocity as the time interval approaches zero:

$$v = \lim_{\Delta t \to 0} \Delta r/\Delta t = \frac{dr}{dt} \tag{4.28}$$

The meaning of the limiting process can be easily understood with the help of Fig. 4.13(a) to (d). In these figures, the thick line represents the path of an object, which is at time t. P_1, P_2 and P_3 represent the positions of the object after times Δt_1, Δt_2 *and* Δt_3. $\Delta r_1, \Delta r_2$ *and* Δr_3 are the displacements of the object in times Δt_1, Δt_2 *and* Δt_3 respectively.



(a) (b) (c) (d)

Fig. 4.13 *As the time interval* Δt *approaches zero, the average velocity approaches the velocity* **v**. *The direction of* $\bar{\boldsymbol{v}}$ *is parallel to the line tangent to the path.*

The direction of the average velocity $\bar{\boldsymbol{v}}$ is shown in figures (a), (b) and (c) for three decreasing values of*t*, i.e. $\Delta\, t_1$, $\Delta\, t_2$, and $\Delta\, t_3$, $(\Delta t_1 > \Delta t_2 > \Delta t_3)$. As $\Delta t \to 0, \Delta r \to 0$ and is along the tangent to the path [Fig. 4.13(d)]. Therefore, **the direction of velocity at any point on the path of an object is tangential to the path at that point and is in the direction of motion**.

We can express **v** in a component form:

$$v = \frac{dr}{dt}$$

$$= \lim_{\Delta t \to 0} \left(\frac{\Delta x}{\Delta t} \hat{\imath} + \frac{\Delta y}{\Delta t} \hat{\jmath} \right) \tag{4.29}$$

$$= \hat{\imath} \lim_{\Delta t \to 0} \frac{\Delta x}{\Delta t} + \hat{\jmath} \lim_{\Delta t \to 0} \frac{\Delta y}{\Delta t}$$

or $v = \hat{\imath} \frac{dx}{dt} + \hat{\jmath} \frac{dy}{dt} = v_x \hat{\imath} + v_y \hat{\jmath}$.

Where $v_x = \frac{dx}{dt}, v_y = \frac{dy}{dt}$ (4.30a)

So, if the expressions for the coordinates *x* and *y* are known as functions of time, we can use these equations to find v_x and v_y.

The magnitude of **v** is then

$$v = \sqrt{v_x^2 + v_y^2} \tag{4.30b}$$

and the direction of **v** is given by the angle θ:

$$\tan\theta = \frac{v_y}{v_x}, \theta = \tan^{-1}\left(\frac{v_y}{v_x}\right) \tag{4.30 c}$$

v_x, v_y and angle θ are shown in Fig. 4.14 for a velocity vector **v**.

Acceleration

The **average acceleration a** of an object for a time interval *t* moving in *x*-*y* plane is the change in velocity divided by the time interval:

$$\bar{a} = \frac{\Delta v}{\Delta t} = \frac{\Delta(v_x \hat{\imath} + v_y \hat{\jmath})}{\Delta t} = \frac{\Delta v_x}{\Delta t} \hat{\imath} + \frac{\Delta v_y}{\Delta t} \hat{\jmath} \tag{4.31a}$$

$$a_x = \frac{d}{dt}\left(\frac{dx}{dt}\right) = \frac{d_x^2}{dt^2}, a_y = \frac{d}{dt}\left(\frac{dy}{dt}\right) = \frac{d_y^2}{dt^2}$$

or $\bar{a} = a_x\, i + a_y\, j$

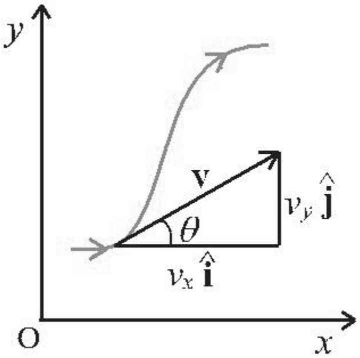


Fig. 4.14 *The components v_x and v_y of velocit y* **v** *and the angle θ it makes with x-axis. Note that $v_x = v\cos\theta$, $v_y = v\sin\theta$.*

The acceleration (instantaneous acceleration) is the limiting value of the average acceleration as the time interval approaches zero:

$$a = \lim_{\Delta t \to 0} \frac{\Delta v}{\Delta t} \qquad (4.32a)$$

Since $\Delta v = \Delta v_x \hat{\imath} + \Delta v_y \hat{\jmath}$. We have

$$a = \hat{\imath} \lim_{\Delta t \to o} \frac{\Delta v_x}{\Delta t} + \hat{\jmath} \lim_{\Delta t \to 0} \frac{\Delta v_y}{\Delta t}$$

Or, a = $a_x \hat{\imath} + a_y \hat{\jmath}$ (4.32b)

where , $a_x = \frac{dv_x}{dt}, a_y = \frac{dv_y}{dt}$ (4.32c)*

As in the case of velocity, we can understand graphically the limiting process used in defining acceleration on a graph showing the path of the object's motion. This is shown in Figs. 4.15(a) to (d). P represents the position of the object at time t and P_1, P_2, P_3 positions after time t_1, t_2, t_3, respectively ($\Delta t_1 > \Delta t_2 > \Delta t_3$). The velocity vectors at points P, P_1, P_2, P_3 are also shown in Figs. 4.15 (a), (b) and (c). In each case of Δt, Δ**v** is obtained using the triangle law of vector addition. By definition, the direction of average acceleration is the same as that of Δ**v**. We see that as Δt decreases, the direction of **v** changes and consequently, the direction of the acceleration changes. Finally, in the limit $\Delta t \to 0$ fig. 4.15(d), the average acceleration becomes the instantaneous acceleration and has the direction as shown.

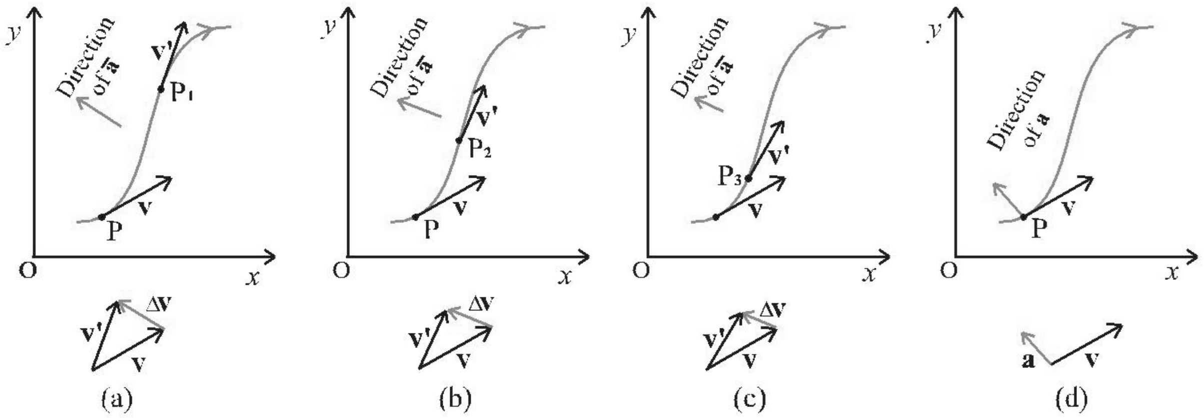


Fig. 4.15 *The average acceleration for three time intervals* (a) *t_1*, (b) *t_2, and* (c) *t_3, ($t_1 > t_2 > t_3$).*(d) *In the limit t 0, the average acceleration becomes the acceleration.*

Note that in one dimension, the velocity and the acceleration of an object are always along the same straight line (either in the same direction or in the opposite direction). However, for motion in two or three dimensions, velocity and acceleration vectors may have any angle between 0° and 180° between them.

Example 4.4 The position of a particle is given by

$$r = 3.0\, t\, \hat{\imath} + 2.0 t^2 \hat{\jmath} + 5.0\, \hat{k}$$

where t is in seconds and the coefficients have the proper units for **r** to be in metres. Find **v**(t) and **a**(t) of the particle. (b) Find the magnitude and direction of **v**(t) at t = 1.0 s.

Answer

$$v(t) = \frac{dr}{dt} = \frac{d}{dt}\left(3.0 t\hat{\imath} + 2.0 t^2 \hat{\jmath} + 5.0\, \hat{k}\right)$$

$$= 3.0\, \hat{\imath} + 4.0\, t\, \hat{\jmath}$$

$$a\,(t) = \frac{dv}{dt} = +4.0\, \hat{\jmath}$$

$a = 40$ ms^{-2} along y-direction

At t = 1.0 s, V= $3.0\hat{\imath} + 4.0\, \hat{\jmath}$

Its magnitude is $v = \sqrt{3^2 + 4^2}$ = 5.0 ms^{-1} and its direction is

$$\theta = \tan^{-1}\left(\frac{v_y}{v_x}\right) = \tan^{-1}\left(\frac{4}{3}\right) \cong 53°\, with\ x - axis$$

4.8 MOTION IN A PLANE WITH CONSTANT ACCELERATION

Suppose that an object is moving in *x*-*y* plane and its acceleration **a** is constant. Over an interval of time, the average acceleration will equal this constant value. Now, let the velocity of the object be $\mathbf{v}_0$ at time $t = 0$ and **v** at time *t*. Then, by definition

$$a = \frac{v-v_o}{t-0} = \frac{v-v_o}{t}$$

or $v = v_o + at$ (4.33a)

In terms of components:

$$v_x = v_{ox} + a_x t$$

$$v_y = v_{oy} + a_y t \qquad (4.33b)$$

Let us now find how the position **r** changes with time. We follow the method used in the one-dimensional case. Let $\mathbf{r_o}$ and **r** be the position vectors of the particle at time 0 and *t* and let the velocities at these instants be $\mathbf{v_o}$ and **v**. Then, over this time interval *t*, the average velocity is $(\mathbf{v_o} + \mathbf{v})/2$. The displacement is the average velocity multiplied by the time interval:

$$r - r_0 = \left(\frac{v + v_0}{2}\right)t = \left(\frac{(v_0 + at) + v_0}{2}\right)t$$

v = $v_0 t + \frac{1}{2}\, at^2$

Or, $r = r_0 + v_0 t + \frac{1}{2}\, at^2$ (4.34a)

It can be easily verified that the derivative of Eq. (4.34a), i.e. $\frac{dr}{dt}$ gives Eq. (4.33a) and it also satisfies the condition that at $t = 0$, $\mathbf{r} = \mathbf{r_o}$. Equation (4.34a) can be written in component form as

$$x = x_0 + v_{0x}t + \frac{1}{2}\, a_x t^2$$

$$y = y_0 + v_{0y}t + \frac{1}{2}\, a_y t^2 \qquad (4.34b)$$

One immediate interpretation of Eq. (4.34b) is that the motions in *x*- and *y*-directions can be treated independently of each other. That is, **motion in a plane (two-dimensions) can be treated as two separate simultaneous one-dimensional motions with constant acceleration along two perpendicular directions**. This is an important result and is useful in analyzing motion of objects in two dimensions. A similar result holds for three dimensions. The choice of perpendicular directions is convenient in many physical situations, as we shall see in section

4.10 for projectile motion.

Example 4.5 A particle starts from origin at $t = 0$ with a velocity 5.0 **î** m/s and moves in x-y plane under action of a force which produces a constant acceleration of $(3.0\,\hat{\imath} + 2.0\,\hat{\jmath})$ m/s^2. (a) What is the y-coordinate of the particle at the instant its x-coordinate is 84 m? (b) What is the speed of the particle at this time?

Answer The position of the particle is given by

$$r(t) = v_0 t + \frac{1}{2} a t^2$$

$$= 5.0\,\hat{\imath} t + \left(\frac{1}{2}\right)(3.0\,\hat{\imath} + 2.0\hat{\jmath})t^2$$

$$= (5.0t + 1.5t^2)\hat{\imath} = 1.0t^2\hat{\jmath}$$

therefore, $x(t) = 5.0t + 1.5t^2$

$$y(t) = +1.0t^2$$

Given $x\,(t) = 84$ m, $t = ?$

$5.0\,t + 1.5\,t^2 = 84 \Rightarrow t = 6$ s

At $t = 6$ s, $y = 1.0\,(6)^2 = 36.0$ m

Now the velocity $v = \frac{dr}{dt} = (5.0 + 3.0t)\hat{\imath} + 2.0t\hat{\jmath}$

$$At\ t = 6s\ v = 23.0\hat{\imath} + 12.0\hat{\jmath}$$

Speed = $|v| = \sqrt{23^2 + 12^2}$ = 26 ms^{-1}

4.9 RELATIVE VELOCITY IN TWO DIMENSIONS

The concept of relative velocity, introduced in section 3.7 for motion along a straight line, can be easily extended to include motion in a plane or in three dimensions. Suppose that two objects A and B are moving with velocities $\mathbf{v_A}$ and $\mathbf{v_B}$ (each with respect to some common frame of reference, say ground.). Then, velocity of object A **relative to that of B is**:

$$\mathbf{v}_{AB} = \mathbf{v}_A - \mathbf{v}_B \qquad (4.35a)$$

and similarly, the velocity of object B *relative tothat of* A is :

$v_{BA} = v_B - v_A$

Therefore $v_{AB} = -v_{BA}$ (4.35b)

And $|v_{AB}| = |v_{BA}|$ (4.35c)

Example 4.6 Rain is falling vertically with a speed of 35 m s^{-1}. A woman rides a bicycle with a speed of 12 m s^{-1} in east to west direction. What is the direction in which she should hold her umbrella?

Answer In Fig. 4.16 $\mathbf{v}_r$ represents the velocity of rain and $\mathbf{v}_b$, the velocity of the bicycle, the woman is riding. Both these velocities are with respect to the ground. Since the woman is riding a bicycle, the velocity of rain as experienced by her is the velocity of rain relative to the velocity of the bicycle she is riding.

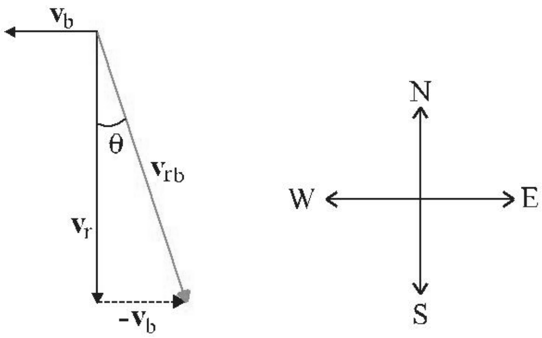


Fig. 4.16

That is $\mathbf{v}_{rb} = \mathbf{v}_r - \mathbf{v}_b$

This relative velocity vector as shown in Fig. 4.16 makes an angle θ with the vertical.

It is given by

$$\text{Tan } \theta = \frac{v_b}{v_r} = \frac{12}{35} = 0.343$$

or, $\theta = 19°$

Therefore, the woman should hold her umbrella at an angle of about 19° with the vertical towards the west.

Note carefully the difference between this Example and the Example 4.1. In Example 4.1, the boy experiences the resultant (vector sum) of two velocities while in this example, the woman experiences the velocity of rain relative to the bicycle (the vector

difference of the two velocities).

4.10 PROJECTILE MOTION

As an application of the ideas developed in the previous sections, we consider the motion of a projectile. An object that is in flight after being thrown or projected is called a **projectile**. Such a projectile might be a football, a cricket ball, a baseball or any other object. The motion of a projectile may be thought of as the result of two separate, simultaneously occurring components of motions. One component is along a horizontal direction without any acceleration and the other along the vertical direction with constant acceleration due to the force of gravity. It was Galileo who first stated this independency of the horizontal and the vertical components of projectile motion in his **Dialogue on the great world systems** (1632).

In our discussion, we shall assume that the air resistance has negligible effect on the motion of the projectile. Suppose that the projectile is launched with velocity v_o that makes an angle θ_o with the x-axis as shown in Fig. 4.17.

After the object has been projected, the acceleration acting on it is that due to gravity which is directed vertically downward:

$$\mathbf{a} = -g\,\mathbf{j}$$

or $a_x = 0,\ a_y = -g$

The components of initial velocity $\mathbf{v_o}$ are:

$$v_{ox} = v_o \cos\theta_o$$

$$v_{oy} = v_o \sin\theta_o$$

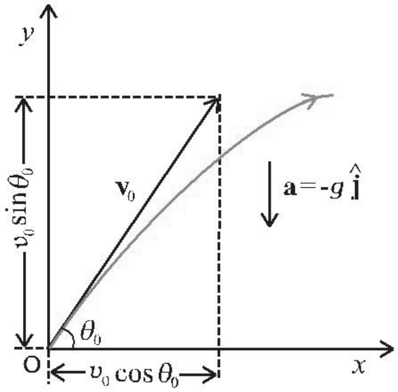


Fig 4.17 *Motion of an object projected with velocity* $\mathbf{v}_o$ *at angle* θ_0.

If we take the initial position to be the origin of the reference frame as shown in Fig. 4.17,

we have: $x_o = 0$, $y_o = 0$

Then, Eq.(4.47b) becomes :

$$x = v_{0x}t = (v_0 cos\ \theta_0)t$$

and $$y = (v_0 sin\ \theta_0)t - \left(\frac{1}{2}\right) gt^2 \qquad (4.38)$$

The components of velocity at time *t* can be obtained using Eq.(4.33b) :

$$v_x = v_{ox} = v_o \cos\theta_o$$

$$v_y = v_o \sin\theta_o - g\ t$$

Equation (4.38) gives the *x*-, and *y*-coordinates of the position of a projectile at time *t* in terms of two parameters - initial speed v_o and projection angle θ_o. Notice that the choice of mutually perpendicular *x*- and *y*-directions for the analysis of the projectile motion has resulted in a simplification. One of the components of velocity, i.e. *x*-component remains constant throughout the motion and only the *y*- component changes, like an object in free fall in vertical direction. This is shown graphically at few instants in Fig. 4.18. Note that at the point of maximum height, $v_y = 0$ and therefore

$$\theta = tan^{-1}\frac{v_y}{v_x} = 0$$

Equation of path of a projectile

What is the shape of the path followed by the projectile? This can be seen by eliminating the time between the expressions for x and y as given in Eq. (4.38). We obtain

$$y = (tan\theta_0)x - \frac{g}{2\ (v_0 cos\theta_0)^2}\ x^2 \qquad (4.40)$$

Now, since g, θ_o and v_o are constants, Eq. (4.40) is of the form $y = a\ x + b\ x^2$, in which *a* and *b* are constants. This is the equation of a parabola, i.e. the path of the projectile is a parabola (Fig. 4.18).

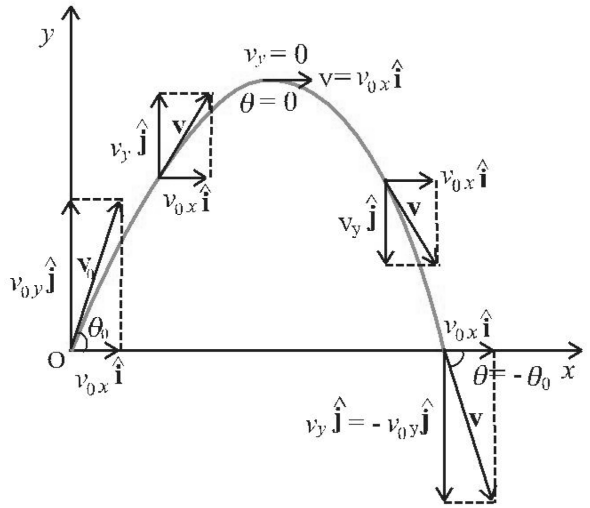


Fig. 4.18 *The path of a projectile is a parabola*

Time of maximum height

How much time does the projectile take to reach the maximum height? Let this time be denoted by t_m. Since at this point, $v_y = 0$, we have from Eq. (4.39):

$$v_y = v_o \sin\theta_o - g\, t_m = 0$$

$$\text{or } t_m = v_o \sin\theta_o / g \qquad (4.41a)$$

The total time T_f during which the projectile is in flight can be obtained by putting $y = 0$ in Eq. (4.38). We get :

$$T_f = 2\,(v_o \sin\theta_o)/g \qquad (4.41b)$$

T_f is known as the **time of flight** of the projectile. We note that $T_f = 2\, t_m$, which is expected because of the symmetry of the parabolic path.

Maximum height of a projectile

The maximum height h_m reached by the projectile can be calculated by substituting $t = t_m$ in Eq. (4.38) :

$$y = h_m = (v_0 sin\theta_0)\left(\frac{v_0 sin\theta_0}{g}\right) - \frac{g}{2}\left(\frac{v_0 sin\theta_0}{g}\right)^2$$

$$\text{Or, } h_m = \left(\frac{v_0 sin\theta_0}{2g}\right)^2$$

Horizontal range of a projectile

The horizontal distance travelled by a projectile from its initial position ($x = y = 0$) to the position where it passes $y = 0$ during its fall is called the **horizontal range**, R. It is the distance travelled during the time of flight T_f . Therefore, the range is

$$R = (v_o \cos \theta_o)\,(T_f)$$

$$= (v_o \cos \theta_o)\,(2\, v_o \sin \theta_o)/g$$

$$R = \left(\frac{v_0^2 sin 2\theta_0}{g}\right)^{\cdot} \qquad (4.43a)$$

Equation (4.43a) shows that for a given projection velocity v_o, R is maximum when $\sin 2\theta_0$ is maximum, i.e., when $\theta_0 = 45^0$.

The maximum horizontal range is, therefore,

$$R_m = \left(\frac{v_0^2}{g}\right)^{\cdot} \qquad (4.43b)$$

Example 4.7 Galileo, in his book **Two new sciences,** stated that "for elevations which exceed or fall short of 45° by equal amounts, the ranges are equal". Prove this statement.

Answer For a projectile launched with velocity $\mathbf{v_o}$ at an angle θ_o, the range is given by

$$R = \frac{v_0^2 sin 2\theta_0}{g}$$

Now, for angles, $(45° + \alpha)$ and $(45° - \alpha)$, $2\theta_o$ is $(90° + 2\alpha)$ and $(90° - 2\alpha)$, respectively. The values of $\sin (90° + 2\alpha)$ and $\sin (90° - 2\alpha)$ are the same, equal to that of $\cos 2\alpha$. Therefore, ranges are equal for elevations which exceed or fall short of 45° by equal amounts α.

Example 4.8 A hiker stands on the edge of a cliff 490 m above the ground and throws a stone horizontally with an initial speed of 15 m s^{-1}. Neglecting air resistance, find the time taken by the stone to reach the ground, and the speed with which it hits the ground. (Take $g = 9.8$ m s^{-2}).

Answer We choose the origin of the x-, and y-axis at the edge of the cliff and $t = 0$ s at the instant the stone is thrown. Choose the positive direction of x-axis to be along the initial velocity and the positive direction of y-axis to be the vertically upward direction. The x-, and y-components of the motion can be treated independently. The equations of motion are:

$$x\,(t) = x_o + v_{ox}\,t$$

$$y\,(t) = y_o + v_{oy}\,t + \frac{1}{2}a_y\,t^2$$

Here, $x_o = y_o = 0$, $v_{oy} = 0$, $a_y = -g = -9.8\ \text{m s}^{-2}$,

$v_{ox} = 15\ \text{m s}^{-1}$.

The stone hits the ground when $y(t) = -\,490$ m.

$$-\,490\ \text{m} = -\frac{1}{2}(9.8)\,t^2.$$

This gives $t = 10$ s.

The velocity components are $v_x = v_{ox}$ and

$$v_y = v_{oy} - g\,t$$

so that when the stone hits the ground :

$v_{ox} = 15\ \text{m s}^{-1}$

$v_{oy} = 0 - 9.8 \times 10 = -\,98\ \text{m s}^{-1}$Therefore, the speed of the stone is

$$\sqrt{v_x^2 + v_y^2} = \sqrt{(15^2 + 98^2)} = 99\ \text{m s}^{-1}$$

Example 4.9 A cricket ball is thrown at a speed of 28 m s^{-1} in a direction 30° above the horizontal. Calculate (a) the maximum height, (b) the time taken by the ball to return to the same level, and (c) the distance from the thrower to the point where the ball returns to the same level.

Answer (a) The maximum height is given by

$$h_m = \left(\frac{v_0 sin\theta_0}{2g}\right)^2 = \left(\frac{28 sin\ 30°}{2(9.8)}\right)^2 m = \frac{14\ x\ 14}{2\ x\ 9.8} = 10.0\ m$$

(b) The time taken to return to the same level is

$$T_f = (2\,v_o \sin\theta_o)/g = (2 \times 28 \times \sin 30°)/9.8$$

$$= 28/9.8\ \text{s} = 2.9\ \text{s}$$

(c) The distance from the thrower to the point where the ball returns to the same level is

$$R = \frac{v_0^2 \sin 2\theta_0}{g} = \frac{28\ \text{x}\ 28\ \text{x} \sin 60^o}{9.8} = 69\ \text{m}$$

SUMMARY

1. *Scalar quantities* are quantities with magnitudes only. Examples are distance, speed, mass and temperature.
2. *Vector quantities* are quantities with magnitude and direction both. Examples are displacement, velocity and acceleration. They obey special rules of vector algebra.
3. A vector **A** multiplied by a real number λ is also a vector, whose magnitude is λ times the magnitude of the vector **A** and whose direction is the same or opposite depending upon whether λ is positive or negative.
4. Two vectors **A** and **B** may be *added graphically* using *head-to-tail method* or *parallelogram method*.
5. Vector addition is *commutative*:

$$\mathbf{A} + \mathbf{B} = \mathbf{B} + \mathbf{A}$$

It also obeys the *associative law* :

$$(\mathbf{A} + \mathbf{B}) + \mathbf{C} = \mathbf{A} + (\mathbf{B} + \mathbf{C})$$

6. A *null* or *zero vector* is a vector with zero magnitude. Since the magnitude is zero, we don't have to specify its direction. It has the properties:

$$\mathbf{A} + \mathbf{0} = \mathbf{A}$$

$$\lambda\mathbf{0} = \mathbf{0}$$

$$0\,\mathbf{A} = \mathbf{0}$$

7. The *subtraction* of vector **B** from **A** is defined as the sum of **A** and **–B**:

$$\mathbf{A} - \mathbf{B} = \mathbf{A} + (-\mathbf{B})$$

8. A vector **A** can be *resolved* into component along two given vectors **a** and **b** lying in the same plane:

$\mathbf{A} = \lambda\,\mathbf{a} + \mu\,\mathbf{b}$ **,** where λ and μ are real numbers.

9. A *unit vector* associated with a vector **A** has magnitude one and is along the vector **A**:

$$\hat{n} = \frac{A}{|A|}$$

The unit vectors $\hat{\imath}, \hat{\jmath}$ *and* $\hat{k}$ are vectors of unit magnitude and point in the direction of the *x*-, *y*- and *z*-axes, respectively in a right handed coordinate system.

10. A vector **A** can be expressed as $\mathbf{A} = A_x\hat{\imath} + A_y\hat{\jmath}$

where A_x, A_y are its components along *x*-, and *y* -axes. If vector **A** makes an angle θ *with the x*- axis

then $A_x = A\cos\theta$, $A_y = A\sin\theta$ *and* $A = |A| = \sqrt{A_x^2 + A_y^2}$, $\tan\theta = \frac{A_y}{A_y}$

11. Vectors can be conveniently added using *analytical method*. If sum of two vectors **A** and **B**, that lie in *x*-*y* plane, is **R**, then:

$\mathbf{R} = R_x\,\mathbf{i} + R_y\,\mathbf{j}$, where, $R_x = A_x + B_x$, and $R_y = A_y + B_y$

12. The *position vector* of an object in *x*-*y* plane is given by $\mathbf{r} = x\mathbf{i} + y\mathbf{j}$ and the *displacement* from position **r** to position **r′** is given by $\mathbf{r} = \mathbf{r}' - \mathbf{r}$

$= (x' - x)\,\mathbf{i} + (y' - y)\,\mathbf{j}$

$= \Delta x\,\mathbf{i} + \Delta y\,\mathbf{j}$

13. If an object undergoes a displacement **r** in time *t*, its *average velocity* is given by $\bar{v} = \frac{\Delta r}{\Delta t}$. The *velocity* of an object at time *t* is the limiting value of the average velocity as Δt tends to zero: $v = \lim_{\Delta t \to 0} \Delta r/\Delta t = \frac{dr}{dt}$

It can be written in unit vector notation as: $v = v_x\hat{\imath} + v_y\hat{\jmath} + v_z\hat{k}$ where

$v_x = \frac{dx}{dt}, v_y = \frac{dy}{dt}, v_z = \frac{dz}{dt}$

When position of an object is plotted on a coordinate system, **v** is always tangent to the curve representing the path of the object.

14. If the velocity of an object changes from **v** to **v′** in time *t*, then its *average acceleration* is

given by $\bar{a} = \frac{v - v\prime}{\Delta t} = \frac{\Delta v}{\Delta t}$

The *acceleration* **a** at any time *t* is the limiting value of $\bar{a}$ *as* $\Delta t \to o$: $a = \lim_{\Delta t \to 0} \frac{\Delta v}{\Delta t} = \frac{dv}{dt}$

In component form, we have: $\mathbf{a} = a_x\,\mathbf{i} + a_y\,\mathbf{j} + a_z\,\mathbf{k}$ where $a_x = \frac{dv_x}{dt}$, $a_y = \frac{dv_y}{dt}$, $a_z = \frac{dv_z}{dt}$

15. If an object is moving in a plane with constant acceleration $a = |a| = \sqrt{a_x^2 + a_y^2}$ and its position vector at time $t = 0$ is $\mathbf{r}_o$, then at any other time *t*, it will be at a point given by: $r = r_0 + v_0 t + \frac{1}{2}at^2$ and its velocity is given by: $\mathbf{v} = \mathbf{v_0} + \mathbf{a}t$ where $\mathbf{v_o}$ is the velocity at time $t = 0$.

In component form :

$$x = x_0 + v_{0x}t + \frac{1}{2}\,a_x t^2$$

$$y = y_0 + v_{0y}t + \frac{1}{2}\,a_y t^2$$

$$v_x = v_{ox} + a_x\,t$$

$$v_y = v_{oy} + a_y\,t$$

Motion in a plane can be treated as superposition of two separate simultaneous one-dimensional motions along two perpendicular directions

16. An object that is in flight after being projected is called a *projectile*. If an object is projected with initial velocity **v₀** making an angle θ_o with *x*-axis and if we assume its initial position to coincide with the origin of the coordinate system, then the position and velocity of the projectile at time *t* are given by :

$$x = (v_o \cos \theta_o)\, t$$

$$y = (v_o \sin \theta_o)\, t - (1/2)\, g\, t^2$$

$$v_x = v_{ox} = v_o \cos\theta_o$$

$$v_y = v_o \sin\theta_o - g\, t$$

The path of a projectile is *parabolic* and is given by :

$$y = (tan\theta_0)x - \frac{g}{2\,(v_0 cos\theta_0)^2}\,x^2$$

The *maximum height* that a projectile attains is :

$$h_m = \left(\frac{v_0 sin\theta_0}{2g}\right)^2$$

The *time* taken to reach this height is: $t_m = v_o \sin\theta_o/g$

The horizontal distance travelled by a projectile from its initial position to the position it passes *y* = 0 during its fall is called the *range*, *R* of the projectile. It is

$$R = \frac{v_0^2 sin2\theta_0}{g}$$

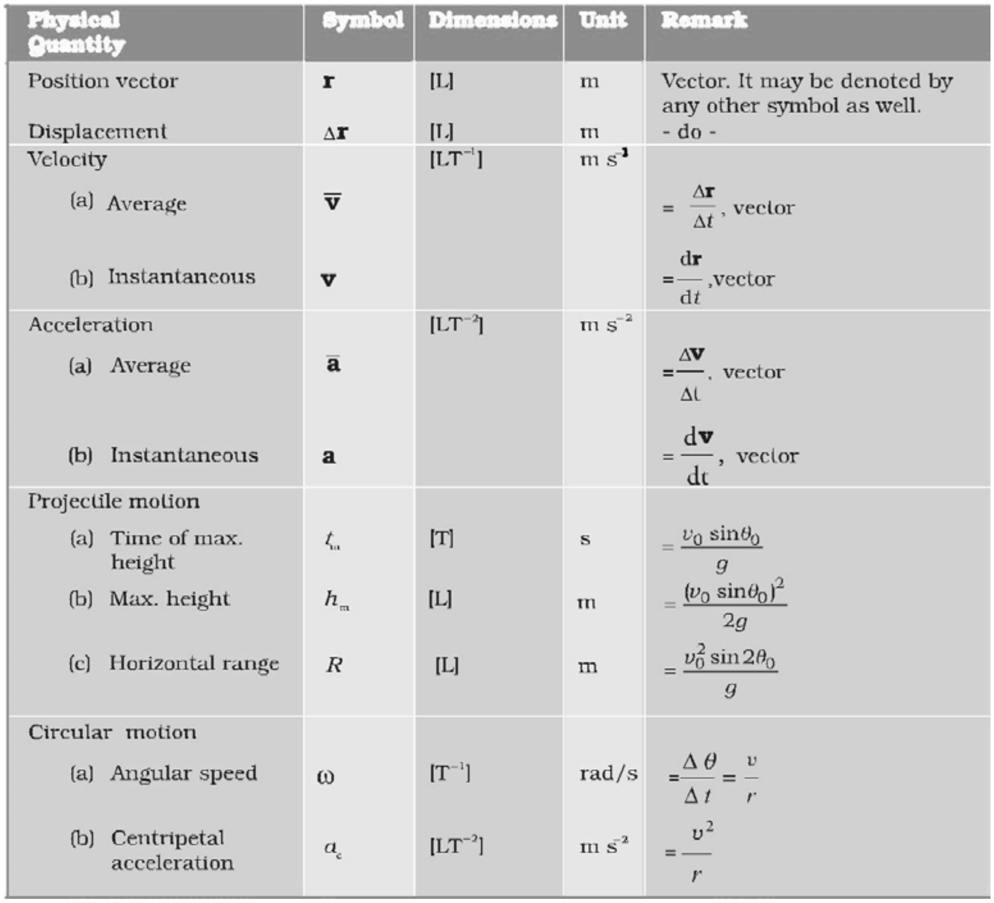
17. When an object follows a circular path at constant speed, the motion of the object is called *uniform circular motion*. The magnitude of its acceleration is $a_c = v^2/R$. The direction of a_c is always towards the centre of the circle.

The angular speed ω, is the rate of change of angular distance.

It is related to velocity v by $v = \omega R$. The acceleration is $a_c = \omega^2 R$.

If T is the time period of revolution of the object in circular motion and ν is its frequency,

we have $\omega = 2\pi\nu$, $v = 2\pi\nu R$, $a_c = 4\pi^2\nu^2 R$



Physical Quantity	Symbol	Dimensions	Unit	Remark
Position vector	$\mathbf{r}$	[L]	m	Vector. It may be denoted by any other symbol as well.
Displacement	$\Delta\mathbf{r}$	[L]	m	- do -
Velocity		$[LT^{-1}]$	$m\ s^{-1}$	
(a) Average	$\bar{\mathbf{v}}$			$= \frac{\Delta\mathbf{r}}{\Delta t}$, vector
(b) Instantaneous	$\mathbf{v}$			$= \frac{d\mathbf{r}}{dt}$, vector
Acceleration		$[LT^{-2}]$	$m\ s^{-2}$	
(a) Average	$\bar{\mathbf{a}}$			$= \frac{\Delta\mathbf{v}}{\Delta t}$, vector
(b) Instantaneous	$\mathbf{a}$			$= \frac{d\mathbf{v}}{dt}$, vector
Projectile motion				
(a) Time of max. height	t_m	[T]	s	$= \frac{v_0 \sin\theta_0}{g}$
(b) Max. height	h_m	[L]	m	$= \frac{(v_0 \sin\theta_0)^2}{2g}$
(c) Horizontal range	R	[L]	m	$= \frac{v_0^2 \sin 2\theta_0}{g}$
Circular motion				
(a) Angular speed	ω	$[T^{-1}]$	rad/s	$= \frac{\Delta\theta}{\Delta t} = \frac{v}{r}$
(b) Centripetal acceleration	a_c	$[LT^{-2}]$	$m\ s^{-2}$	$= \frac{v^2}{r}$

CHAPTER FIVE

LAWS OF MOTION

5.1 INTRODUCTION

In the preceding Chapter, our concern was to describe the motion of a particle in space quantitatively. We saw that uniform motion needs the concept of velocity alone whereas non-uniform motion requires the concept of acceleration in addition. So far, we have not asked the question as to what governs the motion of bodies. In this chapter, we turn to this basic question.

Let us first guess the answer based on our common experience. To move a football at rest, someone must kick it. To throw a stone upwards, one has to give it an upward push. A breeze causes the branches of a tree to swing; a strong wind can even move heavy objects. A boat moves in a flowing river without anyone rowing it. Clearly, some external agency is needed to provide force to move a body from rest. Likewise, an external force is needed also to retard or stop motion. You can stop a ball rolling down an inclined plane by applying a force against the direction of its motion.

In these examples, the external agency of force (hands, wind, stream, etc) is in contact with the object. This is not always necessary. A stone released from the top of a building accelerates downward due to the gravitational pull of the earth. A bar magnet can attract an iron nail from a distance. **This shows that external agencies (e.g. gravitational and magnetic forces) can exert force on a body even from a distance.**

In short, a force is required to put a stationary body in motion or stop a moving body, and some external agency is needed to provide this force. The external agency may or may not be in contact with the body.

So far so good. But what if a body is moving uniformly (e.g. a skater moving straight with constant speed on a horizontal ice slab)? **Is an external force required to keep a body in uniform motion?**

5.2 ARISTOTLE’S FALLACY

The question posed above appears to be simple. However, it took ages to answer it. Indeed, the correct answer to this question given by Galileo in the seventeenth century was the foundation of Newtonian mechanics, which signaled the birth of modern science.

The Greek thinker, Aristotle (384 B.C– 322 B.C.), held the view that if a body is moving, something external is required to keep it moving. According to this view, for example, an arrow shot from a bow keeps flying since the air behind the arrow keeps pushing it. The view was part of an elaborate framework of ideas developed by Aristotle on the motion of bodies in the universe. Most of the Aristotelian ideas on motion are now known to be wrong and need not concern us. For our purpose here, the Aristotelian law of motion may be phrased thus: **An external force is required to keep a body in motion**.

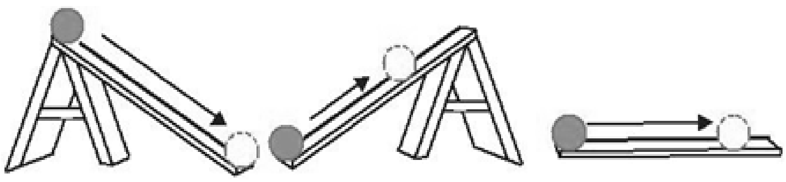
Aristotelian law of motion is flawed, as we shall see. However, it is a natural view that anyone would hold from common experience. Even a small child playing with a simple (non-electric) toy-car on a floor knows intuitively that it needs to constantly drag the string attached to the toy-car with some force to keep it going. If it releases the string, it comes to rest. This experience is common to most terrestrial motion. External forces seem to be needed to keep bodies in motion. Left to themselves, all bodies eventually come to rest.

What is the flaw in Aristotle’s argument? The answer is: a moving toy car comes to rest because the external force of friction on the car by the floor opposes its motion. To counter this force, the child has to apply an external force on the car in the direction of motion. When the car is in uniform motion, there is no net external force acting on it: the force by the child cancels the force (friction) by the floor. The corollary is: if there were no friction, the child would not be required to apply any force to keep the toy car in uniform motion.

The opposing forces such as friction (solids) and viscous forces (for fluids) are always present in the natural world. This explains why forces by external agencies are necessary to overcome the frictional forces to keep bodies in uniform motion. Now we understand where Aristotle went wrong. He coded this practical experience in the form of a basic argument. To get at the true law of nature for forces and motion, one has to imagine a world in which uniform motion is possible with no frictional forces opposing. This is what Galileo did.

5.3 THE LAW OF INERTIA

Galileo studied motion of objects on an inclined plane. Objects (i) moving down an inclined plane accelerate, while those (ii) moving up retard. (iii) Motion on a horizontal plane is an intermediate situation. Galileo concluded that an object moving on a frictionless horizontal plane must neither have acceleration nor retardation, i.e. it should move with constant velocity (Fig. 5.1(a)).



(i) (ii) (iii)

Fig. 5.1(a)

Another experiment by Galileo leading to the same conclusion involves a double inclined plane. A ball released from rest on one of the planes rolls down and climbs up the other. If the planes are smooth, the final height of the ball is nearly the same as the initial height (a little less but never greater). In the ideal situation, when friction is absent, the final height of the ball is the same as its initial height.

If the slope of the second plane is decreased and the experiment repeated, the ball will still reach the same height, but in doing so, it will travel a longer distance. In the limiting case, when the slope of the second plane is zero (i.e. is a horizontal) the ball travels an infinite distance. In other words, its motion never ceases. This is, of course, an idealized situation (Fig. 5.1(b)).

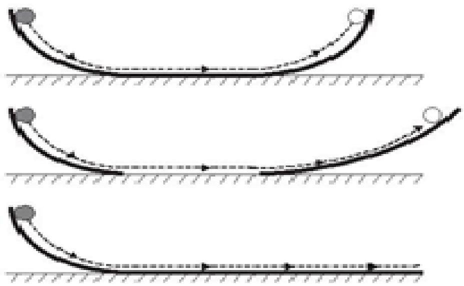


Fig. 5.1(b*) The law of inertia was inferred by Galileo from observations of motion of a ball on a double inclined plane.*

In practice, the ball does come to a stop after moving a finite distance on the horizontal plane, because of the opposing force of friction which can never be totally eliminated. However, if there were no friction, the ball would continue to move with a constant velocity on the horizontal plane. Galileo thus, arrived at a new insight on motion that had eluded Aristotle and those who followed him. The state of rest and the state of uniform linear motion (motion with constant velocity) are equivalent. In both cases, there is no net force acting on the body. It is incorrect to assume that a net force is needed to keep a body in uniform motion. To maintain a body in uniform motion, we need to apply an external force to encounter the frictional force, so that the two forces sum up to zero net external force.

To summarize, if the net external force is zero, a body at rest continues to remain at rest and a body in motion continues to move with a uniform velocity. This property of the body is called inertia. Inertia means **'resistance to change'**. A body does not change its state of rest or uniform motion, unless an external force compels it to change that state.

5.4 NEWTON'S FIRST LAW OF MOTION

Galileo's simple, but revolutionary ideas dethroned Aristotelian mechanics. A new mechanics had to be developed. This task was accomplished almost single handedly by Isaac Newton, one of the greatest scientists of all times. Newton built on Galileo's ideas and laid the foundation of mechanics in terms of three laws of motion that go by his name. Galileo's law of inertia was his starting point which he formulated as the **First Law of motion**: **Everybody continues to be in its state of rest or of uniform motion in a straight line unless compelled by some external force to act otherwise.** The state of rest or uniform linear motion both imply zero acceleration. The first law of motion can, therefore, be simply expressed as:

If the net external force on a body is zero, its acceleration is zero. Acceleration can be non-zero only if there is a net external force on the body.

Ideas on Motion in Ancient Indian Science

Ancient Indian thinkers had arrived at an elaborate system of ideas on motion. Force, the cause of motion, was thought to be of different kinds: force due to continuous pressure (nodan), as the force of wind on a sailing vessel; impact (abhighat), as when a potter's rod strikes the wheel; persistent tendency (sanskara) to move in a straight line (vega) or restoration of shape in an elastic body; transmitted force by a string, rod, etc. The notion of (vega) in the Vaisesika theory of motion perhaps comes closest to the concept of inertia. Vega, the tendency to move in a straight line, was thought to be opposed by contact with objects including atmosphere, a parallel to the ideas of friction and air resistance. It was correctly summarised that the different kinds of motion (translational, rotational and vibrational) of an extended body arise from only the translational motion of its constituent particles. A falling leaf in the wind may have downward motion as a whole (patan) and also rotational and vibrational motion (bhraman, spandan), but each particle of the leaf at an instant only has a definite (small) displacement. There was considerable focus in Indian thought on measurement of motion and units of length and time. It was known that the position of a particle in space can be indicated by distance measured along three axes. Bhaskara (1150 A.D.) had introduced the concept of ‘instantaneous motion’ (tatkalikigati), which anticipated the modern notion of instantaneous velocity using Differential Calculus. The difference between a wave and a current (of water) was clearly understood; a current is a motion of particles of water under gravity and fluidity while a wave results from the transmission of vibrations of water particles

Two kinds of situations are encountered in the application of this law in practice. In some examples, we know that the net external force on the object is zero. In that case we can conclude that the acceleration of the object is zero. For example, a spaceship out in interstellar space, far from all other objects and with all its rockets turned off, has no net external force acting on it. Its acceleration, according to the First Law, must be zero. If it is in motion, it must continue to move with a uniform velocity. More often, however, we do not know all the forces to begin with. In that case, if we know that an object is unaccelerated (i.e. it is either at rest or in uniform linear motion), we can infer from the first law that the net external force on the object must be zero. Gravity is everywhere. For terrestrial phenomena, in particular, every object experiences gravitational force due to the earth. Also objects in motion generally experience friction, viscous drag, etc. If then, on earth, an object is at rest or in uniform linear motion, it is not because there are no forces acting on it, but because the various external forces cancel out i.e. add up to zero net external force.

Consider a book at rest on a horizontal surface Fig. (5.2(a)). It is subject to two external forces: the force due to gravity (i.e. its weight W) acting downward and the upward force on the book by the table, the normal force R. R is a self-adjusting force. This is an example of the kind of situation mentioned above. The forces are not quite known fully but the state of motion is known. We observe the book to be at rest. Therefore, we conclude from the first law that the magnitude of R equals that of W. A statement often encountered is: “Since $W = R$, forces cancel and, therefore, the book is at rest”. This is incorrect reasoning. The correct statement is: “Since the book is observed to be at rest, the net external force on it must be zero, according to the first law. This implies that the normal force R must be equal and opposite to the weight W”

Galileo Galilei (1564 – 1642)

Galileo Galilei, born in Pisa, Italy in 1564 was a key figure in the scientific revolution in Europe about four centuries ago. Galileo proposed the concept of acceleration. From experiments on motion of bodies on inclined planes or falling freely, he contradicted the Aristotelian notion that a force was required to keep a body in motion, and that heavier bodies fall faster than lighter bodies under gravity. He thus arrived at the law of inertia that was the starting point of the subsequent epochal work of Isaac Newton.

Galileo's discoveries in astronomy were equally revolutionary. In 1609, he designed his own telescope (invented earlier in Holland) and used it to make a number of startling observations: mountains and depressions on the surface of the moon; dark spots on the sun; the moons of Jupiter and the phases of Venus. He concluded that the Milky Way derived its luminosity because of a large number of stars not visible to the naked eye. In his masterpiece of scientific reasoning : Dialogue on the Two Chief World Systems, Galileo advocated the heliocentric theory of the solar system proposed by Copernicus, which eventually got universal acceptance.

With Galileo came a turning point in the very method of scientific inquiry. Science was no longer merely observations of nature and inferences from them. Science meant devising and doing experiments to verify or refute theories. Science meant measurement of quantities and a search for mathematical relations between them. Not undeservedly, many regard Galileo as the father of modern science.

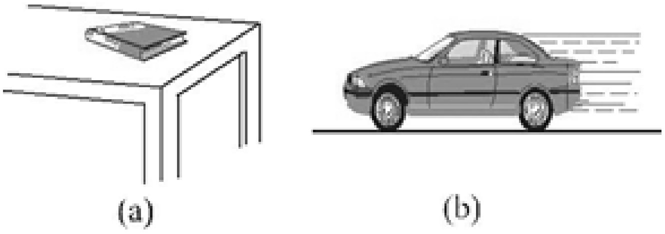


Fig. 5.2 **(a)** *a book at rest on the table, and* **(b)** *a car moving with uniform velocity. The net force is zero in each case.*

Consider the motion of a car starting from rest, picking up speed and then moving on a smooth straight road with uniform speed (Fig (5.2(b)). When the car is stationary, there is no net force acting on it. During pick-up, it accelerates. This must happen due to a net external force. Note, it has to be an external force. The acceleration of the car cannot be accounted for by any internal force. This might sound surprising, but it is true. The only conceivable external force along the road is the force of friction. It is the frictional force that accelerates the car as a whole.

(You will learn about friction in section 5.9). When the car moves with constant velocity, there is no net external force. The property of inertia contained in the First law is evident in many situations. Suppose we are standing in a stationary bus and the driver starts the bus suddenly. We get thrown backward with a jerk. Why? Our feet are in touch with the floor. If there were no friction, we would remain where we were, while the floor of the bus would simply slip forward under our feet and the back of the bus would hit us. However, fortunately, there is some friction between the feet and the floor. If the start is not too sudden, i.e. if the acceleration is moderate, the frictional force would be enough to accelerate our feet along with the bus. But our body is not strictly a rigid body. It is deformable, i.e. it allows some relative displacement between different parts. What this means is that while our feet go with the bus, the rest of the body remains where it is due to inertia. Relative to the bus, therefore, we are thrown backward. As soon as that happens, however, the muscular forces on the rest of the body (by the feet) come into play to move the body along with the bus. A similar thing happens when the bus suddenly stops. Our feet stop due to the friction which does not allow relative motion between the feet and the floor of the bus. But the rest of the body continues to move forward due to inertia. We are thrown forward. The restoring muscular forces again come into play and bring the body to rest.

Example 5.1 An astronaut accidentally gets separated out of his small spaceship accelerating in inter stellar space at a constant rate of 100 m s^{-2}. What is the acceleration of the astronaut the instant after he is outside the spaceship? (Assume that there are no nearby stars to exert gravitational force on him.)

Answer Since there are no nearby stars to exert gravitational force on him and the small spaceship exerts negligible gravitational attraction on him, the net force acting on the astronaut, once he is out of the spaceship, is zero. By the first law of motion the acceleration of the astronaut is zero.

5.5 NEWTON’S SECOND LAW OF MOTION

The first law refers to the simple case when the net external force on a body is zero. The second law of motion refers to the general situation when there is net external force acting on the body. It relates the net external force to the acceleration of the body.

Momentum

Momentum, **P** of a body is defined to be product of its mass *m* and velocity **v**, and is denoted by **p**:

$$\mathbf{p} = m\,\mathbf{v} \qquad (5.1)$$

Momentum is clearly a vector quantity. The following common experiences indicate the importance of this quantity for considering the effect of force on motion.

- Suppose a light-weight vehicle (say a small car) and a heavy weight vehicle (say a loaded truck) are parked on a horizontal road. We all know that a much greater force is needed to push the truck than the car to bring them to the same speed in same time. Similarly, a greater opposing force is needed to stop a heavy body than a light body in the same time, if they are moving with the same speed.

- If two stones, one light and the other heavy, are dropped from the top of a building, a person on the ground will find it easier to catch the light stone than the heavy stone. The mass of a body is thus an important parameter that determines the effect of force on its motion.

- Speed is another important parameter to consider. A bullet fired by a gun can easily pierce human tissue before it stops, resulting in casualty. The same bullet fired with moderate speed will not cause much damage. Thus for a given mass, the greater the speed, the greater is the opposing force needed to stop the body in a certain time. Taken together, the product of mass and velocity, that is momentum, is evidently a relevant variable of motion. The greater the change in the momentum in a given time, the greater is the force that needs to be applied.

- A seasoned cricketer catches a cricket ball coming in with great speed far more easily than a novice, who can hurt his hands in the act. One reason is that the cricketer allows a longer time for his hands to stop the ball. As you may have noticed, he draws in the hands backward in the act of catching the ball (Fig. 5.3). The novice, on the other hand, keeps his hands fixed and tries to catch the ball almost instantly. He needs to provide a much greater force to stop the ball instantly, and this hurts. The conclusion is clear: force not only depends on the change in momentum, but also on how fast the change is brought about. The same change in momentum brought about in a shorter time needs a greater applied force. In short, the greater the rate of change of momentum, the greater is the force.

Fig. 5.3 *Force not only depends on the change in momentum but also on how fast the change is brought about. A seasoned cricketer draws in his hands during a catch, allowing greater time for*

the ball to stop and hence requires a smaller force.

- Observations confirm that the product of mass and velocity (i.e. momentum) is basic to the effect of force on motion. Suppose a fixed force is applied for a certain interval of time on two bodies of different masses, initially at rest, the lighter body picks up a greater speed than the heavier body. However, at the end of the time interval, observations show that each body acquires the same momentum. Thus the same force for the same **time causes the same change in momentum for different bodies**. This is a crucial clue to the second law of motion.

- In the preceding observations, the vector character of momentum has not been evident. In the examples so far, momentum and change in momentum both have the same direction. But this is not always the case. Suppose a stone is rotated with uniform speed in a horizontal plane by means of a string, the magnitude of momentum is fixed, but its direction changes (Fig. 5.4). A force is needed to cause this change in momentum vector.

This force is provided by our hand through the string. Experience suggests that our hand needs to exert a greater force if the stone is rotated at greater speed or in a circle of smaller radius, or both. This corresponds to greater acceleration or equivalently a greater rate of change in momentum vector. This suggests that the greater the rate of change in momentum vector the greater is the force applied

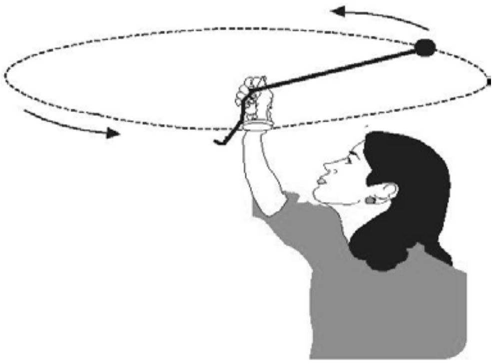


Fig. 5.4 *Force is necessary for changing the direction of momentum, even if its magnitude is constant. We can feel this while rotating a stone in a horizontal circle with uniform speed by means of a string.*

These qualitative observations lead to the **Second Law of motion** expressed by Newton as follows:

The rate of change of momentum of a body is directly proportional to the applied force and takes place in the direction in which the force acts.

Thus, if under the action of a force **F** for time interval *t*, the velocity of a body of mass *m* changes from **v** to **v**+Δ**v** i.e. its initial momentum p = m **v** changes by Δ**p** = m Δ**v**. According to the Second Law,

$$F \propto \frac{\Delta p}{\Delta t}$$

$$F = k\,\frac{\Delta p}{\Delta t}$$

Where *k* is a constant of proportionality. Taking the limit Δ*t* → 0, the term $\frac{\Delta p}{\Delta t}$becomes the *t* derivative or differential co-efficient of p with respect to *t*, denoted by$\frac{dp}{dt}$. Thus

$$F = k\,\frac{dp}{dt} \qquad (5.2)$$

For a body of fixed mass m,

$$\frac{dp}{dt} = \frac{d}{dt}(m\boldsymbol{v}) = m\,\frac{d\boldsymbol{v}}{dt} = m\boldsymbol{a} \qquad (5.3)$$

i.e., the Second law can also be written as

$$F = k\,m\,\boldsymbol{a} \qquad (5.4)$$

Which shows that force is proportional to the product of mass *m* and acceleration **a**.

The unit of force has not been defined so far. In fact, we use Eq. (5.4) to define the unit of force. We, therefore, have the liberty to choose any constant value for *k*. For simplicity, we choose *k* = 1. The Second Law then is

$$F = \frac{dp}{dt} = m\boldsymbol{a} \qquad (5.5)$$

In SI unit force is one that causes an acceleration of 1 m s^{-2} to a mass of 1 kg. This unit is known as newton: 1 N = 1 kg ms^{-2}.

Let us note at this stage some important points about the second law:

1. In the second law, **F** = 0 implies **a** = 0. The second Law is obviously consistent with the first law.

2. The second law of motion is a vector law. It is equivalent to three equations, one for each component of the vectors

$$F_x = \frac{dp_x}{dt} = ma_x$$

$$F_y = \frac{dp_y}{dt} = ma_y$$

$$F_z = \frac{dp_z}{dt} = ma_z \tag{5.6}$$

This means that if a force is not parallel to the velocity of the body, but makes some angle with it, it changes only the component of velocity along the direction of force. The component of velocity normal to the force remains unchanged. For example, in the motion of a projectile under the vertical gravitational force, the horizontal component of velocity remains unchanged (Fig. 5.5).

3. The second law of motion given by Eq. (5.5) is applicable to a single point particle. The force **F** in the law stands for the net external force on the particle and **a** stands for acceleration of the particle. It turns out, however, that the law in the same form applies to a rigid body or, even more generally, to a system of particles. In that case, **F** refers to the total external force on the system and **a** refers to the acceleration of the system as a whole. More precisely, **a** is the acceleration of the centre of mass of the system. **Any internal forces in the system are not to be included in F**.

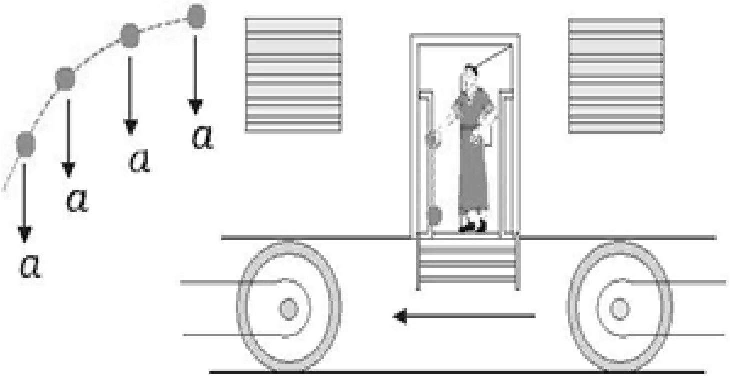


Fig. 5.5 *Acceleration at an instant is determined by the force at that instant. The moment after a stone is dropped out of an accelerated train, it has no horizontal acceleration or force, if air resistance is neglected. The stone carries no memory of its acceleration with the train a moment ago.*

4. The second law of motion is a local relation which means that force **F** at a point in space (location of the particle) at a certain instant of time is related to **a** at that point at that instant. Acceleration here and now is determined by the force here and now, **not by any history of the motion of the particle (See Fig. 5.5)**.

Example 5.2 A bullet of mass 0.04 kg moving with a speed of 90 m s^{-1} enters a heavy wooden block and is stopped after a distance of 60 cm. What is the average resistive force exerted by the block on the bullet?

Answer The retardation 'a' of the bullet (assumed constant) is given by

$$a = -\frac{u^2}{2s}$$

$$= -\frac{90\ x\ 90}{2\ x\ 0.6} ms^{-2}$$

$$= -6750\ ms^{-2}$$

The retarding force, by the Second Law of motion, is

$$= 0.04 \text{ kg x } 6750 \text{ m s}^{-2} = 270 \text{ N}$$

The actual resistive force, and therefore, retardation of the bullet may not be uniform. The answer therefore, only indicates the average resistive force

.***Example 5.3*** The motion of a particle of mass m is described by $y = ut + \frac{1}{2}\ gt^2$. Find 2 the force acting on the particle.

Answer

We know $y = ut + \frac{1}{2}\ gt^2$

Now,

$$\frac{dy}{dt} = u + gt$$

Acceleration, a = dx/dt = g

Then the force is given by Eq. (5.5)

$$F = ma = mg$$

Thus the given equation describes the motion of a particle under acceleration due to gravity and y is the position coordinates in the direction of g.

Impulse

We sometimes encounter examples where a large force acts for a very short duration producing a finite change in momentum of the body. For example, when a ball hits a wall and bounces back, the force on the ball by the wall acts for a very short time when the two are in contact, yet the force is large enough to reverse the momentum of the ball. Often, in these situations, the force and the time duration are difficult to ascertain separately. However, the product of force and time, which is the change in momentum of the body remains a measurable quantity. This product is called impulse:

Impulse = Force x time duration

= Change in momentum

A large force acting for a short time to produce a finite change in momentum is called an *impulsive force*. In the history of science, impulsive forces were put in a conceptually different category from ordinary forces. Newtonian mechanics has no such distinction. Impulsive force is like any other force except that it is large and acts for a short time.

Example 5.4 A batsman hits back a ball straight in the direction of the bowler without changing its initial speed of 12 m s^{-1}. If the mass of the ball is 0.15 kg, determine the impulse imparted to the ball. (Assume linear motion of the ball)

Answer Change in momentum

$= 0.15 \times 12 - (-0.15 \times 12)$

= 3.6 N s,

Impulse = 3.6 N s, in the direction from the batsman to the bowler.

This is an example where the force on the ball by the batsman and the time of contact of the ball and the bat are difficult to know, but the impulse is readily calculated.

5.6 NEWTON’S THIRD LAW OF MOTION

The second law relates the external force on a body to its acceleration. What is the origin of the external force on the body? What agency provides the external force? The simple answer in Newtonian mechanics is that the external force on a body always arises due to some other body. Consider a pair of bodies *A* and *B*. *B* gives rise to an external force on *A*. A natural question is: Does *A* in turn give rise to an external force on *B*? In some examples, the answer seems clear. If you press a coiled spring, the spring is compressed by the force of your hand. The compressed spring in turn exerts a force on your hand and you can feel it. But what if the bodies are not in contact? The earth pulls a stone downwards due to gravity. Does the stone exert a force on them earth? The answer is not obvious since we hardly see the effect of the stone on the earth. The answer according to Newton is: Yes, the stone does exert an equal and opposite force on the earth.

We do not notice it since the earth is very massive and the effect of a small force on its motion is negligible.

Thus, according to Newtonian mechanics, force never occurs singly in nature. Force is the mutual interaction between two bodies. Forces always occur in pairs. Further, the mutual forces between two bodies are always equal and opposite. This idea was expressed by Newton in the form of the **third law of motion**. **To every action, there is always an equal and opposite reaction.**

Newton's wording of the third law is so crisp and beautiful that it has become a part of common language. For the same reason perhaps, misconceptions about the third law abound. Let us note some important points about the third law, particularly in regard to the usage of the terms: action and reaction.

1. The terms action and reaction in the third law mean nothing else but 'force'. Using different terms for the same physical concept can sometimes be confusing. A simple and clear way of stating the third law is as follows :

Forces always occur in pairs. Force on a body A by B is equal and opposite to the force on the body B by A.

2. The terms action and reaction in the third law may give a wrong impression that action comes before reaction i.e. action is the cause and reaction the effect.

There is no cause-effect relation implied in the third law. The force on *A* by *B* and the force on *B* by *A* act at the same instant. By the same reasoning, any one of them may be called action and the other reaction.

3. Action and reaction forces act on different bodies, not on the same body. Consider a pair of bodies *A* and *B*. According to the third law,

$$\mathbf{F}_{AB} = -\,\mathbf{F}_{BA} \qquad (5.8)$$

(Force on *A* by *B*) = – (force on *B* by *A*)

Thus if we are considering the motion of any one body (*A* or *B*), only one of the two forces is relevant. It is an error to add up the two forces and claim that the net force is zero.

However, if you are considering the system of two bodies as a whole, $\mathbf{F}_{AB}$ and $\mathbf{F}_{BA}$ are internal forces of the system ($A + B$). They add up to give a null force. Internal forces in a body or a system of particles thus cancel away in pairs. This is an important fact that enables the second law to be applicable to a body or a system of particles (See Chapter7)

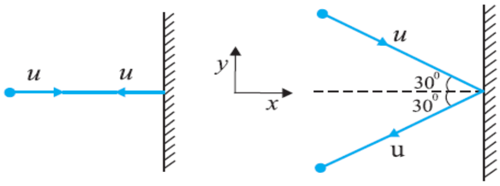
Isaac Newton (1642 – 1727)

Isaac Newton was born in Wools Thorpe, England in 1642, the year Galileo died. His extraordinary mathematical ability and mechanical aptitude remained hidden from others in his school life. In 1662, he went to Cambridge for undergraduate studies. A plague epidemic in 1665 forced the university town to close and Newton had to return to his mother's farm. There in two years of solitude, his dormant creativity blossomed in a deluge of fundamental discoveries in mathematics and physics: binomial theorem for negative and fractional exponents, the beginning of calculus, the inverse square law of gravitation, the spectrum of white light, and so on. Returning to Cambridge, he pursued his investigations in optics and devised a reflecting telescope.

In 1684, encouraged by his friend Edmund Halley, Newton embarked on writing what was to be one of the greatest scientific works ever published: The Principia Mathematica. In it, he enunciated the three laws of motion and the universal law of gravitation, which explained all the three Kepler's laws of planetary motion. The book was packed with a host of path-breaking achievements: basic principles of fluid mechanics, mathematics of wave motion, calculation of masses of the earth, the sun and other planets, explanation of the precession of equinoxes, theory of tides, etc. In 1704, Newton brought out another masterpiece Optics that summarized his work on light and color.

The scientific revolution triggered by Copernicus and steered vigorously ahead by Kepler and Galileo was brought to a grand completion by Newton. Newtonian mechanics unified terrestrial and celestial phenomena. The same mathematical equation governed the fall of an apple to the ground and the motion of the moon around the earth. The age of reason had dawned.

Example 5.5 Two identical billiard balls strike a rigid wall with the same speed but at different angles, and get reflected without any change in speed, as shown in Fig. 5.6. What is (i) the direction of the force on the wall due to each ball? (ii) The ratio of the magnitudes of impulses imparted to the balls by the wall?



(a) (b)

Fig. 5.6

Answer An instinctive answer to (i) might be that the force on the wall in case (a) is normal to the wall, while that in case (b) is inclined at 30° to the normal. This answer is wrong. The force on the wall is normal to the wall in both cases.

How to find the force on the wall? The trick is to consider the force (or impulse) on the ball due to the wall using the second law, and then use the third law to answer (i). Let *u* be the speed of each ball before and after collision with the wall, and m the mass of each ball. Choose the x and y axes as shown in the figure, and consider the change in momentum of the ball in each case:

<u>Case (a)</u>

$$(p_x)_{initial} = mu \qquad (p_y)_{initial} = 0$$

$$(p_x)_{final} = -mu \qquad (p_y)_{final} = 0$$

Impulse is the change in momentum vector. Therefore,

$$x\text{-component of impulse} = -2\,m\,u$$

$$y\text{-component of impulse} = 0$$

Impulse and force are in the same direction. Clearly, from above, the force on the ball due to the wall is normal to the wall, along the negative x-direction. Using Newton’s third law of motion, the force on the wall due to the ball is normal to the wall along the positive x-direction. The magnitude of force cannot be ascertained since the small time taken for the collision has not been specified in the problem.

<u>Case (b)</u>

$$(p_x)_{initial} = \mathrm{mu}\cos 30^o\,, (p_y)_{initial} = -mu\sin 30^o$$

$$(p_x)_{final} = -\,mu\cos 30^o\,, (p_y)_{final} = -mu\sin 30^o$$

Note, while p_x changes sign after collision, p_y does not. Therefore,

$$x\text{-component of impulse} = -2\, m\, u \cos 30°$$

$$y\text{-component of impulse} = 0$$

The direction of impulse (and force) is the same as in (a) and is normal to the wall along the negative x direction. As before, using Newton's third law, the force on the wall due to the ball is normal to the wall along the positive x direction.

The ratio of the magnitudes of the impulses imparted to the balls in (a) and (b) is

$$2mu\,/(2mucos30^0) = \frac{2}{\sqrt{3}} \approx 1.2$$

5.7 CONSERVATION OF MOMENTUM

The second and the third laws of motion lead to an important consequence: the law of conservation of momentum. Take a familiar example. A bullet is fired from a gun. If the force on the bullet by the gun is **F**, the force on the gun by the bullet is **–F**, according to the third law. The two forces act for a common interval of time *t*.

According to the second law, **F** *t* is the change in momentum of the bullet and **–F***t* is the change in momentum of the gun. Since initially, both are at rest, the change in momentum equals the final momentum for each. Thus if $\mathbf{p}_b$ is the momentum of the bullet after firing and $\mathbf{p}_g$ is the recoil momentum of the gun, $\mathbf{p}_g = -\mathbf{p}_b$ *i.e.* $\mathbf{p}_b+\mathbf{p}_g=0$. That is, the total momentum of the (bullet + gun) system is conserved.

Thus in an isolated system (i.e. a system with no external force), mutual forces between pairs of particles in the system can cause momentum change in individual particles, but since the mutual forces for each pair are equal and opposite, the momentum changes cancel in pairs and the total momentum remains unchanged. This fact is known as the **law of conservation of momentum: The total momentum of an isolated system of interacting particles is conserved.**

An important example of the application of the law of conservation of momentum is the collision of two bodies. Consider two bodies A and B, with initial momenta $\mathbf{p}_A$ and $\mathbf{p}_B$. The bodies collide, get apart, with final momenta $\mathbf{p}'_A$ and $\mathbf{p}'_B$ respectively. By the Second Law

$$F_{AB}\,\Delta t = \mathbf{p}'_A - \mathbf{p}'_B \text{ and}$$

$$F_{BA}\,\Delta t = \mathbf{p}'_B - \mathbf{p}_B$$

(Where we have taken a common interval of time for both forces i.e. the time for which the two bodies are in contact.)

Since $\mathbf{F}_{AB} = -\mathbf{F}_{BA}$ by the third law

$$\mathbf{p}'_A - \mathbf{p}_A = -(\mathbf{p}'_B - \mathbf{p}_B)$$

$$\mathbf{p}'_A + \mathbf{p}'_B = \mathbf{p}_A + \mathbf{p}_B \qquad (5.9)$$

Which shows that the total final momentum of the isolated system equals its initial momentum. Notice that this is true whether the collision is elastic or inelastic. In elastic collisions, there is a second condition that the total initial kinetic energy of the system equals the total final kinetic energy (See Chapter 6).

5.8 EQUILIBRIUM OF A PARTICLE

Equilibrium of a particle in mechanics refers to the situation when the net external force on the particle is zero*****. According to the first law, this means that, the particle is either at rest or in uniform motion.

If two forces $\mathbf{F}_1$ and $\mathbf{F}_2$, act on a particle, equilibrium requires

$$\mathbf{F1} = -\mathbf{F2} \qquad (5.10)$$

i.e., the two forces on the particle must be equal and opposite. Equilibrium under three concurrent forces $\mathbf{F}_1$, $\mathbf{F}_2$ and $\mathbf{F}_3$ requires that the vector sum of the three forces is zero.

$$\mathbf{F1} + \mathbf{F2} + \mathbf{F3} = \mathbf{0} \qquad (5.11)$$

In other words, the resultant of any two forces say $\mathbf{F}_1$ and $\mathbf{F}_2$, obtained by the parallelogram law of forces must be equal and opposite to the third force, $\mathbf{F}_3$.

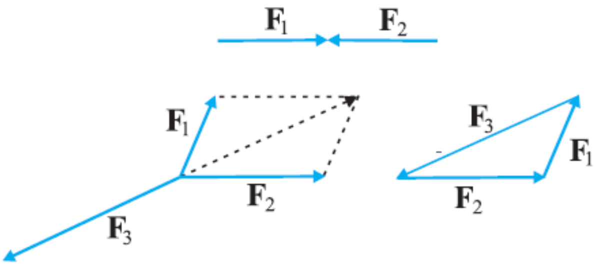


Fig. 5.7 *Equilibrium under concurrent forces.*

In other words, the resultant of any two forces say $\mathbf{F}_1$ and $\mathbf{F}_2$, obtained by the parallelogram law of forces must be equal and opposite to the third force, $\mathbf{F}_3$. As seen in Fig. 5.7, the three forces in equilibrium can be represented by the sides of a triangle with the vector arrows taken in the same sense. The result can be generalized to any number of forces. A particle is in equilibrium under the action of forces $\mathbf{F}_1$, $\mathbf{F}_2$,...$\mathbf{F}_n$if they can be represented by the sides of a closed n-sided polygon with arrows directed in the same sense.

Equation (5.11) implies

$$F_{1x} + F_{2x} + F_{3x} = 0$$

$$F_{1y} + F_{2y} + F_{3y} = 0$$

$$F_{1z} + F_{2z} + F_{3z} = 0 \qquad (5.12)$$

Where F_{1x}, F_{1y} and F_{1z} are the components of F_1 along x, y and z directions respectively.

Example 5.6 See Fig. 5.8 A mass of 6 kg is suspended by a rope of length 2 m from the ceiling. A force of 50 N in the horizontal direction is applied at the mid-point P of the rope, as shown. What is the angle the rope makes with the vertical in equilibrium? (Take g = 10 m s^{-2}). Neglect the mass of the rope

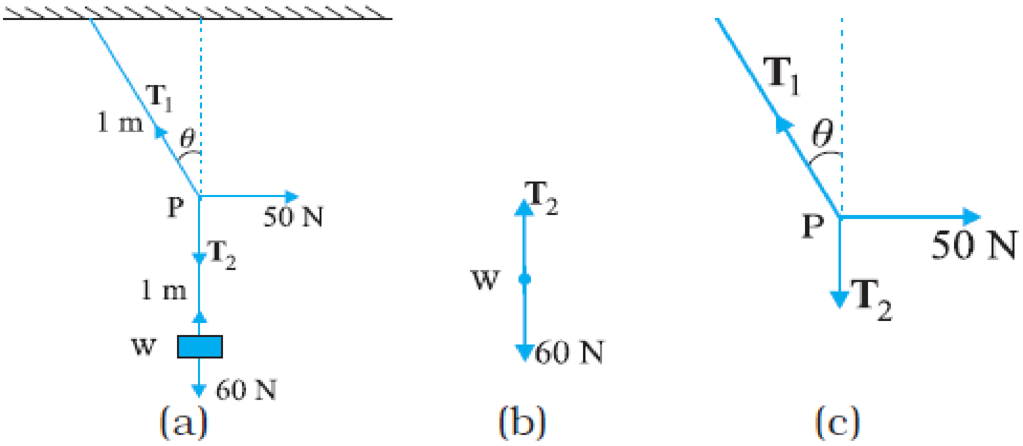


Fig. 5.8

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* *Equilibrium of a body requires not only translational equilibrium (zero net external force) but also rotational equilibrium (zero net external torque), as we shall see in Chapter 7.*

Answer

Figures 5.8(b) and 5.8(c) are known as free-body diagrams. Figure 5.8(b) is the free-body diagram of W and Fig. 5.8(c) is the free-body diagram of point P.

Consider the equilibrium of the weight W. Clearly, $T_2 = 6 \times 10 = 60$ N.

Consider the equilibrium of the point P under the action of three forces - the tensions T_1 and T_2, and the horizontal force 50 N. The horizontal and vertical components of the resultant force must vanish separately:

$$T_1 \cos \theta = T_2 = 60 \text{ N}$$

$$T_1 \sin\theta = 50 \text{ N}$$

Which gives that

$$Tan\ \theta = 5/6 \qquad \text{or}$$

$$\theta = tan^{-1} (5/6) = 40^{o}$$

Note the answer does not depend on the length of the rope (assumed mass less) nor on the point at which the horizontal force is applied.

5.9 COMMON FORCES IN MECHANICS

In mechanics, we encounter several kinds of forces. The gravitational force is, of course, all pervasive. Every object on the earth experiences the force of gravity due to the earth. Gravity also governs the motion of celestial bodies. The gravitational force can act at a distance without the need of any intervening medium.

All the other forces common in mechanics are contact forces*****. As the name suggests, a contact force on an object arises due to contact with some other object: solid or fluid. When bodies are in contact (e.g. a book resting on a table, a system of rigid bodies connected by rods, hinges and other types of supports), there are mutual contact forces (for each pair of bodies) satisfying the third law. The component of contact force normal to the surfaces in contact is called normal reaction. The component parallel to the surfaces in contact is called friction. Contact forces arise also when solids are in contact with fluids. For example, for a solid immersed in a fluid, there is an upward buoyant force equal to the weight of the fluid displaced. The viscous force, air resistance, etc are also examples of contact forces (Fig. 5.9).

Two other common forces are tension in a string and the force due to spring. When a spring is compressed or extended by an external force, a restoring force is generated. This force is usually proportional to the compression or elongation (for small displacements). The spring force F is written as $F = -k\,x$ where x is the displacement and k is the force constant. The negative sign denotes that the force is opposite to the displacement from the unstretched state. For an inextensible string, the force constant is very high. The restoring force in a string is called tension. It is customary to use a constant tension T throughout the string. This assumption is true for a string of negligible mass.

In Chapter 1, we learnt that there are four fundamental forces in nature. Of these, the weak and strong forces appear in domains that do not concern us here. Only the gravitational and electrical forces are relevant in the context of mechanics. The different contact forces of mechanics mentioned above fundamentally arise from electrical forces. This may seem surprising since we are talking of uncharged and non-magnetic bodies in mechanics. At the microscopic level, all bodies are made of charged constituents (nuclei and electrons) and the various contact forces arising due to elasticity of bodies, molecular collisions and impacts, etc. can ultimately be traced to the electrical forces between the charged constituents of different bodies.

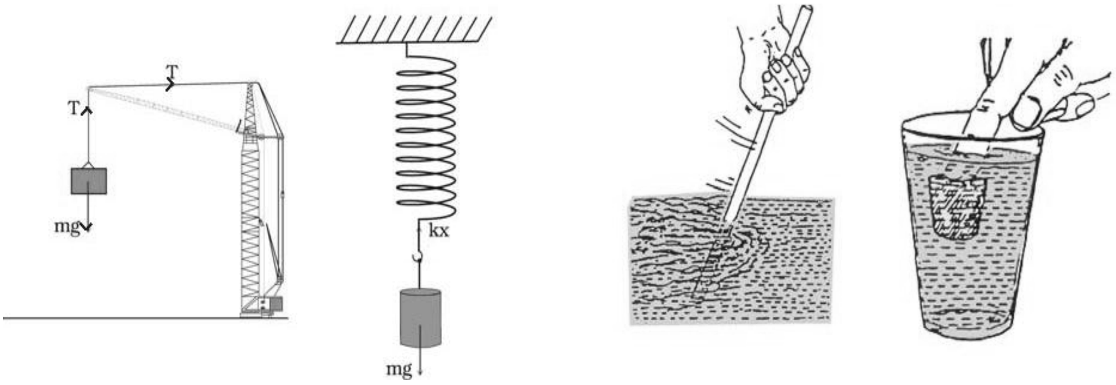

Fig. 5.9 *some examples of contact forces in mechanics.*

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* *We are not considering, for simplicity, charged and magnetic bodies. For these, besides gravity, there are electrical and magnetic non-contact forces.*

The detailed microscopic origin of these forces is, however, complex and not useful for handling problems in mechanics at the macroscopic scale. This is why they are treated as different types of forces with their characteristic properties determined empirically.

5.9.1 Friction

Let us return to the example of a body of mass m at rest on a horizontal table. The force of gravity (*mg*) is cancelled by the normal reaction force (N) of the table. Now suppose a force *F* is applied horizontally to the body. We know from experience that a small applied force may not be enough to move the body. But if the applied force *F* were the only external force on the body, it must move with acceleration *F/m*, however small. Clearly, the body remains at rest because some other force comes into play in the horizontal direction and opposes the applied force *F*, resulting in zero net force on the body. This force f_s parallel to the surface of the body in contact with the table is known as frictional force, or simply friction (Fig. 5.10(a)). The subscript stands for static friction to distinguish it from kinetic friction f_k that we consider later (Fig. 5.10(b)). Note that static friction does not exist by itself.

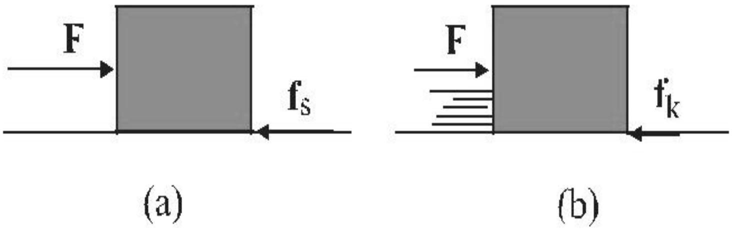


Fig. 5.10 *Static and sliding friction: (a) Impending motion of the body is opposed by static friction. When external force exceeds the maximum limit of static friction, the body begins to move. (b) Once the body is in motion, it is subject to sliding or kinetic friction which opposes relative motion between the two surfaces in contact. Kinetic friction is usually less than the maximum value of static friction.*

When there is no applied force, there is no static friction. It comes into play the moment there is an applied force. As the applied force *F* increases, f_s also increases, remaining equal and opposite to the applied force (up to a certain limit), keeping the body at rest. Hence, it is called **static friction**. Static friction opposes **impending motion**. The term impending motion means motion that would take place (but does not actually take place) under the applied force, if friction were absent.

We know from experience that as the applied force exceeds a certain limit, the body begins to move. It is found experimentally that the limiting value of static friction $(f_s)_{max}$ is independent of the area of contact and varies with the normal force *(N)* approximately as:

$$(f_s)_{max} = \mu_s^N$$

Where μ_s is a constant of proportionality depending only on the nature of the surfaces in contact. The constant μ_s is called the coefficient of static friction. The law of static friction may thus be written as

$$f_s \leq \mu_s \mathrm{N}$$

If the applied force *F* exceeds $(f_s)_{max}$ the body begins to slide on the surface. It is found experimentally that when relative motion has started, the frictional force decreases from the Static maximum value $(f_s)_{max}$. Frictional force that opposes relative motion between surfaces in contact is called kinetic or sliding friction and is denoted by f_k. Kinetic friction, like static friction, is found to be independent of the area of contact. Further, it is nearly independent of the velocity. It satisfies a law similar to that for static friction:

$$f_k = \mu_k N$$

Where μ_k the coefficient of kinetic friction, depends only on the surfaces in contact. As mentioned above, experiments show that μ_k is less than μ_s. When relative motion has begun, the acceleration of the body according to the Second Law is $(F - f_k)/m$. For a body moving with constant velocity, $F = f_k$. If the applied force on the body is removed, its acceleration is $-f_k/m$ and it eventually comes to a stop.

The laws of friction given above do not have the status of fundamental laws like those for gravitational, electric and magnetic forces. They are empirical relations that are only approximately true. Yet they are very useful in practical calculations in mechanics.

Thus, when two bodies are in contact, each experiences a contact force by the other. Friction, by definition, is the component of the contact force parallel to the surfaces in contact, which opposes impending or actual relative motion between the two surfaces. Note that it is not motion, but relative motion that the frictional force opposes. Consider a box lying in the compartment of a train that is accelerating. If the box is stationary relative to the train, it is in fact accelerating along with the train. What forces cause the acceleration of the box? Clearly, the only conceivable force in the horizontal direction is the force of friction. If there were no friction, the floor of the train would slip by and the box would remain at its initial position due to inertia (and hit the back side of the train). This impending relative motion is opposed by the static friction f_s. Static friction provides the same acceleration to the box as that of the train, keeping it stationary relative to the train.

Example 5.7 Determine the maximum acceleration of the train in which a box lying on its floor will remain stationary, given that the co-efficient of static friction between the box and the train's floor is 0.15.

Answer

Since the acceleration of the box is due to the static friction,

$$ma = f_s \leq \mu_s N = \mu_s m g$$

$$i.e.\ a \leq \mu_s g$$

$$\therefore a_{max} = \mu_s g = 0.15 \text{ x } 10 \text{ m s}^{-2} = 1.5 \text{ m s}^{-2}$$

Example 5.8 See Fig. 5.11. A mass of 4 kg rests on a horizontal plane. The plane is gradually inclined until at an angle θ = 15° with the horizontal, the mass just begins to slide. What is the coefficient of static friction between the block and the surface?

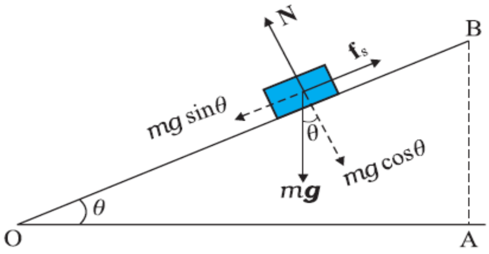


Fig 5.11

Answer The forces acting on a block of mass *m* at rest on an inclined plane are (i) the weight mg acting vertically downwards (ii) the normal force *N* of the plane on the block, and (iii) the static frictional force f_s opposing the impending motion. In equilibrium, the resultant of these forces must be zero. Resolving the weight *mg* along the two directions shown, we have

$$m\,g\sin\theta = f_s\ , \quad m\,g\cos\theta = N$$

As θ increases, the self-adjusting frictional force f_s increases until at $\theta = \theta_{max}$, f_s achieves its maximum value,

$$(f_s)_{\max} = \mu_s N.$$

Therefore,

$$\tan\theta_{max} = \mu_s \text{ or } \theta_{max} = \tan^{-1}\mu_s$$

When θ becomes just a little more than θ_{max}, there is a small net force on the block and it begins to slide. Note that θ_{max} depends only on μ_s and is independent of the mass of the block.

For $\qquad \theta_{max} = 15^0$

$$\mu_s = \tan 15^0$$

$$= 0.27$$

Example 5.9 What is the acceleration of the block and trolley system shown in a Fig. 5.12(a), if the coefficient of kinetic friction between the trolley and the surface is 0.04? What is the tension in the string? (Take g = 10 m s^{-2}). Neglect the mass of the string.

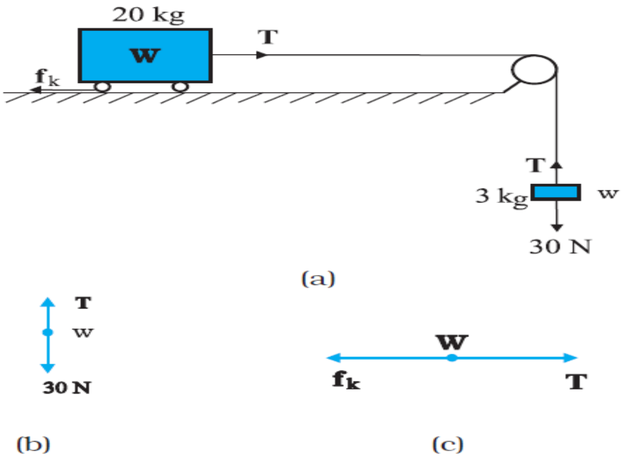


Fig. 5.12

Answer

As the string is inextensible, and the pulley is smooth, the 3 kg block and the 20 kg trolley both have same magnitude of acceleration. Applying second law to motion of the block (Fig. 5.12(b)),

$$30 - T = 3a$$

Apply the second law to motion of the trolley (Fig. 5.12 (c)),

$$T - f_k = 20\,a.$$

Now $f_k = \mu_k N$

Here $\mu_k = 0.04$

$$N = 20 \times 10$$

$$= 200 \text{ N}$$

Thus the equation for the motion of the trolley is

$$T - 0.04 \times 200 = 20\,a \text{ Or } T - 8 = 20a.$$

These equations give

$$a = \frac{22}{23} \text{ m s}^{-2} = 0.96 \text{ m s}^{-2}$$

and $T = 27.1$ N.

Rolling friction

A body like a ring or a sphere rolling without slipping over a horizontal plane will suffer no friction, in principle. At every instant, there is just one point of contact between the body and the plane and this point has no motion relative to the plane. In this ideal situation, kinetic or static friction is zero and the body should continue to roll with constant velocity. We know, in practice, this will not happen and some resistance to motion (rolling friction) does occur, i.e. to keep the body rolling, some applied force is needed. For the same weight, rolling friction is much smaller (even by 2 or 3 orders of magnitude) than static or sliding friction. This is the reason why discovery of the wheel has been a major milestone in human history.

Rolling friction again has a complex origin, though somewhat different from that of static and sliding friction. During rolling, the surfaces in contact get momentarily deformed a little, and this results in a finite area (not a point) of the body being in contact with the surface. The net effect is that the component of the contact force parallel to the surface opposes motion.

We often regard friction as something undesirable. In many situations, like in a machine with different moving parts, friction does have a negative role. It opposes relative motion and thereby dissipates power in the form of heat, etc. Lubricants are a way of reducing kinetic friction in a machine. Another way is to use ball bearings between two moving parts of a machine. (Fig. 5.13(a)) Since the rolling friction between ball bearings and the surfaces in contact is very small, power dissipation is reduced. A thin cushion of air maintained between solid surfaces in relative motion is another effective way of reducing friction (Fig. 5.13(a)).

In many practical situations, however, friction is critically needed. Kinetic friction that dissipates power is nevertheless important for quickly stopping relative motion. It is made use of by brakes in machines and automobiles. Similarly, static friction is important in daily life. We are able to walk because of friction. It is impossible for a car to move on a very slippery road. On an ordinary road, the friction between the tyres and the road provides the necessary external force to accelerate the car.

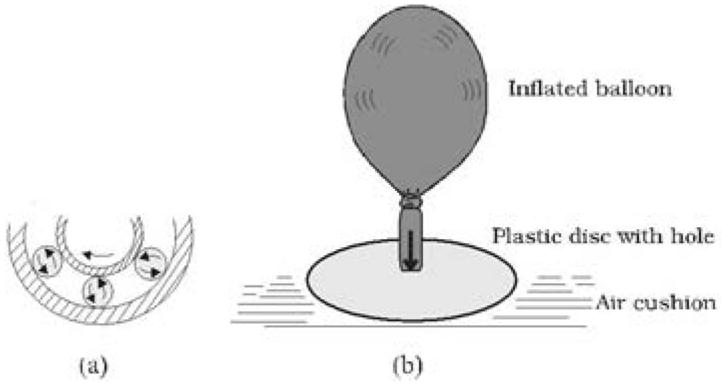


Fig. 5.13 *Some ways of reducing friction. (a) Ball bearings placed between moving parts of a machine. (b) Compressed cushion of air between surfaces in relative motion.*

5.10 CIRCULAR MOTION

We have seen in Chapter 4 that acceleration of a body moving in a circle of radius R with uniform speed v is v^2/R directed towards the centre. According to the second law, the force f providing this acceleration is:

$$f = \frac{mv^2}{R} \quad (5.16)$$

Where m is the mass of the body. This force directed forwards the centre is called the centripetal force. For a stone rotated in a circle by a string, the centripetal force is provided by the tension in the string. The centripetal force for motion of a planet around the sun is the gravitational force on the planet due to the sun. For a car taking a circular turn on a horizontal road, the centripetal force is the force of friction.

The circular motion of a car on a flat and banked road gives interesting application of the laws of motion.

Motion of a car on a level road

Three forces act on the car. (Fig. 5.14(a)

(i) The weight of the car, mg

(ii) Normal reaction, N

(iii) Frictional force, f

As there is no acceleration in the vertical direction

$$N - mg = 0$$

$$N = mg \tag{5.17}$$

The centripetal force required for circular motion is along the surface of the road, and is provided by the component of the contact force between road and the car tyres along the surface. This by definition is the frictional force.

Note that it is the static friction that provides the centripetal acceleration. Static friction opposes the impending motion of the car moving away from the circle. Using equation (5.14) & (5.16) we get the result

$$f \le \mu_s N = \frac{mv^2}{R}$$

$$v^2 \le \frac{\mu_s RN}{m} = \mu_s Rg \qquad [\text{Q}N = \text{mg}]$$

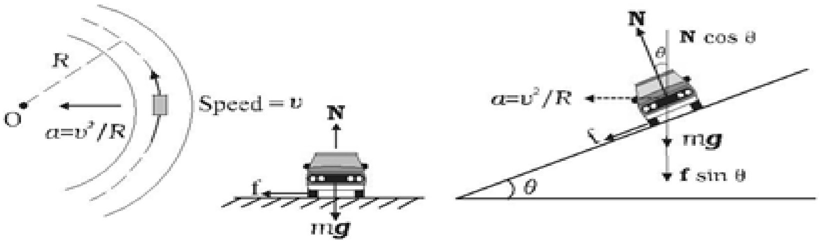


Fig. 5.14 *Circular motion of a car on (a) a level road, (b) a banked road.*

Which is independent of the mass of the car. This shows that for a given value of μ_s and R, there is a maximum speed of circular motion of the car possible, namely

$$V_{max} = \sqrt{\mu_s R g}$$

Motion of a car on a banked road

We can reduce the contribution of friction to the circular motion of the car if the road is banked (Fig. 5.14(b)). Since there is no acceleration along the vertical direction, the net force along this direction must be zero. Hence,

$$N cos\theta = mg + f\ sin\theta \qquad (5.19b)$$

The centripetal force is provided by the horizontal components of *N* and *f*.

$$N\ sin\theta\ +\ f\ cos\ \theta = \frac{mv^2}{R} \qquad (5.20a)$$

But $f \leq \mu s\ N$

Thus to obtain v_{max} we put

$f = \mu_s\ N.$

Then Eqs. (5.19) & (5.20) become

$$N\ cos\theta = mg + \mu_s\ N\ sin\theta \qquad (5.19b)$$

$$N \sin\theta +\ \mu_s N\ cos\theta = mv^2/R \qquad (5.20b)$$

$$N = \frac{mg}{\cos\theta - \mu_s sin\theta}$$

Substituting value of N in Eq. (5.20b), we get

$$mg\frac{(\sin\theta - \ \mu_s \cos\theta)}{\cos\theta - \ \mu_s \sin\theta} = \frac{m\ v_{max}^2}{R}$$

$$\text{or } v_{max} = \left(Rg\frac{\mu_s + \tan\theta}{1 - \mu_s \tan\theta}\right)^{\frac{1}{2}} \qquad (5.21)$$

Comparing this with Eq. (5.18) we see that maximum possible speed of a car on a banked road is greater than that on a flat road.

For $\mu_s = 0$ in Eq. (5.21),

$$v_0 = (Rg\ tan\theta)^{1/2}$$

At this speed, frictional force is not needed at all to provide the necessary centripetal force. Driving at this speed on a banked road will cause little wear and tear of the tyres. The same equation also tells you that for $v < v_o$, frictional force will be up the slope and that a car can be parked only if tan $\theta \leq \mu_s$.

Example 5.10 A cyclist speeding at 18km/h on a level road takes a sharp circular turn of radius 3 m without reducing the speed. The co-efficient of static friction between the tyres and the road is 0.1. Will the cyclist slip while taking the turn?

Answer On an unbanked road, frictional force alone can provide the centripetal force needed to keep the cyclist moving on a circular turn without slipping. If the speed is too large, or if the turn is too sharp (i.e. of too small a radius) or both, the frictional force is not sufficient to provide the necessary centripetal force, and the cyclist slips. The condition for the cyclist not to slip is given by Eq. (5.18):

$$v^2 \leq \mu_s R g$$

Now, R = 3 m, g = 9.8 m s^{-2}, μ_s = 0.1. That is, $\mu_s R g$ = 2.94 $m^2 s^{-2}$. v = 18 km/h = 5 m s^{-1}; i.e., v^2= 25 $m^2 s^{-2}$. The condition is not obeyed. The cyclist will slip while taking the circular turn.

Example 5.11 A circular racetrack of radius 300 m is banked at an angle of 15°. If the coefficient of friction between the wheels of a race-car and the road is 0.2, what is the (a) optimum speed of the race-car to avoid wear and tear on its tyres, and (b) maximum permissible speed to avoid slipping?

Answer On a banked road, the horizontal component of the normal force and the frictional force contribute to provide centripetal force to keep the car moving on a circular turn without slipping. At the optimum speed, the normal reaction's component is enough to provide the needed centripetal force, and the frictional force is not needed. The optimum speed v_o is given by Eq. (5.22):

$$v_o = (R\ g\ \tan\theta)^{1/2}$$

Here R = 300 m, θ= 15°, g = 9.8 m s^{-2}; we have

$$v_o = 28.1 \text{ m s}^{-1}.$$

The maximum permissible speed v_{max} is given by Eq. (5.21):

$$v_{max} = \left(Rg\frac{\mu_s + \tan\theta}{1 - \mu_s\tan\theta}\right)^{\frac{1}{2}} = 38.1 \text{ m s}^{-1}$$

5.11 SOLVING PROBLEMS IN MECHANICS

The three laws of motion that you have learnt in this chapter are the foundation of mechanics. You should now be able to handle a large variety of problems in mechanics. A typical problem in mechanics usually does not merely involve a single body under the action of given forces. More often, we will need to consider an assembly of different bodies exerting forces on each other. Besides, each body in the assembly experiences the force of gravity. When trying to solve a problem of this type, it is useful to remember the fact that we can choose any part of the assembly and apply the laws of motion to that part provided we include all forces on the chosen part due to the remaining parts of the assembly. We may call the chosen part of the assembly as the system and the remaining part of the assembly (plus any other agencies of forces) as the environment. We have followed the same method in solved examples. To handle a typical problem in mechanics systematically, one should use the following steps:

(i) Draw a diagram showing schematically the various parts of the assembly of bodies, the links, supports, etc.

(ii) Choose a convenient part of the assembly as one system. Draw a separate diagram which shows this system

(iii) and all the forces on the system by the remaining part of the assembly. Include also the forces on the system by other agencies. **Do not include the forces on the environment by the system**. A diagram of this type is known as 'a free-body diagram'. (Note this does not imply that the system under consideration is without a net force).

(iv) In a free-body diagram, include information about forces (their magnitudes and directions) that are either given or you are sure of (e.g., the direction of tension in a string along its length). The rest should be treated as unknowns to be determined using laws of motion.

(v) If necessary, follow the same procedure for another choice of the system. In doing so, employ Newton's third law. That is, if in the free-body diagram of *A*, the force on *A* due to *B* is shown as **F,** then in the free-body diagram of *B*, the force on *B* due to *A* should be shown as **–F.**

The following example illustrates the above procedure

Example 5.12 See (Fig. 5.15) A wooden block of mass 2 kg rests on a soft horizontal floor. When an iron cylinder of mass 25 kg is placed on top of the block, the floor yields steadily and the block and the cylinder together go down with an acceleration of 0.1 m s^{-2}. What is the action of the block on the floor (a) before and (b) after the floor yields? Take g = 10 m s^{-2}. Identify the action-reaction pairs in the problem.

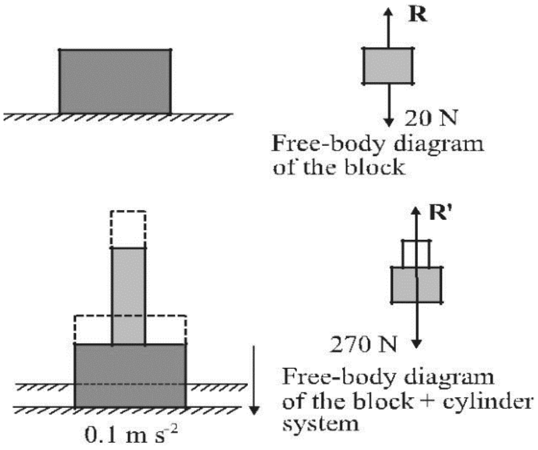


Fig. 5.15

Answer

(a) The block is at rest on the floor. Its free-body diagram shows two forces on the block, the force of gravitational attraction by the earth equal to 2 □10 = 20 N; and the normal force *R* of the floor on the block. By the First Law,

the net force on the block must be zero i.e., *R* = 20 N. Using third law the action of the block (i.e. the force exerted on the floor by the block) is equal to 20 N and directed vertically downwards.

(b) The system (block + cylinder) accelerates downwards with 0.1 m s^{-2}. The free-body diagram of the system shows two forces on the system: the force of gravity due to the earth (270 N); and the normal force *R′* by the floor. Note, the free-body diagram of the system does not show the internal forces between the block and the cylinder. Applying the second law to the system,

$$270 - R' = 27 \times 0.1\text{N ie. } R' = 267.3 \text{ N}$$

By the third law, the action of the system on the floor is equal to 267.3 N vertically downward.

Action-reaction pairs

For (a): (i) The force of gravity (20 N) on the block by the earth (say, action); the force of gravity on the earth by the block (reaction) equal to 20 N directed upwards (not shown in the figure).

(ii) The force on the floor by the block (action); the force on the block by the floor (reaction).

For (b): (i) The force of gravity (270 N) on the system by the earth (say, action); the force of gravity on the earth by the system (reaction), equal to 270 N, directed upwards (not shown in the figure).

(ii) The force on the floor by the system (action); the force on the system by the floor (reaction). In addition, for (b), the force on the block by the cylinder and the force on the cylinder by the block also constitute an action-reaction pair.

The important thing to remember is that an action-reaction pair consists of mutual forces which are always equal and opposite between two bodies. Two forces on the same body which happen to be equal and opposite can never constitute an action-reaction pair. The force of gravity on the mass in (a) or (b) and the normal force on the mass by the floor are not action-reaction pairs. These forces happen to be equal and opposite for (a) since the mass is at rest. They are not so for case (b), as seen already. The weight of the system is 270 N, while the normal force R' is 267.3 N. The practice of drawing free-body diagrams is of great help in solving problems in mechanics. It allows you to clearly define your system and consider all forces on the system due to objects that are not part of the system itself. A number of exercises in this and subsequent chapters will help you cultivate this practice.

SUMMARY

1. Aristotle's view that a force is necessary to keep a body in uniform motion is wrong. A force is necessary in practice to counter the opposing force of friction.

2. Galileo extrapolated simple observations on motion of bodies on inclined planes, and arrived at the law of inertia. Newton's first law of motion is the same law rephrased thus: *"Everybody continues to be in its state of rest or of uniform motion in a straight line, unless compelled by some external force to act otherwise"*. In simple terms, the First Law is **"If external force on a body is zero, its acceleration is zero"**.

3. Momentum (**p**) of a body is the product of its mass *(m)* and velocity ***(v)*** :

$$\boldsymbol{p} = m\boldsymbol{v}$$

4. Newton's second law of motion :

   The rate of change of momentum of a body is proportional to the applied force and takes place in the direction in which the force acts. Thus

$$F = k\frac{dp}{dt} = k\,m\boldsymbol{a}$$

Where F is the net external force on the body and a its acceleration. We set the constant of proportionality $k = 1$ in S.I. Then

$$F = \frac{dp}{dt} = m\boldsymbol{a}$$

The SI unit of force is newton: 1 N = 1 kg m s^{-2}.

(a) The second law is consistent with the First Law (**F**= 0 implies **a**= 0)

(b) It is a vector equation

(c) It is applicable to a particle, and also to a body or a system of particles, provided **F** is the total external force on the system and **a** is the acceleration of the system as a whole.

(d) **F** at a point at a certain instant determines **a** at the same point at that instant. That is the Second Law is a local law; **a** at an instant does not depend on the history of motion.

5. Impulse is the product of force and time which equals change in momentum.

   The notion of impulse is useful when a large force acts for a short time to produce a measurable change in momentum. Since the time of action of the force is very short, one can assume that there is no appreciable change in the position of the body during the action of the impulsive force.

6. Newton’s third law of motion:

To every action, there is always an equal and opposite reaction

In simple terms, the law can be stated thus: Forces *in nature always occur between pairs of bodies. Force on a body A by body B is equal and opposite to the force on the body B by A.*

Action and reaction forces are simultaneous forces. There is no cause-effect relation between action and reaction. Any of the two mutual forces can be called action and the other reaction. Action and reaction act on different bodies and so they cannot be cancelled out. The internal action and reaction forces between different parts of a body do, however, sum to zero.

7. *Law of Conservation of Momentum*

The total momentum of an isolated system of particles is conserved. The law follows from the second and third law of motion.

8. *Friction*

Frictional force opposes (impending or actual) relative motion between two surfaces in contact. It is the component of the contact force along the common tangent to the surface in contact. Static friction f_s opposes impending relative motion; kinetic friction f_k opposes actual relative motion. They are independent of the area of contact and satisfy the following approximate laws:

$$f_s \leq (f_s)_{\max} = \mu_s R$$

$$f_k = \mu_k R$$

μ_s (co-efficient of static friction) and μ_k (co-efficient of kinetic friction) are constants characteristic of the pair of surfaces in contact. It is found experimentally that μ_k is less than μ_s.

Quantity	**Symbol**	**Units**	**Dimensions**	**Remarks**
Momentum	p	Kg m s^{-1} or N s	$[MLT^{-1}]$	Vector
Force	F	N	$[MLT^{-2}]$	F=ma second law
Impulse		Kg m s^{-1} or Ns	$[MLT^{-1}]$	Impulse = force x time =change in momentum
Static friction	f_s	N	$[MLT^{-2}]$	$f_s \leq \mu_s N$
Kinetic friction	f_k	N	$[MLT^{2}]$	$f_s = \mu_k N$

CHAPTER SIX

WORK, ENERGY AND POWER

6.1 INTRODUCTION

The terms ‘work’, ‘energy’ and ‘power’ are frequently used in everyday language. A farmer ploughing the field, a construction worker carrying bricks, a student studying for a competitive examination, an artist painting a beautiful landscape, all are said to be working. In physics, however, the word ‘Work’ covers a definite and precise meaning. Somebody who has the capacity to work for 14-16 hours a day is said to have a large stamina or energy. We admire a long distance runner for her stamina or energy. Energy is thus our capacity to do work. In Physics too, the term ‘energy’ is related to work in this sense, but as said above the term ‘work’ itself is defined much more precisely. The word ‘power’ is used in everyday life with different shades of meaning. In karate or boxing we talk of ‘powerful’ punches. These are delivered at a great speed. This shade of meaning is close to the meaning of the word ‘power’ used in physics. We shall find that there is at best a loose correlation between the physical definitions and the physiological pictures these terms generate in our minds. The aim of this chapter is to develop an understanding of these three physical quantities. Before we proceed to this task, we need to develop a mathematical prerequisite, namely the scalar product of two vectors.

6.1.1 The Scalar Product

We have learnt about vectors and their use in Chapter 4. Physical quantities like displacement, velocity, acceleration, force etc. are vectors. We have also learnt how vectors are added or subtracted. We now need to know how vectors are multiplied. There are two ways of multiplying vectors which we shall come across : one way known as the scalar product gives a scalar from two vectors and the other known as the vector product produces a new vector from two vectors. We shall look at the vector product in Chapter 7. Here we take up the scalar product of two vectors. The scalar product or dot product of any two vectors **A** and **B**, denoted as **A.B** (read **A** dot **B**) is defined as

$$\mathbf{B} = AB\cos\theta \tag{6.1a}$$

Where θ is the angle between the two vectors as shown in Fig. 6.1a. Since A, B and $\cos\theta$ are scalars, the dot product of **A** and **B** is a scalar quantity. Each vector, **A** and **B**, has a direction but their scalar product does not have a direction.

From Eq. (6.1a), we have

$$\mathbf{A.B} = A(B\cos\theta)$$

$$= B\,(A\cos\theta)$$

Geometrically, $B\cos\theta$ is the projection of **B** onto **A** in Fig.6.1 (b) and $A\cos\theta$ is the projection of **A** onto **B** in Fig. 6.1 (c). So, **A·B** is the product of the magnitude of **A** and the component of **B** along **A**. Alternatively, it is the product of the magnitude of **B** and the component of **A** along **B**.

Equation (6.1a) shows that the scalar product follows the commutative law:

$$\mathbf{A.B} = \mathbf{B.A}$$

Scalar product obeys the **distributive law**:

$$\mathbf{A}.(\mathbf{B} + \mathbf{C}) = \mathbf{A.B} + \mathbf{A.C}$$

Further, **A.** (λ**B**) = λ (**A.B**) where λ is a real number.

The proofs of the above equations are left to you as an exercise.

For unit vectors **i, j,k** we have

$$\mathbf{i}\cdot\mathbf{i} = \mathbf{j}\cdot\mathbf{j} = \mathbf{k}\cdot\mathbf{k} = 1$$

$$\mathbf{i}\cdot\mathbf{j} = \mathbf{j}\cdot\mathbf{k} = \mathbf{k}\cdot\mathbf{i} = 0$$

Given two vectors $\mathbf{A} = A_x\mathbf{i} + A_y\mathbf{j} + A_z\mathbf{k}$, $\mathbf{B} = B_x\mathbf{i} + B_y\mathbf{j} + B_z\mathbf{k}$ their scalar product is

$$\boldsymbol{A.B} = Axi + Ayj + AzkBxi + Byj + Bzk$$

$$= AxBx + AyBy + AzBz \qquad (6.1c)$$

From the definition of scalar product and, (Eq. 6.1b) we have:

$$(\text{ i })\ \mathbf{A}\,.\,\mathbf{A} = A_xA_x + A_yA_y + A_zA_z$$

$$\text{Or, } A^2 = A_x^2 + A_y^2 + A_z^2 (6.1c)$$

$$\text{Since } \mathbf{A}\cdot\mathbf{A} = |\mathbf{A}||\mathbf{A}|\cos\theta = A^2$$

(ii) **A.B** = 0, if **A** and **B** are perpendicular.

Example 6.1 Find the angle between force F= $(3i + 4j - 5k)$unit and displacement d = $(5\hat{\imath} + 4\hat{\jmath} + 3\hat{k})$ unit. Also find the projection of **F** on **d**.

Answer $\mathbf{F}.\mathbf{d} = F_x d_x + F_y d_y + F_z d_z$

$= 3\ (5) + 4\ (4) + (-\ 3)\ (3)$

$= 16$ unit

Hence $\mathbf{F}.\mathbf{d}\ = F\mathrm{d}\cos\theta\ = 16$ unit

Now $\mathbf{F}.\mathbf{F} = F^2 = F_x{}^2 + F_y{}^2 + F_z{}^2$

$= 9 + 16 + 25$

$= 50$ unit

and $\mathbf{d}.\mathbf{d} = \ d^2 = d_x{}^2 + d_y{}^2 + d_z{}^2$

$= 25 + 16 + 9$

$= 50$ unit

$$cos\ \theta = 165050 = 1650 = 0.32$$

$$\theta = \cos^{-1}(0.32)$$

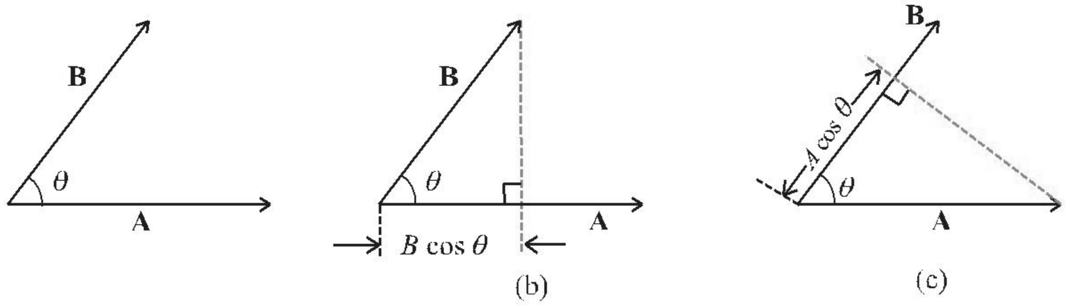


Fig. 6.1*(a) The scalar product of two vectors* ***A*** *and* ***B*** *is a scalar:* ***A.B****= ABcosθ. (b) Bcosθ is the projection of* ***B*** *onto* ***A****. (c) A cos θ is the projection of* ***A*** *onto* ***B****.*

6.2 NOTIONS OF WORK AND KINETIC ENERGY: THE WORK-ENERGY THEOREM

The following relation for rectilinear motion under constant acceleration a has been encountered in Chapter 3,

$$v^2 - u^2 = 2\ as$$

where u and v are the initial and final speeds and s the distance traversed. Multiplying both sides by $m/2$, we have

$$12mv^2-12mu^2=mas=FS \qquad (6.2a)$$

where the last step follows from Newton’s Second Law. We can generalise Eq. (6.1) to three dimensions by employing vectors

$v^2 - u^2 = 2\mathbf{a.d}$

Once again multiplying both sides by $m/2$, we obtain

$$12mv^2-12mu^2=ma.d=Fd \qquad (6.2b)$$

The above equation provides a motivation for the definitions of work and kinetic energy. The left side of the equation is the difference in the quantity ‘half the mass times the square of the speed’ from its initial value to its final value. We call each of these quantities the ‘kinetic energy’, denoted by K. The right side is a product of the displacement and the component of the force along the displacement. This quantity is called ‘work’ and is denoted by W. Eq. (6.2) is then

$$K_f - K_i = W$$

(6.3)

where K_i and K_f are respectively the initial and final kinetic energies of the object. Work refers to the force and the displacement over which it acts. **Work is done by a force on the body over a certain displacement**.

Equation (6.2) is also a special case of the work-energy (WE) theorem: **The change in kinetic energy of a particle is equal to the work done on it by the net force**. We shall generalise the above derivation to a varying force in a later section.

Example 6.2 It is well known that a raindrop falls under the influence of the downward gravitational force and the opposing resistive force. The latter is known to be proportional to the speed of the drop but is otherwise undetermined. Consider a drop of mass1.00 g falling from a height 1.00 km. It hits the ground with a speed of 50.0 m s^{-1}. (a) What is the work done by the gravitational force? What is the work done by the unknown resistive force?

Answer (a) The change in kinetic energy of the drop is

$$K = \frac{1}{2}mv^2$$

$$=12\times10-3\times50\times50$$

$$=1.25 \text{ J}$$

where we have assumed that the drop is initially at rest.

Assuming that g is a constant with a value 10 m/s^2, the work done by the gravitational force is,

$$W_g = mgh$$

$$= 10^{-3} \text{ x } 10 \text{ x } 10^3$$

$$= 10.0 \text{ J}$$

(b) From the work-energy theorem

$$K = W_g + W_r$$

where W_r is the work done by the resistive force on the raindrop. Thus

$$W_r = K - W_g$$

$$= 1.25 - 10$$

$= -\,8.75$ J is negative.

6.3 WORK

As seen earlier, work is related to force and the displacement over which it acts. Consider a constant force **F** acting on an object of mass *m*. The object undergoes a displacement **d** in the positive *x*-direction as shown in Fig. 6.2.

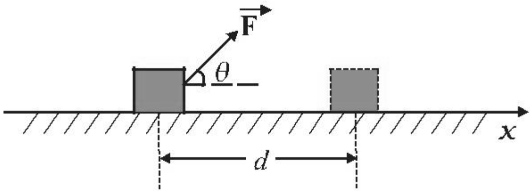


Fig. 6.2 An object undergoes a displacement d under the influence of the force F.

The work done by the force is defined to be the product of component of the force in the direction of the displacement and the magnitude of this displacement. Thus

$$W = (F \cos\theta)d = \mathbf{F}.\mathbf{d} \qquad (6.4)$$

We see that if there is no displacement, there is no work done even if the force is large. Thus, when you push hard against a rigid brick wall, the force you exert on the wall does no work. Yet your muscles are alternatively contracting and relaxing and internal energy is being used up and you do get tired. Thus, the meaning of work in physics is different from its usage in everyday language.

No work is done if :

(i) the displacement is zero as seen in the example above. A weightlifter holding a 150 kg mass steadily on his shoulder for 30 s does no work on the load during this time.

(ii) the force is zero. A block moving on a smooth horizontal table is not acted upon by a horizontal force (since there is no friction), but may undergo a large displacement.

the force and displacement are mutually perpendicular. This is so since, for $\theta = \pi/2$ rad (= 90^o), cos ($\pi/2$) = 0. For the block moving on a smooth horizontal table, the gravitational force *mg* does no work since it acts at right angles to the displacement. If we assume that the moon's orbits around the earth is perfectly circular then the earth's gravitational force does no work. The moon's instantaneous displacement is tangential while the earth's force is radially inwards and $\theta = \pi/2$.

Work can be both positive and negative. If θ is between 0^o and 90^o, cos θ in Eq. (6.4) is positive. If θ is between 90^o and 180^o, cos θ is negative. In many examples the frictional force opposes displacement and $\theta = 180^o$. Then the work done by friction is negative (cos $180^o = -1$).

From Eq. (6.4) it is clear that work and energy have the same dimensions, $[ML^2T^{-2}]$. The SI unit of these is joule (J), named after the famous British physicist James Prescott Joule (1811-1869). Since work and energy are so widely used as physical concepts, alternative units abound and some of these are listed in Table 6.1.

Table 6.1 Alternative Units of Work/Energy in J

Erg	10^{-7} J
Electron volt (eV)	1.6×10^{-19} J
Calorie (cal)	4.186 J
Kilowatt hour (kWh)	3.6×10^{6} J

Example 6.3 A cyclist comes to a skidding stop in 10 m. During this process, the force on the cycle due to the road is 200 N and is directly opposed to the motion. (a) How much work does the road do on the cycle? (b) How much work does the cycle do on the road?

Answer Work done on the cycle by the road is the work done by the stopping (frictional) force on the cycle due to the road.

(a)The stopping force and the displacement make an angle of 180° (π rad) with each other. Thus, work done by the road,

$$
\begin{aligned}
W_r &= Fd\cos\theta \\
&= 200 \times 10 \times \cos\pi \\
&= -2000\ \text{J}
\end{aligned}
$$

It is this negative work that brings the cycle to a halt in accordance with WE theorem.

(b) From Newton's Third Law an equal and opposite force acts on the road due to the cycle. Its magnitude is 200 N. However, the road undergoes no displacement. Thus, work done by cycle on the road is zero.

The lesson of this example is that though the force on a body A exerted by the body B is always equal and opposite to that on B by A (Newton's Third Law); the work done on A by B is not necessarily equal and opposite to the work done on B by A.

6.4 KINETIC ENERGY

As noted earlier, if an object of mass *m* has velocity **v**, its kinetic energy *K* is

$$K= 12mv.v=12mv^2 \qquad (6.5)$$

Kinetic energy is a scalar quantity. The kinetic energy of an object is a measure of the work an object can do by the virtue of its motion. This notion has been intuitively known for a long time. The kinetic energy of a fast flowing stream has been used to grind corn. Sailing ships employ the kinetic energy of the wind. Table 6.2 lists the kinetic energies for various objects.

Table 6.2 Typical kinetic energies (*K*)

Object	Mass (kg)	Speed (ms-1)	K (J)
Car	2000	25	6.3×10^5
Running athlete	70	10	3.5×10^3
Bullet	5×10^{-2}	200	10^3
Stone dropped from 10 m	1	14	10^2
Rain drop at terminal speed	3.5×10^{-5}	9	1.4×10^{-3}

Air molecule	≈ 10^{-26}	500	≈ 10^{-21}

Example 6.4 In a ballistics demonstration a police officer fires a bullet of mass 50.0 g with speed 200 m s^{-1} (see Table 6.2) on soft plywood of thickness 2.00 cm. The bullet emerges with only 10% of its initial kinetic energy. What is the emergent speed of the bullet?

Answer The initial kinetic energy of the bullet is $mv^2/2$ = 1000 J. It has a final kinetic energy of 0.1· 1000 = 100 J. If v_f is the emergent speed of the bullet,

$$\frac{1}{2}mvf^2 = 100\,J$$

$$v_f = \sqrt{\frac{2\,x\,100\,J}{0.05\,kg}}$$

$$= 63.2\ \mathrm{ms}^{-1}$$

The speed is reduced by approximately 68% (not 90%).

6.5 WORK DONE BY A VARIABLE FORCE

A constant force is rare. It is the variable force, which is more commonly encountered. Fig. 6.2 is a plot of a varying force in one dimension.

If the displacement x is small, we can take the force $F(x)$ as approximately constant and the work done is then

$$W = F(x)\,x$$

This is illustrated in Fig. 6.3(a). Adding successive rectangular areas in Fig. 6.3(a) we get the total work done as

$$W \cong \sum_{x_i}^{x_f} F(x)x \tag{6.6}$$

where the summation is from the initial position x_i to the final position x_f.

If the displacements are allowed to approach zero, then the number of terms in the sum increases without limit, but the sum approaches a definite value equal to the area under the curve in Fig. 6.3(b). Then the work done is

$$W = \lim_{\Delta x \to 0} \sum_{x_i}^{x_f} F(x)\Delta x$$

$$= \int_{x_i}^{x_f} F(x)dx \tag{6.7}$$

where '*lim*' stands for the limit of the sum when x tends to zero. Thus, for a varying force the work done can be expressed as a definite integral of force over displacement (see also Appendix 3.1).

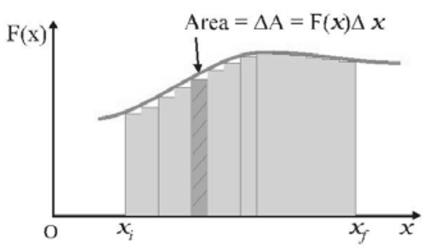


Fig. 6.3(a)

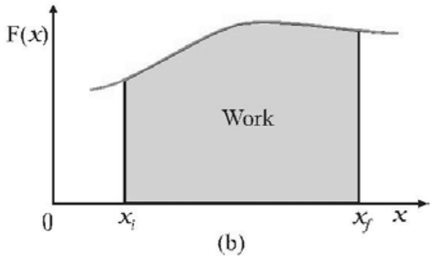


Fig 6.3(b)

Fig. 6.3(a) The shaded rectangle represents the work done by the varying force F(x), over the small displacement x, W = F(x) x.

(b) adding the areas of all the rectangles we find that for x →0, the area under the curve is exactly equal to the work done by F(x).

Example 6.5 A woman pushes a trunk on a railway platform which has a rough surface. She applies a force of 100 N over a distance of 10 m. Thereafter, she gets progressively tired and her applied force reduces linearly with distance to 50 N. The total distance through which the trunk has been moved is 20 m. Plot the force applied by the woman and the frictional force, which is 50 N. Calculate the work done by the two forces over 20 m.

Answer

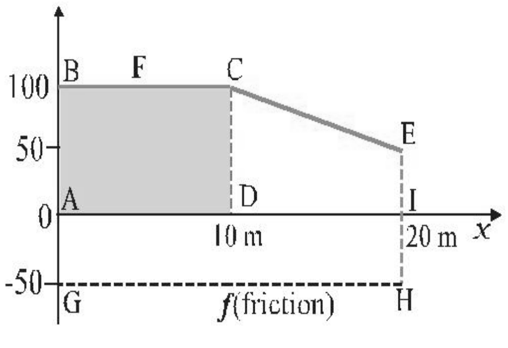


Fig. 6.4 Plot of the force F applied by the woman and the opposing frictional force f.

The plot of the applied force is shown in Fig. 6.4. At x = 20 m, F = 50 N (≠ 0). We are given that the frictional force f is $|\mathbf{f}|$ = 50 N. It opposes motion and acts in a direction opposite to **F**. It is therefore, shown on the negative side of the force axis.

The work done by the woman is

W_F→area of the rectangle ABCD + area ofthe trapezium CEID

$$W_F = 100 \times 10 + \frac{1}{2}(100 + 50) \times 10$$

=1000+750

=1750J

The work done by the frictional force is

W_F→area of the rectangle AGHI

W_f=(−50)·20=− 1000J

The area on the negative side of the force axis has a negative sign.

6.6 THE WORK-ENERGY THEOREM FOR A VARIABLE FORCE

We are now familiar with the concepts of work and kinetic energy to prove the work-energy theorem for a variable force. We confine ourselves to one dimension. The time rate of change of kinetic energy is

$$\frac{dK}{dt} = \frac{d}{dt}(\frac{1}{2}mv^2)$$

$$= m\frac{dv}{dt}v$$

= $F\ v$ (from Newton's Second Law)

$$= F\frac{dx}{dt}$$

Thus $dK = Fdx$

Integrating from the initial position (x_i) to final position (x_f), we have

$$\int_{k_i}^{k_f} dK = \int_{x_i}^{x_f} F\ dx$$

where, K_i and K_f are the initial and final kinetic energies corresponding to x_i and x_f.

$$k_f - K_i = \int_{x_i}^{x_f} F\ dx \tag{6.8a}$$

From Eq. (6.7), it follows that

$$K_f - K_i = W$$ (6.8b)

Thus, the WE theorem is proved for a variable force.

While the WE theorem is useful in a variety of problems, it does not, in general, incorporate the complete dynamical information of Newton's Second Law. It is an integral form of Newton's second law. Newton's second law is a relation between acceleration and force at any instant of time. Work-energy theorem involves an integral over an interval of time. In this sense, the temporal (time) information contained in the statement of Newton's second law is 'integrated over' and is not available explicitly. Another observation is that Newton's second law for two or three dimensions is in vector form whereas the work-energy theorem is in scalar form. In the scalar form, information with respect to directions contained in Newton's second law is not present

Example 6.6 A block of mass m= 1 kg, moving on a horizontal surface with speed v_i= 2 ms^{-1}enters a rough patch ranging from x = 0.10 m to x = 2.01 m. The retarding force F_r on the block in this range is inversely proportional to x over this range, Fr = -k/x for 0.1 <x< 2.01 m = 0 for x < 0.1m and x> 2.01 m

Where $k = 0.5$ J. What is the final kinetic energy and speed v_f of the block as it energy and speed v_f crosses this patch?

Answer From Eq. (6.8a)

$$K_f = K_i + \int_{0.1}^{2.01} \frac{(-k)}{x}\, dx$$

$$= \frac{1}{2} m v_t^2 - k \ln(x)_{0.1}^{2.01}$$

$$= \frac{1}{2} m v_t^2 - k \ln(2.01/0.1)$$

$$= 2\text{-}0.5\ln(20.1)$$

$$= 2\text{-}1.5 = 0.5 \text{ J}$$

$$= v_f = \sqrt{2k\frac{f}{m}} = 1\, ms^{-1}$$

Here, note that ln is a symbol for the natural logarithm to the base e and not the logarithm to the base 10 [ln X = $\log_e$ X = 2.303 $\log_{10}$ X].

6.7 THE CONCEPT OF POTENTIAL ENERGY

The word potential suggests possibility or capacity for action. The term potential energy brings to one's mind 'stored' energy. A stretched bow-string possesses potential energy. When it is released, the arrow flies off at a great speed. The earth's crust is not uniform, but has discontinuities and dislocations that are called fault lines. These fault lines in the earth's crustare like 'compressed springs'. They possess a large amount of potential energy. An earthquake results when these fault lines readjust. Thus, potential energy is the 'stored energy' by virtue of the position or configuration of a body. The body left to itself releases this stored energy in the form of kinetic energy. Let us make our notion of potential energy more concrete

The gravitational force on a ball of mass m is mg. g may be treated as a constant near the earth surface. By 'near' we imply that the height h of the ball above the earth's surface is very small compared to the earth's radius R_E ($h << R_E$) so that we can ignore the variation of g near the earth's surface*****. In what follows we have taken the upward direction to be positive. Let us raise the ball up to a height h. The work done by the external agency against the gravitational force is mgh. This work gets stored as potential energy. Gravitational potential energy of an object, as a function of the height h, is denoted by $V(h)$ and it is the negative of work done by the gravitational force in raising the object to that height.

$$V(h) = mgh$$

If h is taken as a variable, it is easily seen that the gravitational force F equals the negative of the derivative of $V(h)$ with respect to h. Thus,

$$F = \frac{dV(h)}{dh} = -mg$$

The negative sign indicates that the gravitational force is downward. When released, the ball comes down with an increasing speed. Just before it hits the ground, its speed is given by the kinematic relation,

$$v^2 = 2gh$$

This equation can be written as

$$\frac{1}{2}mv^2 = mgh$$

Which shows that the gravitational potential energy of the object at height h, when the object is released, manifests itself as kinetic energy of the object on reaching the ground.

Physically, the notion of potential energy is applicable only to the class of forces where work done against the force gets ‘stored up’ as energy. When external constraints are removed, it manifests itself as kinetic energy. Mathematically, (for simplicity, in one dimension) the potential energy $V(x)$ is defined if the force $F(x)$ can be written as

$$F(x) = -\frac{dV}{dx}$$

This implies that $\int_{x_i}^{x_f} F(x)dx = -\int_{V_i}^{V_f} dV = V_i - V_f$

The work done by a conservative force such as gravity depends on the initial and final positions only. In the previous chapter we have worked on examples dealing with inclined planes. If an object of mass *m* is released from rest, from the top of a smooth (frictionless) inclined plane of height *h*, its speed at the bottom is $\sqrt{2gh}$ irrespective of the angle of inclination. Thus, at the bottom of the inclined plane it acquires a kinetic energy, *mgh*. If the work done or the kinetic energy did depend on other factors such as the velocity or the particular path taken by the object, the force would be called non-conservative.

The dimensions of potential energy are $[ML^2T^{-2}]$ and the unit is joule (J), the same as kinetic energy or work. To reiterate, the change in potential energy, for a conservative force, *V* is equal to the negative of the work done by the force

$$V = -F(x)\,\Delta x \qquad (6.9)$$

In the example of the falling ball considered in this section we saw how potential energy was converted to kinetic energy. This hints at an important principle of conservation in mechanics, which we now proceed to examine

6.8 THE CONSERVATION OF MECHANICAL ENERGY

For simplicity we demonstrate this important principle for one-dimensional motion. Suppose that a body undergoes displacement *x* under the action of a conservative force *F*. Then from the WE theorem we have,

$$K = F(x)\Delta x$$

If the force is conservative, the potential energy function $V(x)$ can be defined such that

$$-\Delta V = F(x)\Delta x$$

The above equations imply that

$$\Delta K + \Delta V = 0$$

$$\Delta (K + V) = 0 \qquad (6.10)$$

which means that $K + V$, the sum of the kinetic and potential energies of the body is a constant. Over the whole path, x_i to x_f, this means that

$$K_i + V(x_i) = K_f + V(x_f) \qquad (6.11)$$

The quantity $K + V(x)$, is called the total mechanical energy of the system. Individually the kinetic energy K and the potential energy $V(x)$ may vary from point to point, but the sumis a constant. The aptness of the term 'conservative force' is now clear.

Let us consider some of the definitions of a conservative force.

- A force $F(x)$ is conservative if it can be derived from a scalar quantity $V(x)$ by the relation given by Eq. (6.9). The three-dimensional generalisation requires the use of a vector derivative, which is outside the scope of this book.
- The work done by the conservative force depends only on the end points. This can be seen from the relation, $W = K_f - K_i = V(x_i) - V(x_f)$ which depends on the end points.
- A third definition states that the work done by this force in a closed path is zero. This is once again apparent from Eq. (6.11) since $x_i = x_f$ Thus, the principle of conservation of total mechanical energy can be stated as

The total mechanical energy of a system is conserved if the forces, doing work on it, are conservative.

The above discussion can be made more concrete by considering the example of the gravitational force once again and that of the spring force in the next section. Fig. 6.5 depicts a ball of mass m being dropped from a cliff of height H.

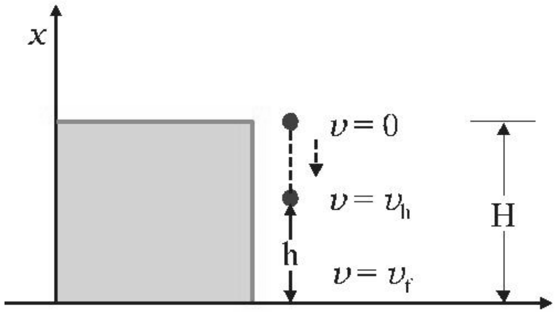


Fig. 6.5 *The conversion of potential energy to kinetic energy for a ball of mass m dropped from a height H.*

The total mechanical energies E_0, E_h, and E_H of the ball at the indicated heights zero (ground level), h and H, are

$$E_H = mgH \tag{6.11a}$$

$$E_H = mgh + \frac{1}{2}mv_h^2 \tag{6.11b}$$

$$E_0 = \frac{1}{2}\, mv^2 \tag{6.11c}$$

The constant force is a special case of a spatially dependent force $F(x)$. Hence, the mechanical energy is conserved. Thus

$$E_H = E_0$$

Or, $$mgH = \frac{1}{2}mv_f^2$$

$$v_f = \sqrt{2gH}$$

a result that was obtained in section 3.7 for a freely falling body.

Further, $E_H = E_h$ which implies,

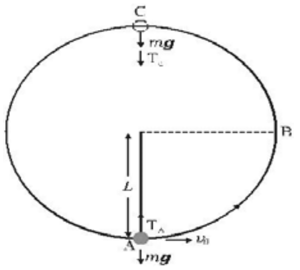
$$v_h^2 = 2g(H - h) \tag{6.11d}$$

and is a familiar result from kinematics.

At the height H, the energy is purely potential. It is partially converted to kinetic at height h and is fully kinetic at ground level. This illustrates the conservation of mechanical energy.

Example 6.7 A bob of mass m is suspended by a light string of length L . It is imparted a horizontal velocity v_o at the lowest point A such that it completes a semi-circular trajectory in the vertical plane with the string becoming slack only on reaching the topmost point, C. This is shown in Fig. 6.6. Obtain an expression for (i) v_o; (ii) the speeds at points B and C; (iii) the ratio of the kinetic energies (K_B/K_C) at B and C. Comment on the nature of the trajectory of the bob after it reaches the point C.

Answer (i) There are two external forces on the bob: gravity and the Tension (T) in the string. The latter does no work since the displacement of the bob is always normal to the string. The potential energy of the bob is thus associated with the gravitational force only. The total



mechanical energy *E* of the system is conserved. We take the potential energy of the system to be zero at the lowest point *A*. ***Fig. 6.6***

Thus, at *A*:

$$E = \frac{1}{2}\, mv_0^2 \qquad (6.12)$$

$$T_A - mg = \frac{mv_0^2}{L} \text{ [Newton's Second Law]}$$

where T_A is the tension in the string at A. At the highest point C, the string slackens, as the tension in the string (T_C) becomes zero.

Thus, at C $$E = \frac{1}{2}mv_C^2 + 2mgL \qquad (6.13)$$

$$mg = \frac{mv_0^2}{L} \text{ [Newton's Second Law]}$$

where v_C is the speed at C. From Eqs. (6.13) and (6.14)

$$E = \frac{5}{2}\, mgL$$

Equating this to the energy at A

$$\frac{5}{2}\, mgL = \frac{1}{2}\, mv_0^2$$

Or $$v_0 = \sqrt{5gL}$$

(ii) It is clear from Eq. (6.14)

$$v_C = \sqrt{gL}$$

At B, the energy is

$$E = \frac{1}{2}\, mv_B^2 + mgL$$

Equating this to the energy at A and employing the result from (i), namely $v_0^2 = 5gL$,

$$\frac{1}{2}\, mv_B^2 + mgL = \frac{1}{2}\, mv_0^2$$

$$= \frac{5}{2}\, mgL$$

$$v_B = \sqrt{3gL}$$

(iii) The ratio of the kinetic energies at B and C is :

$$\frac{K_B}{K_C} = \frac{\frac{1}{2}mv_B^2}{\frac{1}{2}mv_C^2} = \frac{3}{1}$$

At point C, the string becomes slack and the velocity of the bob is horizontal and to the left. If the connecting string is cut at this instant, the bob will execute a projectile motion with horizontal projection akin to a rock kicked horizontally from the edge of a cliff. Otherwise the bob will continue on its circular path and complete the revolution

6.9 THE POTENTIAL ENERGY OF A SPRING

The spring force is an example of a variable force which is conservative. Fig. 6.7 shows a block attached to a spring and resting on a smooth horizontal surface. The other end of the spring is attached to a rigid wall. The spring is light and may be treated as massless. In an ideal spring, the spring force F_s is proportional to x where x is the displacement of the block from the equilibrium position. The displacement could be either positive [Fig. 6.7(b)] or negative [Fig. 6.7(c)]. This force law for the spring is called Hooke's law and is mathematically stated as

$$F_s = -kx$$

The constant k is called the spring constant. Its unit is N m^{-1}. The spring is said to be stiff if k is large and soft if k is small.

Suppose that we pull the block outwards as in Fig. 6.7(b). If the extension is x_m, the work done by the spring force is

$$W_S = \int_0^{x_m} F_s\, dx = -\int_0^{x_m} kx\, dx = \frac{-kx_m^2}{2} \tag{6.15}$$

This expression may also be obtained by considering the area of the triangle as in Fig. 6.7(d). Note that the work done by the external pulling force F is positive since it overcomes the spring force.

$$W = +\frac{k_m^2}{2}$$

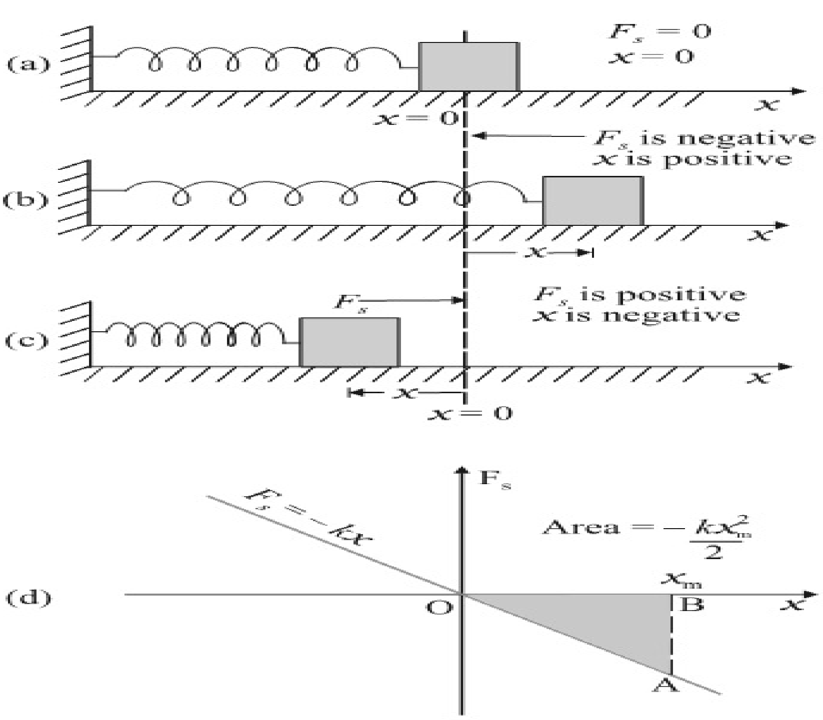


Fig. 6.7

Illustration of the spring force with a block attached to the free end of the spring. (a) The spring force F_s is zero when the displacement x from the equilibrium position is zero. (b) For the stretched spring $x > 0$ and $F_s < 0$ (c) For the compressed spring $x < 0$ and $F_s > 0$.(d) The plot of F_s versus x. The area of the shaded triangle represents the work done by the spring force. Due to the opposing signs of F_s and x, this work done is negative

$$W_s = -kx_m^2 / 2$$

The same is true when the spring is compressed with a displacement x_c (< 0). The spring force does work $W_s = -kx_c^2/2$ while the external force F does work $+kx_c^2/2$. If the block is moved from an initial displacement x_i to a final displacement x_f , the work done by the spring force W_s is

$$W_s = -\int_{x_i}^{x_f} kx dx$$

Thus the work done by the spring force depends only on the end points. Specifically, if the block is pulled from x_i and allowed to return to x_i;

$$W_S = -\int_{x_i}^{X_f} kx\,dx = \frac{kx_i^2}{2} - \frac{kx_i^2}{2} = 0 \qquad (6.18)$$

The work done by the spring force in a cyclic process is zero. We have explicitly demonstrated that the spring force (i) is position dependent only as first stated by Hooke, ($F_s=-kx$); (ii) does work which only depends on the initial and final positions, e.g. Eq. (6.17).

We define the potential energy $V(x)$ of the spring to be zero when block and spring system is in the equilibrium position. For an extension (or compression) x the above analysis suggests that

$$V(x)=\frac{kx^2}{2}$$

You may easily verify that $-\mathrm{d}V/\mathrm{d}x=-k\,x$, the spring force. If the block of mass m in Fig. 6.7 is extended to x_m and released from rest, then its total mechanical energy at any arbitrary point x, where x lies between $-x_m$ and $+x_m$, will be given by

$$\frac{1}{2}kx_m^2=\frac{1}{2}kx^2+\frac{1}{2}mv^2$$

where we have invoked the conservation of mechanical energy. This suggests that the speed and the kinetic energy will be maximum at the equilibrium position, $x = 0$, i.e.,

$$\frac{1}{2}mv_m^2=\frac{1}{2}kx_m^2$$

Where v_m is the maximum speed.

$$v_m=\sqrt{\frac{k}{m}}\,x_m$$

Note that k/m has the dimensions of [T^{-2}] and our equation is dimensionally correct. The kinetic energy gets converted to potential energy and vice versa, however, the total mechanical energy remains constant. This is graphically depicted in Fig. 6.8

Example 6.8 To simulate car accidents, auto manufacturers study the collisions of moving cars with mounted springs of different spring constants. Consider a typical simulation with a car of mass 1000 kg moving with a speed 18.0 km/h on a smooth road and colliding with a horizontally mounted spring of spring constant 6.25×10^3 N m^{-1}. What is the maximum compression of the spring?

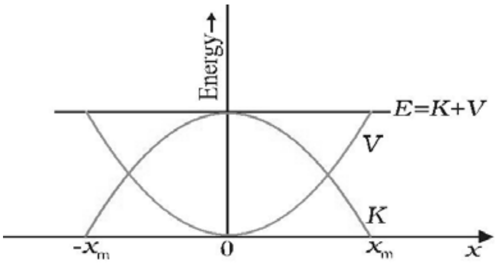


***Fig. 6.8** Parabolic plots of the potential energy V and kinetic energy K of a block attached to a spring obeying Hooke's law. The two plots are complementary, one decreasing as the other increases. The total mechanical energy E = K + V remains constant.*

Answer At maximum compression the kinetic energy of the car is converted entirely into the potential energy of the spring.

The kinetic energy of the moving car is

$$K = \frac{1}{2}mv^2$$

$$= \frac{1}{2} \times 10^3 \times 5 \times 5$$

$$K = 1.25 \times 10^4 \text{ J}$$

where we have converted 18 km h^{-1} to 5 m s^{-1}**[It is useful to remember that 36 km h^{-1} = 10 m s^{-1}]**.At maximum compression x_m, the potential energy *V* of the spring is equal to the kinetic energy *K* of the moving car from the principle of conservation of mechanical energy

$$V = \frac{1}{2}kx_m^2$$

$$= 1.25 \text{ x} 10^4 \text{J}$$

We obtain x_m= 2.00 m

We note that we have idealised the situation. The spring is considered to be massless. The surface has been considered to possess negligible friction.

We conclude this section by making a few remarks on conservative forces.

(i) Information on time is absent from the above discussions. In the example considered above, we can calculate the compression, but not the time over which the compression occurs. A solution of Newton's Second Law for this system is required for temporal information.

(ii) Not all forces are conservative. Friction, for example, is a non-conservative force. The principle of conservation of energy will have to be modified in this case. This is illustrated in Example 6.9.

(iii)The zero of the potential energy is arbitrary. It is set according to convenience. For the spring force we took *V*(*x*) = 0, at *x* = 0, i.e. the unstretched spring had zero potential energy. For the constant gravitational force *mg*, we took $V = 0$ on the earth's surface. Ina later chapter we shall see that for the force due to the universal law of gravitation, the zero is best defined at an infinite distance from the gravitational source. However, once the zero of the potential energy is fixed in a given discussion, it must be consistently adhered to throughout the discussion. You cannot change horses in midstream!

Example 6.9 Consider Example 6.7 taking the coefficient of friction, μ, to be 0.5 and calculate the maximum compression of the spring.

Answer In presence of friction, both the spring force and the frictional force act so as to oppose the compression of the spring as shown in Fig. 6.9.

We invoke the work-energy theorem, rather than the conservation of mechanical energy

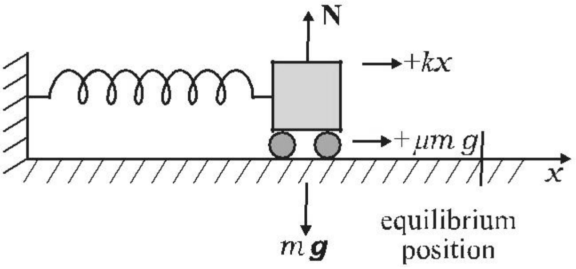


Fig. 6.9*The forces acting on the car.*

The change in kinetic energy is

$$K = K_f - K_i = 0 - \frac{1}{2}\, mv^2$$

The work done by the net force is

$$W = -\frac{1}{2}kx_m^2 - \mu mgx_m$$

Equating we have

$$\frac{1}{2}mv^2 = \frac{1}{2}kx_m^2 + \mu mgx_m$$

Now $\mu mg = 0.5 \times 10^3 \times 10 = 5 \times 10^3$ N (taking g =10.0 m s^{-2}). After rearranging the above equation we obtain the following quadratic equation in the unknown x_m.

$$kx_m^2 + 2\,\mu mgx_m - mv^2 = 0$$

$$x_m = \frac{-\mu mg + [\mu^2 m^2 g^2 + mkv^2]^{-\frac{1}{2}}}{k}$$

where we take the positive square root since x_m is positive. Putting in numerical values we obtain x_m = 1.35 m

which, as expected, is less than the result in Example 6.8.

If the two forces on the body consist of a conservative force F_c and a non-conservative force F_{nc} , the conservation of mechanical energy formula will have to be modified. By the WE theorem

$$(F_c + F_{nc})\,\Delta x = \Delta K$$

But $$F_c\,\Delta x = -\Delta V$$

Hence, $$\Delta(k+v) = F_{nc}\ \Delta x$$

$$\Delta E = F_{nc}\,\Delta x$$

where E is the total mechanical energy. Over the path this assumes the form

$$E_f - E_i\ = W_{nc}$$

Where W_{nc} is the total work done by the non-conservative forces over the path.

Note that unlike the conservative force, W_{nc} depends on the particular path i to f.

6.10 VARIOUS FORMS OF ENERGY: THE LAW OF CONSERVATION OF ENERGY

In the previous section we have discussed mechanical energy. We have seen that it can be classified into two distinct categories: one based on motion, namely kinetic energy; the other on configuration (position), namely potential energy. Energy comes in many a forms which transform into one another in ways which may not often be clear to us.

6.10.1 Heat

We have seen that the frictional force is excluded from the category of conservative forces. However, work is associated with the force of friction. A block of mass m sliding on a rough horizontal surface with speed v_0 comes to a halt over a distance x_0. The work done by the force of kinetic friction f over x_0 is $-f\,x_0$. By the work-energy theorem $\frac{mv_0^2}{2} = fx_0$. If we confine our scope to mechanics, we would say that the kinetic energy of the block is ‘lost’ due to the frictional force. On examination of the block and the table we would detect a slight increase in their temperatures. The work done by friction is not ‘lost’, but is transferred as heat energy. This raises the internal energy of the block and the table. In winter, in order to feel warm, we generate heat by vigorously rubbing our palms together. We shall see later that the internal energy is associated with the ceaseless, often random, motion of molecules. A quantitative idea of the transfer of heat energy is obtained by noting that 1 kg of water releases about 42000 J of energy when it cools by10 °C.

6.10.2 Chemical Energy

One of the greatest technical achievements of humankind occurred when we discovered how to ignite and control fire. We learnt to rub two flint stones together (mechanical energy), got them to heat up and to ignite a heap of dry leaves (chemical energy), which then provided sustained warmth. A matchstick ignites into a bright flame when struck against a specially prepared chemical surface. The lighted matchstick, when applied to a firecracker, results in a spectacular display of sound and light.

Chemical energy arises from the fact that the molecules participating in the chemical reaction have different binding energies. A stable chemical compound has less energy than the separated parts. A chemical reaction is basically a rearrangement of atoms. If the total energy of the reactants is more than the products of the reaction, heat is released and the reaction is said to be an **exothermic** reaction. If the reverse is true, heat is absorbed and the reaction is **endothermic**. Coal consists of carbon and a kilogram of it when burnt releases 3×10^7 J of energy.

Chemical energy is associated with the forces that give rise to the stability of substances. These forces bind atoms into molecules, molecules into polymeric chains, etc. The chemical energy arising from the combustion of coal, cooking gas, wood and petroleum is indispensable to our daily existence.

6.10.3 Electrical Energy

The flow of electrical current causes bulbs to glow, fans to rotate and bells to ring. There are laws governing the attraction and repulsion of charges and currents, which we shall learn later. Energy is associated with an electric current. An urban Indian household consumes about 200 J of energy per second on an average.

6.10.4 The Equivalence of Mass and Energy

Till the end of the nineteenth century, physicists believed that in every physical and chemical process, the mass of an isolated system is conserved. Matter might change its phase, e.g. glacial ice could melt into a gushing stream, but matter is neither created nor destroyed; Albert Einstein (1879-1955) however, showed that mass and energy are equivalent and are related by the relation

$$E = m\,c^2 \tag{6.20}$$

where c, the speed of light in vacuum is approximately 3 x 10^8 m s^{-1}. Thus, a staggering amount of energy is associated with a mere kilogram of matter

$$E = 1x(3x10^8)^2 J = 9x10^{16} J.$$

This is equivalent to the annual electrical output of a large (3000 MW) power generating station.

Table 6.3 Approximate energy associated with various phenomena

Description	Energy
Big Bang	10^{68}
Radio energy emitted by the galaxy during its life time	10^{55}
Rotational energy of the milky way	10^{52}
Energy released in a supernova explosion	10^{44}
Ocean’s hydrogen in fusion	10^{34}
Rotational energy of the earth	10^{29}
Annual solar energy incident on the earth	5×10^{24}
Annual wind energy dissipated near the earth’s surface	10^{22}
Annual global energy usage by human	3×10^{20}
Annual energy dissipated by the tides	10^{20}
Energy release of 15 megaton fusion bomb	10^{17}
Annual electrical output of large generating plant	10^{16}
Thunderstorm	10^{15}
Energy released in burning 1000 kg of coal	3×10^{10}
Kinetic energy of a large jet aircraft	10^{9}
Energy released in burning in 1 litre of gasoline	3×10^{7}
Daily food intake of a human adult	10^{7}
Work done by human heart per beat	0.5
Turning this page	10^{-3}

Flea hop	10^{-7}
Discharge of single neutron	10^{-10}
Typical energy of a proton in a nucleus	10^{-13}
Typical energy of an electron in an atom	10^{-18}
Energy to break one band in DNA	10^{-20}

6.10.5 Nuclear Energy

The most destructive weapons made by man, the fission and fusion bombs are manifestations of the above equivalence of mass and energy [Eq. (6.20)]. On the other hand the explanation of the life-nourishing energy output of the sun is also based on the above equation. In this case effectively four light hydrogen nuclei fuse to form a helium nucleus whose mass is less than the sum of the masses of the reactants. This mass difference, called the mass defect m is the source of energy $(m)c^2$.

In fission, a heavy nucleus like uranium $^{235}{}_{92\mathrm{U}}$, is split by a neutron into lighter nuclei. Once again the final mass is less than the initial mass and the mass difference translates into energy, which can be tapped to provide electrical energy as in nuclear power plants (controlled nuclear fission) or can be employed in making nuclear weapons (uncontrolled nuclear fission). Strictly, the energy E released in a chemical reaction can also be related to the mass defect $m = E/c^2$. However, for a chemical reaction, this mass defect is much smaller than for a nuclear reaction. Table 6.3 lists the total energies for a variety of events, phenomena.

Example 6.10 Examine Tables 6.1-6.3and express (a) The energy required to break one bond in DNA in eV; (b) The kinetic energy of an air molecule (10^{-21} J) in eV; (c) The daily intake of a human adult in kilocalories.

Answer (a) Energy required to break one bond of DNA is

$$\frac{10^{-20} J}{1.6 \times 10^{-19} J/eV} \cong 0.06 \ eV$$

Where the symbol '$\simeq$' stands for approximate. Note 0.1 eV = 100 meV (100 milli electron volt).

(a) The kinetic energy of an air molecule is

$$\frac{10^{-21}J}{1.6\times10^{-19}J/eV}\cong 0.0062eV$$

(c) The average human consumption in a day is

$$\frac{10^{7}J}{4.2\times10^{3}J/kcal}\cong 2400kcal$$

We point out a common misconception created by newspapers and magazines. They mention food values in calories and urge us to restrict diet intake to below 2400 calories. What they should be saying is kilocalories (kcal) and not calories. A person consuming 2400 calories a day will soon starve to death! 1 food calorie is 1 kcal.

6.10.6 The Principle of Conservation of Energy

We have seen that the total mechanical energy of the system is conserved if the forces doing work on it are conservative. If some of the forces involved are non-conservative, part of the mechanical energy may get transformed into other forms such as heat, light and sound. However, the total energy of an isolated system does not change, as long as one accounts for all forms of energy. Energy may be transformed from one form to another but the total energy of an isolated system remains constant. Energy can neither be created, nor destroyed.

Since the universe as a whole may be viewed as an isolated system, the total energy of the universe is constant. If one part of the universe loses energy, another part must gain an equal amount of energy.

The principle of conservation of energy cannot be proved. However, no violation of this principle has been observed. The concept of conservation and transformation of energy into various forms links together various branches of physics, chemistry and life sciences. It provides a unifying, enduring element in our scientific pursuits. From engineering point of view all electronic, communication and mechanical devices rely on some forms of energy transformation.

6.11 POWER

Often it is interesting to know not only the work done on an object, but also the rate at which this work is done. We say a person is physically fit if he not only climbs four floors of a building but climbs them fast. **Power** is defined as the time rate at which work is done or energy is transferred.

The average power of a force is defined as the ratio of the work, *W*, to the total time *t* taken

$$P_{av} = \frac{W}{t}$$

The instantaneous power is defined as the limiting value of the average power as time interval approaches zero,

$$P = \frac{dW}{dt} \tag{6.21}$$

The work dW done by a force F for a displacement $d\mathbf{r}$ is $dW = \mathbf{F}.d\mathbf{r}$. The instantaneous power can also be expressed as

$$P = F.\frac{dr}{dt} = F.v \tag{6.22}$$

where **v** is the instantaneous velocity when the force is **F**.

Power, like work and energy, is a scalar quantity. Its dimensions are $[ML^2T^{-3}]$. In the SI, its unit is called a watt (W). The watt is 1 J s^{-1}. The unit of power is named after James Watt, one of the innovators of the steam engine in the eighteenth century.

There is another unit of power, namely the horse-power (hp)

1 hp = 746 W

This unit is still used to describe the output of automobiles, motorbikes, etc.

We encounter the unit watt when we buy electrical goods such as bulbs, heaters and refrigerators. A 100 watt bulb which is on for 10 hours uses 1 kilowatt hour (kWh) of energy.

$$\begin{aligned} 100 \text{ (watt) x } 10 \text{ (hour)} &= 1000 \text{ watt hour} \\ &= 1 \text{ kilowatt hour (kWh)} \\ &= 10^3 \text{ (W) x } 3600 \text{ (s)} \\ &= 3.6 \text{ x } 10^6 \text{ J} \end{aligned}$$

Our electricity bills carry the energy consumption in units of kWh. Note that kWh is a unit of energy and not of power.

Example 6.11 An elevator can carry a maximum load of 1800 kg (elevator + passengers) is moving up with a constant speed of 2 m s^{-1}. The frictional force opposing the motion is 4000 N. Determine the minimum power delivered by the motor to the elevator in watts as well as in horse power.

Answer The downward force on the elevator is

$$F = m\,g + F_f = (1800 \text{ x} 10) + 4000 = 22000 \text{ N}$$

The motor must supply enough power to balance this force. Hence,

$$P = \mathbf{F}.\,\mathbf{v} = 22000 \text{ x} 2 = 44000 \text{ W} = 59 \text{ hp}$$

6.12 COLLISIONS

In physics we study motion (change in position). At the same time, we try to discover physical quantities, which do not change in a physical process. The laws of momentum and energy conservation are typical examples. In this section we shall apply these laws to commonly encountered phenomena, namely collisions. Several games such as billiards, marbles or carrom involve collisions. We shall study the collision of two masses in an idealised form.

Consider two masses m_1 and m_2. The particle m_1 is moving with speed v_{1i}, the subscript '*i*' implying initial. We can cosider m_2 to be at rest. No loss of generality is involved in making such a selection. In this situation the mass m_1 collides with the stationary mass m_2 and this is depicted in Fig. 6.10.

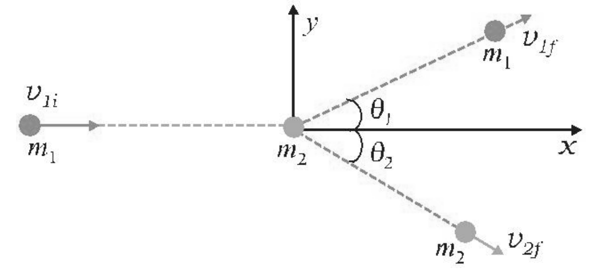


Fig. 6.10 *Collision of mass m_1, with a stationary mass m_2.*

The masses m_1 and m_2 fly-off in different directions. We shall see that there are relationships, which connect the masses, the velocities and the angles.

6.12.1 Elastic and Inelastic Collisions

In all collisions the total linear momentum is conserved; the initial momentum of the system is equal to the final momentum of the system. One can argue this as follows. When two objects collide, the mutual impulsive forces acting over the collision time *t* cause a change in their respective momenta:

$$\mathbf{p}_1 = \mathbf{F}_{12}\Delta t$$

$$\mathbf{p}_2 = \mathbf{F}_{21}\ \Delta t$$

Where $\mathbf{F}_{12}$ is the force exerted on the first particle by the second particle. $\mathbf{F}_{21}$ is likewise the force exerted on the second particle by the first particle. Now from Newton's Third Law, $\mathbf{F}_{12} = -\mathbf{F}_{21}$. This implies $\mathbf{\Delta p}_1 + \mathbf{\Delta p}_2 = \mathbf{0}$

The above conclusion is true even though the forces vary in a complex fashion during the collision time *t*. Since the third law is true at every instant, the total impulse on the first object is equal and opposite to that on the second.

On the other hand, the total kinetic energy of the system is not necessarily conserved. The impact and deformation during collision may generate heat and sound. Part of the initial kinetic energy is transformed into other forms of energy. A useful way to visualise the deformation during collision is in terms of a 'compressed spring'. If the 'spring' connecting the two masses regains its original shape without loss in energy, then the initial kinetic energy is equal to the final kinetic energy but the kinetic energy during the collision time *t* is not constant. Such a collision is called an **elastic collision**. On the other hand the deformation may not be relieved and the two bodies could move together after the collision. A collision in which the two particles move together after the collision is called a **completely inelastic collision**. The intermediate case where the deformation is partly relieved and some of the initial kinetic energy is lost is more common and is appropriately called an **inelastic collision**

6.12.2 Collisions in One Dimension

Consider first a **completely inelastic collision** in one dimension. Then, in Fig. 6.10,

$$\theta_1 = \theta_2$$

$$m_1 v_{1i} = (m_1 + m_2) v_f = 0 \qquad \text{(momentum conservation)}$$

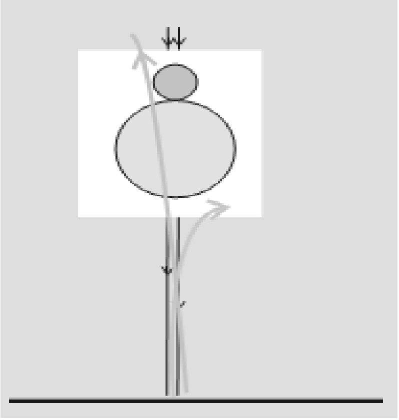
$$v_f = \frac{m_1}{m_1 + m_2} v_{1t} \tag{6.23}$$

The loss in kinetic energy on collision is

$$\Delta K = \frac{1}{2} m_1 v_{1t}^2 - \frac{1}{2} (m_1 + m_2) v_f^2$$

$$= \frac{1}{2} m_1 v_{1t}^2 [1 - \frac{m_1}{m_1 + m_2}]$$

An experiment on head-on collision



In performing an experiment on collision on a horizontal surface, we face three difficulties. One, there will be friction and bodies will not travel with uniform velocities. Two if two bodies of different sizes collide on a table, it would be difficult to arrange them for a head-on collision unless their centres of mass are at the same height above the surface. Three, it will be fairly difficult to measure velocities of the two bodies just before and just after collision.

By performing this experiment in a vertical direction, all the three difficulties vanish. Take two balls, one of which is heavier (basketball/football/volleyball) and the other lighter (tennis ball/rubber ball/table tennis ball). First take only the heavier ball and drop it vertically from some height, say 1 m. Note to which it rises. This gives the velocities near the floor or ground, just before and just after the bounce (by using $v^2=2gh$). Hence you will get the coefficient of restitution. Now take the big ball and a small ball and hold them in your hands one over the other, with the heavier ball below the lighter one, as shown here. Drop them together, taking care that they remain together while falling, and see what happens. You will find that the heavier ball rises less than when it was dropped alone, while the lighter one shoots up to about 3 m. With practice, you will be able to hold the ball properly so that the lighter ball rises vertically up and does not fly sideways. This is head-on collision. You can try to find the best combination of balls which gives you the best effect. You can measure the masses on a standard balance. We leave it to you to think how you can determine the initial and final velocities of the balls.

$$= \frac{1}{2}\,\frac{m_1 m_2}{m_1+m_2}\,v_{1t}^2$$

which is a positive quantity as expected.

Consider next an elastic collision. Using the above nomenclature with $\theta_1=\theta_2=0$, the momentum and kinetic energy conservation equations are

$$m_1 v_{1t} = m_1 v_{1f} + m_2 v_{2f} \tag{6.24}$$

$$m_1 v^2{}_{1t} = m_1 v_{1f} + m_2 v_{2f} \tag{6.25}$$

From Eqs. (6.24) and (6.25) it follows that,

$$v_{1i}^2 - v_{2i}^2 = (v_{1i} - v_{1f})(v_{1i} + v_{1f})$$

$$\text{Hence } {v_{1f}}^2 = v_{1i} + v_{1f}$$

Substituting this in Eq. (6.24), we obtain

$$v_{1f} = \frac{(m_1 - m_2)}{m_1 + m_2} v_{1i}$$

$$\text{and } v_{2f} = \frac{2m_1 v_{1i}}{m_1 + m_2}$$

Thus, the 'unknowns' $\{v_{1f}, v_{2f}\}$ are obtained in terms of the 'knowns' $\{m_1, m_2, v_{1i}\}$. Special cases of our analysis are interesting.

Case I: If the two masses are equal

$$v_{1f} = 0$$

$$v_{2f} = v_{1i}$$

The first mass comes to rest and pushes off the second mass with its initial speed on collision.

Case II: If one mass dominates, e.g.$m_2 >> m_1$

$$v_{1f} \simeq - v_{1i} \qquad v_{2f} \simeq 0$$

The heavier mass is undisturbed while the lighter mass reverses its velocity.

Example 6.12 **Slowing down of neutrons**: In a nuclear reactor a neutron of high speed (typically 10^7 m s^{-1}) must be slowed to 10^3 m s^{-1} so that it can have a high probability of interacting with isotope $^{235}{}_{92}$ U and causing it to fission. Show that a neutron can lose most of its kinetic energy in an elastic collision with a light nuclei like deuterium or carbon which has a mass of only a few times the neutron mass. The material making up the light nuclei, usually heavy water (D_2O) or graphite, is called a moderator.

Answer The initial kinetic energy of the neutron is

$$K_{1i} = \frac{1}{2} m_1 v_{1f}^2$$

while its final kinetic energy from Eq. (6.27)

$$= K_{1f} = \frac{1}{2} m_1 \left(\frac{m_1 - m_2}{m_1 + m_2}\right)^2 v_{1i}^2$$

The fractional kinetic energy lost is

$$f_1 = \frac{K_{1f}}{K_{1i}} = \left(\frac{m_1 - m_2}{m_1 + m_2}\right)^2$$

while the fractional kinetic energy gained by the moderating nuclei K_{2f}/K_{1i} is

$f_2 = 1 - f_1$(elastic collision)

$$= \frac{4\,m_1 m_2}{(m_1 + m_2)^2}$$

One can also verify this result by substituting from Eq. (6.28).

For deuterium $m_2 = 2m_1$ and we obtain $f_1 = 1/9$ while $f_2 = 8/9$. Almost 90% of the neutron's energy is transferred to deuterium. For carbon $f_1 = 71.6\%$ and $f_2 = 28.4\%$. In practice, however, this number is smaller since head-on collisions are rare.

If the initial velocities and final velocities of both the bodies are along the same straight line, then it is called a one-dimensional collision, or **head-on collision.** In the case of small spherical bodies, this is possible if the direction of travel of body 1 passes through the centre of body 2 which is at rest. In general, the collision is two-dimensional, where the initial velocities and the final velocities lie in a plane.

6.12.3 Collisions in Two Dimensions

Fig. 6.10 also depicts the collision of a moving mass m_1 with the stationary mass m_2. Linear momentum is conserved in such a collision. Since momentum is a vector this implies three equations for the three directions $\{x, y, z\}$. Consider the plane determined by the final velocity directions of m_1 and m_2 and choose it to be the x-y plane. The conservation of the z-component of the linear momentum implies that the entire collision is in the x-y plane. The x- and y-component equations are

$$m_1 v_{1i} = m_1 v_{1f} \cos\theta_1 + m_2 v_{2f} \cos\theta_2$$

(6.29)

$$0 = m_1 v_{1f} \sin\theta_1 - m_2 v_{2f} \sin\theta_2$$

(6.30)

One knows $\{m_1, m_2, v_{1i}\}$ in most situations. There are thus four unknowns $\{v_{1f}, v_{2f}, \theta_1 and \theta_2\}$, and only two equations. If $\theta_1 = \theta_2 = 0$, we regain Eq. (6.24) for one dimensional collision.

If, further the collision is elastic,

$$\frac{1}{2}\, m_1 v_{1i}^2 = \frac{1}{2} m_1 v_{1f}^2 + \frac{1}{2} m_2 v_{2f}^2 \qquad (6.31)$$

We obtain an additional equation. That still leaves us one equation short. At least one of the four unknowns, say θ_1, must be made known for the problem to be solvable. For example, θ_1 can be determined by moving a detector in an angular fashion from the x to the y axis. Given$\{m_1, m_2, v_{1i}, \theta_1\}$ we can determine $\{v_{1f}, v_{2f}, \theta_2\}$ from Eqs. (6.29)-(6.31).

Example 6.13 Consider the collision depicted in Fig. 6.10 to be between two billiard balls with equal masses $m_1 = m_2$. The first ball is called the cue while the second ball is called the target. The billiard player wants to 'sink' the target ball in a corner pocket, which is at an angle $\theta_2 = 37°$. Assume that the collision is elastic and that friction and rotational motion are not important. Obtain θ_1.

Answer From momentum conservation, since the masses are equal

$$v_{1i} = v_{1f} + v_{2f}$$

$$v_{1i}^2 = \left(v_{1f} + v_{2f}\right).\left(v_{1f} + v_{2f}\right)$$

$$= v_{1f}^2 + v_{2f}^2 + 2 v_{1f}\, v_{2f}$$

$\cos(\theta_1 + 37°)\}$ (6.32)

Since the collision is elastic and $m_1 = m_2$ it follows from conservation of kinetic energy that

$$v_{1i}^2 = v_{1f}^2 + v_{2f}^2 \qquad (6.33)$$

Comparing Eqs. (6.32) and (6.33), we get

$$\cos(\theta_1 + 37°) = 0 \text{ or } \theta_1 + 37° = 90°$$

Thus, $\theta_1 = 53°$

This proves the following result: when two equal masses undergo a glancing elastic collision with one of them at rest, after the collision, they will move at right angles to each other.

The matter simplifies greatly if we consider spherical masses with smooth surfaces, and assume that collision takes place only when the bodies touch each other. This is what happens in the games of marbles, carrom and billiards.

In our everyday world, collisions take place only when two bodies touch each other. But consider a comet coming from far distances to the sun, or alpha particle coming towards a nucleus and going away in some direction. Here we have to deal with forces involving action at a distance. Such an event is called scattering. The velocities and directions in which the two particles go away depend on their initial velocities as well as the type of interaction between them, their masses, shapes and sizes.

SUMMARY

1. The *work-energy theorem* states that the change in kinetic energy of a body is the work done by the net force on the body.

$$K_f - K_i = W_{net}$$

2. A force is *conservative* if (i) work done by it on an object is path independent and depends only on the end points $\{x_i, x_j\}$, or (ii) the work done by the force is zero for an arbitrary closed path taken by the object such that it returns to its initial position.

3. For a conservative force in one dimension, we may define a *potential energy* function $V(x)$ such that

$$F\ (x) = -\ \frac{dv}{dx}$$

$$or\ V_i - V_f = \int_{x_i}^{x_f} (x) dx$$

4. The principle of conservation of mechanical energy states that the total mechanical energy of a body remains constant if the only forces that act on the body are conservative.

5. The *gravitational potential energy* of a particle of mass m at a height x about the earth's surface is

$$V(x) = m\,g\,x$$

Where the variation of g with height is ignored.

6. The elastic potential energy of a spring of force constant k and extension x is

$$V(x) = \frac{1}{2}\,kx^2$$

7. The scalar or dot product of two vectors **A** and **B** is written as **A.B** and is a scalar Quantity given by : **A·B** = $AB \cos\theta$, where θ is the angle between **A** and **B**. It can be positive, negative or zero depending upon the value of θ. The scalar product of two vectors can be interpreted as the product of magnitude of one vector and component of the other vector along the first vector. For unit vectors:

$$\mathbf{i} \cdot \mathbf{i} = \mathbf{j} \cdot \mathbf{j} = \mathbf{k} \cdot \mathbf{k} = 1 \text{and} \mathbf{i} \cdot \mathbf{j} = \mathbf{j} \cdot \mathbf{k} = \mathbf{k} \cdot \mathbf{i} = 0$$

Scalar product obeys the commutative and distributive law.

CHAPTER SEVEN

SYSTEMS OF PARTICLES AND ROTATIONAL MOTION

7.1 INTRODUCTION

In the earlier chapters we primarily considered the motion of a single particle (A particle is represented as a point mass. It has practically no size). We applied the results of our study even to the motion of bodies of finite size, assuming that motion of such bodies can be described in terms of the motion of a particle.

Any real body which we encounter in daily life has a finite size. In dealing with the motion of extended bodies (bodies of finite size) often the idealised model of a particle is inadequate. In this chapter we shall try to go beyond this inadequacy. We shall attempt to build an understanding of the motion of extended bodies. An extended body, in the first place, is a system of particles. We shall begin with the consideration of motion of the system as a whole. The centre of mass of a system of particles will be a key concept here We shall discuss the motion of the centre of mass of a system of particles and usefulness of this concept in understanding the motion of extended bodies. A large class of problems with extended bodies can be solved by considering them to be rigid bodies. Ideally a rigid body is a body with a perfectly definite and unchanging shape. The distances between different pairs of such a body do not change. It is evident from this definition of a rigid body that no real body is truly rigid, since real bodies deform under the influence of forces. But in many situations the deformations are negligible. Thus, in a number of situations involving bodies such as wheels, tops, steel beams, molecules and planets on the other hand, we can ignore that they warp, bend or vibrate and treat them as rigid.

7.1.1 What kind of motion can a rigid body have?

Let us try to explore this question by taking some examples of the motion of rigid bodies. Let us begin with a rectangular block sliding down an inclined plane without any sidewise movement.

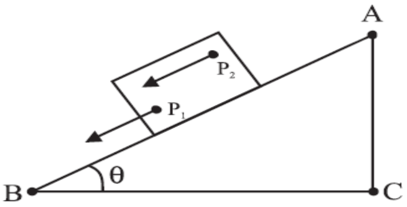


Fig 7.1*Translational (sliding) motion of a block downan inclined plane. (Any point like P_1 or P_2 of the block moves with the same velocity at any instant of time.)*

The block is a rigid body. Its motion down the plane is such that all the particles of the body are moving together, i.e. they have the same velocity at any instant of time. The rigid body here is in pure translational motion (Fig. 7.1).**In pure translational motion at any instant of time every particle of the body has the same velocity.**

Consider now the rolling motion of a solid metallic or wooden cylinder down the same inclined plane (Fig. 7.2). The rigid body in this problem, namely the cylinder, shifts from the top to the bottom of the inclined plane, and thus, has translational motion. But as Fig. 7.2 shows, all its particles are not moving with the same velocity at any instant. The body therefore, is not in pure translation. Its motion is translation plus 'something else.'

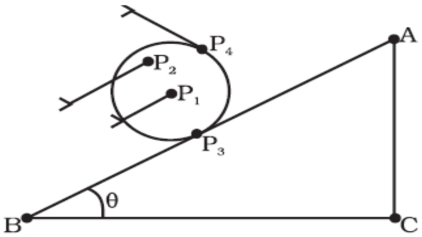
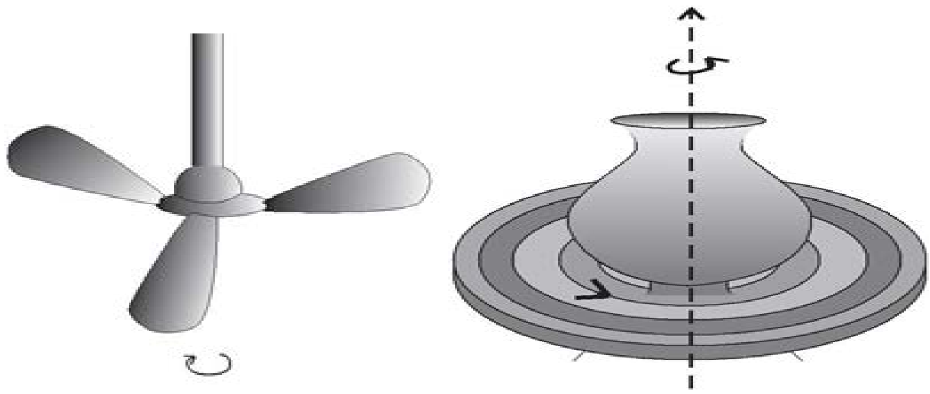


Fig. 7.2 *Rolling motion of a cylinder It is not pure translational motion. Points P_1, P_2, P_3 and P_4 have different velocities (shown by arrows) at any instant of time. In fact, the velocity of the point of contact P_3 is zero at any instant, if the cylinder rolls without slipping.*

In order to understand what this 'something else' is, let us take a rigid body so constrained that it cannot have translational motion. The most common way to constrain a rigid body so that it does not have translational motion is to fix it along a straight line.

The only possible motion of such a rigid body is **rotation**. The line along which the body is fixed is termed as its **axis of rotation**. If you look around, you will come across many examples of rotation about an axis, a ceiling fan, a potter's wheel, a giant wheel in a fair, a merry-go-round and so on (Fig 7.3(a) and (b)).



(a) A ceiling fan *(b) A potter's wheel.*

Fig. 7.3*Rotation about a fixed axis*

Let us try to understand what rotation is, what characterises rotation. You may notice that in rotation of a rigid body about a fixed **axis, every particle of the body moves in a circle, which lies in a plane perpendicular to the axis and has its centre on the axis**.Fig.7.4 shows the rotational motion of a rigid body about a fixed axis (the *z*-axis of the frame of reference). Let P_1 be a particle of the rigid body, arbitrarily chosen and at a distance r_1 from fixed axis.

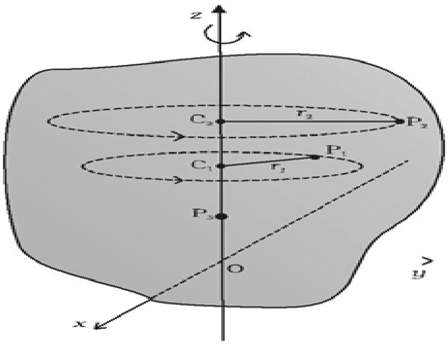


Fig. 7.4 *A rigid body rotation about the z-axis(Each point of the body such as P_1orP_2 describes a circle with its centre (C_1 or C_2) on the axis. The radius of the circle ($r_1$or r_2) is the perpendicular distance of the point (P_1 or P_2) from the axis. A point on the axis like P_3 remains stationary).*

The particle P_1 describes a circle of radius $r_1$with its centre C_1on the fixed axis. The circlelies in a plane perpendicular to the axis. The figure also shows another particle P_2 of the rigid body, P_2 is at a distance r_2 from the fixed axis. The particle P_2 moves in a circle of radius r_2 and with centre C_2 on the axis. This circle, too, lies in a plane perpendicular to the axis. Note that the circles described by P_1 and P_2 may lie in different planes; both these planes, however, are perpendicular to the fixed axis. For any particle on the axis like P_3, $r = 0$. Any such particle remains stationary while the body rotates. This is expected since the axis is fixed.

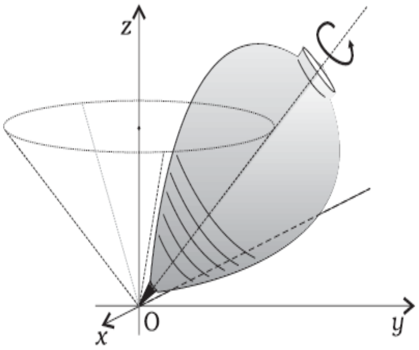


Fig. 7.5 (a)*A spinning top (The point of contact of the top with the ground, its tip O, is fixed.)*

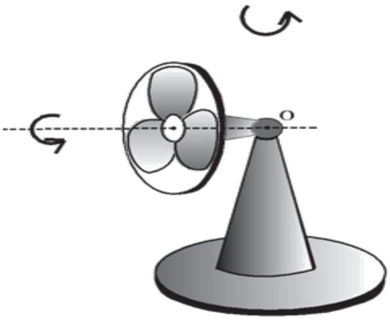


Fig. 7.5 (b)*an oscillating table fan. The pivot of thefan, point O, is fixed.*

In some examples of rotation, however, the axis may not be fixed. A prominent example of this kind of rotation is a top spinning in place [Fig. 7.5(a)]. (We assume that the top does not slip from place to place and so does not have translational motion.) We know from experience that the axis of such a spinning top moves around the vertical through its point of contact with the ground, sweeping out a cone as shown in Fig. 7.5(a). (This movement of the axis of the top around the vertical is termed **precession**.) Note, the **point of contact of the top withground is fixed**. The axis of rotation of the topat any instant passes through the point of contact. Another simple example of this kind of rotation is the oscillating table fan or a pedestal fan. You may have observed that the axis of rotation of such a fan has an oscillating (sidewise) movement in a horizontal plane about the vertical through the point at which the axis is pivoted (point O in Fig. 7.5(b)).

While the fan rotates and its axis moves sidewise, this point is fixed. Thus, in more general cases of rotation, such as the rotation of a top or a pedestal fan, **one point and notone**

line, of the rigid body is fixed. In this casethe axis is not fixed, though it always passes through the fixed point. In our study, however, we mostly deal with the simpler and special case of rotation in which one line (i.e. the axis) is fixed. Thus, for us rotation will be about a fixed axis only unless stated otherwise.

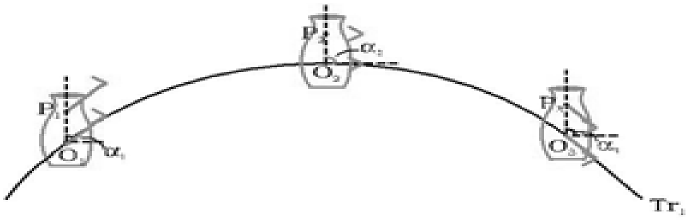


Fig. 7.6(a) *Motion of a rigid body which is pure translation.*

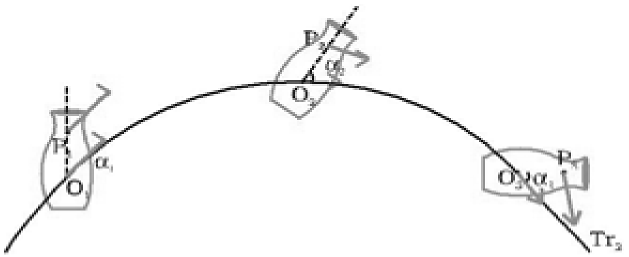


Fig. 7.6(b) *Motion of a rigid body which is a combination of translation and rotation*

Fig 7.6 (a) and 7.6 (b) *illustrate different motions of the same body. Note P is an arbitrary point of the body; O is the centre of mass of the body, which is defined in the next section. Suffice to say here that the trajectories of O are the translational trajectories* Tr_1 *and* Tr_2 *of the body. The positions O and P at three different instants of time are shown by* O_1, O_2, *and* O_3, *and* P_1, P_2 *and* P_3 *respectively in Fig. 7.6 (a) and (b) both. As seen from Fig. 7.6(a), at any instant the velocities of any particles like O and P of the body are the same in pure translation. Notice, in this case the orientation of OP, i.e. the angle OP makes with a fixed direction, say the horizontal, remains the same, i.e.* $\alpha_1 = \alpha_2 = \alpha_3$. *Fig. 7.6 (b) illustrates a case of combination of translation and rotation. In this case, at any instants the velocities of O and P differ. Also,* α_1, α_2 *and* α_3 *may all be different.*

The rolling motion of a cylinder down an inclined plane is a combination of rotation about a fixed axis and translation. Thus, the ‘something else’ in the case of rolling motion which we referred to earlier is rotational motion. You will find Fig. 7.6(a) and (b) instructive from this point of view. Both these figures show motion of the same body along identical translational trajectory. In one case, Fig. 7.6(a), the motion is a pure translation; in the other case [Fig. 7.6(b)] it is a combination of translation and rotation. (You may try to reproduce the two types of motion shown using a rigid object like a heavy book.)

We now recapitulate the most important observations of the present section: **The motionof a rigid body which is not pivoted or fixed in some way is either a pure translation or a combination of translation and rotation. The motion of a rigid body which is pivoted or fixed in some way is rotation.** The rotationmay be about an axis that is fixed (e.g. a ceiling fan) or moving (e.g. an oscillating table fan). We shall, in the present chapter, consider rotational motion about a fixed axis only.

7.2 CENTRE OF MASS

We shall first see what the centre of mass of a system of particles is and then discuss its significance. For simplicity we shall start with a two particle system. We shall take the line joining the two particles to be the x- axis.

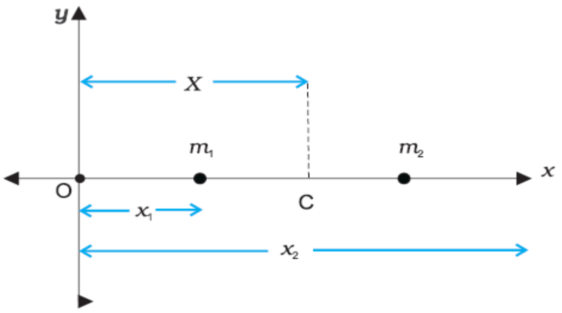


Fig. 7.7

Let the distances of the two particles be x_1 and x_2 respectively from some origin O. Let m_1 and m_2 be respectively the masses of the two particles.

The centre of mass of the system is that point C which is at a distance X from O, where X is given by

$$X = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2} \tag{7.1}$$

In Eq. (7.1), X can be regarded as the mass-weighted mean of x_1 and x_2. If the two particles have the same mass $m_1 = m_2 = m$, then

$$X = \frac{m\,x_1 + \,m\,x_2}{2m} = \frac{(x_1 + \,x_2)}{2}$$

Thus, for two particles of equal mass the centre of mass lies exactly midway between them.

If we have *n* particles of masses m_1, m_2, ... m_n respectively, along a straight line taken as the *x*- axis, then by definition the position of the centre of the mass of the system of particles is given by

$$X = \frac{m_1x_1 + \,m_2x_2 + \,\ldots + m_nx_n}{m_1 + \,m_2 + \,\ldots + m_n} = \frac{\sum m_ix_i}{\sum x_i} \qquad (7.2)$$

Where x_1, x_2,...x_n are the distances of the particles from the origin; *X* is also measured from the same origin. The symbol $\sum$ (the Greek letter sigma) denotes summation, in this case over *n* particles. The sum $\sum m_i = M$ is the total mass of the system.

Suppose that we have three particles, not lying in a straight line. We may define *x* and *y*-axes in the plane in which the particles lie and represent the positions of the three particles by coordinates (x_1,y_1), (x_2,y_2) and (x_3,y_3) respectively. Let the masses of the three particles be m_1, m_2 and m_3 respectively. The centre of mass C of the system of the three particles is defined and located by the coordinates (*X, Y)* given by

$$X = \frac{m_1x_1 + \,m_2x_2 + m_3x_3}{m_1 + \,m_2 + m_3} \qquad (7.3a)$$

$$Y = \frac{m_1y_1 + \,m_2y_2 + m_3y_3}{m_1 + \,m_2 + m_3} \qquad (7.3b)$$

For the particles of equal mass $m = m_1 = m_2 = m_3$,

$$X = \frac{m\,x_1 + \,m\,x_2 + m\,x_3}{3m} = \frac{(x_1 + \,x_2 + \,x_3)}{3}$$

$$Y = \frac{m\,y_1 + \,m\,y_2 + m\,y_3}{3m} = \frac{y_1 + \,y_2 + \,y_3)}{3}$$

Thus, for three particles of equal mass, the centre of mass coincides with the centroid of the triangle formed by the particles.

Results of Eqs. (7.3a) and (7.3b) are generalised easily to a system of *n* particles, not necessarily lying in a plane, but distributed in space. The centre of mass of such a system is at (*X*, *Y*, *Z*), where

$$X = \frac{\sum m_i x_i}{M} \qquad (7.4a)$$

$$Y = \frac{\sum m_i y_i}{M} \qquad (7.4b)$$

$$Z = \frac{\sum m_i z_i}{M} \qquad (7.4c)$$

Here $M = \ m_i$ is the total mass of the system. The index *i* runs from 1 to *n; m_i* is the mass of the i^{th} particle and the position of the i^{th} particle is given by (x_i, y_i, z_i).Eqs. (7.4a), (7.4b) and (7.4c) can be combined into one equation using the notation of position vectors. Let $\mathbf{r}_i$ be the position vectorof the i^{th} particle and **R** be the position vector of the centre of mass:

The sum on the right hand side is a vector sum.

$$r_i = x_i\hat{\boldsymbol{\imath}} + y_i\hat{\boldsymbol{\jmath}} + z_i\hat{k}$$

$$R = X\,\hat{\boldsymbol{\imath}} + Y\hat{\boldsymbol{\jmath}} + Z\,\hat{\boldsymbol{k}}$$

Then $$R = \frac{\sum m_i r_i}{M}$$

Note the economy of expressions we achieve by use of vectors. If the origin of the frame of reference (the coordinate system) is chosen to be the centre of mass then $\sum m_i\, x_i = 0$ for the given system of particles.

A rigid body, such as a metre stick or a flywheel, is a system of closely packed particles; Eqs. (7.4a), (7.4b), (7.4c) and (7.4d) are therefore, applicable to a rigid body. The number of particles (atoms or molecules) in such a body is so large that it is impossible to carry out the summations over individual particles in these equations. Since the spacing of the particles is small, we can treat the body as a continuous distribution of mass. We subdivide the body into *n* small elements of mass; m_1, m_2... m_n; the i^{th} element m_i is taken to be located about the point (x_i, y_i, z_i). The coordinates of the centre of mass are then approximately given by

$$X = \frac{\sum m_i x_i}{\sum m_i},\ Y = \frac{\sum m_i y_i}{\sum m_i}, Z = \frac{\sum m_i z_i}{\sum m_i}$$

As we make *n* bigger and bigger and each m_i *smaller* and smaller, these expressions become exact. In that case, we denote the sums over *i* by integrals. Thus,

$$\sum m_i \rightarrow \int dm \;\square M,$$

$$\sum (m_i)x_i \rightarrow \int x\, dm,\ \sum (m_i)y_i \rightarrow \int y\, dm,$$

$$\text{and} \qquad \sum (m_i)z_i \rightarrow \int z dm$$

Here *M* is the total mass of the body. The coordinates of the centre of mass now are

$$X = \frac{1}{M}\int x\, dm,\ Y = \frac{1}{M}\int y\, dm$$

And $$Z = \frac{1}{M}\int z\, dm \qquad (7.5\ a)$$

The vector expression equivalent to these three scalar expressions is

$$\boldsymbol{R} = \frac{1}{M}\int \boldsymbol{r}\, dm \tag{7.5 b}$$

If we choose, the centre of mass as the origin of our coordinate system,

$$R\ (x, y, z) = 0$$

i.e $$\int r\, dm = 0$$

Or $$\int x\, dm = \int y\, dm \int z\, dm = 0 \tag{7.6}$$

Often we have to calculate the centre of mass of homogeneous bodies of regular shapes like rings, discs, spheres, rods etc. (By a homogeneous body we mean a body with uniformly distributed mass.) By using symmetry consideration, we can easily show that the centres of mass of these bodies lie at their geometric centres.

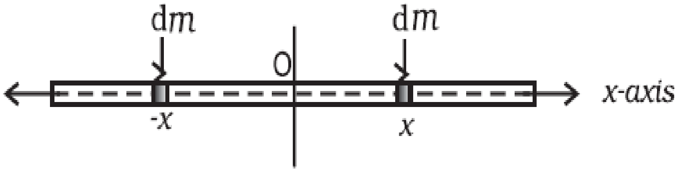


Fig. 7.8 *Determining the CM of a thin rod.*

Let us consider a thin rod, whose width and breath (in case the cross section of the rod is rectangular) or radius (in case the cross section of the rod is cylindrical) is much smaller than its length. Taking the origin to be at the geometric centre of the rod and *x*-axis to be along the length of the rod, we can say that on account of reflection symmetry, for every element *dm* of the rod at *x*, there is an element of the same mass *dm* located at *–x* (Fig. 7.8).

The net contribution of every such pair to the integral and hence the integral $\int x\, dm$ itself is zero. From Eq. (7.6), the point for which the integral itself is zero, is the centre of mass. Thus, the centre of mass of a homogenous thin rod coincides with its geometric centre. This can be understood on the basis of reflection symmetry.

The same symmetry argument will apply to homogeneous rings, discs, spheres, or even thick rods of circular or rectangular cross section. For all such bodies you will realise that for every element *dm* at a point (*x, y, z*) one can always take an element of the same mass at the point (*-x,-y,-z*). (In other words, the origin is a point of reflection symmetry for these bodies.) As a result, the integrals in Eq. (7.5 a) all are zero. This means that for all the above bodies, their centre of mass coincides with their geometric centre.

Example 7.1 Find the centre of mass of three particles at the vertices of an equilateral triangle. The masses of the particles are 100g, 150g, and 200g respectively. Each side of the equilateral triangle is 0.5m long.

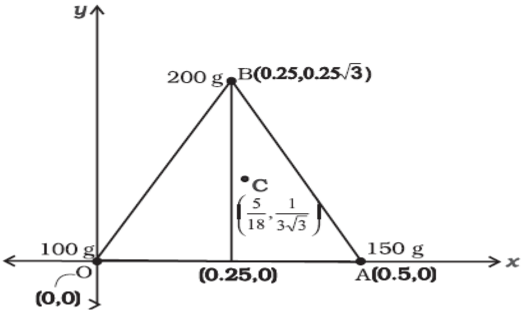


Fig. 7.9

With the *X* and *Y* axes chosen as shown in Fig. 7.9, the coordinates of points O, A and B forming the equilateral triangle are respectively (0,0), (0.5,0), (0.25, 0.25√3).

Let the masses 100 g, 150g and 200g be located at O, A and B be respectively. Then,

$$X = \frac{m_1x_1 + m_2x_2 + m_3x_3}{m_1 + m_2 + m_3}$$

$$= \frac{\left(100\ (0) + 150(0.5) + 200(0.25)\right)\ \mathrm{g\ m}}{(100 + 150 + 200)\mathrm{g}}$$

$$= \frac{75 + 50\ \mathrm{m}}{450} = \frac{125\ \mathrm{m}}{450} = \frac{5}{18}m$$

$$\mathrm{Y} = \frac{\left(100\ (0) + 150(0) + 200(0.25\sqrt{3})\right)\ \mathrm{g\ m}}{(100+150+200)\mathrm{g}}$$

$$= \frac{50\sqrt{3}\ \mathrm{m}}{450}$$

$$= \frac{\sqrt{3}\ \mathrm{m}}{9} = \frac{1}{3\sqrt{3}}\ \mathrm{m}$$

The centre of mass C is shown in the figure. Note that it is not the geometric centre of the triangle OAB. Why?

Example 7.2 Find the centre of mass of a triangular lamina.

Answer The lamina (*LMN*) may be subdivided into narrow strips each parallel to the base *(MN)* as shown in Fig. 7.10

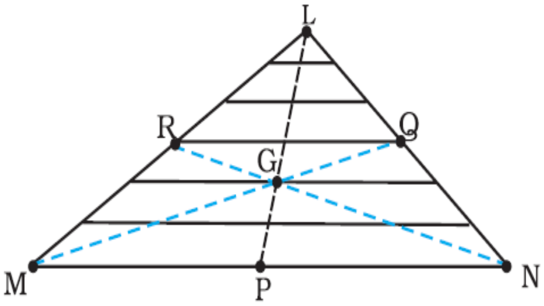


Fig. 7.10

By symmetry each strip has its centre of mass at its midpoint. If we join the midpoint of all the strips we get the median LP. The centre of mass of the triangle as a whole therefore, has to lie on the median LP. Similarly, we can argue that it lies on the median MQ and NR. This means the centre of mass lies on the point of concurrence of the medians, i.e. on the centroid G of the triangle.

Example 7.3 Find the centre of mass of a uniform L-shaped lamina (a thin flat plate) with dimensions as shown. The mass of the lamina is 3 kg

Answer Choosing the *X* and *Y* axes as shown in Fig. 7.11 we have the coordinates of the vertices of the L-shaped lamina as given in the figure. We can think of the L-shape to consist of 3 squares each of length 1m. The mass of each square is 1kg, since the lamina is uniform. The centres of mass C_1, C_2 and C_3 of the squares are, by symmetry, their geometric centres and have coordinates (1/2, 1/2), (3/2, 1/2), (1/2, 3/2) respectively. We take the masses of the squares to be concentrated at these points. The centre of mass of the whole L shape (*X*, *Y*) is the centre of mass of these mass points.

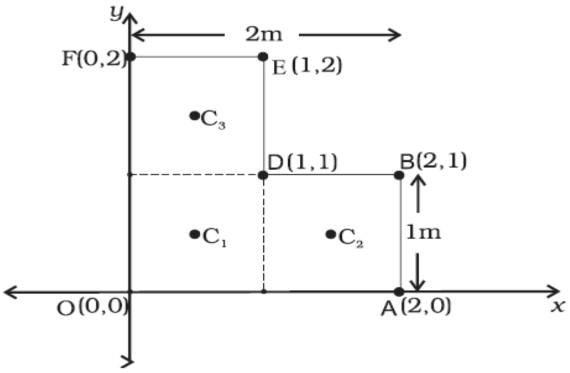


Fig. 7.11

Hence

$$X = \frac{(1\,(1/2) + 1(3/2) + 1(1/2))\text{k g m}}{(1+1+1)\text{kg}} = \frac{5}{6}\,\text{m}$$

$$Y = \frac{(1\,(1/2) + 1(1/2) + 1(3/2))\text{k g m}}{(1+1+1)\text{kg}} = \frac{5}{6}\,\text{m}$$

The centre of mass of the L-shape lies on the line OD. We could have guessed this without calculations. Can you tell why? Suppose, the three squares that make up the L shaped lamina of Fig. 7.11 had different masses. How will you then determine the centre of mass of the lamina?

7.3 MOTION OF CENTRE OF MASS

Equipped with the definition of the centre of mass, we are now in a position to discuss its physical importance for a system of particles. We may rewrite Eq.(7.4d) as

$$MR = \sum m_i\, r_i = m_1 r_1 + m_2 r_2 \ldots\ldots + m_n r_n \qquad (7.7)$$

Differentiating the two sides of the equation with respect to time we get

$$\mathrm{M}\frac{\mathrm{dR}}{\mathrm{dt}} = \mathrm{m_1}\frac{\mathrm{dr_1}}{\mathrm{dt}} + \mathrm{m_2}\frac{\mathrm{dr_2}}{\mathrm{dt}} + \cdots + \mathrm{m_n}\frac{\mathrm{dr}_n}{\mathrm{dt}}$$

Or

$$MV = m_1 v_1 + m_2 v_2 + \ldots + m_n v_n \qquad (7.8)$$

Where $\mathbf{v}_1$(=d$\mathbf{r}_1$/dt) is the velocity of the first particle $\mathbf{v}_2$(=$d\mathbf{r}_2/dt$) is the velocity of the second particle etc. and **V**= d**R**/d$t$is the velocity of the centre of mass. Note that we assumed the masses m_1, m_2, ... etc. do not change in time. We have therefore, treated them as constants in differentiating the equations with respect to time.

Differentiating Eq.(7.8) with respect to time, we obtain

$$M\frac{\mathrm{d}\mathbf{V}}{\mathrm{dt}} = \frac{\mathrm{m_1 d}\mathbf{v_1}}{\mathrm{dt}} + \frac{\mathrm{m_2 d}\mathbf{v_2}}{\mathrm{dt}} + \cdots + \frac{\mathrm{m_n d}\mathbf{v_n}}{\mathrm{dt}}$$

Or

$$MA = m_1 a_1 + m_2 a_2 + \ldots + m_n a_n \qquad (7.9)$$

Where $\mathbf{a}_1$(=d$\mathbf{v}_1$/dt)is the acceleration of the first particle, $\mathbf{a}_2$(=d$\mathbf{v}_2$/dt**)** is the acceleration of the second particle etc. and A (=d**V**/dt) is the acceleration of the centre of mass of the system of particles.

Now, from Newton's second law, the force acting on the first particle is given by $\mathbf{F}_1 = m_1\mathbf{a}_1$.The force acting on the second particle is given by $\mathbf{F}_2 = m_2\mathbf{a}_2$ and so on. Eq. (7.9) may be written as

$$MA = F_1 + F_2 + \ldots + F_n \qquad (7.10)$$

Thus, the total mass of a system of particles times the acceleration of its centre of mass is the vector sum of all the forces acting on the system of particles.

Note when we talk of the force $\mathbf{F}_1$ on the first particle, it is not a single force, but the vector sum of all the forces on the first particle; likewise for the second particle etc. Among these forces on each particle there will be **external** forces exerted by bodies outside the system and also **internal** forces exerted by the particles on one another. We know from Newton's third law that these internal forces occur in equal and opposite pairs and in the sum of forces of Eq. (7.10), their contribution is zero. Only the external forces contribute to the equation. We can then rewrite Eq. (7.10) as

$$MA = F_{ext} \qquad (7.11)$$

Where $\mathbf{F}_{ext}$ represents the sum of all external forces acting on the particles of the system. Eq. (7.11) states that **the centre of mass of a system of particles moves as if all the mass of the system was concentrated at the centre of mass and all the external forces were applied at that point.**

Notice, to determine the motion of the centre of mass no knowledge of internal forces of the system of particles is required; for this purpose we need to know only the external forces.

To obtain Eq. (7.11) we did not need to specify the nature of the system of particles. The system may be a collection of particles in which there may be all kinds of internal motions, or it may be a rigid body which has either pure translational motion or a combination of translational and rotational motion. Whatever is the system and the motion of its individual particles, the centre of mass moves according to Eq. (7.11).

Instead of treating extended bodies as single particles as we have done in earlier chapters, we can now treat them as systems of particles. We can obtain the translational component of their motion, i.e. the motion centre of mass of the system, by taking the mass of the whole system to be concentrated at the centre of mass and all the external forces on the system to be acting at the centre of mass.

This is the procedure that we followed earlier in analysing forces on bodies and solving problems without explicitly outlining and justifying the procedure. We now realise that in earlier studies we assumed, without saying so, that rotational motion and/or internal motion of the particles were either absent or negligible. We no longer need to do this. We have not only found the justification of the procedure we followed earlier; but we also have found how to describe and separate the translational motion of (1) a rigid body which may be rotating as well, or (2) a system of particles with all kinds of internal motion.

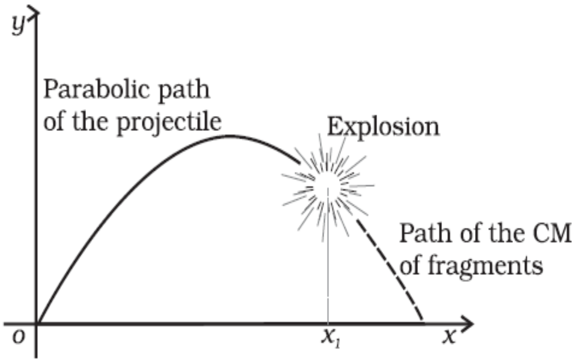


Fig. 7.12 *The centre of mass of the fragments of the projectile continues along the same parabolic path which it would have followed if there were no explosion*

Figure 7.12 is a good illustration of Eq. (7.11). A projectile, following the usual parabolic trajectory, explodes into fragments midway in air. The forces leading to the explosion are internal forces. They contribute nothing to the motion of the centre of mass. The total external force, namely, the force of gravity acting on the body, is the same before and after the explosion. The centre of mass under the influence of the external force continues, therefore, along the same parabolic trajectory as it would have followed if there were no explosion.

7.4 LINEAR MOMENTUM OF A SYSTEM OF PARTICLES

Let us recall that the linear momentum of a particle is defined as

$$p = mv \tag{7.12}$$

Let us also recall that Newton’s second law written in symbolic form for a single particle is

$$F = \frac{dp}{dt} \tag{7.13}$$

Where **F** is the force on the particle. Let us consider a system of *n* particles with masses m_1, m_2,...m_n respectively and velocities $\mathbf{v}_1$, $\mathbf{v}_2$,.......$\mathbf{v}_n$ respectively. The particles may be interacting and have external forces acting on them. The linear momentum of the first particle is $m_1\mathbf{v}_1$, of the second particle is $m_2\mathbf{v}_2$ and soon.

For the system of *n* particles, the linear momentum of the system is defined to be the vector sum of all individual particles of the system,

$$P = p_1 + p_1 + \ldots + p_n$$

$$= m_1 v_1 + m_2 v_2 + \ldots + m_n v_n \qquad (7.14)$$

Comparing this eq. (7.8)

$$p = mv \qquad (7.15)$$

Thus, **the total momentum of a system of particles is equal to the product of the total mass of the system and the velocity of its centre of mass**. Differentiating Eq. (7.15) with respect to time,

$$\frac{dp}{dt} = M\frac{dV}{dt} = MA \qquad (7.16)$$

Comparing Eq. (7.16) and Eq. (7.11)

$$\frac{dp}{dt} = F_{ext} \qquad (7.17)$$

This is the statement of **Newton's second law extended to a system of particles.** Suppose now, that the sum of external forces acting on a system of particles is zero. Then from Eq.(7.17)

$$\frac{dp}{dt} = 0 \text{ Or } \qquad P = \text{constant} \quad (7.48a)$$

Thus, when the total external force acting on a system of particles is zero, the total linear momentum of the system is constant. This is the law of conservation of the total linear momentum of a system of particles. Because of Eq. (7.15), this also means that when the total external force on the system is zero the velocity of the centre of mass remains constant. (We assume throughout the discussion on systems of particles in this chapter that the total mass of the system remains constant.)

Note that on account of the internal forces, i.e. the forces exerted by the particles on one another, the individual particles may have complicated trajectories. Yet, if the total external force acting on the system is zero, the centre of mass moves with *a* constant velocity, i.e., moves uniformly in a straight line like a free particle.

The vector Eq. (7.18a) is equivalent to three scalar equations,

$$P_x = c_1,\ P_y = c_2 \text{ and } P_z = c_3 \qquad (7.18\text{ b})$$

Here P_x, P_y and P_z are the components of the total linear momentum vector **P** along the *x, y* and *z* axes respectively; c_1, $c_2$and $c_3$areconstants.

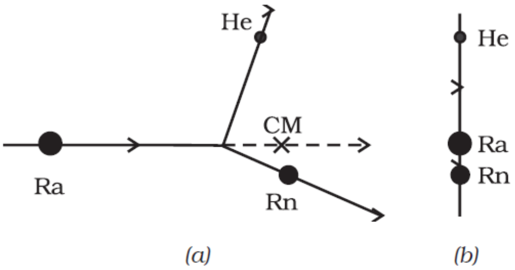


Fig. 7.13 (a) *A heavy nucleus (Ra) splits into a lighter nucleus (Rn) and an alpha particle (He). The CM of the system is in uniform motion. (b)The same splitting of the heavy nucleus (Ra) with the centre of mass at rest. The two product particles fly back to back.*

As an example, let us consider the radioactive decay of a moving unstable particle, like the nucleus of radium. A radium nucleus disintegrates into a nucleus of radon and an alpha particle. The forces leading to the decay are internal to the system and the external forces on the system are negligible. So the total linear momentum of the system is the same before and after decay. The two particles produced in the decay, the radon nucleus and the alpha particle, move in different directions in such a way that their centre of mass moves along the same path along which the original decaying radium nucleus was moving [Fig. 7.13(a)].

If we observe the decay from the frame of reference in which the centre of mass is at rest, the motion of the particles involved in the decay looks particularly simple; the product particles move back to back with their centre of mass remaining at rest as shown in Fig.7.13 (b).

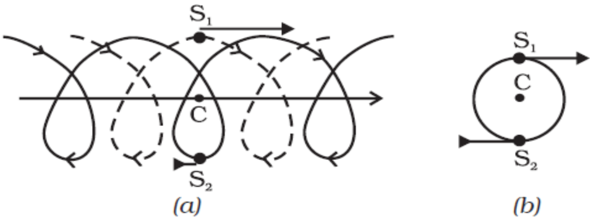


Fig. 7.14 (a) *Trajectories of two stars, S_1(dotted line) and S_2 (solid line) forming a binary system with their centre of mass C in uniform motion. (b) The same binary system, with the centre of mass C at rest.*

In many problems on the system of particles as in the above radioactive decay problem, it is convenient to work in the centre of mass frame rather than in the laboratory frame of reference.

In astronomy, binary (double) stars is a common occurrence. If there are no external forces, the centre of mass of a double star moves like a free particle, as shown in Fig.7.14 (a).

The trajectories of the two stars of equal mass are also shown in the figure; they look complicated. If we go to the centre of mass frame, then we find that there the two stars are moving in a circle, about the centre of mass, which is at rest. Note that the position of the stars have to be diametrically opposite to each other [Fig. 7.14(b)]. Thus in our frame of reference, the trajectories of the stars are a combination of (i) uniform motion in a straight line of the centre of mass and (ii) circular orbits of the stars about the centre of mass.

As can be seen from the two examples, **separating** the motion of different parts of a system into motion **of the centre of mass and motion about the centre of mass** is a very useful technique that helps in understanding the motion of the system.

7.5 VECTOR PRODUCT OF TWO VECTORS

We are already familiar with vectors and their use in physics. In chapter 6 (Work, Energy, Power) we defined the scalar product of two vectors. An important physical quantity, work, is defined as a scalar product of two vector quantities, force and displacement. We shall now define another product of two vectors. This product is a vector. Two important quantities in the study of rotational motion, namely, moment of a force and angular momentum, are defined as vector products.

Definition of Vector Product

A vector product of two vectors **a** and **b** is a vector **c** such that

(i) Magnitude of **c** = $c = ab\sin\theta$ where a and b are magnitudes of **a** and **b** and θ is the angle between the two vectors.

(ii) **c** is perpendicular to the plane containing **a** and **b**.

(iii) If we take a right handed screw with its head lying in the plane of **a** and **b** and the screw perpendicular to this plane, and if we turn the head in the direction from **a** to **b**, then the tip of the screw advances in the direction of **c**. This right handed screw rule is illustrated in Fig. 7.15a.

Alternately, if one curls up the fingers of right hand around a line perpendicular to the plane of the vectors **a** and **b** and if the fingers are curled up in the direction from **a** to **b**, then the stretched thumb points in the direction of **c**, as shown in Fig. 7.15b.

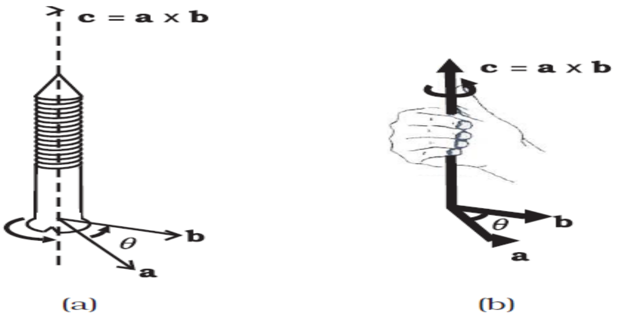


Fig. 7.15 (a)*Rule of the right handed screw for defining the direction of the vector product of two vectors. (b) Rule of the right hand for defining the direction of the vector product.*

A simpler version of the right hand rule is the following: Open up your right hand palm and curl the fingers pointing from **a** to **b**. Your stretched thumb points in the direction of **c**.

It should be remembered that there are two angles between any two vectors **a** and **b** . In Fig. 7.15 (a) or (b) they correspond to θ (as shown) and ($360^0 - \theta$). While applying either of the above rules, the rotation should be taken through the smaller angle ($<180^0$) between **a** and **b**. It is θ here.

Because of the cross used to denote the vector product, it is also referred to as cross product.

- Note that scalar product of two vectors is commutative as said earlier, a.b = b.a The vector product, however, is not commutative, i.e., $\mathbf{a} \times \mathbf{b} \neq \mathbf{b} \times \mathbf{a}$.

  The magnitude of both **a** × **b** and **b** × **a** is the same (ab sinθ); also, both of them are perpendicular to the plane of **a** and **b**. But the rotation of the right-handed screw in case of **a** × **b** is from **a** to **b**, whereas in case of **b** × **a** it is from **b** to **a**. This means the two vectors are in opposite directions. We have

  $$\mathbf{a}\,.\mathbf{b} =- \mathbf{b}.\mathbf{a}$$

- Another interesting property of a vector product is its behaviour under reflection. Under reflection (i.e. on taking the mirror image) we have $x \rightarrow -x, y \rightarrow -y$ **and** $z \rightarrow -z$.
- As a result all the components of a vector change sign and thus $a \rightarrow -a, b \rightarrow -b$. What happens to **a** × **b** under reflection?

  $$\mathbf{a} \times \mathbf{b} \rightarrow (-\mathbf{a}).(-\mathbf{b}) = \mathbf{a}.\mathbf{b}$$

  Thus, **a** × **b** does not change sign under reflection.

- Both scalar and vector products are distributive with respect to vector addition. Thus,

  a. (**b**+ **c**)= **a**.**b** + **a**.**c** **a.**

  (b+**c)**= **a** .**b** +**a. c**

- We may write **c** = **a** × **b** in the component form. For this we first need to obtain some elementary cross products:

  (i) a × **a** = **0** (**0** is a null vector, i.e. a vector with zero magnitude). This follows since magnitude of a × a is a^2 sin 0° = 0.

  From this follow the results

$$\text{(i) } \hat{\mathbf{i}}\text{x}\hat{\mathbf{i}} = \hat{\mathbf{j}}\text{x}\hat{\mathbf{j}} = \hat{\mathbf{k}}\text{x}\hat{\mathbf{k}} = \widehat{\mathbf{0}} \text{ and}$$

$$\text{(ii) } \hat{\mathbf{i}}\text{x}\hat{\mathbf{j}} = \widehat{\boldsymbol{k}}$$

Note that the magnitude of $\hat{\imath}$ x $\hat{\jmath}$ is sin 90° or 1, scince $\hat{\imath}$ and $\hat{\jmath}$ both have unit magnitude and the angle between them is 90°.

Thus $\hat{\boldsymbol{\imath}}\text{x}\hat{\boldsymbol{\jmath}}$ is a unit vector. A unit vector perpendicular to the plane of $\hat{\mathbf{i}}$and$\hat{\mathbf{j}}$, and related to them by the right hand screw rule is $\widehat{\mathbf{k}}$. Hence, the above result. You may verify similarly,

j x k = i and **kx i = j**

From the rule for commutation of the cross product, it follows:

j x i = - k, k x j = -i and **ix k = -j**

Note if $\hat{\boldsymbol{\imath}}, \hat{\boldsymbol{\jmath}}and\widehat{\boldsymbol{k}}$occur cyclically in the above vector product relation, the vector product is Positive. If $\hat{\boldsymbol{\imath}}, \hat{\boldsymbol{\jmath}}and\widehat{\boldsymbol{k}}$ do not occur in cyclic order, the vector product is negative.

Now

$$\begin{aligned}\mathbf{a}.\mathbf{b} &= \left(a_x\hat{\boldsymbol{\imath}} + a_y\hat{\boldsymbol{\jmath}} + a_z\widehat{\boldsymbol{k}}\right).\left(b_x\hat{\boldsymbol{\imath}} + b_y\hat{\boldsymbol{\jmath}} + b_z\widehat{\boldsymbol{k}}\right)\\ &= a_xb_y\widehat{\boldsymbol{k}} - a_xb_z\hat{\boldsymbol{\jmath}} - a_yb_x\widehat{\boldsymbol{k}} + a_yb_z\hat{\boldsymbol{\imath}} + a_zb_x\hat{\boldsymbol{\jmath}} - a_zb_y\hat{\boldsymbol{\imath}}\\ &= \left(a_yb_z - a_zb_x\right)\hat{\boldsymbol{\imath}} + (a_zb_x - a_xb_z)\hat{\boldsymbol{\jmath}} + (a_xb_y - a_yb_x)\,\widehat{\boldsymbol{k}}\end{aligned}$$

We have used the elementary cross products in obtaining the above relation. The expression for **a** × **b** can be put in a determinant form which is easy to remember.

$$\text{a x b} = \begin{vmatrix} \hat{\text{i}} & \hat{\text{j}} & \hat{\text{k}} \\ \text{a}_\text{x} & \text{a}_\text{y} & \text{a}_\text{z} \\ \text{b}_\text{x} & \text{b}_\text{y} & \text{b}_\text{z} \end{vmatrix}$$

Example 7.4*Find the scalar and vector products of two vectors a = (3i – 4j + 5k) and b = (– 2i + j – 3k)*

Answer

$$\mathbf{a}\cdot\mathbf{b} = (3i - 4j + 5k)\cdot(-2i + j - 3k)$$

$$= -6 - 4 - 15$$

$$= -25$$

$$\mathrm{a \times b} = \begin{vmatrix} \hat{\imath} & \hat{\jmath} & \hat{k} \\ 3 & -4 & 5 \\ -2 & 1 & -3 \end{vmatrix} = 7\hat{\imath} - \hat{\jmath} - 5\hat{k}$$

Note that $\mathrm{b \times a} = -7\hat{\imath} + \hat{\jmath} + 5\hat{k}$

7.6 ANGULAR VELOCITY AND ITS RELATION WITH LINEAR VELOCITY

In this section we shall study what is angular velocity and its role in rotational motion. We have seen that every particle of a rotating body moves in a circle. The linear velocity of the particle is related to the angular velocity. The relation between these two quantities involves a vector product which we learnt about in the last section.

Let us go back to Fig. 7.4. As said above, in rotational motion of a rigid body about a fixed axis, every particle of the body moves in a circle, which lies in a plane perpendicular to the axis and has its centre on the axis. In Fig. 7.16 we redraw Fig. 7.4, showing a typical particle (at a point P) of the rigid body rotating about a fixed axis (taken as the *z*-axis). The particle describes a circle with a centre C on the axis.

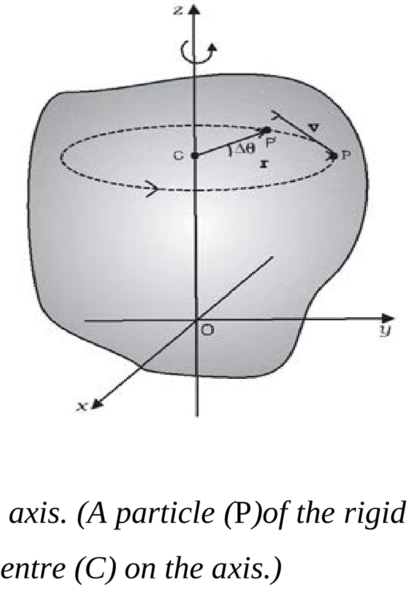


Fig. 7.16 *Rotation about a fixed axis. (A particle (*P*)of the rigid body rotating about the fixed (z-) axis moves in a circle with centre (C) on the axis.)*

The radius of the circle is *r*, the perpendicular distance of the point P from the axis. We also show the linear velocity vector **v** of the particle at P. It is along the tangent at P to the circle.

Let P′ be the position of the particle after an interval of time *t* (Fig. 7.16). The angle PCP′ describes the angular displacement $\Delta\theta$ of the particle in time Δt. The average angular velocity of the particle over the interval *t* is $\Delta\theta/\Delta t$. As Δt tends to zero (i.e. takes smaller and smaller values), the ratio $\Delta\theta/\Delta t$ approaches a limit which is the instantaneous angular velocity $d\theta/dt$ of the particle at the position P. We denote the instantaneous angular velocity by ω (the Greek letter omega). We know from our study of circular motion that the magnitude of linear velocity *v* of a particle moving in a circle is related to the angular velocity of the particle ω by the simple relation $\upsilon=\omega r$, where *r* is the radius of the circle.

We observe that at any given instant the relation $v=\omega r$ applies to all particles of the rigid body. Thus for a particle at a perpendicular distance r_i from the fixed axis, the linear velocity at a given instant v_i is given by

$$\omega = d\theta/dt v_i = \omega r_i$$

The index *i* runs from 1 to *n*, where *n* is the total number of particles of the body.

For particles on the axis, ***r*=0**, and hence $v = \omega r = 0$. Thus, particles on the axis are stationary. This verifies that the axis is *fixed*.

Note that we use the same angular velocity Ω for all the particles. **We therefore, refer to ω as the angular velocity of the whole body**. **We have characterised pure translation of a body by all parts of the body having the same velocity at any instant of time. Similarly, we may characterise pure rotation by all parts of the body having the same angular velocity at any instant of time**. Note that this characterisation of the rotation of a rigid body about a fixed axis is **just another way** of saying as in Sec. 7.1 that each particle of the body moves in a circle, which lies in a plane perpendicular to the axis and has the centre on the axis.

In our discussion so far the angular velocity appears to be a scalar. In fact, it is a vector. We shall not justify this fact, but we shall accept it. For rotation about a fixed axis, the angular velocity vector lies along the axis of rotation, and points out in the direction in which a right handed screw would advance, if the head of the screw is rotated with the body. (See Fig. 7.17a).

The magnitude of this vector is referred as above

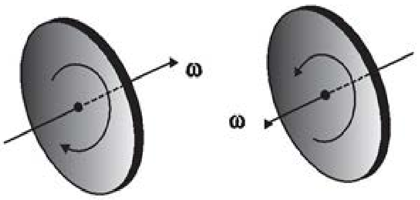


Fig. 7.17 (a) *If the head of a right handed screw rotates with the body, the screw advances in the direction of the angular velocity **ω**. If the sense (clockwise or anticlockwise) of rotation of the body changes, so does the direction of **ω***

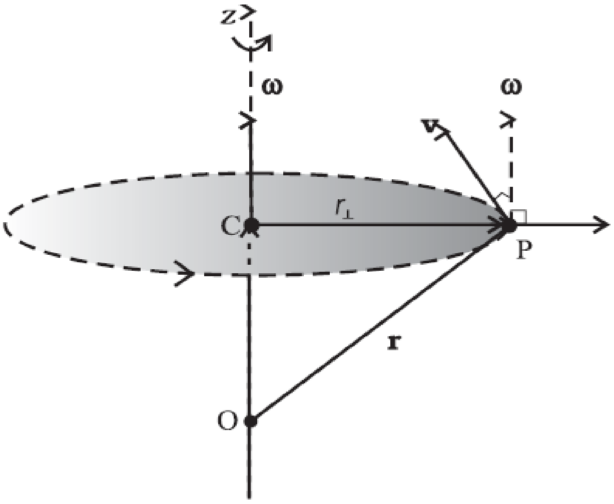


Fig. 7.17 (b) *The angular velocity vector **ω** is directed along the fixed axis as shown. The linear velocity of the particle at P is **v**=**ω** × **r**. It is perpendicular to both **ω** and **r** and is directed along the tangent to the circle described by the particle.*

We shall now look at what the vector product **ω** × **r** corresponds to. Refer to Fig. 7.17(b) which is a part of Fig. 7.16 reproduced to show the path of the particle P. The figure shows the vector **ω** directed along the fixed (*z*-) axis and also the position vector **r** = **OP** of the particle at P of the rigid body with respect to the origin O. Note that the origin is chosen to be on the axis of rotation.

Now $\omega \times \mathbf{r} = \omega \times \mathbf{OP} = \omega \times (\mathbf{OC} + \mathbf{CP})$

But $\omega \times \mathbf{OC} = \mathbf{0}$ **as ω is** along **OC**

Hence $\omega \times \mathbf{r} = \omega \times \mathbf{CP}$

The vector ω x **CP** is perpendicular to ω, i.e.to **CP**, the *z*-axis and also to the radius of the circle described by the particle at P. It is therefore, along the tangent to the circle at P. Also, the magnitude of **ω** × **CP** is ω (CP) since ***ω*** and **CP** are perpendicular to each other. We shall denote **CP** by **r** and not by **r**, as we did earlier.

Thus, $\boldsymbol{\omega} \times \mathbf{r}$ is a vector of magnitude ωr and is along the tangent to the circle described by the particle at P. The linear velocity vector **v** at P has the same magnitude and direction. Thus,

$$v = \omega \times r \tag{7.20}$$

In fact, the relation, Eq. (7.20), holds good even for rotation of a rigid body with one point fixed, such as the rotation of the top [Fig. 7.6(a)]. In this case **r** represents the position vector of the particle with respect to the fixed point taken as the origin.

We note that **for rotation about a fixed axis, the direction of the vector ω does not change with time. Its magnitude may, however, change from instant to instant. For the more general rotation, both the magnitude and the direction of ω may change from instant to instant.**

7.6.1 Angular acceleration

You may have noticed that we are developing the study of rotational motion along the lines of the study of translational motion with which we are already familiar. Analogous to the kinetic variables of linear displacement and velocity (**v**) in translational motion, we have angular displacement and angular velocity ($\boldsymbol{\omega}$) in rotational motion. It is then natural to define in rotational motion the concept of angular acceleration in analogy with linear acceleration defined as the time rate of change of velocity in translational motion. We define angular acceleration **α** as the time rate of change of angular velocity; Thus,

$$\alpha = d\omega/dt \tag{7.21}$$

If the axis of rotation is fixed, the direction of **ω** and hence, that of **α** is fixed. In this case the vector equation reduces to a scalar equation

$$\alpha = d\omega/dt \tag{7.22}$$

7.7 TORQUE AND ANGULAR MOMENTUM

In this section, we shall acquaint ourselves with two physical quantities which are defined as vector products of two vectors. These as we shall see, are especially important in the discussion of motion of systems of particles, particularly rigid bodies.

7.7.1 Moment of force (Torque)

We have learnt that the motion of a rigid body in general is a combination of rotation and translation. If the body is fixed at a point or along a line, it has only rotational motion. We know that force is needed to change the translational state of a body, i.e. to produce linear acceleration. We may then ask, what is the analogue of force in the case of rotational motion? To look into the question in a concrete situation let us take the example of opening or closing of a door. A door is a rigid body which can rotate about a fixed vertical axis passing through the hinges. What makes the door rotate? It is clear that unless a force is applied the door does not rotate. But any force does not do the job. A force applied to the hinge line cannot produce any rotation at all, whereas a force of given magnitude applied at right angles to the door at its outer edge is most effective in producing rotation. It is not the force alone, but how and where the force is applied is important in rotational motion.

The rotational analogue of force is **moment of force**. It is also referred to as **torque**. (We shall use the words moment of force and torque interchangeably.) We shall first define the moment of force for the special case of a single particle. Later on we shall extend the concept to systems of particles including rigid bodies. We shall also relate it to a change in the state of rotational motion, i.e. is angular acceleration of a rigid body.

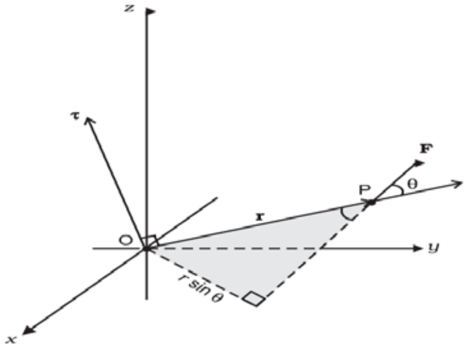


Fig. 7.18 *τ=**r** x **F**,τ is perpendicular to the plane containing **r** and **F**, and its direction is given by the right handed screw rule.*

If a force acts on a single particle at a point P whose position with respect to the origin O is *l = r p given* by the position vector (Fig. 7.18), the moment of the force acting on the particle with respect to the origin O is defined as the vector product

$$\tau = r \times F \tag{7.23}$$

The moment of force (or torque) is a vector quantity. The symbol **τ** stands for the greek latter **tau** The magnitude of τ is

$$\tau = r \times F \sin\theta$$

Where r is the magnitude of position vector **r**, i.e. the length OP, F is the magnitude of force **F** and θ is the angle between **r** and **F** as shown Moment of force has dimensions M L^2 T^{-2}. Its dimensions are the same as those of work or energy. It is, however, a very different physical quantity than work. Moment of a force is a vector, while work is a scalar. The SI unit of moment of force is Newton-metre (Nm). The magnitude of the moment of force may be written

$$\tau = (r\sin\theta)F = r_{\perp}F$$

(Or) $$\tau = rF\ sin\theta = rF_{\perp}$$

Where $r = r$ sinθ is the perpendicular distance of line of action of **F** form the origin and F (= F sin θ) is the component of **F** in the direction perpendicular to **r**. Note that $\tau = 0$ if $r = 0, F_{\perp} = 0$ or $\theta = 0^0$ or 180^0. Thus, the moment of a force vanishes if either the magnitude of the force is zero, or if the line of action of the force passes through the origin.

One may note that since **r** × **F** is a vector product, properties of a vector product of two vectors apply to it. If the direction of **F** is reversed, the direction of the moment of force is reversed. If directions of both **r** and **F** are reversed, the direction of the moment of force remains the same.

7.7.2 Angular momentum of a particle

Just as the moment of a force is the rotational analogue of force, the quantity angular momentum is the rotational analogue of linear momentum. We shall first define angular momentum for the special case of a single particle and look at its usefulness in the context of single particle motion. We shall then extend the definition of angular momentum to systems of particles including rigid bodies.

Like moment of a force, angular momentum is also a vector product. It could also be referred to as moment of (linear) momentum. From this term one could guess how angular momentum is defined.

Consider a particle of mass m and linear momentum **p** at a position **r** relative to the origin O. The angular momentum **l** of the particle with respect to the origin O is defined to be

$$\mathbf{l} = \mathbf{r} \times \mathbf{p} \tag{7.25a}$$

The magnitude of the angular momentum vector is

$$l = r\ p\ sin\theta \tag{7.26a}$$

Where p is the magnitude of **p** and θ is the angle between **r** and **p**. We may write

Or $$r_{\perp}\text{p} \tag{7.26b}$$

Where r (= r sinθ) is the perpendicular distance of the directional line of **p** from the origin and p (= p sinθ) is the component of **p** in a direction perpendicular to **r**. We expect the angular momentum to be zero (l = 0), if the linear momentum vanishes (p = 0), if the particle is at the origin (r = 0), or if the directional line of **p** passes through the origin $\theta = 0^0$ or 180^0.

The physical quantities, moment of a force and angular momentum, have an important relation between them. It is the rotational analogue of the relation between force and linear momentum. For deriving the relation in the context of a single particle, we differentiate **l** = **r** × **p** with respect to time,

$$\frac{dl}{dt} = \frac{d}{dt}(r\text{x}p)$$

Applying the product rule for differentiation to the right hand side,

$$\frac{d}{dt}(r \text{ x } p) = \frac{dr}{dt} \,.p + r \text{ x} \frac{dp}{dt}$$

Now, the velocity of the particle is **v** = d**r**/dt and **p** = m**v**

Because of this $\frac{dr}{dt}\text{x}\, p = v \text{ x}\, mv = 0$

As the vector product of two parallel vectors vanishes. Further, since d**p**/dt = **F**,

$$r\ x\ \frac{dp}{dt} = r\ x\ F = \tau$$

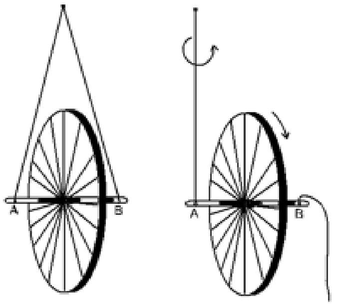
Hence $\frac{d}{dt}(r\text{x}p) = \tau$

Or $\frac{dl}{dt} = \tau$ (7.27)

Thus, the time rate of change of the angular momentum of a particle is equal to the torque acting on it. This is the rotational analogue of the equation **F** = d**p**/dt, which expresses Newton's second law for the translational motion of a single particle.

An experiment with the bicycle rim

Take a bicycle rim and extend its axle on both sides. Tie two strings at both ends A and B, as shown in the adjoining figure. Hold both the strings together in one hand such that the rim is vertical. If you leave one string, the rim will tilt. Now keeping the rim in vertical position with both the strings in one hand, put the wheel in fast rotation around the axle with the other hand. Then leave one string, say B, from your hand, and observe what happens.



Initially After

The rim keeps rotating in a vertical plane and the plane of rotation turns around the string A which you are holding. We say that the axis of rotation of the rim or equivalently its angular momentum precesses about the string A.

The rotating rim gives rise to an angular momentum. Determine the direction of this angular momentum. When you are holding the rotating rim with string A, a torque is generated. (We leave it to you to find out how the torque is generated and what its direction is.) The effect of the torque on the angular momentum is to make it precess around an axis perpendicular to both the angular momentum and the torque. Verify all these statements.

Torque and angular momentum for a system of particles

To get the total angular momentum of a system of particles about a given point we need to add vectorially the angular momenta of individual particles. Thus, for a system of *n* particles,

$$L = I_1 + I_2 + \ldots + I_n = \sum_{i=1}^{n} I_i$$

The angular momentum of the i^{th} particle is given by

$$\mathbf{l}_i = \mathbf{r}_i \times \mathbf{p}_i$$

Where $\mathbf{r}_i$ is the position vector of the i^{th} particle with respect to a given origin and $\mathbf{p} = (m_i \mathbf{v}_i)$ is the linear momentum of the particle. (The particle has mass m_i and velocity $\mathbf{v}_i$) We may write the total angular momentum of a system of particles as x

$$L = \sum I_i = \sum_i r_i \times p_i \tag{7.25b}$$

This is a generalisation of the definition of angular momentum (Eq. 7.25a) for a single particle to a system of particles.

Using Eqs. (7.23) and (7.25b), we get

$$\frac{dL}{dt} = \frac{d}{dt}\left(\sum I_i\right) = \sum_i \frac{dI_i}{dt} = \sum_i \tau_i \tag{7.28a}$$

Where τ_i is the torque acting on the i_{th} particle:

$$\tau_i = r_i \times F_i$$

The force Fi on the i_{th} particle is the vector sum of external forces F_i^{ext} acting on the particle and the internal forces F_i^{int} exerted on it by the other particles of the system. We may therefore separate the contribution of the external and the internal forces to the total torque

$$\tau = \sum_i \tau_i = \sum_i r_i\ x\ F_i \text{ as}$$

$$\tau = \tau_{ext} + \tau_{int}$$

Where $\tau_{ext} = \sum_i r_i\ x\ F_i^{ext}$

and $\tau_{int} = \sum_i r_i\ x\ F_i^{int}$

We shall assume not only Newton’s third law, i.e. the forces between any two particles of the system are equal and opposite but also that these forces are directed along the line joining of the two particles. In this case the contribution of the internal forces to the total torque on the system is zero. Since the torque resulting from each action-reaction pair of forces is zero. We thus have, $\tau_{int} = 0$ and therefore $\tau = \tau_{ext}$

Since $\tau = \sum \tau_i,$ it follows from Eq.(7.28a)

That $$\frac{dl}{dt} = \tau_{ext} \tag{7.28b}$$

Thus the time rate of the total angular acting on the system taken about the same point. Eq. (7.28b) is the generalization of the single particle case of Eq. (7.23) to a system of particles. Note that when we have only one particle there are no internal forces or torques. Eq. (7.28b) is the rotational analogue of

$$\frac{dP}{dt} = F_{ext} \tag{7.17}$$

Note that like Eq. (7.17), Eq. (7.28b) holds good for any system of particles, whether it is a rigid body or its individual particles have all kinds of internal motion.

Conservation of angular momentum

If $\tau_{ext} = 0$ Eq. (7.28b) reduces to

$$\frac{dL}{dt} = 0$$

Or L = constant. (7.29a)

Thus, if the total external torque on a system of particles is zero, then the total angular momentum of the system is conserved. i.e. remains constant. Eq. (7.29a) is equivalent to three scalar equations.

$$L_x = K_1, L_y = K_2 \; and \; K_z = K_3 \tag{7.29b}$$

Here $K_1, K_2 and\, K_3$ are constants: $L_x, L_y and\, L_z$ are the components of the total angular momentum vector L along the x,y and z axes respectively. The statement that the total angular momentum is conserved means that each of these three components is conserved.

Eq. (7.29a) is the rotational analogue of Eq. (7.18a), i.e. the conservation law of the total linear momentum for a system of particles. Like Eq. (7.18a), it has applications in many practical situations. We shall look at a few of the interesting applications later on in this chapter.

Example 7.5 Find the torque of a force $7\hat{\imath} + 3\hat{\jmath} - 5\hat{k}$ about the origin. The force acts on a particle whose position vector is $\hat{\imath} - \hat{\jmath} + \hat{k}$.

Answer Here $r = \hat{\imath} - \hat{\jmath} + \hat{k}\ and\ F = 7\hat{\imath} + 3\hat{\jmath} - 5\hat{k}$

$$\tau = \begin{vmatrix} \hat{\imath} & \hat{\jmath} & \hat{k} \\ 1 & -1 & 1 \\ 7 & 3 & -5 \end{vmatrix} = (5-3)\hat{\imath} - (-5-7)\hat{\jmath} + (3-(-7))\hat{k}$$

Or $\tau = 2\hat{\imath} + 12\hat{\jmath} + 10\hat{k}$

Example 7.6 Show that the angular momentum about any point of a single particle moving with constant velocity remains constant throughout the motion.

Answer Let the particle with velocity **v** be at point P at some instant *t*. We want to calculate the angular momentum of the particle about an arbitrary point O.

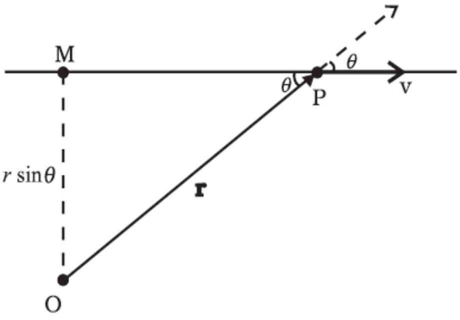


Fig 7.19

The angular momentum is **l** = **r** × *m***v**. Its magnitude is *mvr* sin*θ*, where *θ* is the angle between **r** and **v** as shown in Fig. 7.19. Although the particle changes position with time, the line of direction of **v** remains the same and hence OM = *r sinθ.* is a constant.

Further, the direction of **l** is perpendicular to the plane of **r** and **v**. It is into the page of the figure. This direction does not change with time. Thus, **l** remains the same in magnitude and direction and is therefore conserved. Is there any external torque on the particle?

7.8 EQUILIBRIUM OF A RIGID BODY

We are now going to concentrate on the motion of rigid bodies rather than on the motion of general systems of particles.

We shall recapitulate what effect the external forces have on a rigid body. (Henceforth we shall omit the adjective 'external' because unless stated otherwise, we shall deal with only external forces and torques.) The forces change the translational state of the motion of the rigid body, i.e. they change its total linear momentum in accordance with Eq. (7.17). But this is not the only effect the forces have. The total torque on the body may not vanish. Such a torque changes the rotational state of motion of the rigid body, i.e. it changes the total angular momentum of the body in accordance with Eq. (7.28 b).

A rigid body is said to be in mechanical equilibrium, if both its linear momentum and angular momentum are not changing with time, or equivalently, the body has neither linear acceleration nor angular acceleration.

This means

(1) the total force, i.e. the vector sum of the forces, on the rigid body is zero;

$$F_1 + F_2 + \ldots + F_n = \sum_{i=1}^{n} F_i = 0 \qquad (7.30a)$$

If the total force on the body is zero, then the total linear momentum of the body does not change with time. Eq. (7.30a) gives the condition for the translational equilibrium of the body.

(2) The total torque, i.e. the vector sum of the torques on the rigid body is zero,

$$\tau_1 + \tau_2 + \ldots + \tau_n = \sum_{i=1}^{n} \tau_i = 0 \qquad (7.30b)$$

If the total torque on the rigid body is zero, the total angular momentum of the body does not change with time. Eq. (7.30 b) gives the condition for the rotational equilibrium of the body.

One may raise a question, whether the rotational equilibrium condition [Eq. 7.30(b)] remains valid, if the origin with respect to which the torques are taken is shifted. One can show that if the translational equilibrium condition [Eq. 7.30(a)] holds for a rigid body, then such a shift of origin does not matter, i.e. the rotational equilibrium condition is independent of the location of the origin about which the torques are taken. Example 7.7 gives a proof of this result in a special case of a couple, i.e. two forces acting on a rigid body in translational equilibrium. The generalisation of this result to n forces is left as an exercise.

Eq. (7.30a) and Eq. (7.30b), both, are vector equations. They are equivalent to three scalar equations each. Eq. (7.30a) corresponds to

$$\sum_{i=1}^{n} F_{ix} = 0, \sum_{i=1}^{n} F_{iy} = 0, \sum_{i=1}^{n} F_{iz} = 0 \qquad (7.31a)$$

Where F_{ix}, F_{iy} and F_{iz} are respectively the x, y and z components of the forces $\mathbf{F}_i$. Similarly, Eq. (7.30b) is equivalent to three scalar equations

$$\sum_{i=1}^{n} \tau_{ix} = 0, \sum_{i=1}^{n} \tau_{iy} = 0, \sum_{i=1}^{n} \tau_{iz} = 0 \qquad (7.31b)$$

Whereτ_{ix}, τ_{iy} and τ_{iz} are respectively the x, y and z components of the torque τ_i

Eq. (7.31a) and (7.31b) give six independent conditions to be satisfied for mechanical equilibrium of a rigid body. In a number of problems all the forces acting on the body are coplanar. Then we need only three conditions to be satisfied for mechanical equilibrium. Two of these conditions correspond to translational equilibrium; the sum of the components of the forces along any two perpendicular axes in the plane must be zero. The third condition corresponds to rotational equilibrium. The sum of the components of the torques along any axis perpendicular to the plane of the forces must be zero.

The conditions of equilibrium of a rigid body may be compared with those for a particle, which we considered in earlier chapters. Since consideration of rotational motion does not apply to a particle, only the conditions for translational equilibrium (Eq. 7.30 a) apply to a particle. Thus, for equilibrium of a particle the vector sum of all the forces on it must be zero. Since all these forces act on the single particle, they must be concurrent. Equilibrium under concurrent forces was discussed in the earlier chapters.

A body may be in partial equilibrium, i.e., it may be in translational equilibrium and not in rotational equilibrium, or it may be in rotational equilibrium and not in translational equilibrium.

Consider a light (i.e. of negligible mass) rod (AB), at the two ends (A and B) of which two parallel forces both equal in magnitude are applied perpendicular to the rod as shown in Fig. 7.20(a).

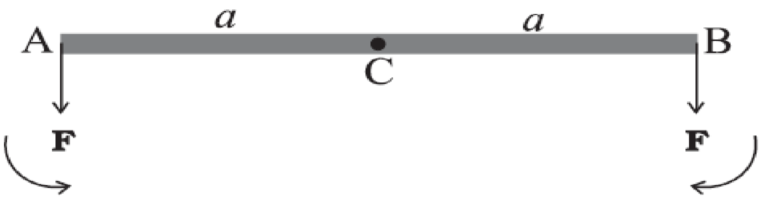


Fig. 7.20 (a)

Let C be the midpoint of AB, CA = CB = a. the moment of the forces at A and B will both be equal in magnitude (aF), but opposite in sense as shown. The net moment on the rod will be zero. The system will be in rotational equilibrium, but it will not be in translational equilibrium; $\sum F \neq 0$

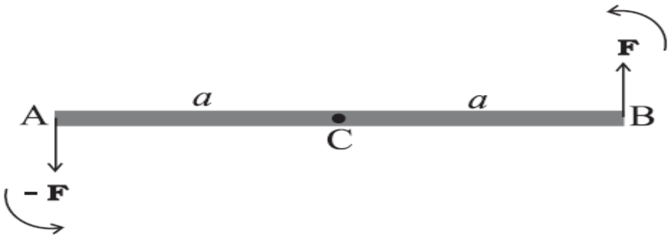


Fig. 7.20 (b)

The force at B in Fig. 7.20(a) is reversed in Fig. 7.20(b). Thus, we have the same rod with two equal and opposite forces applied perpendicular to the rod, one at end A and the other at end B. Here the moments of both the forces are equal, but they are not opposite; they act in the same sense and cause anticlockwise rotation of the rod. The total force on the body is zero; so the body is in translational equilibrium; but it is not in rotational equilibrium. Although the rod is not fixed in any way, it undergoes pure rotation (i.e. rotation without translation).

A pair of equal and opposite forces with different lines of action is known as a **couple**. A couple produces rotation without translation.

When we open the lid of a bottle by turning it, our fingers are applying a couple to the lid [Fig. 7.21(a)]. Another known example is a compass needle in the earth’s magnetic field as shown in the Fig. 7.21(b). The earth’s magnetic field exerts equal forces on the north and south poles. The force on the North Pole is towards the north, and the force on the South Pole is toward the south. Except when the needle points in the north-south direction; the two forces do not have the same line of action. Thus there is a **couple** acting on the needle due to the earth's magnetic field.

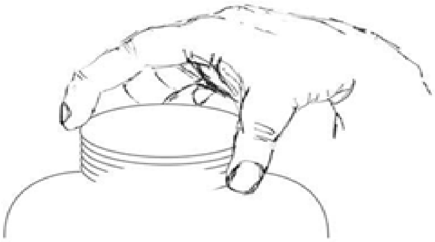


Fig. 7.21(a) *Our fingers apply a couple to turn the lid.*

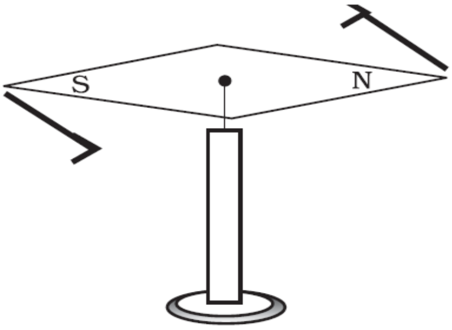


Fig. 7.21(b) *The Earth's magnetic field exerts equal and opposite forces on the poles of a compass needle. These two forces form a couple.*

Example 7.7 Show that moment of a couple does not depend on the point about which you take the moments.

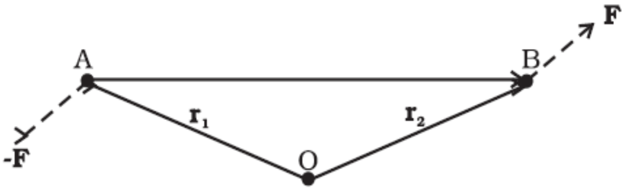


Fig. 7.22

Consider a couple as shown in Fig. 7.22 acting on a rigid body. The forces **F** and **-F** act respectively at points B and A. These points have position vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ with respect to origin O. Let us take the moments of the forces about the origin.

The moment of the couple = sum of the moments of the two forces making the couple

$$= \mathbf{r}_1 \times (-\mathbf{F}) + \mathbf{r}_2 \times \mathbf{F}$$
$$= \mathbf{r}_2 \times \mathbf{F} - \mathbf{r}_1 \times \mathbf{F}$$
$$= (\mathbf{r}_2 - \mathbf{r}_1) \times \mathbf{F}$$

But $\mathbf{r}_1 + \mathbf{AB} = \mathbf{r}_2$, and hence $\mathbf{AB} = \mathbf{r}_2 - \mathbf{r}_1$. The moment of the couple, therefore, is $\mathbf{AB} \times \mathbf{F}$. Clearly this is independent of the origin, the point about which we took the moments of the forces.

7.8.1 Principle of moments

An ideal lever is essentially a light (i.e. of negligible mass) rod pivoted at a point along its length. This point is called the fulcrum. A see-saw on the children's playground is a typical example of a lever. Two forces F_1 and F_2, parallel to each other and usually perpendicular to the lever, as shown here, act on the lever at distances d_1 and d_2 respectively from the fulcrum as shown in Fig. 7.23.

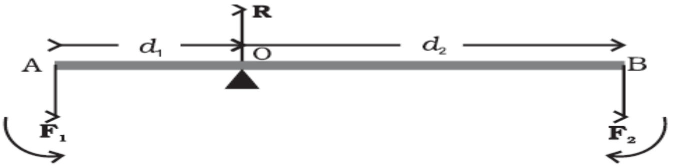


Fig. 7.23.

The lever is a system in mechanical equilibrium. Let **R** be the reaction of the support at the fulcrum; **R** is directed opposite to the forces F_1 and F_2. For translational equilibrium,

$$R - F_1 - F_2 = 0 \qquad \text{(i)}$$

For considering rotational equilibrium we take the moments about the fulcrum; the sum of moments must be zero,

$$d_1F_1 - d_2F_2 = 0 \qquad \text{(ii)}$$

Normally the anticlockwise (clockwise) moments are taken to be positive (negative). Note R acts at the fulcrum itself and has zero moment about the fulcrum.

In the case of the lever force F_1 is usually some weight to be lifted. It is called the *load* and its distance from the fulcrum d_1 is called the *load arm*. Force F_2 is the *effort* applied to lift the load; distance d_2 of the effort from the fulcrum is the *effort arm.*

Eq. (ii) can be written as

$$d_1F_1 = d_2\,F_2 \qquad (7.32a)$$

or load arm × load = effort arm × effort

The above equation expresses the principle of moments for a lever. Incidentally the ratio F_1/F_2 is called the Mechanical Advantage (M.A.);

$$M.A = \frac{F_1}{F_2} = \frac{d_2}{d_1} \qquad (7.32b)$$

If the effort arm d_2 is larger than the load arm, the mechanical advantage is greater than one. Mechanical advantage greater than one means that a small effort can be used to lift a large load. There are several examples of a lever around you besides the see-saw. The beam of a balance is a lever. Try to find more such examples and identify the fulcrum, the effort and effort arm, and the load and the load arm of the lever in each case.

You may easily show that the principle of moment holds even when the parallel forces F_1 and F_2 are not perpendicular, but act at some angle, to the lever.

7.8.2 Centre of gravity

Many of you may have the experience of balancing your notebook on the tip of a finger. Figure 7.24 illustrates a similar experiment that you can easily perform. Take an irregular-shaped cardboard and a narrow tipped object like a pencil. You can locate by trial and error a point G on the cardboard where it can be balanced on the tip of the pencil. (The cardboard remains horizontal in this position.) This point of balance is the centre of gravity (CG) of the cardboard. The tip of the pencil provides a vertically upward force due to which the cardboard is in mechanical equilibrium. As shown in the Fig. 7.24, the reaction of the tip is equal and opposite to $M\mathbf{g}$, the total weight of (i.e., the force of gravity on) the cardboard and hence the cardboard is in translational equilibrium. It is also in rotational equilibrium; if it were not so, due to the unbalanced torque it would tilt and fall. There are torques on the card board due to the forces of gravity like $m_1\mathbf{g}$, $m_2\mathbf{g}$…. etc, acting on the individual particles that make up the cardboard.

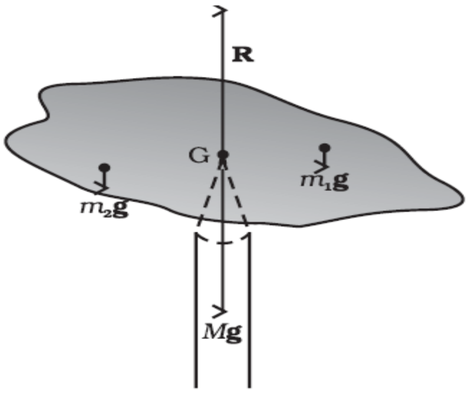


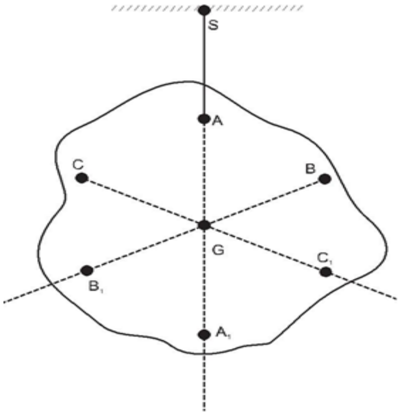
***Fig. 7.24** Balancing a cardboard on the tip of a pencil. The point of support,* G*, is the centre of gravity.*

The CG of the cardboard is so located that the total torque on it due to the forces $m_1\mathbf{g}$, $m_2\mathbf{g}$ ….etc. is zero. If $\mathbf{r}_i$ is the position vector of the i^{th} particle of an extended body with respect to its CG, then the torque about the CG, due to the force of gravity on the particle is $\boldsymbol{\tau}_i = \mathbf{r}_i \times m_i\mathbf{g}$. The total gravitational torque about the CG is zero, i.e

$$\tau_g = \sum \tau_i = \sum r_i \times m_i g = 0 \qquad (7.33)$$

We may therefore, define the CG of a body as that point where the total gravitational torque on the body is zero.

We notice that in Eq. (7.33), **g** is the same for all particles, and hence it comes out of the summation. This gives, since **g** is nonzero,$\sum m_i\mathbf{r}_i = \mathbf{0}$. Remember that the position vectors($\mathbf{r}_i$) are taken with respect to the CG. Now, in accordance with the reasoning given below Eq. (7.4a) in Sec. 7.2, if the sum is zero, the origin must be the centre of mass of the body. Thus, the centre of gravity of the body coincides with the centre of mass. We note that this is true because the body being small, **g** does not vary from one point of the body to the other. If the body is so extended that **g** varies from part to part of the body, then the centre of gravity and centre of mass will not coincide. Basically, the two are different concepts. The centre of mass has nothing to do with gravity. It depends only on the distribution of mass of the body.



7.25 *Determining the centre of gravity of a body of irregular shape. The centre of gravity G lies on the vertical* AA_1 *through the point of suspension of the body A.*

In Sec. 7.2 we found out the position of the centre of mass of several regular, homogeneous objects. Obviously the method used there gives us also the centre of gravity of these bodies, if they are small enough.

Figure 7.25 illustrates another way of determining the CG of an regular shaped body like a cardboard. If you suspend the body from some point like A, the vertical line through A passes through the CG. We mark the vertical AA$_1$. We then suspend the body through other points like B and C. The intersection of the verticals gives the CG. Explain why the method works. Since the body is small enough, the method allows us to determine also its centre of mass.

Example 7.8 A metal bar 70 cm long and 4.00 kg in mass supported on two knife-edges placed 10 cm from each end. A 6.00 kg weight is suspended at 30 cm from one end. Find the reactions at the knife-edges. (Assume the bar to be of uniform cross section and homogeneous.)

Answer

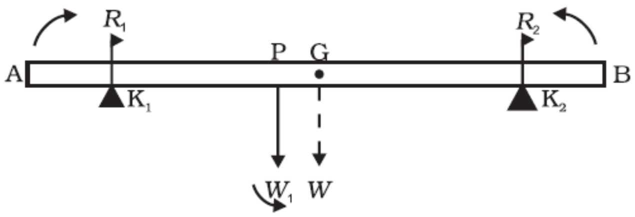


Fig. 7.26

Figure 7.26 shows the rod AB, the positions of the knife edges K$_1$ and K$_2$, the centre of gravity of the rod at G and the suspended weight at P.

Note the weight of the rod W acts at its centre of gravity G. The rod is uniform in cross section and homogeneous; hence G is at the centre of the rod; AB = 70 cm. AG = 35 cm, AP 30 cm, PG = 5 cm, $AK_1 = BK_2 = 10$ cm and K_1G $K_2G = 25$ cm. Also, W= weight of the rod = 4.00 kg and W_1= suspended weight = 6.00 kg; $R_1$and $R_2$are the normal reactions of the support at the knife edges.

For translational equilibrium of the rod,

$$R_1 + R_2 - W_1 - W = 0 \quad \text{(i)}$$

Note W_1 and W act vertically down and $R_1$and R_2 act vertically up.

For considering rotational equilibrium, we take moments of the forces. A convenient point to take moments about is G. The moments of R_2 and W_1 are anticlockwise (+ve), whereas the moment of R_1 is clockwise (-ve).

For rotational equilibrium,

$$-R_1(K_1G) + W_1(PG) + R_2(K_2G) = 0 \quad \text{(ii)}$$

It is given that $W = 4.00g$ N and $W_1 = 6.00g$ N, where g = acceleration due to gravity. We take $g = 9.8\ \text{m/s}^2$.

With numerical values inserted, from (i)

$$R_1 + R_2 - 4.00g - 6.00g = 0$$

$$\text{Or} \quad R_1 + R_2 = 10.00g\ \text{N} \quad \text{(iii)}$$

$$= 98.00\ \text{N}$$

From (ii) $-0.25R_1 + 0.05W_1 + 0.25R_2 = 0$

Or $\quad R_2 - R_1 = 1.2g\ \text{N} = 11.76\ \text{N}$ (iv)

From (iii) and (iv), $R_1 = 54.88$ N

$R_2 = 43.12$ N

Thus the reactions of the support are about 55 N at K_1 and 43 N at K_2.

Example 7.9 A 3m long ladder weighing20 kg leans on a frictionless wall. Its feet rest on the floor 1 m from the wall as shown in Fig.7.27. Find the reaction forces of the wall and the floor.

Answer

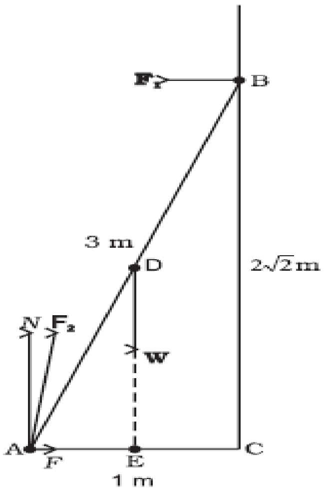


Fig. 7.27

The ladder AB is 3 m long, its foot A is at distance AC = 1 m from the wall. From Pythagoras theorem, BC = $\sqrt[2]{2}$ m. The forces on the ladder are its weight W acting at its centre of gravity D, reaction forces F_1 and F_2 of the wall and the floor respectively. Force F_1 is perpendicular to the wall, since the wall is frictionless. Force F_2 is resolved into two components, the normal reaction N and the force of friction F. Note that F prevents the ladder from sliding away from the wall and is therefore directed toward the wall.

For translational equilibrium, taking the forces in the vertical direction,

$$N - W = 0 \qquad \text{(i)}$$

Taking the forces in the horizontal direction,

$$F - F_1 = 0 \qquad \text{(ii)}$$

For rotational equilibrium, taking the moments of the forces about A,

$$\sqrt[2]{2}\ F_1 - (1/2)\, W = 0 \qquad \text{(iii)}$$

Now $W = 20\ g = 20 \times 9.8\ N = 196.0\ N$

From (i) $N = 196.0$

From (iii) $F_1 = \frac{W}{\sqrt[4]{2}} = \frac{196.0}{\sqrt[4]{2}} = 34.6\ N$

From (ii) $F = F_1 = 34.6\ N$

$$F_2 = \sqrt{F^2 + N^2} = 199.0\ N$$

The force F_2 makes an angle α with the horizontal

$$\text{Tan}\alpha = N/F = \sqrt[4]{2},\ \alpha = \tan^{-1}(\sqrt[4]{2}) \approx 80^{\circ}$$

7.9 MOMENT OF INERTIA

We have already mentioned that we are developing the study of rotational motion parallel to the study of translational motion with which we are familiar. We have yet to answer one major question in this connection. **What is the analogue of mass in rotational motion?**

We shall attempt to answer this question in the present section. To keep the discussion simple, we shall consider rotation about a fixed axis only. Let us try to get an expression for *the* **kinetic energy of a rotating body**. We know that for a body rotating about a fixed axis, each particle of the body moves in a circle with linear velocity given by Eq. (7.19). (Refer to Fig. 7.16). For a particle at a distance from the axis, the linear velocity $v_i = r_i\omega$. The kinetic energy of motion of this particle is

$$k_i = \frac{1}{2}m_i{v_i}^2 = \frac{1}{2}m_i{r_i}^2\omega^2$$

Where m_i is the mass of the particle. The total kinetic energy K of the body is then given by the sum of the kinetic energies of individual particles,

$$K = \sum_{i=1}^{n} k_i = \frac{1}{2}\sum_{i=1}^{n}(m_i\, r_i^2\omega^2)$$

Here n is the number of particles in the body.

(i) Note ω is the same for all particles, Hence, taking ω out of the sum

(ii) $K = \frac{1}{2}\omega^2\sum_{i=1}^{n}(m_i\, r_i^2)$

We define a new parameter characterising.

(iii) The rigid body, called the moment of inertia I, given by

$$I = \sum_{i=1}^{n} m_i\, r_i^2 \qquad (7.34)$$

With this definition

$$K = \frac{1}{2}I\omega^2 \qquad (7.35)$$

Note that the parameter I is independent of the magnitude of the angular velocity. It is a characteristic of the rigid body and the axis about which it rotates.

Compare Eq. (7.35) for the kinetic energy of a rotating body with the expression for the kinetic energy of a body in linear (translational) motion,

$$K = \frac{1}{2}\, mv^2$$

Here m is the mass of the body and v is its velocity. We have already noted the analogy between angular velocity ω (in respect of rotational motion about a fixed axis) and linear velocity v (in respect of linear motion). It is then evident that the parameter, moment of inertia I, is the desired rotational analogue of mass. In rotation (about a fixed axis), the moment of inertia plays a similar role as mass does in linear motion. We now apply the definition Eq. (7.34), to calculate the moment of inertia in two simple cases.

(a) Consider a thin ring of radius R and mass M, rotating in its own plane around its centre with angular velocity ω. Each mass element of the ring is at a distance R from the axis, and moves with a speed $R\omega$. The kinetic energy is therefore,

$$K = \frac{1}{2}Mv^2 = \frac{1}{2}MR^2\omega^2$$

Comparing with Eq. (7.35) we get $I = MR^2$ for the ring

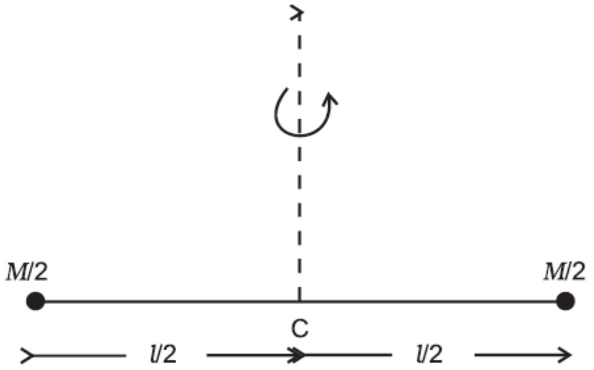


Fig. 7.28 *A light rod of length l with a pair of masses rotating about an axis through the centre of mass of the system and perpendicular to the rod. The total mass of the system is M.*

(b) Next, take a rigid mass less rod of length l with a pair of small masses, rotating about an axis through the centre of mass perpendicular to the rod (Fig. 7.28). Each mass $M/2$ is at a distance $l/2$ from the axis. The moment of inertia of the masses is therefore given by

$$(M/2)\,(l/2)^2 + (M/2)(l/2)^2$$

Thus, for the pair of masses, rotating about the axis through the centre of mass perpendicular to the rod

$$I = Ml^2 / 4$$

Table 7.1 gives the moment of inertia of various familiar regular shaped solids about specific axes. As the mass of a body resists a change in its state of linear motion, it is a measure of its inertia in linear motion. Similarly, as the moment of inertia about a given axis of rotation resists a change in its rotational motion, it can be regarded as a measure of rotational inertia of the body; it is a measure of the way in which different parts of the body are distributed at different distances from the axis. Unlike the mass of a body, the moment of inertia is not a fixed quantity but depends on the orientation and position of the axis of rotation with respect to the body as a whole. As a measure of the way in which the mass of a rotating rigid body is distributed with respect to the axis of rotation, we can define a new parameter, the **radius of gyration**. It is related to the moment of inertia and the total mass of the body.

Notice from the Table 7.1 that in all cases, we can write I = Mk^2, where k has the dimension of length. For a rod, about the perpendicular axis at its midpoint, $k^2=L^2/12$, **i.e.** $k^2 = \frac{L}{\sqrt{12}}$. Similarly, $k=R/2$ for the circular disc about its diameter. The length k is a geometric property of the body and axis of rotation. It is called the **radius of gyration**. **The radius of gyration of a body about an axis** may be defined as the distance from the axis of a mass point whose mass is equal to the mass of the whole body and whose moment of inertia is equal to the moment of inertia of the body about the axis.

Thus, the moment of inertia of a rigid body depends on the mass of the body, its shape and size; distribution of mass about the axis of rotation, and the position and orientation of the axis of rotation.

From the definition, Eq. (7.34), we can infer that the dimensions of moments of inertia we ML^2 and its SI units are kg m^2.

The property of this extremely important quantity I as a measure of rotational inertia of the body has been put to a great practical use. The machines, such as steam engine and the automobile engine, etc., that produce rotational motion have a disc with a large moment of inertia, called a **flywheel**. Because of its large moment of inertia, the flywheel resists the sudden increase or decrease of the speed of the vehicle. It allows a gradual change in the speed and prevents jerky motions, thereby ensuring a smooth ride for the passengers on the vehicle.

7.10 THEOREMS OF PERPENDICULAR AND PARALLEL AXES

These are two useful theorems relating to moment of inertia. We shall first discuss the theorem of perpendicular axes and its simple yet instructive application in working out the moments of inertia of some regular-shaped bodies.

Theorem of perpendicular axes

This theorem is applicable to bodies which are planar. In practice this means the theorem applies to flat bodies whose thickness is very small compared to their other dimensions (e.g. length, breadth or radius).

Fig. 7.29 illustrates the theorem. It states that **the moment of inertia of a planar body (lamina) about an axis perpendicular to its plane is equal to the sum of its moments of inertia about two perpendicular axes concurrent with perpendicular axis and lying in the plane of the body.**

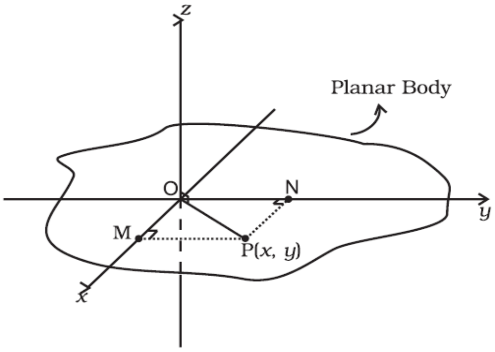
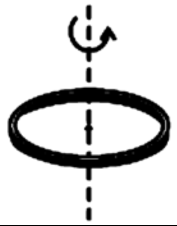
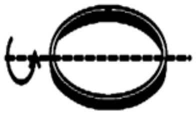
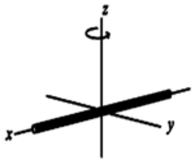
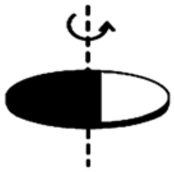
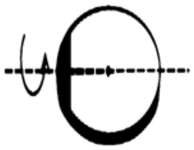
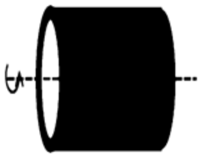
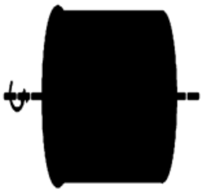
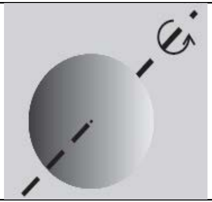


Fig. 7.29 *Theorem of perpendicular axes applicable to a planar body; x and y axes are two perpendicular axes in the plane and the z-axis is perpendicular to the plane.*

Table 7.1Moments of Inertia of some regular shaped bodies about specific axes

Z	Body	Axis	Figure	I
1	Thin circular ring, radius R	Perpendicular to plane, at center		MR^2
2	Thin circular ring, radius R	Diameter		$MR^2/2$
3	Thin rod, length L	Perpendicular to rod, at mid-point		$ML^2/12$
4	Circular disc, Radius R	Perpendicular to disc at center		$MR^2/2$
5	Circular disc, Radius R	Diameter		$MR^2/4$
6	Hollow cylinder, Radius R	Axis of cylinder		MR^2
7	Solid cylinder, Radius R	Axis of cylinder		$MR^2/2$
8	Solid sphere, Radius R	diameter		$2MR^2/5$

The figure shows a planar body. An axis perpendicular to the body through a point O is taken as the z-axis. Two mutually perpendicular axes lying in the plane of the body and concurrent with z-axis, i.e. passing through O, are taken as the x and y-axes. The theorem states that

$$I_z = I_x + I_y \qquad (7.36)$$

Let us look at the usefulness of the theorem through an example.

Example 7.10 What is the moment of inertia of a disc about one of its diameters?

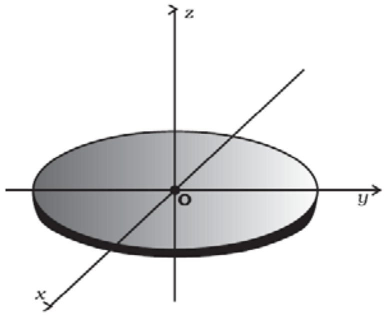


Fig. 7.30 *M.I. of a disc about a diameter, given its M.I. about the perpendicular axis through its centre.*

Answer We assume the moment of inertia of the disc about an axis perpendicular to it and through its centre to be known; it is $MR^2/2$, where M is the mass of the disc and R is its radius (Table 7.1)

The disc can be considered to be a planar body. Hence the theorem of perpendicular axes is applicable to it. As shown in Fig. 7.30, we take three concurrent axes through the centre of the disc, O as the x,y,z axes; x and y-axes lie in the plane of the disc and z is perpendicular to it. By the theorem of perpendicular axes,

$$I_z = I_x + I_y$$

Now, x and y axes are along two diameters of the disc, and by symmetry the moment of inertia of the disc is the same about any diameter. Hence

$$I_x = I_y$$

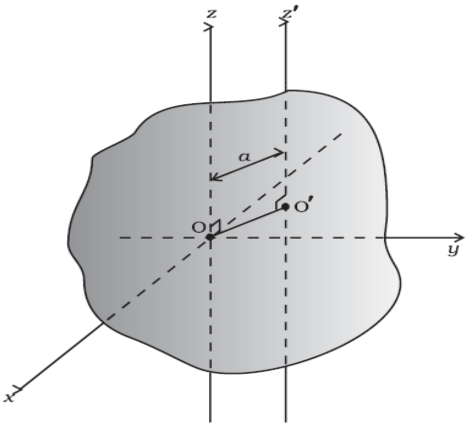
And $I_z = 2 I_x$

But $I_z = MR^2/2$

So finally, $I_x = I_z/2 = MR^2/4$

Thus the moment of inertia of a disc about any of its diameter is $MR^2/4$.

Find similarly the moment of inertia of a ring about any of its diameter. Will the theorem be applicable to a solid cylinder?



7.31The theorem of parallel axes the z and z′ axes are two parallel axes separated by a distance a; O is the centre of mass of the body, ***OO***’ = a.

7.10.1 Theorem of parallel axes

This theorem is applicable to a body of any shape. It allows to find the moment of inertia of a body about any axis, given the moment of inertia of the body about a parallel axis through the centre of mass of the body. We shall only state this theorem and not give its proof. We shall, however, apply it to a few simple situations which will be enough to convince us about the usefulness of the theorem. The theorem may be stated as follows:

The moment of inertia of a body about any axis is equal to the sum of the moment of inertia of the body about a parallel axis passing through its centre of mass and the product of its mass and the square of the distance between the two parallel axes. As shown in the Fig. 7.31, z and z′ are two parallel axes separated by a distance a. The z-axis passes through the centre of mass O of the rigid body. Then according to the theorem of parallel axes

$$I_{z'} = I_z + Ma^2 \quad (7.37)$$

Where I_z and $I_{z'}$ are the moments of inertia of the body about the z and z' axes respectively, M is the total mass of the body and a is the perpendicular distance between the two parallel axes.

Example 7.11 What is the moment of inertia of a rod of mass *M*, length *l* about an axis perpendicular to it through one end?

Answer For the rod of mass *M* and length *l*, $I = Ml^2/12$. Using the parallel axes theorem, $I' = I + Ma^2$ with $a = l/2$ we get,

$$I' = M\frac{l^2}{12} + M\left(\frac{l}{2}\right)^2 + \frac{ml^2}{3}$$

We can check this independently since *I* is half the moment of inertia of a rod of mass 2*M* and length 2*l* about its midpoint,

$$I' = 2M\ \frac{4l^2}{12} \text{x} \frac{1}{2} = \frac{ml^2}{3}$$

Example 7.12 What is the moment of inertia of a ring about a tangent to the circle of the ring?

Answer: The tangent to the ring in the plane of the ring is parallel to one of the diameters of the ring. The distance between these two parallel axes is *R*, the radius of the ring. Using the parallel axes theorem,

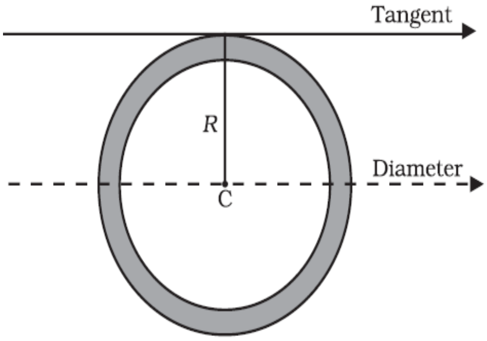


Fig. 7.32

$$I_{tangent} = I_{dia} + MR^2 = \frac{MR^2}{2} + MR^2 = \frac{3}{2}MR^2$$

7.11 KINEMATICS OF ROTATIONAL MOTION ABOUT A FIXED AXIS

We have already indicated the analogy between rotational motion and translational motion. For example, the angular velocity **ω** plays the same role in rotation as the linear velocity **v** in translation. We wish to take this analogy further. In doing so we shall restrict the discussion only to rotation about fixed axis. This case of motion involves only one degree of freedom, i.e., needs only one independent variable to describe the motion. This in translation corresponds to linear motion. This section is limited only to kinematics. We shall turn to dynamics in later sections.

We recall that for specifying the angular displacement of the rotating body we take any particle like P (Fig.7.33) of the body. Its angular displacement θ in the plane it moves is the angular displacement of the whole body; θ is measured from a fixed direction in the plane of motion of P, which we take to be the x' - axis, chosen parallel to the x-axis. Note, as shown, the axis of rotation is the z – axis and the plane of the motion of the particle is the x - y plane. Fig. 7.33 also shows θ_0, the angular displacement at $t = 0$.

We also recall that the angular velocity is the time rate of change of angular displacement, $\boldsymbol{\omega} = \mathrm{d}\boldsymbol{\theta}/\mathrm{d}t$. Note since the axis of rotation is fixed, there is no need to treat angular velocity as a vector. Further, the angular acceleration, $\boldsymbol{\alpha} = \mathrm{d}\boldsymbol{\omega}/\mathrm{d}t$.

The kinematical quantities in rotational motion, angular displacement (**θ**), angular velocity (**ω**) and angular acceleration (α) respectively correspond to kinematic quantities in linear motion, displacement (x), velocity (v) and acceleration (a). We know the kinematical equations of linear motion with uniform (i.e. constant) acceleration:

$$v = v_0 + at \text{(a)}$$

$$x = x_0 + v_0 t + \frac{1}{2}at^2 \text{(b)}$$

$$v^2 = v_0^2 + 2ax \text{(c)}$$

Where x_0 = initial displacement and v_0= initial velocity. The word ‘initial’ refers to values of the quantities at $t = 0$ the corresponding kinematic equations for rotational motion with uniform angular acceleration are:

$$\omega = \omega_0 + \alpha t (7.38)$$

$$\theta = \theta_0 + w_0 t + \frac{1}{2}\alpha t^2 \qquad (7.39)$$

$$\text{And } \omega^2 = \omega_0^2 + 2\alpha(\theta - \theta_0) \qquad (7.40)$$

Whereθ_0= initial angular displacement of the rotating body, and ω = initial angular velocity of the body.

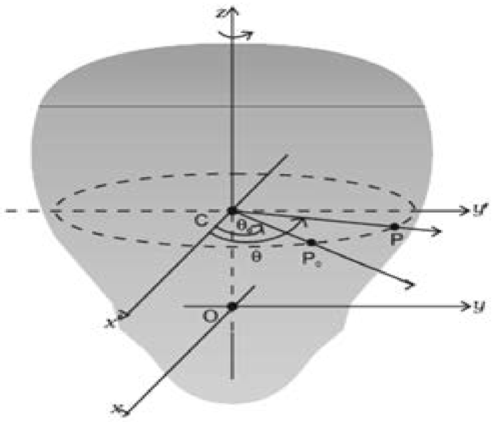


Fig. 7.33*specifying the angular position of a rigid body*

Example 7.13 Obtain Eq.(7.38) from first principles

Answer The angular acceleration is uniform, hence

$$\frac{d\omega}{dt} = \alpha = constant \qquad (i)$$

Integrating this equation,

$$\omega = \int \alpha dt + c$$

$= \alpha t + c$ (as α) is constant

At t=0 thus, $\omega = \omega_0 (given)$

From (i) we get at $t = 0, \omega = c = \omega$

Thus, $\omega = \alpha t + \omega_0$ as required

With the definition of $\omega = \frac{d\theta}{dt}$ we may integrate Eq. (7.38) to get Eq. (7.39). This derivation and the derivation of Eq. (7.40) is left as an exercise.

Example 7.14 motor wheel is increased from 1200 rpm the angular speed of a to 3120 rpm in 16 seconds. (i) What is its angular acceleration, assuming the acceleration to be uniform? (ii) How many revolutions does the engine make during this time?

Answer

(i) We shall use $\omega = \omega_0 + at$

ω_0Initial angular speed in rad/s

$$= 2\pi \text{ xAngular speed in rev/s}$$

$$= \frac{2\pi \; angular \; speed \; in \; rev/min}{60 \; s/min}$$

$$= \frac{2\pi \text{ x } 1200}{60}\text{rad/s}$$

$$= 40\,\pi \text{ rad/s}$$

Similarly ω = final angular speed in rad/s

$$= \frac{2\pi \text{ x } 3120}{60}\text{Rad/s}$$

$$= 104\,\pi \text{ rad/s}$$

Angular acceleration

$$\alpha = \frac{\omega - \omega_0}{t} = 4\pi \text{ rad/s}^2$$

The angular acceleration of the engine = 4 π rad/s^2

(ii) The angular displacement in time *t* is given by

$$\theta = \omega_0 t + \frac{1}{2}at^2$$

$$= \left(40\pi \text{ x } 16 \text{ x} + \frac{1}{2} \text{x } 4\pi \text{ x} 16^2\right) rad$$

$$= (640\,\pi + 512\,\pi) \text{ rad}$$

$$= 1152\,\pi \text{ rad}$$

Number of revolutions = $\frac{1152\,\pi}{2\pi}$ = 576

7.12 DYNAMICS OF ROTATIONAL MOTION ABOUT A FIXED AXIS

Table 7.2 lists quantities associated with linear motion and their analogues in rotational motion. We have already compared kinematics of the two motions. Also, we know that in rotational motion moment of inertia and torque play the same role as mass and force respectively in linear motion. Given this we should be able to guess what the other analogues indicated in the table are. For example, we know that in linear motion, work done is given by F dx, in rotational motion about a fixed axis it should be $\tau\ d\theta$, since we already know the correspondence $d\ x \rightarrow d\theta$ and $F \rightarrow \tau$. It is, however, necessary that these correspondences are established on sound dynamical considerations. This is what we now turn to. Before we begin, we note *a* simplification that arises in the case of rotational motion about a fixed axis. Since the axis is fixed, only those components of torques, which are along the direction of the fixed axis need to be considered in our discussion. Only these components can cause the body to rotate about the axis. A component of the torque perpendicular to the axis of rotation will tend to turn the axis from its position. We specifically assume that there will arise necessary forces of constraint to cancel the effect of the perpendicular components of the (external) torques, so that the fixed position of the axis will be maintained. The perpendicular components of the torques therefore need not be taken into account. This means that for our calculation of torques on a rigid body:

(1) We need to consider only those forces that lie in planes perpendicular to the axis. Forces which are parallel to the axis will give torques perpendicular to the axis and need not be taken into account.

(2) We need to consider only those components of the position vectors which are perpendicular to the axis. Components of position vectors along the axis will result in torques perpendicular to the axis and need not be taken into account.

Work done by a torque

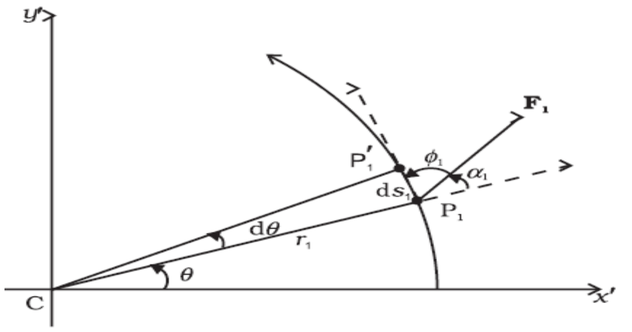


Fig. 7.34 *Work done by a force* $\mathbf{F}_1$ *acting on a particle of a body rotating about a fixed axis; the particle describes a circular path with centre C on the axis; arc* $P_1P'_1(ds_1)$ *gives the displacement of the particle.*

Figure 7.34 shows a cross-section of a rigid body rotating about a fixed axis, which is taken as the z-axis (perpendicular to the plane of the page; see Fig. 7.33). As said above we need to consider only those forces which lie in planes perpendicular to the axis. Let F_1 be one such typical force acting as shown on a particle of the body at point P_1 with its line of action in a plane perpendicular to the axis. For convenience we call this to be the x′ –y′ plane (coincident with the plane of the page). The particle at P_1 describes a circular path of radius r_1 with centre C on the axis; $CP_1 = r_1$.

In time t, the point moves to the position P_1' . The displacement of the particle ds_1, therefore, has magnitude $ds_1 = r_1 d\theta$ and direction tangential at P_1 to the circular path as shown. Here dθ is the angular displacement of the particle, $d\theta = P_1CP_1'$ .The work done by the force on the particle is

$$dW_1 = \mathbf{F}_1 .\ ds_1 = F_1 ds_1 \cos\varphi_1 = F_1 (r_1\, d\theta) \sin\alpha_1$$

Where φ_1 is the angle between $\mathbf{F_1}$ and the tangent

Table 7.2 Comparison of Translational and Rotational Motion

Linear Motion	**Rotational motion about a Fixed Axis**
Displacement x	Angular displacement θ
Velocity $v = dx/dt$	Angular velocity $\omega = d\theta/dt$
Acceleration $a = dv/dt$	Angular acceleration $\alpha = d\omega/dt$
Mass M	Moment of inertia I
Force $F = Ma$	Torque $\tau = I\alpha$
Work $dW = F\, ds$	Work $W = \tau d\theta$
Kinetic energy $K = Mv^2/2$	Kinetic energy $K = I\omega^2/2$
Power $P = F\, v$	Power $P = \tau\omega$
Linear momentum $p = Mv$	Angular momentum $L = I\omega$

At P_1 and α_1 is the angle between F1 and the radius vector $\mathbf{OP}_1$; $\varphi_1 + \alpha_1 = 90^0$.

The torque due to $\mathbf{F}_1$ about the origin is $\mathbf{OP}_1 \times \mathbf{F}_1$. Now $\mathbf{OP}_1 = \mathbf{OC} + \mathbf{OP}_1$. [Refer to Fig. 7.17(b).] Since **OC** is along the axis, the torque resulting from it is excluded from our consideration. The effective torque due to $\mathbf{F}_1$ is $\boldsymbol{\tau}_1 = \mathbf{CP} \times \mathbf{F}_1$; it is directed along the axis of rotation and has a magnitude $\tau_1 = r_1 F_1 \sin\alpha$, Therefore,

$$dW_1 = \tau_1\, d\theta$$

If there are more than one forces acting on the body, the work done by all of them can be added to give the total work done on the body. Denoting the magnitudes of the torques due to the different forces as $\tau_1,\tau_2, \ldots$ etc,

$$d\,W = (\tau_1 + \tau_2 + ...)\, d\theta$$

Remember, the forces giving rise to the torques act on different particles, but the angular displacement $d\theta$ is the same for all particles. Since all the torques considered are parallel to the fixed axis, the magnitude τ of the total torque is just the algebraic sum of the magnitudes of the torques, i.e., $\tau = \tau_1 + \tau_2 + ...$

We have

$$dW = \tau\, d\theta \qquad (7.41)$$

This expression gives the work done by the total (external) torque τ which acts on the body rotating about a fixed axis. Its similarity with the corresponding expression

$$dW = F\, ds$$

For linear (translational) motion is obvious.

Dividing both sides of Eq. (7.41) by dt gives

$$P = \frac{dW}{dt} = r\frac{d\theta}{dt} = \tau\omega \text{ Or}$$

$$P = \tau\omega \qquad (7.42)$$

This is the instantaneous power. Compare this expression for power in the case of rotational motion about a fixed axis with the expression for power in the case of linear motion,

$$P = Fv$$

In a perfectly rigid body there is no internal motion. The work done by external torques is therefore, not dissipated and goes on to increase the kinetic energy of the body. The rate at which work is done on the body is given by Eq. (7.42). This is to be equated to the rate at which kinetic energy increases. The rate of increase of kinetic energy is

$$\frac{d}{dt}\left(\frac{I\,\omega^2}{2}\right) = I\frac{2\omega}{2}\frac{d\omega}{dt}$$

We assume that the moment of inertia does not change with time. This means that the mass of the body does not change, the body remains rigid and also the axis does not change its position with respect to the body.

Since $\alpha = \frac{d\omega}{dt}$, we get

$$\frac{d}{dt}\left(\frac{I\,\omega^2}{2}\right) = I\omega\alpha$$

Equating rates of work done and of increase in kinetic energy,

$$\tau\omega = I\,\omega\,\alpha$$

$$\tau = I\,\alpha \qquad (7.43)$$

Eq. (7.43) is similar to Newton's second law for linear motion expressed symbolically a

$$F = ma$$

Just as force produces acceleration, torque produces angular acceleration in a body. The angular acceleration is directly proportional to the applied torque and is inversely proportional to the moment of inertia of the body. Eq.(7.43) can be called Newton's second law for rotation about a fixed axis.

Example 7.15 A cord of negligible mass is wound round the rim of a fly wheel of mass 20 kg and radius 20 cm. A steady pull of 25 N is applied on the cord as shown in Fig. 7.35. The flywheel is mounted on a horizontal axle with frictionless bearings.

(a) Compute the angular acceleration of the wheel.

(b) Find the work done by the pull, when 2m of the cord is unwound.

(c) Find also the kinetic energy of the wheel at this point. Assume that the wheel starts from rest.

(d) Compare answers to parts (b) and (c).

Answer

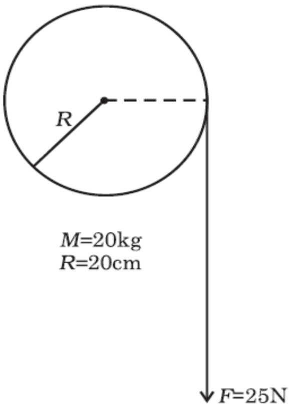


Fig. 7.35

(a) We use $I\,\alpha = \tau$

The torque $\tau = F\,R$

= 25 x 0.20 Nm (as R = 0.20m)

=5.0 Nm

I = M. I. of flywheel about its axis = $MR^2/2$

$$= \frac{20.0 \text{ X}(0.2)^2}{2} = 0.4\ kg\ m^2$$

α = *angu*lar acceleration

= 5.0 N m/0.4 kg m^2 = 12.35 s^{-2}.

(b) Work done by the pull unwinding 2m of the cord

= 25N X 2 = 50 J

(c) Let ω be the final angular velocity

Kinetic energy gained = $\frac{1}{2}\ I\omega^2$

Since the wheel starts from rest. Now

$$\omega^2 = {\omega_0}^2 + 2a\theta, \qquad \omega_0 = 0$$

The angular displacement θ = length of unwound string/ radius of wheel

= 2 m/0.2 m = 10 rad

$$\omega^2 = 2 \text{ X } 12.5 \text{ X } 10.0 = 250\ (rad/s)^2$$

K.E gained = ½ X 0.4 X 250 = 50J

(d) The answers are the same, i.e. the kinetic energy gained by the wheel = work done by the force. There is no loss of energy due to friction.

7.13 ANGULAR MOMENTUM IN CASE OF ROTATION ABOUT A FIXED AXIS

We have studied in section 7.7, the angular momentum of a system of particles. We already know from there that the time rate of total angular momentum of a system of particles about a point is equal to the total external torque on the system taken about the same point. When the total external torque is zero, the total angular momentum of the system is conserved.

We now wish to study the angular momentum in the special case of rotation about a fixed axis. The general expression for the total angular momentum of the system is

$$L = \sum_{i=1}^{N} r_i\, \text{x} p_i \qquad (7.25b)$$

We first consider the angular momentum of a typical particle of the rotating rigid body. We then sum up the contributions of individual particles to get **L** of the whole body.

For a typical particle **l** = **r** × **p**. As seen in the last section **r** = **OP** = **OC** + **CP** [Fig. 7.17(b)].

With **p** = m **v**,

$$\mathbf{l} = (\mathbf{OC} \text{ x} m \, \mathbf{v}) + (\mathbf{CP} \text{ x} m \, \mathbf{v})$$

The magnitude of the linear velocity **v** of the particle at P is given by $v = \omega r$ where r is the length of CP or the perpendicular distance of P from the axis of rotation. Further, **v** is tangential at P to the circle which the particle describes. Using the right-hand rule one can check that **CP** × **v** is parallel to the fixed axis. The unit vector along fixed axis (chosen as the *z*-axis) is $\mathbf{k}^{\mu}$. Hence

$$\mathbf{CP} \text{ x } m\boldsymbol{v} = r\,(mv)\mathbf{k}^{\mu}$$

$$= mr^2\omega \, \mathbf{k}^{\mu} \quad (\text{since } v = \omega \, r_{\perp})$$

Similarly, we can check that **OC** × **v** is perpendicular to the fixed axis. Let us denote the part of **l** along the fixed axis (i.e. the *z*-axis) by $\mathbf{l}_z$, then

$$\mathbf{l}_z = \mathbf{CP} \text{ x } m\boldsymbol{v} = mr^2\omega_{\perp}\mathbf{k}^{\mu}$$

$$\text{and} \quad \mathbf{l} = \mathbf{l}_z + \mathbf{OC} \text{x} m\mathbf{v}$$

We note that $\mathbf{l}_z$ is parallel to the fixed axis, but **l** is not. In general, for a particle, the angular momentum **l** is not along the axis of rotation, i.e. for a particle, **l** and **ω** are not necessarily parallel. Compare this with the corresponding fact in translation. For a particle, **p** and **v** are always parallel to each other.

For computing the total angular momentum of the whole rigid body, we add up the contribution of each particle of the body.

$$\text{Thus} \quad \mathbf{L} = \sum \boldsymbol{l}_i = \sum \boldsymbol{l}_{iz} + \sum \mathbf{OC}_i \ \mathbf{x} \ m_i \, \mathbf{v}_i$$

We denote by **L** and $\mathbf{L}_z$ the components of L respectively perpendicular to the *z*-axis and along the *z*-axis;

$$L_z = \sum \mathrm{L_{iz}} = \left(\sum_i m_i r_i^2\right) \omega k^{\mu}$$

Or

$$L_z = \mathrm{I} \, \omega k^{\mu} \qquad (7.44b)$$

The last step follows since the perpendicular distance of the i^{th} particle from the axis is r_i; and by definition the moment of inertia of the body about the axis of rotation is $I=\sum m_i r_i^2$.

Note $$L = L_z + L\perp \tag{7.44c}$$

The rigid bodies which we have mainly considered in this chapter are symmetric about the axis of rotation, i.e. the axis of rotation is one of their symmetry axes. For such bodies, for a given $\mathbf{OC}_i$, for every particle which has a velocity $\mathbf{v}_i$, there is another particle of velocity $-\mathbf{v}_i$ located diametrically opposite on the circle with centre C_i described by the particle. Together such pairs will contribute zero to **L**⊥ and as a result for symmetric bodies **L**⊥ is zero, and hence bodies, which are not symmetric about the axis of rotation, **L** is not equal to $\mathbf{L}_z$ and hence **L** does not lie along the axis of rotation.

Referring to table 7.1, can you tell in which cases $\mathbf{L} = \mathbf{L}_z$ will not apply?

Let us differentiate Eq. (7.44b). Since $\boldsymbol{k^\mu}$is a fixed (constant) vector, we get

$$\frac{d}{dt}L_z = \left(\frac{d}{dt}\ I\omega\right)k^\mu$$

Now, Eq. (7.28b) states

$$\frac{d\boldsymbol{L}}{dt} = \boldsymbol{\tau}$$

As we have seen in the last section, only those components of the external torques which are along the axis of rotation need to be taken into account, when we discuss rotation about a τ=τk^μ fixed axis. This means we can take k, Since L=Lz+L⊥ and the direction of Lz (vector$\boldsymbol{k^\mu}$) is fixed, it follows that for rotation about afixed axis,

$$\frac{d\boldsymbol{L_z}}{dt} = \tau\boldsymbol{k^\mu} \tag{7.45a}$$

And $$\frac{d\boldsymbol{L}}{dt} = 0 \tag{7.45b}$$

Thus, for rotation about a fixed axis, the component of angular momentum perpendicular to the fixed axis is constant.

As $\boldsymbol{L_z} = I\ \omega\boldsymbol{k^\mu}$, we get from Eq. (7.45a),

$$\frac{d}{dt}\ I\boldsymbol{\omega} = \ \boldsymbol{\tau} \tag{7.45c}$$

If the moment of inertia *I* does not change with time,

$$\frac{d}{dt} I\omega = I \frac{d}{dt} \omega = I\alpha$$

And we get from Eq. (7.45 c),

$$\boldsymbol{\tau} = I\alpha \qquad (7.43)$$

We have already derived this equation using the work - kinetic energy route.

7.13.1 Conservation of angular momentum

We are now in a position to revisit the principle of conservation of angular momentum in the context of rotation about a fixed axis. From Eq. (7.45c), if the external torque is zero,

$L_z = I\omega =$ constant (7.46) For symmetric bodies, from Eq. (7.44d), L_z may be replaced by L .(L and L_z are respectively the magnitudes of **L** and $\mathbf{L}_z$.)

This then is the required form, for fixed axis rotation, of Eq. (7.29a), which expresses the general law of conservation of angular momentum of a system of particles. Eq. (7.46) applies to many situations that we come across in daily life. You may do this experiment with your friend. Sit on a swivel chair with your arms folded and feet not resting on, i.e., away from, the ground. Ask your friend to rotate the chair rapidly.

Fig 7.36 (a) *A demonstration of conservation of angular momentum. A girl sits on a swivel chair and stretches her arms/brings her arms closer to the body.*

While the chair is rotating with considerable angular speed stretch your arms horizontally. What happens? Your angular speed is reduced. If you bring back your arms closer to your body, the angular speed increases again. This is a situation where the principle of conservation of angular momentum is applicable. If friction in the rotational mechanism is neglected, there is no external torque about the axis of rotation of the chair and hence $I\omega$ is constant. Stretching the arms increases I about the axis of rotation, resulting in decreasing the angular speed ω. Bringing the arms closer to the body has the opposite effect.

A circus acrobat and a diver take advantage of this principle. Also, skaters and classical, Indian or western, dancers performing a pirouette on the toes of one foot display 'mastery' over this principle. Can you explain?

7.14 ROLLING MOTION

One of the most common motions observed in daily life is the rolling motion. All wheels used in transportation have rolling motion. For specificness we shall begin with the case of a disc, but the result will apply to any rolling body rolling on a level surface. We shall assume that the disc rolls without slipping. This means that at any instant of time the bottom of the disc which is in contact with the surface is at rest on the surface.

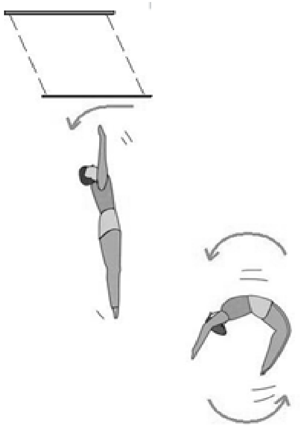


Fig 7.36 (b) *an acrobat employing the principle of conservation of angular*

We have remarked earlier that rolling motion is a combination of rotation and translation. We know that the translational motion of a system of particles is the motion of its centre of mass.

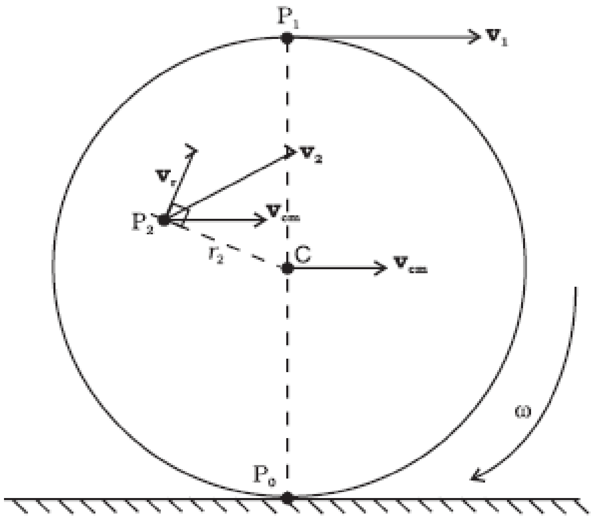


Fig. 7.37 *The rolling motion (without slipping) of a disc on a level surface. Note at any instant, the point of contact P_0 of the disc with the surface is at rest; the centre of mass of the disc moves with velocity, v_{cm}. The disc rotates with angular velocity about its axis which passes through C; $v_{cm} = R\omega$, where R is the radius of the disc.*

Let $\mathbf{v}_{cm}$ be the velocity of the centre of mass and therefore the translational velocity of the disc. Since the centre of mass of the rolling disc is at its geometric centre C (Fig. 7.37), $\mathbf{v}_{cm}$ is the velocity of C. It is parallel to the level surface. The rotational motion of the disc is about its symmetry axis, which passes through C. Thus, the velocity of any point of the disc, like P_0, P_1 or P_2, consists of two parts, one is the translational velocity $\mathbf{v}_{cm}$ and the other is the linear velocity $\mathbf{v}_r$ on account of rotation. The magnitude of $\mathbf{v}_r$ is $v_r = r\omega$, where ω is the angular velocity of the rotation of the disc about the axis and *r* is the distance of the point from the axis (i.e. from C). The velocity $\mathbf{v}_r$ is directed perpendicular to the radius vector of the given point with respect to C. In Fig. 7.37, the velocity of the point P_2 ($\mathbf{v}_2$) and its components $\mathbf{v}_r$ and $\mathbf{v}_{cm}$ are shown; $\mathbf{v}_r$ here is perpendicular to CP_2.It is easy to show that $\mathbf{v}_z$ is perpendicular to the line P_OP_2. Therefore the line passing through P_O and parallel to ω is called the instantaneous axis of rotation.

For At P_o, the linear velocity, $\mathbf{v}_r$, due to rotation is directed exactly opposite to the translational velocity $\mathbf{v}_{cm}$. Further the magnitude of $\mathbf{v}_r$ here is $R\omega$, where *R* is the radius of the disc. The condition that P_o is instantaneously at rest requires $v_{cm} = R\omega$. Thus for the disc the condition for rolling without slipping is (7.47) Incidentally, this means that the velocity of point P_1 at the top of the disc ($\mathbf{v}_1$) has a magnitude $v_{cm} + R\omega$ or 2 v_{cm} and is directed parallel to the level surface. The condition (7.47) applies to all rolling bodies.

7.14.1 Kinetic Energy of Rolling Motion

Our next task will be to obtain an expression for the kinetic energy of a rolling body. The kinetic energy of a rolling body can be separated into kinetic energy of translation and kinetic energy of rotation. This is a special case of a general result for a system of particles, according to which the kinetic energy of a system of particles (K) can be separated into the kinetic energy of motion of the centre of mass (translation) ($MV^2/2$) and kinetic energy of rotational motion about the centre of mass of the system of particles (K'). Thus,

$$K = K' + MV^2/2 \qquad (7.48)$$

We assume this general result (see Exercise 7.31), and apply it to the case of rolling motion. In our notation, the kinetic energy of the centre of mass, i.e., the kinetic energy of translation, of the rolling body is $mv^2_{cm}/2$, where m is the mass of the body and v_{cm} is the centre of the mass velocity. Since the motion of the rolling body about the centre of mass is rotation, K' represents the kinetic energy of rotation of the body; $K'=I\omega^2/2$, where I is the moment of inertia about the appropriate axis, which is the symmetry axis of the rolling body. The kinetic energy ofa rolling body, therefore, is given by

$$K = \frac{1}{2}I\omega^2 + \frac{1}{2}mv_{cm}^2 \qquad (7.49a)$$

Substituting $I = mk^2$ where k = the corresponding radius of gyration of the body and $v_{cm} = R\omega$, we get

$$K = \frac{1}{2}\frac{mk^2v_{cm}^2}{R^2} + \frac{1}{2}\,mv_{cm}^2$$

Or

$$K = \frac{1}{2}\,m\,v_{cm}^2\,\left(1 + \frac{k^2}{R^2}\right) \qquad (7.49b)$$

Equation (7.49b) applies to any rolling body: a disc, a cylinder, a ring or a sphere.

Example 7.16 Three bodies, a ring, a solid cylinder and a solid sphere roll down the same inclined plane without slipping. They start from rest. The radii of the bodies are identical. Which of the bodies reaches the ground with maximum velocity?

Answer We assume conservation of energy of the rolling body, i.e. there is no loss of energy due to friction etc. The potential energy lost by the body in rolling down the inclined plane (= *mgh*) must, therefore, be equal to kinetic energy gained. (See Fig.7.38) Since the bodies start from rest the kinetic energy gained is equal to the final kinetic energy of the bodies.

From Eq. (7.49b) $K = \frac{1}{2}\, m\, v^2 \left(1 + \frac{k^2}{R^2}\right)$,

Where v is the final velocity of (the centre of mass of) the body. Equating *K* and *mgh*,

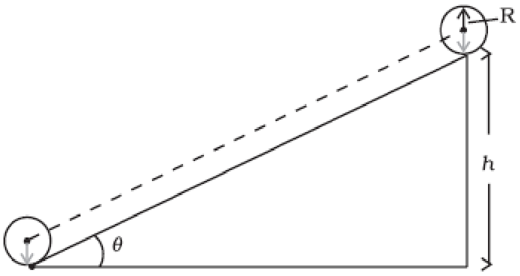


Fig.7.38

$$mgh = \frac{1}{2}\, m\, v^2 \left(1 + \frac{k^2}{R^2}\right)$$

Or $$v^2 = \frac{2gh}{\left(1+\frac{k^2}{R^2}\right)}$$

Note is independent of the mass of the rolling body; for a ring, $k^2 = R^2$

$$v_{ring} = \sqrt{\frac{2gh}{1+1}}$$

$$= \sqrt{gh}$$

For a solid cylinder $k^2 = R^2/2$

$$v_{disc} = \sqrt{\frac{2gh}{1+ 1/2}} = \sqrt{\frac{4gh}{3}}$$

For a solid sphere $k^2 = 2R^2/5$

$$v_{sphere} = \sqrt{\frac{2gh}{1+2/5}}$$

$$= \sqrt{\frac{10gh}{7}}$$

From the results obtained it is clear that among the three bodies the sphere has the greatest and the ring has the least velocity of the centre of mass at the bottom of the inclined plane. Suppose the bodies have the same mass. Which body has the greatest rotational kinetic energy while reaching the bottom of the inclined plane?

SUMMARY

1. Ideally, a rigid body is one for which the distances between different particles of the body do not change, even though there are forces on them.
2. A rigid body fixed at one point or along a line can have only rotational motion. A rigid body not fixed in some way can have either pure translation or a combination of translation and rotation.
3. In rotation about a fixed axis, every particle of the rigid body moves in a circle which lies in a plane perpendicular to the axis and has its centre on the axis. Every Point in the rotating rigid body has the same angular velocity at any instant of time.
4. In pure translation, every particle of the body moves with the same velocity at any instant of time.
5. Angular velocity is a vector. Its magnitude is ω = dθ/dt and it is directed along the axis of rotation. For rotation about a fixed axis, this vector ω has a fixed direction.
6. The vector or cross product of two vector a and b is a vector written as $a \times b$. The magnitude of this vector is $ab \sin\theta$ and its direction is given by the right handed screw or the right hand rule.
7. The linear velocity of a particle of a rigid body rotating about a fixed axis is given by $v = \omega \times r$. Where r is the position vector of the particle with respect to an origin along the fixed axis. The relation applies even to more general rotation of a rigid body with one point fixed. In that case **r** is the position vector of the particle with respect to the fixed point taken as the origin.
8. The centre of mass of a system of particles is defined as the point whose position vector is

$$R = \frac{\sum m_i r_i}{M}$$

9. Velocity of the centre of mass of a system of particles is given by $V = P/M$. Where **P** is the linear momentum of the system. The centre of mass moves as if all the mass of the system is concentrated at this point and all the external force act at it. If the total external force on the system is zero. Then the total linear momentum of the system is constant.
10. The angular momentum of a system of n particles about the origin is

$$L = \sum_{i=1}^{n} r_i \times p_i$$

The torque or moment of force on a system of n particles about the origin is

$$\tau = \sum_{1} r_f \times F_f$$

The force F_f acting on the ith particle includes the external as well as internal forces. Assuming Newton's third law and that forces between any two particles act along the line joining the particles. We can show $\tau_{int} = 0$ and

$$\frac{dL}{dt} = \tau_{ext}$$

11. A rigid body is in mechanical equilibrium if

- It is in translational equilibrium. i.e., the total external force on it is zero: $\sum F_f = 0$. and
- It is in rotational equilibrium. i.e. the total external torque on it is zero: $\sum \tau_i = \sum r_f \times F_f = 0$.

12. The centre of gravity of an extended body is that point where the total gravitational torque on the body is zero.
13. The moment of inertia of a rigid body about an axis is defined by the formula $I = \sum m_f r_f^2$ where r_i is the perpendicular distance of the ith point of the body from the axis. The kinetic energy of rotation is $K = \frac{1}{2} I\omega^2$.
14. The theorem of parallel axes: $\grave{I}_Z = I_Z - Ma^2$. Allows us to determine the moment of inertia of a rigid body about an axis as the sum of the moment of inertia of the body about a parallel axis through its centre of mass and the product of mass and square of the perpendicular distance between these two axes.
15. Rotation about a fixed axis is directly analogous to linear motion in respect of kinematics and dynamics.
16. The angular acceleration of a rigid body rotating about a fixed axis is given by $I\alpha = \tau$. If the external torque τ is zero, the component of angular momentum about the fixed axis $I\omega$ of such a rotating body is constant.
17. For rolling motion without slipping $v_{cm} = R\omega$, where v_{cm} is the velocity of translation (i.e. of the centre of mass), *R* is the radius and *m* is the mass of the body. The kinetic energy of such a

    Rolling body is a sum of kinetic energy of translation and rotation:

$$K = \frac{1}{2}\, m v_{cm}^2 + \frac{1}{2} I \omega^2$$

Quantity	**symbols**	**Dimensions**	**Units**	**Remarks**
Angular velocity	ω	$[T^{-1}]$	Rad s^{-1}	v = ω x r
Angular momentum	L	$[ML^2T^{-1}]$	J s	L = r x p
Torque	τ	$[ML^2T^{-2}]$	N m	τ = r x F
Moment of inertia	I	$[ML^2]$	Kg m^2	$I = \sum m_i \, {r_i}^2$

CHAPTER EIGHT

OSCILLATIONS

8.1 INTRODUCTION

In our daily life we come across various kinds of motions. You have already learnt about some of them, e.g. rectilinear motion and motion of a projectile. Both these motions are non-repetitive. We have also learnt about uniform circular motion and orbital motion of planets in the solar system. In these cases, the motion is repeated after a certain interval of time, that is, it is periodic. In your childhood you must have enjoyed rocking in a cradle or swinging on a swing. Both these motions are repetitive in nature but different from the periodic motion of a planet. Here, the object moves to and fro about a mean position. The pendulum of a wall clock executes a similar motion. There are leaves and branches of a tree oscillating in breeze, boats bobbing at anchor and the surging pistons in the engines of cars. All these objects execute a periodic to and fro motion. Such a motion is termed as oscillatory motion. In this chapter we study this motion.

The study of oscillatory motion is basic to physics; its concepts are required for the understanding of many physical phenomena. In musical instruments like the sitar, the guitar or the violin, we come across vibrating strings that produce pleasing sounds. The membranes in drums and diaphragms in telephone and speaker systems vibrate to and fro about their mean positions. The vibrations of air molecules make the propagation of sound possible. Similarly, the atoms in a solid oscillate about their mean positions and convey the sensation of temperature. The oscillations of electrons in the antennas of radio, TV and satellite transmitters convey information.

The description of a periodic motion in general, and oscillatory motion in particular, requires some fundamental concepts like period, frequency, displacement, amplitude and phase. These concepts are developed in the next section.8.2

8.2 PERIODIC AND OSCILLATORY MOTIONS

Fig 8.1 shows some periodic motions. Suppose an insect climbs up a ramp and falls down it comes back to the initial point and repeats the process identically. If you draw a graph of its height above the ground versus time, it would look something like Fig. 8.1 (a). If a child climbs up a step, comes down, and repeats the process, its height above the ground would look like that in Fig 8.1 (b).

When you play the game of bouncing a ball off the ground, between your palm and the ground, its height versus time graph would look like the one in Fig 8.1 (c). Note that both the curved parts in Fig 8.1 (c) are sections of a parabola given by the Newton's equation of motion (see section 3.6),

$$h = ut + \frac{1}{2}\,gt^2 \text{ for downward motion and}$$

$$h = ut - \frac{1}{2}gt^2 \text{ for upward motion}$$

with different values of u in each case. These are examples of periodic motion. Thus, a motion that repeats itself at regular intervals of time is called periodic motion.

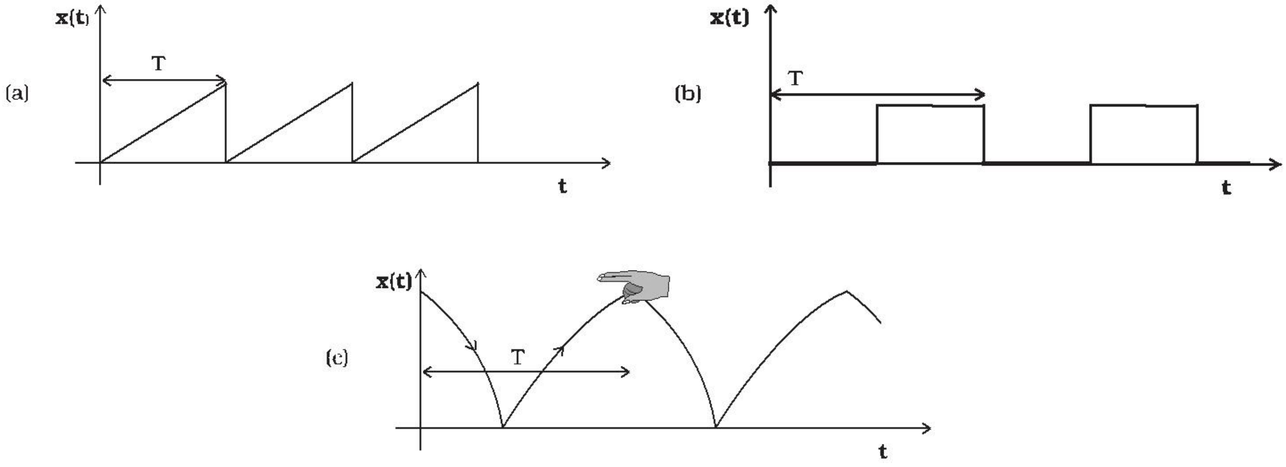


Fig 8.1 *Examples of periodic motion. The period T is shown in each case.*

Very often the body undergoing periodic motion has an equilibrium position somewhere inside its path. When the body is at this position no net external force acts on it. Therefore, if it is left there at rest, it remains there forever. If the body is given a small displacement from the position, a force comes into play which tries to bring the body back to the equilibrium point, giving rise to oscillations or vibrations. For example, a ball placed in a bowl will be in equilibrium at the bottom. If displaced a little from the point, it will perform oscillations in the bowl. Every oscillatory motion is periodic, but every periodic motion need not be oscillatory. Circular motion is a periodic motion, but it is not oscillatory.

There is no significant difference between oscillations and vibrations. It seems that when the frequency is small, we call it oscillation (like the oscillation of a branch of a tree), while when the frequency is high, we call it vibration (like the vibration of a string of a musical instrument).

Simple harmonic motion is the simplest form of oscillatory motion. This motion arises when the force on the oscillating body is directly proportional to its displacement from the mean position, which is also the equilibrium position. Further, at any point in its oscillation, this force is directed towards the mean position.

In practice, oscillating bodies eventually come to rest at their equilibrium positions, because of the damping due to friction and other dissipative causes. However, they can be forced to remain oscillating by means of some external periodic agency. We discuss the phenomena of damped and forced oscillations later in the chapter.

Any material medium can be pictured as a collection of a large number of coupled oscillators. The collective oscillations of the constituents of a medium manifest themselves as waves. Examples of waves include water waves, seismic waves, electromagnetic waves. We shall study the wave phenomenon in the next chapter.

8.2.1 Period and frequency

We have seen that any motion that repeats itself at regular intervals of time is called periodic motion. The smallest interval of time after which the motion is repeated is called its period. Let us denote the period by the symbol T. Its SI unit is second. For periodic motions, which are either too fast or too slow on the scale of seconds, other convenient units of time are used. The period of vibrations of a quartz crystal is expressed in units of microseconds (10–6 s) abbreviated as μs. On the other hand, the orbital period of the planet Mercury is 88 earth days. The Halley's comet appears after every 76 years. The reciprocal of T gives the number of repetitions that occur per unit time. This quantity is called the frequency of the periodic motion. It is represented by the symbol ν. The relation between v and T is

$$\upsilon = 1/T \tag{8.1}$$

The unit of ν is thus s^{-1}. After the discoverer of radio waves, Heinrich Rudolph Hertz (1857-1894), a special name has been given to the unit of frequency. It is called hertz (abbreviated as Hz).

$$\text{Thus, 1 hertz} = 1\text{ Hz} = 1\text{ oscillation per second} = 1s^{-1} \tag{8.2}$$

Note, that the frequency, ν, is not necessarily an integer.

Example 8.1 On an average a human heart is found to beat 75 times in a minute. Calculate its frequency and period.

Answer The beat frequency of heart = 75/ (1 min)

= 75/(60 s)

= 1.25 s–1= 1.25 Hz

The time period T= 1/(1.25 s–1) = 0.8 s

8.2.2 Displacement

In section 4.2, we defined displacement of a particle as the change in its position vector. In this chapter, we use the term displacement in a more general sense. It refers to change with time of any physical property under consideration. For example, in case of rectilinear motion of a steel ball on a surface, the distance from the starting point as a function of time is its position displacement. The choice of origin is a matter of convenience. Consider a block attached to a spring, the other end of which is fixed to a rigid wall [see Fig. 8.2(a)].

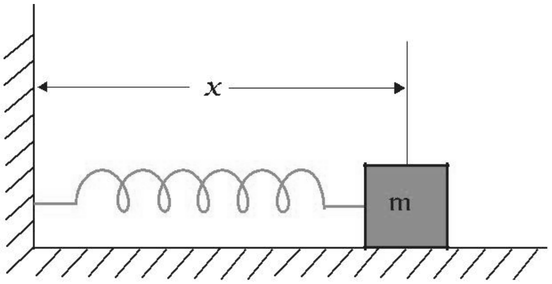


Fig. 8.2(a) A block attached to a spring, the other end of which is fixed to a rigid wall. The block moves on a frictionless surface. The motion of the block can be described in terms of its distance or displacement x from the wall**.**

Generally it is convenient to measure displacement of the body from its equilibrium position. For an oscillating simple pendulum, the angle from the vertical as a function of time may be regarded as a displacement variable [see Fig.8.2(b)]. The term displacement is not always to be referred in the context of position only. There can be many other kinds of displacement variables. The voltage across a capacitor, changing with time in an a.c. circuit, is also a displacement variable. In the same way, pressure variations in time in the propagation of sound wave, the changing electric and magnetic fields in a light wave are examples of displacement in different contexts. The displacement variable may take both positive and negative values. In experiments on oscillations, the displacement is measured for different times.

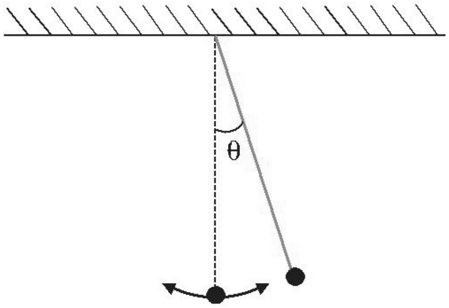


Fig.8.2(b) An oscillating simple pendulum; its motion can be described in terms of angular displacement θ from the vertical

The displacement can be represented by a mathematical function of time. In case of periodic motion, this function is periodic in time. One of the simplest periodic functions is given by

$$f(t) = A \cos\omega t \tag{8.3a}$$

If the argument of this function, ωt, is increased by an integral multiple of 2π radians, the value of the function remains the same. The function f (t) is then periodic and its period, T, is given by

$$T = 2\pi/\omega \tag{8.3b}$$

Thus, the function f (t) is periodic with period T,

$$f(t) = f(t+T)$$

The same result is obviously correct if we consider a sine function, f (t) = A sin ωt. Further, a linear combination of sine and cosine functions like, f (t) = A sinωt + B cosωt is also a periodic function with the same period Taking,

$$A = D\cos\varphi \text{ and } B = D$$

sinφ Eq. (8.3c) can be written as, $f(t) = D\sin(\omega t + \varphi)$, (8.3d)

Here D and φ are constant given by

$$D = \sqrt{A^2 + B^2} \quad \textit{and} \quad \tan^{-1}\frac{B}{A}$$

The great importance of periodic sine and cosine functions is due to a remarkable result proved by the French mathematician, Jean Baptiste Joseph Fourier (1768-1830): **Any periodic function can be**

expressed as a superposition of sine and cosine functions of different time periods with suitable coefficients.

Example 8.2 Which of the following functions of time represent (a) periodic and (b) non-periodic motion? Give the period for each case of periodic motion [ω is any positive constant]. (i) sin ωt + cos ωt (ii) sin ωt + cos 2 ωt + sin 4 ωt (iii) $e^{-\omega t}$ (iv) log (ωt).

Answer

(i) sin ωt + cos ωt is a periodic function, it can also be written as $\sqrt{2} \sin(\omega t + \pi/4)$.

Now $\sqrt{2} \sin(\omega t + \pi/4) = \sqrt{2} \sin(\omega t + \pi/4 + 2\pi)$

$= \sqrt{2} \sin[\omega(t + 2\pi/\omega) + \pi/4]$

The periodic time of the function is $2\pi/\omega$.

(ii) This is an example of a periodic motion. It can be noted that each term represents a periodic function with a different angular frequency. Since period is the least interval of time after which a function repeats its value, sin ωt has a period $T_0 = 2\pi/\omega$; cos $2\omega t$ has a period $\pi/\omega = T_0/2$; and sin $4\omega t$ has a period $2\pi/4\omega = T_0/4$. The period of the first term is a multiple of the periods of the last two terms. Therefore, the smallest interval of time after which the sum of the three terms repeats is T_0, and thus the sum is a periodic function with a period $2\pi/\omega$.

(iii) The function $e^{-\omega t}$ is not periodic, it decreases monotonically with increasing time and tends to zero as $t \to \infty$ and thus, never repeats its value.

(iv) The function log(ωt) increases mono-tonically with time t. It, therefore, never repeats its value and is a non- periodic function. It may be noted that as $t \to \infty$, log(ωt) diverges to ∞. It, therefore, cannot represent any kind of physical displacement.

8.3 SIMPLE HARMONIC MOTION

Let us consider a particle vibrating back and forth about the origin of an x-axis between the limits +A and –A as shown in Fig. 8.3. In between these extreme positions the particle moves in such a manner that its speed is maximum when it is at the origin and zero when it is at ± A. The time t is chosen to be zero when the particle is at +A and it returns to +A at t = T. In this section we will describe this motion. Later, we shall discuss how to achieve it. To study the motion of this particle, we record its positions as a function of time by taking ‘snapshots’ at regular intervals of time. A set of such snapshots is shown in Fig. 8.4. The position of the particle with reference to the origin gives its displacement at any instant of time.

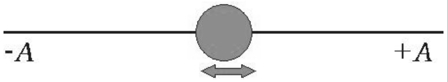


Fig. 8.3 *A particle vibrating back and forth about the origin of x-axis, between the limits +A and –A.*

For such a motion the displacement x(t) of the particle from a certain chosen origin is found to vary with time as,

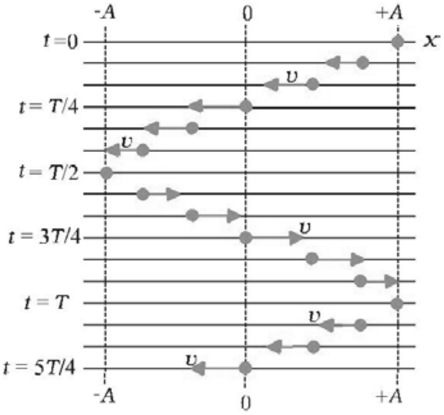


Fig. 8.4 *A sequence of 'snapshots' (taken at equal intervals of time) showing the position of a particle as it oscillates back and forth about the origin along an x-axis, between the limits +A and –A. The length of the vector arrows is scaled to indicate the speed of the particle. The speed is maximum when the particle is at the origin and zero when it is at ± A. If the time t is chosen to be zero when the particle is at +A, then the particle returns to +A at t = T, where T is the period of the motion. The motion is then repeated. It is represented by Eq. (8.4) for φ = 0.*

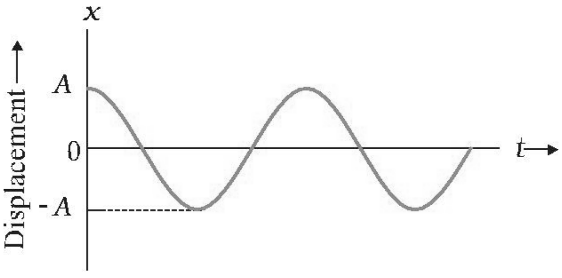


Fig. 8.5 *A graph of x as a function of time for the motion represented by Eq. (8.4)*

$$x(t) = A\cos(\omega t + \varphi) \qquad (8.4)$$

in which A, ω, and φ are constants.

$$\begin{array}{ccccc} x(t) = & A & Cos(\overbrace{\omega t}) & + & \varphi \\ \uparrow & \uparrow & \uparrow & & \uparrow \\ \text{Displacement} & \text{Amplitude} & \text{Angular Phase frequency constant} & & \text{Phase} \end{array}$$

Fig. 8.6 A reference of the quantities in Eq. (8.4).

The motion represented by Eq. (8.4) is called simple harmonic motion (SHM); a term that means the periodic motion is a sinusoidal function of time. Equation (8.4), in which the sinusoidal function is a cosine function, is plotted in Fig. 8.5. The quantities that determine the shape of the graph are displayed in Fig. 8.6 along with their names.

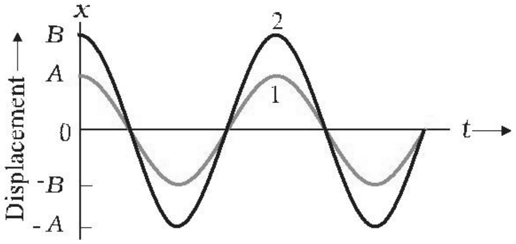


Fig. 8.7 (a) *A plot of displacement as a function of time as obtained from Eq. (8.4) with φ = 0. The curves 1 and 2 are for two different amplitudes A and B*

We shall now define these quantities.

The quantity A is called the amplitude of the motion. It is a positive constant which represents the magnitude of the maximum displacement of the particle in either direction. The cosine function in Eq. (8.4) varies between the limits ±1, so the displacement x(t) varies between the limits ± A. In Fig. 8.7 (a), the curves 1 and 2 are plots of Eq. (8.4) for two different amplitudes A and B. The difference between these curves illustrates the significance of amplitude.

The time varying quantity, (ωt + φ), in Eq. (8.4) is called the phase of the motion. It describes the state of motion at a given time. The constant φ is called the phase constant (or phase angle). The value of φ depends on the displacement and velocity of the particle at t = 0. This can be understood better by considering Fig. 8.7(b). In this figure, the curves 3 and 4 represent plots of Eq. (8.4) for two values of the phase constant φ. It can be seen that the phase constant signifies the initial conditions. The constant ω, called the angular frequency of the motion, is related to the period T.

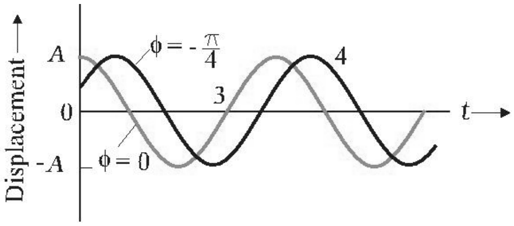


Fig. 8.7 (b) *A plot obtained from Eq. 8.4. The curves3 and 4 are for φ= 0 and -π /4 respectively. The amplitude A is same for both the plots.*

To get their relationship, let us consider Eq. (8.4) with φ = 0; it then reduces to,

$$x(t) = A\cos\omega t \tag{8.5}$$

Now since the motion is periodic with a period T, the displacement x (t) must return to its initial value after one period of the motion; that is, x(t) must be equal to x (t+T) for all t. Applying this condition to Eq. (8.5) leads to,

$$A\cos\omega t = A\cos\omega(t+T) \tag{8.6}$$

As the cosine function first repeats itself when its argument (the phase) has increased by 2π, Eq. (8.6) gives,

$$\omega(t+T) = \omega t + 2\pi$$

$$\text{or} \qquad \omega T = 2\pi$$

Thus, the angular frequency is, $\omega = 2\pi/T$ (8.7)

The SI unit of angular frequency is radians per second. To illustrate the significance of period T, sinusoidal functions with two different periods are plotted in Fig. 8.8.

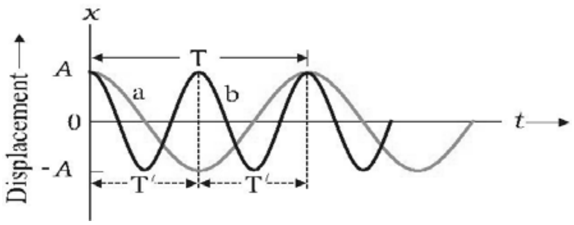


Fig. 8.7 (b) *A plot obtained from Eq. 8.4. The curves3 and 4 are for φ= 0 and -π /4 respectively. The amplitude A is same for both the plots.*

In this plot the SHM represented by curve a, has a period T and that represented by curve b, has a period $T^{/} = T/2$.

We have had an introduction to simple harmonic motion. In the next section we will discuss the simplest example of simple harmonic motion. It will be shown that the projection of uniform circular motion on a diameter of the circle executes simple harmonic motion.

Example 8.3 Which of the following functions of time represent (a) simple harmonic motion and (b) periodic but not simple harmonic? Give the period for each case. (1) sin ωt – cos ωt (2) sin2ωt

Answer

(a) $\sin \omega t - \cos \omega t$

$= \sin \omega t - \sin (\pi/2 - \omega t)$

$= 2 \cos (\pi/4) \sin (\omega t - \pi/4)$

$= \sqrt{2} \sin (\omega t - \pi/4)$

This function represents a simple harmonic motion having a period $T = 2\pi/\omega$ and a phase angle $(-\pi/4)$ or $(7\pi/4)$

(b) $\sin^2 \omega t = ½ - ½ \cos 2 \omega t$

The function is periodic having a period $T = \pi/\omega$. It also represents a harmonic motion with the point of equilibrium occurring at ½ instead of zero.

8.4 SIMPLE HARMONIC MOTION AND UNIFORM CIRCULAR MOTION

In 1610, Galileo discovered four principal moons of the planet Jupiter. To him, each moon seemed to move back and forth relative to the planet in a simple harmonic motion; the disc of the planet forming the midpoint of the motion. The record of his observations, written in his own hand, is still available. Based on his data, the position of the moon Callisto relative to Jupiter is plotted in Fig. 8.9. In this figure, the circles represent Galileo's data points and the curve drawn is a best fit to the data. The curve obeys Eq. (8.4), which is the displacement function for SHM. It gives a period of about 16.8 days.

It is now well known that Callisto moves with essentially a constant speed in an almost circular orbit around Jupiter. Its true motion is uniform circular motion. What Galileo saw and what we can also see, with a good pair of binoculars, is the projection of this uniform circular motion on a line in the plane of motion. This can easily be visualized by performing a simple Tie a ball to the end of a string and make it move in a horizontal plane about a fixed point with a constant angular speed.

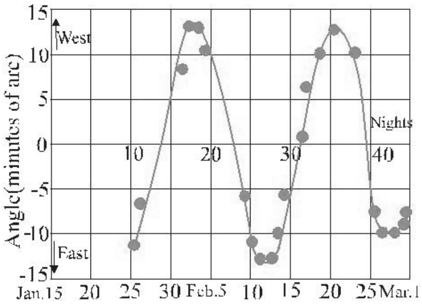


Fig. 8.9 *The angle between Jupiter and its moon Callis to as seen from earth. The circles are based on Galileo's measurements of 1610. The curve is a best fit suggesting a simple harmonic motion. At Jupiter's mean distance,10 minutes of arc corresponds to about 2 ×106 km.*

The ball would then perform a uniform circular motion in the horizontal plane. Observe the ball sideways or from the front, fixing your attention in the plane of motion. The ball will appear to execute to and fro motion along a horizontal line with the point of rotation as the midpoint. You could alternatively observe the shadow of the ball on a wall which is perpendicular to the plane of the circle. In this process what we are observing is the motion of the ball on a diameter of the circle normal to the direction of viewing. This experiment provides an analogy to Galileo's observation.

In Fig. 8.10, we show the motion of a reference particle P executing a uniform circular motion with (constant) angular speed ω in a reference circle. The radius A of the circle is the magnitude of the particle's position vector. At any time t, the angular position of the particle is $\omega t + \varphi$, where φ is its angular position at t = 0.

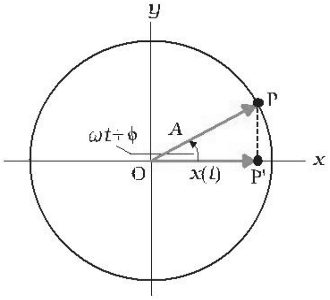


Fig. 8.10 *The motion of a reference particle P executing a uniform circular motion with (constant) angular speed ω in a reference circle of radius A.*

The projection of particle P on the x-axis is a point P′ , which we can take as a second particle. The projection of the position vector of particle P on the x-axis gives the location x(t) of P′ . Thus we have,

$$x(t) = A \cos(\omega t + \varphi)$$

which is the same as Eq. (8.4). This shows that if the reference particle P moves in a uniform circular motion, its projection particle P′ executes a simple harmonic motion along a diameter of the circle.

From Galileo's observation and the above considerations, we are led to the conclusion that circular motion viewed edge-on is simple harmonic motion. In a more formal language we can say that: **Simple harmonic motion is the projection of uniform circular motion on a diameter of the circle in which the latter motion takes place.**

Example 8.4 Fig. 8.11 depicts two circular motions. The radius of the circle, the period of revolution, the initial position and the sense of revolution are indicated on the figures. Obtain the simple harmonic motions of the x-projection of the radius vector of the rotating particle P in each case.

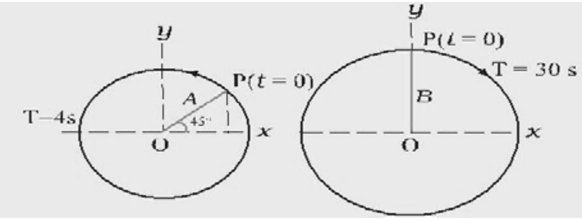


Fig. 8.11

Answer

(a) At t = 0, OP makes an angle of 45° = π/4 rad with the (positive direction of) x-axis. After time t, it covers an angle 2Tπt/T in the anticlockwise sense, and makes an angle of 2πt/T + π/4 with the x-axis.

The projection of OP on the x-axis at time t is given by,

$$x(t) = A \cos(2/T \;\; t + \pi/4)$$

For T = 4s, $x\,(t) = A \cos\left(\frac{2}{4}\; t + \frac{\pi}{4}\right)$

which is a SHM of amplitude A, period 4 s and an initial phase* = π/4

In this case at t = 0, OP makes an angle of 90o = π/2 with the x-axis. After a time t, it 2 covers an angle of 2/T t in the clockwise sense and makes an angle of π/2-2/T t with the x-axis. The projection of OP on the x-axis at time t is given by

$$x\ (t) = B\cos\left(\frac{\pi}{2} - \frac{2}{T}\ t\right)$$

$$x\ (t) = B\sin\left(\frac{2}{T}\ t\right)$$

For T = 30 s, $x\ (t) = B\sin\left(\frac{1}{15}\ t\right)$

Writing this as $x\ (t) = B\cos\left(\frac{1}{15}\ t - \frac{\pi}{2}\right)$

and comparing with Eq. (8.4). We find that this represents a SHM of amplitude B, period 30 s, and initial phase of π/2

8.5 VELOCITY AND ACCELERATION IN SIMPLE HARMONIC MOTION

It can be seen easily that the magnitude of velocity, v, with which the reference particle P (Fig. 8.10) is moving in a circle is related to its angular speed, ω, as

$$v = \omega A \tag{8.8}$$

where A is the radius of the circle described by the particle P. The magnitude of the velocity vector v of the projection particle is ωA ; its projection on the x-axis at any time t, as shown in Fig. 8.12, is

$$v(t) = -\omega A\sin(\omega t + \varphi) \tag{8.9}$$

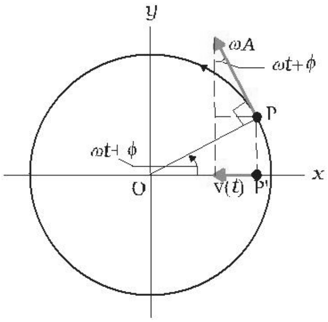


Fig. 8.12 *The velocity, v (t), of the particle P' is the projection of the velocity v of the reference particle, P.*

**The natural unit of angle is radian, defined through the ratio of arc to radius. Angle is a dimensionless quantity. Therefore it is not always necessary to mention the unit 'radian' when we use π, its multiples or submultiples. The conversion between radian and degree is not similar to that between metre and centimetre or mile. If the argument of a trigonometric function is stated without units, it is understood that the unit is radian. On the other hand, if degree is to be used as the unit of angle, then it must be shown explicitly. For example, sin(150) means sine of 15 degree, but sin(15) means sine of 15 radians. Hereafter, we will often drop 'rad' as the unit, and it should be understood that whenever angle is mentioned as a numerical value, without units, it is to be taken as radians.*

The negative sign appears because the velocity component of P is directed towards the left, in the negative direction of x. Equation (8.9) expresses the instantaneous velocity of the particle P′ (projection of P). Therefore, it expresses the instantaneous velocity of a particle executing SHM. Equation (8.9) can also be obtained by differentiating Eq. (8.4) with respect to time as,

$$\nu (t) = \frac{d}{dt} x(t) \tag{8.10}$$

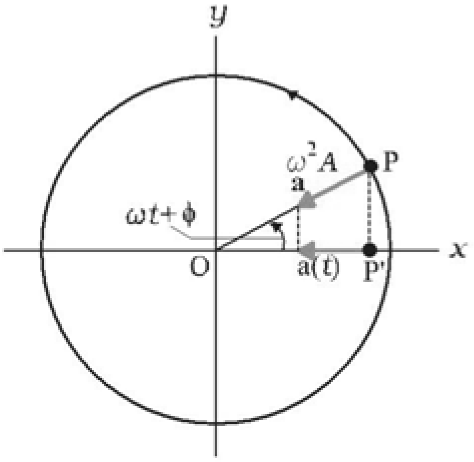


Fig. 8.13 *The acceleration, a(t), of the particle P′ is the projection of the acceleration a of the reference particle P.*

We have seen that a particle executing a uniform circular motion is subjected to a radial acceleration a directed towards the centre. Figure 8.13 shows such a radial acceleration a of the reference particle P executing uniform circular motion. The magnitude of the radial acceleration of P is ωA. Its projection on the x-axis at any time t is,

$$a (t) = -\omega A \cos (\omega t + \varphi)$$

$$= -\omega x\,(t) \qquad (8.11)$$

which is the acceleration of the particle P′ projection of particle P).Equation (8.11),therefore, represents the instantaneous acceleration of the particle P′ , which is executing SHM. Thus Eq. (8.11) expresses the acceleration of a particle executing SHM. It is an important result for SHM. It shows that in SHM the acceleration is proportional to the displacement and is always directed towards the mean position. Eq. (8.11) can also be obtained by differentiating Eq. (8.9) with respect to time as,

$$a(t) = \frac{d}{dt}\, v(t) \qquad (8.12)$$

The inter –relationship between the displacement of a particle executing simple harmonic motion, its velocity and acceleration can be seen in Fig. 8.8. In this figure (a) is a plot of Eq. (8.4) with $\varphi = 0$ and (b) depicts Eq. (8.9) also with $\varphi = 0$. Similar to the amplitude A in Eq. (8.4), the positive quantity ωA in Eq. (8.9) is called the velocity amplitude *v*. In Fig. 8.8(b), it can be seen that the velocity of the oscillating particle varies between the limits $\pm v_m = \pm \omega A$. Note that the curve of v(t) is shifted (to the left) from the curve of x(t) by one quarter period and thus the particle velocity lags behind the displacement by a phase angle of $\pi/2$; when the magnitude of displacement is the greatest, the magnitude of the velocity is the least. When the magnitude of displacement is the least, the velocity is the greatest. Figure 8.8(c) depicts the variation of the particle acceleration a(t). It is seen that when the displacement has its greatest positive value, the acceleration has its greatest negative value and vice versa. When the displacement is zero, the acceleration is also zero.

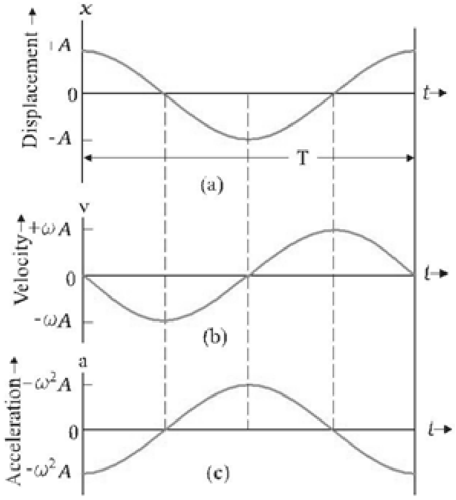


Fig. 8.14 *The particle displacement, velocity and acceleration in a simple harmonic motion. (a) The displacement x (t) of a particle executing SHM with phase angle φ equal to zero. (b) The velocity v (t) of the particle. (c) The acceleration a (t) of the particle.*

Example 8.5 A body oscillates with SHM according to the equation (in SI units), $x = 5 \cos [2\pi t+\pi/4]$. At t = 1.5 s, calculate the (a) displacement, (b) speed and (c) acceleration of the body.

Answer

The angular frequency ω of the body = 2π s–1 and its time period T = 1 s.

At $t = 1.5$ s

(a) displacement = (5.0 m) cos [(2π s–1) × 1.5 s + π/4]

$= (5.0 \text{ m}) \cos [(3\pi + \pi/4)]$

$= –5.0 \times 0.707 \text{ m}$

$= –3.535 \text{ m}$

(b) Using Eq. (8.9), the speed of the body

$= – (5.0 \text{ m})(2\pi \text{ s}^{–1}) \sin [(2\pi \text{ s}^{–1}) \times 1.5 \text{ s} + \pi/4]$

$= – (5.0 \text{ m})(2\pi \text{ s}^{–1}) \sin [(3\pi + \pi/4)]$

$= 10\pi \times 0.707 \text{ m s}^{–1}$

$= 22 \text{ m s}^{–1}$

(c) Using Eq.(8.10), the acceleration of the body

$= –(2\pi \text{ s}^{–1})^2 \times \text{displacement}$

$= – (2\pi \text{ s}^{–1})^2 \times (–3.535 \text{ m})$

$= 80 \text{ m s}^{–2}$

8.6 FORCE LAW FOR SIMPLE HARMONIC MOTION

In Section8.3, we described the simple harmonic motion. Now we discuss how it can be generated. Newton’s second law of motion relates the force acting on a system and the corresponding acceleration produced. Therefore, if we know how the acceleration of a particle varies with time, this law can be used to learn about the force, which must act on the particle to give it that acceleration. If we combine Newton’s second law and Eq. (8.11), we find that for simple harmonic motion,

$$F(t) = ma$$

$$= -m\omega^2 x(t)$$

$$\text{or} \quad F(t) = -k\,x(t) \qquad (8.13)$$

$$\text{where} \quad k = m\omega^2 \qquad (8.8a)$$

$$\text{or} \quad \omega = \sqrt{\frac{k}{m}} \qquad (8.8b)$$

Equation (8.13) gives the force acting on the particle. It is proportional to the displacement and directed in an opposite direction. Therefore, it is a restoring force. Note that unlike the centripetal force for uniform circular motion that is constant in magnitude, the restoring force for SHM is time dependent. The force law expressed by Eq. (8.13) can be taken as an alternative definition of simple harmonic motion. It states:

Simple harmonic motion is the motion executed by a particle subject to a force, which is proportional to the displacement of the particle and is directed towards the mean position.

Since the force F is proportional to x rather than to some other power of x, such a system is also referred to as a **linear harmonic oscillator**. Systems in which the restoring force is a non-linear function of x are termed as non-linear harmonic or anharmonic oscillators.

Example 8.6 Two identical springs of spring constant k are attached to a block of mass m and to fixed supports as shown in Fig. 8.15. Show that when the mass is displaced from its equilibrium position on either side, it executes a simple harmonic motion. Find the period of oscillations.

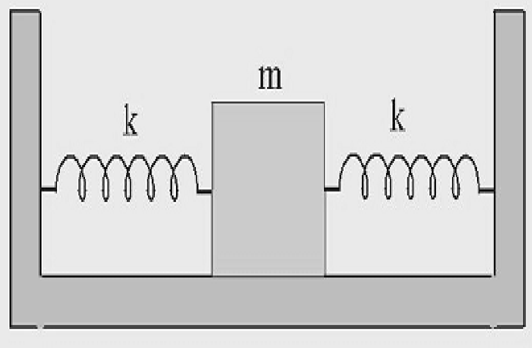


Fig. 8.15

***Answer** Let the mass be displaced by a small distance x to the right side of the equilibrium position, as shown in Fig. 8.16. Under this situation the spring on the left side gets*

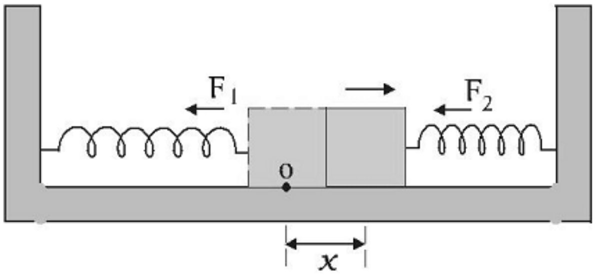


Fig. 8.16

elongated by a length equal to *x* and that on the right side gets compressed by the same length. The forces acting on the mass are then,

F_1 = –k x (force exerted by the spring on the left side, trying to pull the mass towards the mean position)

F_2 = –k x (force exerted by the spring on the right side, trying to push the mass towards the mean position)

The net force, *F*, acting on the mass is then given by,

$F = -2kx$

Hence the force acting on the mass is proportional to the displacement and is directed towards the mean position; therefore, the motion executed by the mass is simple harmonic. The time period of oscillations is,

$$T = 2\pi \sqrt{\frac{m}{2k}}$$

8.7 ENERGY IN SIMPLE HARMONIC MOTION

A particle executing simple harmonic motion has kinetic and potential energies, both varying between the limits, zero and maximum.

In section8.5 we have seen that the velocity of a particle executing SHM, is a periodic function of time. It is zero at the extreme positions of displacement. Therefore, the kinetic energy (*K*) of such a particle, which is defined as

$$K = \frac{1}{2}mv^2$$

$$= \frac{1}{2}\, m\omega^2 A^2 \sin^2(\omega t + \varphi)$$

$$= \tfrac{1}{2} kA^2 \sin^2(\omega t + \varphi) \quad (8.15)$$

is also a periodic function of time, being zero when the displacement is maximum and maximum when the particle is at the mean position. Note, since the sign of v is immaterial in K, the period of K is $T/2$.

What is the potential energy (PE) of a particle executing simple harmonic motion? In Chapter 6, we have seen that the concept of potential energy is possible only for conservative forces. The spring force $F = -kx$ is a conservative force, with associated potential energy

$$U = \tfrac{1}{2}\, kx^2 \quad (8.16)$$

Hence the potential energy of a particle executing simple harmonic motion is,

$$U = \frac{1}{2}\, kx^2$$

$$= \tfrac{1}{2}\, kA^2 \cos^2(\omega t + \varphi) \quad (8.17)$$

Thus the potential energy of a particle executing simple harmonic motion is also periodic, with period $T/2$, being zero at the mean position and maximum at the extreme displacements.

It follows from Eqs. (8.15) and (8.17) that the total energy, E, of the system is,

$$E = U + K$$

$$= \tfrac{1}{2} kA^2 \cos^2(\omega t + \varphi) + \tfrac{1}{2} kA^2 \sin^2(\omega t + \varphi)$$

$$= \tfrac{1}{2} kA^2 [\cos^2(\omega t + \varphi) + \sin^2(\omega t + \varphi)]$$

The quantity within the square brackets above is unity and we have,

$$E = \frac{1}{2} kA^2$$

The total mechanical energy of a harmonic oscillator is thus independent of time as expected for motion under any conservative force. The time and displacement dependence of the potential and kinetic energies of a linear simple harmonic oscillator are shown in Fig. 8.17.

It is observed that in a linear harmonic oscillator, all energies are positive and peak twice during every period. For $x = 0$, the energy is all kinetic and for $x = \pm A$ it is all potential.

In between these extreme positions, the potential energy increases at the expense of kinetic energy. This behaviour of a linear harmonic oscillator suggests that it possesses an element of springiness and an element of inertia. The former stores its potential energy and the latter stores its kinetic energy.

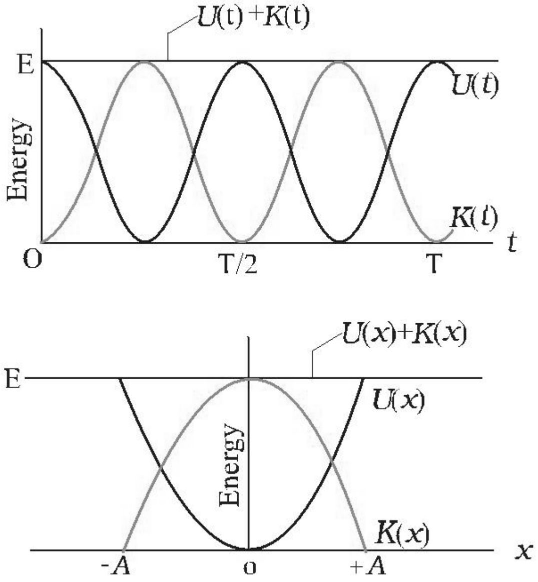


Fig. 8.17 (a) Potential energy U(t), kinetic energy K(t)and the total energy E as functions of time t for a linear harmonic oscillator. All energies are positive and the potential and kinetic energies peak twice in every period of the oscillator. (b) Potential energy U(x), kinetic energy K(x) and the total energy E as functions of position x for a linear harmonic oscillator with amplitude A. For x = 0, the energy is all kinetic and for x = ± A it is all potential.

Example 8.7 A block whose mass is 1 kg is fastened to a spring. The spring has a spring constant of 50 N m^{-1}. The block is pulled to a distance $x = 10$ cm from its equilibrium position at $x = 0$ on a frictionless surface from rest at $t = 0$. Calculate the kinetic, potential and total energies of the block when it is 5 cm away from the mean position.

Answer The block executes SHM, its angular frequency, as given by Eq. (8.8b), is

$$\omega = \sqrt{\frac{k}{m}}$$

$$= \sqrt{\frac{50\ N\ m^{-1}}{1\ kg}}$$

$$= 7.07 \text{ rad s}^{-1}$$

Its displacement at any time t is then given by,

$$x(t) = 0.1 \cos (7.07t)$$

Therefore, when the particle is 5 cm away from the mean position, we have

$$0.05 = 0.1 \cos (7.07t)$$

Or $\cos (7.07t) = 0.5$ and hence

$$\text{Sin } (7.07\text{t}) = \sqrt{3/2} = 0.866,$$

Then the velocity of the block at $x = 5$ cm is

$$= 0.1 \times 7.07 \times 0.866 \text{ m s}^{-1}$$

$$= 0.61 \text{ m s}^{-1}$$

Hence the K.E. of the block,

$$= \frac{1}{2}mv^2$$

$$= ½[1\text{kg} \times (0.6123 \text{ m s}^{-1})^2]$$

$$= 0.19 \text{ J}$$

The P.E. of the block,

$$= \frac{1}{2}kx^2$$

$$= ½(50 \text{ N m}^{-1} \times 0.05 \text{ m} \times 0.05 \text{ m})$$

$$= 0.0625 \text{ J}$$

The total energy of the block at $x = 5$ cm,

$$= \text{K.E.} + \text{P.E.}$$

$$= 0.25 \text{ J}$$

we also know that at maximum displacement, K.E. is zero and hence the total energy of the system is equal to the P.E. Therefore, the total energy of the system,

$$= \tfrac{1}{2}(50\ \text{N m}^{-1} \times 0.1\ \text{m} \times 0.1\ \text{m})$$
$$= 0.25\ \text{J}$$

which is same as the sum of the two energies at a displacement of 5 cm. This is in conformity with the principle of conservation of energy.

8.8 SOME SYSTEMS EXECUTING SIMPLE HARMONIC MOTION

There are no physical examples of absolutely pure **simple harmonic motion**. In practice we come across systems that execute simple harmonic motion approximately under certain conditions. In the subsequent part of this section, we discuss the motion executed by some such systems.

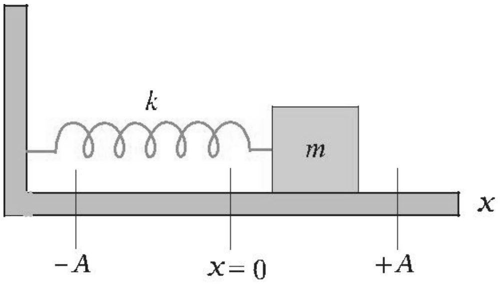


Fig. 8.18 *A linear simple harmonic oscillator consisting of a block of mass m attached to a spring. The block moves over a frictionless surface. Once pulled to the side and released, it executes simple harmonic motion.*

8.8.1 Oscillations due to a Spring

The simplest observable example of simple harmonic motion is the small oscillations of a block of mass *m* fixed to a spring, which in turn is fixed to a rigid wall as shown in Fig. 8.18. The block is placed on a frictionless horizontal surface. If the block is pulled on one side and is released, it then executes a to and fro motion about a mean position. Let $x = 0$, indicate the position of the centre of the block when the spring is in equilibrium. The positions marked as $-A$ and $+A$ indicate the maximum displacements to the left and the right of the mean position. We have already learnt that springs have special properties, which were first discovered by the English physicist Robert Hooke. He had shown that such a system when deformed, is subject to a restoring force, the magnitude of which is proportional to the deformation or the displacement and acts in opposite direction. This is known as Hooke’s law (Chapter 9). It holds good for displacements small in comparison to the length of the spring. At any time *t*, if the displacement of the block from its mean position is *x*, the restoring force F acting on the block is,

$$F(x) = -k\,x \qquad (8.19)$$

The constant of proportionality, k, is called the spring constant, its value is governed by the elastic properties of the spring. A stiff spring has large k and a soft spring has small k. Equation (8.19) is same as the force law for SHM and therefore the system executes a simple harmonic motion. From Eq. (8.8) we have,

$$\omega = \sqrt{k/m} \qquad (8.20)$$

and the period, T, of the oscillator is given by,

$$T = 2\sqrt{\frac{m}{k}} \qquad (8.21)$$

Equations (8.20) and (8.21) tell us that a large angular frequency and hence a small period is associated with a stiff spring (high k) and a light block (small m).

Example 8.8 A 5 kg collar is attached to a spring of spring constant 500 N m^{-1}. It slides without friction over a horizontal rod. The collar is displaced from its equilibrium position by 10.0 cm and released. Calculate (a) the period of oscillation, (b) the maximum speed and (c) maximum acceleration of the collar.

Answer (a) The period of oscillation as given byEq. (8.21) is,

$$T = 2\sqrt{\frac{m}{k}}$$

$$= 2\pi\sqrt{\frac{5.0\,kg}{500\,Nm^{-1}}}$$

$$= \frac{2\pi}{10}s$$

(b) The velocity of the collar executing SHM is given by,

$$v(t) = -A\omega\sin(\omega t + \varphi)$$

The maximum speed is given by,

$$v_m = A\omega$$

$$= 0.1\ x\ \sqrt{\frac{500\ Nm^{-1}}{5\ kg}}$$

$$= 1\ s^{-1}$$

and it occurs at $x = 0$

(c) The acceleration of the collar at the displacement $x\ (t)$ from the equilibrium is given by,

$$a\ (t) = -\omega^2\ x(t)$$

$$= -\frac{k}{m}\ x(t)$$

Therefore the maximum acceleration is,

$$a_{max} = \omega^2\ A$$

$$= \frac{500\ Nm^{-1}}{5\ kg}\ x\ 0.1\ m$$

$$= 10\ ms^{-2}$$

and it occurs at the extremities.

8.8.2 The Simple Pendulum

It is said that Galileo measured the periods of a swinging chandelier in a church by his pulse beats. He observed that the motion of the chandelier was periodic. The system is a kind of pendulum. You can also make your own pendulum by tying a piece of stone to a long unstretchable thread, approximately 100 cm long. Suspend your pendulum from a suitable support so that it is free to oscillate. Displace the stone to one side by a small distance and let it go. The stone executes a to and fro motion, it is periodic with a period of about two seconds. Is this motion simple harmonic? To answer this question, we consider a **simple pendulum**, which consists of a particle of mass m (called the bob of the pendulum) suspended from one end of an unstretchable, massless string of length L fixed at the other end as shown in Fig. 8.19(a). The bob is free to swing to and fro in the plane of the page, to the left and right of a vertical line through the pivot point.

The forces acting on the bob are the force **T**, tension in the string and the gravitational force $\mathbf{F_g}$(= m **g**), as shown in Fig. 8.19(b). The string makes an angle θ with the vertical. We resolve the force $\mathbf{F_g}$ into a radial component $F_g \cos\theta$ and a tangential component $F_g \sin\theta$. The radial component is cancelled by the tension, since there is no motion along the length of the string. The tangential component produces a restoring torque about the pendulum's pivot point. This

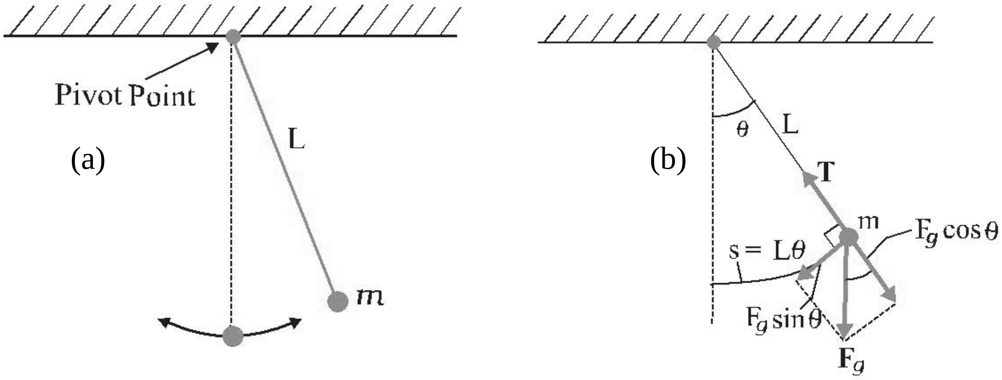


Fig. 8.19 *(a) A simple pendulum. (b) The forces acting on the bob are the force due to gravity,* F_g *(= mg), and the tension T in the string. (b) The tangential component* F_g *of the gravitational force is a restoring force that tends to bring the pendulum back to the central position.*

torque always acts opposite to the displacement of the bob so as to bring it back towards its central location. The central location is called the **equilibrium position** ($\theta = 0$), because at this position the pendulum would be at rest if it were not swinging

The restoring torque τ is given by,

$$\tau = -L\,(F_g \sin\theta) \tag{8.22}$$

where the negative sign indicates that the torque acts to reduce θ, and L is the length of the moment arm of the force $F_g \sin\theta$ about the pivot point. For rotational motion we have,

$$\tau = I\,\alpha \tag{8.23}$$

where I is the pendulum's rotational inertia about the pivot point and α is its angular acceleration about that point. From Eqs. (8.22) and (8.23) we have,

$$-L\,(F_g \sin\theta) = I\,\alpha$$

(8.24)

Substituting the magnitude of F_g, i.e. *mg*, we have,

$$-L\, mg \sin\theta = I\, \alpha$$

$$\alpha = \frac{mgL}{I} \sin\theta \qquad (8.25)$$

We can simplify Eq. (8.25) if we assume that the displacement θ is small. We know that sin θ can be expressed as,

$$\text{Sin}\theta = 1 - \theta/3! + \theta/5! \pm \cdots \qquad (8.26)$$

where θ is in radians.

Now if θ is small, sin θ can be approximated by θ and Eq. (8.25) can then be written as,

$$\alpha = -\frac{mgL}{I}\theta \qquad (8.27)$$

In Table 8.1, we have listed the angle θ in degrees, its equivalent in radians, and the value of the function sin θ . From this table it can be seen that for θ as large as 20 degrees, sin θ is nearly the same as θ **expressed in radians**.

Table 8.1 sin θ as a function of angle θ

θ (degrees)	θ (radians)	Sin θ
0	0	0
5	0.087	0.087
10	0.174	0.174
15	0.262	0.256
20	0.349	0.342

Equation (8.27) is the angular analogue of Eq. (8.11) and tells us that the angular acceleration of the pendulum is proportional to the angular displacement θ but opposite in sign. Thus as the pendulum moves to the right, its pull to the left increases until it stops and begins to return to the left. Similarly, when it moves towards left, its acceleration to the right tends to return it to the right and so on, as it swings to and fro in SHM. Thus the motion of a **simple pendulum swinging through small angles is approximately SHM**.

Comparing Eq. (8.27) with Eq. (8.11), we see that the angular frequency of the pendulum is,

$$\omega = \sqrt{\frac{mgL}{I}}$$

and the period of the pendulum, T, is given by,

$$T = 2\pi\sqrt{\frac{I}{mgL}} \tag{8.28}$$

All the mass of a simple pendulum is centred in the mass m of the bob, which is at a radius of L from the pivot point. Therefore, for this system, we can write $I = m\,L^2$ and substituting this in Eq. (8.28) we get,

$$\mathrm{T} = 2\pi\sqrt{\frac{\mathrm{L}}{\mathrm{g}}} \tag{8.29}$$

Equation (8.29) represents a simple expression for the time period of a simple pendulum.

Example 8.9 What is the length of a simple pendulum, which ticks seconds?

Answer From Eq. (8.29), the time period of a simple pendulum is given by

$$\mathrm{T} = 2\pi\sqrt{\frac{\mathrm{L}}{\mathrm{g}}}$$

From this relation one gets,

$$L = \frac{gT^2}{4^2}$$

The time period of a simple pendulum, which ticks seconds, is 2 s. Therefore, for $g = 9.8$ m s^{-2} and $T = 2$ s, L is

$$T = \frac{9.8\ (ms^{-2})4\ s^2}{4^2} = 1\ m$$

SHM - how small should the amplitude be?

When you perform the experiment to determine the time period of a simple pendulum, your teacher tells you to keep the amplitude small. But have you ever asked how small is small? Should the amplitude to 5^0, $2^{0,}$ 1^0, or 0.5^0? Or could it be 10^0, 20^0, or 30^0?

To appreciate this, it would be better to measure the time period for different amplitudes, up to large amplitudes. Of course, for large oscillations, you will have to take care that the pendulum oscillates in a vertical plane. Let us denote the time period for small-amplitude oscillations as T (0) and write the time period for amplitudeθ_0 as $T(\theta_0\ ) = cT$ (0), where c is the multiplying factor. If you plot a graph of c versus θ_0, you will get values somewhat like this:

θ_0	:	20^0	45^0	50^0	70^0	90^0
c	:	1.02	1.04	1.05	1.10	1.18

This means that the error in the time period is about 2% at an amplitude of 20^0, 5% at an amplitude of 50^0, and 10% at an amplitude of 70^0 and 18% at an amplitude of 90^0.

In the experiment, you will never be able to measure T (0) because this means there are no oscillations. Even theoretically, sin θ is exactly equal to θ only for $\theta = 0$. There will be some inaccuracy for all other values of θ. The difference increases with increasing θ . Therefore we have to decide how much error we can tolerate. No measurement is ever perfectly accurate. You must also consider questions like these: What is the accuracy of the stopwatch? What is your own accuracy in starting and stopping the stopwatch? You will realise that the accuracy in your measurements at this level is never better than 5% or 10%. Since the above table shows that the time period of the pendulum increases hardly by 5% at an amplitude of 50^0 over its low amplitude value, you could very well keep the amplitude to be 50° in your experiments.

8.9 DAMPED SIMPLE HARMONIC MOTION

We know that the motion of a simple pendulum, swinging in air, dies out eventually. Why does it happen? This is because the air drag and the friction at the support oppose the motion of the pendulum and dissipate its energy gradually. The pendulum is said to execute **damped oscillations**. In damped oscillations, although the energy of the system is continuously dissipated, the oscillations remain apparently periodic. The dissipating forces are generally the frictional forces. To understand the effect of such external forces on the motion of an oscillator, let us consider a system as shown in Fig. 8.20. Here a block of mass m oscillates vertically on a spring with spring constant k. The block is connected to a vane through a rod (the vane and the rod are considered to be massless). The vane is submerged in a liquid. As the block oscillates up and down, the vane also moves along with it in the liquid. The up and down motion of the vane displaces the liquid, which in turn, exerts an inhibiting drag force (viscous drag) on it and thus on the entire oscillating system. With time, the mechanical energy of the block-spring system decreases, as energy is transferred to the thermal energy of the liquid and vane.

Let the damping force exerted by the liquid on the system be* $\mathbf{F}_d$. Its magnitude is proportional to the velocity **v** of the vane or the block. The force acts in a direction opposite to the direction of **v**. This assumption is valid only when the vane moves slowly. Then for the motion along the *x*-axis (vertical direction as shown in Fig. 8.20), we have

$$\mathbf{F}_d = -b\,\mathbf{v} \tag{8.30}$$

where b is a **damping constant** that depends on the characteristics of the liquid and the vane. The negative sign makes it clear that the force is opposite to the velocity at every moment.

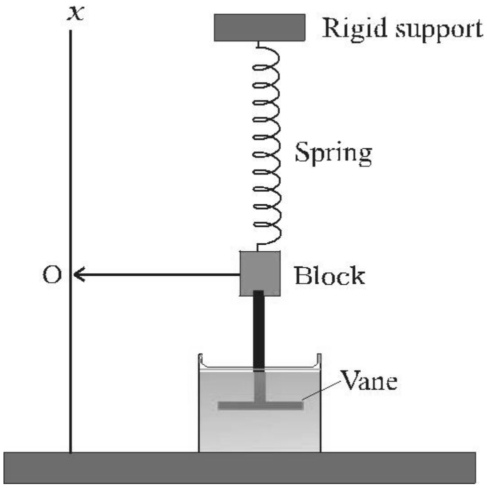


Fig. 8.20 *A damped simple harmonic oscillator. The vane immersed in a liquid exerts a damping force on the block as it oscillates up and down.*

When the mass m is attached to the spring and released, the spring will elongate a little and the mass will settle at some height. This position, shown by O in Fig 8.20, is the equilibrium position of the mass. If the mass is pulled down or pushed up a little, the restoring force on the block due to the spring is $\mathbf{F}_S = -k\mathbf{x}$, where **x** is the displacement of the mass from its equilibrium position. Thus the total force acting on the mass at any time t is $\mathbf{F} = -k\mathbf{x} - b\mathbf{v}$. If $\mathbf{a}(t)$ is the acceleration of the mass at time t, then by Newton's second law of motion for force components along the *x*-axis, we have

$$m\, a(t) = -k\, x(t) - b\, v(t) \tag{8.31}$$

Here we have dropped the vector notation because we are discussing one-dimensional motion. Substituting dx/dt for $v(t)$ and d^2x/dt^2 for the acceleration $a(t)$ and rearranging gives us the differential equation,

$$m\, d^2 x/ dt^2 + b\, dx/dt + kx = 0 \tag{8.32}$$

The solution of Eq. (8.32) describes the motion of the block under the influence of a damping force which is proportional to velocity. The solution is found to be of the form

$$x(t) = A\, e^{-b\,t/2m} \cos (\omega' t + \varphi) \tag{8.33}$$

where a is the amplitude and ω' is the angular frequency of the damped oscillator given by,

$$\omega' = \sqrt{\frac{k}{m} - \frac{b^2}{4m^2}} \tag{8.34}$$

In this function, the cosine function has a period $2\pi/\omega'$ but the function $x(t)$ is not strictly periodic because of the factor $e^{-b\,t/2m}$ which decreases continuously with time. However, if the decrease is small in one time period T, the motion represented by Eq. (8.33) is approximately periodic.

The solution, Eq. (8.33), can be graphically represented as shown in Fig. 8.21. We can regard it as a cosine function whose amplitude, which is $Ae^{-b\,t/2m}$, gradually decreases with time.

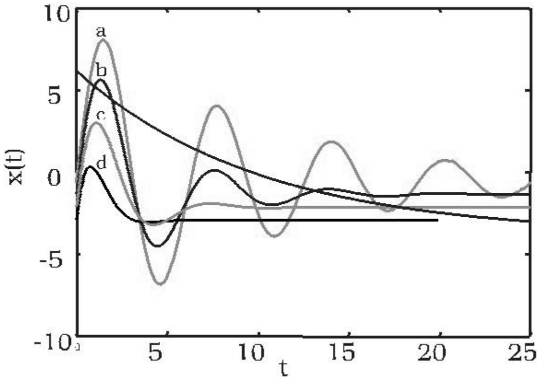


Fig. 8.21 *Displacement as a function of time in damped harmonic oscillations. Damping goes on increasing successively from curve* ***a*** *to* **d**.

If $b = 0$ (there is no damping), then Eqs. (8.33) and (8.34) reduce to Eqs. (8.4) and (8.8b), expressions for the displacement and angular frequency of an undamped oscillator. We have seen that the mechanical energy of an undamped oscillator is constant and is given by Eq. (8.18) ($E = 1/2\, k A^2$). If the oscillator is damped, the mechanical energy is not constant but decreases with time. If the damping is small, we can find E (t) by replacing A in Eq. (8.18) by $Ae^{-bt/2m}$, the amplitude of the damped oscillations. Thus we find,

$$E(t) = \frac{1}{2}\, kA^2 e^{\left(\frac{-bt}{m}\right)} \tag{8.35}$$

Equation (8.35) shows that the total energy of the system decreases exponentially with time. Note that small damping means that the dimensionless ratio b/km is much less than 1

Example 8.10 For the damped oscillator shown in Fig. 8.20, the mass m of the block is 200 g, k = 90 N m^{-1} and the damping constant b is 40 g s^{-1}. Calculate (a) the period of oscillation, (b) time taken for its amplitude of vibrations to drop to half of its initial value and (c) the time taken for its mechanical energy to drop to half its initial value.

Answer (a) We see that km= 90×0.2 = 18 kg N m^{-1} = kg^2 s^{-2}; therefore$\sqrt{km} = 4.243 kgs^{-1}$, and b=0.04 kgs^{-1} Therefore b is much less than$\sqrt{km}$. Hence the time period T from Eq. (8.34) is given by

$$T = 2\pi\sqrt{\frac{m}{k}}$$

$$= 2\sqrt{\frac{0.2\;kg}{90\;Nm^{\pm 1}}}$$

= 0.3 s

(b) Now, from Eq. (8.33), the time, $T_{1/2}$, for the amplitude to drop to half of its initial value is given by,

$$T_{\frac{1}{2}} = \frac{\ln\frac{1}{2}}{\frac{b}{2m}} = \frac{0.639}{40}\;2\quad 200\; s$$

= 6.93 s

(c) For calculating the time, $t_{1/2}$, for its mechanical energy to drop to half its initial value we make use of Eq. (8.35). From this equation we have,

$$E\,(t_{1/2})/E\,(0) = \exp\,(-bt_{1/2}/m)$$

Or $\quad \frac{1}{2} = \exp(-bt_{\frac{1}{2}}/m)$

$$\ln\left(\frac{1}{2}\right) = -(bt_{\frac{1}{2}}/m)$$

$$t_{\frac{1}{2}} = \frac{0.693}{40\ \mathrm{gs}^{-1}}\ \ 200\ \mathrm{g}$$

$$= 3.16\ \mathrm{s}$$

This is just half of the decay period for amplitude. This is not suprising, because, according to Eqs. (8.33) and (8.35), energy depends on the square of the amplitude. Notice that there is a factor of 2 in the exponents of the two exponentials.

8.10 FORCEDOSCILLATIONS AND RESONANCE

A person swinging in a swing without anyone pushing it or a simple pendulum, displaced and released, are examples of free oscillations. In both the cases, the amplitude of swing will gradually decrease and the system would, ultimately, come to a halt. Because of the ever-present dissipative forces, the free oscillations cannot be sustained in practice. They get damped as seen in section 8.9. However, while swinging in a swing if you apply a push periodically by pressing your feet against the ground, you find that not only the oscillations can now be maintained but the amplitude can also be increased. Under this condition the swing has **forced,** or **driven, oscillations**. In case of a system executing driven oscillations under the action of a harmonic force, two angular frequencies are important: (1) **the natural** angular frequency ω of the system, which is the angular frequency at which it will oscillate if it were displaced from equilibrium position and then left to oscillate freely, and (2) the angular frequency ω of the external force causing the driven oscillations.

Suppose an external force $F(t)$ of amplitude F_0 that varies periodically with time is applied to a damped oscillator. Such a force can be represented as,

$$F(t) = F_0 \cos \omega t_d \qquad (8.36)$$

The motion of a particle under the combined action of a linear restoring force, damping force and a time dependent driving force represented by Eq. (8.36) is given by,

$$m\,a(t) = -k\,x(t) - bv(t) + F_0 \cos \omega t_d \qquad (8.37a)$$

Substituting d^2x/dt^2 for acceleration in Eq. (8.37a) and rearranging it, we get

$$m\frac{d_x^2}{dt^2} + b\ \frac{dx}{dt} + \ kx + F_0 \cos \omega t_d \qquad (8.37b)$$

This is the equation of an oscillator of mass m on which a periodic force of (angular) frequency ω

is applied. The oscillator initially oscillates with its natural frequency ω. When we apply the external periodic force, the oscillations with the natural frequency die out, and then the body oscillates with the (angular) frequency of the external periodic force. Its displacement, after the natural oscillations die out, is given by

$$x(t) = A\cos(\omega t_d + \varphi) \qquad (8.38)$$

where t is the time measured from the moment when we apply the periodic force.

The amplitude A is a function of the forced frequency ω_d and the natural frequency ω. Analysis shows that it is given by

$$A = \frac{F}{m_d^2 + b^{\frac{1}{2}}} \qquad (8.39a)$$

$$Tan\,\varphi = -\frac{v_0}{\omega_d x_o} \qquad (8.39b)$$

where m is the mass of the particle and v_0 and $x_0$are the velocity and the displacement of the particle at time $t = 0$, which is the moment when we apply the periodic force. Equation (8.39) shows that the amplitude of the forced oscillator depends on the (angular) frequency of the driving force. We can see a different behavior of the oscillator when ω is far from ω and when it is close to ω. We consider these two cases.

(a) Small Damping, Driving Frequency far from Natural Frequency : In this case, ωb will be much smaller than $m(\omega^2 - \omega^2_d)$, and we can neglect that term. Then Eq. (8.39) reduces to

$$A = \frac{F}{m_d^2}$$

Figure 8.22 shows the dependence of the displacement amplitude of an oscillator on the angular frequency of the driving force for different amounts of damping present in the system. It may be noted that in all the cases the amplitude is greatest when $\omega_d/\omega = 1$. The curves in this figure show that smaller the damping, the taller and narrower is the resonance peak.

If we go on changing the driving frequency, the amplitude tends to infinity when it equals the natural frequency. But this is the ideal case of zero damping, a case which never arises in a real system as the damping is never perfectly zero. You must have experienced in a swing that when the timing of your push exactly matches with the time period of the swing, your swing gets the maximum amplitude. This amplitude is large, but not infinity, because there is always some damping in your swing. This will become clear in the (b).

(b) Driving Frequency Close to Natural

ω_d is very close to $m(\omega^2 - \omega^2_d)$ would be much less than ωb, for any reasonable value of b, then Eq.

(8.39) reduces to

$$A = \frac{F}{m_d^2} \qquad (8.40)$$

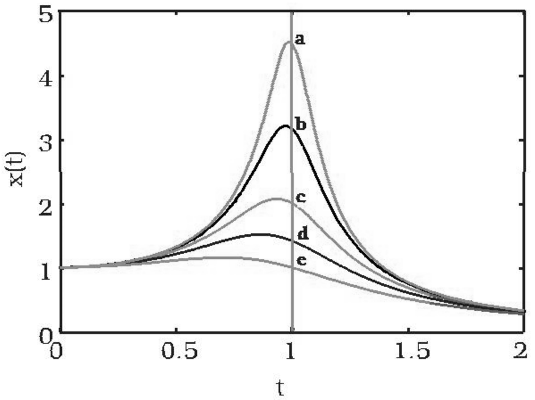


Fig. 8.22 *The amplitude of a forced oscillator as a function of the angular frequency of the driving force. The amplitude is greatest near* $\omega / \omega = 1$*. The five curves correspond to different extents of damping present in the system. Curve* **a** *corresponds to the least damping, and damping goes on increasing successively in curves* ***b, c, d,e****. Notice that the peak shifts to the left with increasing b.*

This makes it clear that the maximum possible amplitude for a given driving frequency is governed by the driving frequency and the damping, and is never infinity. The phenomenon of increase in amplitude when the driving force is close to the natural frequency of the oscillator is called **resonance**.

In our daily life we encounter phenomena which involve resonance. Your experience with swings is a good example of resonance. You might have realised that the skill in swinging to greater heights lies in the synchronisation of the rhythm of pushing against the ground with the natural frequency of the swing.

To illustrate this point further, let us consider a set of five simple pendulums of assorted lengths suspended from a common rope as shown in Fig. 8.23. The pendulums 1 and 4 have the same lengths and the others have different lengths. Now let us set pendulum 1 into motion. The energy from this pendulum gets transferred to other pendulums through the connecting rope and they start oscillating. The driving force is provided through the connecting rope. The frequency of this force is the frequency with which pendulum 1 oscillates. If we observe the response of pendulums 2, 3 and 5, they first start oscillating with their natural frequencies of oscillations and different amplitudes, but this motion is gradually damped and not sustained. Their frequencies of oscillation gradually change and ultimately they oscillate with the frequency of pendulum 1, i.e. the frequency of the driving force but with different amplitudes. They oscillate with small amplitudes. The response of pendulum 4 is in contrast to this set of pendulums. It oscillates with the same frequency as that of pendulum 1 and its amplitude gradually picks up and becomes very large. A resonance-like response is seen. This happens because in this the condition for resonance is satisfied, i.e. the natural frequency of the system coincides with that of the driving force.

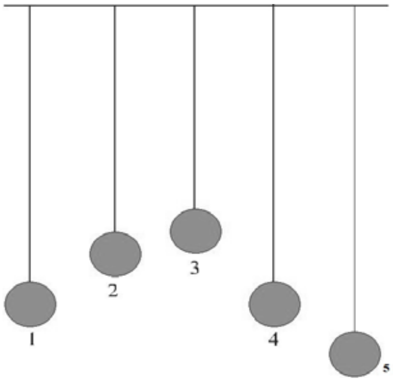


Fig. 8.23 *A system of five simple pendulums suspended from a common rope*

All mechanical structures have one or more natural frequencies, and if a structure is subjected to a strong external periodic driving force that matches one of these frequencies, the resulting oscillations of the structure may rupture it. The Tacoma Narrows Bridge at Puget Sound, Washington, USA was opened on July 1, 1940. Four months later winds produced a pulsating resultant force in resonance with the natural frequency of the structure. This caused a steady increase in the amplitude of oscillations until the bridge collapsed. It is for the same reason the marching soldiers break steps while crossing a bridge. Aircraft designers make sure that none of the natural frequencies at which a wing can oscillate match the frequency of the engines in flight. Earthquakes cause vast devastation. It is interesting to note that sometimes, in an earthquake, short and tall structures remain unaffected while the medium height structures fall down. This happens because the natural frequencies of the short structures happen to be higher and those of taller structures lower than the frequency of the seismic waves.

SUMMARY

1. The motions which repeat themselves are called *periodic motions.*
2. The *period T* is the time required for one complete oscillation, or cycle. It is related to the frequency v by,

   $$T = 1/v$$

   The *frequency* of periodic or oscillatory motion is the number of oscillations per unit time. In the SI, it is measured in hertz:

   $$1 \text{ hertz} = 1 \text{ Hz} = 1 \text{ oscillation per second} = 1\text{s}^{-1}$$

3. In *simple harmonic motion* (SHM), the displacement $x(t)$ of a particle from its equilibrium position is given by,

   $$x(t) = A\cos(\omega t + \varphi) \quad \text{(displacement)},$$

   in which A is the *amplitude* of the displacement, the quantity $(\omega t + \varphi)$ is the phase of the motion, and φ is the *phase constant*. The *angular frequency* ω is related to the period and frequency of the motion by,

   $$\frac{2}{T} \quad 2 \quad \text{(angular frequency)}.$$

4. Simple harmonic motion is the projection of uniform circular motion on the diameter of the circle in which the latter motion occurs.
5. The particle velocity and acceleration during SHM as functions of time are given by,

   $$v(t) = -\omega A\sin(\omega t + \varphi) \quad \text{(velocity)},$$

   $$a(t) = -\omega^2 A\cos(\omega t + \varphi)$$

   Thus we see that both velocity and acceleration of a body executing simple harmonic motion are periodic functions, having the velocity *amplitude* $v_m = \omega A$ and *acceleration amplitude* $a_m = \omega^2 A$, respectively.
6. The force acting simple harmonic motion is proportional to the displacement and is always directed towards the centre of motion.
7. A particle executing simple harmonic motion has, at any time, kinetic energy $K = ½ mv^2$ and potential energy $U = ½ kx^2$. If no friction is present the mechanical

energy of the system, $E = K + U$ always remains constant even though K and U change with time

8. A particle of mass m oscillating under the influence of a Hooke's law restoring force given by $F = -k\,x$ exhibits simple harmonic motion with

$$\omega = \sqrt{\frac{k}{m}}$$

$$T = 2\pi\sqrt{\frac{m}{k}}$$

Such a system is also called a linear oscillator.

9. The motion of a simple pendulum swinging through small angles is approximately simple harmonic. The period of oscillation is given by,

$$T = 2\pi\sqrt{\frac{L}{g}}$$

10. The mechanical energy in a real oscillating system decreases during oscillations because external forces, such as drag, inhibit the oscillations and transfer mechanical energy to thermal energy. The real oscillator and its motion are then said to be *damped*. If the *damping force* is given by $F_d = -bv$, where v is the velocity of the oscillator and b is a *damping constant*, then the displacement of the oscillator is given by,

$$x(t) = A\,e^{-bt/2m}\cos(\omega' t + \varphi)$$

where ω', the angular frequency of the damped oscillator, is given by

$$\omega' = \sqrt{\frac{k}{m} - \frac{b^2}{4m^2}}$$

If the damping constant is small then $\omega' \approx \omega$, where ω is the angular frequency of the undamped oscillator. The mechanical energy E of the damped oscillator is given by

$$E(t) = 1/2\,kA^2\,e^{\,bt/m}$$

11. If an external force with angular frequency ω acts on an oscillating system with natural angular frequency ω, the system oscillates with angular frequency ω . The amplitude of oscillations is the greatest when

$$\omega_d \quad = \omega$$

a condition called *resonance*.

CHAPTER NINE

GRAVITATION

9.1 Introduction

Early in our lives, we become aware of the tendency of all material objects to be attracted towards the earth. Anything thrown up falls down towards the earth, going uphill is lot more tiring than going downhill, raindrops from the clouds above fall towards the earth and there are many other such phenomena. Historically it was the Italian Physicist Galileo (1564-1642) who recognised the fact that all bodies, irrespective of their masses, are accelerated towards the earth with a constant acceleration. It is said that he made a public demonstration of this fact. To find the truth, he certainly did experiments with bodies rolling down inclined planes and arrived at a value of the acceleration due to gravity which is close to the more accurate value obtained later.

A seemingly unrelated phenomenon, observation of stars, planets and their motion has been the subject of attention in many countries since the earliest of times. Observations since early times recognised stars which appeared in the sky with positions unchanged year after year. The more interesting objects are the planets which seem to have regular motions against the background of stars. The earliest recorded model for planetary motions proposed by Ptolemy about 2000 years ago was a 'geocentric' model in which all celestial objects, stars, the sun and the planets, all revolved around the earth. The only motion that was thought to be possible for celestial objects was motion in a circle. Complicated schemes of motion were put forward by Ptolemy in order to describe the observed motion of the planets. The planets were described as moving in circles with the center of the circles themselves moving in larger circles. Similar theories were also advanced by Indian astronomers some 400 years later. However a more elegant model in which the Sun was the center around which the planets revolved – the 'heliocentric' model – was already mentioned by Aryabhatta (5th century A.D.) in his treatise. A thousand years later, a Polish monk named Nicolas Copernicus (1473-1543) proposed a definitive model in which the planets moved in circles around a fixed central sun. His theory was discredited by the church, but notable amongst its supporters was Galileo who had to face prosecution from the state for his beliefs.

It was around the same time as Galileo, a nobleman called Tycho Brahe (1546-1601) hailing from Denmark, spent his entire lifetime recording observations of the planets with the naked eye. His compiled data were analysed later by his assistant Johannes Kepler (1571-1640). He could extract from the data three elegant laws that now go by the name of Kepler's laws. These laws were known to Newton and enabled him to make a great scientific leap in proposing his universal law of gravitation.

9.2 Kepler's Laws

The three laws of Kepler can be stated as follows:

1. **Law of orbits:** All planets move in elliptical orbits with the Sun situated at one of the foci of the ellipse (Fig. 9.1a). This law was a deviation from the Copernican model which allowed only circular orbits. The ellipse, of which the circle is a special case, is a closed curve which can be drawn very simply as follows.

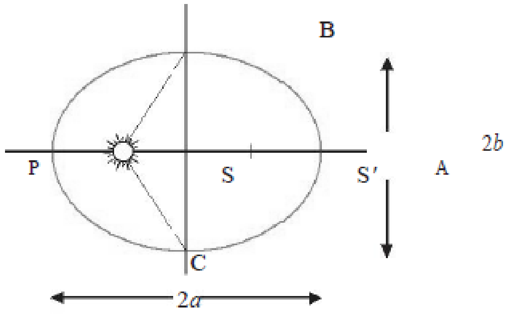


Fig. 9.1(a) *An ellipse traced out by a planet around the sun. The closest point is P and the farthest point is A, P is called the perihelion and A the aphelion. The semi major axis is half the distance AP.*

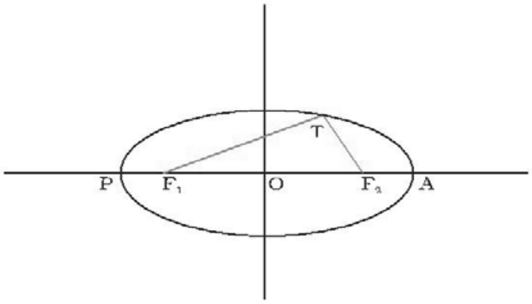


Fig. 9.1(b) *Drawing an ellipse. A string has its ends fixed at F_1 and F_2. The tip of a pencil holds the string taut and is moved around.*

Select two points F_1 and F_2. Take a length of a string and fix its ends at F_1 and F_2 by pins. With the tip of a pencil stretch the string taut and then draw a curve by moving the pencil keeping the string taut throughout. (Fig. 9.1(b)) The closed curve you get is called an ellipse. Clearly for any point T on the ellipse, the sum of the distances from F_1 and F_2 is a constant. F_1, F_2 are called the focii. Join the points F_1 and F_2 and extend the line to intersect the ellipse at points P and A as shown in Fig. 9.1(b). The midpoint of the line PA is the centre of the ellipse O and the length PO = AO is called the semi-major axis of the ellipse. For a circle, the two focii merge into one and the semi-major axis becomes the radius of the circle.

2. Law of areas: The line that joins any planet to the sun sweeps equal areas in equal intervals of time (Fig. 9.2). This law comes from the observations that planets appear to move slower when they are farther from the sun than when they are nearer.

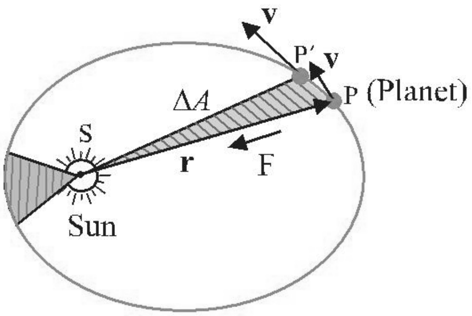


Fig. 9.2 *The planet P moves around the sun in an elliptical orbit. The shaded area is the area A swept out in a small interval of time*

3. Law of periods: The square of the time period of revolution of a planet is proportional to the cube of the semi-major axis of the ellipse traced out by the planet.

The table below gives the approximate time periods of revolution of nine planets around the sun along with values of their semi-major axes

Table 1 Data from measurement of planetary motions given below confirm Kepler's Law of Periods

a ≡ Semi-major axis in units of 1010 m.

T ≡ Time period of revolution of the planet in years(y).

Q ≡ The quotient (T^2/a^3) in units of 10^{-34} S^2 $m^{-3.}$

Table 1 Data from measurement of planetary motions given below confirm Kepler's Law of Periods

Planet	**a**	**T**	**Q**
Mercury	5.79	0.24	2.95
Venus	10.8	0.615	3.00
Earth	15.0	1	2.96
Mars	22.8	1.88	2.98
Jupiter	77.8	11.9	3.01
Saturn	143	29.5	2.98
Uranus	287	84	2.98
Neptune	450	165	2.99
Pluto	590	248	2.99
Mars	22.8	1.88	2.98
Jupiter	77.8	11.9	3.01

The law of areas can be understood as a consequence of conservation of angular momentum which is valid for any central force. A central force is such that the force on the planet is along the vector joining the sun and the planet. Let the sun be at the origin and let the position and momentum of the planet be denoted by r and p respectively. Then the area swept out by the planet of mass m in time interval t is (Fig. 9.2) A given by

$$\Delta \mathrm{A} = \frac{1}{2}(\mathrm{r \; x \; vt}) \qquad (9.1)$$

Hence $\frac{\Delta \mathrm{A}}{\mathrm{t}} = \frac{1}{2} \; \frac{\mathrm{r \; x \; p}}{\mathrm{m}}$ since (v = p/m)

$$= \frac{L}{2m} \qquad (9.2)$$

where v is the velocity, **L** is the angular momentum equal to (**r** × **p**). For a central force, which is directed along **r**, **L** is a constant as the planet goes around. Hence, **∆A/∆t** is a constant according to the last equation. This is the law of areas. Gravitation is a central force and hence the law of areas follows.

Example 9.1 Let the speed of the planet at the perihelion P in Fig. 9.1(a) be v_P and the Sun-planet distance SP be r_P. Relate $\{r_P, v_P\}$ to the corresponding quantities at the aphelion $\{r_A, v_A\}$. Will the planet take equal times to traverse BAC and CPB?

Answer The magnitude of the angular momentum at P is $L_p = m_p r_p v_p$, since inspection tells us that rp and vp are mutually perpendicular. Similarly, $LA = m_p r_A v_A$. From angular momentum conservation

$$m_p\ r_p\ v_p = m_p\ r_A\ v_A$$

$$\text{or}\ \ (v_p/v_A) = (r_A/r_p)$$

$$\text{Since } r_A > r_p,\ v_p > v_A\ .$$

The area SBAC bounded by the ellipse and the radius vectors SB and SC is larger than SBPC in Fig. 9.1. From Kepler’s second law, equal areas are swept in equal times. Hence the planet will take a longer time to traverse BAC than CPB.

9.3 UNIVERSAL LAW OF GRAVITATION

Legend has it that observing an apple falling from a tree, Newton was inspired to arrive at an universal law of gravitation that led to an explanation of terrestrial gravitation as well as of Kepler’s laws. Newton’s reasoning was that the moon revolving in an orbit of radius Rm was subject to a centripetal acceleration due to earth’s gravity of magnitude

$$a_m = \frac{V^2}{R_m} = \frac{4\pi^2 R_m}{T^2} \qquad (9.3)$$

where V is the speed of the moon related to the time period T by the relation $V = \frac{2\pi\, R_m}{T}$. The time period T is about 27.3 days and R_m was already known then to be about 3.84 × 108 m. If we substitute these numbers in equation (9.3), we get a value of am much smaller than the value of acceleration due to gravity g on the surface of the earth, arising also due to earth's gravitational attraction.

Central Forces

We know the time rate of change of the angular momentum of a single particle about the origin is $\frac{dl}{dt} = r \times F$.

The angular momentum of the particles is conserved. If the torque = r x F due to the force F on it vanishes. This happens either when F is zero or when F is along r. We are interested in forces which satisfy the latter condition. Central forces satisfy this condition. A central force is always directed towards or away from a fixed point. i.e. along the position vector of the point of application of the force with respect to the fixed point. (See figure below.) Further, the magnitude of a central force F depends on r, the distance of the point of application of the force from the fixed point: F= F(*r*).

In the motion under a central force the angular momentum is always conserved. Two important results follow from this:

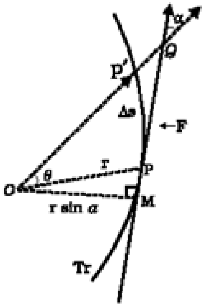
(1) The motion of a particle under the central force is always confined to plane.

(2) The position vector of the particle with respect to the centre of the force (i.e. the fixed point) has a constant areal velocity. In other words the position vector sweeps out equal areas in equal times as the particle moves under the influence of the central force.

Try to prove both these results. You may need to know that the areal velocity is given by:

$$\frac{dA}{dt} = \frac{1}{2} rv \sin\alpha$$

An immediate application of the above discussion can be made to the motion of a planet under the gravitational force of the sun. For convenience the sun may be taken to be so heavy that it is at rest. The gravitational force of the sun on the planet is directed towards the sun. This force also satisfies the requirement F=F(r), since $F = G\, m_1 m_2/r^2$ when m_1 and m_2 are respectively the masses of the planet and the sun and G is the universal constant of gravitation. The two results (1) and (2) described above. Therefore apply to the motion of the planet. In fact the result (2) is the well - known second law of Kepler.



Tr is the trajectory of the particle under the central force. At a position P, the force is direct along OP, O is the centre of the force taken as the origin. In time Δt, the particle moves from P to P\` arc PP\` = Δs = vΔt. The tangent PQ at P to the trajectory gives the direction of the velocity at P. The area swept in Δt is the area of sector

POP\` = (r sin α) PP\`/2 = (rv sin α) Δt/2).

This clearly shows that the force due to earth's gravity decreases with distance. If one assumes that the gravitational force due to the earth decreases in of the earth, we will proportion to the inverse square of the distance from the center have $a_m \, \alpha \, R_m^{-2}$; g α R_E^{-2} and we get

$$\frac{g}{a_m} = \frac{R_m^2}{R_E^2} \, ; 3600 \tag{9.4}$$

in agreement with a value of g; 9.8 m s^{-2} and the value of am from Eq. (9.3). These observations led Newton to propose the following Universal Law of Gravitation:

Everybody in the universe attracts every other body with a force which is directly proportional to the product of their masses and inversely proportional to the square of the distance between them. The quotation is essentially from Newton's famous treatise called 'Mathematical Principles of Natural Philosophy' (Principia for short).

Stated Mathematically, Newton's gravitation law reads: The force F on a point mass m2 due to another point mass m1 has the magnitude

$$|F| = G\frac{m_1 m_2}{r^2} \tag{9.5}$$

Equation (9.5) can be expressed in vector form as

$$F = G\frac{m_1 m_2}{r^2}\ (-\hat{r}) = -G\frac{m_1 m_2}{r^2}\ (\hat{r})$$

$$= \ -G\ \frac{m_1 m_2}{|r|^3}\hat{r}$$

where G is the universal gravitational constant,$\hat{r}$ is the unit vector from m_1 to m_2 and $r = r_2 - r_1$ as shown in Fig. 9.3.

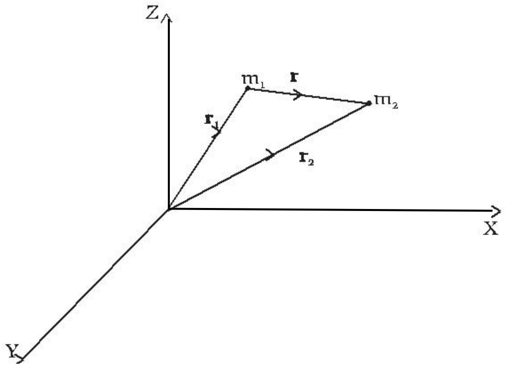


Fig. 9.3 *Gravitational force on* m_1 *due to* m_2*is along r where the vector r is* $(r_2 – r_1)$.

The gravitational force is attractive, i.e., the force F is along – r. The force on point mass m_1 due to m_2 is of course – F by Newton’s third law. Thus, the gravitational force F_{12} on the body 1 due to 2 and F_{21} on the body $_2$ due to $_1$ are related as $F_{12} = – F_{21}$.

Before we can apply Eq. (9.5) to objects under consideration, we have to be careful since the law refers to point masses whereas we deal with extended objects which have finite size. . If we have a collection of point masses, the force on any one of them is the vector sum of the gravitational forces exerted by the other point masses as shown in Fig 9.4.

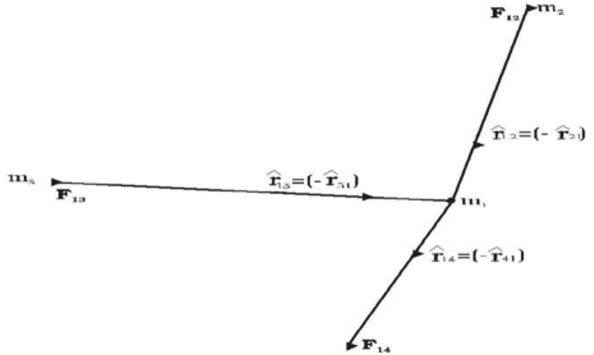


Fig. 9.4 *Gravitational force on point mass* m_1*is the vector sum of the gravitational forces exerted by* m_2, m_3 *and* m_4.

$$F_1 = G\frac{m_2 m_1}{r_{21}^2}\,\hat{r}_{21} + G\frac{m_3 m_1}{r_{31}^2}\,\hat{r}_{31} + G\frac{m_4 m_1}{r_{41}^2}\,\hat{r}_{41}$$

Example 9.4 (a) What is the force acting on a mass 2m placed at the centroid G of the triangle? (b) What is the force if the mass at the vertex A is doubled?

Take AG = BG = CG = 1m (see Fig. 9.5)

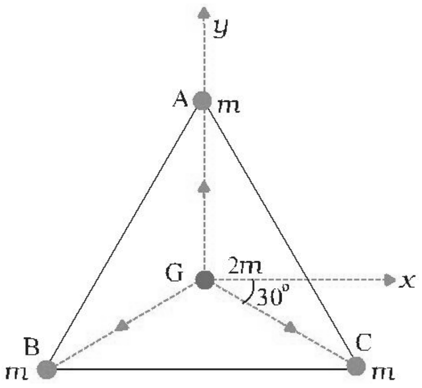


Fig. 9.5 *Three equal masses are placed at the three vertices of the ABC. A mass 2m is placed at the centroid G.*

Answer (a) The angle between GC and the positive *x*-axis is 30° and so is the angle between GB and the negative *x*-axis. The individual forces in vector notation are

$$F_{GA} = \frac{Gm\,(2m)}{1}\,\hat{j}$$

$$F_{GB} = \frac{Gm\,(2m)}{1}\,(-\hat{\imath}\cos 30° - \hat{j}\sin 30°)$$

$$F_{GC} = \frac{Gm\,(2m)}{1}\,(-\hat{\imath}\cos 30° - \hat{j}\sin 30°)$$

From the principle of superposition and the law of vector addition, the resultant gravitational force $\mathbf{F}_R$ on (2*m*) is

$F_R = F_{GA} + F_{GB} + F_{GC}$

$F_R = 2Gm^2\,\hat{j} + 2Gm^2\,(-\,\hat{\imath}\cos 30° -\,\hat{j}\sin 30°) + 2Gm^2\,(-\,\hat{\imath}\cos 30° -\,\hat{j}\sin 30°)$

Alternatively, one expects on the basis of symmetry that the resultant force ought to be zero.

(b) By symmetry the *x*-component of the force cancels out. The *y*-component survives.

$$\mathbf{F}_R = 4Gm^2\hat{\mathbf{j}} - 2Gm^2\hat{\mathbf{j}} = 2Gm^2\hat{\mathbf{j}}$$

For the gravitational force between an extended object (like the earth) and a point mass, Eq. (8.5) is not directly applicable. Each point mass in the extended object will exert a force on the given point mass and these force will not all be in the same direction. We have to add up these forces vectorially for all the point masses in the extended object to get the total force. This is easily done using calculus. For two special cases, a simple law results when you do that:

(1) The force of attraction between a hollow spherical shell of uniform density and a point mass situated outside is just as if the entire mass of the shell is concentrated at the centre of the shell.

Qualitatively this can be understood as follows: Gravitational forces caused by the various regions of the shell have components along the line joining the point mass to the centre as well as along a direction perpendicular to this line. The components perpendicular to this line cancel out when summing over all regions of the shell leaving only a resultant force along the line joining the point to the centre. The magnitude of this force works out to be as stated above.

(2) The force of attraction due to a hollow spherical shell of uniform density, on a point mass situated inside it is zero.

Qualitatively, we can again understand this result. Various regions of the spherical shell attract the point mass inside it in various directions. These forces cancel each other completely.

Newton’s Principia

Kepler had formulated his third law by 1619. The announcement of the underlying universal law of gravitation came about seventy years later with the publication in 1687 of Newton’s masterpiece **Philosophiae Naturalis Principia Mathematica**, often simply called the **Principia**.

Around 1685, Edmund Halley (after whom the famous Halley’s comet is named), came to visit Newton at Cambridge and asked him about the nature of the trajectory of a body moving under the influence of an inverse square law. Without hesitation Newton replied that it had to be an ellipse, and further that he had worked it out long ago around 1665 when he was forced to retire to his farm house from Cambridge on account of a plague outbreak. Unfortunately, Newton had lost his papers. Halley prevailed upon Newton to produce his work in book form and agreed to bear the cost of publication. Newton accomplished this feat in eighteen months of superhuman effort. The **Principia** is a singular scientific masterpiece and in the words of Lagrange it is “the greatest production of the human mind.” The Indian born astrophysicist and Nobel laureate S. Chandrasekhar spent ten years writing a treatise on the **Principia**. His book, Newton’s **Principia for the Common Reader** brings into sharp focus the beauty, clarity and breath taking economy of Newton’s methods.

9.4 THE GRAVITATIONAL CONSTANT

The value of the gravitational constant G entering the Universal law of gravitation can be determined experimentally and this was first done by English scientist Henry Cavendish in 1798. The apparatus used by him is schematically shown in figure.8.6

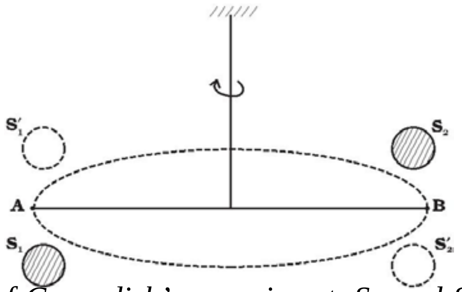


Fig. 9.6 *Schematic drawing of Cavendish’s experiment. S_1 and S_2 are large spheres which are kept on either side (shown shades) of the masses at A or B. When the big spheres are taken to the other side of the masses (shown by dotted circles), the bar AB rotates a little since the torque reverses direction. The angle of rotation can be measured experimentally.*

The bar AB has two small lead spheres attached at its ends. The bar is suspended from a rigid support by a fine wire. Two large lead spheres are brought close to the small ones but on opposite sides as shown. The big spheres attract the nearby small ones by equal and opposite force as shown. There is no net force on the bar but only a torque which is clearly equal to F times the length of the bar, where F is the force of attraction between a big sphere and its neighbouring small sphere. Due to this time as the restoring torque, the suspended wire gets twisted till such time as the restoring of the wire equals the gravitational torque. If θ is the angle of twist of the suspended wire, the restoring torque is proportional to θ, equal to τθ. Where τ is the restoring couple per unit angle of twist. τ can be measured independently e.g. by applying a known torque and measuring the angle of twist. The gravitational force between the spherical balls is the same as if their masses are concentrated at their centers. Thus if d is the separation between the centers of the big and its neighbouring small ball, M and m their masses, the gravitational force between the big sphere and its neighouring small ball is.

$$F = G\frac{Mm}{d^2} \tag{9.6}$$

If L is the length of the bar AB , then the torque arising out of F is F multiplied by L. At equilibrium, this is equal to the restoring torque and hence

$$G\frac{Mm}{d^2}L = T\theta \tag{9.7}$$

Observation of θ thus enables one to calculate G from this equation. Since Cavendish's experiment, the measurement of G has been refined and the currently accepted value is

$$G = 6.67 \times 10^{-11}\ \text{N m}^2/\text{kg}^2 \tag{9.8}$$

9.5 ACCELERATION DUE TO GRAVITY OF THE EARTH

The earth can be imagined to be a sphere made of a large number of concentric spherical shells with the smallest one at the centre and the largest one at its surface. A point outside the earth is obviously outside all the shells. Thus, all the shells exert a gravitational force at the point outside just as if their masses are concentrated at their common centre according to the result stated in the last section. The total mass of all the shells combined is just the mass of the earth. Hence, at a point outside the earth, the gravitational force is just as if its entire mass of the earth is concentrated at its center.

For a point inside the earth, the situation is different. This is illustrated in Fig. 9.7.

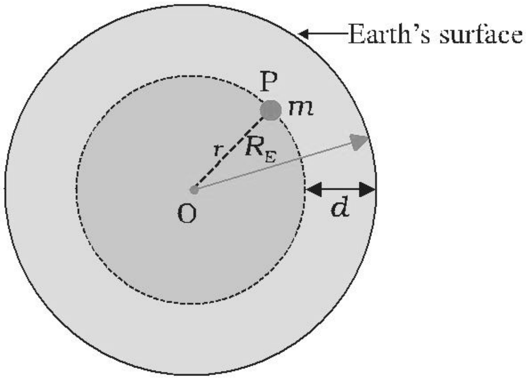


Fig. 9.7 *The mass m is in a mine located at a depth d below the surface of the Earth of mass M_E and radius R_E. We treat the Earth to be spherically symmetric.*

Again consider the earth to be made up of concentric shells as before and a point mass m situated at a distance r from the centre. The point P lies outside the sphere of radius r. For the shells of radius greater than r, the point P lies inside. Hence according to result stated in the last section, they exert no gravitational force on mass *m* kept at P. The shells with radius ≤ r make up a sphere of radius r for which the point P lies on the surface. This smaller sphere therefore exerts a force on a mass m at P as if its mass m_r is concentrated at the center. Thus the force on the mass m at P has a magnitude

$$F = \frac{\mathrm{Gm(m_r)}}{\mathrm{r}^2} \tag{9.9}$$

We assume that the entire earth is of uniform density and hence its mass is

$$M_E = \frac{4\pi}{3} R_E^3\, \rho$$

where M_E is the of the earth R_E is its radius and ρ is the density. On the other hand the mass of the sphere M_r of radius r is $\frac{4\pi}{3}\ \rho r^3$ and hence

$$F = \mathrm{Gm}\left(\frac{4\pi}{3}\rho\right)\frac{r^3}{r^2} = Gm\ \left(\frac{M_E}{R_E^3}\right)\frac{r^3}{r^2}$$

$$= \frac{G\ mM_E}{R_E^3} r \tag{9.10}$$

If the mass m is situated on the surface of earth, then r = R_E and the gravitational force on it is, from Eq. (8.10)

$$F = G\frac{M_E m}{R_E^2} \tag{9.11}$$

The acceleration experienced by the mass *m*, which is usually denoted by the symbol *g* is related to F by Newton's 2nd law by relation F = *mg*. Thus

$$g = \frac{F}{m} = \frac{GM_E}{R_E^2} \tag{9.12}$$

Acceleration *g* is readily measurable. R_E is a known quantity. The measurement of G by Cavendish's experiment (or otherwise), combined with knowledge of *g* and R_E enables one to estimate M_E from Eq. (9.12). This is the reason why there is a popular statement regarding Cavendish: "Cavendish weighed the earth".

9.6 ACCELERATION DUE TO GRAVITY BELOW AND ABOVE THE SURFACE OF EARTH

Consider a point mass *m* at a height *h* above the surface of the earth as shown in Fig. 9.8(a). The radius of the earth is denoted by R_E. Since this point is outside the earth, its distance from the centre of the earth is (R_E+ h).

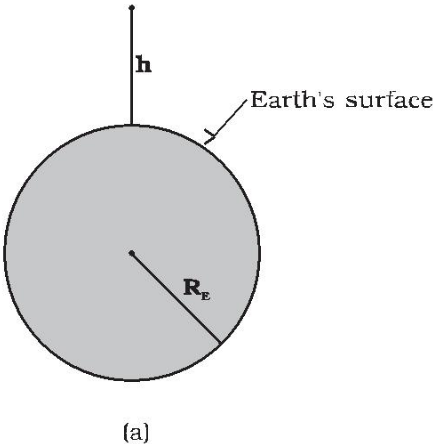


Fig. 9.8 (a) *g at a height h above the surface of the earth.*

If F (h) denoted the magnitude of the force on the point mass m, we get from Eq. (9.5):

$$F(h) = \frac{GM_E m}{(R_E+h)^2} \tag{9.13}$$

The acceleration experienced by the point mass is F(h)/m≡ g(h)

$$g(h) = \frac{F(h)}{m} = \frac{GM_E}{(R_E+h)^2} \qquad (9.14)$$

This is clearly less than the value of g on the surface of the earth: g = $\frac{GM_E}{(R_E)^2}$.

For h<<R_E, we can expand the RHS of Eq. (9.14):

$$g = \frac{GM}{R_E^2\left(1+\frac{h}{R_E}\right)^2} = g\left(1+\frac{h}{R_E}\right)^{-2}(h)$$

For $\frac{h}{R_E} \ll 1$. using binomial expansion

$$g(h) \cong g\left(1-\frac{2h}{R_E}\right) \qquad (9.15)$$

Equation (9.15) thus tells us that for small heights h above the value of g decreases by a factor $(1-2h/R_E)$.

Now, consider a point mass m at a depth d below the surface of the earth (Fig. 9.8(b)), so that its distance from the center of the earth is $(R_E - d)$ as shown in the figure. The earth can be thought of as being composed of a smaller sphere of radius $(R_E - d)$ and a spherical shell of thickness d. The force on m due to the outer shell of thickness d is zero because the result quoted in the previous section. As far as the smaller sphere of radius $(R_E - d)$ is concerned, the point mass is outside it and hence according to the result quoted earlier, the force due to this smaller sphere is just as if the entire mass of the smaller sphere is concentrated at the centre. If M_s is the mass of the smaller sphere, then,

$$M_s / M_E = (R_E - \mathrm{d})^3 / R_E^3 \qquad (9.16)$$

Since mass of a sphere is proportional to be cube of its radius.

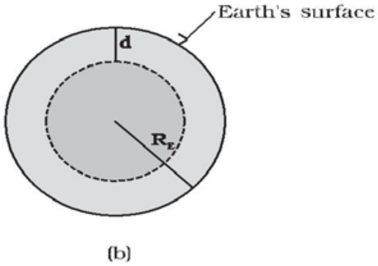


Fig. 9.8 (b) *g at a depth d. In this case only the smaller sphere of radius (R_E –d) contributes to g.*

Thus the force on the point mass is

$$F(d) = G\,M_s\,m\,/\,(R_E\text{-}d)^2 \qquad (9.17)$$

Substituting for M_s from above, we get

$$F(d) = G\,M_s\,m\,/\,(R_E\text{-}d)\,/R_E^3 \qquad (9.18)$$

and hence the acceleration due to gravity at a depth d.

$$g(d) = \frac{F(d)}{m} \text{ is}$$

$$g(d) = \frac{F(d)}{m} = \frac{GM_E}{R_E^3}\,(R_E - d)$$

$$= g\,\frac{R_E - d}{R_E} = g(1 - \frac{d}{R_E}) \qquad (9.19)$$

Thus, as we go down below earth's surface, the acceleration due gravity decreases by a factor $(1-d/R_E)$ The remarkable thing about acceleration due to earth's gravity is that it is maximum on its surface decreasing whether you go up or down.

9.7 GRAVITATIONAL POTENTIAL ENERGY

We had discussed earlier the notion of potential energy as being the energy stored in the body at its given position. If the position of the particle changes on account of forces acting on it, then the change in its potential energy is just the amount of work done on the body by the force. As we had discussed earlier, forces for which the work done is independent of the path are the conservative forces.

The force of gravity is a conservative force and we can calculate the potential energy of a body arising out of this force, called the gravitational potential energy. Consider points close to the surface of earth, at distances from the surface much smaller than the radius of the earth. In such cases, the force of gravity is practically a constant equal to mg, directed towards the center of the earth. If we consider a point at a height h_1 from the surface of the earth and another point vertically above it at a height h_2 from the surface, the work done in lifting the particle of mass m from the first to the second position is denoted by W_{12}

$$W_{12} = \text{Force} \times \text{displacement}$$

$$= mg\,(h_2 - h_1) \qquad (9.20)$$

we associate a potential energy $W(h)$ at a point at a height h above the surface such that

$$W(h) = mgh + W_o \qquad \text{(where } W_o = \text{constant) ;}$$

(9.21)

then it is clear that W_{12} If $= W(h_2) - W(h_1)$ (9.22)

The work done in moving the particle is just the difference of potential energy between its final and initial positions. Observe that the constant W_o cancels out in Eq. (8.22). Setting $h = 0$ in the last equation, we get $W\,(h = 0) = W_o$. $h = 0$ means points on the surface of the earth. Thus, W_o is the potential energy on the surface of the earth.

If we consider points at arbitrary distance from the surface of the earth, the result just derived is not valid since the assumption that the gravitational force mg is a constant is no longer valid. However, from our discussion we know that a point outside the earth, the force of gravitation on a particle directed towards the center of the earth is

$$F = G\,\frac{M_E m}{d^2} \qquad (9.23)$$

where M_E = mass of earth, m = mass of the particle and r its distance from the center of the earth. If we now calculate the work done in lifting a particle from $r = r_1$ to $r = r_2$ ($r_2 > r_1$) along a vertical path, we get instead of Eq. (9.20)

$$W_{12} = \int_{r_1}^{r_2} \left(\frac{GMm}{r^2}\right) dr$$

$$= -GM_E m\left(\frac{1}{r_2} - \frac{1}{r_1}\right) \qquad (9.24)$$

In place of Eq. (9.21), we can thus associate a potential energy $W(r)$ at a distance r, such that

$$W(r) = -\frac{GM_E m}{r} + W_1 \qquad (9.25)$$

valid for $r > R$,

so that once again $W_{12} = W(r_2) - W(r_1)$.

Setting r = infinity in the last equation, we get W (r = infinity) = W_1 . Thus, W_1 is the potential energy at infinity. One should note that only the difference of potential energy between two points has a definite meaning from Eqs. (9.22) and (9.24). One conventionally sets W_1 equal to zero, so that the potential energy at a point is just the amount of work done in displacing the particle from infinity to that point.

We have calculated the potential energy at a point of a particle due to gravitational forces on it due to the earth and it is proportional to the mass of the particle. The gravitational potential due to the gravitational force of the earth is defined as the potential energy of a particle of unit mass at that point. From the earlier discussion, we learn that the gravitational potential energy associated with two particles of masses m_1 and m_2 separated by distance by a distance r is given by

$$V = -G\,\frac{m_1 m_2}{r} \quad \text{(if we choose } V = 0 \text{ as } r \to \infty)$$

It should be noted that an isolated system of particles will have the total potential energy that equals the sum of energies (given by the above equation) for all possible pairs of its constituent particles. This is an example of the application of the superposition principle.

Example 9.3 Find the potential energy of a system of four particles placed at the vertices of a square of side l. Also obtain the potential at the centre of the square.

Answer Consider four masses each of mass mat the corners of a square of side l; See Fig. 8.9.

We have four mass pairs at distance l and two diagonal pairs at distance $\sqrt{2l}$

Hence,

$$W(r) = -4\,\frac{Gm^2}{l} - 2\,\frac{Gm^2}{\sqrt{2l}}$$

$$= -\frac{2Gm^2}{l}\left(2 + \frac{1}{\sqrt{2}}\right) = -5.41\,\frac{Gm^2}{l}$$

The gravitational potential at the centre of the square$(r = \sqrt{2l})/2$ is

$$U(r) = 4\sqrt{2}\,\frac{Gm}{l}$$

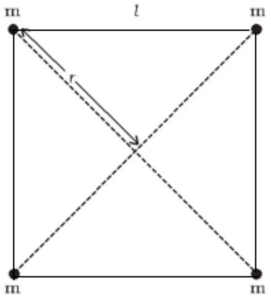


Fig. 9.9

9.8 ESCAPE SPEED

If a stone is thrown by hand, we see it falls back to the earth. Of course using machines we can shoot an object with much greater speeds and with greater and greater initial speed, the object scales higher and higher heights. A natural query that arises in our mind is the following: 'can we throw an object with such high initial speeds that it does not fall back to the earth?'

The principle of conservation of energy helps us to answer this question. Suppose the object did reach infinity and that its speed there was V_f. The energy of an object is the sum of potential and kinetic energy. As before W_1 denotes that gravitational potential energy of the object at infinity. The total energy of the projectile at infinity then is

$$E(\infty) = W_1 + \frac{mV_f^2}{2} \tag{9.26}$$

If the object was thrown initially with a speed V_i from a point at a distance $(h+R_E)$ from the center of the earth (R_E = radius of the earth), its energy initially was

$$E(h + R_E) = \frac{1}{2}mV_i^2 - \frac{GmM_E}{(h+R_E)} + W_1 \tag{9.27}$$

By the principle of energy conservation Eqs. (9.26) and (9.27) must be equal. Hence

$$\frac{mV_i^2}{2} - \frac{GmM_E}{(h+R_E)} = \frac{mV_f^2}{2} \tag{9.28}$$

The R.H.S. is a positive quantity with a minimum value zero hence so must be the L.H.S. Thus, an object can reach infinity as long as V_i is such that

$$\frac{mV_i^2}{2} - \frac{GmM_E}{(h+R_E)} \geq 0 \tag{9.29}$$

The minimum value of V_i corresponds to the case when the L.H.S. of Eq. (9.29) equals zero.

Thus, the minimum speed required for an object to reach infinity (i.e. escape from the earth) corresponds to

$$\frac{1}{2}m(V_i^2)min = \frac{GmM_E}{(h+R_E)} \tag{9.30}$$

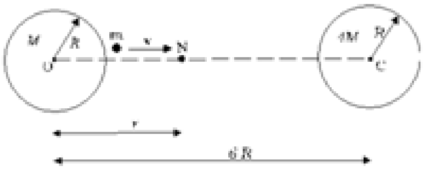
If the object is thrown from the surface of the earth, h=0, and we get

$$(V_i)min = \frac{\sqrt{2GM_E}}{R_E} \tag{9.31}$$

Using the value of g and R_E, numerically $(V_i)_{min} \approx$ 11.2 km/s. This is called the escape speed, sometimes loosely called the escape velocity.

Equation (9.32) applies equally well to an object thrown from the surface of the moon with g replaced by the acceleration due to Moon's gravity on its surface and r_E replaced by the radius of the moon. Both are smaller than their values on earth and the escape speed for the moon turns out to be 2.3 km/s, about five times smaller. This is the reason that moon has no atmosphere. Gas molecules if formed on the surface of the moon having velocities larger than this will escape the gravitational pull of the moon.

Example 9.4 Two uniform solid spheres of equal radii *R*, but mass *M* and 4 *M* have a center to centre separation 6 *R*, as shown in Fig.9.10. The two spheres are held fixed. A projectile of mass *m* is projected from the surface of the sphere of mass *M* directly towards the centre of the second sphere. Obtain an expression for the minimum speed v of the projectile so that it reaches the surface of the second sphere.



Answer The projectile is acted upon by two mutually opposing gravitational forces of the two spheres.

The neutral point N (see Fig.9.10) is defined as the position where the two forces cancel each other exactly. If ON = *r*, we have

$$G\frac{Mm}{r^2} = 4G\frac{Mm}{(6R-r)^2}$$

$$(6R - r)^2 = 4r^2$$

$$6R - r = \pm 2r$$

$$r = 2R \text{ or } -6R.$$

The neutral point $r = -6R$ does not concern us in this example. Thus ON = $r = 2R$. It is sufficient to project the particle with a speed which would enable it to reach N. Thereafter, the greater gravitational pull of $4M$ would suffice. The mechanical energy at the surface of M is

$$E_i = \frac{1}{2}mv^2 - \frac{GMm}{R} - \frac{4GMm}{5R}$$

At the neutral point N, the speed approaches zero. The mechanical energy at N is purely potential.

$$E_N = -\frac{GMm}{R} - \frac{4GMm}{5R}$$

$$\frac{1}{2}mv^2 - \frac{GM}{R} - \frac{4GM}{5R} = -\frac{GM}{2R} - \frac{GM}{R}$$

$$\text{Or } v^2 = \frac{2GM}{R}\left(\frac{4}{5} - \frac{1}{2}\right)$$

$$v = \left(\frac{3GM}{5R}\right)^{\frac{1}{2}}$$

A point to note is that the speed of the projectile is zero at N, but is nonzero when it strikes the heavier sphere 4 M. The calculation of this speed is left as an exercise to the students.

9.9 EARTH SATELLITES

Earth satellites are objects which revolve around the earth. Their motion is very similar to the motion of planets around the Sun and hence Kepler's laws of planetary motion are equally applicable to them. In particular, their orbits around the earth are circular or elliptic. Moon is the only natural satellite of the earth with a near circular orbit with a time period of approximately 27.3 days which is also roughly equal to the rotational period of the moon about its own axis. Since, 1957, advances in technology have enabled many countries including India to launch artificial earth satellites for practical use in fields like telecommunication, geophysics and meteorology.

We will consider a satellite in a circular orbit of a distance ($R_E + h$) from the centre of the earth, where R_E = radius of the earth. If m is the mass of the satellite and V its speed, the centripetal force required for this orbit is

$$F(centripetal) = \frac{mV^2}{(R_E+h)} \tag{9.33}$$

directed towards the center. This centripetal force is provided by the gravitational force, which is

$$F(gravitation) = \frac{GmM_E}{(R_E+h)^2} \tag{9.34}$$

Where M_E is the mass of the earth. Equating R.H.S of Eqs. (9.33) and (9.34) and cancelling out m, we get

$$V^2 = \frac{GM_E}{(R_E+h)} \tag{9.35}$$

Thus V decreases as h increases. From equation (9.35) the speed V for h = 0 is

$$V^2\ (h = 0) = GM/R_E = gR_E \tag{9.36}$$

where we have used the relation $g = GM / R_E^2$. In every orbit, the satellite traverses a distance $2\pi(R_E + h)$ with speed V. It's time period T therefore is

$$T = \frac{2\pi(R_E+h)}{V} = \frac{2\pi(R_E+h)^{\frac{3}{2}}}{\sqrt{GM_E}} \tag{9.37}$$

on substitution of value of V from Eq. (9.35). Squaring both sides of Eq. (9.37), we get

$$T^2 = k\,(R_E + h)^3 \quad (\text{where } k = 4\,\pi^2 / GM_E) \tag{9.38}$$

which is Kepler's law of periods, as applied to motion of satellites around the earth. For a satellite very close to the surface of earth h can be neglected in comparison to R_E in Eq. (9.38). Hence, for such satellites, T is T_o, where

$$T_0 = 2\pi\sqrt{\frac{RE}{g}} \tag{9.39}$$

If we substitute the numerical values g **;** 9.8 m s^{-2} and R_E = 6400 km., we get

$$T_0 = 2\pi\sqrt{\frac{6.4\ x\ 10^6}{9.8}}\ s$$

This is approximately 85 minutes.

Example 9.5 The planet Mars has two moons, phobos and delmos. (i) phobos has a period 7 hours, 39 minutes and an orbital radius of 9.4 x 10^3 km. Calculate the mass of mars. (ii) Assume that earth and mars move in circular orbits around the sun, with the martian orbit being 1.52 times the orbital radius of the earth. What is the length of the martian year in days?

Answer (i) We employ Eq. (9.38) with the sun's mass replaced by the martian mass M_m

$$T^2 = \frac{4\pi^2 R^3}{GM_m}$$

$$M_m = \frac{4\pi^2 R^3}{G\,T^2}$$

$$M_m = \frac{4\times(3.14)^2\times(9.4)^3\times10^{18}}{6.67\times10^{-11}\times(459\times60)^2}$$

$$M_m = \frac{4\times(3.14)^2\times(9.4)^3\times10^{18}}{6.67\times(4.59\times6)\times10^{-5}\,.}$$

$$= 6.48\times10^{23}\text{ kg}$$

(ii) Once again Kepler's third law comes to our aid,

$$\frac{T_M^2}{T_E^2} = \frac{R_{MS}^3}{R_{ES}^3}$$

where R_{MS} is the mars -sun distance and R_{ES} is the earth-sun distance.

T_M = $(1.52)^{3/2}$ × 365 = 684 days

We note that the orbits of all planets except Mercury, Mars and Pluto are very close to being circular. For example, the ratio of the semi-minor to semi-major axis for our Earth is,

$$b/a = 0.99986$$

Example 9.6 Weighing the Earth: You are given the following data: g = 9.81 ms^{-2}, R_E = 6.37 x 10^6 m, the distance to the moon R = 3.84 x 10^8 m and the time period of the moon's revolution is 27.3 days. Obtain the mass of the Earth ME in two different ways.

Answer From Eq. (9.12) we have

$$M_E = \frac{gR_E^2}{G}$$

$$= \frac{9.81 \times \left(6.37 \times 10^{6}\right)^{2}}{6.67 \times 10^{-11}}$$

$$= 5.97 \times 10^{24} \text{ kg.}$$

The moon is a satellite of the Earth. From the derivation of Kepler’s third law [see Eq. (9.38)]

$$T^{2} = \frac{4\pi^{2} R^{3}}{G\, M_{E}}$$

$$M_{E} = \frac{4\pi^{2} R^{3}}{G T^{2}}$$

$$= \frac{4 \times 3.14^{2} \times 3.84^{3} \times 10^{24}}{6.67 \times 10^{-11} \times (27.3 \times 24 \times 60 \times 60)^{2}}$$

$$= 6.02 \times 10^{24} \text{ kg}$$

Both methods yield almost the same answer, the difference between them being less than 1%.

Example 9.7 Express the constant k of Eq. (9.38) in days and kilometers. Given k = 10^{-13} s^{2} m^{-3}. The moon is at a distance of 3.84 x 10^{5} km from the earth. Obtain its time-period of revolution in days.

Answer Given

$$k = 10^{-13}\, s^{2} m^{-3}$$

$$= 10^{-13} \times \frac{1}{(24 \times 60 \times 60)^{2}} \times \frac{1}{(1/1000)^{3} km^{3}}$$

$$= 1.33 \cdot 10^{-14}\, d^{2}\ \ km^{-3}$$

Using Eq. (9.38) and the given value of k the time period of the moon is

$$T^{2} = (1.33 \times 10^{-14})(3.84 \times 10^{5})^{3}$$

$$T = 27.3 \text{ d}$$

Note that Eq. (9.38) also holds for elliptical orbits if we replace ($R_E + h$) by the semi-major axis of the ellipse. The earth will then be at one of the foci of this ellipse.

9.10 ENERGY OF AN ORBITING SATELLITE

Using Eq. (9.35), the kinetic energy of the satellite in a circular orbit with speed v is

$$K.E = \frac{1}{2} m v^{2}$$

$$= \frac{GmM_E}{2(R+h)}, \qquad (9.40)$$

Considering gravitational potential energy at infinity to be zero, the potential energy at distance (R_e+h) from the center of the earth is

$$P.E = \frac{GmM_E}{(R_E+H)} \qquad (9.41)$$

The K.E is positive whereas the P.E is negative. However, in magnitude the K.E. is half the P.E, so that the total E is

$$E = K.E + P.E = \frac{GmM_E}{2(R_E+H)} \qquad (9.42)$$

The total energy of an circularly orbiting satellite is thus negative, with the potential energy being negative but twice is magnitude of the positive kinetic energy.

When the orbit of a satellite becomes elliptic, both the *K.E.* and *P.E.* vary from point to point. The total energy which remains constant is negative as in the circular orbit case. This is what we expect, since as we have discussed before if the total energy is positive or zero, the object escapes to infinity. Satellites are always at finite distance from the earth and hence their energies cannot be positive or zero.

Example 9.8 A 400 kg satellite is in a circular orbit of radius $2R_E$ about the Earth. How much energy is required to transfer it to a circular orbit of radius $4R_E$? What are the changes in the kinetic and potential energies?

Answer Initially

$$E_i = -\frac{GM_E m}{4R_E}$$

While finally

$$E_f = -\frac{GM_E m}{8R_E}$$

The change in the total energy is

$$E = E_f - E_i$$

$$= \frac{GM_E m}{8R_E} = \left(\frac{GM_E}{R_E^2}\right)\frac{mR_E}{8} E = \frac{gmR_E}{8} = \frac{9.81\times400\times6.37\times10^6}{8} = 3.13\times10^9 J$$

The kinetic energy is reduced and it mimicsΔE, namely $\Delta K = K_f - K_i = -3.13 \times 10^9$ J

The change in the potential energy is twice the change in the total energy, namely

$$\Delta V = V_f - V_i = 6.25 \text{ x } 10^9 \text{ J}$$

9.11 GEOSTATIONARY AND POLAR SATELLITES

An interesting phenomenon arises if in we arrange the value of (R + h) such that T in Eq. (9.37) becomes equal to 24 hours. If the circular orbit is in the equatorial plane of the earth, such a satellite, having the same period as the period of rotation of the earth about its own axis would appear stationery viewed from a point on earth. The (R_E+ h) for this purpose works out to be large as compared to R_E:

$$R_E + H = \left(\frac{T^2 G M_E}{4\pi^2}\right)^{1/3} \qquad (9.43)$$

And for T = 24 hours, h works out to be 35800 km.

Which is much larger than Re. Sattelites in a circular orbits and the earth in the equatorial plane with T = 24 hours are called Geostationery Satellites. Clearly, since the earth rotates with the same period, the satellite would appear fixed from any point on earth. It takes very powerful rockets to throw up a satellite to such large heights above the earth but this has been done in view of the several benefits of many practical applications.

India’s Leap into Space

India entered the space age with the launching of the low orbit satellite Aryabhatta in 1975. In the first few years of its programme the launch vehicles were provided by the erstwhile Soviet Union. Indigenous launch vehicles were employed in the early 1980’s to send the Rohini series of satellites into space. The programme to send polar satellites into space began in late 1980’s. A series of satellites labelled IRS (Indian Remote Sensing Satellites) have been launched and this programme is expected to continue in future. The satellites have been employed for surveying, weather prediction and for carrying out experiments in space. The INSAT (Indian National Satellite) series of satellites were designed and made operational for communications and weather prediction purposes beginning in 1982. European launch vehicles have been employed in the INSAT series. India tested its geostationary launch capability in 2001 when it sent an experimental communications satellite (GSAT-1) into space. In 1984 Rakesh Sharma became the first Indian astronaut. The Indian Space Research Organisation (ISRO) is the umbrella organisation that runs a number of centre. Its main lauch centre at Sriharikota (SHAR) is 100 km north of Chennai. The National Remote Sensing Agency (NRSA) is near Hyderabad. Its national centre for research in space and allied sciences is the Physical

Research Laboratory (PRL) at Ahmedabad.

It is known that electromagnetic waves above a certain frequency are not reflected from ionosphere. Radio waves used for radio broadcast which are in the frequency range 2 MHz to 10 MHz, are below the critical frequency. They are therefore reflected by the ionosphere. Thus radio waves broadcast from an antenna can be received at points far away where the direct wave fail to reach on account of the curvature of the earth. Waves used in television broadcast or other forms of communication have much higher frequencies and thus cannot be received beyond the line of sight. A Geostationery satellite, appearing fixed above the broadcasting station can however receive these signals and broadcast them back to a wide area on earth. The INSAT group of satellites sent up by India are one such group of Geostationary satellites widely used for telecommunications in India.

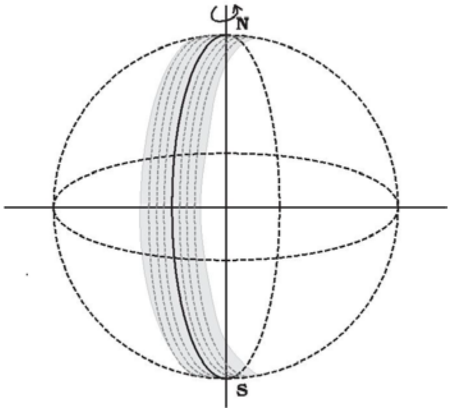


Fig. 9.11 *A Polar satellite. A strip on earth's surface (shown shaded) is visible from the satellite during one cycle. For the next revolution of the satellite, the earth has rotated a little on its axis so that an adjacent strip becomes visible.*

Another class of satellites are called the Polar satellites (Fig. 9.11). These are low altitude (hl 500 to 800 km) satellites, but they go around the poles of the earth in a north-south direction whereas the earth rotates around its axis in an east-west direction. Since its time period is around 100 minutes it crosses any altitude many times a day. However, since its height h above the earth is about 500-800 km, a camera fixed on it can view only small strips of the earth in one orbit. Adjacent strips are viewed in the next orbit, so that in effect the whole earth can be viewed strip by strip during the entire day. These satellites can view polar and equatorial regions at close distances with good resolution. Information gathered from such satellites is extremely useful for remote sensing, meterology as well as for environmental studies of the earth.

9.12 WEIGHTLESSNESS

Weight of an object is the force with which the earth attracts it. We are conscious of our own weight when we stand on a surface, since the surface exerts a force opposite to our weight to keep us at rest. The same principle holds good when we measure the weight of an object by a spring balance hung from a fixed point e.g. the ceiling. The object would fall down unless it is subject to a force opposite to gravity. This is exactly what the spring exerts on the object. This is because the spring is pulled down a little by the gravitational pull of the object and in turn the spring exerts a force on the object vertically upwards.

Now, imagine that the top end of the balance is no longer held fixed to the top ceiling of the room. Both ends of the spring as well as the object move with identical acceleration g. The spring is not stretched and does not exert any upward force on the object which is moving down with acceleration g due to gravity. The reading recorded in the spring balance is zero since the spring is not stretched at all. If the object were a human being, he or she will not feel his weight since there is no upward force on him. Thus, when an object is in free fall, it is weightless and this phenomenon is usually called the phenomenon of weightlessness.

In a satellite around the earth, every part and parcel of the satellite has an acceleration towards the center of the earth which is exactly the value of earth’s acceleration due to gravity at that position. Thus in the satellite everything inside it is in a state of free fall. This is just as if we were falling towards the earth from a height. Thus, in a manned satellite, people inside experience no gravity. Gravity for us defines the vertical direction and thus for them there are no horizontal or vertical directions, all directions are the same. Pictures of astronauts floating in a satellite reflect show this fact.

SUMMARY

1. Newton's law of universal gravitation states that the gravitational force of attraction between any two particles of masses m_1 and m_2 separated by a distance r has the magnitude

$$F = \frac{Gm_1m_2}{r^2}$$

where G is the universal gravitational constant, which has the value 6.672×10^{-11} N m^2 kg^{-2}.

2. If we have to find the resultant gravitational force acting on the particle m due to a number of masses M_1, M_2, ….M_n etc., we use the principle of superposition. Let F_1, F_2, ….F_n be the individual forces due to M_1, M_2, ….M_n, each given by the law of gravitation. From the principle of superposition each force acts independently and uninfluenced by the other bodies.

The resultant force F_R is then found by vector addition

$$F_R = F_1 + F_2 + \ldots\ldots + F_n = \sum_{i=1}^{n} \boldsymbol{F_i}$$

where the symbol 'Σ' stands for summation.

3. Kepler's laws of planetary motion state that

(a) All planets move in elliptical orbits with the Sun at one of the focal points

(b) The radius vector drawn from the sun to a planet sweeps out equal areas in equal time intervals. This follows from the fact that the force of gravitation on the planet is central and hence angular momentum is conserved.

(c) The square of the orbital period of a planet is proportional to the cube of the semi-major axis of the elliptical orbit of the planet.

The period T and radius R of the circular orbit of a planet about the Sun are related by

$$T^2 = \left(\frac{4\pi^2}{GM_s}\right)R^3$$

where M_s is the mass of the Sun. Most planets have nearly circular orbits about the Sun. For elliptical orbits, the above equation is valid if R is replaced by the semi-major axis, a.

4. The acceleration due to gravity.

   (a) at a height h above the Earth's surface

$$g(h) = \frac{GM_E}{(R_E+h)^2}$$

$$\approx \frac{GM_E}{R_E^2}\left[1-\frac{2h}{R_E}\right] \quad \text{for h} \ll R_E$$

$$\text{g(h)} = g(0)\left[1-\frac{2h}{R_E}\right] \quad \text{where } g(0) = \frac{GM_E}{(R_E)^2}$$

   (b) at depth d below the earth surface

$$g(d) = \frac{GM_E}{R_E^2}\left[1-\frac{d}{R_E}\right] = g(0)\left[1-\frac{d}{R_E}\right]$$

5. The gravitational force is a conservative force, and therefore a potential energy function can be defined. The *gravitational potential energy* associated with two particles separated by a distance r is given by

$$V = -\frac{Gm_1m_2}{r}$$

   where V is taken to be zero at $r \to \infty$. The total potential energy for a system of particles is the sum of energies for all pairs of particles, with each pair represented by a term of the form given by above equation. This prescription follows from the principle of superposition.

6. If an isolated system consists of a particle of mass m moving with a speed v in the vicinity of a massive body of mass M, the total mechanical energy of the particle is given by

$$E = \frac{1}{2}mv^2 - \frac{GMm}{r}$$

   That is, the total mechanical energy is the sum of the kinetic and potential energies. The total energy is a constant of motion.

7. If m moves in a circular orbit of radius a about M, where $M >> m$, the total energy of the system is

$$E = -\frac{GMm}{2a}$$

with the choice of the arbitrary constant in the potential energy given in the point 5., above. The total energy is negative for any bound system, that is, one in which the orbit is closed, such as an elliptical orbit. The kinetic and potential energies are

$$K = \frac{GMm}{2a}$$

$$V = \frac{GMm}{a}$$

8. The escape speed from the surface of the Earth is

$$V_e = \sqrt{\frac{2GM_E}{R_E}} = \sqrt{2gR_E}$$

and has a value of 11.2 km s^{-1}.

9. If a particle is outside a uniform spherical shell or solid sphere with a spherically symmetric internal mass distribution, the sphere attracts the particle as though the mass of the sphere or shell were concentrated at the centre of the sphere.

10. If a particle is inside a uniform spherical shell, the gravitational force on the particle is zero. If a particle is inside a homogeneous solid sphere, the force on the particle acts toward the centre of the sphere. This force is exerted by the spherical mass interior to the particle.

11. A geostationary (geosynchronous communication) satellite moves in a circular orbit in the equatorial plane at a approximate distance of 4.22×10^{4} km from the Earth's centre.

Physical Quantity	Symbol	Dimensions	Units	Remarks
Gravitational constant	G	$[M^{-1}L^{3}T^{-2}]$	$Nm^{2}kg^{-2}$	6.67×10^{-11}
Gravitational Potential Energy	V(r)	$[ML^{2}T^{-2}]$	J	$-\frac{GMm}{r}$
Gravitational Potential	U(r)	$[L^{2}T^{-3}]$	JKg^{-1}	$\frac{GM}{r}$
Gravitational Intensity	E or g	$[LT^{-2}]$	Ms^{-2}	$\frac{GM}{r^2}\hat{r}$

CHAPTERTEN

MECHANICAL PROPERTIES OF SOLIDS

10.1 INTRODUCTION

In Chapter 7, we studied the rotation of the bodies and then realised that the motion of a body depends on how mass is distributed within the body. We restricted ourselves to simpler situations of rigid bodies. A rigid body generally means a hard solid object having a definite shape and size. But in reality, bodies can be stretched, compressed and bent. Even the appreciably rigid steel bar can be deformed when a sufficiently large external force is applied on it. This means that solid bodies are not perfectly rigid.

A solid has definite shape and size. In order to change (or deform) the shape or size of a body, a force is required. If you stretch a helical spring by gently pulling its ends, the length of the spring increases slightly. When you leave the ends of the spring, it regains its original size and shape. The property of a body, by virtue of which it tends to regain its original size and shape when the applied force is removed, is known as **elasticity** and the deformation caused is known as **elastic** deformation. However, if you apply force to a lump of putty or mud, they have no gross tendency to regain their previous shape, and they get permanently deformed. Such substances are called **plastic** and this property is called **plasticity.** Putty and mud are close to ideal plastics.

The elastic behaviour of materials plays an important role in engineering design. For example, while designing a building, knowledge of elastic properties of materials like steel, concrete etc. is essential. The same is true in the design of bridges, automobiles, ropeways etc. One could also ask — can we design an aeroplane which is very light but sufficiently strong? Can we design an artificial limb which is lighter but stronger? Why does a railway track have a particular shape like **I**? Why is glass brittle while brass is not? Answers to such questions begin with the study of how relatively simple kinds of loads or forces act to deform different solids bodies. In this chapter, we shall study the elastic behaviour and mechanical properties of solids which would answer many such questions.

10.2 ELASTIC BEHAVIOUR OF SOLIDS

We know that in a solid, each atom or molecule is surrounded by neighbouring atoms or molecules. These are bonded together by interatomic or intermolecular forces and stay in a stable equilibrium position. When a solid is deformed, the atoms or molecules are displaced from their equilibrium positions causing a change in the interatomic (or intermolecular) distances. When the deforming force is removed, the interatomic forces tend to drive them back to their original positions. Thus the body regains its original shape and size. The restoring mechanism can be visualised by taking a model of spring-ball system shown in the Fig. 10.1. Here the balls represent atoms and springs represent interatomic forces.

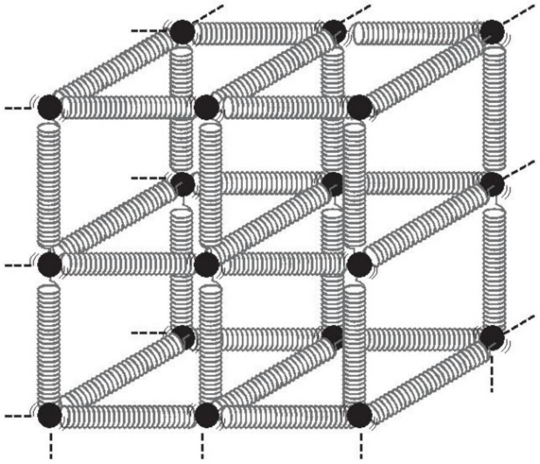


Fig.10.1 *Spring-ball model for the illustration of elastic behaviour of solids*

If you try to displace any ball from its equilibrium position, the spring system tries to restore the ball back to its original position. Thus elastic behaviour of solids can be explained in terms of microscopic nature of the solid. Robert Hooke, an English physicist (1635 - 1703 A.D) performed experiments on springs and found that the elongation (change in the length) produced in a body is proportional to the applied force or load. In 1676, he presented his law of elasticity, now called Hooke’s law.

We shall study about it in Section 10.4. This law, like Boyle’s law, is one of the earliest quantitative relationships in science. It is very important to know the behaviour of the materials under various kinds of load from the context of engineering design.

10.3 STRESS AND STRAIN

When a force is applied on body, it is deformed to a small or large extent depending upon the nature of the material of the body and the magnitude of the deforming force. The deformation may not be noticeable visually in many materials but it is there. When a body is subjected to a deforming force, a restoring force is developed in the body. This restoring force is equal in magnitude but opposite in direction to the applied force. The restoring force per unit area is known as **stress.** If F is the force applied and A is the area of cross section of the body,

$$\text{Magnitude of the stress} = F/A \qquad (10.1)$$

The SI unit of stress is N m^{-2} or pascal (Pa) and its dimensional formula is [ML^{-1}T^{-2}].

There are three ways in which a solid may change its dimensions when an external force acts on it. These are shown in Fig. 10.2. In Fig.10.2(a), a cylinder is stretched by two equal forces applied normal to its cross-sectional area. The restoring force per unit area in this case is called **tensile stress**. If the cylinder is compressed under the action of applied forces, the restoring force per unit area is known as **compressive stress**. Tensile or compressive stress can also be termed as longitudinal stress.

$$\text{Longitudinal strain} = \frac{L}{L} \qquad (10.2)$$

However, if two equal and opposite deforming forces are applied parallel to the cross-sectional area of the cylinder, as shown in Fig. 10.2(b), there is relative displacement between the opposite faces of the cylinder. The restoring force per unit area developed due to the applied tangential force is known as **tangential** or **shearing stress**.

Robert Hooke (1635 – 1703 A.D.)

Robert Hooke was born on July 18, 1635 in Freshwater, Isle of Wight. He was one of the most brilliant and versatile seventeenth century English scientists. He attended Oxford University but never graduated. Yet he was an extremely talented inventor, instrument-maker and building designer. He assisted Robert Boyle in the construction of Boylean air pump. In 1662, he was appointed as Curator of Experiments to the newly founded Royal Society. In 1665, he became Professor of Geometry in Gresham College where he carried out his astronomi-cal observations. He built a Gregorian reflecting telescope; discovered the fifth star in the trapezium and an asterism in the constellation Orion; suggested that Jupiter rotates on its axis; plotted detailed sketches of Mars which were later used in the 110th century to determine the planet's rate of rotation; stated the inverse square law to describe planetary motion, which Newton modified later etc. He was elected Fellow of Royal Society and also served as the Society's Secretary from 1667 to 1682. In his series of observations presented in Micrographia, he suggested wave theory of light and first used the word 'cell' in a biological context as a result of his studies of cork.

> Robert Hooke is best known to physicists for his discovery of law of elasticity: **Ut tensio, sic vis** (This is a Latin expression and it means as the distortion, so the force). This law laid the basis for studies of stress and strain and for understanding the elastic materials.

As a result of applied tangential force, there is a relative displacement *x* between opposite faces of the cylinder as shown in the Fig. 10.2(b). The strain so produced is known as **shearing strain** and it is defined as the ratio of relative displacement of the faces *x* to the length of the cylinder *L*.

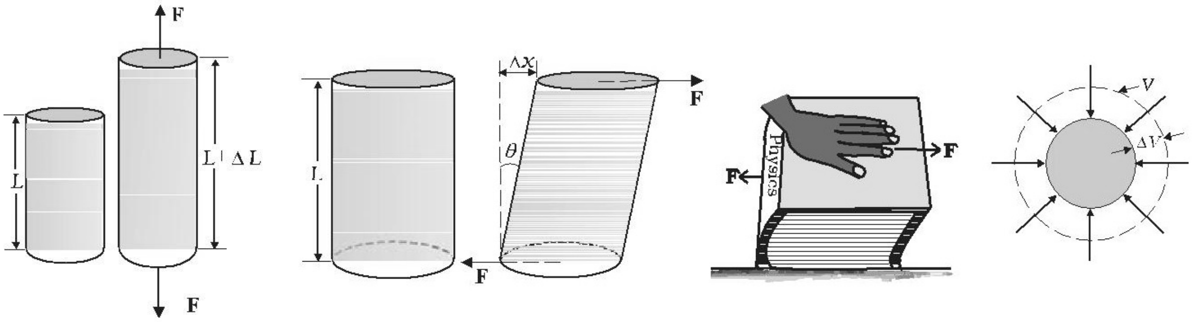
$$\text{Shearing strain } \frac{x}{L} = tan\,\theta \qquad (10.3)$$

where θ is the angular displacement of the cylinder from the vertical (original position of the cylinder). Usually θ is very small, tan θ is nearly equal to angle θ, (if θ= 10° , for example, there is only 1% difference between θ and tan θ).

It can also be visualised, when a book is pressed with the hand and pushed horizontally, as shown in Fig. 10.2 (c).

$$\text{Thus, shearing strain} = tan\,\theta \approx \theta \qquad (10.4)$$

In Fig. 10.2 (d), a solid sphere placed in the fluid under high pressure is compressed uniformly on all sides. The force applied by the fluid acts in perpendicular direction at each point of the surface and the body is said to be under hydraulic compression. This leads to decrease in its volume without any change of its geometrical shape.



(a) **(b)** **(c)** **(d)**

Fig. 10.2 *(a) Cylinder subjected to tensile stress stretches it by an amount L. (b) A cylinder subjected toshearing (tangential) stress deforms by an angle θ .(c) A book subjected to a shearing stress(d) A solid sphere subjected to a uniform hydraulic stress shrinks in volume by an amount V.*

The body develops internal restoring forces that are equal and opposite to the forces applied by the fluid (the body restores its original shape and size when taken out from the fluid). The internal restoring force per unit area in this case is known as **hydraulic stress** and in magnitude is equal to the hydraulic pressure (applied force per unit area).

The strain produced by a hydraulic pressure is called **volume strain** and is defined as the ratio of change in volume (V) to the original volume (V).

$$\text{Volume strain} = \frac{V}{V} \qquad (10.5)$$

Since the strain is a ratio of change in dimension to the original dimension, it has no units or dimensional formula.

10.4 HOOKE’S LAW

Stress and strain take different forms in the situations depicted in the Fig. (10.2). For small deformations the stress and strain are proportional to each other. This is known as Hooke’s law. Thus stress α strain

$$\text{stress} = k.\ \text{strain} \qquad (10.6)$$

where k is the proportionality constant and is known as modulus of elasticity.

Hooke’s law is an empirical law and is found to be valid for most materials. However, there are some materials which do not exhibits this linear relationship.

10.5 STRESS-STRAIN CURVE

The relation between the stress and the strain for a given material under tensile stress can be found experimentally. In a standard test of tensile properties, a test cylinder or a wire is stretched by an applied force. The fractional change in length (the strain) and the applied force needed to cause the strain are recorded. The applied force is gradually increased in steps and the change in length is noted. A graph is plotted between the stress (which is equal in magnitude to the applied force per unit area) and the strain produced. A typical graph for a metal is shown in Fig. 10.3. Analogous graphs for compression and shear stress may also be obtained. The stress-strain curves vary from material to material. These curves help us to understand how a given material deforms with increasing loads. From the graph, we can see that in the region between O to A, the curve is linear. In this region, Hooke’s law is obeyed.The body regains its original dimensions when the applied force is removed. In this region, the solid behaves as an elastic body.

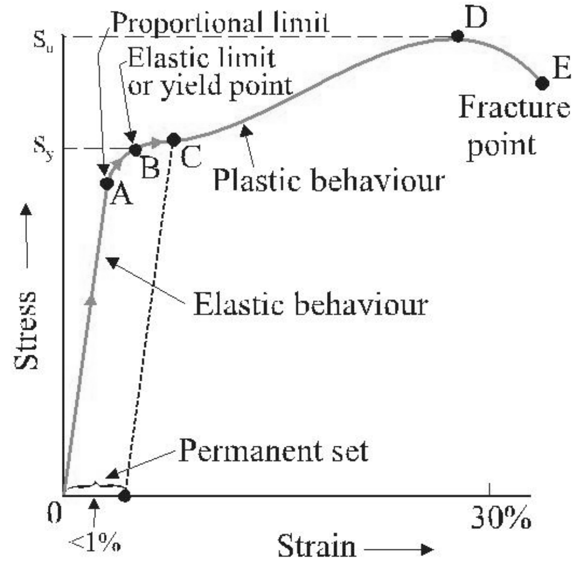


Fig. 10.3 *A typical stress-strain curve for a metal.*

In the region from A to B, stress and strain are not proportional. Nevertheless, the body still returns to its original dimension when the load is removed. The point B in the curve is known as **yield point** (also known as **elastic limit**) and the corresponding stress is known as yield strength (σ_y) of the material.

If the load is increased further, the stress developed exceeds the yield strength and strain increases rapidly even for a small change in the stress. The portion of the curve between B and D shows this. When the load is removed, say at some point C between B and D, the body does not regain its original dimension. In this case, even when the stress is zero, the strain is not zero. The material is said to have a **permanent set**. The deformation is said to be **plastic deformation**. The point D on the graph is the ultimate **tensile strength** (S_u) of the material. Beyond this point, additional strain is produced even by a reduced applied force and fracture occurs at point E. If the ultimate strength and fracture points D and E are close, the material is said to be brittle. If they are far apart, the material is said to be ductile.

As stated earlier, the stress-strain behaviour varies from material to material. For example, rubber can be pulled to several times its original length and still returns to its original shape. Fig. 10.4 shows stress-strain curve for the elastic tissue of aorta, present in the heart. Note that although elastic region is very large, the material does not obey Hooke's law over most of the region. Secondly, there is no well defined plastic region. Substances like tissue of aorta, rubbers etc. which can be stretched to cause large strains are called **elastomers**.

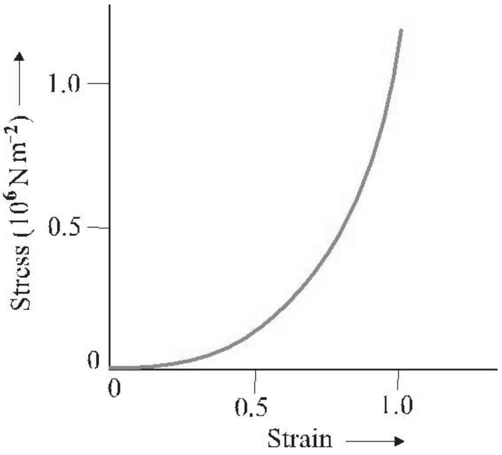


Fig. 10.4 *Stress-strain curve for the elastic tissue of Aorta, the large tube (vessel) carrying blood from the heart.*

10.6 ELASTIC MODULI

The proportional region within the elastic limit of the stress-strain curve (region OA in Fig. 10.3) is of great importance for structural and manufacturing engineering designs. The ratio of stress and strain, called **modulus of elasticity**, is found to be a characteristic of the material.

10.6.1 Young's Modulus

Experimental observation show that for a given material, the magnitude of the strain produced is same whether the stress is tensile or compressive. The ratio of tensile (or compressive) stress (σ) to the longitudinal strain (ε) is defined as **Young's modulus** and is denoted by the symbol **Y**.

$$Y = \sigma / \varepsilon \qquad (10.7)$$

From Eqs. (10.1) and (10.2), we have

$$Y = (F/A)/(L/L)$$

$$= (F.L)/(A.L) \qquad (10.8)$$

Since strain is a dimensionless quantity, the unit of Young's modulus is the same as that of stress *i.e.*, N m^{-2} or Pascal (Pa). Table 10.1 gives the values of Young's moduli and yield strengths of some materials.

From the data given in Table 10.1, it is noticed that for metals Young's moduli are large. Therefore, these materials require a large force to produce small change in length. To increase the length of a thin steel wire of 0.1 cm^2 cross-sectional area by 0.1%, a force of 2000 N is required. The force required to produce the same strain in aluminium, brass and copper wires having the same cross-sectional area are 6100 N, 1000 N and 1100 N respectively. It means that steel is more elastic than copper, brass and aluminium. It is for this reason that steel is preferred in heavy-duty machines and in structural designs. Wood, bone, concrete and glass have rather small Young's moduli.

Table 10.1 Young's moduli and yield strengths of some materials.

Substance	Density ρ (kg m^{-3})	Young's modulus Y(10^9 n/m^2)	Ultimate strength, Su (10^6 Nm^{-2})	Yield strength, S_y (10^6 Nm^{-2})
Aluminium	2710	70	110	95
Copper	8890	110	400	200
Iron (wrought)	7800-7900	190	330	170
Steel	7860	200	400	250
Glass#	2190	65	50	-
Concrete	2320	30	40	-
Wood#	525	13	50	-
Bone#	1900	9	170	-
Polystyrene	1050	3	48	-

Example 10.1 A structural steel rod has a radius of 10 mm and a length of 1.0 m. A 100 kN force stretches it along its length. Calculate (a) stress, (b) elongation, and (c) strain on the rod. Young's modulus, of structural steel is $2.0 \cdot 10^{11}$ N m^{-2}.

Answer We assume that the rod is held by a clamp at one end, and the force *F* is applied at the other end, parallel to the length of the rod. Then the stress on the rod is given by

$$Stress = \frac{F}{A} = \frac{F}{\pi r^2} = \frac{100 \text{ x } 10^3\ N}{3.14 \text{ x } 10^2\ m^2} = 3.18 \text{ x } 10^8\ Nm^{-2}$$

The elongation,

$$L = \frac{\left(\frac{F}{A}\right) L}{Y} = \frac{3.18 \text{ x } 10^8\ Nm^{-2} \text{ x } 1m}{2 \text{ x } 10^{11}\ Nm^{-2}} = 1.510\ mm$$

The strain is given by

$$\text{Strain} = L/L$$

$$= (1.510 \times 10^{-3}\ \text{m})/(1\text{m})$$

$$= 1.510 \times 10^{-3}$$

$$= 0.16\%$$

Example 10.2 A copper wire of length 2.2m and a steel wire of length 1.6 m, both of diameter 3.0 mm, are connected end to end. When stretched by a load, the net elongation is found to be 0.70 mm. Obtain the load applied.

Answer The copper and steel wires are under a tensile stress because they have the same tension (equal to the load *W*) and the same area of cross-section *A*. From Eq. (10.7) we have stress = strain · Young's modulus. Therefore

$$W/A = Y_c \times (\Delta L_c/L_c) = Y_s \times (\Delta L_s/L_s)$$

where the subscripts c and s refer to copper and stainless steel respectively. Or,

$$\Delta L_c / \Delta L_s = (Ys/Yc) \times (Lc/Ls)$$

Given $L_c = 2.2$ m, $L_s = 1.6$ m,

From Table 10.1, $Y_c = 1.1 \times 10^{11}\ \text{N.m}^{-2}$, and

$Y = 2.0 \times 10^{11}\ \text{N.m}^{-2}$.

$L_c/L_s = (2.0 \times 10^{11}/1.1 \times 10^{11}) \times (2.2/1.6) = 2.5$.

The total elongation is given to be

$L_c + L_s = 7.0 \times 10^{-4}$ m

Solving the above equations,

$L_c = 5.0 \times 10^{-4}$m, and $L_s = 2.0 \times 10^{-4}$ m.

Therefore $W = (A \times Y_c \times \Delta L_c)/L_c$

$$= \pi\,(1.5 \times 10^{-3})^2 \times [(5.0 \times 10^{-4} \times 1.1 \times 10^{11})/2.2]$$

$$= 1.8 \times 10^2\ \text{N}$$

Example 10.3 In a human pyramid in a circus, the entire weight of the balanced group is supported by the legs of a performer who is lying on his back (as shown in Fig. 10.5). The combined mass of all the persons performing the act, and the tables, plaques etc. involved is 280 kg. The mass of the performer lying on his back at the bottom of the pyramid is 60 kg. Each thighbone (femur) of this performer has a length of 50 cm and an effective radius of 2.0 cm. Determine the amount by which each thighbone gets compressed under the extra load.

Fig. 10.5 *Human pyramid in a circus.*

Answer Total mass of all the performers, tables, plaques etc.

= 280 kg

Mass of the performer = 60 kg

Mass supported by the legs of the performer at the bottom of the pyramid= 280 – 60 = 220 kg

Weight of this supported mass= 220 kg wt. = 220 x (9.8) N = 2156 N

Weight supported by each thighbone of the performer = ½ (2156) N = 1078 N.

From Table 10.1, the Young’s modulus for bone is given by $Y = 9.4 \times 10^{9}\ \mathrm{N\ m^{-2}}$.

Length of each thighbone $L = 0.5$ m

The radius of thighbone = 2.0 cm

Thus the cross-sectional area of the thighbone $A = \pi\ (2 \times 10^{-2})^2\ \mathrm{m^2} = 1.26 \cdot 10^{-3}\ \mathrm{m^2}$.

Using Eq. (10.8), the compression in each thighbone (L) can be computed as

$L = [(F \times L)/(Y \times A)]$

$= [(1078 \times 0.5)/(9.4 \times 10^{10} \times 1.26 \times 10^{-3})]$

$= 4.55 \times 10^{-5}$ m or 4.55×10^{-3} cm.

This is a very small change!

The fractional decrease in the thighbone is

$\Delta L/L = 0.0000101$ or 0.00101%.

10.6.2 Determination of Young's Modulus of the Material of a Wire

A typical experimental arrangement to determine the Young's modulus of a material of wire under tension is shown in Fig. 10.6. It consists of two long straight wires of same length and equal radius suspended side by side from a fixed rigid support. The wire A (called the *reference wire*) carries a millimetre main scale M and a pan to place a weight. The wire B (called the *experimental wire*) of uniform area of cross-section also carries a pan in which known weights can be placed. A vernier scale V is attached to a pointer at the bottom of the experimental wire B, and the main scale M is fixed to the reference wire A. The weights placed in the pan exert a downward force and stretch the experimental wire under a tensile stress. The elongation of the wire (increase in length) is measured by the vernier arrangement. The reference wire is used to compensate for any change in length that may occur due to change in room temperature, since any change in length of the reference wire due to temperature change will be accompanied by an equal change in experimental wire. (We shall study these temperature effects in detail in Chapter 11.)

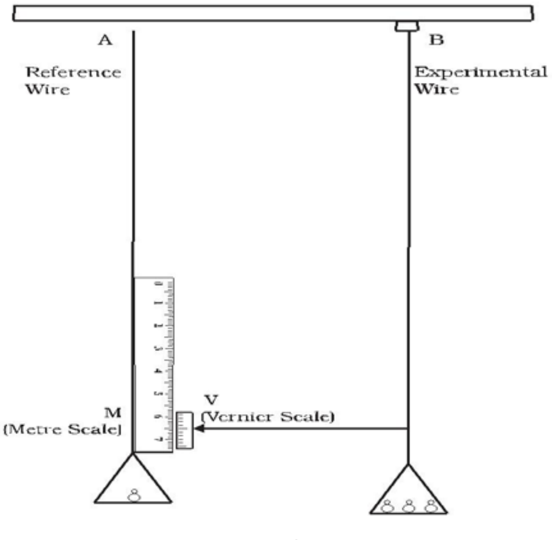


Fig. 10.6 *An arrangement for the determination of Young's modulus of the material of a wire.*

Both the reference and experimental wires are given an initial small load to keep the wires straight and the vernier reading is noted. Now the experimental wire is gradually loaded with more weights to bring it under a tensile stress and the vernier reading is noted again. The difference between two vernier readings gives the elongation produced in the wire. Let r and L be the initial radius and length of the experimental wire, respectively. Then the area of cross-section of the wire would be πr^2. Let M be the mass that produced an elongation L in the wire. Thus the applied force is equal to Mg, where g is the acceleration due to gravity. From Eq. (10.8), the Young's modulus of the material of the experimental wire is given by

$$Y = \frac{\sigma}{\varepsilon} = \frac{Mg}{\pi r^2} \cdot \frac{L}{\Delta L}$$

$$= \frac{MgL}{(\pi r^2)\Delta L}$$

10.6.3 Shear Modulus

The ratio of shearing stress to the corresponding shearing strain is called the *shear modulus* of the material and is represented by G. It is also called the *modulus of rigidity*

G = shearing stress (σ_s)/shearing strain

$$G = (F/A)/(x/L)$$

$$= (F \cdot L)/(A \cdot x) \qquad (10.10)$$

Similarly, from Eq. (10.4)

$$G = (F/A)/\theta$$

$$= F/(A \cdot \theta) \ (10.11)$$

The shearing stress σ_s can also be expressed as

$$\sigma_s = G \cdot \theta \qquad (10.12)$$

SI unit of shear modulus is N m^{-2} or Pa. The shear moduli of a few common materials are given in Table 10.2. It can be seen that shear modulus (or modulus of rigidity) is generally less than Young's modulus (from Table 10.1). For most materials $G \approx Y/3$.

Table 10.2 Shear moduli *(G)* of some common materials

Material	G (10^{10} Nm^{-2} or GPa)
Aluminium	25
Brass	36
Copper	42
Glass	23
Iron	70
Lead	5.6
Nickel	77
Steel	84
Tungsten	150
Wood	10

Example 10.4 A square lead slab of side 50cm and thickness 10 cm is subject to a shearing force (on its narrow face) of $10.0 \cdot 10^4$ N. The lower edge is riveted to the floor. How much will the upper edge be displaced?

Answer The lead slab is fixed and the force is applied parallel to the narrow face as shown in Fig. 10.7. The area of the face parallel to which this force is applied is

$$A = 50 \text{ cm x } 10 \text{ cm}$$

$$= 0.5 \text{ m x } 0.1 \text{ m}$$

$$= 0.05 \text{ m}^2$$

Therefore, the stress applied is

$$= (10.4 \text{ x } 10^4 \text{ N}/0.05 \text{ m}^2)$$

$$= 1.80 \text{ x } 10^6 \text{ N.m}^{-2}$$

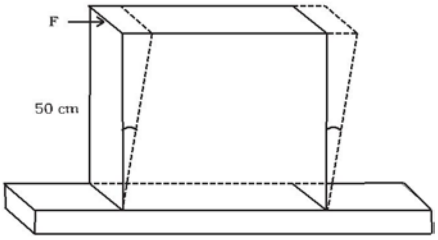


Fig. 10.7

We know that shearing strain = (x/L)= Stress $/G$.

Therefore the displacement $x = (\text{Stress}\cdot L)/G$

$$= (1.8 \text{ x } 10^{6} \text{ N m}^{-2}\cdot\ 0.5\text{m})/(5.6 \text{ x } 10^{10} \text{ N m}^{-2})$$

$$= 1.6 \text{ x } 10^{-4} \text{ m} = 0.16 \text{ mm}$$

10.6.4 Bulk Modulus

In Section (10.3), we have seen that when a body is submerged in a fluid, it undergoes a hydraulic stress (equal in magnitude to the hydraulic pressure). This leads to the decrease in the volume of the body thus producing a strain called volume strain [Eq. (10.5)]. The ratio of hydraulic stress to the corresponding hydraulic strain is called *bulk modulus*. It is denoted by symbol B.

$$B = -p/(\Delta V/V) \qquad (10.13)$$

The negative sign indicates the fact that with an increase in pressure, a decrease in volume occurs. That is, if p is positive, V is negative. Thus for a system in equilibrium, the value of bulk modulus B is always positive. SI unit of bulk modulus is the same as that of pressure *i.e.*, N m^{-2}or Pa. The bulk moduli of a few common materials are given in Table 10.3.

The reciprocal of the bulk modulus is called *compressibility* and is denoted by k. It is defined as the fractional change in volume per unit increase in pressure.

$$k = (1/B) = -(1/p)\cdot(\Delta V/V)$$

It can be seen from the data given in Table 10.3 that the bulk moduli for solids are much larger than for liquids, which are again much larger than the bulk modulus for gases (air).

Table 10.3 Bulk moduli *(B)* of some common Materials

Material Solids	B (10^{10} Nm^{-2} or GPa)
Aluminium	72
Brass	61
Copper	140
Glass	37
Iron	100
Nickel	260
Steel	160
Tungsten	150
Wood	10
Liquids	
Water	2.2
Ethanol	0.10
Carbon disulphide	1.56
Glycerine	4.76
Mercury	25
Gases	
Air (at STP)	1.0×10^{-4}

Thus solids are least compressible whereas gases are most compressible. Gases are about a million times more compressible than solids! Gases have large compressibilities, which vary with pressure and temperature. The incompressibility of the solids is primarily due to the tight coupling between the neighbouring atoms. The molecules in liquids are also bound with their neighbours but not as strong as in solids. Molecules in gases are very poorly coupled to their neighbours.

Table 10.4 shows the various types of stress, strain, elastic moduli, and the applicable state of matter at a glance.

Type of stress	**Stress**	**Strain**	**Change in**		**Elastic modulus**	**Name of modulus**	**State of Mater**
			shape	**volume**			
Tensile or compressive	Two equal and opposite forces perpendicular to opposite faces($\sigma = F/A$)	Elongation or compression parallel to force direction ($\Delta L/L$) (longitudinal strain)	Yes	No	$Y = (F \times L)/(A \times L)$	Young’s modulus	Solid
Shearing	Two equal and opposite forces parallel to oppoiste surfaces [forces in each case such that total force and total torque on the body vanishes($\sigma_s = F/A$)	Pure shear, θ	Yes	No	$G = (F \times \theta)/A$	Shear modulus	Solid
Hydraulic	Forces perpendicular everywhere to the surface, force per unit area (pressure) same everywhere.	Volume change(compression or elongation ($\Delta V/V$)	No	Yes	$B = -p/(\Delta V/V)$	Bulk modulus	Solid, liquid and gas

10.7 APPLICATIONSOF ELASTIC BEHAVIOUR OF MATERIALS

The elastic behaviour of materials plays an important role in everyday life. All engineering designs require precise knowledge of the elastic behaviour of materials. For example while designing a building, the structural design of the columns, beams and supports require knowledge of strength of materials used. Have you ever thought why the beams used in construction of bridges, as supports etc. have a cross-section of the type **I**? Why does a heap of sand or a hill have a pyramidal shape? Answers to these questions can be obtained from the study of structural engineering which is based on concepts developed here.

Cranes used for lifting and moving heavy loads from one place to another have a thick metal rope to which the load is attached. The rope is pulled up using pulleys and motors. Suppose we want to make a crane, which has a lifting capacity of 10 tonnes or metric tons (1 metric ton = 1000 kg). How thick should the steel rope be? We obviously want that the load does not deform the rope permanently. Therefore, the extension should not exceed the elastic limit. From Table 10.1, we find that mild steel has a yield strength (S_y) of about 300 □ 10^6 N m^{-2}. Thus, the area of cross-section (A) of the rope should at least be corresponding to a radius of about 1 cm for a rope of circular cross-section.

$$A \geq W/S_y = Mg/S_y \qquad (10.15)$$

$$= (10^4 \text{ kg x } 10 \text{ m s}^{-2})/(300 \text{ x } 10^6 \text{ N m}^{-2})$$

$$= 3.3 \text{ x } 10^{-4} \text{ m}^2$$

Generally a large margin of safety (of about a factor of ten in the load) is provided. Thus a thicker rope of radius about 3 cm is recommended. A single wire of this radius would practically be a rigid rod. So the ropes are always made of a number of thin wires braided together, like in pigtails, for ease in manufacture, flexibility and strength.

A bridge has to be designed such that it can withstand the load of the flowing traffic, the force of winds and its own weight. Similarly, in the design of buildings use of beams and columns is very common. In both the cases, the overcoming of the problem of bending of beam under a load is of prime importance. The beam should not bend too much or break. Let us consider the case of a beam loaded at the centre and supported near its ends as shown in Fig. 10.8. A bar of length l, breadth b, and depth $d$when loaded at the centre by a load W sags by an amount given by

$$\delta = W\,l^3/(4bd^3Y) \qquad (10.16)$$

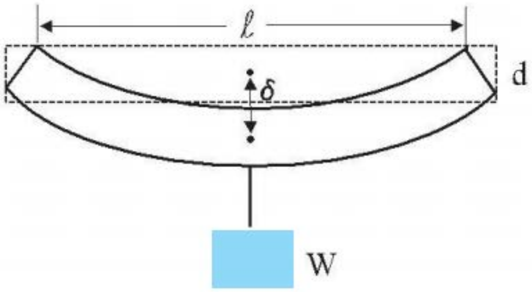


Fig. 10.8 *A beam supported at the ends and loaded at the centre.*

This relation can be derived using what you have already learnt and a little calculus. From Eq. (10.16), we see that to reduce the bending for a given load, one should use a material with a large Young's modulus *Y*. For a given material, increasing the depth *d* rather than the breadth *b* is more effective in reducing the bending, since δ is proportional to d^{-3} and only to b^{-1}(of course the length *l* of the span should be as small as possible). But on increasing the depth, unless the load is exactly at the right place (difficult to arrange in a bridge with moving traffic), the deep bar may bend as shown in Fig. 10.10(b). This is called buckling. To avoid this, a common compromise is the cross-sectional shape shown in Fig. 10.10(c). This section provides a large load-bearing surface and enough depth to prevent bending. This shape reduces the weight of the beam without sacrificing the strength and hence reduces the cost.

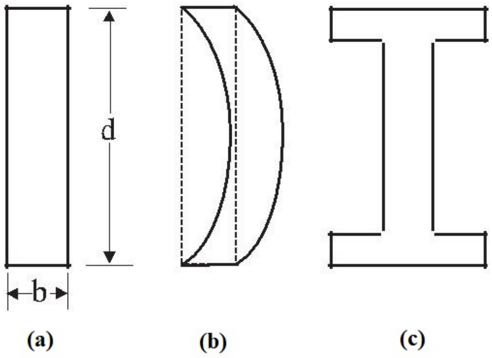


Fig. 10.10(a) *Different cross-sectional shapes of abeam. (a) Rectangular section of a bar; (b) A thin bar and how it can buckle; (c) Commonly used section for a load bearing bar.*

Use of pillars or columns is also very common in buildings and bridges. A pillar with rounded ends as shown in Fig. 10.10(a) supports less load than that with a distributed shape at the ends [Fig. 10.10(b)]. The precise design of a bridge or a building has to take into account the conditions under which it will function, the cost and long period, reliability of usable materials etc.

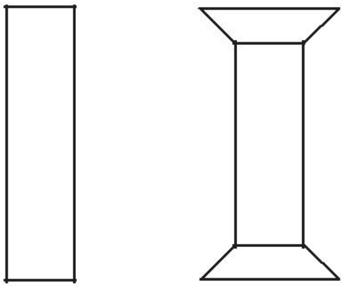


Fig. 10.10(b) *Pillars or columns: (a) a pillar with rounded ends, (b) Pillar with distributed ends.*

The answer to the question why the maximum height of a mountain on earth is ~10 km can also be provided by considering the elastic properties of rocks. A mountain base is not under uniform compression and this provides some shearing stress to the rocks under which they can flow. The stress due to all the material on the top should be less than the critical shearing stress at which the rocks flow.

At the bottom of a mountain of height h, the force per unit area due to the weight of the mountain is $h\rho g$ where ρ is the density of the material of the mountain and g is the acceleration due to gravity. The material at the bottom experiences this force in the vertical direction, and the sides of the mountain are free. Therefore this is not a case of pressure or bulk compression. There is a shear component, approximately $h\rho g$ itself. Now the elastic limit for a typical rock is 30×10^7 N m^{-2}.

Equating this to $h\rho g$, with $\rho = 3 \times 10^3$ kg m^{-3}

Gives $h\rho g = 30 \times 10^7$ N m^{-2}.

Or $h = 30 \times 10^7 \text{ N m}^{-2}/(3 \times 10^3 \text{ kg m}^{-3} \times 10 \text{ m s}^{-2}$

which is more than the height of Mt. Everest!

SUMMARY

1. Stress is the restoring force per unit area and strain is the fractional change in dimension. In general there are three types of stresses

   (a) tensile stress — longitudinal stress (associated with stretching) or compressive stress (associated with compression),

   (b) shearing stress, and

   (c) hydraulic stress.

2. For small deformations, stress is directly proportional to the strain for many materials. This is known as Hooke’s law. The constant of proportionality is called modulus of elasticity. Three elastic moduli *viz.*, Young’s modulus, shear modulus and bulk modulus are used to describe the elastic behaviour of objects as they respond to deforming forces that act on them. A class of solids called elastomers does not obey Hooke’s law.

3. When an object is under tension or compression, the Hooke’s law takes the form

   $$F/A = Y\,(\Delta L/L)$$

   where $\Delta L/L$ is the tensile or compressive strain of the object, F is the magnitude of the applied force causing the strain, A is the cross-sectional area over which F is applied (perpendicular to A) and Y is the Young’s modulus for the object. The stress is F/A.

4. A pair of forces when applied parallel to the upper and lower faces, the solid deforms so that the upper face moves sideways with respect to the lower. The horizontal displacement L of the upper face is perpendicular to the vertical height L. This type of deformation is called shear and the corresponding stress is the shearing stress. This type of stress is possible only in solids.

5. In this kind of deformation the Hooke’s law takes the form

   $$F/A = G \text{ x } \Delta L/L$$

   where L is the displacement of one end of object in the direction of the applied force F, and G is the shear modulus.

CHAPTER ELEVEN

MECHANICAL PROPERTIES OF FLUIDS

11.1 INTRODUCTION

In this chapter, we shall study some common physical properties of liquids and gases. Liquids and gases can flow and are therefore, called fluids. It is this property that distinguishes liquids and gases from solids in a basic way.

Fluids are everywhere around us. Earth has an envelop of air and two-thirds of its surface is covered with water. Water is not only necessary for our existence; every mammalian body constitute mostly of water. All the processes occurring in living beings including plants are mediated by fluids. Thus understanding the behavior and properties of fluids is important.

How are fluids different from solids? What is common in liquids and gases? Unlike a solid, a fluid has no definite shape of its own. Solids and liquids have a fixed volume, whereas a gas fills the entire volume of its container. We have learnt in the previous chapter that the volume of solids can be changed by stress. The volume of solid, liquid or gas depends on the stress or pressure acting on it. When we talk about fixed volume of solid or liquid, we mean its volume under atmospheric pressure. The difference between gases and solids or liquids is that for solids or liquids the change in volume due to change of external pressure is rather small. In other words solids and liquids have much lower compressibility as compared to gases.

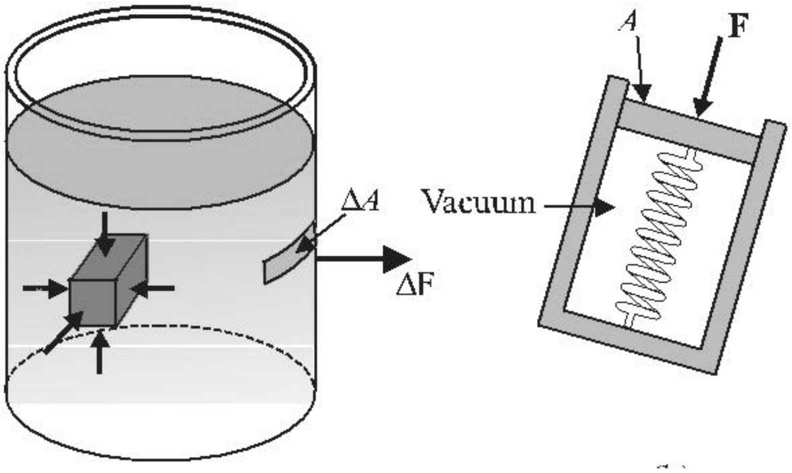
Shear stress can change the shape of a solid keeping its volume fixed. The key property of fluids is that they offer very little resistance to shear stress; their shape changes by application of very small shear stress. The shearing stress of fluids is about million times smaller than that of solids.

11.2 PRESSURE

A sharp needle when pressed against our skin pierces it. Our skin, however, remains intact when a blunt object with a wider contact area (say the back of a spoon) is pressed against it with the same force. If an elephant were to step on A man’s chest, his ribs would crack.

A circus performer across whose chest a large Light, but strong wooden plank is placed first, is saved from this accident. Such everyday experiences convince us that both the force and its coverage area are important. Smaller the area on which the force acts, greater is the impact. This concept is known as pressure.

When an object is submerged in a fluid at rest, the fluid exerts a force on its surface. This force is always normal to the object's surface. This is so because if there were a component of force parallel to the surface, the object will also exert a force on the fluid parallel to it; as a consequence of Newton's third law. This force will cause the fluid to flow parallel to the surface. Since the fluid is at rest, this cannot happen. Hence, the force exerted by the fluid at rest has to be perpendicular to the surface in contact with it. This is shown in Fig.11.1 (a).The normal force exerted by the fluid at a point may be measured. An idealized form of one such pressure-measuring device is shown in Fig. 11.1(b). It consists of an evacuated chamber with a spring that is calibrated to measure the force acting on the piston. This device is placed at a point inside the fluid. The inward force exerted by the fluid on the piston is balanced by the outward spring force and is thereby measured.



(a) (b)

Fig. 11.1 *(a) The force exerted by the liquid in the beaker on the submerged object or on the walls is normal (perpendicular) to the surface at all points.*

(b) *An idealised device for measuring pressure.*

If F is the magnitude of this normal force on the piston of area A then the average pressure**P_{ave}** is defined as the normal force acting per unit area

$$P_{ave} = \frac{F}{A} \tag{11.1}$$

* STP means standard temperature (0^0C) and 1 atm pressure.

In principle, the piston area can be made arbitrarily small. The pressure is then defined in a limiting sense as

$$\mathrm{P} = \lim_{A\to 0}\frac{F}{A} \tag{11.2}$$

Pressure is a scalar quantity. We remind the reader that it is the component of the force normal to the area under consideration and not the (vector) force that appears in the numerator in Eqs. (11.1) and (11.2). Its dimensions are $[ML^{-1}T^{-2}]$. The SI unit of pressure is N m^{-2}. It has been named as pascal (Pa) in honour of the French scientist Blaise Pascal (1623-1662) who carried out pioneering studies on fluid pressure. A common unit of pressure is the atmosphere (atm), i.e. the pressure exerted by the atmosphere at sea level (1 atm = 1.013 x105 Pa).Another quantity, that is indispensable in describing fluids, is the density ρ. For a fluid of mass m occupying volume V,

$$\rho = \frac{m}{V} \tag{11.3}$$

The dimensions of density are $[ML^{-3}]$. Its SI unit is kg m^{-3}. It is a positive scalar quantity. A liquid is largely incompressible and its density is therefore, nearly constant at all pressures. Gases, on the other hand exhibit a large variation in densities with pressure.

The density of water at 4^oC (277 K) is1.0 x 10^3 kg m^{-3}. The relative density of a substance is the ratio of its density to the density of water at 4^oC. It is a dimensionless positive scalar quantity. For example the relative density of aluminum is 2.7. Its density is 2.7 x10^3 kg m^{-3}. The densities of some common fluids are displayed in Table 11.1.

Table 11.1 Densities of some common fluids at STP* $\pi/2$ A=π

Fluid	ρ (kg m^{-3})
Water	1.00×10^3
Sea Water	1.03×10^3
Mercury	13.6×10^3
Ethyl alcohol	0.806×10^3
Whole blood	1.06×10^3
Air	1.29
Oxygen	1.43
Hydrogen	9.0×10^{-2}
Interstellar space	$\approx 10^{-20}$

Example 11.1 The two thigh bones(femurs), each of cross-sectional area 10 cm^2 support the upper part of a human body of mass 40 kg. Estimate the average pressure sustained by the femurs.

Answer: Total cross-sectional area of the femurs is A = 2 x 10 cm^2 = 20 x 10^{-4} m^2. The force acting on them is F = 40 kg wt = 400 N (taking g = 10 m s^{-2}). This force is acting vertically down and hence, normally on the femurs. Thus, the average pressure is

$$P_{av} = \frac{F}{A} = 2 \times 10^5 \text{ N m}^{-2}$$

11.2.1 Pascal's Law

The French scientist Blaise Pascal observed that the pressure in a fluid at rest is the same at all points if they are at the same height. This fact may be demonstrated in a simple way.

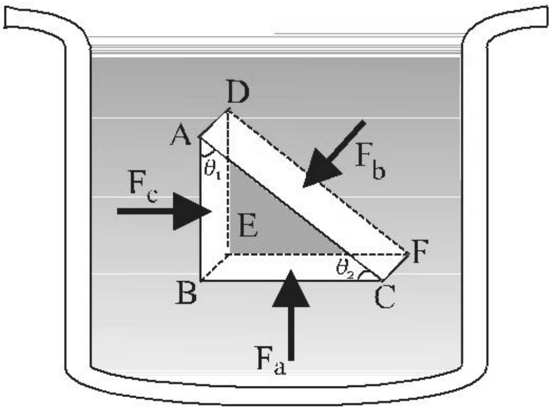


Fig. 11.2 *Proof of Pascal's law. ABC-DEF is an element of the interior of a fluid at rest. This element is in the form of a right-angled prism. The element is small so that the effect of gravity can be ignored, but it has been enlarged for the sake of clarity.*

form of a right-angled prism. In principle, this prismatic element is very small so that every part of it can be considered at the same depth from the liquid surface and therefore, the effect of the gravity is the same at all these points. But for clarity we have enlarged this element. The forces on this element are those exerted by the rest of the fluid and they must be normal to the surfaces of the element as discussed above. Thus, the fluid exerts pressures P_a, P_b and P_c onthis element of area corresponding to the normal forces Fa, Fb and Fc as shown in Fig. 11.2 on the faces BEFC, ADFC and ADEB denoted by A_a, A_b and A_c respectively. Then

$$F_b \sin\theta = F_c, \quad F_b \cos\theta = F_a \text{(by equilibrium)}$$

$$A_b \sin\theta = A_c, \quad A_b \cos\theta = A_a \text{(by geometry)}$$

$$\frac{F_b}{A_b} = \frac{F_c}{A_c} = \frac{F_a}{A_a} \; ; \quad P_b = P_c = P_a \qquad (11.4)$$

Hence, pressure exerted is same in all directions in a fluid at rest. It again reminds us that like other types of stress, pressure is not a vector quantity. No direction can be assigned to it. The force against any area within (or bounding) a fluid at rest and under pressure is normal to the area, regardless of the orientation of the area.

Now consider a fluid element in the form of a horizontal bar of uniform cross-section. The bar is in equilibrium. The horizontal forces exerted at its two ends must be balanced or the pressure at the two ends should be equal. This proves that for a liquid in equilibrium the pressure is same at all points in a horizontal plane. Suppose the pressure were not equal in different parts of the fluid, then there would be a flow as the fluid will have some net force acting on it. Hence in the absence of flow the pressure in the fluid must be same everywhere. Wind is flow of air due to pressure differences.

11.2.2 Variation of Pressure with Depth

Consider a fluid at rest in a container. In Fig. 11.3 point 1 is at height h above a point 2. The pressures at points 1 and 2 are P_1 and P_2 respectively. Consider a cylindrical element of fluid having area of base A and height h. As the fluid is at rest the resultant horizontal forces should be zero and the resultant vertical forces should balance the weight of the element. The forces acting in the vertical direction are due to the fluid pressure at the top (P_1A) acting downward, at the bottom (P_2A) acting upward. If mg is weight of the fluid in the cylinder we have

$$(P_2 - P_1)\, A = mg$$

(11.5)

Now, if ρ is the mass density of the fluid, we have the mass of fluid to be $m = \rho V = \rho hA$ so that

$$P_2 - P_1 = \rho g h \qquad (11.6)$$

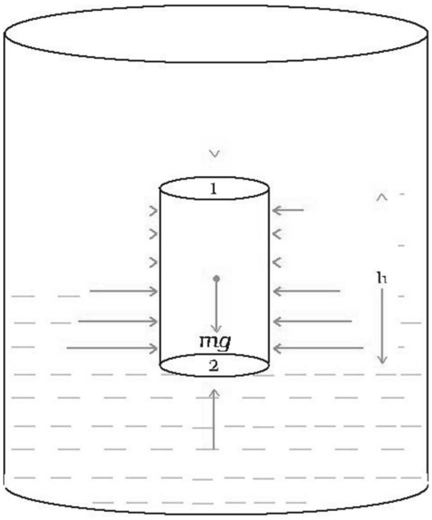


Fig. 11.3 *Fluid under gravity. The effect of gravity is illustrated through pressure on a vertical cylindrical column.*

Pressure difference depends on the vertical distance h between the points (1 and 2), mass density of the fluid ρ and acceleration due to gravity *g*. If the point 1 under discussion is shifted to the top of the fluid (say water), which is open to the atmosphere, P_1 may be replaced by atmospheric pressure (P_a) and we replace P_2 by P. Then Eq. (11.6) gives

$$P = P_a + \rho g h \qquad (11.7)$$

Thus, the pressure P, at depth below the surface of a liquid open to the atmosphere is greater than atmospheric pressure by an amount ρgh. The excess of pressure, $P - P_a$, at depth h is called a gauge pressure at that point.The area of the cylinder is not appearing in the expression of absolute pressure in Eq. (11.7). Thus, the height of the fluid column is important and not cross sectional or base area or the shape of the container. The liquid pressure is the same at all points at the same horizontal level (same depth). The result is appreciated through the example of hydrostatic paradox. Consider three vessels A, B and C [Fig.11.4] of different shapes. They are connected at the bottom by a horizontal pipe. On filling with water the level in the three vessels is the same though they hold different amounts of water. This is so, because water at the bottom has the same pressure below each section of the vessel.

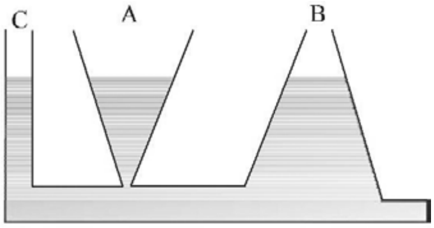


Fig 11.4 *Illustration of hydrostatic paradox. The three vessels A, B and C contain different amounts of liquids, all upto the same height.*

Example 11.2: What is the pressure on a swimmer 10 m below the surface of a lake?

Answer

Here h = 10 m *and* ρ = 1000 kg m^{-3}. Take g = 10 m s^{-2} From Eq. (11.7)

$$P = P_a + \rho g h$$

$$= 1.01 \times 10^5 \text{ Pa} + 1000 \text{ kg m}^{-3} \times 10 \text{ m s}^{-2} \times 10 \text{ m}$$

$$= 2.01 \times 10^5 \text{ Pa} \approx 2 \text{ atm}$$

=

This is a 100% increase in pressure from surface level. At a depth of 1 km the increase in pressure is 100 atm Submarines are designed to withstand such enormous pressures.

11.2.3 Atmospheric Pressure and GaugePressure

The pressure of the atmosphere at any point is equal to the weight of a column of air of unit cross sectional area extending from that point to the top of the atmosphere. At sea level it is 1.013 x 10^5 Pa (1 atm). Italian scientist Evangelista Torricelli (1608-1647) devised for the first time, a method for measuring atmospheric pressure. A long glass tube closed at one end and filled with mercury is inverted into a trough of mercury as shown in Fig.11.5 (a). This device is known as mercury barometer. The space above the mercury column in the tube contains only mercury vapour whose pressure P is so small that it may be neglected. The pressure inside the column at point A must equal the pressure at point B, which is at the same level. Pressure at B = atmospheric pressure = P_a

$$P_a = \rho g h \qquad \textit{Pressure at A} \qquad (11.8)$$

whereρ is the density of mercury and h is the height of the mercury column in the tube.

In the experiment it is found that the mercury column in the barometer has a height of about 76 cm at sea level equivalent to one atmosphere (1 atm). This can also be obtained using the value of ρ in Eq. (11.8). A common way of stating pressure is in terms of cm or mm of mercury (Hg). A pressure equivalent of 1 mm is called a torr (after Torricelli).

1 torr = 133 Pa.

The mm of Hg and torr are used in medicine and physiology. In meteorology, a common unit is the bar and millibar.

$$1 \text{ bar} = 10^5 \text{ Pa}$$

An open-tube manometer is a useful instrument for measuring pressure differences. It consists of a U-tube containing a suitable liquid i.e. a low density liquid (such as oil) for measuring small pressure differences and a high density liquid (such as mercury) for large pressure differences. One end of the tube is open to the atmosphere and other end is connected to the system whose pressure we want to measure [see Fig. 11.5 (b)]. The pressure P at A is equal to pressure at point B. What we normally measure is the gauge pressure, which is $P-P_a$, given by Eq. (11.8) and is proportional to manometer height h.

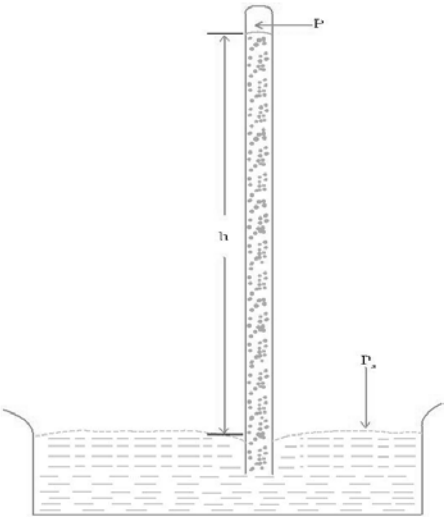


Fig 11.5 (a) The mercury barometer.

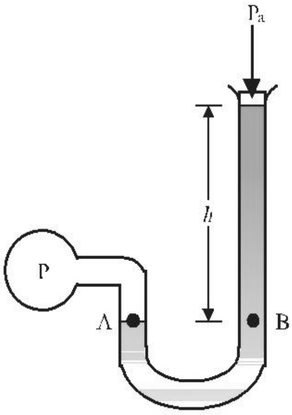


Fig 11.5 (b) Two pressure measuring devices.

Pressure is same at the same level on both sides of the U-tube containing a fluid. For liquids the density varies very little over wide ranges in pressure and temperature and we can treat it safely as a constant for our present purposes. Gases on the other hand, exhibit large variations of densities with changes in pressure and temperature. Unlike gases, liquids are therefore, largely treated as incompressible.

Example 11.3 The density of the atmosphere at sea level is 1.29 kg/m^3. Assume that it does not change with altitude. Then how high would the atmosphere extend?

Answer We use Eq. (11.7)

ρgh= 1.29 kg m^{-3} x 9.8 m s^{-2} x h m = 1.01 x 10^{5}Pa $\therefore h$ = 7989 m≈8 km

In reality the density of air decreases with height. So does the value of g. The atmospheric cover extends with decreasing pressure over 100 km. We should also note that the sea level atmospheric pressure is not always 760 mm of Hg. A drop in the Hg level by 10 mm or more isa sign of an approaching storm.

Example 11.4: At a depth of 1000 m in an ocean (a) what is the absolute pressure? (b)What is the gauge pressure? (c) Find the force acting on the window of area 20 cm × 20 cm of a submarine at this depth density of sea waterdepth, the interior of which is maintained at sea-level atmospheric pressure. (The is 1.03 x 10^3 kg m^{-3}, g= 10 m s^{-2}.)

Answer Here h= 1000 m and ρ= 1.03x10^{3}kg m^{-3}.

(a) From Eq. (11.6), absolute pressure $P = P_a + \rho gh$

= 1.01 x11^5 Pa

+ 1.03 x10^3 kg m^{-3}x10 m s^{-2}x1000 m

= 104.01 x10^5 Pa

≈104 atm

(b) Gauge pressure is $P - P_a = \rho gh = P_g$

P_g= 1.03x10^{3}kg m^{-3} x10ms^{-2} x1000 m

= 103 x10^5 Pa ≈103 atm

(c) The pressure outside the submarine is $P = P_a + \rho gh$and the pressure inside it is P_a. Hence, the net pressure acting on the window is gauge pressure, $P_g = \rho gh$. Since the area of the window is A = 0.04 m^2, the force acting on it is

$F = P_g A = 103\text{x}10^5\text{Pax}0.04\ \text{m}^2 = 4.12\text{x}10^5\text{N}$

11.2.4 Hydraulic Machines

Let us now consider what happens when we change the pressure on a fluid contained in a vessel. Consider a horizontal cylinder with a piston and three vertical tubes at different points. The pressure in the horizontal cylinderis indicated by the height of liquid column in the vertical tubes. It is necessarily the same in all. If we push the piston, the fluid level rises in all the tubes, again reaching the same level in each one of them.

This indicates that when the pressure on the cylinder was increased, it was distributed uniformly throughout. We can say **whenever external pressure is applied on any part of a fluid contained in a vessel, it is transmitted undiminished and equally in all directions. This is the Pascal's law for transmission of fluid pressure and has many applications in daily life.**

A number of devices such as **hydraulic lift** and **hydraulic brakes** are based on the Pascal's law. In these devices fluids are used for transmitting pressure. In a hydraulic lift as shown in Fig. 11.6 two pistons are separated by the space filled with a liquid. A piston of small cross section A1 is used to exert a force F1 directly on the liquid. The pressure is$P = \frac{F_1}{A_1}$transmitted throughout the liquid to the larger cylinder attached with a larger piston of area A_2, which results in an upward force of $P \times A_2$. Therefore, the piston is capable of supporting a large force (large weight of, say a car, or a truck, placed on the platform)

$$F_2 = PA_2 = \frac{F_1 A_2}{A_1}$$

By changing the force at A_1, the platform can bemoved up or down. Thus, the applied force has been increased by a factor of $\frac{A_2}{A_1}$ and this factoris the mechanical advantage of the device. The example below clarifies it.

Archemedes' Principle

Fluid appears to provide partial support to the objects placed in it. When a body is wholly or partially immersed in a fluid at rest, the fluid exerts pressure on the surface of the body in contact with the fluid. The pressure is greater on lower surfaces of the body than on the upper surfaces as pressure in a fluid increases with depth. The resultant of all the forces is an upward force called buoyant force. Suppose that a cylindrical body is immersed in the fluid. The upward force on the bottom of the body is more than the downward force on its top. The fluid exerts a resultant upward force or buoyant force on the body equal to (P_2-P_1) A. We have seen in equation 11.4 that $(P_2-P_1)A = \rho ghA$. Now hA is the volume of the solid and ρhA is the weight of an equivalent volume of the fluid. $(P_2-P_1)A = mg$. Thus the upward force exerted is equal to the weight of the displaced fluid.

The result holds true irrespective of the shape of the object and here cylindrical object is considered only for convenience. This is Archimedes' principle. For totally immersed objects the volume of the fluid displaced by the object is equal to its own volume. If the density of the immersed object is more than that of the fluid, the object will sink as the weight of the body is more than the upward thrust. If the density of the object is less than that of the fluid, it floats in the fluid partially submerged. To calculate the volume submerged. Suppose the total volume of the object is Vs and a part Vp of it is submerged in the fluid. Then the upward force which is the weight of the displaced fluid is ρfgVp, which must equal the weight of the body; ρsgVs = ρfgVporρs/ρf = Vp/VsThe apparent weight of the floating body is zero.

This principle can be summarized as; 'the loss of weight of a body submerged (partially or fully) in a fluid is equal to the weight of the fluid displaced'.

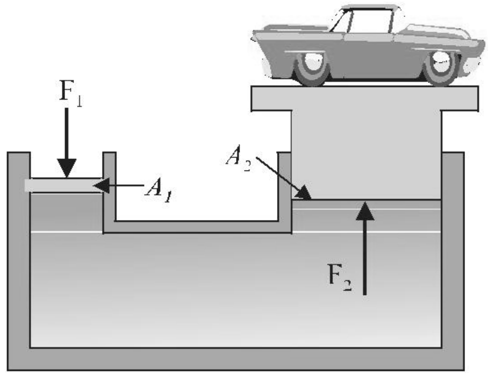


Fig 11.6 *Schematic diagram illustrating the principle behind the hydraulic lift, a device used to lift heavy loads.*

Example 11.5 Two syringes of different cross sections (without needles) filled with water are connected with a tightly fitted rubber tube filled with water. Diameters of the smaller piston and larger piston are 1.0 cm and 3.0 cm respectively. (a) Find the force exerted on the larger piston when a force of 11 N is applied to the smaller piston. (b) If the smaller piston is pushed in through 6.0 cm, how much does the larger piston move out?

Answer (a) Since pressure is transmitted undiminished throughout the fluid,

$$F2 = \frac{A1}{A2}F1 = \frac{\Pi(\frac{3}{2}\times10^{-2}m^2)}{\Pi(\frac{1}{2}\times10^{-2}m^2)}\times10N = 90N$$

(b) Water is considered to be perfectly incompressible. Volume covered by the movement of smaller piston inwards is equal to volume moved outwards due to the larger piston.

$$L_1 A_1 = L_2 A_2$$

$$L2 = \frac{A1}{A2}L1 = \frac{\Pi(\frac{1}{2}\times10^{-2}m^2)}{\Pi(\frac{3}{2}\times10^{-2}m^2)}\times6\times10^{-2}m =$$

$$0.67\times10^{-2}m = 0.67cm$$

Note, atmospheric pressure is common to bothpistons and has been ignored.

Example 11.6 In a car lift compressed air exerts a force F1 on a small piston having a radius of 5.0 cm. This pressure is transmitted to a second piston of radius15 cm (Fig 11.7). If the mass of the car to be lifted is 1350 kg, calculate F1. What is the pressure necessary to accomplish this task? ($g = 9.8\ ms^{-2}$).

Answer: Since pressure is transmitted undiminished throughout the fluid,

$$F2 = \frac{A1}{A2}F1 = \frac{5\times10^{-2}m^2}{15\times10^{-2}m^2}\times1350N\times9.8\ m\ s^{-2}$$

$$= 1470 \text{ N}$$

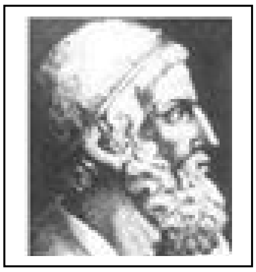
$$\approx 1.5 \times 10^3 \text{ N}$$

The air pressure that will produce this force is

$$P = \frac{F1}{A1} = \frac{1.5 \times 10^{-2} m^2}{\Pi(5\times10^{-2}))^2 m^2} \times 1.9\times10^5 \text{ Pa}$$

This is almost double the atmospheric pressure. Hydraulic brakes in automobiles also work on the same principle. When we apply a little force on the pedal with our foot the master piston moves inside the master cylinder, and the pressure caused is transmitted through the brake oil to act on a piston of larger area. A large force acts on the piston and is pushed down expanding the brake shoes against brake lining. In this way a small force on the pedal produces a large retarding force on the wheel. An important advantage of the system is that the pressure set up by pressing pedal is transmitted equally to all cylinders attached to the four wheels so that the braking effort is equal on all wheel.

Archimedes (287 – 212 B.C.)



Archimedes was a Greek philosopher, mathematician, scientist and engineer. He invented the catapult and devised a system of pulleys and levers to handle heavy loads. The king of his native city Syracuse, Hiero II asked him to determine if his gold crown was alloyed with some cheaper metal such as silver without damaging the crown. The partial loss of weight he experienced while lying in his bathtub suggested a solution to him. According to legend, he ran naked through the streets of Syracuse exclaiming “Eureka, eure

11.3 STREAMLINE FLOW

So far we have studied fluids at rest. The studyof the fluids in motion is known as fluid dynamics. When a water -tap is turned on slowly, the water flow is smooth initially, but loses its smoothness when the speed of the outflow is increased. In studying the motion of fluids we focus our attention on what is happening to various fluid particles at a particular point in space at a particular time. The flow of the fluid is said to be **steady** if at any given point, the velocity of each passing fluid particle remains constant in time. This does not mean that the velocity at different points in space is same. The velocity of a particular particle may change as it moves from one point to another. That is, at some other point the particle may have a different velocity, but every other particle which passes the second point behaves exactly as the previous particle that has just passed that point. Each particle follows a smooth path, and the paths of the particles do not cross each other.

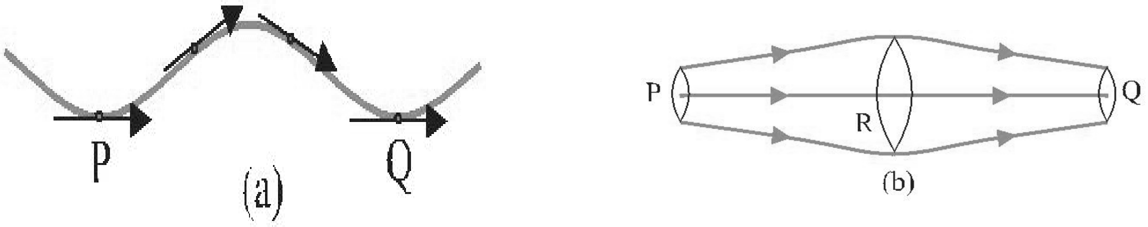


Fig. 11.7 *The meaning of streamlines. (a) A typical trajectory of a fluid particle. (b) A region of streamline flow.*

The path taken by a fluid particle under a steady flow is a streamline. It is defined as a curve whose tangent at any point is in the direction of the fluid velocity at that point. Consider the path of a particle as shown in Fig.11.7 (a), the curve describes how a fluid particle moves with time. The curve PQ is like a permanent map of fluid flow, indicating how the fluid streams. No two streamlines can cross, for if they do, an oncoming fluid particle can go either one way or the other and the flow would not be steady. Hence, in steady flow, the map of flow is stationary in time. How do we draw closely spaced streamlines? If we intend to show streamline of every flowing particle, we would end up with a continuum of lines. Consider planes perpendicular to the direction of fluid flow e.g., at three points P, R and Q in Fig.11.7 (b). The plane pieces are so chosen that their boundaries be determined by the same set of streamlines. This means that number of fluid particles crossing the surfaces as indicated at P, R and Q is the same. If area of cross-sections at these points are AP,AR and AQ and speeds of fluid particles are vP, vR and vQ, then mass of fluid ÄmP crossing at AP in a small interval of time Ät is ρPAPvPÄt. Similarly mass of fluid ÄmR flowing or crossing at AR in a small interval of time Ät is ρAvÄt and mass of fluid Äm is ρQAQvQÄt crossing at AQ. The mass of liquidflowing out equals the mass flowing in, holds in all cases. Therefore,

(11.9)

$$\rho_P A_P v_P \ddot{A}t=\rho_R A_R v_R \ddot{A}t=\rho_Q A_Q v_Q \ddot{A}t$$

For flow of incompressible fluids

$\rho_P = \rho_R = \rho_Q$

Equation (11.9) reduces to

$$A_P v_P = A_R v_R = A_Q v_Q \qquad (11.11)$$

Which is called the equation of continuity and it is a statement of conservation of mass in flow of incompressible fluids. In general

$$Av = \text{constant} \qquad (11.11)$$

Av gives the volume flux or flow rate and remains constant throughout the pipe of flow. Thus, at narrower portions where the streamlines are closely spaced, velocity increases and its vice versa. From (Fig 11.7b) it is clear that AR>AQ or vR<vQ, the fluid is accelerated while passing from R to Q. This is associated with a change in pressure in fluid flow in horizontal pipes.Steady flow is achieved at low flow speeds. Beyond a limiting value, called critical speed, this flow loses steadiness and becomes turbulent. One sees this when a fast flowingstream encounters rocks, small foamy whirlpool-like regions called ‘white water rapids are formed.Figure 11.8 displays streamlines for some typical flows. For example, Fig. 11.8(a) describes a laminar flow where the velocities at different points in the fluid may have different magnitudes but their directions are parallel. Figure 11.8 (b) gives a sketch of turbulent flow.

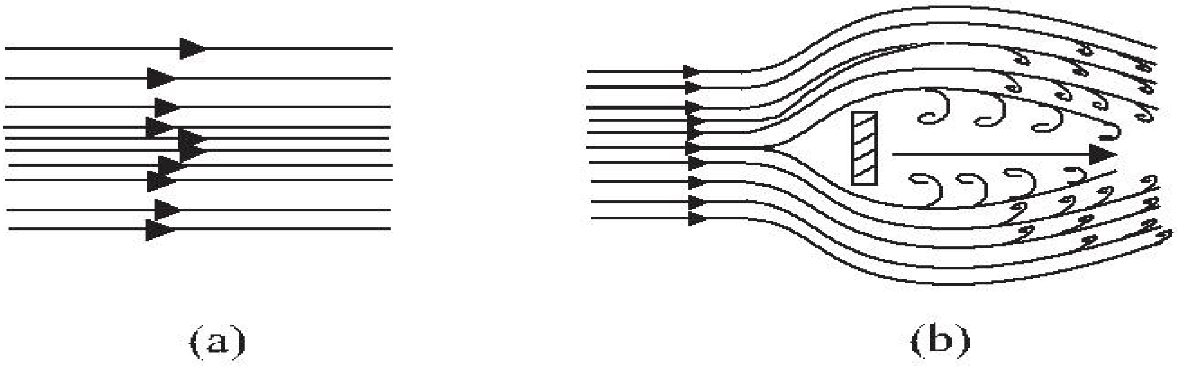


Fig. 11.8 *(a) Some streamlines for fluid flow. (b)A jet of air striking a flat plate placed perpendicular to it. This is an example of turbulent flow.*

11.4 BERNOULLI'S PRINCIPLE

Fluid flow is a complex phenomenon. But we can obtain some useful properties for steady or streamline flows using the conservation of energy.Consider a fluid moving in a pipe of varying cross-sectional area. Let the pipe be at varying heights as shown in Fig. 11.9. We now suppose that an incompressible fluid is flowing through the pipe in a steady flow. Its velocity must change as a consequence of equation of continuity. A force is required to produce this acceleration, which is caused by the fluid surrounding it, the pressure must be different in different regions. Bernoulli's equation is a general expression that relates the pressure difference between two points in a pipe to both velocity changes (kinetic energy change) and elevation (height) changes (potential energychange). The Swiss Physicist Daniel Bernoulli developed this relationship in 1738.

Consider the flow at two regions 1 (i.e. BC) and 2 (i.e. DE). Consider the fluid initially lying between B and D. In an infinitesimal time interval t, this fluid would have moved. Suppose v_1 is the speed at B and v_2 at D, then fluid initially at B has moved a distance v_{1t} to C (v_{1t} is small enough to assume constant cross-section along BC). In the same interval t the fluid initially at D moves to E, a distance equal to v_{2t}. Pressures P_1 and P_2 act as shown on the plane faces of areas A_1 and A_2 binding the two regions. The work done on the fluid at left end (BC) is $W_1 = P_1A_1(v_1t) = P_1V$. Since the same volume V passes through both theregions (from the equation of continuity) the work done by the fluid at the other end (DE) is$W_2=P_2A_2(v_2\ t) = P_2\ V$ or, the work done on the fluid is $-P_2\Delta V$. So the total work done on the fluid is

$$W_1 - W_2 = (P_1 - P_2)\ \Delta V$$

Part of this work goes into changing the kinetic energy of the fluid, and part goes into changing the gravitational potential energy. If the density of the fluid is ρ and $m = \rho A_1 v_1 t = \rho \Delta V$ is the mass passing through the pipe in time t, then change in gravitational potential energy is

$$U = \rho g\ V\ (h_2 - h_1)$$

The change in its kinetic energy is

$$\Delta K = \frac{1}{2}\rho \Delta V(v_2{}^2 - v_1{}^2)$$

We can employ the work – energy theorem (Chapter 6) to this volume of the fluid and this yields

$$(P_1 - P_2)\Delta V = \frac{1}{2}\rho \Delta V(v_2{}^2 - v_1{}^2) + \rho g \Delta V\ (h_2 - h_1)$$

We now divide each term by ΔV to obtain

$$(P_1-P_2)=\frac{1}{2}\rho(v_2{}^2-v_1{}^2)+\rho g\,(h_2-h_1)$$

We can rearrange the above terms to obtain

$$P_1+\frac{1}{2}\rho_1\,v_1{}^2+\rho g h_1=P_2+\frac{1}{2}\rho 2\,v_2{}^2+\rho g h_2$$

(11.12)

Daniel Bernoulli was a Swiss scientist and mathematician who along with Leonard Euler had the distinction of winning the French Academy prize for mathematics ten times. He also studied medicine and served as a professor of anatomy and botany for a while at Basle, Switzerland. His most well known work was in hydrodynamics, a subject he developed from a single principle: the conservation of energy. His work included calculus, probability, the theory of vibrating strings, and applied mathematics. He has been called the founder of mathematical physics.

This is **Bernoulli's equation**. Since 1 and 2refer to any two locations along the pipeline,we may write the expression in general as

$$P+\frac{1}{2}\rho v^2+\rho g h=constant \qquad (11.13)$$

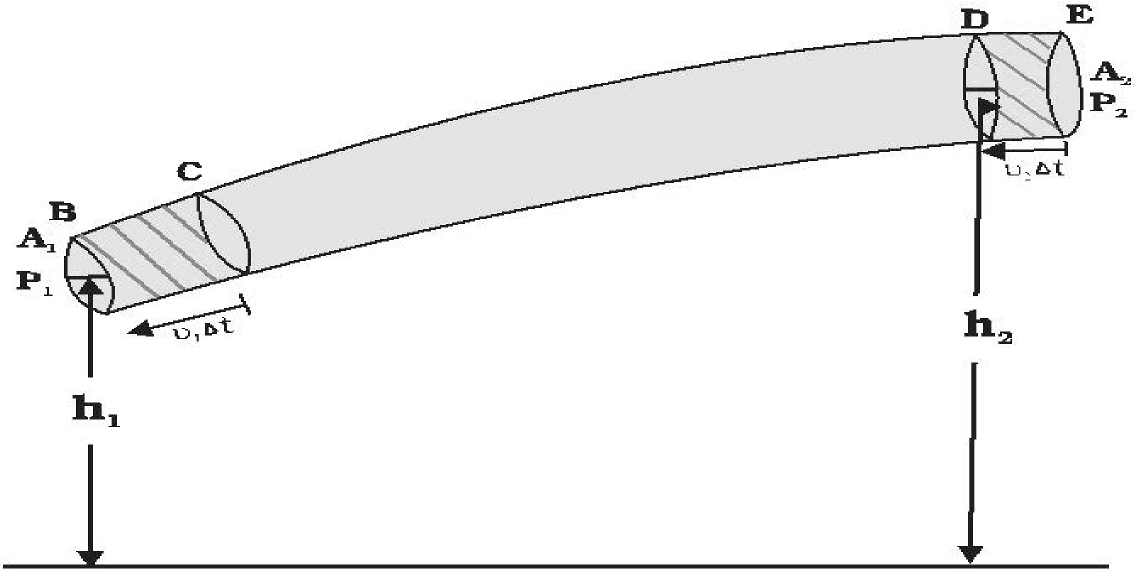


Fig. 11.9 *The flow of an ideal fluid in a pipe of varying cross section. The fluid in a section of length* v_1 *t moves to the section of length* v_2 *t in time t.*

In words, the Bernoulli's relation may be stated as follows: As we move along a streamline the sum of the pressure (*P*), the kinetic energy per unit volume $\frac{v^2}{2}$andthe potential energy per unit volume (ρgh) remains a constant. Note that in applying the energy conservation principle, there is an assumption that no energy is lost due to friction. But in fact, when fluids flow, some energy does get lost due to internal friction. This arises due to the fact that in a fluid flow, the different layers of the fluid flow with different velocities. These layers exert frictional forces on each other resulting in a loss of energy. This property of the fluid is called viscosity and is discussed in more detail in a later section. The lost kinetic energy of the fluid gets converted into heat energy. Thus, Bernoulli's equation ideally applies to fluids with zero viscosity or non-viscous fluids. Another

restriction on application of Bernoulli theorem is that the fluids must be incompressible, as the elastic energy of the fluid is also not taken into consideration. In practice, it has a large number of useful applications and can help explain a wide variety of phenomena for low viscosity incompressible fluids. Bernoulli's equation also does not hold for non-steady or turbulent flows, because in that situation velocity and pressure are constantly fluctuating in time.

When a fluid is at rest i.e. its velocity is zero everywhere, Bernoulli's equation becomes

$$P_1+\rho gh_1= P_2+\rho\, gh_2$$

$$(P_1-P_2) = \rho g\,(h_2-h_1)$$ which is same as Eq. (11.6).

11.4.1 Speed of Efflux: Torricelli's Law

The word efflux means fluid outflow. Torricelli discovered that the speed of efflux from an open tank is given by a formula identical to that of a freely falling body. Consider a tank containing a liquid of density ρ with a small hole in its side at a height y_1 from the bottom (see Fig. 11.11). The air above the liquid, whose surface is at height y_2, is at pressure *P*. From the equation of continuity [Eq. (11.11)] we have

$$v_1\, A_1 = v_2\, A_2$$

$$\frac{A_1}{A_2} v_1 = v_2$$

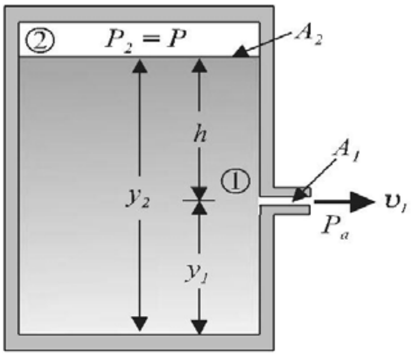


Fig. 11.11 *Torricelli's law. The speed of efflux, v_1, from the side of the container is given by the application of Bernoulli's equation. If the container is open at the top to the atmosphere then* $v_1 = \sqrt{2gh}$

If the cross sectional area of the tank A_2 is much larger than that of the hole ($A_2 >> A_1$), then we may take the fluid to be approximately at rest at the top, i.e. $v_2 = 0$. Now applying the Bernoulli equation at points 1 and 2 and noting that at the hole $P_1 = P_a$, the atmospheric pressure, we have from Eq. (11.12)

$$P_a + \frac{1}{2}\rho v_1^2 + \rho g_1 y = P + \rho g y$$

Taking $y_2 - y_1 = h$ we have

$$v_1 = \sqrt{2gh + \frac{2(P-P_a)}{\rho}}$$

When $P >> P_a$ and $2gh$ may be ignored, the speed of efflux is determined by the container pressure. Such a situation occurs in rocket propulsion. On the other hand if the tank is open to the atmosphere, then $P = P_a$ and

$$v_1 = \sqrt{2gh} \qquad (11.15)$$

This is the speed of a freely falling body.Equation (11.15) is known as **Torricelli's law**.

11.4.2 Venturi-meter

The Venturi-meter is a device to measure the flow speed of incompressible fluid. It consists of a tube with a broad diameter and a small constriction at the middle as shown in Fig. (11.11). A manometer in the form of a U-tube is also attached to it, with one arm at the broad neck point of the tube and the other at constriction as shown in Fig. (11.11). The manometer contains a liquid of density ρ_m. The speed v_1 of the liquid flowing through the tube at the broad neck area A is to be measured from equation of continuity Eq. (11.11) the speed at the constriction becomes $v_2=(Av_2/a_1)$ Then using Bernoulli's equation, we get

$$P_1+\frac{1}{2}\rho v_1^2 = P_2+\frac{1}{2}\rho v_1^2 (A/a)^2 \quad \text{so that}$$

$$P_1-P_2=\frac{1}{2}\rho v_1^2 [(A/a)^2-1] \tag{11.16}$$

This pressure difference causes the fluid in the U tube connected at the narrow neck to rise in comparison to the other arm. The difference in height *h* measure the pressure difference.

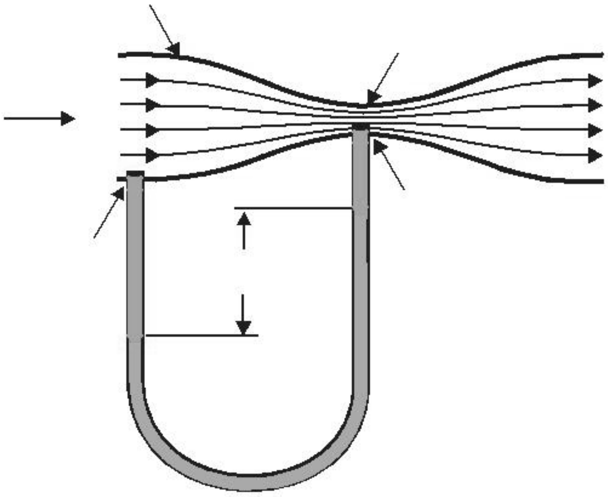


Fig. 11.11 A schematic diagram of Venturi-meter.

$$P_1-P_2=\rho_m gh=\frac{1}{2}\rho v_1^2 [(A/a)^2-1]$$

$$v_1=[\sqrt{(2\rho_m gh/\rho)}]\,[(A/a)^2-1]^{-1/2} \tag{11.17}$$

The principle behind this meter has many applications. The carburetor of automobile has a Venturi channel (nozzle) through which air flows with a large speed. The pressure is then lowered at the narrow neck and the petrol (gasoline) is sucked up in the chamber to provide the correct mixture of air to fuel necessary for combustion. Filter pumps or aspirators, Bunsen burner, atomisers and sprayers [See Fig. 11.12] used for perfumes or to spray insecticides work on the same principle.

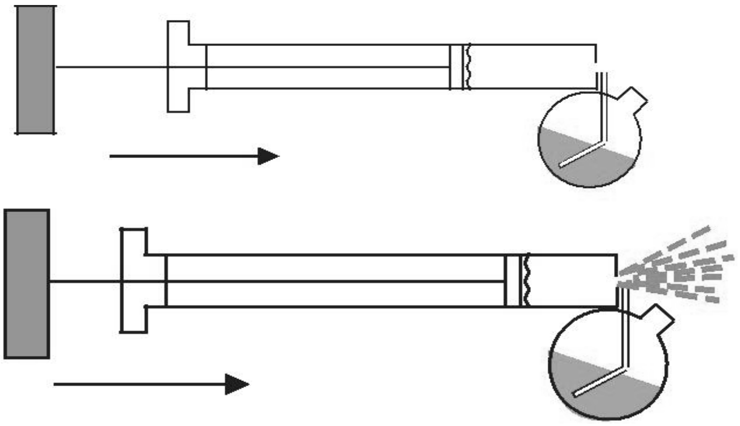


Fig. 11.12 *The spray gun. Piston forces air at high speeds causing a lowering of pressure at the neck of the container*

Example 11.7 **Blood velocity:** The flow of blood in a large artery of an anesthetised dog is diverted through a Venturi meter. The wider part of the meter has a cross-sectional area equal to that of the artery. A = 8 mm^2. The narrower part has an area a = 4 mm^2. The pressure drop in the artery is 24 Pa. What is the speed of the blood in the artery?

Answer We take the density of blood from Table11.1 to be 1.06 x 10^3 kg m^{-3}. The ratio of the area is A/a = 2.

Using Eq. (11.17) we obtain

$$v_1 = \sqrt{\frac{2\text{x}24 \text{ pa}}{1060 \text{ Kg m}^{-3}\text{x } (2^2-1)}} = 0.125 \text{ ms}^{-1}$$

11.4.3 Blood Flow and Heart Attack

Bernoulli's principle helps in explaining blood flow in artery. The artery may get constricted due to the accumulation of plaque on its inner walls. In order to drive the blood through this constriction a greater demand is placed on the activity of the heart. The speed of the flow of the blood in this region is raised which lowers the pressure inside and the artery may collapse due to the external pressure. The heart exerts further pressure to open this artery and forces the blood through. As the blood rushes through the opening, the internal pressure once again drops due to same reasons leading to a repeat collapse. This may result in heart attack.

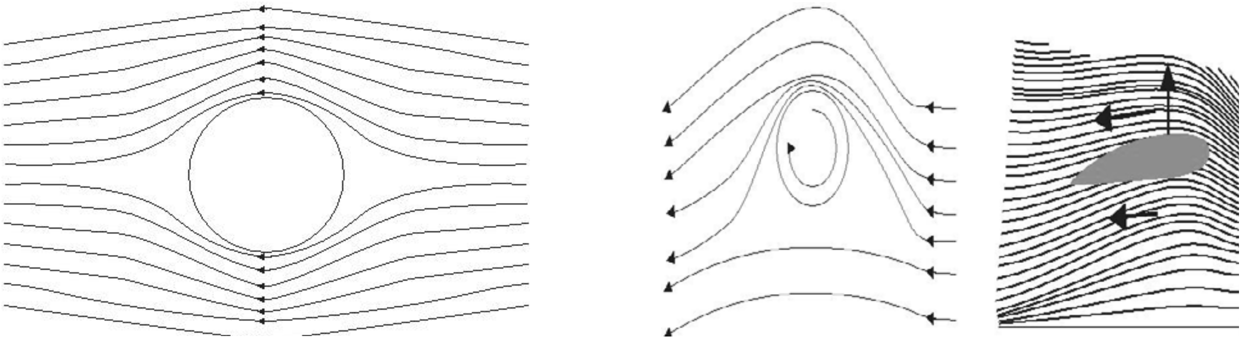
11.4.4 Dynamic Lift

Dynamic lift is the force that acts on a body, such as airplane wing, a hydrofoil or a spinning ball, by virtue of its motion through a fluid. In many games such as cricket, tennis, baseball, or golf, we notice that a spinning ball deviates from its parabolic trajectory as it moves through air. This deviation can be partly explained on the basis of Bernoulli’s principle.

(i) **Ball moving without spin**: Fig. 11.13(a)shows the streamlines around a non-spinning ball moving relative to a fluid. From the symmetry of streamlines it is clear that the velocity of fluid (air) above and below the ball at corresponding points is the same resulting in zero pressure difference. The air therefore, exerts no upward or downward force on the ball.

(ii) **Ball moving with spin**: A ball which isspinning drags air along with it. If the surface is rough more air will be dragged. Fig 11.13(b) shows the streamlines of air for a ball which is moving and spinning at the same time. The ball is moving forward and relative to it the air is moving backwards. Therefore, the velocity of air above the ball relative to it is larger and below it is smaller. The stream lines thus get crowded above and rarified below.

This difference in the velocities of air results in the pressure difference between the lower and upper faces and there is a net upward force on the ball. This dynamic lift due to spinning is called **Magnus effect**.



(a) **(b)** **(c)**

Fig 11.13 *(a) Fluid streaming past a static sphere. (b) Streamlines for a fluid around a sphere spinning clockwise.(c) Air flowing past an aerofoil.*

Aerofoil or lift on aircraft wing: Figure 11.13shows an aerofoil, which is a solid piece shaped to provide an upward dynamic lift when it moves horizontally through air. The cross-section of the wings of an aeroplane looks somewhat like the aerofoil shown in Fig. 11.13 (c) with streamlines around it. When the aerofoil moves against the wind, the orientation of the wing relative to flow direction causes the streamlines to crowd together above the wing more than those below it. The flow speed on top is higher than that below it. There is an upward force resulting in a dynamic lift of the wings and this balances the weight of the plane. The following example illustrates this.

Example 11.8 A fully loaded Boeing aircraft has a mass of 3.3 x 10^5 kg. Its total wing area is 500 m^2. It is in level flight with a speed of 960 km/h. (a) Estimate the pressure difference between the lower and upper surfaces of the wings (b) Estimate the fractional increase in the speed of the air on the upper surface of the wing relative to the lower surface. [The density of air is $\rho = 1.2$ kg m^{-3}]

Answer (a) The weight of the Boeing aircraft isbalanced by the upward force due to the pressure difference

$$P \times A = 3.3\text{x}10^5\text{kg x } 9.8$$

$$P = (3.3\text{x}10^5\text{kg x } 9.8 \text{ m s}^{-2}) / 500 \text{ m}^2$$

$$= 6.5 \text{ x } 10^3 \text{ Nm}^{-2}$$

(b) We ignore the small height difference between the top and bottom sides in Eq. (11.12). The pressure difference between them is then

$$\Delta P = \frac{1}{2}\rho(v_2^2 - v_1^2)$$

wherev_2 is the speed of air over the upper surface and v_1 is the speed under the bottom surface.

$$v_2 - v_1 = \frac{2\Delta P}{\rho(v_2 + v_1)}$$

Taking the average speed$v_{av}=(v_2+v_1)/2=960$ km/h=267 ms^{-1}

we have

$$\frac{v_2 - v_1}{v_{av}} = \frac{\Delta P}{\rho v_{av}^2} = 0.08$$

The speed above the wing needs to be only 8% higher than that below.

11.5 VISCOSITY

Most of the fluids are not ideal ones and offer some resistance to motion. This resistance to fluid motion is like an internal friction analogous to friction when a solid moves on a surface. It is called viscosity. This force exists when there is relative motion between layers of the liquid. Suppose we consider a fluid like oil enclosed between two glass plates as shown in Fig. 11.15 (a). The bottom plate is fixed while the top plate is moved with a constant velocity **v** relative to the fixed plate. If oil is replaced by honey, a greater force is required to move the plate with the same velocity. Hence we say that honey is more viscous than oil. The fluid in contact with a surface has the same velocity as that of the surfaces. Hence, the layer of the liquid in contact with top surface moves with a velocity **v** and the layer of the liquid in contact with the fixed surface is stationary. The velocities of layers increase uniformly from bottom (zero velocity) to the top layer (velocity **v**). For any layer of liquid, its upper layer pullsit forward while lower layer pulls it backward. This results in force between the layers. This type of flow is known as laminar. The layers of liquid slide over one another as the pages of a book do when it is placed flat on a table and a horizontal force is applied to the top cover. When a fluid is flowing in a pipe or a tube, then velocity of the liquid layer along the axis of the tube is maximum and decreases gradually as we move towards the walls where it becomes zero, Fig. 11.14 (b). The velocity on a cylindrical surface in a tube is constant.

On account of this motion, a portion of liquid, which at some instant has the shape ABCD, take the shape of AEFD after short interval of time (t). During this time interval the liquid has undergone a shear strain of x/l. Since, the strain in a flowing fluid increases with time continuously. Unlike a solid, here the stress is found experimentally to depend on ‘rate of change of strain’ or ‘strain rate’ i.e. $x/(l\ t)$ or v/l instead of strain itself. The coefficient of viscosity (pronounced ‘eta’) for a fluid is defined as the ratio of shearing stress to the strain rate.

$$\eta = \frac{F/A}{v/l} = \frac{Fl}{vA} \quad (11.18)$$

The SI unit of viscosity is poiseiulle (Pl). Its other units areN s m^{-2} or Pa s. The dimensions

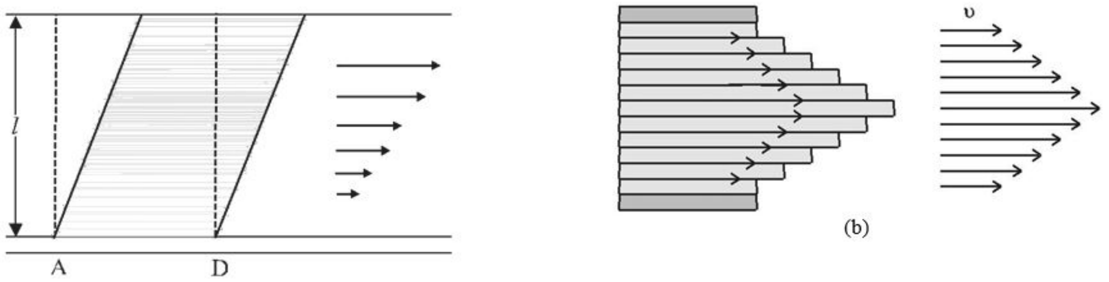


Fig 11.14 *(a) A layer of liquid sandwiched between two parallel glass plates in which the lower plate is fixed and the upper one is moving to the right with velocity* **v** *velocity distribution for viscous flow in a pipe.*

of viscosity are [ML^{-1}T^{-1}]. Generally thin liquids like water, alcohol etc. are less viscous than thick liquids like coal tar, blood, glycerin etc. The coefficients of viscosity for some common fluids are listed in Table 11.2. We point out two facts about blood and water that you may find interesting. As Table 11.2 indicates, blood is ‘thicker’ (more viscous) than water. Further therelative viscosity (η/η_{water}) of blood remains constant between 0^{o}C and 37^{o}C.The viscosity of liquids decreases with temperature while it increases in the case of gases.

Example 11.9 A metal block of area 0.11 m^2 is connected to a 0.011 kg mass via a string that passes over an ideal pulley (considered mass less and frictionless), as in Fig. 11.15. A liquid with a film thickness of 0.30 mm is placed between the block andthetableWhen released the block moves to the rightwith a constant speed of 0.085 m s^{-1}. Findthe coefficient of viscosity of the liquid.

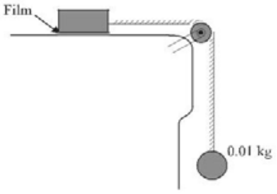


Fig. 11.15 *Measurement of the coefficient ofviscosity of a liquid.*

Answer The metal block moves to the right because of the tension in the string. The tension *T* is equal in magnitude to the weight of the suspended mass m. Thus the shear force *F* is $F = T = mg$ = 0.011 kg x 9.8 m s^{-2}= 9.8x10^{-2}N shearing stress on the fluid $= \frac{F}{A} = \frac{9.8\times10^{-2}}{0.11}$

$$\text{strain rate} = \frac{v}{l} = \frac{0.085}{0.030}$$

$$\eta = \frac{\text{stress}}{\text{strain rate}}$$

$$= \frac{9.8\times10^{-2}\ \text{N}\times0.30\times10^{-3}\ \text{m}}{0.085\ \text{ms}^{-1}\times0.10\ \text{m}^2} = 3.45\text{x}10^{-3}\ \text{pas}$$

Table11.2 The viscosities of some fluids

Fluid	**T (°C)**	**Viscocity (mPI)**
Water	20	1.0
	110	0.3
Blood	37	2.7
Machine oil	16	113
	38	34
Glycerine	20	830
Honey		200
Air	0	0.017
	40	0.019

11.5.1 Stokes' Law

When a body falls through a fluid it drags the layer of the fluid in contact with it. A relative motion between body experiences a retarding force. Falling of a raindrop and swinging of a pendulum bob are some common examples of such motion. It is seen that the viscous force is proportional to the velocity of the object and is opposite to the direction of motion. The other quantities on which the force F depends on viscosity η of the fluid and radius a of the sphere. Sir George G. Stokes (1819-1903), an English scientist enunciated clearly the viscous drag force F as

$$F = 6\Pi\eta\, av \qquad (11.19)$$

This is known as Stokes' law. We shall not derive Stokes' law.This law is an interesting example of retarding force which is proportional to velocity. We can study its consequences on an object falling through a viscous medium. We consider a raindrop in air. It accelerates initially due to gravity. As the velocity increases, the retarding force also increases. Finally when viscous force plus buoyant force becomes equal to force due to gravity, the net force becomes zero and so does the acceleration. The sphere (raindrop) then descends with a constant velocity. Thus in equilibrium, this terminal velocity v_t is given by

$$6\pi\eta avt = (4\pi/3)\ a3\ (\rho-\sigma)g$$

where ρ and σ are mass densities of sphere and the fluid respectively. We obtain

$$v_t = 2a2(\rho-\sigma)g\ /\ (9\eta) \qquad (11.20)$$

So the terminal velocity v_t depends on the square of the radius of the sphere and inversely on the viscosity of the medium.You may like to refer back to Example 6.2 in this context.

Example 11.11The terminal velocity of a copper ball of radius 2.0 mm falling through a tank Ofoil at 20°C is 6.5 cm s^{-1}. Compute the viscosity of the oil at 20°C. Density of oil is 1.5 $X10^3$ kg m^{-3}, density of copper is 8.9 $x10^3$ kg m^{-3}.

Answer We have $v_t = 6.5\cdot 11^{-2}ms^{-1}$,$a = 2\cdot 11^{-3}m$,$g = 9.8\ ms^{-2}$,$\rho = 8.9\cdot 11^{3}kg\ m^{-3}$,

$\sigma = 1.5\cdot 11^{3}\ kg\ m^{-3}$. From Eq. (11.20)

$$\eta = \frac{2}{9} \times \frac{2\times10^{-3}m^2\times9.8ms^{-2}}{6.5\times10^{-2}ms^{-1}} \times 7.4\times10^{3}Kgm^{-3}$$

$$=9.9\times10^{-1}\text{Kg m}^{-1}\text{s}^{-1}$$

11.6 REYNOLDS NUMBER

When the rate of flow of a fluid is large, the flow no longer remain laminar, but becomes turbulent. In a turbulent flow the velocity of the fluids at any point in space varies rapidly and randomly with time. Some circular motions called eddies are also generated. An obstacle placed in the path of a fast moving fluid causes turbulence [Fig. 11.8 (b)]. The smoke rising from a burning stack of wood, oceanic currents are turbulent. Twinkling of stars is the result of atmospheric turbulence. The wakes in the water and in the air left by cars, aeroplanes and boats are also turbulent.

Osborne Reynolds (1842-1912) observed that turbulent flow is less likely for viscous fluid flowing at low rates. He defined a dimensionless number, whose value gives one an approximate idea whether the flow would be turbulent.

This number is called the Reynolds

$$R_e=\rho\ vd/\eta \qquad (11.21)$$

where ρ is the density of the fluid flowing with a speed v, d stands for the dimension of the pipe, and η is the viscosity of the fluid. Re is a dimensionless number and therefore, it remains same in any system of units. It is found that flow is streamline or laminar for Re less than 1100. The flow is turbulent for $R_e > 2000$. The flow becomes unsteady for Re between 1100 and 2000. The critical value of Re (known as critical Reynolds number), at which turbulence sets, is found to be the same for the geometrically similar flows. For example when oil and water with their different densities and viscosities, flow in pipes of same shapes and sizes, turbulence sets in at almost the same value of Re. Using this fact a small scale laboratory model can be set up to study the character of fluid flow. They are useful in designing of ships, submarines, are useful in designing of racing cars and aeroplanes.

Rescan also be written as

$$R_e=\rho v_2/(\eta v/d)=\rho A v_2/(\eta A v/d)$$

(11.20)

Thus Re represents the ratio of inertial force (force due to inertia i.e. mass of moving fluid or due to inertia of obstacle in its path) to viscous force.Turbulence dissipates kinetic energy usually in the form of heat. Racing cars and planes are engineered to precision in order to minimise turbulence. The design of such vehicles involves experimentation and trail anderror. On the other hand turbulence (like friction) is sometimes desirable. Turbulence promotes mixing and increases the rates of transfer of mass, momentum and energy. The blades of a kitchen mixer induce turbulent flow and provide thick milk shakes as well as beat eggs into a uniform texture.

Example 11.11 The flow rate of water froma tap of diameter 1.25 cm is 0.48 L/min. The coefficient of viscosity of water is 10^{-3} Pa s. After sometime the flow rate is increased to 3 L/min. Characterize the flow for both the flow rates.

Answer Let the speed of the flow be v and the diameter of the tap be d = 1.25 cm. The volume

of the water flowing out per second is

$$Q = v \pi d^2 / 4$$

$$v = 4 Q / d^2$$

We then estimate the Reynolds number to be

$$R_e = 4\rho Q / \pi d \eta$$
$$= 4 \text{ x} 10^3 \text{ kg m}^{-3} \text{ x } Q / (3.14 \ 1.25 \ 10^{-2} \text{ m x } 10^{-3} \text{ Pa s})$$
$$= 1.019 \times 10^8 \text{ m}^{-3} \text{ s } Q$$

Since initially $Q = 0.48 \text{ L / min} = 8 \text{ cm}^3/\text{ s} = 8 \cdot 11^{-6} \text{m}^3\text{s}^{-1}$,we obtain,

$$R_e = 815$$

Since this is below 1000, the flow is steady. After some time when

$$Q = 3 \text{ L / min} = 50 \text{ cm}^3/\text{ s} = 5 \text{x} 10^{-5} \text{m}^3\text{s}^{-1},$$

we obtain, $R_e = 5095$

The flow will be turbulent. You may carry out an experiment in your washbasin to determine the transition from laminar to turbulent flow.

11.7 SURFACE TENSION

You must have noticed that, oil and water do not mix; water wets you and me but not ducks; mercury does not wet glass but water sticks to it, oil rises up a cotton wick, inspite of gravity, Sap and water rise up to the top of the leaves of the tree, hairs of a paint brush do not cling together when dry and even when dipped in water but form a fine tip when taken out of it. All these and many more such experiences are related with the free surfaces of liquids. As liquids have no definite shape but have a definite volume, they acquire a free surface when poured in a container.

These surfaces possess some additional energy. This phenomenon is known as surface tension and it is concerned with only liquid as gases do not have free surfaces. Let us now understand this phenomenon.

11.7.1 Surface Energy

A liquid stays together because of attraction between molecules. Consider a molecule well inside a liquid. The intermolecular distances are such that it is attracted to all the surrounding molecules [Fig. 11.16(a)]. This attraction results in a negative potential energy for the molecule, which depends on the number and distribution of molecules around the chosen one. But the average potential energy of all the molecules is the same. This is supported by the fact that to take a collection of such molecules (the liquid) and to disperse them far away from each other in order to evaporate or vaporise, the heat of evaporation required is quite large. For water it is of the order of 40 kJ/mol.

Let us consider a molecule near the surface Fig. 11.16(b). Only lower half side of it is surrounded by liquid molecules. There is some negative potential energy due to these, but obviously it is less than that of a molecule in bulk, i.e., the one fully inside. Approximately it is half of the latter. Thus, molecules on a liquid surface have some extra energy in comparison to molecules in the interior. A liquid thus tends to have the least surface area which external conditions permit. Increasing surface area requires energy. Most surface phenomenon can be understood in terms of this fact. What is the energy required for having a molecule at the surface? As mentioned above, roughly it is half the energy required to remove it entirely from the liquid i.e., half the heat of evaporation.

Finally, what is a surface? Since a liquid consists of molecules moving about, there cannot be a perfectly sharp surface. The density of the liquid molecules drops rapidly to zero around $z = 0$ as we move along the direction indicated Fig 11.16 (c) in a distance of the order of a few molecular sizes.

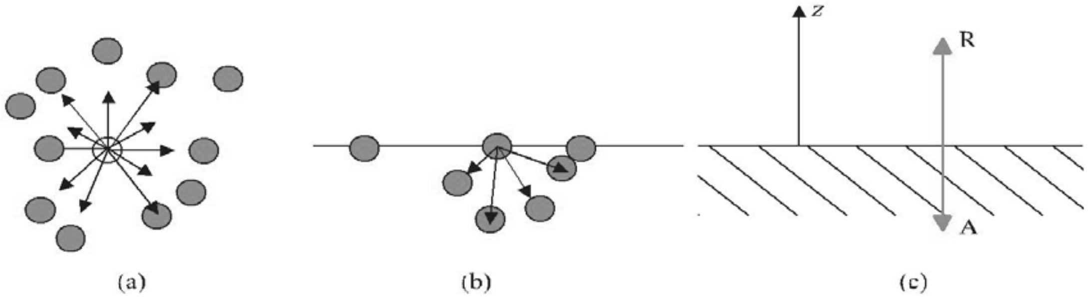


Fig. 11.16 *Schematic picture of molecules in a liquid, at the surface and balance of forces. (a) Molecule inside a liquid. Forces on a molecule due to others are shown. Direction of arrows indicates attraction of repulsion. (b) Same, for a molecule at a surface. (c) Balance of attractive (A) and repulsive (R) forces.*

11.7.2 Surface Energy and Surface Tension

As we have discussed that an extra energy is associated with surface of liquids, the creation of more surface (spreading of surface) keeping other things like volume fixed requires additional energy. To appreciate this, consider a horizontal liquid film ending in bar free to slide over parallel guides Fig (11.17).

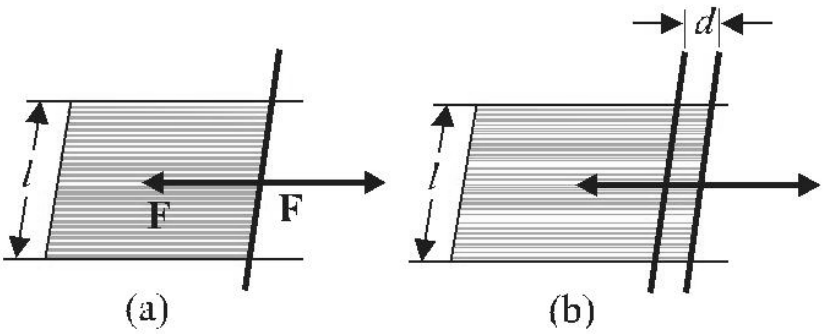


Fig. 11.17 Stretching a film. (a) A film in equilibrium;(b) The film stretched an extra distance.

ce increases, the system now has more energy, this means that some work has been done against an internal force. Let this internal force be **F**, the work done by the applied force is $\mathbf{F}\cdot\mathbf{d}=Fd$. From conservation of energy, this isstored as additional energy in the film. If the surface energy of the film is S per unit area, the extra area is $2dl$**.** A film has two sides and the liquid in between, so there are two surfaces and the extra energy is

$$S(2dl)= Fd \qquad (11.23)$$

$$\text{Or, } S=Fd/2dl=F/2l \qquad (11.24)$$

This quantity S is the magnitude of surface tension. It is equal to the surface energy per unit area of the liquidinterface and is also equal to the force per unit length exerted by the fluid on the movable bar.

So far we have talked about the surface of one liquid. More generally, we need to consider fluid surface in contact with other fluids or solid surfaces. The surface energy in that case depends on the materials on both sides of the surface. For example, if the molecules of the materials attract each other, surface energy is reduced while if they repel each other the surface energy is increased. Thus, more appropriately, the surface energy is the energy of the interface between two materials and depends on both of them.

We make the following observations from above:

(i) Surface tension is a force per unit length (or surface energy per unit area) acting in the plane of the interface between the plane of the liquid and any other substance; it also is the extra energy that the molecules at the interface have as compared to molecules in the interior.

(ii) At any point on the interface besides the boundary, we can draw a line and imagine equal and opposite surface tension forces *S* per unit length of the line acting perpendicular to the line, in the plane of the interface. The line is in equilibrium. To be more specific, imagine a line of atoms or molecules at the surface. The atoms to the left pull the line towards them; those to the right pull it towards them! This line of atoms is in equilibrium under tension. If the line really marks the end of the interface, as in Figure 11.16 (a) and (b) there is only the force *S* per unit length acting inwards.

(iii)Table 11.3 gives the surface tension of various liquids. The value of surface tension depends on temperature. Like viscosity, the surface tension of a liquid usually falls with temperature.

Table 11.3 Surface tension of some liquids at the temperatures indicated with the heats of the vaporization

Liquid	Temp ($°C$)	Surface Tension (N/m)	Heat of vaparisation
Helium	-270	0.000239	0.115
Oxygen	-183	0.0132	7.1
Ethanol	20	0.0227	40.6
Water	20	0.0727	44.16
Mercury	20	0.4355	63.2

A fluid will stick to a solid surface if the surface energy between fluid and the solid is smaller than the sum of surface energies between solid-air, and fluid-air. Now there is cohesion between the solid surface and the liquid. It can be directly measured experimentally as schematically shown in Fig. 11.18. A flat vertical glass plate, below which a vessel of some liquid is kept, forms one arm of the balance. The plate is balanced by weights on the other side, with its horizontal edge just over water. The vessel is raised slightly till the liquid just touches the glass plate and pulls it down a little because of surface tension. Weights are added till the plate just clears water.

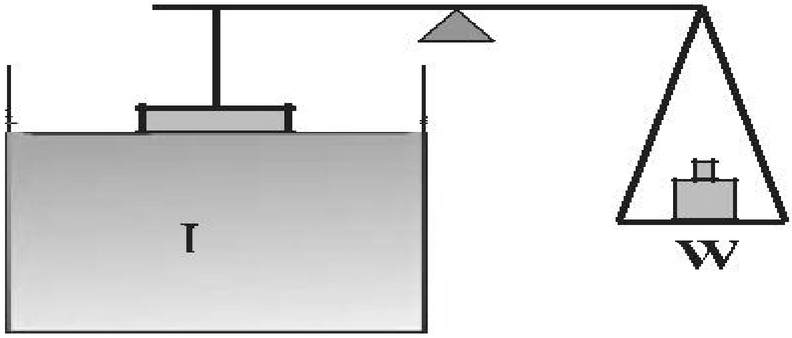


Fig. 11.18 *Measuring Surface Tension.*

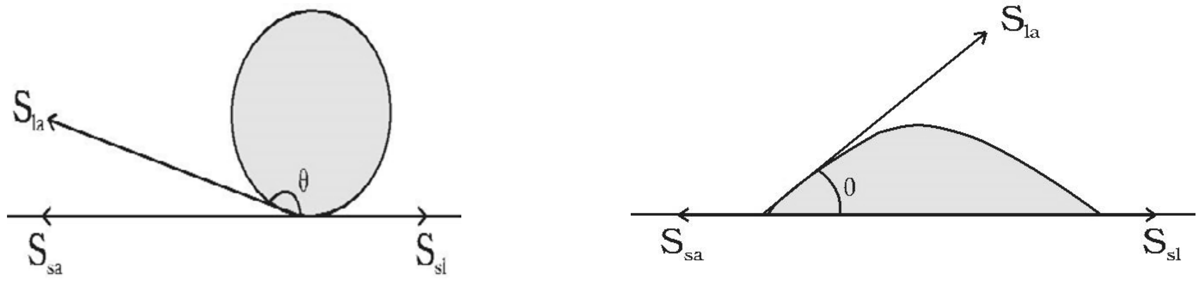
Suppose the additional weight required is *W*. Then from Eq. 11.24 and the discussion given there, the surface tension of the liquid-air interface is

$$S_{la} = (W/2l) = (mg/2l) \qquad (11.25)$$

where m is the extra mass and *l* is the length of the plate edge. The subscript (la) emphasises the fact that the liquid-air interface tension is involved.

11.7.3 Angle of Contact

The surface of liquid near the plane of contact, with another medium is in general curved. The angle between tangent to the liquid surface at the point of contact and solid surface inside the liquid is termed as angle of contact. It is denoted by θ. It is different at interfaces of different pairs of liquids and solids. The value of θ determines whether a liquid will spread on the surface of a solid or it will form droplets on it. For example, water forms droplets on lotus leaf as shown in Fig. 11.19 (a) while spreads over a clean plastic plate as shown in Fig. 11.19(b).



(a) **(b)**

Fig. 11.19 *Different shapes of water drops with interfacial tensions (a) on a lotus leaf (b) on a clean plastic plate.*

We consider the three interfacial tensions at all the three interfaces, liquid-air, solid-air and solid-liquid denoted by S_{la}, S_{sa}&S_{sl} respectively as given in Fig. 11.19 (a) and (b). At the line of contact, the surface forces between the three media must be in equilibrium. From the Fig. 11.19(b) the following relation is easily derived.

$$S_{la}\cos\theta+S_{sl}=S_{sa} \qquad (11.26)$$

The angle of contact is an obtuse angle if Ssl>Slaas in the case of water-leaf interface while it is an acute angle if $S_{sl}<S_{la}$ as in the case of water-plastic interface. When θ is anobtuse angle then molecules of liquids are attracted strongly to themselves and weakly to those of solid, it costs a lot of energy to create a liquid-solid surface, and liquid then does not wet the solid. This is what happens with water on a waxy or oily surface, and with mercury on any surface. On the other hand, if the molecules of the liquid are strongly attracted to those of the solid, this will reduce S_{sl} and therefore, cosθ may increase or θ may decrease. In this case θ is an acute angle. This is what happens for water on glass or on plastic and for kerosene oil on virtually anything (it just spreads). Soaps, detergents and dying substances are wetting agents. When they are added the angle of contact becomes small so that these may penetrate well and become effective. Water proofing agents on the other hand are added to create a large angle of contact between the water and fibres.

11.7.4 Drops and Bubbles

One consequence of surface tension is that free liquid drops and bubbles are spherical if effects of gravity can be neglected. You must have seen this especially clearly in small drops just formed in a high-speed spray or jet, and in soap bubbles blown by most of us in childhood. Why are drops and bubbles spherical? What keeps soap bubbles stable?

As we have been saying repeatedly, a liquid-air interface has energy, so for a given volume the surface with minimum energy is the one with the least area. The sphere has this property. Though it is out of the scope of this book, but you can check that a sphere is better than at least a cube in this respect! So, if gravity and other forces (e.g. air resistance) were ineffective, liquid drops would be spherical.

Another interesting consequence of surface tension is that the pressure inside a spherical drop Fig. 11.20(a) is more than the pressure outside. Suppose a spherical drop of radius r is in equilibrium. If its radius increase by r. The extra surface energy is

$$[4\pi(r+\Delta r)^2 - 4\pi r^2]\, S_{la} = 8\pi r \Delta r\, S_{la} \qquad (11.27)$$

If the drop is in equilibrium this energy cost is balanced by the energy gain due to expansion under the pressure difference ($P_i - P_o$) between the inside of the bubble and the outside. The work done is

$$w = (p_i - p_o)\,4\pi r^2 \Delta r \qquad (11.28)$$

So that

$$(p_i - p_o) = \left(\frac{2S_{1a}}{r}\right) \qquad (11.29)$$

In general, for a liquid-gas interface, the convex side has a higher pressure than the concave side. For example, an air bubble in a liquid, would have higher pressure inside it. See Fig 11.20 (b).

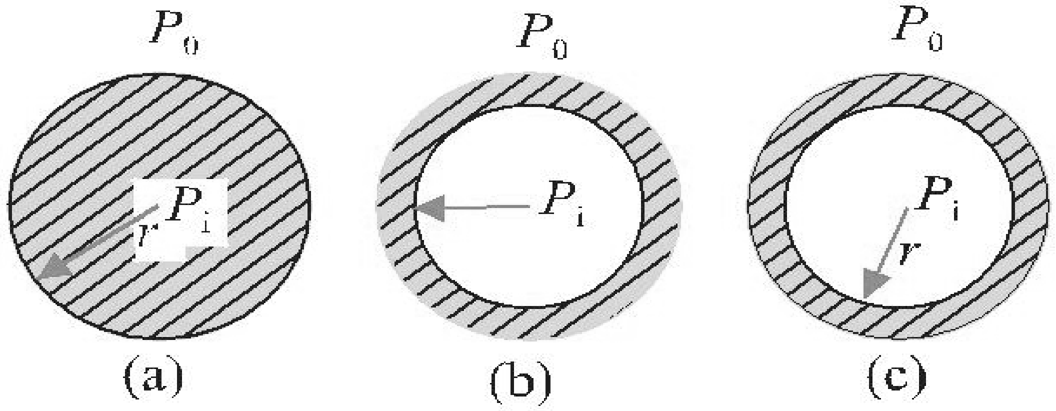


Fig. 11.20 *Drop, cavity and bubble of radius r.*

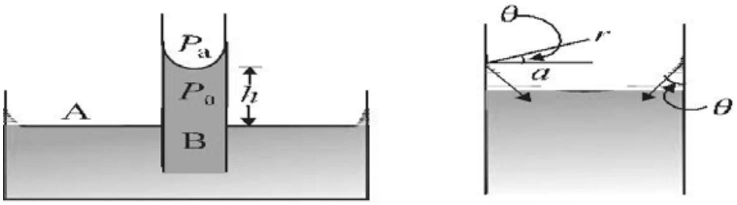
A bubble Fig 11.20 (c) differs from a drop and a cavity; in this it has two interfaces. Applying the above argument we have for a bubble

$$(P_i - P_o) = (4\, S_{la}/r) \qquad (11.30)$$

This is probably why you have to blow hard,but not too hard, to form a soap bubble. A little extra air pressure is needed inside!

11.7.5 Capillary Rise

One consequence of the pressure difference across a curved liquid-air interface is the well-known effect that water rises up in a narrow tube in spite of gravity. The word capilla means hair in Latin; if the tube were hair thin, the rise would be very large. To see this, consider a vertical capillary tube of circular cross section (radius a) inserted into an open vessel of water (Fig. 11.21). The contact angle between water and glass is acute. Thus the surface of water in the capillary is concave. This means that there is a pressure difference between the two sides of the top surface. This is given by



(a) (b)

Fig. 11.21 *Capillary rise, (a) Schematic picture of an arrow tube immersed water.(b) Enlarged picture near interface.*

$$(P_i - P_o) = (2S/r) = 2S/(a \sec \theta)$$
$$= (2S/a)\cos\theta \qquad (11.31)$$

Thus the pressure of the water inside the tube, just at the meniscus (air-water interface) is less than the atmospheric pressure. Consider the two points A and B in Fig. 11.21(a). They must be at the same pressure, namely

$$P_0 + h\rho\ g = P_i = P_A \qquad (11.32)$$

whereρ is the density of water and h is called the capillary rise [Fig. 11.21(a)]. Using Eq. (11.31) and (11.32) we have

$$h\rho\ g = (P_i - P_0) = (2S\cos\theta)/a \qquad (11.33)$$

The discussion here, and the Eqs. (11.28) and (11.29) make it clear that the capillary rise is due to surface tension. It is larger, for a smaller a. Typically it is of the order of a few cm for fine capillaries. For example, if $a = 0.05$ cm, using the value of surface tension for water (Table 11.3), we find that $h = 2S/(\rho\, g\, a)$

$$= \frac{2 \times 0.073\, Nm^{-1}}{10^3 kgm^{-3} \times 9.8 ms^{-2} \times 5 \times 10^{-4} m}$$

$$= 2.98 \times 10^{-2} \text{ m} = 2.98 \text{ cm}$$

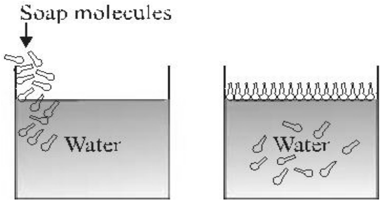
Notice that if the liquid meniscus is convex, as for mercury, i.e., if $\cos\theta$ is negative then from Eq. (11.32) for example, it is clear that the liquid will be lower in the capillary !

11.7.6 Detergents and Surface Tension

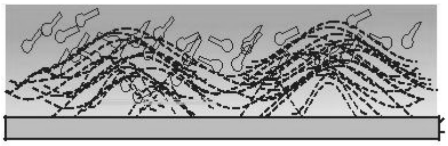
We clean dirty clothes containing grease and oil stains sticking to cotton or other fabrics by adding detergents or soap to water, soaking clothes in it and shaking. Let us understand this process better.

Washing with water does not remove grease stains. This is because water does not wet greasy dirt; i.e., there is very little area of contact between them. If water could wet grease, the flow of water could carry some grease away. Something of this sort is achieved through detergents. The molecules of detergents are hairpinshaped, with one end attracted to water and the other to molecules of grease, oil or wax, thus tending to form water-oil interfaces. The result is shown in Fig. 11.22 as a sequence of figures.

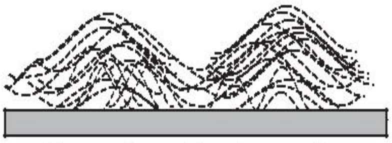
In our language, we would say that addition of detergents, whose molecules attract at one end and say, oil on the other, reduces drastically the surface tension S (water-oil). It may even become energetically favourable to form such interfaces, i.e., globs of dirt surrounded by detergents and then by water. This kind of process using surface active detergents or surfactants is important not only for cleaning, but also in recovering oil, mineral ores etc.



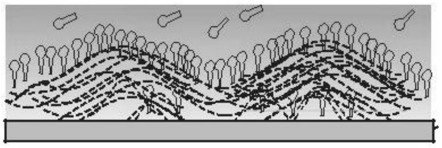
Soap molecule head attracted to water



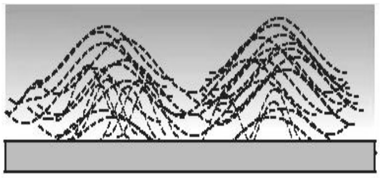
Detergent is added, the 'inert' waxy ends of its molecules are attracted to boundary where water meets dirt.



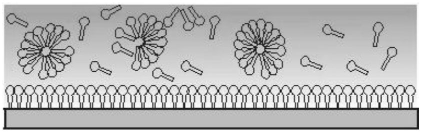
Platter with particles of greasy dirt.



Inert ends surround dirt and the platter dirt can now be dislodged say by moving water.



Water is added; dirt is not dislodged.



Dirt is held suspended, surrounded by soap molecules.

Fig. 11.22 *Detergent action in terms of what detergent molecules do.*

Example 11.12 The lower end of acapillary tube of diameter 2.00 mm is dipped 8.00 cm below the surface of water in a beaker. What is the pressure required in the tube in order to blow a hemispherical bubble at its end in water? The surface tension of water at temperature of the experiments is 7.30×10^{-2} Nm^{-1}. 1 atmospheric pressure = 1.01×10^5 Pa, density of water = 1000 kg/m^3, g = 9.80 m s^{-2}. Also calculate the excess pressure.

Answer The excess pressure in a bubble of gas in a liquid is given by 2S/r, where S is the surface tension of the liquid-gas interface. You should note there is only one liquid surface in this case. (For a bubble of liquid inA gas, there are two liquid surfaces, so the formula for excess pressure in that case is 4S/r.) The radius of the bubble is r. Now the pressure outside the bubble P_o equals atmospheric pressure plus the pressure due to 8.00 cm of water column. That is

$$P_o = (1.01 \times 10^5 \text{Pa} + 0.08 \text{ m} \times 1000 \text{ kg m}^{-3} \times 9.80 \text{ m s}^{-2})$$

$$= 1.01784 \times 10^5 \text{ Pa}$$

Therefore, the pressure inside the bubble is

$$P_i = P_o + 2S/r$$

$$= 1.01784 \times 10^5 \text{ Pa} + (2 \times 7.3 \times 10^{-2} \text{ Pa m}/10^{-3} \text{ m})$$

$$= (1.01784 + 0.00146) \times 10^5 \text{ Pa}$$

$$= 1.02 \times 10^5 \text{ Pa}$$

where the radius of the bubble is taken to be equal to the radius of the capillary tube, since the bubble is hemispherical ! (The answer has been rounded off to three significant figures.) The excess pressure in the bubble is 146 Pa.

SUMMARY

1. The basic property of a fluid is that it can flow. The fluid does not have any resistance to change of its shape. Thus, the shape of a fluid is governed by the shape of its container.
2. A liquid is incompressible and has a free surface of its own. A gas is compressible and it expands to occupy all the space available to it.
3. If F is the normal force exerted by a fluid on an area A then the average pressure $P_{av}$is defined as the ratio of the force to area

$$P_{av}=F/A$$

4. The unit of the pressure is the pascal (Pa). It is the same as N m^{-2}. Other common units of pressure are

   1 atm = 1.01×10^5 Pa

   1 bar = 10^5 Pa

   1 torr = 133 Pa = 0.133 kPa

   1 mm of Hg = 1 torr = 133 Pa

5. Pascal's law states that Pressure in a fluid at rest is same at all points which are at the same height. A change in pressure applied to an enclosed fluid is transmitted undiminished to every point of the fluid and the walls of the containing vessel.
6. The pressure in a fluid varies with depth h according to the expression $P = P_a+\rho gh$
   where ρ is the density of the fluid, assumed uniform.
7. The volume of an incompressible fluid passing any point every second in a pipe of non uniformcrossection is the same in the steady flow.

   v A = constant (v is the velocity and A is the area of crossection)

   The equation is due to mass conservation in incompressible fluid flow.
8. Bernoulli's principle states that as we move along a streamline, the sum of the pressure (P), the kinetic energy per unit volume ($\rho v^2/2$) and the potential energy per unit volume (ρgy) remains a constant.

$$P +\rho\, v^2/2 +\rho gy= \text{constant}$$

The equation is basically the conservation of energy applied to non viscuss fluid motion in steady state. There is no fluid which have zero viscosity, so the above statement is true only approximately. The viscosity is like friction and converts the kinetic energy to heat energy.

9. Though shear strain in a fluid does not require shear stress, when a shear stress is applied to a fluid, the motion is generated which causes a shear strain growing with time. The ratio of the shear stress to the time rate of shearing strain is known as coefficient of viscosity, η.

   where symbols have their usual meaning and are defined in the text.

10. *Stokes' law* states that the viscous drag force **F** on a sphere of radius a moving with velocity **v** through a fluid of viscosity is, $\mathbf{F} = -6\pi\eta a\mathbf{v}$.

11. The onset of turbulence in a fluid is determined by a dimensionless parameter is called the *Reynolds number* given by

$$R_e = \rho v d/\eta$$

   Where d is a typical geometrical length associated with the fluid flow and the other symbols have their usual meaning.

12. Surface tension is a force per unit length (or surface energy per unit area) acting in the plane of interface between the liquid and the bounding surface. It is the extra energy that the molecules at the interface have as compared to the interior.

CHAPTER TWELVE

THERMAL PROPERTIES OF MATTER

12.1 INTRODUCTION

We all have common-sense notions of heat and temperature. Temperature is a measure of 'hotness' of a body. A kettle with boiling water is hotter than a box containing ice. In physics, we need to define the notion of heat, temperature, etc., more carefully. In this chapter, you will learn what heat is and how it is measured, and study the various processes by which heat flows from one body to another. Along the way, you will find out why blacksmiths heat the iron ring before fitting on the rim of a wooden wheel of a bullock cart and why the wind at the beach often reverses direction after the sun goes down. You will also learn what happens when water boils or freezes, and its temperature does not change during these processes even though a great deal of heat is flowing into or out of it.

12.2 TEMPERATURE AND HEAT

We can begin studying thermal properties of matter with definitions of temperature and heat. Temperature is a relative measure, or indication of hotness or coldness. A hot utensil is said to have a high temperature, and ice cube to have a low temperature. An object that has a higher temperature than another object is said to be hotter. Note that hot and cold are relative terms, like tall and short. We can perceive temperature by touch. However, this temperature sense is somewhat unreliable and its range is too limited to be useful for scientific purposes.

We know from experience that a glass of ice-cold water left on a table on a hot summer day eventually warms up whereas a cup of hot tea on the same table cools down. It means that when the temperature of body, ice-cold water or hot tea in this case, and its surrounding medium are different, heat transfer takes place between the system and the surrounding medium, until the body and the surrounding medium are at the same temperature. We also know that in the case of glass tumbler of ice cold water, heat flows from the environment to the glass tumbler, whereas in the case of hot tea, it flows from the cup of hot tea to the environment. So, we can say that heat is the form of energy transferred between two (or more) systems or a system and its surroundings by virtue of temperature difference. The SI unit of heat energy transferred is expressed in joule (J) while SI unit of temperature is Kelvin (K), and °C is a commonly used unit of temperature. When an object is heated, many changes may take place. Its temperature may rise; it may expand or change state. We will study the effect of heat on different bodies in later sections.

12.3 MEASUREMENT OF TEMPERATURE

A measure of temperature is obtained using a thermometer. Many physical properties of materials change sufficiently with temperature to be used as the basis for constructing thermometers. The commonly used property is variation of the volume of a liquid with temperature. For example, a common thermometer (the liquid-in-glass type) with which you are familiar. Mercury and alcohol are the liquids used in most liquid-in-glass thermometers.

Thermometers are calibrated so that a numerical value may be assigned to a given temperature. For the definition of any standard scale, two fixed reference points are needed. Since all substances change dimensions with temperature, an absolute reference for expansion is not available. However, the necessary fixed points may be correlated to physical phenomena that always occur at the same temperature. The ice point and the steam point of water are two convenient fixed points and are known as the freezing and boiling points. These two points are the temperatures at which pure water freezes and boils under standard pressure. The two familiar temperature scales are the Fahrenheit temperature scale and the Celsius temperature scale. The ice and steam point have values 32 °F and 212 °F respectively, on the Fahrenheit scale and 0 °C and 100 °C on the Celsius scale. On the Fahrenheit scale, there are 180 equal intervals between two reference points, and on the celsius scale, there are 100.

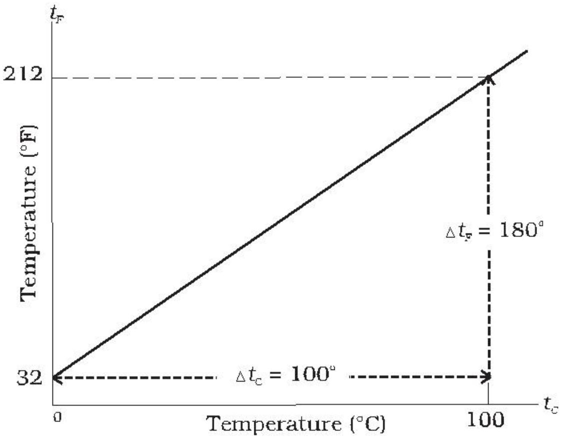


Fig. 12.1 *A plot of Fahrenheit temperature (tF) versus Celsius temperature (tc).*

A relationship for converting between the two scales may be obtained from a graph of Fahrenheit temperature (tF) versus Celsius temperature (tC) in a straight line (Fig. 12.1), whose equation is

$$\frac{t_F - 32}{180} = \frac{t_C}{100} \quad (12.1)$$

12.4 IDEAL-GAS EQUATION AND ABSOLUTE TEMPERATURE

Liquid-in-glass thermometers show different readings for temperatures other than the fixed points because of differing expansion properties. A thermometer that uses a gas, however, gives the same readings regardless of which gas is used. Experiments show that all gases at low densities exhibit same expansion behaviour. The variables that describe the behaviour of a given quantity (mass) of gas are pressure, volume, and temperature (P, V, and T) (where T = t + 273.15; t is the temperature in °C). When temperatureis held constant, the pressure and volume of a quantity of gas are related as PV = constant. This relationship is known as Boyle's law, after Robert Boyle (1627-1691) the English Chemist who discovered it. When the pressure is held constant, the volume of a quantity of the gas is related to the temperature as V/T = constant. This relationship is known as Charles' law, after the French scientist Jacques Charles (1747-1823). Low density gases obey these laws, which may be combined into a single relationship.

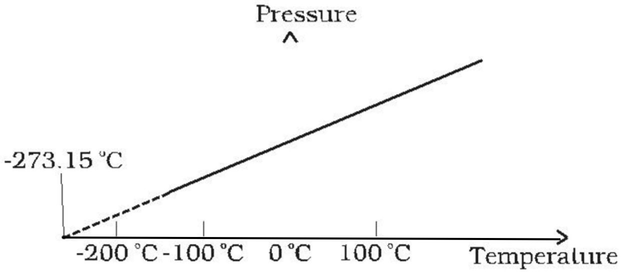


Fig. 12.2 *Pressure versus temperature of a low gas temperature and kept at constant volume*

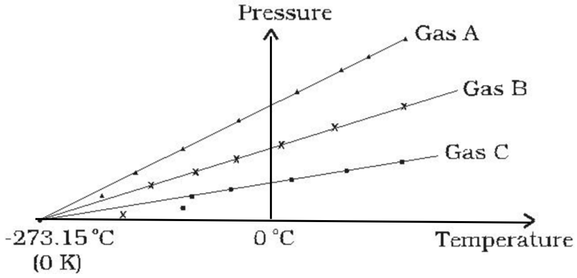


Fig. 12.3 *Aplot of pressure versus density extrapolation of lines for low density gases indicates the same absolute zero temperature.*

Notice that since PV = constant and V/T = constant for a given quantity of gas, then PV/T should also be a constant. This relationship is known as ideal gas law. It can be written in a more general form that applies not just to a given quantity of a single gas but to any quantity of any dilute gas and is known as ideal-gas equation:

$$\frac{PV}{T} = \mu R \ \ Or \ \ PV = \mu RT \tag{12.2}$$

where, μ is the number of moles in the sample of gas and R is called universal gas constant: R = 8.31 J $mol^{-1}K^{-1}$

In Eq. 12.2, we have learnt that the pressure and volume are directly proportional to temperature: $PV \propto T$. This relationship allows a gas to be used to measure temperature in a constant volume gas thermometer. Holding the volume of a gas constant, it gives P T. Thus, with a constant-volume gas thermometer, temperature is read in terms of pressure. A plot of pressure versus temperature gives a straight line in this case, as shown in Fig. 12.2.

However, measurements on real gases deviate from the values predicted by the ideal gas law at low temperature. But the relationship is linear over a large temperature range, and it looks as though the pressure might reach zero with decreasing temperature if the gas continued to be a gas. The absolute minimum temperature for an ideal gas, therefore, inferred by extrapolating the straight line to the axis, as in Fig. 12.3. This temperature is found to be – 273.15 °C and is designated as absolute zero. Absolute zero is the foundation of the Kelvin temperature scale or absolute scale temperature named after the British scientist Lord Kelvin. On this scale, – 273.15 °C is taken as the zero point, that is 0 K (Fig. 12.4).

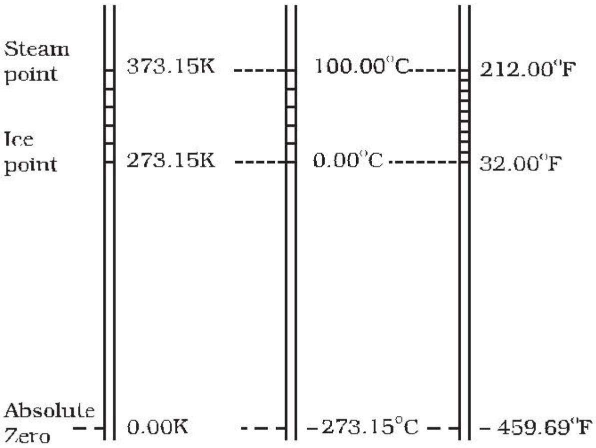


Fig. 12.4 Comparison of the Kelvin, Celsius and Fahrenheit temperature scales.

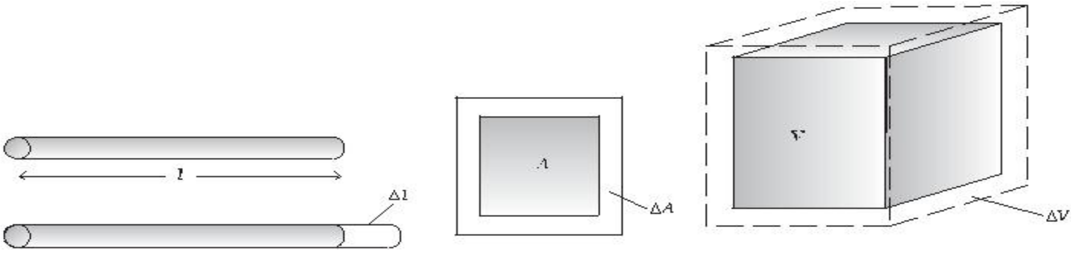
The size of the unit for Kelvin temperature is the same Celsius degree, so temperature on these scales are related by

$$T = t_C + 273.15 \quad (12.3)$$

12.5 THERMAL EXPANSION

You may have observed that sometimes sealed bottles with metallic lids are so tightly screwed that one has to put the lid in hot water for some time to open the lid. This would allow the metallic cover to expand, thereby loosening it to unscrew easily. In case of liquids, you may have observed that mercury in a thermometer rises, when the thermometer is put in slightly warm water. If we take out the thermometer from the warm water the mercury level down to room temperature.

It is our common experience that most substances expand on heating and contract on cooling. A change in the temperature of a body causes change in its dimensions. The increase in the dimensions of a body due to the increase in its temperature is called thermal expansion. The expansion in length is called linearexpansion. The expansion in area is called area expansion. The expansion in volume is called volume expansion (Fig. 12.5).



$\frac{\Delta l}{l} = \alpha_l \Delta t$ $\frac{\Delta A}{A} = \alpha_A \Delta t$ $\frac{\Delta V}{V} = \alpha_V \Delta t$

a) Linear expansion (b) Area expansion (c) Volume expansion

Fig. 12.5 Thermal Expansion.

If the substance is in the form of a long rod, then for small change in temperature, T, the fractional change in length, l/l, is directly proportional to T.

$$\frac{\Delta l}{l} = \alpha_1 \Delta T \tag{12.4}$$

where α_1 is known as the coefficient of linear expansion and is characteristic of the material of the rod. In Table 12.1 are given typical average values of the coefficient of linear expansion for some materials in the temperature range 0 °C to 100 °C. From this Table, compare the value of αl for glass and copper. We find that copper expands about five times more than glass for the same rise in temperature. Normally, metals expand more and have relatively high values of α_l.

Table 12.1 Values of coefficient of linear expansion for some materials

Materials	α_l (10^{-5} K^{-1})
Aluminium	2.5
Brass	1.8
Iron	1.2

Copper	1.7
Silver	1.9
Gold	1.4
Glass (pyrex)	0.32
Lead	0.29

Similarly, we consider the fractional change in volume, ΔV/V, of a substance for temperature change ΔT and define the coefficient of volume expansion, α_V as

$$\frac{\Delta V}{V\,t} = \alpha_V$$

Here α_V is also a characteristic of the substance but is not strictly a constant. It depends in general on temperature (Fig 12.6). It is seen that α_V becomes constant only at a high temperature.

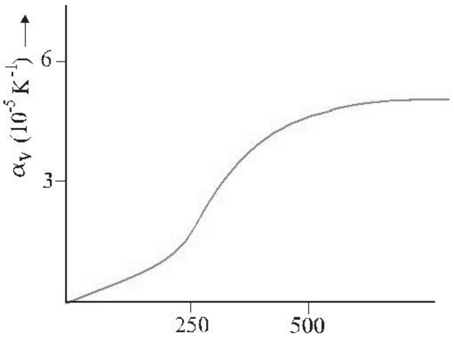


Fig. 12.6 *Coefficient of volume expansion of copperas a function of temperature.*

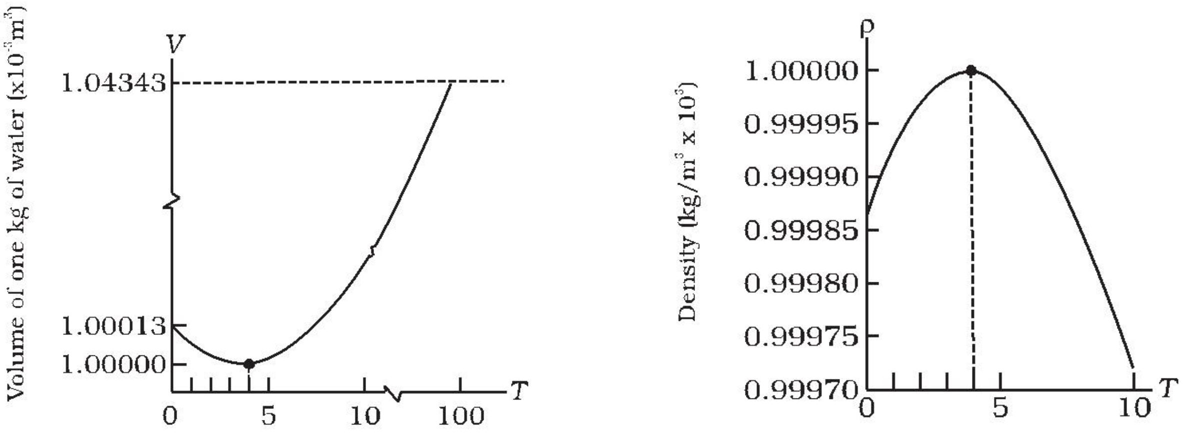
Table 12.2 gives the values of co-efficient of volume expansion of some common substances in the temperature range 0 –100 °C. You can see that thermal expansion of these substances (solids and liquids) is rather small, with materials like pyrex glass and invar (a special iron-nickel alloy) having particularly low values of α_V. From this Table we find that the value of α_V for alcohol (ethyl) is more than mercury and expands more than mercury for the same rise in temperature.

Table 12.2 Values of coefficient of volume expansion for some substances

Materials	α_v (K^{-1})
Aluminium	7×10^{-5}
Brass	6×10^{-5}
Iron	3.55×10^{-5}
Paraffin	58.8×10^{-5}
Glass (ordinary)	2.5×10^{-5}
Glass (pyrex)	1×10^{-5}
Hard rubber	2.4×10^{-4}
Invar	2×10^{-6}
Mercurry	18.2×10^{-5}
Water	20.7×10^{-5}
Alcohol (ethyl)	120×10^{-5}

Water exhibits an anomalous behavour; it contracts on heating between 0 °C and 4 °C. The volume of a given amount of water decreases as it is cooled from room temperature, until its temperature reaches 4 °C, [Fig. 12.7(a)]. Below 4 °C, the volume increases, and therefore the density decreases [Fig. 12.7(b)]. This means that water has a maximum density at 4 °C. This property has an important environmental effect: Bodies of water, such asl akes and ponds, freeze at the top first. As a lake cools toward 4 °C, water near the surface loses energy to the atmosphere, becomes denser, and sinks; the warmer, less dense water near the bottom rises.

However, once the colder water on top reaches temperature below 4 °C, it becomes less dense and remains at the surface, where it freezes. If water did not have this property, lakes and ponds would freeze from the bottom up, which would destroy much of their animal and plant life.



(a) Temperature (°C) (b) Temperature (°C)

Fig. 12.7 Thermal expansion of water

Gases at ordinary temperature expand more than solids and liquids. For liquids, the coefficient of volume expansion is relatively independent of the temperature. However, for gases it is dependent on temperature. For an ideal gas, the coefficient of volume expansion at constant pressure can be found from the ideal gas equation:

$$PV = \mu RT$$

At constant pressure $P\Delta V = \mu R\Delta T$

$$\frac{\Delta V}{V} = \frac{\Delta T}{T}$$

i.e $\alpha_V = \frac{1}{T}$ for Ideal gas

At 0 °C, $\alpha v = 3.7 \times 10^{-3}$ K^{-1}, which is much larger than that for solids and liquids. Equation (12.6) shows the temperature dependence of αv; it decreases with increasing temperature. For a gas at room temperature and constant pressure α_v is about 3300×10^{-6} K^{-1}, as much as order(s) of magnitude larger than the coefficient of volume expansion of typical liquids.

There is a simple relation between the coefficient of volume expansion (αv) and coefficient of linear expansion (αl). Imagine a cube of length, l, that expands equally in all directions, when its temperature increases by T. We have

$$\Delta l = \alpha_l \, l\Delta T$$

so, $\Delta V = (l + \Delta l)^3 - l^3;\ 3l^2\Delta l$

In equation (12.7), terms in $(\Delta l)^2$ and $(\Delta l)^3$have been neglected since l is small compared to l. So

$$\Delta V = \frac{3V\Delta l}{l} = \alpha V \alpha_l \Delta t$$

Which gives, $\alpha_v = 3\alpha_l$ (12.9)

What happens by preventing the thermal expansion of a rod by fixing its ends rigidly? Clearly, the rod acquires a compressive strain due to the external forces provided by the rigid support at the ends. The corresponding stress set up in the rod is called thermal stress. For example, consider a steel rail of length 5 m and area of cross section 40 cm2 that is prevented from expanding while the temperature rises by 10 °C. The coefficient of linear expansion of steel is αl(steel) = 1.2×10^{-5} K^{-1}. Thus, the compressive strain is

$(\Delta l/l) = \alpha_{l(steel)}\ \ \Delta T = 1.2 \times 10^{-5} \times 10 = 1.2 \times 10^{-4}$.

Young's modulus of steel is $Y_{(steel)} = 2 \times 1012\ N\ m^{-2}$.

Therefore, the thermal stress developed is

$\Delta F/A = Y_{steel}\ (\Delta l/l) = 2.4x107\ Nm^{-2}$, which corresponds to an external force of

$\Delta F = AY_{steel}\ (\Delta l/l) = 2.4\ x\ 107\ x\ 40\ x\ 10^{-4}$ j105N.

If two such steel rails, fixed at their outer ends, are in contact at their inner ends, a force of this magnitude can easily bend the rails.

Example 12.1 Show that the coefficient of area expansions, (A/A)/ T, of a rectangular sheet of the solid is twice its linear expansivity, α_l.

Answer

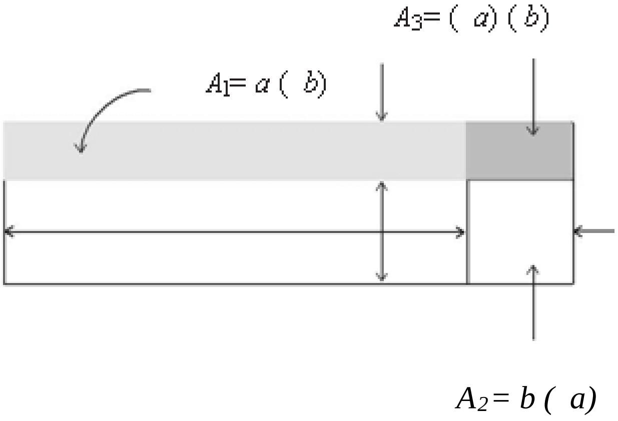


Fig. 12.8

Consider a rectangular sheet of the solid material of length a and breadth b (Fig. 12.8). When the temperature increases by ΔT, a Increases by $\Delta a = \alpha_1 a \Delta T$ and b increases by $\Delta b = \alpha_1 b \Delta T$. From Fig. 12.8,

the increase in area $\Delta A = \Delta A_1 + \Delta A_2 + \Delta A_3$

$$A = a\Delta b + b\Delta a + (\Delta a)(\Delta b)$$

$$= a\alpha_1 b\Delta T + b\alpha_1 a\Delta T + {\alpha_1}^2 ab(\Delta T)^2$$

$$= \alpha_1 ab\Delta T(2 + \alpha_1\Delta T) = \alpha_1 A\Delta T(2 + \alpha_1\Delta T)$$

since $\alpha_1 \Delta T;\ 10^{-5} K^{-1}$,

from table 12.1, the product α_1 for fractional temperature is small in comparision with 2 and may be neglected. Hence, $\left(\frac{\Delta A}{A}\right)\frac{1}{\Delta T} \cong 2\alpha_1$

Example 12.2 A blacksmith fixes iron ring on the rim of the wooden wheel of a bullock cart. The diameter of the rim and the iron ring are 5.243 m and 5.231 m respectively at 27 °C. To what temperature should the ring be heated so as to fit the rim of the wheel?

Answer

Given, T1= 27 °C, L_{T1}= 5.231 m, L_{T2}= 5.243 m

So, $L_{T2}=L_{T1}\ [1+\alpha_l\ (T_2–T_1)]$

5.243 m = 5.231 m [1 + 1.20×10–5 K^{-1} (T2–27 °C)] or T_2 = 218 °C.

12.6 SPECIFIC HEAT CAPACITY

$$\frac{\Delta F}{A} = Y_{steel}\left(\frac{\Delta l}{l}\right) 2.4 \text{ x } 10^7 Nm^{-2}$$

Take some water in a vessel and start heating it on a burner. Soon you will notice that bubbles begin to move upward. As the temperature is raised the motion of water particles increases till it becomes turbulent as water starts boiling. What are the factors on which the quantity of heat required to raise the temperature of a substance depend? In order to answer this question in the first step, heat a given quantity of water to raise its temperature by, say 20 °C and note the time taken. Again take the same amount of water and raise its temperature by 40 °C using the same source of heat. Note the time taken by using a stopwatch. You will find it takes about twice the time and therefore, double the quantity of heat required raising twice the temperature of same amount of water.

In the second step, now suppose you take double the amount of water and heat it, using the same heating arrangement, to raise the temperature by 20 °C, you will find the time taken is again twice that required in the first step.

In the third step, in place of water, now heat the same quantity of some oil, say mustard oil, and raise the temperature again by 20 °C. Now note the time by the same stopwatch. You will find the time taken will be shorter and therefore, the quantity of heat required would be less than that required by the same amount of water for the same rise in temperature.The above observations show that the quantity of heat required to warm a given substance depends on its mass, m, the change in temperature, T and the nature of substance. The change in temperature of a substance, when a given quantity of heat is absorbed or rejected by it, is characterised by a quantity called the heat capacity of that substance. We define heatcapacity, S of a substance as

$$S = \frac{\Delta Q}{\Delta T} \qquad (12.10)$$

where Q is the amount of heat supplied to the substance to change its temperature from T to T + T.

You have observed that if equal amount of heat is added to equal masses of different substances, the resulting temperature changes will not be the same. It implies that every substance has a unique value for the amount of heat absorbed or rejected to change the temperature of unit mass of it by one unit. This quantity is referred to as the **specific heat capacity** of the substance.

If Q stands for the amount of heat absorbed or rejected by a substance of mass m when it undergoes a temperature change T, then the specific heat capacity, of that substance is given by

$$s = \frac{S}{m} = \frac{1}{m}\left(\frac{\Delta Q}{\Delta T}\right)$$

The specific heat capacity is the property of the substance which determines the change in the temperature of the substance (undergoing no phase change) when a given quantity of heat is absorbed (or rejected) by it. It is defined as the amount of heat per unit mass absorbed or rejected by the substance to change its temperature by one unit. It depends on the nature of the substance and its temperature. The SI unit of specific heat capacity is J kg^{-1} $\text{K}^{-1.}$

If the amount of substance is specified in terms of moles μ, instead of mass m in kg, we can define heat capacity per mole of the substance by

$$C = \frac{S}{\mu} = \frac{1}{\mu}\frac{\Delta Q}{\Delta T} \qquad (12.12)$$

Where C is known as molar specific heat capacity of the substance. Like S, C also depends on the nature of the substance and its temperature. The SI unit of molar specific heat capacity is J mol^{-1} K^{-1}.

However, in connection with specific heat capacity of gases, additional conditions may be needed to define C. In this case, heat transfer can be achieved by keeping either pressure or volume constant. If the gas is held under constant pressure during the heat transfer, then it is called the molar specific heat capacity at constant pressure and is denoted by Cp. On the other hand, if the volume of the gas is maintained during the heat transfer, then the corresponding molar specific heat capacity is called molar specific heat capacity at constant volume and is denoted by Cv. For details see Chapter 12. Table 12.3 lists measured specific heat capacity of some substances at atmospheric pressure and ordinary temperature while Table 12.4 lists molar specific heat capacities of some gases.

Table 12.3 Specific heat capacity of some substances at room temperature and atmospheric pressure

Substance	Specific heat capacity ($J\ kg^{-1}\ K^{-1}$)	Substance	Specific heat capacity ($J\ kg^{-1}\ K^{-1}$)
Aluminium	900.0	Ice	2060
Carbon	506.5	Glass	840
Copper	386.4	Iron	450
Lead	127.7	Kerosene	2128
Silver	236.1	Edible oil	1965
Tungesten	134.4	Mercury	140
Water	4186.0		

From Table 12.3 you can note that water has the highest specific heat capacity compared to other substances. For this reason water is used as a coolant in automobile radiators as well as a heater in hot water bags. Owing to its high specific heat capacity, the water warms up much more slowly than the land during summer and consequently wind from the sea has a cooling effect. Now, you can tell why in desert areas, the earth surface warms up quickly during the day and cools quickly at night.

Table 12.4 Molar specific heat capacities of some gases

Gas	C_p(J mol^{-1}K^{-1})	C_v (J mol^{-1}K^{-1})
He	20.8	12.5
H_2	28.8	20.4
N_2	29.1	20.8
O_2	29.4	21.1
CO_2	37.0	28.5

12.7 CALORIMETRY

A system is said to be isolated if no exchange or transfer of heat occurs between the system and its surroundings. When different parts of an isolated system are at different temperature, a quantity of heat transfers from the part at higher temperature to the part at lower temperature. The heat lost by the part at higher temperature is equal to the heat gained by the part at lower temperature.

Calorimetry means measurement of heat. When a body at higher temperature is brought in contact with another body at lower temperature, the heat lost by the hot body is equal to the heat gained by the colder body, provided no heat is allowed to escape to the surroundings. A device in which heat measurement can be made is called a calorimeter. It consists a metallic vessel and stirrer of the same material like copper or aluminium. The vessel is kept inside a wooden jacket which contains heat insulating materials like glass wool etc. The outer jacket acts as a heat shield and reduces the heat loss from the inner vessel. There is an opening in the outer jacket through which a mercury thermometer can be inserted into the calorimeter. The following example provides a method by which the specific heat capacity of a given solid can be determined by using the principle; heat gained is equal to the heat lost.

Example 12.3 A sphere of aluminium of 0.047 kg placed for sufficient time in a vessel containing boiling water, so that the sphere is at 100 °C. It is then immediately transfered to 0.14 kg copper calorimeter containing 0.25 kg of water at 20 °C. The temperature of water rises and attains a steady state at 23 °C. Calculate the specific heat capacity of aluminium.

Answer In solving this example we shall use the fact that at a steady state, heat given by an aluminium sphere will be equal to the heat absorbed by the water and calorimeter.

Mass of aluminium sphere (m1) = 0.047 kg

Initial temp. of aluminium sphere = 100 °C

Final temp. = 23 °C

Change in temp (T) = (100 °C - 23 °C) = 77 °C Let specific heat capacity of aluminium be s_{Al}.

The amount of heat lost by the aluminium sphere $= m_1 s_{Al}\, T = 0.047 kg. s_{Al}. \; 77\,^0C$

Mass of water (m_2) = 0.25 kg

Mass of calorimeter (m_3) = 0.14 kg

Initial temp. of water and calorimeter = 20 °C

Final temp. of the mixture = 23 °C

Change in temp. (T_2) = 23 °C – 20 °C = 3 °C

Specific heat capacity of water (sw)

= 4.18 × 103 J kg^{-1} K^{-1}

Specific heat capacity of copper calorimeter

= 0.386 × 103 J kg^{-1} K^{-1}

The amount of heat gained by water and

calorimeter $= m_2 s_w \Delta T_2 + m_3 s_{cu}$

$= (m_2 sw + m_3 s_{cu}) (\Delta T_2)$

= 0.25 kg ×4.18 × 103 J kg^{-1} K^{-1} + 0.14 kg ×0.386 × 103 J kg^{-1} K^{-1}) (23 °C – 20 °C)

In the steady state heat lost by the aluminium sphere = heat gained by water + heat gained by calorimeter.

So, 0.047 kg × s_{Al} × 77 °C

$= (0.25\text{ kg} \times 4.18 \times 103\text{ J kg}^{-1}\text{ K}^{-1} + 0.14\text{ kg} \times 0.386 \times 103\text{ J kg}^{-1}\text{ K}^{-1})(3\text{ °C})$

$s_{Al} = 0.912\text{ kJ kg}^{-1}\text{K}^{-1}$.

12.8 CHANGE OF STATE

Matter normally exists in three states: solid, liquid, and gas. A transition from one of these states to another is called a change of state. Two common changes of states are solid to liquid and liquid to gas (and vice versa). These changes can occur when the exchange of heat takes place between the substance and its surroundings. To study the change of state on heating or cooling, let us perform the following activity.

Take some cubes of ice in a beaker. Note the temperature of ice (0 °C). Start heating it slowly on a constant heat source. Note the temperature after every minute. Continuously stir the mixture of water and ice. Draw a graph between temperature and time (Fig. 12.9). You will observe no change in the temperature so long as there is ice in the beaker. In the above process, the temperature of the system does not change even though heat is being continuously supplied. The heat supplied is being utilized in changing the state from solid (ice) to liquid (water).

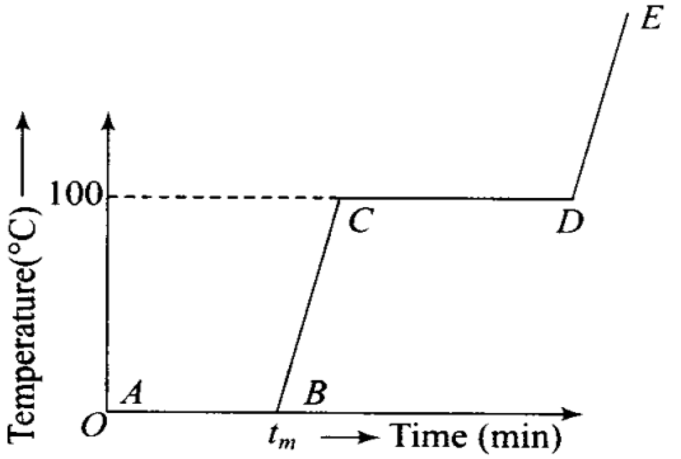


Fig. 12.9 *A plot of temperature versus time showing the changes in the state of ice on heating(not to scale).*

The change of state from solid to liquid is called melting and from liquid to solid is called fusion. It is observed that the temperature remains constant until the entire amount of the solid substance melts. That is, both the solid and liquid states of the substance coexist in thermal equilibrium during the change of states from solid to liquid. The temperature at which the solid and the liquid states of the substance are in thermal equilibrium with each other is called its melting point. It is characteristic of the substance. It also depends on pressure. The melting point of a substance at standard atmospheric pressure is called its normal melting point. Let us do the following activity to understand the process of melting of ice.

Take a slab of ice. Take a metallic wire and fix two blocks, say 5 kg each, at its ends. Put the wire over the slab as shown in Fig. 12.10. You will observe that the wire passes through the ice slab. This happens due to the fact that just below the wire, ice melts at lower temperature due to increase in pressure. When the wire has passed, water above the wire freezes again. Thus the wire passes through the slab and the slab does not split. This phenomenon of refreezing is called regelation. Skating is possible on snow due to the formation of water below the skates. Water is formed due to the increase of pressure and it acts as a lubricant.

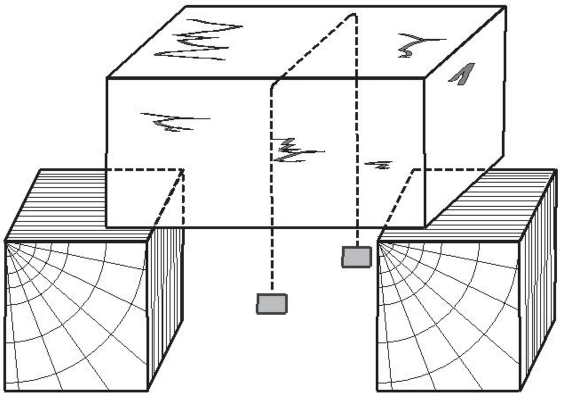


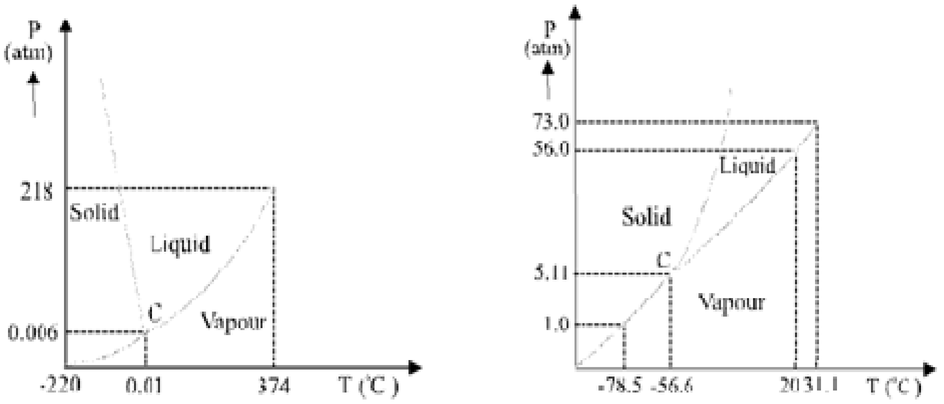
Fig. 12.10

After the whole of ice gets converted into water and as we continue further heating, we shall see that temperature begins to rise. The temperature keeps on rising till it reaches nearly100 °C when it again becomes steady. The heat supplied is now being utilised to change water from liquid state to vapour or gaseous state.

The change of state from liquid to vapour (or gas) is called vaporisation. It is observed that the temperature remains constant until the entire amount of the liquid is converted into vapour. That is, both the liquid and vapour states of the substance coexist in thermal equilibrium, during the change of state from liquid to vapour. The temperature at which the liquid and the vapour states of the substance coexist is called its boiling point. Let us do the following activity to understand the process of boiling of water.

Triple Point

The temperature of a substance remains constant during its change of state (phase change). A graph between the temperature T and the Pressure P of the substance is called a phase diagram or P – T diagram. The following figure shows the phase diagram of water and CO2. Such a phase diagram divides the P – T plane into a solid-region, the vapour-region and the liquid-region. The regions are separated by the curves such as sublimation curve (BO), fusioncurve (AO) andvaporisation curve (CO). The points on sublimation curve represent statesin which solid and vapour phases coexist. The point on the sublimation curve BO represent states in which the solid and vapour phases co-exist. Points on the fusion curve AO represent states in which solid and liquid phase coexist. Points on the vapourisation curve CO represent states in which the liquid and vapour phases coexist. The temperature and pressure at which the fusion curve, the vaporisation curve and the sublimation curve meet and all the three phases of a substance coexist is called the triple point of the substance. For example the triple point of water is represented by the temperature 273.16 K and pressure 6.12×10–3Pa.



Pressure-temperature phase diagrams for (a) water and (b) CO2 (not to the scale)

Take a round-bottom flask, more than half filled with water. Keep it over a burner and fix a thermometer and steam outlet through the cork of the flask (Fig. 12.11). As water gets heated in the flask, note first that the air, which was dissolved in the water, will come out as small bubbles. Later, bubbles of steam will form at the bottom but as they rise to the cooler water near the top, they condense and disappear. Finally, as the temperature of the entire mass of the water reaches 100 °C, bubbles of steam reach the surface and boiling is said to occur. The steam in the flask may not be visible but as it comes out of the flask, it condenses as tiny droplets of water, giving a foggy appearance.

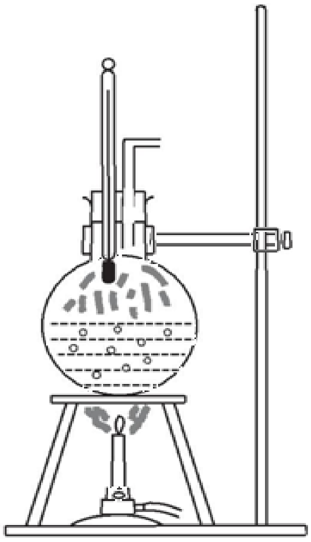


Fig. 12.12 Boiling process

If now the steam outlet is closed for a few seconds to increase the pressure in the flask, you will notice that boiling stops. More heat would be required to raise the temperature (depending on the increase in pressure) before boiling begins again. Thus boiling point increases with increase in pressure.

Let us now remove the burner. Allow water to cool to about 80 °C. Remove the thermometer and steam outlet. Close the flask with the airtight cork. Keep the f lask turned upside down on the stand. Pour ice-cold water on the flask. Water vapours in the flask condense reducing the pressure on the water surface inside the flask. Water begins to boil again, now at a lower temperature. Thus boiling point decreases with decrease in pressure.

This explains why cooking is difficult on hills. At high altitudes, atmospheric pressure is lower, reducing the boiling point of water as compared to that at sea level. On the other hand, boiling point is increased inside a pressure cooker by increasing the pressure. Hence cooking is faster. The boiling point of a substance at standard atmospheric pressure is called its **normal boiling point**.

However, all substances do not pass through the three states: solid-liquid-gas. There are certain substances which normally pass from the solid to the vapour state directly and vice versa. The change from solid state to vapour state without passing through the liquid state is called

sublimation, and the substance is said to sublime. Dry ice (solid CO2) sublimes, so also iodine. During the sublimation process both the solid and vapour states of a substance coexist in thermal equilibrium.

12.8.1 Latent Heat

In Section 12.8, we have learnt that certain amount of heat energy is transferred between a substance and its surroundings when it undergoes a change of state. The amount of heat per unit mass transferred during change of state of the substance is called latent heat of the substance for the process. For example, if heat is added to a given quantity of ice at –10 °C, the temperature of ice increases until it reaches its melting point (0 °C). At this temperature, the addition of more heat does not increase the temperature but causes the ice to melt, or changes its state. Once the entire ice melts, adding more heat will cause the temperature of the water to rise. A similar situation occurs during liquid gas change of state at the boiling point. Adding more heat to boiling water causes vaporisation, without increase in temperature.

Table 12.5 Temperatures of the change of state and latent heats for various substances at 1 atm pressure

Substance	Melting Point (°C)	L_f (105J kg^{-1})	Boiling Point (°C)	L_v (105J kg^{-1})
Ethyl alcohol	–124	1.0	78	8.5
Gold	1063	0.645	2660	15.8
Lead	328	0.25	1744	8.67
Mercury	–39	0.12	357	2.7
Nitrogen	–210	0.26	–196	2.0
Oxygen	–219	0.14	–183	2.1
Water	0	3.33	100	22.6

The heat required during a change of state depends upon the heat of transformation and the mass of the substance undergoing a change of state. Thus, if mass m of a substance undergoes a change from one state to the other, then the quantity of heat required is given by

$$Q = m L \quad \text{or}$$

$$L = Q/m \qquad (12.13)$$

where L is known as latent heat and is a characteristic of the substance. Its SI unit is J kg–1. The value of L also depends on the pressure. Its value is usually quoted at standard atmospheric pressure. The latent heat for a solid-liquid state change is called the latent heat of fusion (Lf), and that for a liquid-gas state change is called the latent heat of vaporization (L_v). These are often referred to as the heat of fusion and the heat of vaporization. A plot of temperature versus heat energy for a quantity of water is shown in Fig. 12.12. The latent heats of some substances, their freezing and boiling points, are given in Table 12.5.

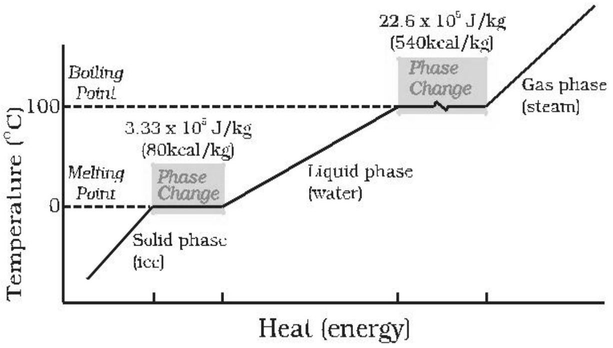


Fig. 12.12 *Temperature versus heat for water at1 atm pressure (not to scale).*

Note that when heat is added or removed during a change of state, the temperature remains constant. Note in Fig. 12.12 that the slopes of the phase lines are not all the same, which indicates that specific heats of the various states are not equal. For water, the latent heat of fusion and vaporization are $L_f = 3.33 \times 105$ J kg^{-1} and $L_v = 22.6 \times 105$ J kg^{-1} respectively. That is 3.33 × 105 J of heat are needed to melt 1 kg of ice at 0 °C, and 22.6 × 105 J of heat are needed to convert 1 kg of water to steam at 100 °C. So, steam at 100 °C carries 22.6 × 105 J kg^{-1} more heat than water at 100 °C. This is why burns from steam are usually more serious than those from boiling water.

Example 12.4 When 0.15 kg of ice of 0 °C mixed with 0.30 kg of water at 50 °C in a container, the resulting temperature is 6.7 °C. Calculate the heat of fusion of ice. (s= 4186 Jkg^{-1} K^{-1}).

Answer

Heat lost by water = msw $(\theta f – \theta i)_w$

= (0.30 kg) (4186 J kg–1 K–1) (50.0 °C – 6.7 °C) = 54376.14 J

Heat required to melt ice = m_2L_f = (0.15 kg) L_f

Heat required to raise temperature of ice

water to final temperature = mIsw $(\theta f–\theta i)_I$ = (0.15 kg) (4186 J kg–1 K –1) (6.7 °C – 0 °C)

= 4206.93 J

Heat lost = heat gained

54376.14 J = (0.15 kg)Lf + 4206.93 J

L_f= 3.34×105J kg$^{–1.}$

Example 12.5 Calculate the heat required□ to convert 3 kg of ice at–12 °C kept in a calorimeter to steam at 100 °C at atmospheric pressure. Given specific heat capacity of ice = 2100 J kg$^{–1}$ K$^{–1}$, specific heat capacity of water = 4186 J kg$^{–1}$ K$^{–1}$, latent heat of fusion of ice = 3.35 × 105 J kg$^{–1}$ and latent heat of steam = 2.256 ×106 J kg$^{–1}$.

Answer

We have, Mass of the ice, m = 3 kg specific heat capacity of ice, s_{ice}

= 2100 J kg$^{–1}$ K$^{–1}$ specific heat capacity of water, s_{water}

= 4186 J kg$^{–1}$ K$^{–1}$ latent heat of fusion of ice, Lf ice

= 3.35 × 105 J kg$^{–1}$

latent heat of steam, L_{steam}

= 2.256 × 106 J kg$^{–1}$

Now, Q = heat required to convert 3 kg of ice at –12 °C to steam at 100 °C,

Q_1 = heat required to convert ice at –12 °C to ice at 0 °C.

= m s_{ice} T_1 = (3 kg) (2100 J kg$^{–1}$)

K–1) [0–(–12)]°C = 75600 J

Q_2 = heat required to melt ice at 0 °C to water at 0 °C

= m $L_{f\ ice}$= (3 kg) (3.35 × 105J kg–1)

= 1005000 J

Q_3 = heat required to convert water

at 0 °C to water at 100 °C.

= ms_wT_2 = (3kg) (4186 J kg$^{–1}$K$^{–1}$) (100 °C)

= 1255800 J

Q_4 = heat required to convert water at 100 °C to steam at 100 °C.

= m L_{steam} = (3 kg) (2.256×106 J kg$^{–1}$)

= 6768000 J

So, Q = Q_1+ Q_2 + Q_3 + Q_4

= 75600J + 1005000 J + 1255800 J + 6768000 J

= 9.1×106 J

12.9 HEAT TRANSFER

We have seen that heat is energy transfer from one system to another or from one part of a system to another part, arising due toTemperature difference. What are the different ways by which this energy transfer takes place? There are three distinct modes of heat transfer: conduction, convection and radiation (Fig. 12.13).

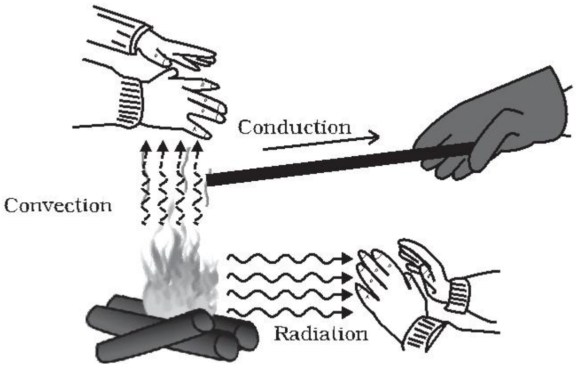


Fig. 12.13 heating by conduction, convection and radiation

12.9.1 Conduction

Conduction is the mechanism of transfer of heat between two adjacent parts of a body because of their temperature difference. Suppose one end of a metallic rod is put in a flame, the other end of the rod will soon be so hot that you cannot hold it by your bare hands. Here heat transfer takes place by conduction from the hot end of the rod through its different parts to the other end. Gases are poor thermal conductors while liquids have conductivities intermediate between solids and gases.

Heat conduction may be described quantitatively as the time rate of heat flow in a material for a given temperature difference. Consider a metallic bar of length L and uniform cross section A with its two ends maintained at different temperatures. This can be done, for example, by putting the ends in thermal contact with large reservoirs at temperatures, say, T_C and T_D respectively (Fig. 12.14). Let us assume the ideal condition that the sides of the bar are fully insulated so that no heat is exchanged between them.

After sometime, a steady state is reached; the temperature of the bar decreases uniformly with distance from T_C to T_D; ($T_C>T_D$). The reservoir at C supplies heat at a constant rate, which transfers through the bar and is given out at the same rate to the reservoir at D.

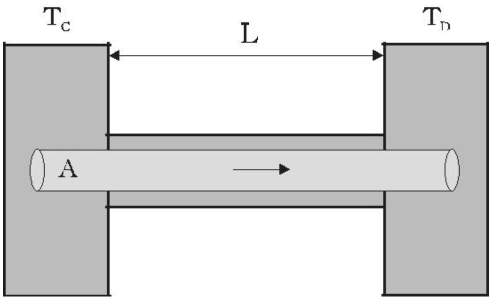


Fig. 12.14 Steady state heat flow by conduction in a bar with its two ends maintained at temperatures T_C and T_D; ($T_C > T_D$).

It is found experimentally that in this steady state, the rate of flow of heat (or heat current) H is proportional to thetemperature difference (TC – TD) and the area of cross section A and is inversely proportional to the length L:

$$H = K_A \frac{T_C - T_D}{L} \qquad (12.14)$$

The constant of proportionality K is called the thermal conductivity of the material. Thegreater the value of K for a material, the more rapidly will it conduct heat. The SI unit of K is J S^{-1} m^{-1} K^{-1} or W m^{-1} K^{-1}. The thermal conductivities of various substances are listed in Table 12.5. These values vary slightly with temperature, but can be considered to be constant over a normal temperature range.

Compare the relatively large thermal conductivities of the good thermal conductors, the metals, with the relatively small thermal conductivities of some good thermal insulators, such as wood and glass wool. You may have noticed that some cooking pots have copper coating on the bottom. Being a good conductor of heat, copper promotes the distribution of heat over the bottom of a pot for uniform cooking. Plastic foams, on the other hand, are good insulators, mainly because they contain pockets of air. Recall that gases are poor conductors, and note the low thermal conductivity of air in the Table 12.5. Heat retention and transfer are important in many other applications. Houses made of concrete roofs get very hot during summer days, because thermal conductivity of concrete (though much smaller than that of a metal) is still not small enough. Therefore, people usually prefer to give a layer of earth or foam insulation on the ceiling so that heat transfer is prohibited and keeps the room cooler. In some situations, heat transfer is critical. In a nuclear reactor, for example, elaborate heat transfer systems need to be installed so that the enormous energy produced by nuclear fission in the core transits out sufficiently fast, thus preventing the core from overheating.

Materials	Thermal conductivity	Non-metals	Thermal conductivity	Gases	Thermal conductivity

	$(\text{J s}^{-1}\ \text{m}^{-1}\ \text{K}^{-1})$		$(\text{J s}^{-1}\ \text{m}^{-1}\ \text{K}^{-1})$		$(\text{J s}^{-1}\ \text{m}^{-1}\ \text{K}^{-1})$
Silver	406	Insulating brick	0.15	Air	0.024
Copper	385	Concrete	0.8	Argon	0.016
Aluminium	205	Body fat	0.20	Hydrogen	0.14
Brass	109	Felt	0.04		
Steel	50.2	Glass	0.8		
Lead	34.7	Ice	1.6		
Mercury	8.3	Glasswool	0.04		
		Wood	0.12		
		Water	0.8		

Example 12.6 What is the temperature of the steel-copper junction in the steady state of the system shown in Fig. 12.15. Length of the steel rod = 15.0 cm, length of the copper rod = 10.0 cm, temperature of the furnace = 300 °C, temperature of the other end = 0 °C. The area of cross section of the steel rod is twice that of the copper rod. (Thermal conductivity of steel = 50.2 $\text{J s}^{-1}\ \text{m}^{-1}\text{K}^{-1}$; and of copper = 385 $\text{J s}^{-1}\text{m}^{-1}\text{K}^{-1}$).

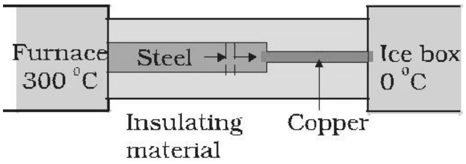


Fig. 12.15

Answer

The insulating material around the rods reduces heat loss from the sides of the rods. Therefore, heat flows only along the length of the rods. Consider any cross section of the rod. In the steady state, heat flowing into the element must equal the heat flowing out of it; otherwise there would be a net gain or loss of heat by the element and its temperature would not be steady. Thus in the steady state, rate of heat flowing across a cross section of the rod is the same at every point along the length of the combined steel-copper rod. Let T be the temperature of the steel-copper junction in the steady state. Then,

$$\frac{K_1 A_1 300T}{L_1} = \frac{K_2 A_2 (T-0)}{L_2}$$

where 1 and 2 refer to the steel and copper rod respectively. For $A_1 = 2A_2$, $L_1 = 15.0$ cm,

$L_2 = 10.0$ cm, $K_1 = 50.2$ J $s^{-1}m^{-1}K^{-1}$, $K_2 = 385$ Js^{-1} m^{-1} K^{-1}, we have

$$\frac{50.2 \times 2(300 - T)}{15} = \frac{385\,T}{10}$$

which gives T = 44.4 °C

Example 12.7 An iron bar ($L_1 = 0.1$ m, $A_1 = 0.02$ m^2, $K_1 = 79$ W m^{-1} K^{-1}) and a brass bar ($L_2 = 0.1$m, $A_2 = 0.02$ m^2, $K_2 = 109$ W $m^{-1}K^{-1}$) are soldered end to end as shown in Fig. 12.16.

The free ends of the iron bar and brass bar are maintained at 373 K and 273 K respectively. Obtain expressions for and hence compute (i) the temperature of the junction of the two bars, (ii) the equivalent thermal conductivity of the compound bar, and (iii) the heat current through the compound bar.

Answer

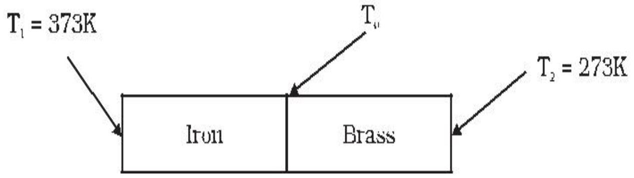


Fig 12.16

Given, $L_1 = L_2 = L = 0.1$ m, $A_1 = A_2 = A = 0.02$ m^2 $K_1 = 79$ W $m^{-1}K^{-1}$, $K_2 = 109$ W $m^{-1}K^{-1}$, $T_1 = 373$ K, and $T_2 = 273$ K.

Under steady state condition, the heat current (H1) through iron bar is equal to the heat current (H2) through brass bar.

So, $H = H_1 = H_2$

$$= \frac{K_1A_1(T_1-T_2)}{L_2} = \frac{K_2\,A_2\,(T_1-T_2\,)}{L_2}$$

For $A_1 = A_2 = A$ and $L_1 = L_2 = L$, this equation leads to

K1(T1– T0) = K2(T0– T2)

Thus the junction temperature T0 of the two bars is

$$T_0 = \frac{K_1T_1 + K_2\,T_2}{K_1 + K_2}$$

Using this equation, the heat current H through either bar is $= \frac{K_1A(T_1-T_0)}{L} = \frac{K_2\,A\,(T_0-T_2\,)}{L}$

$$= \frac{K_1K_2\,A(T_1-T_0)}{L}\ \frac{A(T_1-T_2)}{L\,[\frac{1}{K_1}-\frac{1}{K_2}]}$$

Using these equations, the heat current H' through the compound bar of length $L_1 + L_2 = 2L$ and the equivalent thermal conductivity K', of the compound bar are given

(i) $T = K_1T_1 + K_2T_2/K_1 + K_2$

= 315 K

(ii) K= $\frac{2K_1K_2}{K_1+K_2}$

$$= \frac{91.6\,Wm^{-1}K^{-1}\,x\,0.02\,m^2\,x\,(373K-273K)}{2\,x\,0.1\,m}$$

= [2 x (79 $Wm^{-1}K^{-1}$) x (109 $Wm^{-1}K^{-1}$)]/[79 $Wm^{-1}K^{-1}$ + 109 $Wm^{-1}K^{-1}$]

= 91.6 W m^{-1} K^{-1}

(iii) H =

$$H = \frac{KA\,(T_{1}{\_}T_2)}{2L}$$

$$= \frac{91.6\,Wm^{-1}K^{-1}\,x\;\;0.02\,m^2\,x\,(373K-273K)}{2\,x\,0.1\,m}$$

= 916.1 W

12.9.2 Convection

Convection is a mode of heat transfer by actual motion of matter. It is possible only in fluids. Convection can be natural or forced. In natural convection, gravity plays an important part. When a fluid is heated from below, the hot part expands and, therefore, becomes less dense. Because of buoyancy, it rises and the upper colder part replaces it. This again gets heated, rises up and is replaced by the colder part of the fluid. The process goes on. This mode of heat transfer is evidently different from conduction. Convection involves bulk transport of different parts of the fluid. In forced convection, material is forced to move by a pump or by some other physical means. The common examples of forced convection systems are forced-air heating systems in home, the human circulatory system, and the cooling system of an automobile engine. In the human body, the heart acts as the pump that circulates blood through different parts of the body, transferring heat by forced convection and maintaining it at a uniform temperature.

Natural convection is responsible for many familiar phenomena. During the day, the ground heats up more quickly than large bodies of water do. This occurs both because the water has a greater specific heat and because mixing currents disperse the absorbed heat throughout the great volume of water. The air in contact with the warm ground is heated by conduction. It expands, becoming less dense than the surrounding cooler air. As a result, the warm air rises (air currents) and other air moves (winds) to fill the space-creating a sea breeze near a large body of water. Cooler air descends, and a thermal convection cycle is set up, which transfers heat away from the land. At night, the ground loses its heat more quickly, and the water surface is warmer than the land. As a result, the cycle is reveresed (Fig. 12.17).

The other example of natural convection is the steady surface wind on the earth blowing in from north-east towards the equator, the so called trade wind. A resonable explanation is as follows : the equatorial and polar regions of the earth receive unequal solar heat. Air at the earth's surface near the equator is hot while the air in the upper atmosphere of the poles is cool. In the absence of any other factor, a convection current would be set up, with the air at the equatorial surface rising and moving out towards the poles, descending and streaming in towards the equator. The rotation of the earth, however, modifies this convection current. Because of this, air close to the equator has an eastward speed of 1600 km/h, while it is zero close to the poles. As a result, the air descends not at the poles but at 30° N (North) latitude and returns to the equator. This is called **trade wind**.

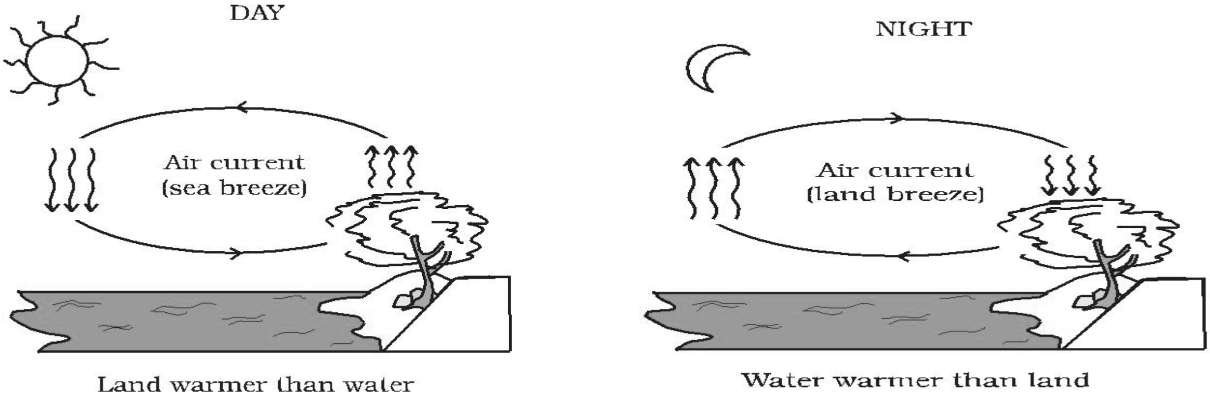


Fig. 12.17 *Convection cycles.*

12.9.3 Radiation

Conduction and convection require some material as a transport medium. These modes of heat transfer cannot operate between bodies separated by a distance in vacuum. But the earth does receive heat from the sun across a huge distance and we quickly feel the warmth of the fire nearby even though air conducts poorly and before convection can set in. The third mechanism for heat transfer needs no medium; it is called radiation and the energy so radiated by electromagnetic waves is called radiant energy. In an electromagnetic wave electric and magnetic fields oscillate in space and time. Like any wave, electromagnetic waves can have different wavelengths and can travel in vacuum with the same speed, namely the speed of light i.e., 3×10^8 m s^{-1} . You will learn these matters in more details later, but you now know why heat transfer by radiation does not need any medium and why it is so fast. This is how heat is transfered to the earth from the sun through empty space. All bodies emit radiant energy, whether they are solid, liquid or gases. The electromagnetic radiation emitted by a body by virtue of its temperature like the radiation by a red hot iron or light from a filament lamp is called thermal radiation.

When this thermal radiation falls on other bodies, it is partly reflected and partly absorbed. The amount of heat that a body can absorb by radiation depends on the colour of the body.

We find that black bodies absorb and emit radiant energy better than bodies of lighter colours. This fact finds many applications in our daily life. We wear white or light coloured clothes in summer so that they absorb the least heat from the sun. However, during winter, we use dark coloured clothes which absorb heat from the sun and keep our body warm. The bottoms of the utensils for cooking food are blackened so that they absorb maximum heat from the fire and give it to the vegetables to be cooked.

Similarly, a Dewar flask or thermos bottle is a device to minimise heat transfer between the contents of the bottle and outside. It consists of a double-walled glass vessel with the inner and outer walls coated with silver. Radiation from the inner wall is reflected back into the contents of the bottle. The outer wall similarly reflects back any incoming radiation. The space between the walls is evacuted to reduce conduction and convection losses and the flask is supported on an insulator like cork. The device is, therefore, useful for preventing hot contents (like milk) from getting cold, or alternatively to store cold contents (like ice).

12.10 NEWTON’S LAW OF COOLING

We all know that hot water or milk when left on a table begins to cool gradually. Ultimately it attains the temperature of the surroundings. To study how a given body can cool on exchanging heat with its surroundings, let us perform the following activity.

Take some water, say 300 ml, in a calorimeter with a stirrer and cover it with two holed lid. Fix a thermometer through a hole in the lid and make sure that the bulb of thermometer is immersed in the water. Note the reading of the thermometer. This reading $T_1$is the temperature of the surroundings.Heat the water kept in the calorimeter till it attains a temperature, say, 40 °C above room temperature (i . e . , temperature of the surroundings). Then stop heating the water by removing the heat source. Start the stop-watch and note the reading of the thermometer after fixed interval of time, say after every one minute of stirring gently with the stirrer. Continue to note the temperature (T_2) of water till it attains a temperature about 5 °C above that of the surroundings. Then plot a graph by taking each value of temperature $T = T_2 – T_1$along y axis and the corespondingvalue of t along x-axis (Fig. 12.18).

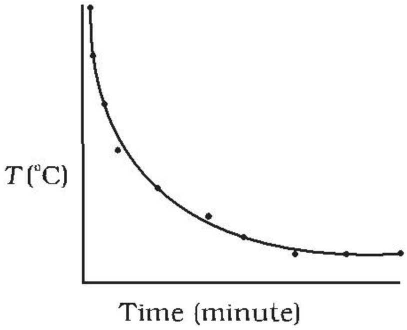


Fig. 12.18 *Curve showing cooling of hot water with time.*

From the graph you will infer how the cooling of hot water depends on the difference of its temperature from that of the surroundings. You will also notice that initially the rate of cooling is higher and decreases as the temperature of the body falls.

The above activity shows that a hot body loses heat to its surroundings in the form of heat radiation. The rate of loss of heat depends on the difference in temperature between the body and its surroundings. Newton was the first to study, in a systematic manner, the relation between the heat lost by a body in a given enclosure and its temperature.

According to Newton's law of cooling, the rate of loss of heat, – dQ/dt of the body is directly proportional to the difference of temperature $T = (T_2 – T_1)$ of the body and the surroundings.The law holds good only for small difference of temperature. Also, the loss of heat by radiation depends upon the nature of the surface of the body and the area of the exposed surface. We can write

$$-\frac{dQ}{dt} = k(T_2 - T_1\ ) \qquad (12.15)$$

wherek is a positive constant depending upon the area and nature of the surface of the body. Suppose a body of mass m and specific heat capacity s is at temperature T_2. Let T_1 be the temperature of the surroundings. If the temperature falls by a small amount dT_2 in time dt, then the amount of heat lost is

$$dQ = ms\ dT_2$$

Rate of loss of heat is given by

$$\frac{dQ}{dt} = ms\ \frac{dT_2}{dt} \qquad (12.16)$$

From Eqs. (12.15) and (12.16) we have

$$-ms\ \frac{dT_2}{dt} = k(T_2 - T_1)$$

$$\frac{dT_2}{T_2 - T_1} = \ -\frac{k}{ms}dt = \ -kdt \qquad (12.17)$$

where $K = k/m\ s$

On integrating

$$\log_e (T_2 - T_1) = - K\ t + c$$

(12.18)

or $T_2 = T_1 + C'$ e-Kt; where $C' = e^c$

Equation (12.19) enables you to calculate the time of cooling of a body through a particular range of temperature.

For small temperature differences, the rate of cooling, due to conduction, convection, and radiation combined, is proportional to the difference in temperature. It is a valid approximation in the transfer of heat from a radiator to a room, the loss of heat through the wall of a room, or the cooling of a cup of tea on the table.

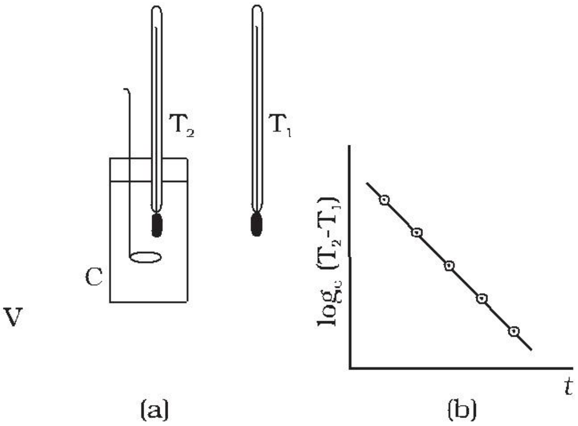


Fig. 12.19 *Verification of Newton's Law of cooling.*

Newton's law of cooling can be verified with the help of the experimental set-up shown in Fig. 12.19(a). The set-up consists of a double walled vessel (V) containing water in between the two walls. A copper calorimeter (C) containing hot water is placed inside the double walled vessel. Two thermometers through the corks are used to note the temperatures T_2 of water in calorimeter and T_1 of hot water in between the double walls respectively. Temperature of hot water in the calorimeter is noted after equal intervals of time. A graph is plotted between $\log_e (T_2 - T_1)$ and time (t). The nature of the graph is observed to be a straight line having a negative slope as shown in Fig. 12.19(b). This is in support of Eq. (12.18).

Example 12.8 A pan filled with hot food cools from 94 °C to 86 °C in 2 minutes when the room temperature is at 20 °C. How long will it take to cool from 71 °C to 69 °C?

Answer The average temperature of 94 °C and86 °C is 90 °C, which is 70 °C above the room temperature. Under these conditions the pan cools 8 °C in 2 minutes.

Using Eq. (12.17), we have

$$\frac{change\ in\ temperature\ (K)}{Time\ (T)}$$

$$\frac{8\ °C}{2\ min} = K\ (70\ °C)$$

The average of 69 °C and 71 °C is 70 °C, which is 50 °C above room temperature. K is the same for this situation as for the original.

$$\frac{2\ °C}{Time} = \ K\ (50\ °C)$$

When we divide above two equations, we have

$$\frac{8\frac{C}{2}min}{2\ C/time} = \frac{K(70\ C)}{K\ (50\ C)}$$

Time = 0.7 min

= 42 s

SUMMARY

1. Heat is a form of energy that flows between a body and its surrounding medium by virtue of temperature difference between them. The degree of hotness of the body is quantitatively represented by temperature.

2. A temperature-measuring device (thermometer) makes use of some measurable property (called thermometric property) that changes with temperature. Different thermometers lead to different temperature scales. To construct a temperature scale, two fixed points are chosen and assigned some arbitrary values of temperature. The two numbers fix the origin of the scale and the size of its unit.

3. The Celsius temperature (t_C) and the Farenheit temperare (t_F) are related

$$t_F = \left(\frac{9}{5}\right) t_C + 32$$

4. The ideal gas equation connecting pressure (P), volume (V) and absolute temperature (T) is:

$$PV = \mu RT$$

where μ is the number of moles and R is the universal gas constant.

5. In the absolute temperature scale, the zero of the scale is the absolute zero of temperature– the temperature where every substance in nature has the least possible molecular activity. The Kelvin absolute temperature scale (T) has the same unit size as the Celsius scale (T_c), but differs in the origin :

$$T_C = T - 273.15$$

6. The coefficient of linear expansion (α_l) and volume expansion (α_v) are defined by the relations :

$$\frac{\Delta l}{l} = \alpha_1 \Delta T$$

$$\frac{\Delta V}{V} = \alpha_v \Delta T$$

where$l$ and V denote the change in length l and volume V for a change of temperature T. The relation between them is :

$$\alpha_v = 3\,\alpha_l$$

7. The specific heat capacity of a substance is defined by

$$S = \frac{1}{m}\frac{Q}{T}$$

wherem is the mass of the substance and Q is the heat required to change its temperature by T. The specific heat capacity of a substance is defined by

$$C = 1/\mu\left(\frac{Q}{\Delta T}\right)$$

where μ is the number of moles of the substance

8. The latent heat of fusion (L_f) is the heat per unit mass required to change a substance from solid into liquid at the same temperature and pressure. The latent heat of vaporisation (L_v) is the heat per unit mass required to change a substance from liquid to the vapour state without change in the temperature and pressure.

9. The three modes of heat transfer are conduction, convection and radiation.

10. In conduction, heat is transferred between neighbouring parts of a body through molecular collisions, without any flow of matter. For a bar of length L and uniform cross section A with its ends maintained at temperatures T_C and T_D, the rate of flow of heat H is

$$H = KA\left(\frac{T_C - T_D}{L}\right)$$

where K is the thermal conductivity of the material of the bar

11. Newton's Law of Cooling says that the rate of cooling of a body is proportional to the excess temperature of the body over the surroundings:

$$\frac{dQ}{dt} = -k\ (T_2 - T_1)$$

Where T_1 is the temperature of the surrounding medium and T_2 is the temperature of the body

CHAPTER THIRTEEN

THERMODYNAMICS

13.1 INTRODUCTION

In previous chapter we have studied thermal properties of matter. In this chapter we shall study laws that govern thermal energy. We shall study the processes where work is converted into heat and vice versa. In winter, when we rub our palms together, we feel warmer; here work done in rubbing produces the ‘heat’. Conversely, in a steam engine, the ‘heat’ of the steam is used to do useful work in moving the pistons, which in turn rotate the wheels of the train. In physics, we need to define the notions of heat, temperature, work, etc. more carefully. Historically, it took a long time to arrive at the proper concept of ‘heat’. Before the modern picture, heat was regarded as a fine invisible fluid filling in the pores of a substance. On contact between a hot body and a cold body, the fluid (called caloric) flowed from the colder to the hotter body! This is similar to what happens when a horizontal pipe connects two tanks up to different heights. The flow continues until the levels of water in the two tanks are the same. Likewise, in the ‘caloric’ picture of heat, heat flows until the ‘caloric levels’ (i.e., the temperatures) equalize. In time, the picture of heat as a fluid was discarded in favour of the modern concept of heat as a form of energy. An important experiment in this connection was due to Benjamin Thomson (also known as Count Rumford) in 1798. He observed that boring of a brass cannon generated a lot of heat, indeed enough to boil water. More significantly, the amount of heat produced depended on the work done (by the horses employed for turning the drill) but not on the sharpness of the drill. In the caloric picture, a sharper drill would scoop out more heat fluid from the pores; but this was not observed. A most natural explanation of the observations was that heat was a form of energy and the experiment demonstrated conversion of energy from one form to another–from work to heat.

Thermodynamics is the branch of physics that deals with the concepts of heat and temperature and the inter-conversion of heat and other forms of energy. Thermodynamics is a macroscopic science. It deals with bulk systems and does not go into the molecular constitution of matter. In fact, its concepts and laws were formulated in the nineteenth century before the molecular picture of matter was firmly established. Thermodynamic description involves relatively few macroscopic variables of the system, which are suggested by common sense and can be usually measured directly. A microscopic description of a gas, for example, would involve specifying the co-ordinates and velocities of the huge number of molecules constituting the gas. The description in kinetic theory of gases is not so detailed but it does involve molecular distribution of velocities. Thermodynamic description of a gas, on the other hand, avoids the molecular description altogether. Instead, the state of a gas in thermodynamics is specified by macroscopic variables such as pressure, volume, temperature, mass and composition that are felt by our sense perceptions and are measurable*.

The distinction between mechanics and thermodynamics is worth bearing in mind. In mechanics, our interest is in the motion of particles or bodies under the action of forces and torques. Thermodynamics is not concerned with the motion of the system as a whole. It is concerned with the internal macroscopic state of the body. When a bullet is fired from a gun, what changes is the mechanical state of the bullet (its kinetic energy, in particular), not its temperature. When the bullet pierces a wood and stops, the kinetic energy of the bullet gets converted into heat, changing the temperature of the bullet and the surrounding layers of wood. Temperature is related to the energy of the internal (disordered) motion of the bullet, not to the motion of the bullet as a whole.

13.2 THERMAL EQUILIBRIUM

Equilibrium in mechanics means that the net external force and torque on a system are zero. The term ‘equilibrium’ in thermodynamics appears in a different context: we say the state of a system is an equilibrium state if the macroscopic variables that characterize the system do not change in time. For example, a gas inside a closed rigid container, completely insulated from its surroundings, with fixed values of pressure, volume, temperature, mass and composition that do not change with time, is in a state of thermodynamic equilibrium.

In general, whether or not a system is in a state of equilibrium depends on the surroundings and the nature of the wall that separates the system from the surroundings. Consider two gases A and B occupying two different containers. We know experimentally that pressure and volume of a given mass of gas can be chosen to be its two independent variables.

Let the pressure and volume of the gases be (P_A, V_A) and (P_B, V_B) respectively. Suppose first that the two systems

are put in proximity but are separated by an adiabatic wall – an insulating wall (can be movable) that does not allow flow of energy (heat) from one to another. The systems are insulated from the rest of the surroundings also by similar adiabatic walls. The situation is shown schematically in Fig. 13.1 (a). In this case, it is found that any possible pair of values (P_A, V_A) will be in equilibrium with any possible pair of values (P_B, V_B). Next, suppose that the adiabatic wall is replaced by a diathermic wall – a conducting wall that allows energy flow (heat) from one to another. It is then found that the macroscopic variables of the systems A and B change spontaneously until both the systems attain equilibrium states. After that there is no change in their states. The situation is shown in Fig. 13.1(b). The pressure and volume variables of the two gases change to (PB′ , VB′) and (PA′ , VA′) such that the new states of A and B are in equilibrium with each other**.

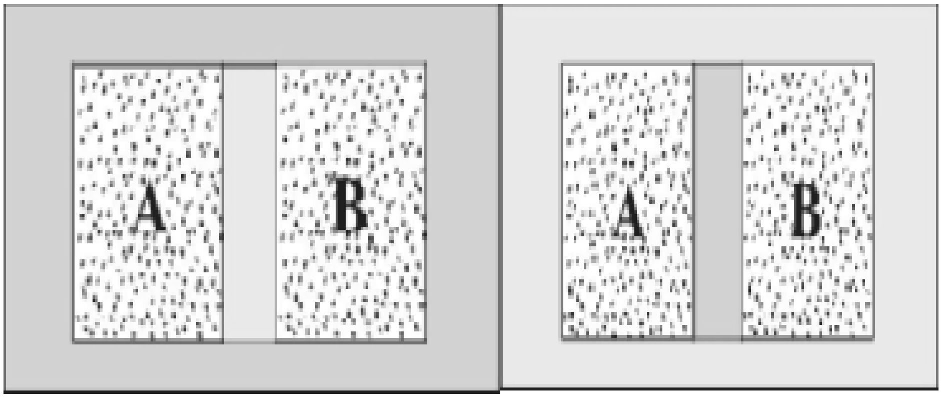
There is no more energy flow from one to another. We then say that the system A is in thermal equilibrium with the system B. What characterizes the situation of thermal equilibrium between two systems? You can guess the answer from your experience. In thermal equilibrium, the temperatures of the two systems are equal. We shall see how does one arrive at the concept of temperature in thermodynamics? The Zeroth law of thermodynamics provides the clue.

* *Thermodynamics may also involve other variables that are not so obvious to our senses e.g. entropy, enthalpy, etc., and they are all macroscopic variables.*

** *Both the variables need not change. It depends on the constraints. For instance, if the gases are in containers of fixed volume, only the pressures of the gases would change to achieve thermal equilibrium.*

13.3 ZEROTH LAW OF THERMODYNAMICS

Imagine two systems A and B, separated by an adiabatic wall, while each is in contact with a third system C, via a conducting wall [Fig. 13.2(a)]. The states of the systems (i.e., their macroscopic variables) will change until both A and B come to thermal equilibrium with C. After this is achieved, suppose that the adiabatic wall between A and B is replaced by a conducting wall and C is insulated from A and B by an adiabatic wall [Fig.13.2(b)]. It is found that the states of A and B change no further i.e. they are found to be in thermal equilibrium with each other. This observation forms the basis of the Zeroth Law of Thermodynamics, which states that 'two systems in thermal equilibrium with a third system separately are in thermal equilibrium with each other'. R.H. Fowler formulated this law in 1931 long after the first and second Laws of thermodynamics were stated and so numbered.



(a) (b)

Fig. 13.1 *(a) Systems A and B (two gases) separated by an adiabatic wall – an insulating wall that does not allow flow of heat. (b) The same systems A and B separated by a diathermic wall – a conducting wall that allows heat to flow from one to another. In this case, thermal equilibrium is attained in due course.*

The Zeroth Law clearly suggests that when two systems A and B, are in thermal equilibrium, there must be a physical quantity that has the same value for both. This thermodynamic variable whose value is equal for two systems in thermal equilibrium is called temperature (T). Thus, if A and B are separately in equilibrium with C, $T_A = T_C$ and $T_B = T_C$. This implies that $T_A = T_B$ i.e., the systems A and B are also in thermal equilibrium.

We have arrived at the concept of temperature formally via the Zeroth Law. The next question is: how to assign numerical values to temperatures of different bodies ? In other words, how do we construct a scale of temperature? Thermometry deals with this basic question to which we turn in the next section.

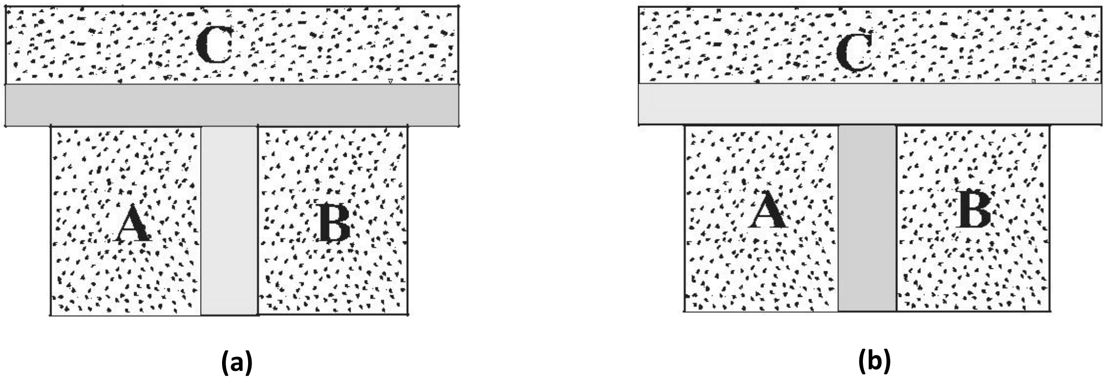


Fig. 13.2 *(a) Systems A and B are separated by an adiabatic wall, while each is in contact with a third system C via a conducting wall. (b) The adiabatic wall between A and B is replaced by a conducting wall, while C is insulated from A and B by an adiabatic wall.*

13.4 HEAT, INTERNAL ENERGY AND WORK

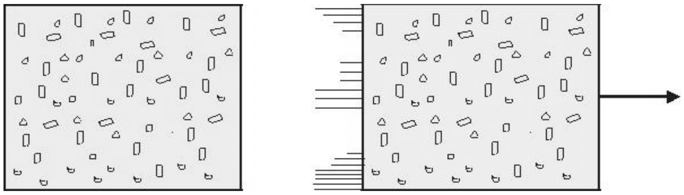
The Zeroth Law of Thermodynamics led us to the concept of temperature that agrees with our commonsense notion. Temperature is a markerof the 'hotness' of a body. It determines the direction of flow of heat when two bodies are placed in thermal contact. Heat flows from the body at a higher temperature to the one at lower temperature. The flow stops when the temperatures equalize; the two bodies are then in thermal equilibrium. We saw in some detail how to construct temperature scales to assign temperatures to different bodies. We now describe the concepts of heat and other relevant quantities like internal energy and work.

The concept of internal energy of a system is not difficult to understand. We know that every bulk system consists of a large number of molecules. Internal energy is simply the sum of the kinetic energies and potential energies of these molecules. We remarked earlier that in thermodynamics, the kinetic energy of the system, as a whole, is not relevant. Internal energy is thus, the sum of molecular kinetic and potential energies in the frame of reference relative to which the centre of mass of the system is at rest. Thus, it includes only the (disordered) energy associated with the random motion of molecules of the system. We denote the internal energy of a system by U.

Though we have invoked the molecular picture to understand the meaning of internal energy, as far as thermodynamics is concerned, U is simply a macroscopic variable of the system. The important thing about internal energy is that it depends only on the state of the system, not on how that state was achieved. Internal energy U of a system is an example of a thermodynamic 'state variable' – its value depends only on the given state of the system, not on history i.e. not on the 'path' taken to arrive at that state. Thus, the internal energy of a given mass of gas depends on its state described by specific values of pressure, volume and temperature. It does not depend on how this state of the gas came about. Pressure, volume, temperature, and internal energy are thermodynamic state variables of the system (gas) (see section 13.7). If we neglect the small intermolecular forces in a gas, the internal energy of a gas is just the sum of kinetic energies associated with various random motions of its molecules. We will see in the next chapter that in a gas this motion is not only translational (i.e. motion from one point to another in the volume of the container); it also includes rotational and vibrational motion of the molecules (Fig. 13.3).

What are the ways of changing internal energy of a system? Consider again, for simplicity, the system to be a certain mass of gas contained in a cylinder with a movable piston as shown in Fig. 13.4. Experience shows there are two ways of changing the state of the gas (and hence its internal energy). One way is to put the cylinder in contact with a body at a higher temperature than that of the gas. The temperature difference will cause a flow of energy (heat) from the hotter body to the gas, thus increasing the internal energy of the gas. The other way is to push the piston down i.e. to do work on the system, which again results in increasing the internal energy of the gas. Of course, both these things could happen in the reverse direction. With surroundings at a lower temperature, heat would flow from the gas to the surroundings. Likewise, the gas could push the piston up and do work on the surroundings. In short, heat and work are two different modes of altering the state of a thermodynamic system and changing its internal energy.

The notion of heat should be carefully distinguished from the notion of internal energy. Heat is certainly energy, but it is the energy in transit. This is not just a play of words. The distinction is of basic significance. The state of a thermodynamic system is characterized by its internal energy, not heat. A statement like 'a gas in a given state have a certain amount of heat' is as meaningless as the statement that 'a gas in a given state has a certain amount of work'. In contrast, 'a gas in a given state has a certain amount of internal energy' is a perfectly meaningful statement. Similarly, the statements 'a certain amount of heat is supplied to the system' or 'a certain amount of work was done by the system' are perfectly meaningful. To summarize, heat and work in thermodynamics are not state variables. They are modes of energy transfer to a system resulting in change in its internal energy, which, as already mentioned, is a state variable. In ordinary language, we often confuse heat with internal energy. The distinction between them is sometimes ignored in elementary physics books. For proper understanding of thermodynamics, however, the distinction is crucial.



(a)(b)

Fig. 13.3(a) *Internal energy U of a gas is the sum of the kinetic and potential energies of its molecules when the box is at rest. Kinetic energy due to various types of motion (translational, rotational, vibrational) is to be included in U. (b) If the same box is moving as a whole with some velocity, the kinetic energy of the box is not to be included in U.*

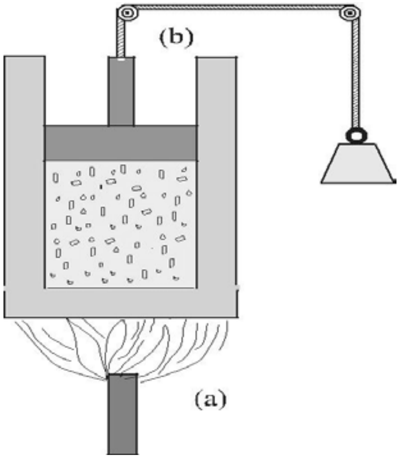


Fig. 13.4 *Heat and work are two distinct modes of energy transfer to a system that results in change in its internal energy. (a) Heat is energy transfer due to temperature difference between the system and the surroundings. (b) Work is energy transfer brought about by means (e.g. moving the piston by raising or lowering some weight connected to it) that do not involve such a temperature difference.*

13.5 FIRST LAW OF THERMODYNAMICS

We have seen that the internal energy *U* of a system can change through two modes of energy transfer: heat and work. Let

ΔQ = Heat supplied to the system by the surroundings

ΔW= Work done by the system on the surroundings

ΔU = Change in internal energy of the system.

The general principle of conservation of energy then implies that

$$\Delta Q = \Delta U + \Delta W \qquad (13.1)$$

i.e. the energy (Q) supplied to the system goes in partly to increase the internal energy of the system (U) and the rest in work on the environment (W). Equation (13.1) is known as the First Law of Thermodynamics. It is simply the general law of conservation of energy applied to any system in which the energy transfer from or to the surroundings is taken into account.

Let us put Eq. (13.1) in the alternative form

$$\Delta Q - \Delta W = \Delta U \qquad (13.2)$$

Now, the system may go from an initial state to the final state in a number of ways. For example, to change the state of a gas from (P_1, V_1) to (P_2, V_2), we can first change the volume of the gas from V_1 to V_2, keeping its pressure constant i.e. we can first go the state (P_1, V_2) and then change the pressure of the gas from P_1 to P_2, keeping volume constant, to take the gas to (P_2, V_2). Alternatively, we can first keep the volume constant and then keep the pressure constant. Since U is a state variable, ΔU depends only on the initial and final states and not on the path taken by the gas to go from one to the other. However, ΔQ and ΔW will, in general, depend on the path taken to go from the initial to final states. From the First Law of Thermodynamics, Eq. (13.2), it is clear that the combination $\Delta Q - \Delta W$, is however, path independent. This shows that if a system is taken through a process in which $\Delta U = 0$ (for example, isothermal expansion of an ideal gas, see section 13.8), does work. Since force is pressure times area, and area times displacement is volume, work done by the system against a constant pressure P is $\Delta W = P\Delta V$ where ΔV is the change in volume of the gas. Thus, for this case, Eq. (13.1) gives

$$\Delta Q = \Delta U + P\Delta V \qquad (13.3)$$

As an application of Eq. (13.3), consider the change in internal energy for 1 g of water when we go from its liquid to vapour phase. The measured latent heat of water is 2256 J/g. i.e., for 1 g of water ΔQ = 2256 J. At atmospheric pressure, 1 g of water has a volume 1 cm^3 in liquid phase and 1671 cm^3 in vapour phase.

Therefore,

$\Delta W = P\,(V_g - V_l) = 1.013 \times 10^5 \times (1670) \times 10^{-6} = 169.2$J Equation (13.3) then gives

$$\Delta U = 2256 - 169.2 = 2086.8 \text{ J}$$

We see that most of the heat goes to increase the internal energy of water in transition from the liquid to the vapor phase.

13.6 SPECIFIC HEAT CAPACITY

Suppose an amount of heat ΔQ supplied to a substance changes its temperature from T to $T + \Delta T$. We define heat capacity of a substance (see Chapter 11) to be

$$\mathrm{s} = \frac{\Delta \mathrm{Q}}{\Delta \mathrm{T}}$$

We expect Q and, therefore, heat capacity S to be proportional to the mass of the substance. Further, it could also depend on the temperature, i.e., a different amount of heat may be needed for a unit rise in temperature at different temperatures. To define a constant characteristic of the substance and independent of its amount, we divide S by the mass of the substance m in kg:

$$s = \frac{S}{m} = \frac{1}{m}\frac{\Delta Q}{\Delta T} \qquad (13.5)$$

s is known as the specific heat capacity of the substance. It depends on the nature of the substance and its temperature. The unit of specific heat capacity is J kg K^{-1}.If the amount of substance is specified in terms of moles μ (instead of mass m in kg), we can define heat capacity

$$\Delta \mathrm{Q} = \Delta \mathrm{W}$$

i.e., heat supplied to the system is used up entirely by the system in doing work on the environment.

If the system is a gas in a cylinder with a movable piston, the gas in moving the piston per mole of the substance by

$$c = \frac{S}{\mu} = \frac{1}{\mu}\frac{\Delta Q}{\Delta T}$$

C is known as molar specific heat capacity of the substance. Like *s*, *C* is independent of the amount of substance. *C* depends on the nature of the substance, its temperature and the conditions under which heat is supplied. The unit of *C* is J mo1^{-1} K^{-1}. As we shall see later (in connection with specific heat capacity of gases), additional conditions may be needed to define *C* or *s*. The idea in defining *C* is that simple predictions can be made in regard to molar specific heat capacities.

Table 13.1 lists measured specific and molar heat capacities of solids at atmospheric pressure and ordinary room temperature. We will see in Chapter 14 that predictions of specific heats of gases generally agree with experiment. We can use the same law of equipartition of energy that we use there to predict molar specific heat capacities of solids. Consider a solid of *N* atoms, each vibrating about its mean position. An oscillator in one dimension has average energy of $2 \times ½\ k_B T = k_B T$. In three dimensions, the average energy is $3\ k_B T$. For a mole of a solid, the total energy is

$$U = 3\ k_B T \times N_A = 3\ RT$$

Now, at constant pressure, $\Delta Q = \Delta U + P\ \Delta V \cong \Delta U$, since for a solid ΔV is negligible. Therefore,

$$C = \frac{\Delta Q}{\Delta T} = \frac{\Delta U}{\Delta T} = 3\mathrm{R}$$

Table 13.1 Specific and molar heat capacities of some solids at room temperature and atmospheric pressure

Substance	**Specific heat (J kg^{-1} K^{-1})**	**Molar specific Heat (J mol-1 K^{-1})**
Aluminium	900.0	24.4
Carbon	506.5	6.1
Copper	386.4	24.5
Lead	127.7	26.5
Silver	236.1	25.5
Tungsten	134.4	24.9

As Table 13.1 shows, the experimentally measured values which generally agrees with predicted value 3R at ordinary temperatures. (Carbon is an exception.) The agreement is known to break down at low temperatures.

Specific heat capacity of water. The old unit of heat was calorie. One calorie was earlier defined to be the amount of heat required to raise the temperature of 1g of water by 1°C. With more precise measurements, it was found that the specific heat of water varies slightly with temperature. Figure 13.5 shows this variation in the temperature range 0 to 100 °C.

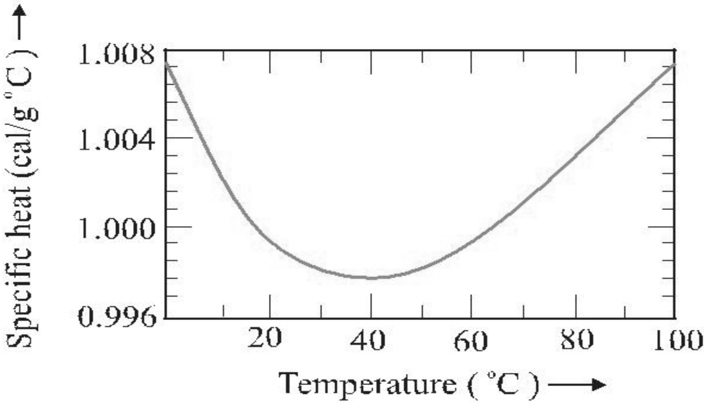


Fig.13.5 *Variation of specific heat capacity of water with temperature.*

For a precise definition of calorie, it was, therefore, necessary to specify the unit temperature interval. One calorie is defined to be the amount of heat required to raise the temperature of 1g of water from 14.5 °C to 15.5 °C. Since heat is just a form of energy, it is preferable to use the unit joule, J.In SI units, the specific heat capacity of water is 4186 J kg^{-1} K^{-1} i.e. 4.186 J g^{-1} K^{-1}. The socalled mechanical equivalent of heat defined as the amount of work needed to produce 1 cal of heat is in fact just a conversion factor between two different units of energy : calorie to joule. Since in SI units, we use the unit joule for heat, work or any other form of energy, the term mechanical equivalent is now superfluous and need not be used.

As already remarked, the specific heat capacity depends on the process or the conditions under which heat capacity transfer takes place. For gases, for example, we can define two specific heats: **specific heat capacity at constant volume and specific heat capacity at constant pressure**.

For an ideal gas, we have a simple relation.

$$C_p - C_v = R \qquad 13.8)$$

Where C_p and C_v are molar specific heat capacities of an ideal gas at constant pressure and volume respectively and R is the universal gas constant. To prove the relation, we begin with Eq. (13.3) for 1 mole of the gas :

$$\Delta Q = \Delta U + P \Delta V$$

If ΔQ is absorbed at constant volume, $\Delta V = 0$

$$C_V = \left(\frac{\Delta Q}{\Delta T}\right)_v = \left(\frac{\Delta U}{\Delta T}\right)_v = \frac{U}{T} \tag{13.9}$$

Where the subscript v is dropped in the last step, since U of an ideal gas depends only on temperature. (The subscript denotes the quantity kept fixed.) If, on the other hand, ΔQ is absorbed at constant pressure,

$$C_P = \left(\frac{\Delta Q}{\Delta T}\right)_P = \left(\frac{\Delta U}{\Delta T}\right)_P + P\left(\frac{\Delta V}{\Delta T}\right)_P$$

The subscript p can be dropped from the first term since U of an ideal gas depends only on T. Now, for a mole of an ideal gas

$$PV = RT$$

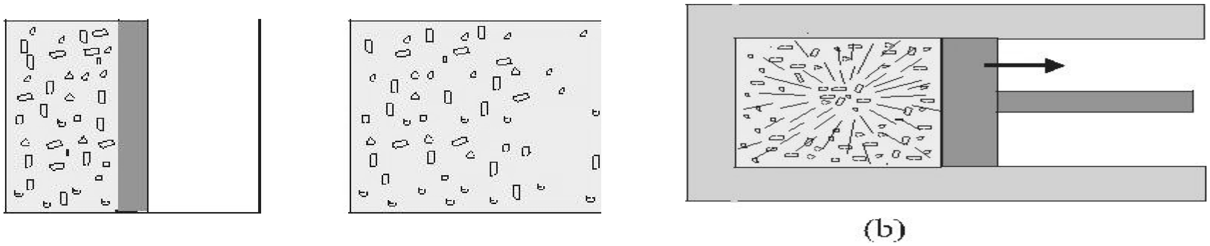
Which gives

$$P = \left(\frac{V}{T}\right)_p = R \tag{13.11}$$

Equations (13.9) to (13.11) give the desired relation, Eq. (13.8).

13.7 THERMODYNAMIC STATE VARIABLES AND EQUATION OF STATE

Every equilibrium state of a thermodynamic system is completely described by specific values of some macroscopic variables, also called state variables. For example, an equilibrium state of a gas is completely specified by the values of pressure, volume, temperature, and mass (and composition if there is a mixture of gases). A thermodynamic system is not always in equilibrium. For example, a gas allowed to expand freely against vacuum is not an equilibrium state [Fig. 13.6(a)]. During the rapid expansion, pressure of the gas may not be uniform throughout. Similarly, a mixture of gases undergoing an explosive chemical reaction (e.g. a mixture of petrol vapour and air when ignited by a spark) is not an equilibrium state; again its temperature and pressure are not uniform [Fig. 13.6(b)]. Eventually, the gas attains a uniform temperature and pressure and comes to thermal and mechanical equilibrium with its surroundings.



(a)

(b)

Fig. 13.6 *(a) The partition in the box is suddenly removed leading to free expansion of the gas. (b) A mixture of gases undergoing an explosive chemical reaction. In both situations, the gas is not in equilibrium and cannot be described by state variables.*

In short, thermodynamic state variables describe equilibrium states of systems. The various state variables are not necessarily independent. The connection between the state variables is called the equation of state. For example, for an ideal gas, the equation of state is the ideal gas relation

$$P\,V = \mu\,R\,T$$

For a fixed amount of the gas i.e. given μ, there are thus, only two independent variables, say P and V or T and V. The pressure-volume curve for a fixed temperature is called an isotherm. Real gases may have more complicated equations of state. The thermodynamic state variables are of two kinds: extensive and intensive. Extensive variables indicate the ‘size’ of the system. Intensive variables such as pressure and temperature do not. To decide which variable is extensive and which intensive, think of a relevant system in equilibrium, and imagine that it is divided into two equal parts. The variables that remain unchanged for each part are intensive. The variables whose values get halved in each part are extensive. It is easily seen, for example, that internal energy U, volume V, total mass M are extensive variables. Pressure P, temperature T, and density ρ are intensive variables. It is a good practice to check the consistency of thermodynamic equations using this classification of variables. For example, in the equation

$$\Delta Q = \Delta\, U + P\,\Delta V$$

Quantities on both sides are extensive*. (The product of an intensive variable like P and an extensive quantity ΔV is extensive.)

13.8 THERMODYNAMIC PROCESSES

13.8.1 Quasi-static process

Consider a gas in thermal and mechanical equilibrium with its surroundings. The pressure of the gas in that case equals the external pressure and its temperature is the same as that of its surroundings. Suppose that the external pressure is suddenly reduced (say by lifting the weight on the movable piston in the container). The piston will accelerate outward. During the process, the gas passes through states that are not equilibrium states. The non-equilibrium states do not have well-defined pressure and temperature. In the same way, if a finite temperature difference exists between the gas and its surroundings, there will be a rapid exchange of heat during which the gas will pass through non-equilibrium states. In due course, the gas will settle to an equilibrium state with well-defined temperature and pressure equal to those of the surroundings. The free expansion of a gas in vacuum and a mixture of gases undergoing an explosive chemical reaction, mentioned in section 13.7 are also examples where the system goes through non-equilibrium states. Non-equilibrium states of a system are difficult to deal with. It is, therefore, convenient to imagine an idealized process in which at every stage the system is an equilibrium state. Such a process is, in principle, infinitely slow-hence the name quasi-static (meaning nearly static). The system changes its variables (P,T,V) so slowly that it remains in thermal and mechanical equilibrium with its surroundings throughout. In a quasi-static process, at every stage, the difference in the pressure of the system and the external pressure is infinitesimally small. The same is true of the temperature difference between the system and its surroundings. To take a gas from the state (P, T) to another state (P' , T') via a quasi-static process, we change the external pressure by a very small amount, allow the system to equalize its pressure with that of the surroundings and continue the process infinitely slowly until the system achieves the pressure P' . Similarly, to change the temperature, we introduce an infinitesimal temperature difference between the system and the surrounding reservoirs and by choosing reservoirs of progressively different temperatures T to T', the system achieves the temperature T'.

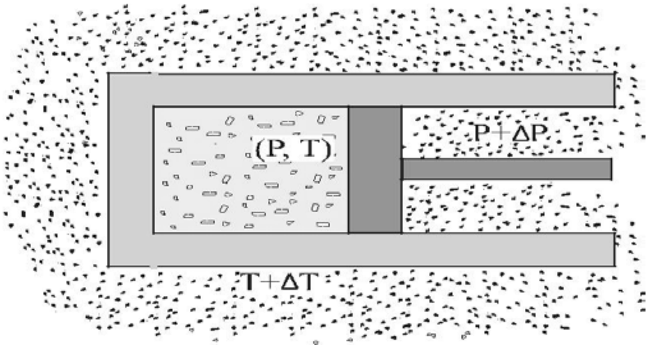


Fig. 13.7 *In a quasi-static process, the temperature of the surrounding reservoir and the external pressure differ only infinitesimally from the temperature and pressure of the system.*

A quasi-static process is obviously a hypothetical construct. In practice, processes that are sufficiently slow and do not involve accelerated motion of the piston, large temperature gradient, etc. are reasonably approximation to an ideal quasi-static process. We shall from now on deal with quasi-static processes only, except when stated otherwise.

A process in which the temperature of the system is kept fixed throughout is called an isothermal process. The expansion of a gas in a metallic cylinder placed in a large reservoir of fixed temperature is an example of an isothermal process. (Heat transferred from the reservoir to the system does not materially affect the temperature of the reservoir, because of its very large heat capacity.) In isobaric processes the pressure is constant while in isochoric processes the volume is constant. Finally, if the system is insulated from the surroundings and no heat flows between the system and the surroundings, the process is adiabatic. The definitions of these special processes are summarized in Table. 13.2.

Table 13.2 some special thermodynamic processes

Type of processes	**Feature**
Isothermal	Temperature constant
Isobaric	Pressure constant
Isochoric	Volume constant
Adiabatic	No heat flow between the system and the surroundings ($\Delta Q = 0$)

We now consider these processes in some detail:

Isothermal process

For an isothermal process (T fixed), the ideal gas equation gives

$$PV = \text{constant}$$

i.e., pressure of a given mass of gas varies inversely as its volume. This is nothing but Boyle's Law. Suppose an ideal gas goes isothermally (at temperature T) from its initial state (P_1, V_1) to the final state (P_2, V_2). At any intermediate stage with pressure P and volume change from V to V +Δ V (ΔV small) ΔW = P ΔV Taking (ΔV→0) and summing the quantity W over the entire process,

$$W = \int_{V_1}^{V_2} PdV \quad \text{as } (P=\mu RT/V)$$

$$=RT\int_{V_1}^{V_2} \frac{dV}{V} \; RT \; \ln\left(\frac{V2}{V1}\right) \qquad (13.12)$$

where in the second step we have made use of the ideal gas equation PV = μRT and taken the constants out of the integral. For an ideal gas, internal energy depends only on temperature. Thus, there is no change in the internal energy of an ideal gas in an isothermal process. The First Law of Thermodynamics then implies that heat supplied to the gas equals the work done by the gas: Q = W. Note from Eq. (13.13) that for $V_2>V_1$, W> 0; and for $V_2<V_1$, W< 0. That is, in an isothermal expansion, the gas absorbs. We can calculate, as before, the work done in an adiabatic change of an ideal gas from the state (P_1, V_1, T_1) to the state (P_2, V_2, T_2) heat and does work while in an isothermal compression, work is done on the gas by the environment and heat is released.

Adiabatic process

In an adiabatic process, the system is insulated from the surroundings and heat absorbed or released is zero. From Eq. (13.1), we see that work done by the gas results in decrease in its

internal energy (and hence its temperature for an ideal gas). We quote without proof (the result that you will learn in higher courses) that for an adiabatic process of an ideal gas.

$$P\,V^{\gamma} = \text{constant} \qquad (13.13)$$

where γ is the ratio of specific heats (ordinary or molar) at constant pressure and at constant volume.

$$\gamma = \frac{C_P}{C_V}$$

Thus if an ideal gas undergoes a change in its state adiabatically from (P_1, V_1) to (P_2, V_2):

$$P_1V_1^{\gamma} = P_2V_2^{\gamma} \qquad (13.14)$$

Fig.ure13.8 shows the P-V curves of an ideal gas for two adiabatic processes connecting two isotherms.

$$W = \int_{V_1}^{V_2} PdV$$

$$= \text{constant} \int_{V_1}^{V_2} \frac{dV}{V^{\gamma}} = \text{constant} \left[\frac{V^{-\gamma+1}}{1-\gamma}\right]_{V_1}^{V^2}$$

$$\gamma = \frac{C_p}{C_v}$$

$$= \frac{constant}{1-\gamma}\left[\frac{1}{V_2^{\gamma-1}} - \frac{1}{V_1^{\gamma-1}}\right] \qquad (13.15)$$

From Eq. (13.34), the constant is $P_1V_1^{\gamma}$or P_2V_2

$$W = \frac{1}{1-\gamma}\left[\frac{P_2V_2^{\gamma}}{V_2^{\gamma-1}} - \frac{P_1V_1^{\gamma}}{V_1^{\gamma-1}}\right]$$

$$= \frac{1}{1-\gamma}[P_2V_2P_1V_1] = \frac{R(T_1 - T_2)}{1-\gamma} \qquad (13.16)$$

As expected, if work is done by the gas in an adiabatic process ($W > 0$), from Eq. (13.16), $T_2 < T_1$. On the other hand, if work is done on the gas ($W < 0$), we get $T_2 > T_1$ i.e., the temperature of the gas rises.

Isochoric process

In an isochoric process, V is constant. No work is done on or by the gas. From Eq. (13.1), the heat absorbed by the gas goes entirely to change its internal energy and its temperature. The change in temperature for a given amount of heat is determined by the specific heat of the gas at constant volume.

Isobaric process

In an isobaric process, P is fixed. Work done by the gas is

$$W=P(V_2-V_1)=\mu R(T_2-T_1) \tag{13.17}$$

Since temperature changes, so does internal energy. The heat absorbed goes partly to increase internal energy and partly to do work. The change in temperature for a given amount of heat is determined by the specific heat of the gas at constant pressure.

Cyclic process

In a cyclic process, the system returns to its initial state. Since internal energy is a state variable, $\Delta U = 0$ for a cyclic process. From

Eq. (13.1), the total heat absorbed equals the work done by the system.

13.9 HEAT ENGINES

Heat engine is a device by which a system is made to undergo a cyclic process that results in conversion of heat to work.

1. It consists of a working substance–the system. For example, a mixture of fuel vapour and air in a gasoline or diesel engine or steam in a steam engine are the working substances.
2. The working substance goes through a cycle consisting of several processes. In some of these processes, it absorbs a total amount of heat Q_1 from an external reservoir at some high temperature T_1.
3. In some other processes of the cycle, the working substance releases a total amount of heat Q_2 to an external reservoir at some lower temperature T_2.
4. The work done (W) by the system in a cycle is transferred to the environment via some arrangement (e.g. the working substance may be in a cylinder with a moving piston that transfers mechanical energy to the wheels of a vehicle via a shaft).

The basic features of a heat engine are schematically represented in Fig. 13.9.

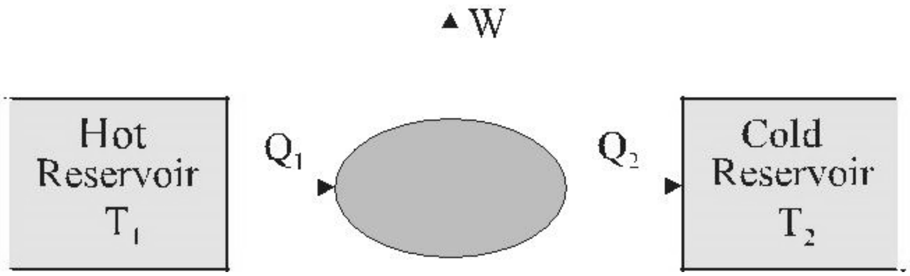


Fig. 13.9 *Schematic representation of a heat engine. The engine takes heat* Q_1 *from a hot reservoir at temperature* T_1*, releases heat* Q_2 *to a cold reservoir at temperature* T_2 *and delivers work W to the surroundings.*

The cycle is repeated again and again to get useful work for some purpose. The discipline of thermodynamics has its roots in the study of heat engines. A basic question relates to the efficiency of a heat engine. The efficiency (η) of a heat engine is defined by

$$\eta = W/Q_1 \tag{13.18}$$

where Q_1 is the heat input i.e., the heat absorbed by the system in one complete cycle and W is the work done on the environment in a cycle. In a cycle, a certain amount of heat (Q_2) may also be rejected to the environment. Then, according to the First Law of Thermodynamics, over one complete cycle,

$$W = Q_1 - Q_2 \tag{13.19}$$

$$\text{i.e., } \eta = 1 - \left({}^{Q2}/_{Q1}\right) \tag{13.20}$$

For $Q_2 = 0$, $\eta = 1$, i.e., the engine will have 100% efficiency in converting heat into work. Note that the First Law of Thermodynamics i.e., the energy conservation law does not rule out such an engine. But experience shows that such an ideal engine with $\eta = 1$ is never possible, even if we can eliminate various kinds of losses associated with actual heat engines. It turns out that there is a fundamental limit on the efficiency of a heat engine set by an independent principle of nature, called the Second Law of Thermodynamics (section 13.11).

The mechanism of conversion of heat into work varies for different heat engines. Basically, there are two ways: the system (say a gas or a mixture of gases) is heated by an external furnace, as in a steam engine; or it is heated internally by an exothermic chemical reaction as in an internal combustion engine. The various steps involved in a cycle also differ from one engine to another. For the purpose of general analysis, it is useful to conceptualise a heat engine as having the following essential ingredients.

13.10 REFRIGERATORS AND HEAT PUMPS

A refrigerator is the reverse of a heat engine. Here the working substance extracts heat Q_2 from the cold reservoir at temperature T_2, some external work W is done on it and heat Q_1 is released to the hot reservoir at temperature T_1 (Fig. 13.10).

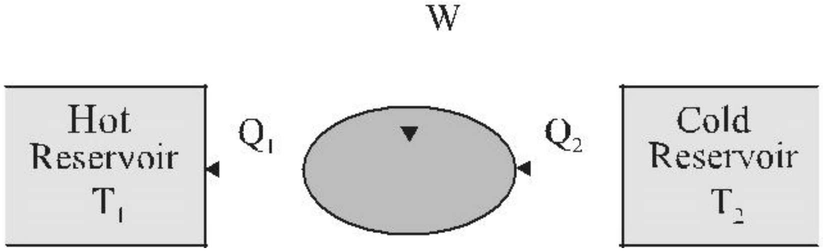
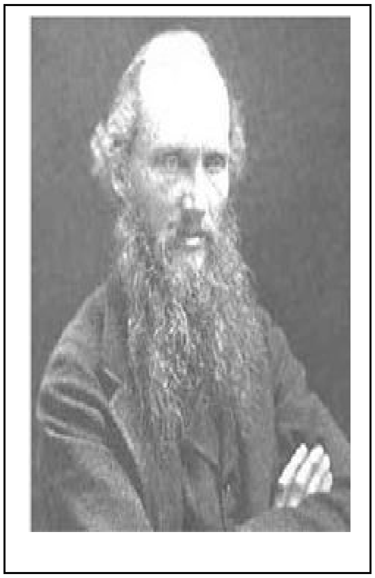
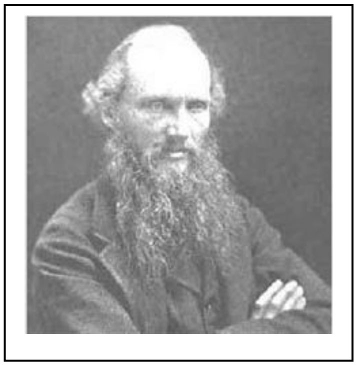


Fig.13.10 *Schematic representation of a refrigerator or a heat pump, the reverse of a heat engine.*

Pioneers of Thermodynamics



Lord Kelvin (William Thomson) (1824-1907), born in Belfast, Ireland, is among the foremost British scientists of the nineteenth century. Thomson played a key role in the development of the law of conservation of energy suggested by the work of James Joule (1818-1889), Julius Mayer (1814-1878) and Hermann Helmholtz (1821-1894). He collaborated with Joule on the so-called Joule-Thomson effect : cooling of a gas when it expands into vacuum. He introduced the notion of the absolute zero of temperature and proposed the absolute temperature scale, now called the Kelvin scale in his honour. From the work of Sadi Carnot (1796-1832), Thomson arrived at a form of the Second Law of Thermodynamics. Thomson was a versatile physicist, with notable contributions to electromagnetic theory and hydrodynamics.



Rudolf Clausius (1822-1888), born in Poland, is generally regarded asthe discoverer of the Second Law of Thermodynamics. Based on the work of Carnot and Thomson, Clausius arrived at the important notion of entropy that led him to a fundamental version of the Second Law of Thermodynamics that states that the entropy of an isolated system can never decrease. Clausius also worked on the kinetic theory of gases and obtained the first reliable estimates of molecular size, speed, mean free path, etc

A heat pump is the same as a refrigerator. What term we use depends on the purpose of the device. If the purpose is to cool a portion of space, like the inside of a chamber, and higher temperature reservoir is surrounding, we call the device a refrigerator; if the idea is to pump heat into a portion of space (the room in a building when the outside environment is cold), the device is called a heat pump.

In a refrigerator the working substance (usually, in gaseous form) goes through the following steps : (a) sudden expansion of the gas from high to low pressure which cools it and converts it into a vapour-liquid mixture, (b) absorption by the cold fluid of heat from the region to be cooled converting it into vapour, (c) heating up of the vapour due to external work done on the system, and (d) release of heat by the vapour to the surroundings, bringing it to the initial state and completing the cycle. The coefficient of performance (α) of a refrigerator is given by

$$\frac{Q_2}{W} \tag{13.21}$$

where Q_2 is the heat extracted from the cold reservoir and W is the work done on the system–the refrigerant. (α for heat pump is defined as Q_1/W) Note that while η by definition can never exceed 1, α can be greater than 1. By energy conservation, the heat released to the hot reservoir is

$$Q_1 = W + Q_2$$

$$\frac{Q_2}{Q_1 - Q_2} \tag{13.22}$$

In a heat engine, heat cannot be fully converted to work; likewise a refrigerator cannot work without some external work done on the system, i.e., the coefficient of performance in Eq. (13.21) cannot be infinite.

13.11 SECOND LAW OF THERMODYNAMICS

The First Law of Thermodynamics is the principle of conservation of energy. Common experience shows that there are many conceivable processes that are perfectly allowed by the First Law and yet are never observed. For example, nobody has ever seen a book lying on a table jumping to a height by itself. But such a thing would be possible if the principle of conservation of energy were the only restriction. The table could cool spontaneously, converting some of its internal energy into an equal amount of mechanical energy of the book, which would then hop to a height with potential energy equal to the mechanical energy it acquired. But this never happens. Clearly, some additional basic principle of nature forbids the above, even though it satisfies the energy conservation principle. This principle, which disallows many phenomena consistent with the First Law of Thermodynamics is known as the Second Law of Thermodynamics.

The Second Law of Thermodynamics gives a fundamental limitation to the efficiency of a heat engine and the co-efficient of performance of a refrigerator. In simple terms, it says that efficiency of a heat engine can never be unity. According to Eq. (13.20), this implies that heat released to the cold reservoir can never be made zero. For a refrigerator, the Second Law says that the co-efficient of performance can never be infinite. According to Eq. (13.21), this implies that external work (W) can never be zero. The following two statements, one due to Kelvin and Planck denying the possibility of a perfect heat engine, and another due to Clausius denying the possibility of a perfect refrigerator or heat pump, are a concise summary of these observations. bring both the system and surroundings to their initial states with no other effect anywhere? Experience suggests that for most processes in nature this is not possible. The spontaneous processes of nature are irreversible. Several examples can be cited. The base of a vessel on an oven is hotter than its other parts. When the vessel is removed, heat is transferred from the base to the other parts, bringing the vessel to a uniform temperature (which in due course cools to the temperature of the surroundings). The process cannot be reversed; a part of the vessel will not get cooler spontaneously and warm up the base. It will violate the Second Law of Thermodynamics, if it did. The free expansion of a gas is irreversible. The combustion reaction of a mixture of petrol and air ignited by a spark cannot be reversed. Cooking gas leaking from a gas cylinder in the kitchen diffuses to the entire room. The diffusion process will not spontaneously reverse and bring the gas back to the cylinder. The stirring of a liquid in thermal contact with a reservoir will convert the work done into heat, increasing the internal energy of the reservoir. The process cannot be reversed exactly; otherwise it would amount to conversion of heat entirely into work, violating the Second Law of Thermodynamics. Irreversibility is a rule rather an exception in nature.

Irreversibility arises mainly from two causes: one, many processes (like a free expansion, or an explosive chemical reaction) take the system to non-equilibrium states; two, most processes involve friction, viscosity and other dissipative effects (e.g., a moving body coming to a stop and losing its mechanical energy as heat to the floor and the body; a rotating blade in a liquid coming to a stop due to viscosity and losing its mechanical energy with corresponding gain in the internal energy of the liquid). Since dissipative effects are present everywhere and can be minimised but not fully eliminated, most processes that we deal with are irreversible.

A thermodynamic process (state i→ state f) is reversible if the process can be turned back such that both the system and the surroundings return to their original states, with no other change anywhere else in the universe. From the preceding discussion, a reversible process is an idealized notion. A process is reversible only if it is quasi-static (system in equilibrium with the surroundings at every stage) and there are no dissipative effects. For example, a quasi-static isothermal expansion of an ideal gas in a cylinder fitted with a frictionless movable piston is a reversible process.

Why is reversibility such a basic concept in thermodynamics? As we have seen, one of the concerns of thermodynamics is the efficiency with which heat can be converted into work. The Second Law of Thermodynamics rules out the possibility of a perfect heat engine with 100% efficiency. But what is the highest efficiency possible for a heat engine working between two reservoirs at temperatures T_1 and T_2? It turns out that a heat engine based on idealised reversible processes achieves the highest efficiency possible. All other engines involving irreversibility in any way (as would be the case for practical engines) have lower than this limiting efficiency.

13.12 CARNOT ENGINE

Suppose we have a hot reservoir at temperature T_1 and a cold reservoir at temperature T_2. Whatis the maximum efficiency possible for a heat engine operating between the two reservoirs and what cycle of processes should be adopted to achieve the maximum efficiency? Sadi Carnot, a French engineer, first considered this question in 1824. Interestingly, Carnot arrived at the correct answer, even though the basic concepts of heat and thermodynamics had yet to be firmly established.

We expect the ideal engine operating between two temperatures to be a reversible engine. Irreversibility is associated with dissipative effects, as remarked in the preceding section, and lowers efficiency. A process is reversible if it is quasi-static and non-dissipative. We have seen that a process is not quasi-static if it involves finite temperature difference between the system and the reservoir. This implies that in a reversible heat engine operating between two temperatures, heat should be absorbed (from the hot reservoir) isothermally and released (to the cold reservoir) isothermally. We thus have identified two steps of the reversible heat engine: isothermal process at temperature T_1 absorbing heat Q_1 from the hot reservoir, and another isothermal process at temperature T_2 releasing heat Q_2 to the cold reservoir.

To complete a cycle, we need to take the system from temperature T_1 to T_2 and then back from temperature T_2 to T_1. Which processes should we employ for this purpose that are reversible? A little reflection shows that we can only adopt reversible adiabatic processes for these purposes, which involve no heat flow from any reservoir. If we employ any other process that is not adiabatic, say an isochoric process, to take the system from one temperature to another, we shall need a series of reservoirs in the temperature range T_2 to T_1 to ensure that at each stage the process is quasi-static. (Remember again that for a process to be quasi-static and reversible, there should be no finite temperature difference between the system and the reservoir.) But we are considering a reversible engine that operates between only two temperatures. Thus adiabatic processes must bring about the temperature change in the system from T_1 to T_2 and T_2 to T_1 in this engine.

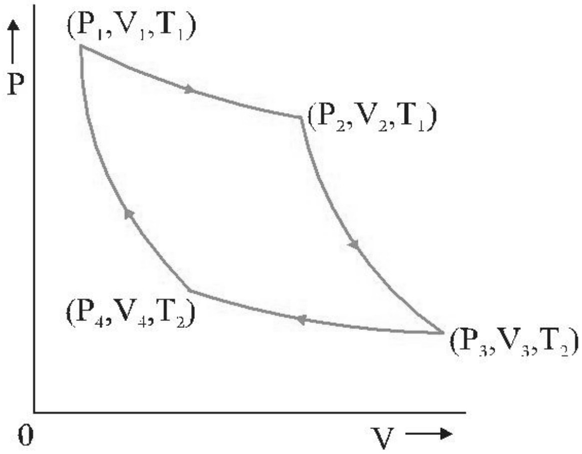


Fig. 13.11 *Carnot cycle for a heat engine with an ideal gas as the working substance.*

A reversible heat engine operating between two temperatures is called a Carnot engine. We have just argued that such an engine must have the following sequence of steps constituting one cycle, called the Carnot cycle, shown in Fig. 13.11. We have taken the working substance of the Carnot engine to be an ideal gas.

(a) Step 1 →2 Isothermal expansion of the gas taking its state from (P_1, V_1, T_1) to (P_2, V_2, T_1).The heat absorbed by the gas (Q_1) from the reservoir at temperature T_1 is given byEq. (13.12). This is also the work done ($W_{1\to2}$) by the gas on the environment.

$$W_{1\to2} = Q_1 = \mu R T_1 \ln\left(\frac{V_2}{V_1}\right) \tag{13.23}$$

(b) *Step* 2→3 Adiabatic expansion of the gas

from (P_2, V_2, T_1) to (P_3, V_3, T_2) Work

done by the gas, using Eq. (13.16), is

$$W_{2\to3} = \frac{R(T_1 - T_2)}{\gamma - 1} \tag{13.24}$$

(c) *Step* 3→4 Isothermal compression of the gas from (P_3, V_3, T_2) to (P_4, V_4, T_2).

Heat released (Q_2) by the gas to the reservoir at temperature T_2 is given by Eq. (13.13). This is also the work done ($W_{3\to4}$) on the gas by the environment.

$$W_{3\to4} = Q_2 = RT_2 \ln\left(\frac{V_3}{V_4}\right) \quad (13.25)$$

(d) *Step* 4⟶1 Adiabatic compression of the gas from (P_4, V_4, T_2) to (P_1,V_1, T_1).

Work done on the gas, [using Eq.(13.16)], is

$$W_{4\to1} = \frac{R(T_1-T_2)}{\gamma-1} \quad (13.26)$$

From Eqs. (13.23) to (13.26) total work done by the gas in one complete cycle is

$$W = W_{1\to2} + W_{2\to3} + W_{3\to4} + W_{4\to1}$$

$$= \mu RT_1 \ln\left(\frac{V_2}{V_1}\right) - \mu RT_2 \ln\left(\frac{V_3}{V_4}\right) \quad (13.27)$$

The efficiency η of the Carnot engine is

$$\frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

$$1 - \frac{T_2}{T_1} = \frac{\ln(V_3/V_4)}{\ln(V_2/V_1)} \quad (13.28)$$

Now since step 2→ 3 is an adiabatic process,

$$T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$$

$$\text{i.e.} \qquad \frac{V_2}{V_3} = \left(\frac{T_2}{T_1}\right)^{\frac{1}{\gamma-1}} \quad (13.29)$$

Similarly, since step 4 ⟶ 1 is an adiabatic process

$$T_2 V_4^{\gamma-1} = T_1 V_1^{\gamma-1}$$

$$\frac{V_1}{V_4} = \left(\frac{T_2}{T_1}\right)^{\frac{1}{\gamma-1}} \quad (13.30)$$

From Eqs. (13.29) and (13.30),

$$\left(\frac{V_3}{V_4}\right) = \left(\frac{V_2}{V_1}\right) \quad (13.31)$$

Using Eq. (13.31) in Eq. (13.28), we get

$$1 - \frac{T_2}{T_1}\ \text{(carnot engine)} \tag{13.32}$$

We have already seen that a Carnot engine is a reversible engine. Indeed it is the only reversible engine possible that works between two reservoirs at different temperatures. Each step of the Carnot cycle given in Fig. 13.11 can be reversed. This will amount to taking heat Q_2 from the cold reservoir at T_2, doing work W on the system, and transferring heat Q_1 to the hot reservoir. This will be a reversible refrigerator. We next establish the important result (sometimes called Carnot's theorem) that (a) working between two given temperatures T_1 and T_2 of the hot and cold reservoirs respectively, no engine can have efficiency more than that of the Carnot engine and (b) the efficiency of the Carnot engine is independent of the nature of the working substance.

To prove the result (a), imagine a reversible (Carnot) engine R and an irreversible engine I working between the same source (hot reservoir) and sink (cold reservoir). Let us couple the engines, I and R, in such a way so that I acts like a heat engine and R acts as a refrigerator. Let I absorb heat Q_1 from the source, deliver work W' and release the heat Q_1- W' to the sink. We arrange so that R returns the same heat Q_1 to the source, taking heat Q_2 from the sink and requiring work $W = Q_1 – Q_2$ to be done on it.

Now suppose $\eta_R < \eta_i$ i.e. if R were to act as an engine it would give less work output than that of I i.e. $W < W'$ for a given Q_1. With R acting like a refrigerator, this would mean$Q_2 = Q_1 – W > Q_1 – W'$. Thus on the whole the coupled I-R system extracts heat $(Q_1 – W) – (Q_1 – W') = (W' – W)$ from the cold reservoir and delivers the same amount of workin one cycle, without any change in the source or anywhere else. This is clearly against the Kelvin-Planck statement of the Second Law of Thermodynamics. Hence the assertion $\eta_i > \eta_R$ is wrong. No engine can have efficiency greater

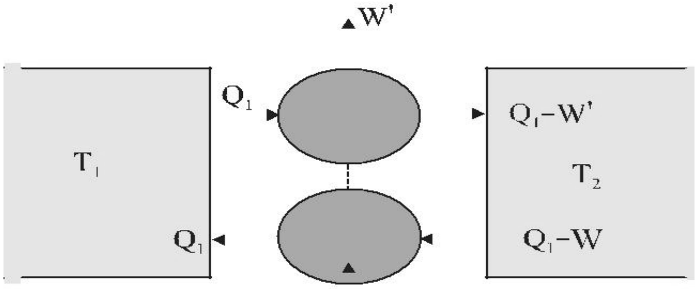


Fig. 13.13 *An irreversible engine (I) coupled to a reversible refrigerator (R). If W '> W, this would amount to extraction of heat W' – W from the sink and its full conversion to work, in contradiction with the Second Law of Thermodynamics.*

than that of the Carnot engine. A similar argument can be constructed to show that a reversible engine with one particular substance cannot be more efficient than the one using another substance. The maximum efficiency of a Carnot engine given by Eq. (13.32) is independent of the nature of the system performing the Carnot cycle of operations. Thus we are justified in using an ideal gas as a system in the calculation of efficiency η of a Carnot engine. The ideal gas has a simple equation of state, which allows us to readily calculate η, but the final result for η, [Eq. (13.32)], is true for any Carnot engine.

This final remark shows that in a Carnot cycle,

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \qquad (13.33)$$

is a universal relation independent of the nature of the system. Here Q_1 and Q_2 are respectively, the heat absorbed and released isothermally (from the hot and to the cold reservoirs) in a Carnot engine. Equation (13.33), can, therefore, be used as a relation to define a truly universal thermodynamic temperature scale that is independent of any particular properties of the system used in the Carnot cycle. Of course, for an ideal gas as a working substance, this universal temperature is the same as the ideal gas temperature introduced in section 13.11.

SUMMARY

1. The zeroth law of thermodynamics states that ‘two systems in thermal equilibrium with a third system are in thermal equilibrium with each other’. The Zeroth Law leads to the concept of temperature.
2. Internal energy of a system is the sum of kinetic energies and potential energies of the molecular constituents of the system. It does not include the over-all kinetic energy of the system. Heat and work are two modes of energy transfer to the system. Heat is the energy transfer arising due to temperature difference between the system and the surroundings. Work is energy transfer brought about by other means, such as moving the piston of a cylinder containing the gas, by raising or lowering some weight connected to it.
3. The first law of thermodynamics is the general law of conservation of energy applied to any system in which energy transfer from or to the surroundings (through heat and work) is taken into account. It states that $\Delta Q = \Delta U + \Delta W$ where Q is the heat supplied to the system, ΔW is the work done by the system and ΔU is the change in internal energy of the system.
4. The specific heat capacity of a substance is defined by

$$S = \frac{1}{m}\frac{\Delta Q}{\Delta T}$$

Where m is the mass of the substance and Q is the heat required to change its temperature by T. The molar specific heat capacity of a substance is defined by

$$C = \frac{1}{\mu}\frac{\Delta Q}{\Delta T}$$

where μ is the number of moles of the substance. For a solid, the law of equipartition of energy gives $C = 3R$

which generally agrees with experiment at ordinary temperatures.

Calorie is the old unit of heat. 1 calorie is the amount of heat required to raise the temperature of 1 g of water from 14.5 °C to 15.5 °C. 1 cal = 4.186 J.

5. For an ideal gas, the molar specific heat capacities at constant pressure and volume satisfy the relation

   $$C_p - C_v = R \text{ where } R \text{ is}$$

   the universal gas constant.

6. Equilibrium states of a thermodynamic system are described by state variables. The value of a state variable depends only on the particular state, not on the path used to arrive at that state. Examples of state variables are pressure (P), volume (V), temperature (T), and mass (m). Heat and work are not state variables. An Equation of State (like the ideal gas equation $PV = \mu RT$) is a relation connecting different state variables.

7. A quasi-static process is an infinitely slow process such that the system remains in thermal and mechanical equilibrium with the surroundings throughout. In a quasi-static process, the pressure and temperature of the environment can differ from those of the system only infinitesimally.

8. In an isothermal expansion of an ideal gas from volume V_1 to V_2 at temperature T the heat absorbed (Q) equals the work done (W) by the gas, each given by

   $$Q = W = \mu RT \ln\left(\frac{V_2}{V_1}\right)$$

9. In an adiabatic process of an ideal gas

   $$PV^{\gamma} = \text{constant}$$

   $$where\ \gamma = \frac{C_p}{C_v}$$

   Work done by an ideal gas in an adiabatic change of state from (P_1, V_1, T_1) to (P_2, V_2, T_2) is

   $$W = \frac{R(T_1 - T_2)}{\gamma - 1}$$

10. Heat engine is a device in which a system undergoes a cyclic process resulting in conversion of heat into work. If Q_1 is the heat absorbed from the source, Q_2 is the heat released to the sink, and the work output in one cycle is W, the efficiency $\eta$of the engine is:$\frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1}$

11. In a refrigerator or a heat pump, the system extracts heat Q_2 from the cold reservoir and releases Q_1 amount of heat to the hot reservoir, with work W done on the system. The co-efficient of performance of a refrigerator is given by $\alpha = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2}$

12. The second law of thermodynamics disallows some processes consistent with the First Law of Thermodynamics. It states

    Kelvin-Planck statement

    No process is possible whose sole result is the absorption of heat from a reservoir and complete conversion of the heat into work.

    Clausius statement

    No process is possible whose sole result is the transfer of heat from a colder object to a hotter object.

    Put simply, the Second Law implies that no heat engine can have efficiency η equal to

    1 or no refrigerator can have co-efficient of performance α equal to infinity.

13. A process is reversible if it can be reversed such that both the system and the surroundings return to their original states, with no other change anywhere else in the universe. Spontaneous processes of nature are irreversible. The idealized reversible process is a quasi-static process with no dissipative factors such as friction, viscosity, etc.

14. Carnot engine is a reversible engine operating between two temperatures T_1 (source) and T_2(sink). The Carnot cycle consists of two isothermal processes connected by two adiabatic processes. The efficiency of a Carnot engine is given by $\eta = 1 - \frac{T_2}{T_1}$

    (carnot engine)

    No engine operating between two temperatures can have efficiency greater than that of the Carnot engine.

15. If Q > 0, heat is added to the system

    If Q < 0, heat is removed to the system

    If W >0, Work is done by the system

    If W < 0, Work is done on the system

CHAPTER 14

KINETIC THEORY

14.1 INTRODUCTION

Boyle discovered the law named after him in 1661. Boyle, Newton and several others tried to explain the behaviour of gases by considering that gases are made up of tiny atomic particles. The actual atomic theory got established more than 150 years later. Kinetic theory explains the behaviour of gases based on the idea that the gas consists of rapidly moving atoms or molecules. This is possible as the inter-atomic forces, which are short range forces that are important for solids and liquids, can be neglected for gases. The kinetic theory was developed in the nineteenth century by Maxwell, Boltzmann and others. It has been remarkably successful. It gives a molecular interpretation of pressure and temperature of a gas, and is consistent with gas laws and Avogadro's hypothesis. It correctly explains specific heat capacities of many gases. It also relates measurable properties of gases such as viscosity, conduction and diffusion with molecular parameters, yielding estimates of molecular sizes and masses. This chapter gives an introduction to kinetic theory.

14.2 MOLECULAR NATURE OF MATTER

Richard Feynman, one of the great physicists of 20th century considers the discovery that "Matter is made up of atoms" to be a very significant one. Humanity may suffer annihilation (due to nuclear catastrophe) or extinction (due to environmental disasters) if we do not act wisely. If that happens, and all of scientific knowledge were to be destroyed then Feynman would like the 'Atomic Hypothesis' to be communicated to the next generation of creatures in the universe. Atomic Hypothesis: All things are made of atoms - little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another. Speculation that matter may not be continuous, existed in many places and cultures. Kanada in India and Democritus in Greece had suggested that matter may consist of indivisible constituents.

Atomic Hypothesis in Ancient India and Greece

Though John Dalton is credited with the introduction of atomic viewpoint in modern science, scholars in ancient India and Greece conjectured long before the existence of atoms and molecules. In the Vaiseshika school of thought in India founded by Kanada (Sixth century B.C.) the atomic picture was developed in considerable detail. Atoms were thought to be eternal, indivisible, infinitesimal and ultimate parts of matter. It was argued that if matter could be subdivided without an end, there would be no difference between a mustard seed and the Meru mountain. The four kinds of atoms (**Paramanu** — Sanskrit word for the smallest particle) postulated were Bhoomi (Earth), Ap (water), Tejas (fire) and Vayu (air) that have characteristic mass and other attributes, were propounded. Akasa (space) was thought to have no atomic structure and was continuous and inert. Atoms combine to form different molecules (e.g. two atoms combine to form a diatomic molecule dvyanuka, three atoms form a tryanuka or a triatomic molecule), their properties depending upon the nature and ratio of the constituent atoms. The size of the atoms was also estimated, by conjecture or by methods that are not known to us. The estimates vary. In Lalitavistara, a famous biography of the Buddha written mainly in the second century B.C., the estimate is close to the modern estimate of atomic size, of the order of 10^{-10} m.

In ancient Greece, Democritus (Fourth century B.C.) is best known for his atomic hypothesis. The word ‘atom’ means ‘indivisible’ in Greek. According to him, atoms differ from each other physically, in shape, size and other properties and this resulted in the different properties of the substances formed by their combination. The atoms of water were smooth and round and unable to ‘hook’ on to each other, which is why liquid /water flows easily. The atoms of earth were rough and jagged, so they held together to form hard substances. The atoms of fire were thorny which is why it caused painful burns. These fascinating ideas, despite their ingenuity, could not evolve much further, perhaps because they were intuitive conjectures and speculations not tested and modified by quantitative experiments - the hallmark of modern science.

The scientific ‘Atomic Theory’ is usually credited to John Dalton. He proposed the atomic theory to explain the laws of definite and multiple proportions obeyed by elements when they combine into compounds. The first law says that any given compound has, a fixed proportion by mass of its constituents. The second law says that when two elements form more than one compound, for a fixed mass of one element, the masses of the other elements are in ratio of small integers.

To explain the laws Dalton suggested, about 200 years ago, that the smallest constituents of an element are atoms. Atoms of one element are identical but differ from those of other elements. A small number of atoms of each element combine to form a molecule of the compound. Gay Lussac’s law, also given in early 19th century, states: When gases combine chemically to yield another gas, their volumes are in the ratios of small integers. Avogadro’s law (or hypothesis) says: Equal volumes of all gases at equal temperature and pressure have the same number of molecules. Avogadro’s law, when combined with Dalton’s theory explains Gay Lussac’s law. Since the elements are often in the form of molecules, Dalton’s atomic theory can also be referred to as the molecular theory of matter. The theory is now well accepted by scientists. However even at the end of the nineteenth century there were famous scientists who did not believe in atomic theory!

From many observations, in recent times we now know that molecules (made up of one or more atoms) constitute matter. Electron microscopes and scanning tunnelling microscopes enable us to even see them. The size of an atom is about an angstrom (10^{-10} m). In solids, which are tightly packed, atoms are spaced about a few angstroms (2 Å) apart. In liquids the separation between atoms is also about the same. In liquids the atoms are not as rigidly fixed as in solids, and can move around. This enables a liquid to flow. In gases the interatomic distances are in tens of angstroms. The average distance a molecule can travel without colliding is called the **mean free path**. The mean free path, in gases, is of the order of thousands of angstroms. The atoms are much freer in gases and can travel long distances without colliding. If they are not enclosed, gases disperse away. In solids and liquids the closeness makes the interatomic force important. The force has a long range attraction and short range repulsion. The atoms attract when they are at a few angstroms but repel when they come closer. The static appearance of a gas is misleading.

The gas is full of activity and the equilibrium is a dynamic one. In dynamic equilibrium, molecules collide and change their speeds during the collision. Only the average properties are constant.

Atomic theory is not the end of our quest, but the beginning. We now know that atoms are not indivisible or elementary. They consist of a nucleus and electrons. The nucleus itself is made up of protons and neutrons. The protons and neutrons are again made up of quarks. Even quarks may not be the end of the story. There may be string like elementary entities. Nature always has surprises for us, but the search for truth is often enjoyable and the discoveries beautiful. In this chapter, we shall limit ourselves to understanding the behaviour of gases (and a little bit of solids), as a collection of moving molecules in incessant motion.

14.3 BEHAVIOUR OF GASES

Properties of gases are easier to understand than those of solids and liquids. This is mainly because in a gas, molecules are far from each other and their mutual interactions are negligible except when two molecules collide. Gases at low pressures and high temperatures much above that at which they liquefy (or solidify) approximately satisfy a simple relation between their pressure, temperature and volume given by (see Ch. 11)

$$PV = KT \qquad \text{for a given sample of the gas.} \qquad (14.1)$$

Here T is the temperature in kelvin or (absolute) scale. K is a constant for the given sample but varies with the volume of the gas. If we now bring in the idea of atoms or molecules then K is proportional to the number of molecules, (say) N in the sample. We can write $K = N\,k$. Observation tells us that this k is same for all gases. It is called Boltzmann constant and is denoted by k.

$$\text{As } \frac{P_1V_1}{N_1T_1} = \frac{P_2V_2}{N_2T_2} = \text{constant} = \mathrm{k_B} \qquad (14.2)$$

if P, V and T are same, then N is also same for all gases. This is Avogadro's hypothesis, that the number of molecules per unit volume is same for all gases at a fixed temperature and pressure. The number in 22.4 litres of any gas is 6.02×10^{23}. This is known as Avogadro number and is denoted by N_A. The mass of 22.4 litres of any gas is equal to its molecular weight in grams at S.T.P (standard temperature 273 K and pressure 1 atm). This amount of substance is called a mole (see Chapter 2 for a more precise definition). Avogadro had guessed the equality of numbers in equal volumes of gas at a fixed temperature and pressure from chemical reactions. Kinetic theory justifies this hypothesis.

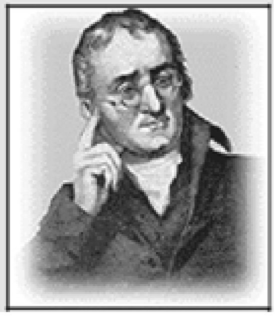
The perfect gas equation can be written as

$$PV = \mu RT \qquad (14.3)$$

Where μ is the number of moles and $R = N_A$

k_B is a universal constant. The temperature T is absolute temperature.

John Dalton (1766- 1844)



He was an English chemist. When different types of atoms combine, they obey certain simple laws. Dalton's atomic theory explains these laws in a simple way. He also gave a theory of colour blindness.

Amedeo Avogadro (1776 – 1856)

He made a brilliant guess that equal volumes of gases have equal number of molecules at the same temperature and pressure. This helped in understanding the combination of different gases in a very simple way. It is now called Avogadro's hypothesis (or law). He also suggested that the smallest constituent of gases like hydrogen, oxygen and nitrogen are not atoms but diatomic molecules.

Choosing kelvin scale for absolute temperature, $R = 8.314 \text{ J mol}^{-1}\text{K}^{-1}$.

$$\text{Here } \frac{M}{M_0} = \frac{N}{N_A} \qquad (14.4)$$

where M is the mass of the gas containing N molecules, M_0 is the molar mass and N_A the Avogadro's number. Using Eqs. (14.4) and (14.3) can also be written as

$$PV = k_B NT \quad \text{or} \quad P = k_B nT$$

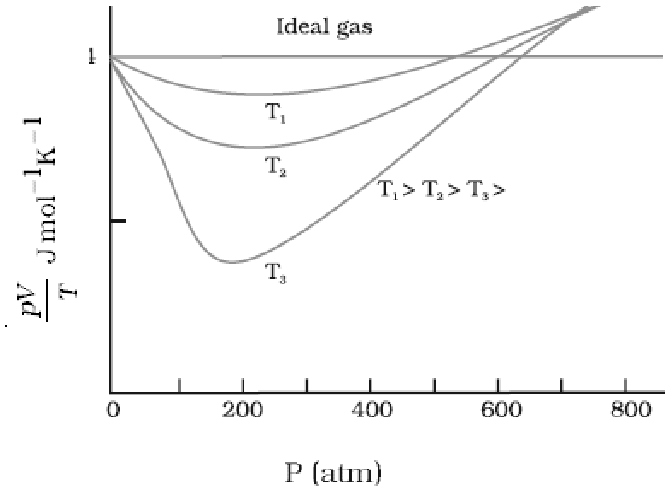


Fig.14.1 *Real gases approach ideal gas behaviour at low pressures and high temperatures.*

where n is the number density, i.e. number of molecules per unit volume. k_B is the Boltzmann constant introduced above. Its value in SI units is 1.38×10^{-23} J K^{-1}.

Another useful form of Eq. (14.3) is

$$\rho = \frac{RT}{M_0} \tag{14.5}$$

Where ρ is the mass density of the gas.

A gas that satisfies Eq. (14.3) exactly at all pressures and temperatures is defined to be an **ideal gas**. An ideal gas is a simple theoretical model of a gas. No real gas is truly ideal. Fig. 14.1 shows departures from ideal gas behaviour for a real gas at three different temperatures. Notice that all curves approach the ideal gas behaviour for low pressures and high temperatures.

At low pressures or high temperatures the molecules are far apart and molecular interactions are negligible. Without interactions the gas behaves like an ideal one.

If we fix μ and T in Eq. (14.3), we get

$$PV = \text{constant} \tag{14.6}$$

i.e., keeping temperature constant, pressure of a given mass of gas varies inversely with volume. This is the famous **Boyle's law**. Fig. 14.2 shows comparison between experimental P-V curves and the theoretical curves predicted by Boyle's law. Once again you see that the agreement is good at high temperatures and low pressures. Next, if you fix P, Eq. (14.1) shows that $V = T$ i.e., for a fixed pressure, the volume of a gas is proportional to its absolute temperature T **(Charles' law)**. See Fig. 14.3.

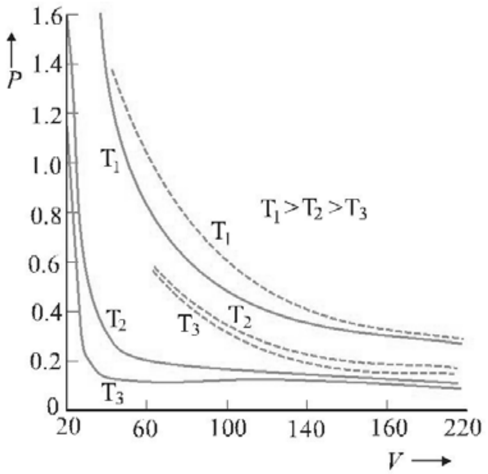


Fig.14.2 *Experimental P-V curves (solid lines) for steam at three temperatures compared with Boyle's law (dotted lines). P is in units of 22 atm and V in units of 0.09 litre*

Finally, consider a mixture of non-interacting Ideal gases: μ_1 moles of gas 1, μ_2 moles of gas 2, etc. in a vessel of volume V at temperature T and pressure P. It is then found that the equation of state of the mixture is:

$$PV = (\mu_1 + \mu_2 + \dots)RT$$

$$P = \mu_1(RT/V) + \mu_2(RT/V)\dots$$

$$= P_1 + P_2 + \dots$$

Clearly $P_1 = \mu_1 R T/V$ is the pressure gas 1 Would exert at the same conditions of volume and temperature if no other gases were present. This is called the partial pressure of the gas. Thus, the total pressure of a mixture of ideal gases is the sum of partial pressures. This is Dalton's law of partial pressures.

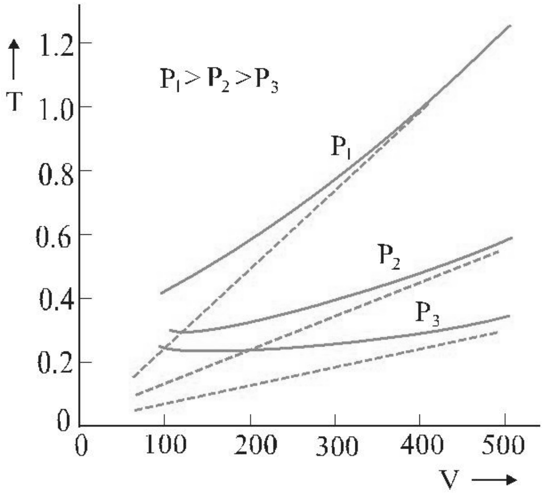


Fig. 14.3 *Experimental T-V curves (solid lines) for CO_2 at three pressures compared with Charles' law (dotted lines). T is in units of 300 K and V in units of 0.14 litres.*

We next consider some examples which give us information about the volume occupied by the molecules and the volume of a single molecule.

Example 14.1 The density of water is 1000 kg m^{-3}. The density of water vapour at 100 °C and 1 atm pressure is 0.6 kg m^{-3}. The volume of a molecule multiplied by the total number gives, what is called, molecular volume. Estimate the ratio (or fraction) of the molecular volume to the total volume occupied by the water vapour under the above conditions of temperature and pressure.

Answer For a given mass of water molecules, the density is less if volume is large. So the volume of the vapour is 1000/0.6 =/(6×10^{-4}) times larger. If densities of bulk water and water molecules are same, then the fraction of molecular volume to the total volume in liquid state is 1. As volume in vapour state has increased, the fractional volume is less by the same amount, i.e. 6×10^{-4}.

Example 14.2 Estimate the volume of a water molecule using the data in Example 14.1.

Answer In the liquid (or solid) phase, the molecules of water are quite closely packed.

The density of water molecule may therefore, be regarded as roughly equal to the density of bulk water = 1000 kg m^{-3}. To estimate the volume of a water molecule, we need to know the mass of a single water molecule. We know that 1 mole of water has a mass approximately equal to (2 + 16)g = 18 g = 0.018 kg.

Since 1 mole contains about 6×10^{23} molecules (Avogadro's number), the mass of a molecule of water is $(0.018)/(6 \times 10^{23})$ kg = 3×10^{-26} kg. Therefore, a rough estimate of the volume of a water molecule is as follows:

Volume of a water molecule

$$= (3 \times 10^{-26}\ \text{kg})/\ (1000\ \text{kg m}^{-3})$$

$$= 3 \times 10^{-29}\ \text{m}^3$$

$$= (4/3)\,\pi\ (\text{Radius})^3$$

Hence, Radius $\approx\ 2 \times 10^{-10}$ m = 2 Å

Example 14.3 What is the average distance between atoms (interatomic distance) in water? Use the data given in Examples 14.1 and 14.2.

Answer: A given mass of water in vapour state has 1.67×10^3 times the volume of the same mass of water in liquid state (Ex. 14.1). This is also the increase in the amount of volume available for each molecule of water. When volume increases by 10^3 times the radius increases by $V^{1/3}$ or 10 times, i.e., 10 × 2 Å = 20 Å. So the average distance is 2 × 20 = 40 Å.

Example 14.4 A vessel contains two non-reactive gases: neon (monatomic) and oxygen (diatomic). The ratio of their partial pressures is 3:2. Estimate the ratio of (i) number of molecules and (ii) mass density of neon and oxygen in the vessel. Atomic mass of Ne = 20.2 u, molecular mass of O_2 = 32.0 u.

Answer Partial pressure of a gas in a mixture is the pressure it would have for the same volume and temperature if it alone occupied the vessel. (The total pressure of a mixture of non-reactive gases is the sum of partial pressures due to its constituent gases.) Each gas (assumed ideal) obeys the gas law. Since V and T are common to the two gases, we have $P_1V = \mu_1 RT$ and $P_2V = \mu_2 RT$, i.e. $(P_1/P_2) = (\mu_1 / \mu_2)$. Here 1 and 2 refer to neon and oxygen respectively. Since $(P_1/P_2) = (3/2)$ (given), $(\mu_1/ \mu_2) = 3/2$.

(i) By definition $\mu_1 = (N_1/N_A)$ and $\mu_2 = (N_2/N_A)$ where N_1 and N_2 are the number of molecules of 1 and 2, and N_A is the Avogadro's number. Therefore, $(N_1/N_2) = (\mu_1 / \mu_2) = 3/2$.

(ii) We can also write $\mu_1 = (m_1/M_1)$ and $\mu_2 = (m_2/M_2)$ where m_1 and m_2 are the masses of 1 and 2; and M_1 and M_2 are their molecular masses. (Both m_1 and M_1; as well as m_2 and M_2 should be expressed in the same units). If ρ_1 and ρ_2 are the mass densities of 1 and 2 respectively, we have

$$\frac{1}{2} \quad \frac{\mathrm{m}_1/\mathrm{V}}{\mathrm{m}_2/\mathrm{V}} = \frac{\mathrm{m}_1}{\mathrm{m}_2} \cdot \frac{1}{2} \quad = \frac{\mathrm{M1}}{\mathrm{M2}}$$

$$= \frac{3}{2} \quad \frac{20.2}{32.0} = 0.947$$

14.4 KINETIC THEORY OF AN IDEAL GAS

Kinetic theory of gases is based on the molecular picture of matter. A given amount of gas is a collection of a large number of molecules (typically of the order of Avogadro's number) that are in incessant random motion. At ordinary pressure and temperature, the average distance between molecules is a factor of 10 or more than the typical size of a molecule (2 Å). Thus the interaction between the molecules is negligible and we can assume that they move freely in straight lines according to Newton's first law. However, occasionally, they come close to each other, experience intermolecular forces and their velocities change. These interactions are called collisions. The molecules collide incessantly against each other or with the walls and change their velocities. The collisions are considered to be elastic. We can derive an expression for the pressure of a gas based on the kinetic theory.

We begin with the idea that molecules of a gas are in incessant random motion, colliding against one another and with the walls of the container. All collisions between molecules among themselves or between molecules and the walls are elastic. This implies that total kinetic energy is conserved. The total momentum is conserved as usual.

14.4.1 Pressure of an Ideal Gas

Consider a gas enclosed in a cube of side l. Take the axes to be parallel to the sides of the cube, as shown in Fig. 14.4. A molecule with velocity (v_x, v_y, v_z) hits the planar wall parallel to yz-

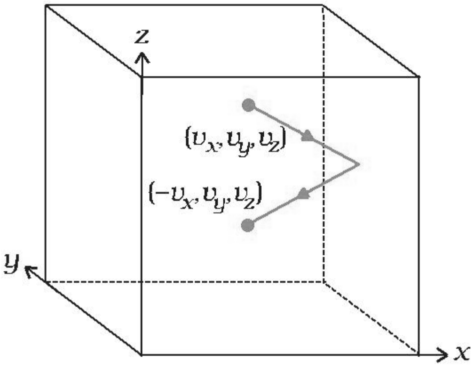


Fig. 14.4 *Elastic collision of a gas molecule with the wall of the container*

plane of area A (= l^2). Since the collision is elastic, the molecule rebounds with the same velocity; its y and z components of velocity do not change in the collision but the x-component reverses sign. That is, the velocity after collision is ($-v_x$, v_y, v_z). The change in momentum of the molecule is: $-mv_x - (mv_x) = -2mv_x$. By the principle of conservation of momentum, the momentum imparted to the wall in the collision= $2mv_x$.

To calculate the force (and pressure) on the wall, we need to calculate momentum imparted to the wall per unit time. In a small time interval t, a molecule with x-component of velocity v_x will hit the wall if it is within the distance $v_x\Delta t$ from the wall. That is, all molecules within the volume $Av_x\Delta t$ only can hit the wall in time t. But, on the average, half of these are moving towards the wall and the other half away from the wall. Thus the number of molecules with velocity (v_x, v_y, v_z) hitting the wall in time Δt is ½ $Av_x \Delta t\, n$ where n is the number of molecules per unit volume. The total momentum transferred to the wall by these molecules in time Δt is:

$$Q = (2mv_x)\left(\tfrac{1}{2}\, n A v_x \Delta t\right) \tag{14.10}$$

The force on the wall is the rate of momentum transfer $Q/\,t$

and pressure is force per unit area $P = Q/(A/\Delta t) = n\, m\, v_x^2$ (14.11)

Actually, all molecules in a gas do not have the same velocity; there is a distribution in velocities. The above equation therefore, stands for pressure due to the group of molecules with speed v_x in the x-direction and n stands for the number density of that group of molecules.

The total pressure is obtained by summing over the contribution due to all groups:

$$P = nm\overline{V_x^2} \tag{14.12}$$

where $\overline{v^2}_x$ is the average of v_x^2 . Now the gas is isotropic, i.e. there is no preferred direction of velocity of the molecules in the vessel. Therefore, by symmetry,

$$\overline{V_x^2} = \overline{V_y^2} = \overline{V_z^2}$$

$$= 1/3 \ (\overline{V_x^2} + \overline{V_y^2} + \overline{V_z^2}) = 1/3 \ \ \overline{V^2} \qquad (14.13)$$

where v is the speed and v^2 denotes the mean of the squared speed.

Thus

$$P = (1/3)\ n\ m\ \overline{v^2} \qquad (14.14)$$

Some remarks on this derivation. First, though we choose the container to be a cube, the shape of the vessel really is immaterial. For a vessel of arbitrary shape, we can always choose a small infinitesimal (planar) area and carry through the steps above. Notice that both A and t do not appear in the final result. By Pascal’s law, given in Ch. 10, pressure in one portion of the gas in equilibrium is the same as anywhere else. Second, we have ignored any collisions in the derivation. Though this assumption is difficult to justify rigorously, we can qualitatively see that it will not lead to erroneous results. The number of molecules hitting the wall in time t was found to be ½ $n\ Av_x\ t$. Now the collisions are random and the gas is in a steady state. Thus, if a molecule with velocity (v_x, v_y, v_z) acquires a different velocity due to collision with some molecule, there will always be some other molecule with a different initial velocity which after a collision acquires the velocity (v_x, v_y, v_z). If this were not so, the distribution of velocities would not remain steady. In any case we are finding v_x^2. Thus, on the whole, molecular collisions (if they are not too frequent and the time spent in a collision is negligible compared to time between collisions) will not affect the calculation above.

Founders of Kinetic Theory of Gases

James Clerk Maxwell (1831 – 1879), born in Edinburgh, Scotland, was among the greatest physicists of the nineteenth century. He derived the thermal velocity distribution of molecules in a gas and was among the first to obtain reliable estimates of molecular parameters from measurable quantities like viscosity, etc. Maxwell's greatest achievement was the unification of the laws of electricity and magnetism (discovered by Coulomb, Oersted, Ampere and Faraday) into a consistent set of equations now called Maxwell's equations. From these he arrived at the most important conclusion that light is an electromagnetic wave. Interestingly, Maxwell did not agree with the idea (strongly suggested by the Faraday's laws of electrolysis) that electricity was particulate in nature.

Ludwig Boltzmann (1844 – 1906) Vienna, Austria, worked on the kinetic theory of gases independently of Maxwell. A firm advocate of atomism, that is basic to kinetic theory, Boltzmann provided a statistical interpretation of the Second Law of thermodynamics and the concept of entropy. He is regarded as one of the founders of classical statistical mechanics. The proportionality constant connecting energy and temperature in kinetic theory is known as Boltzmann's constant in his honour.

14.4.2 Kinetic Interpretation of Temperature

Equation (14.14) can be written as

$$PV = (1/3)\, nV\, m\, \overline{v^2} \tag{14.15a}$$

$$PV = (2/3)\, N \times 1/2\, m\, \overline{v^2} \tag{14.15b}$$

where N (= nV) is the number of molecules in the sample. The quantity in the bracket is the average translational kinetic energy of the molecules in the gas.

Since the internal energy E of an ideal gas is purely kinetic*

$$E = N \times (1/2)\, m\, \overline{v^2} \tag{14.16}$$

Equation (14.15) then gives :

$$PV = (2/3)\, E \tag{14.17}$$

We are now ready for a kinetic interpretation of temperature. Combining Eq. (14.17) with the ideal gas Eq. (14.3), we get

$$E = (3/2)\, k_B\, NT \tag{14.18}$$

$$E/N = \tfrac{1}{2}\, m\, \overline{v^2} = (3/2)\, k_B T \tag{14.19}$$

i.e., the average kinetic energy of a molecule is proportional to the absolute temperature of the gas; it is independent of pressure, volume or the nature of the ideal gas. This is a fundamental result relating temperature, a macroscopic measurable parameter of a gas (a thermodynamic variable as it is called) to a molecular quantity, namely the average kinetic energy of a molecule. The two domains are connected by the Boltzmann constant. We note in passing that Eq. (14.18) tells us that internal energy of an ideal gas depends only on temperature, not on pressure or volume. With this interpretation of temperature, kinetic theory of an ideal gas is completely consistent with the ideal gas equation and the various gas laws based on it.

For a mixture of non-reactive ideal gases, the total pressure gets contribution from each gas in the mixture. Equation (14.14) becomes

$$P = \frac{1}{3}\left[n_1 m_1 \overline{v^2} + n_2 m_2 \overline{v^2} \ldots \ldots\right] \tag{14.20}$$

In equilibrium, the average kinetic energy of the molecules of different gases will be equal.

That is,

$$\frac{1}{2}m_1\overline{v_1^2} = \frac{1}{2}m_2\overline{v_2^2} = \frac{3}{2}k_bT \qquad (14.21)$$

which is Dalton's law of partial pressures. From Eq. (14.19), we can get an idea of the typical speed of molecules in a gas. At a temperature $T = 300$ K, the mean square speed of a molecule in nitrogen gas is:

**E denotes the translational part of the internal energy U that may include energies due to other degrees of freedom also. See section 14.5.*

$$m\ \frac{M\ N_2}{N_A} = 28 \quad \frac{4.65\ x\ 10^{-26}}{6.02\ x\ 10^{26}}\ \ kg$$

$$\overline{v^2} = 3\frac{k_BT}{m} = (516)^2\ m^2s^{-2}$$

The square root of $\overline{v^2}$ is known as root mean square (rms) speed and is denoted by v_{rms},

(We can also write $\overline{v^2}$ as $< v^2 >$.)

$$v_{rms} = 516\ \ m\,s^{-1}$$

The speed is of the order of the speed of sound in air. It follows from Eq. (14.19) that at the same temperature, lighter molecules have greater rms speed.

Example 14.5 A flask contains argon and chlorine in the ratio of 2:1 by mass. The temperature of the mixture is 27 °C. Obtain the ratio of (i) average kinetic energy per molecule, and (ii) root mean square speed v_{rms} of the molecules of the two gases. Atomic mass of argon = 39.9 u; Molecular mass of chlorine = 70.9 u.

Answer The important point to remember is that the average kinetic energy (per molecule) of any (ideal) gas (be it monatomic like argon, diatomic like chlorine or polyatomic) is always equal to (3/2) k_BT. It depends only on temperature, and is independent of the nature of the gas.

(i) Since argon and chlorine both have the same temperature in the flask, the ratio of average kinetic energy (per molecule) of the two gases is 1:1.

(ii) Now ½ $m\ v_{rms}^2$ = average kinetic energy per molecule = (3/2) k_BT where m is the mass of a molecule of the gas. Therefore,

$$\frac{v_{rms_{Ar}}^2}{v_{rms_{Cl}}^2} = \frac{m_{Cl}}{m_{Ar}} = \frac{M_{Cl}}{M_{Ar}} = \frac{70.9}{39.9} = 1.77$$

where *M* denotes the molecular mass of the gas. (For argon, a molecule is just an atom of argon.) Taking square root of both sides,

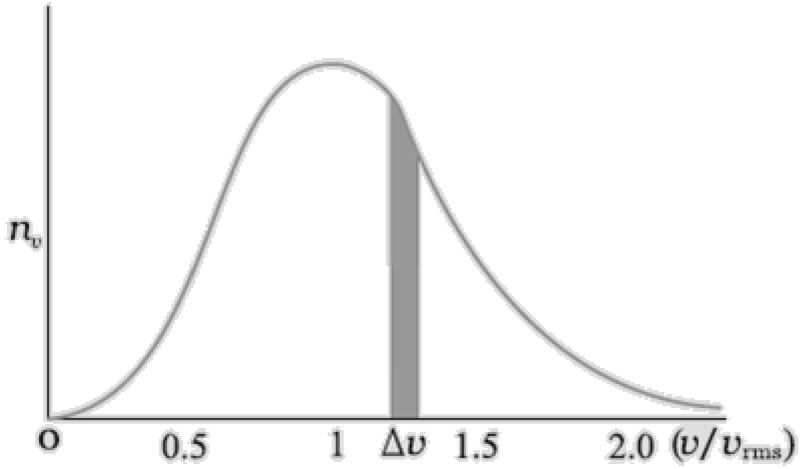
$$\frac{v_{rms_{Ar}}}{v_{rms_{Cl}}} = 1.33$$

You should note that the composition of the mixture by mass is quite irrelevant to the above calculation.

Maxwell Distribution Function

In a given mass of gas, the velocities of all molecules are not the same, even when bulk parameters like pressure, volume and temperature are fixed. Collisions change the direction and the speed of molecules. However in a state of equilibrium, the distribution of speeds is constant or fixed.

Distributions are very important and useful when dealing with systems containing large number of objects. As an example consider the ages of different persons in a city. It is not feasible to deal with the age of each individual. We can divide the people into groups: children up to age 20 years, adults between ages of 20 and 60, old people above 60. If we want more detailed information we can choose smaller intervals, 0-1, 1-2,..., 99-100 of age groups. When the size of the interval becomes smaller, say half year, the number of persons in the interval will also reduce, roughly half the original number in the one year interval. The number of persons $dN(x)$ in the age interval x and $x+dx$ is proportional to dx or $dN(x) = n_x\, dx$. We have used n_x to denote the number of persons at the value of x.



Maxwell distribution of molecular speeds

In a similar way the molecular speed distribution gives the number of molecules between the speeds v and v+ dv. d$N(v)$ = $4p\ N\ a^3 e^{-bv2}\ v^2$ dv = n_vdv. This is called Maxwell distribution. The plot of n_v against v is shown in the figure. The fraction of the molecules with speeds v and v+dv is equal to the area of the strip shown. The average of any quantity like v^2 is defined by the integral $<v^2>$ = $(1/N)\int v^2$ d$N(v)$ = **Å** $(3k_B\ T/m)$ which agrees with the result derived from more elementary considerations.

Any other proportion by mass of argon and chlorine would give the same answers to (i) and (ii), provided the temperature remains unaltered.

Example 14.6 Uranium has two isotopes of masses 235 and 238 units. If both are present in Uranium hexafluoride gas which would have the larger average speed ? If atomic mass of fluorine is 19 units, estimate the percentage difference in speeds at any temperature.

Answer At a fixed temperature the average energy = ½ $m <v^2>$ is constant. So smaller the mass of the molecule, faster will be the speed. The ratio of speeds is inversely proportional to the square root of the ratio of the masses. The masses are 349 and 352 units. So

$$v_{349} / v_{352} = (352/349)^{1/2} = 1.0044 .$$

Hence difference $\frac{V}{V}$ = 0.44 %.

[^{235}U is the isotope needed for nuclear fission. To separate it from the more abundant isotope ^{238}U, the mixture is surrounded by a porous cylinder. The porous cylinder must be thick and narrow, so that the molecule wanders through individually, colliding with the walls of the long pore. The faster molecule will leak out more than the slower one and so there is more of the lighter molecule (enrichment) outside the porous cylinder (Fig. 14.5). The method is not very efficient and has to be repeated several times for sufficient enrichment].

When gases diffuse, their rate of diffusion is inversely proportional to square root of the masses (see Exercise 14.12). Can you guess the explanation from the above answer?

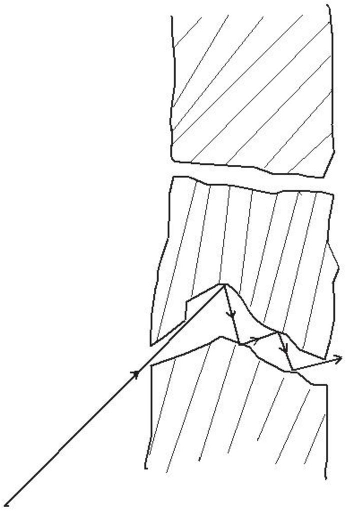


Fig. 14.5 *Molecules going through a porous wall.*

Example 14.7 (a) When a molecule (or an elastic ball) hits a (massive) wall, it rebounds with the same speed. When a ball hits a massive bat held firmly, the same thing happens. However, when the bat is moving towards the ball, the ball rebounds with a different speed. Does the ball move faster or slower? (Ch.6 will refresh your memory on elastic collisions.)

(b) When gas in a cylinder is compressed by pushing in a piston, its temperature rises. Guess at an explanation of this in terms of kinetic theory using (a) above.

(c) What happens when a compressed gas pushes a piston out and expands? What would you observe?

(d) Sachin Tendulkar uses a heavy cricket bat while playing. Does it help him in anyway?

Answer (a) Let the speed of the ball be u relative to the wicket behind the bat. If the bat is moving towards the ball with a speed V relative to the wicket, then the relative speed of the ball to bat is $V + u$ towards the bat. When the ball rebounds (after hitting the massive bat) its speed, relative to bat, is $V + u$ moving away from the bat. So relative to the wicket the speed of the rebounding ball is $V + (V + u) = 2V + u$, moving away from the wicket. So the ball speeds up after the collision with the bat. The rebound speed will be less than u if the bat is not massive. For a molecule this would imply an increase in temperature.

You should be able to answer (b) (c) and (d) based on the answer to (a).

(Hint: Note the correspondence, piston → bat, cylinder → wicket, molecule → ball.)

14.5 LAW OF EQUIPARTITION OF ENERGY

The kinetic energy of a single molecule is

$$E_t=1/2\ mv_x^2 + 1/2\ mv_y^2 + 1/2\ mv_z^2 \tag{14.22}$$

For a gas in thermal equilibrium at temperature T the average value of energy denoted by < $_t$ > is

$$E_t=< \frac{1}{2}mv_x^2 >< \frac{1}{2}mv_y^2 >< \frac{1}{2}mv_z^2 > \frac{3}{2}k_BT \tag{14.23}$$

Since there is no preferred direction, Eq. (14.23) implies

$$< \frac{1}{2}mv_x^2 > \quad \frac{1}{2}k_BT\ , < \frac{1}{2}mv_y^2 > \frac{1}{2}k_BT$$

$$< \frac{1}{2}mv_z^2 > \frac{1}{2}k_BT \tag{14.24}$$

A molecule free to move in space needs three coordinates to specify its location. If it is constrained to move in a plane it needs two; and if constrained to move along a line, it needs just one coordinate to locate it. This can also be expressed in another way. We say that it has one degree of freedom for motion in a line, two for motion in a plane and three for motion in space. Motion of a body as a whole from one point to another is called translation. Thus, a molecule free to move in space has three translational degrees of freedom. Each translational degree of freedom contributes a term that contains square of some variable of motion, e.g., ½ mv_x^2 and similar terms in v_y and v_z. In, Eq. (14.24) we see that in thermal equilibrium, the average of each such term is ½ k_BT.

Molecules of a monatomic gas like argon have only translational degrees of freedom. But what about a diatomic gas such as O_2 or N_2? A molecule of O_2 has three translational degrees of freedom. But in addition it can also rotate about its centre of mass. Figure 14.6 shows the two independent axes of rotation 1 and 2, normal to the axis joining the two oxygen atoms about which the molecule can rotate*. The molecule thus has two rotational degrees of freedom, each of which contributes a term to the total energy consisting of translational energy t and rotational energy r.

$$t_r = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \frac{1}{2}I_1^2\omega_1^2 + \frac{1}{2}I_2^2\omega_2^2 \qquad (14.25)$$

where ω_1 and ω_2 are the angular speeds about the axes 1 and 2 and I_1, I_2 are the corresponding moments of inertia. Note that each rotational degree of freedom contributes a term to the energy that contains square of a rotational variable of motion.

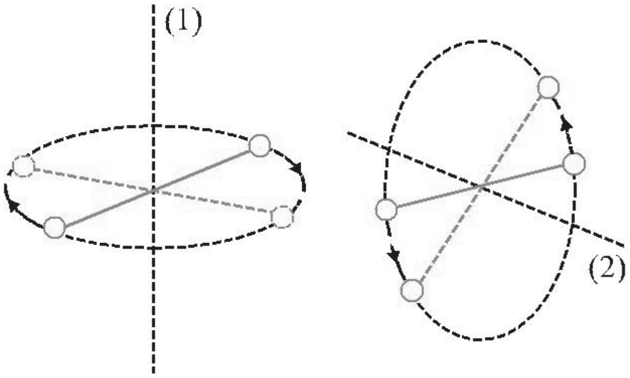


Fig. 14.6 *The two independent axes of rotation of a diatomic molecule*

We have assumed above that the O_2 molecule is a ‘rigid rotator’, i.e. the molecule does not vibrate. This assumption, though found to be true (at moderate temperatures) for O_2, is not always valid. Molecules like CO even at moderate temperatures have a mode of vibration, i.e. its atoms oscillate along the interatomic axis like a one-dimensional oscillator, and contribute a vibrational energy term ε_v to the total energy:

$$\varepsilon_V = \frac{1}{2} m \frac{dy^2}{dt} = \frac{1}{2} k y^2 \qquad (14.26)$$

where k is the force constant of the oscillator and y the vibrational co-ordinate.

Once again the vibrational energy terms in Eq. (14.26) contain squared terms of vibrational variables of motion *y* and d*y*/d*t*.

At this point, notice an important feature in Eq. (14.26). While each translational and rotational degree of freedom has contributed only one 'squared term' in Eq.(14.26), one vibrational mode contributes two 'squared terms' : kinetic and potential energies.

Each quadratic term occurring in the expression for energy is a mode of absorption of energy by the molecule. We have seen that in thermal equilibrium at absolute temperature T, for each translational mode of motion, the average energy is ½ k_BT. A most elegant principle of classical statistical mechanics (first proved by Maxwell) states that this is so for each mode of energy: translational, rotational and vibrational. That is, in equilibrium, the total energy is equally distributed in all possible energy modes, with each mode having an average energy equal to ½ k_BT. This is known as the **law of equipartition of energy**. Accordingly, each translational and rotational degree of freedom of a molecule contributes ½ k_BT to the energy while each vibrational frequency contributes 2 × ½ $k_BT = k_BT$, since a vibrational mode has both kinetic and potential energy modes.

The proof of the law of equipartition of energy is beyond the scope of this book. Here we shall apply the law to predict the specific heats of gases theoretically. Later we shall also discuss briefly, the application to specific heat of solids.

14.6 SPECIFIC HEAT CAPACITY

14.6.1 Monatomic Gases

The molecule of a monatomic gas has only three translational degrees of freedom. Thus, the average energy of a molecule at temperature *T* is (3/2)k_BT . The total internal energy of a mole of such a gas is

$$U = \frac{3}{2} K_B T\, N_A = \frac{3}{2}\, RT \qquad (14.27)$$

The molar specific heat at constant volume, C_v, is

$$C_v \text{ (mono atomic gas)} = \frac{dU}{dT} = \frac{3}{2}RT \qquad (14.28)$$

$$\text{For an ideal gas } C_p - C_v = R \qquad (14.29)$$

Where C_p is molar specific heat at constant pressure. Thus

$$C_p = \frac{5}{2} R \qquad (14.30)$$

The ratio of specific heats $\frac{C_p}{C_v} = \frac{5}{3}$ (14.31)

14.6.2 Diatomic Gases

As explained earlier, a diatomic molecule treated as a rigid rotator like a dumbbell has 5 degrees of freedom: 3 translational and 2 rotational. Using the law of equipartition of energy, the total internal energy of a mole of such a gas is

$$U = \frac{5}{2}K_BT\,N_A = \frac{5}{2}RT \qquad (14.32)$$

The molar specific heats are given by

$$C_p = \frac{5}{2} R \text{ (rigid diatomic)} \quad C_v = \frac{7}{2} R \qquad (14.33)$$

$$\gamma = \frac{7}{5} \text{ (rigid diatomic)} \qquad (14.34)$$

If the diatomic molecule is not rigid but has in addition a vibrational mode

$$U = \left[\frac{5}{2}k_BT + k_BT\right]N_A = \frac{7}{2}RT$$

$$C_v = \frac{7}{2}R, C_p = \frac{9}{2}R,\ \gamma = \frac{9}{7}R \qquad (14.35)$$

14.6.3 Polyatomic Gases

In general a polyatomic molecule has 3 translational, 3 rotational degrees of freedom and a certain number (f) of vibrational modes. According to the law of equipartition of energy, it is easily seen that one mole of such a gas has

$$U = \left(\frac{3}{2}k_BT + \frac{3}{2}k_BT + fk_BT\right)N_A$$

$$\text{i.e. } C_v = (3 + f)\,R,\ C_p = (4 + f)\,R,\ \frac{f}{f} \qquad (14.36)$$

Note that $C_p - C_v = R$ is true for any ideal gas, whether mono, di or polyatomic.

Table 14.1 summarises the theoretical predictions for specific heats of gases ignoring any vibrational modes of motion. The values are in good agreement with experimental values of specific heats of several gases given in Table 14.2. Of course, there are discrepancies between predicted and actual values of specific heats of several other gases (not shown in the table), such as Cl_2, C_2H_6 and many other polyatomic gases. Usually, the experimental values for specific heats of these gases are greater than the predicted values given in Table14.1 suggesting that the agreement can be improved by including vibrational modes of motion in the calculation. The law of equipartition of energy is thus well verified experimentally at ordinary temperatures.

Table 14.1 Predicted values of specific heat capacities of gases (ignoring vibrational modes)

Nature of Gas	**C_V (J $Mol^{-1}k^{-1}$)**	**C_P (J $Mol^{-1}k^{-1}$)**	**C_P-C_V (J $Mol^{-1}k^{-1}$)**	**γ**
Mono atomic	12.5	20.8	8.31	1.67
Diatomic	20.8	29.1	8.31	1.40
Triatomic	24.93	33.24	8.31	1.33

Table 14.2 Measured values of specific heat capacities of some gases

Nature of Gas	**Gas**	**C_V (J $Mol^{-1}k^{-1}$)**	**C_P (J $Mol^{-1}k^{-1}$)**	**C_P-C_V (J $Mol^{-1}k^{-1}$)**	**γ**
Mono atomic	He	12.5	20.8	8.30	1.66
Mono atomic	Ne	12.7	20.8	8.12	1.64
Mono atomic	Ar	12.5	20.8	8.30	1.67
Diatomic	H_2	20.4	28.8	8.45	1.41
Diatomic	O_2	21.0	29.3	8.32	1.40
Diatomic	N_2	20.8	29.1	8.32	1.40
Triatomic	H_2O	27.0	35.4	8.35	1.31
Polyatomic	CH_4	27.1	35.4	8.36	1.31

Example 14.8 A cylinder of fixed capacity 44.8 litres contains helium gas at standard temperature and pressure. What is the amount of heat needed to raise the temperature of the gas in the cylinder by 15.0 °C ? ($R = 8.31$ J $mo1^{-1}$ K^{-1}).

Answer Using the gas law $PV = \mu RT$, you can easily show that 1 mol of any (ideal) gas at standard temperature (273 K) and pressure (1 atm = 1.01×10^5 Pa) occupies a volume of 22.4 litres. This universal volume is called molar volume. Thus the cylinder in this example contains 2 mol of helium. Further, since helium is monatomic, its predicted (and observed) molar specific heat at constant volume, $C_v = (3/2)\ R$, and molar specific heat at constant pressure, $C_p = (3/2)\ R + R = (5/2)\ R$. Since the volume of the cylinder is fixed, the heat required is determined by C_v. Therefore,

Heat required = no. of moles × molar specific heat × rise in temperature

$= 2 \times 1.5\ R \times 15.0 = 45\ R$

$= 45 \times 8.31 = 374$ J.

14.6.4 Specific Heat Capacity of Solids

We can use the law of equi-partition of energy to determine specific heats of solids. Consider a solid of N atoms, each vibrating about its mean position. An oscillation in one dimension has average energy of $2 \times ½\ k_BT = k_BT$. In three dimensions, the average energy is $3\ k_BT$. For a mole of solid, $N = N_A$, and the total energy is

$$U = 3\ k_BT \times N_A = 3\ RT$$

Now at constant pressure $\Delta Q = \Delta U + P\Delta V$

$= \Delta U$, since for a solid ΔV is negligible. Hence,

$$= \frac{\partial Q}{\partial T} = \frac{\partial U}{\partial T} = 3\mathrm{R} \qquad (14.37)$$

Table 14.3 Specific Heat Capacity of some solids at room temperature and atmospheric pressure

Substance	**Specific heat ($\mathbf{J\ Kg^{-1}k^{-3}}$)**	**Molar specific Heat ($\mathbf{Jmol^{-3}K^{-1}}$)**
Aluminium	900.0	24.4
Carbon	506.5	6.1
Copper	386.4	24.5
Lead	127.7	26.5
Silver	236.1	25.5
Tungsten	134.4	24.9

As Table 14.3 shows the prediction generally agrees with experimental values at ordinary temperature (Carbon is an exception).

14.6.5 Specific Heat Capacity of Water

We treat water like a solid. For each atom average energy is 3kBT. Water molecule has three atoms, two hydrogen and one oxygen. So it has

$U = 3 \times 3\ k_B T \times N_A = 9\ RT$ and $C = \Delta Q/\Delta T = \Delta U / \Delta T = 9R$.

This is the value observed and the agreement is very good. In the calorie, gram, degree units, water is defined to have unit specific heat. As 1 calorie = 4.179 joules and one mole of water is 18 grams, the heat capacity per mole is ~ 75 J mol^{-1} K^{-1} ~ 9R. However with more complex molecules like alcohol or acetone the arguments, based on degrees of freedom, become more complicated.

Lastly, we should note an important aspect of the predictions of specific heats, based on the classical law of equi-partition of energy. The predicted specific heats are independent of temperature. As we go to low temperatures, however, there is a marked departure from this prediction. Specific heats of all substances approach zero as T ⇨ 0. This is related to the fact that degrees of freedom get frozen and ineffective at low temperatures. According to classical physics degrees of freedom must remain unchanged at all times. The behaviour of specific heats at low temperatures shows the inadequacy of classical physics and can be explained only by invoking quantum considerations, as was first shown by Einstein. Quantum mechanics requires a minimum, nonzero amount of energy before a degree of freedom comes into play. This is also the reason why vibrational degrees of freedom come into play only in some cases.

14.7 MEAN FREE PATH

Molecules in a gas have rather large speeds of the order of the speed of sound. Yet a gas leaking from a cylinder in a kitchen takes considerable time to diffuse to the other corners of the room. The top of a cloud of smoke holds together for hours. This happens because molecules in a gas have a finite though small size, so they are bound to undergo collisions. As a result, they cannot move straight unhindered; their paths keep getting incessantly deflected.

Seeing is Believing

Can one see atoms rushing about. Almost but not quite. One can see pollen grains of a flower being pushed around by molecules of water. The size of the grain is ~ 10-5 m. In 1827, a Scottish botanist Robert Brown, while examining, under a microscope, pollen grains of a flower suspended in water noticed that they continuously moved about in a zigzag, random fashion.

Kinetic theory provides a simple explanation of the phenomenon. Any object suspended in water is continuously bombarded from all sides by the water molecules. Since the motion of molecules is random, the number of molecules hitting the object in any direction is about the same as the number hitting in the opposite direction. The small difference between these molecular hits is negligible compared to the total number of hits for an object of ordinary size, and we do not notice any movement of the object.

When the object is sufficiently small but still visible under a microscope, the difference in molecular hits from different directions is not altogether negligible, i.e. the impulses and the torques given to the suspended object through continuous bombardment by the molecules of the medium (water or some other fluid) do not exactly sum to zero. There is a net impulse and torque in this or that direction. The suspended object thus, moves about in a zigzag manner and tumbles about randomly. This motion called now ‘Brownian motion’ is a visible proof of molecular activity.

In the last 50 years or so molecules have been seen by scanning tunneling and other special microscopes.

In 1987 Ahmed Zewail, an Egyptian scientist working in USA was able to observe not only the molecules but also their detailed interactions. He did this by illuminating them with flashes of laser light for very short durations, of the order of tens of femto seconds and photographing them. (1 femto-second = 10-15 s). One could study even the formation and breaking of chemical bonds. That is really seeing!

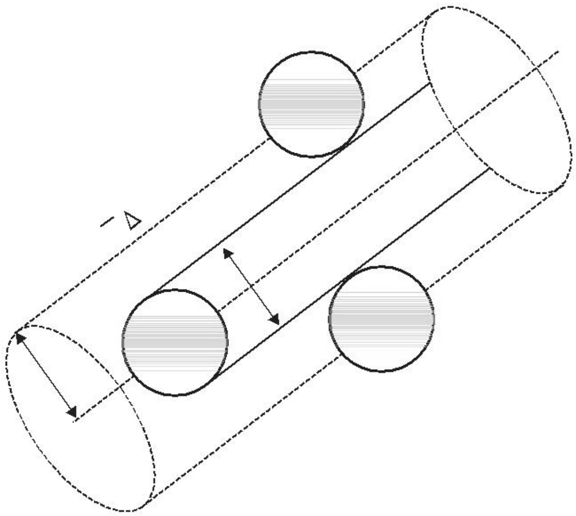


Fig. 14.7 *The volume swept by a molecule in time t in which any molecule will collide with it.*

Suppose the molecules of a gas are spheres of diameter d. Focus on a single molecule with the average speed <v>. It will suffer collision with any molecule that comes within a distance d between the centres. In time t, it sweeps a volume πd^2 <v> t wherein any other molecule will collide with it (see Fig. 14.7). If n is the number of molecules per unit volume, the molecule suffers $n\pi d^2$ <v> Δt collisions in time Δt. Thus the rate of collisions is $n\pi d^2$ <v> or the time between two successive collisions is on the average,

$$\tau = \frac{1}{n\pi <v> d^2} \tag{14.38}$$

The average distance between two successive collisions, called the mean free path l, is:

$$l = < v > \tau = 1/(n\pi d^2) \tag{14.39}$$

In this derivation, we imagined the other molecules to be at rest. But actually all molecules are moving and the collision rate is determined by the average relative velocity of the molecules. Thus we need to replace <v> by <□ > in Eq. (14.38). A more exact treatment gives

$$l \ \frac{1}{\sqrt{2}} nd^2 \tag{14.40}$$

Let us estimate l and τ for air molecules with average speeds <v> = (485 m/s). At STP,

n = (0.02 x 1023)/ (22.4 x 10^{-3})

=2.7 x 1025 m^{-3}

Taking, d = 2 × 10^{-10} m,

τ = 6.1 × 10^{-10} s and l=2.9 x 10^{-7} m ≈1500 d (14.41)

As expected, the mean free path given by Eq. (14.40) depends inversely on the number density and the size of the molecules. In a highly evacuated tube n is rather small and the mean free path can be as large as the length of the tube.

Example 14.9 Estimate the mean free path for a water molecule in water vapour at 373 K. Use information from Exercises 14.1 and Eq. (14.41) above.

Answer

The d for water vapour is same as that of air. The number density is inversely

proportional to absolute temperature.

So $n = \ 2.7\ x\ 10^{25}\ \ \frac{273}{373}\ 2\ 10^{25}\ m^{-3}$

$$\frac{1}{2}m\overline{(v^2)} = \frac{3}{2}k_BT\ , v_{rms} = v -\frac{1}{2}\sqrt{\left(\frac{3k_BT}{m}\right)}$$

Hence, mean free path l = 4x10-7 m.

Note that the mean free path is 100 times the interatomic distance ~ 40 Å = 4 ×10^{-9} m calculated earlier. It is this large value of mean free path that leads to the typical gaseous behaviour. Gases cannot be confined without a container. Using, the kinetic theory of gases, the bulk measurable properties like viscosity, heat conductivity and diffusion can be related to the microscopic parameters like molecular size. It is through such relations that the molecular sizes were first estimated.

SUMMARY

1. The ideal gas equation connecting pressure (P), volume (V) and absolute temperature (T) is PV = μ RT = k_B NT\

   Where μ is the number of moles and N is the number of molecules. R and k_B are universal constants.

   R = 8.314 J mol^{-1} K^{-1}, $k_B = \frac{R}{N_A} = 1.38 \, x \, 10^{-23} \, JK^{-1}$.

   Real gases satisfy the ideal gas equation only approximately, more so at low pressures and high temperatures.

2. Kinetic theory of an ideal gas gives the relation

$$P = \frac{1}{3} nm\overline{(v^2)}$$

   Where n is number density of molecules, m the mass of the molecule and $\overline{((v^2))}$ is the mean of squared speed. Combined with the ideal gas equation it yields a kinetic interpretation of temperature.

$$\frac{1}{2} m\overline{((v^2))} = \frac{3}{2} k_B T \, , v_{rms} = v -^{\frac{1}{2}} \sqrt{\frac{3k_B T}{m}}$$

   This tells us that the temperature of a gas is a measure of the average kinetic energy of a molecule, independent of the nature of the gas or molecule. In a mixture of gases at a fixed temperature the heavier molecule has the lower average speed.

3. The translational kinetic energy

   $E = \frac{3}{2} k_B NT$ This leads to a relation $PV = \frac{2}{3} E$

4. The law of equi-partition of energy states that if a system is in equilibrium at absolute temperature T, the total energy is `distributed equally in different energy modes of

absorption, the energy in each mode being equal to ½ k_B T. Each translational and rotational degree of freedom corresponds to one energy mode of absorption and has energy ½ k_B T. Each vibrational frequency has two modes of energy (kinetic and potential) with corresponding energy equal to

$$2 \times ½\, k_B T = k_B T.$$

5. Using the law of equi-partition of energy, the molar specific heats of gases can be determined and the values are in agreement with the experimental values of specific heat of several gases. The agreement can be improved by including vibrational modes of motion.
6. The mean free path l is the average distance covered by a molecule between two successive collisions:

$$\bar{l} = \frac{1}{\sqrt{2nd^2}}$$

where n is the number density and d the diameter of the molecule.

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VOCATIONAL BRIDGE COURSE

PHYSICS- I YEAR (w.e.f 2018-19)

Weightage of Marks

S.No.	Name of the Chapter	No of periods	Weightage
1.	Physical World	01	01
2.	Units and Measurements	05	01
3.	Motion in a Straight Line	05	01
4.	Motion in a Plane	07	04
5.	Laws of Motion	05	04
6.	Work, Energy and Power	08	04
7.	System of Particles and Rotational Motion	08	04
8.	Oscillations	05	04
9.	Gravitation	05	04
10.	Mechanical Properties of Solids	03	01
11.	Mechanical Properties of Fluids	05	01+01
12.	Thermal Properties of Matter	06	04+01
13.	Thermodynamics	04	04
14.	Kinetic Theory	02	01
	Total	69	40

ANDHRA PRADESH BOARD OF INTERMEDIATE EDUCATION, VIJAYAWADA

VOCATIONAL BRIDGE COURSE2018-2019

MODEL QUESTION PAPER

Time: 1 ½ Hours **Physics – I Year (w.e.f 2018-2019)** **Max. Marks: 25**

–

Section – A 5 x 1 = 5

Instructions:

Answer any **five** of the following questions

Each question carries **one** mark.

1. What are the fundamental forces in nature .
2. Distinguish between accuracy and precision
3. Define acceleration?
4. State the Units of stress and strain.
5. What is angle of Contact?
6. Why the liquid drops and bubbles are spherical?
7. What are the lower and upper fixed points in Fahrenheit scale?
8. When does a real gas behave like an ideal gas?

Section – B 5 x 4 = 20

Instructions:

Answer any **five** of the following questions

Each question carries **four** marks.

9.State parallelogram law of vectors? Derive an expression for the magnitude?

10.Mention the methods to decrease friction?

11.What are Collisions? Explain the possible types of Collisions?

12. Define Angular velocity? Derive V= rw?

13.What is seconds Pendulum? Calculate its length on the earth?

14.What is escape velocity? Obtain an expression for it.

15.Explain conduction, convection and radiation of heat with examples?

16. Compare Isothermal and adiabatic process.

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VOCATIONAL BRIDGE COURSE

QUESTION BANK

Physics – I Year (w.e.f 2018-19)

Chapter 1: PHYSICAL WORLD

Very Short Answer Questions

1. What is Physics?
2. What is the discovery of C.V. Raman?
3. What are the fundamental forces in matter?
4. What is the contribution of Chandra Sekhar to Physics?
5. Which year is called as international year of Physics?

Chapter 2: UNITS & MEASUREMENTS

Very Short Answer Questions

1. Distinguish between accuracy and precision.
2. What are the different types of errors that can occur in a measurement?
3. How can systematic errors be minimized or eliminated?
4. Distinguish between fundamental units and derived units.
5. Why do we have different units for the same physical quantity?
6. Express unified atomic mass unit in kg.
7. Write the dimension formula for the following (a) Power (b) Universal Gravitational constant (G)

Chapter 3: MOTION IN STRAIGHT LINE

Very Short Answer Questions

1. How is average velocity different from instantaneous velocity?
2. Give an example where the velocity an object is zero but its acceleration is not zero.
3. A vehicle travels half the distance L with speed v_1 and the other half with speed v2. What is the average speed?

4. Can the velocity of an object be in a direction other than the direction of acceleration of the object?
5. Define acceleration ?

Chapter 4: MOTION IN A PLANE

Very Short Answer Questions

1. The vertical component of a vector is equal to its horizontal component. What is the angle made by the vector with x-axis?
2. What is the acceleration of a projectile at the top of its trajectory?
3. A = i + j . What is the angle between the vector and x-axis?
4. When two right angled vectors of magnitude 7 units and 24 units combine, what is the magnitude of their resultant?

Short Answer Questions

1. If P = 2i + 4j + 14k and Q = 4i + 4j+ 10k find the magnitude of **P** + **Q**.
2. State Parallelogram law of Vectors. Derive an expression for the magnitude.
3. Define unit vector, null vector and position vector.
4. Show that the trajectory of an object thrown at certain angle with the horizontal is parabola.
5. Derive an equation for Time of flight and Range of a projectile.

Chapter 5: LAWS OF MOTION

Very Short Answer Questions

1. What is inertia?
2. When a bullet is fired from a gun, the gun gives a kick in the backward direction. Explain.
3. Why does a heavy rifle not recoil as strongly as a light rifle using the same cartridges?
4. If a bomb at rest explodes into two pieces, the pieces must travel in opposite direction. Explain.
5. Define force.
6. Why does the car with a flattened tyre stop sooner than the one with inflated tyres?
7. What happens to the coefficient of friction if the weight of the body is doulbled?

Short Answer Questions

1. Define the terms momentum and impulse. State and explain the law of conservation of linear momentum.
2. Explain the terms limiting friction, dynamic friction and rolling friction.
3. Explain advantages and disadvantages of friction.
4. Mention the methods used to decrease friction.
5. Derive the equation of motion F = ma.

Chapter 6: WORK, ENERGY AND POWER

Very Short Answer Questions

1. State the conditions under which a force does not work.
2. State the relation between the kinetic energy and momentum of a body.

Short Answer Questions

1. Define: Work, Power and Energy. State their SI units.
2. What is potential energy? Derive an expression for the gravitational potential energy.
3. State and explain the law of conservation of energy?
4. Develop the notions of work and kinetic energy and show that it leads to work-energy theorem.
5. What are collisions? Explain the possible types of collisions?
6. State and prove law of conservation of energy in case of a freely falling body.

Chapter 7: SYSTEM OF PARTICLES AND ROTATIONAL MOTION

Very Short Answer Questions

1. Is it necessary that a mass should be present at the centre of mass of any system?
2. Why are spokes provided in a bicycle wheel?
3. Why do we prefer a spanner of longer arm as compared to the spanner of shorter arm?
4. By spinning eggs on a table top, how will you distinguish a hard boiled egg from a raw egg?

Short Answer Questions

1. Distinguish between centre of mass and centre of gravity.
2. Define vector product. Explain the properties of a vector product.
3. Define angular velocity (u). Derive $v = r\ \omega$.

4. Define angular acceleration and torque. Establish the relation between angular acceleration and torque.

5. State and explain perpendicular and parallel axes theorems?

Chapter 8: OSCILLATIONS

Short Answer Questions

1. Define simple harmonic motion? Give two examples.
2. Show that the motion of a simple pendulum is simple harmonic and hence derive an equation for its time period.
3. What is seconds pendulum? Calculate its length on the earth ($g = 9.8\ m/s^2$)
4. A girl is swinging seated in a awing. What is the effect on the frequency of oscillation if she stands? Explain.
5. The bob of a simple pendulum is a hollow sphere filled with water. How will the period of oscillation charge, if the water begins to drain out of the hollow sphere?
6. The bob of a simple pendulum is made of wood. What will be the effect on the time period if the wooden bob is replaced by an identical bob of aluminum?
7. A pendulum clock gives correct time at the equator. Will it gain or lose time if it is taken to the poles? If so, why?

Chapter 9: GRAVITATION

Very Short Answer Questions

1. What is the time period of revolution of geostationary satellite?
2. What are polar satellites?

Short Answer Questions

1. State Kepler’s law of planetary motion.
2. Derive the relation between acceleration due to gravity(g) at the surface of a planet and Gravitational constant (G).
3. What is orbital velocity? Obtain its expression.
4. What is escape velocity? Obtain an expression for it.
5. What is geostationary satellite? State its uses.

Chapter 10: MECHANICAL PROPERTIES OF SOLIDS

Very Short Answer Questions

1. State Hooker’s law of elasticity.
2. State the units of stress and strain
3. State the units of modulus of elasticity.
4. State the examples of nearly perfect elastic bodies.
5. State the examples of nearly plastic bodies.
6. Define Young’s modulus and bulk modulus

Short Answer Questions

1. Describe the behaviour of a wire under gradually increasing load.
2. Define modulus of elasticity, stress, strain and poisson’s ratio?

Chapter 11: MECHANICAL PROPERTIES OF FLUIDS

Very Short Answer Questions

1. Define coefficient Viscosity.
2. What is the principle behind the carburetor of an automobile?
3. What is magnus effect.
4. What are drops and bubbles spherical?
5. Give the expression for the excess pressure in liquid drop.
6. Give the expression for the excess pressure in an air bubble inside the liquid.
7. Give the expression for the soap bubble in air.
8. What are water proofing agents.
9. What are water wetting agents?
10. What is angle of contact?
11. Mention any one example that obey Bernoulli’s theorem.
12. When water flows through a pipe, which of the layers moves fastest and slowest.
13. Explain Bernoulli’s theorem.

Chapter 12: THERMAL PROPERTIES OF MATTER

Very Short Answer Questions

1. Distinguish between heat and temperature.
2. What are the lower and upper fixing points in Fahrenheit scales?
3. Do the values of coefficients of expansion differ, when the temperatures are measured on Centigrade scale or on Fahrenheit scale.
4. Can a substance contract on heating? Give an example.

5. Why gaps are left between rails on a railway track?
6. Why do liquids have no linear and areal expansion?
7. What is latent heat of fusion?
8. Why utensils are coated black?
9. Why the bottom of the utensils are made of copper?
10. Sate Weins displacement law?
11. Ventilators are provided in rooms just below the roof. Why?
12. Does a body radiate heat at 9 K?
13. Does a body radiate heat at 0^oC?
14. Sate the different modes of transmission of heat.
15. Define coefficient of thermal conductivity.
16. What is greenhouse effect.
17. Explain global warming.
18. State the conditions under which Newton's law of cooling is applicable.
19. The roofs of buildings are often painted while during summer. Why?

hort Answer Questions

1. Explain Celsius and Fahrenheit scales of temperature. Obtain the relation between Celsius and Fahrenheit scales of temperature.
2. Two identical rectangular strips, one of copper and the other of steel, are riveted together to form a compound bar. What will happen on heating?
3. Pendulum clocks generally go fast in winter and slow in summer. Why?
4. In what way is the anomalous behavior of water advantageous of aquatic animals?
5. Explain conduction, convection and radiation with examples.

Chapter 13: THERMODYNAMICS

Very Short Answer Questions

1. Define Thermal equilibrium. How does it lead to Zeroth Law of Thermodynamics?
2. What thermodynamic variables can be defined by Zeroth Law
3. Define molar specific heat capacity.
4. Why a heat engine with 100% efficiency can never be realized in practice?

Short Answer Questions

1. State and explain first law of thermodynamics
2. State and explain 2nd law of thermodynamics
3. Define two principle specific heats of a gas. What is greater and Why?

4. Compare isothermal and adiabatic process.
5. Explain qualitatively the working of a heat engine.
6. How is heat engine different from a refrigerator.

Chapter 14: KINETIC THEORY

1. Define mean free path.
2. When does a real gas behave line an ideal gas?
3. State Boyle’s Law.
4. Sate Charles Law.
5. Sate Dalton’s law of partial pressure.

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CHAPTER-1

ATOMIC STRUCTURE

In this chapter we start with the experimental observations made by scientists towards the end of nineteenth and beginning of twentieth century. These established that atoms can be further divided into sub- atomic particles. i.e. electrons, protons and neutrons - a concept very different from that of Dalton. The major problems before the scientists at that time were:

- to account for the stability of atom after the discovery of sub-atomic particles,
- to compare the behavior of one element from other in terms of both physical and chemical properties.
- to explain the formation of different kinds of molecules by the combination of different atoms and
- to understand the origin and nature of radiation absorbed or emitted by atoms by the combination of different atoms and to understand the origin and nature of the radiation absorbed or emitted by atoms.

1.1 Sub-atomic particles:

Dalton's atomic theory was able to explain the law of conservation, law of constant proportion and law of multiple proportions very successfully. However, it failed to explain the results of many experiments; for example, it was known that substances like glass or ebonite when rubbed with silk or fur generate electricity. Many different kinds of sub-atomic particles were discovered in the twentieth century. However, in this section we will talk about only two particles, namely electron and proton.

In 1830, Michael Faraday showed that if electricity is passed through a solution of an electrolyte, chemical reactions occurred at the electrodes, which resulted in the liberation and deposition of matter at the electrodes. He formulated certain laws which you will study in second year. These results suggested the particulate nature of electricity:

An insight into the structure of atom was obtained from the experiments on electrical discharge through gases. Before we discuss these results we need to keep in mind a basic rule regarding the behaviour of charged particles: "Like charges repel each other and unlike charges attract each other".

In mid 1850s many scientists mainly Faraday began to study electrical discharge in partially evacuated tubes, known as cathode discharge tubes. It is depicted in Fig.1.1 (a). A cathode ray tube is made of glass containing two thin pieces of metal, called electrodes, sealed in it. The electrical discharge through the gases could be observed only at very low pressures and at very high voltages. The pressure of different gases could be adjusted by evacuation. When sufficiently high voltage is applied across the electrodes, current starts flowing through a stream of particles moving in the tube from the negative electrode (cathode) to the positive electrode (anode). These were called cathode rays or cathode ray particles.

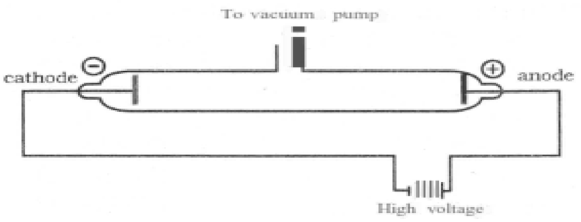


Fig. I.I(a). A cathode ray discharge tube

The results of these experiments are summarized below.

(i) The cathode rays start from cathode and move towards the anode.

(ii) These rays themselves are not visible but their behavior can be observed with the help of certain kind of materials (fluorescent or phosphorescent) which glow when hit by them. Television picture tubes are cathode ray tubes and television pictures result due to fluorescence on the television screen coated with certain fluorescent or phosphorescent materials.

(iii) In the absence of electrical or magnetic field these rays travel in straight lines (Fig. 1.2).

(iv) In the presence of electrical or magnetic field, the behaviour of cathode rays is similar to that expected from negatively charged particles, suggesting that the cathode rays consist of negatively charged particles, called electrons.

(v) The characteristics of cathode rays (electrons) do not depend upon the material of electrodes and the nature of the gas present in the cathode ray tube. Thus, we can conclude that electrons are basic constituents of all the atoms.

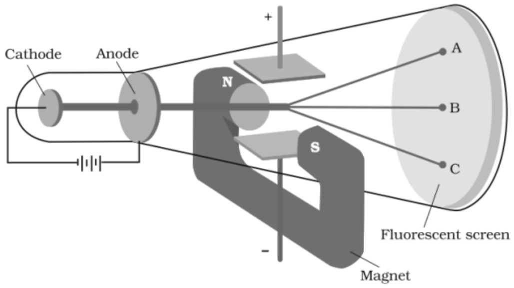


Fig. 1.2 The apparatus to determine the charge to mass ratio of electron

Charge on the Electron

R.A. Millikan (1868-1953) devised a method known as oil drop experiment (1906-14) to determine the charge on the electrons. He found that the charge on the electron to be -1.6 x 10^{-19}C. The present accepted value of electrical charge is -1.6022 X 10^{-19}C. The mass of the electron (m_e) was determined by combining these results with Thomson's value of e/m_e ratio.

$$m_e = \frac{e}{e/m_e} = \\ = 9.1094\ 10^{-31}\,\text{kg} \qquad (1.1)$$

Discovery of Protons and Neutrons

Electrical discharge carried out in the modified cathode ray tube led to the discovery of particles carrying positive charge, also known as canal rays. The characteristics of these positively charged particles are listed below.

(i) unlike cathode rays, the nature of positively charged particles depends upon the nature of gas present in the cathode ray tube. These are simply the positively charged gaseous ions.

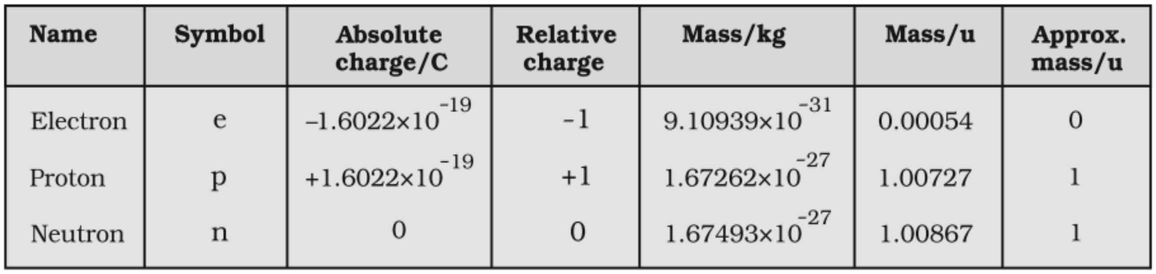
(ii) The charge to mass ratio of the particles is found to depend on the gas from which these originate.

(iii) Some of the positively charged particles carry a multiple of the fundamental unit of electrical charge.

(iv) The behaviour of these particles in the magnetic or electrical field is opposite to that observed for electron or cathode rays.

The smallest and lightest positive ion was obtained from hydrogen gas and was called proton. This positively charged particle was characterised in 1919. Later, a need was felt for the presence of electrically neutral particle as one of the constituents of atom. These particles were discovered by Chadwick (1932) by bombarding a thin sheet of beryllium by α-particles, when electrically neutral particles having a mass slightly greater than that of the protons were emitted. He named these particles as neutrons. The important properties of these fundamental particles are given in Table 1.1.

Table 1.1 Properties of Fundamental Particles



Name	Symbol	Absolute charge/C	Relative charge	Mass/kg	Mass/u	Approx. mass/u
Electron	e	-1.6022×10^{-19}	-1	9.10939×10^{-31}	0.00054	0
Proton	p	$+1.6022\times10^{-19}$	+1	1.67262×10^{-27}	1.00727	1
Neutron	n	0	0	1.67493×10^{-27}	1.00867	1

1.2 Atomic Models

Observations obtained from the experiments mentioned in the previous sections have suggested that Dalton's indivisible atom is composed of sub-atomic particles carrying positive and negative charges. Different atomic models were proposed to explain the distributions of these charged particles in an atom. Although some of these models were not able to explain the stability of atoms, two of these models, proposed by J. J. Thomson and Emest Rutherford are discussed below.

1.2.1 Thomson’s Model of atom

In 1904 Sir J. J. Thomson proposed the first definite theory as to the internal structure of the atom. According to this theory the atom was assumed to consist of a sphere of uniform dispersal of about 10^{-10}m positive charge with electrons embedded in it such that the number of electrons equal to the number of positive charges and the atom as a whole is electrically neutral.

This model of atom was able to explain the electrical neutrality of atom, but it could not explain the results of gold foil scattering experiment carried out by Rutherford.

1.2.2 Rutherford’s Scattering Experiment

Rutherford performed a scattering experiment in 1911 to find out the arrangement of electrons and protons. He bombarded a thin gold foil with a stream of fast moving positively charged α-particles emitting from radium.

1.2.3 Rutherford’s Nuclear model of a atom

This model resulted from conclusion drawn from experiments on the scattering of alpha particles from a radioactive source when the particles were passed through thin sheets of metal foil. According to him

(i) Most of the space in the atom is empty as most of the α-particles passed through the foil without any deviation.

(ii) A few positively charged α-particles are deflected. The deflection must be due to huge repulsive force showing that the positive charge of the atom is not spread throughout the atom. The positive charge has to be concentrated in a very small volume that repelled and deflected the positively charged α-particles. This very small segment of the atom was called nucleus by Rutherford.

(iii) Calculations by Rutherford showed that the volume occupied by the nucleus is negligibly small as compared to the total volume of the atom. The diameter of the atom is about 10^{-10} m while that of nucleus is 10^{-15} m. One can appreciate this difference in size by realizing that if a cricket ball represents a nucleus, then radius of the atom would be about 5 km.

On the basis of above observations and conclusions, Rutherford proposed the nuclear model of atom. According to this model:

(a) An atom consists of a tiny positively charged nucleus at its centre.

(b) The positive charge of the nucleus is due to protons. The mass of the nucleus, on the other hand, is due to protons and some neutral particles each having mass almost equal to the mass of proton. Protons and neutrons present in the nucleus are collectively also known as nucleons. The total number of nucleons is termed as mass number (A) of the atom.

(c) The nucleus is surrounded by electrons that travel around the nucleus with very high speed in circular paths called orbits. Thus, Rutherford’s model of atom resembles the solar system in which the sun plays the role of the nucleus and the planets that of revolving electrons.

(d) The number of electrons in an atom is equal to the number of protons in it. Thus, the total positive charge of the nucleus exactly balances the total negative charge in the atom making it electrically neutral. The number of protons in an atom is called its atomic number (Z).

(e) Electrons and the nucleus are held together by electrostatic forces of attraction.

1.2.4 Defects of Rutherford's model

1. According to Rutherford's model, an atom consists of a positive nucleus with the electrons moving around it in circular orbits. However, according to electromagnetic theory of J. C. Maxwell that whenever an electron is subjected to acceleration, it emits radiation and loses energy. As a result of this, its orbit should become smaller and smaller and finally it should drop into the nucleus by following a spiral path. This means that atom would collapse and thus Rutherford's model failed to explain stability of atoms.
2. Another drawback of the Rutherford's model is that it says nothing about the electronic structure of the atoms i.e., how the electrons are distributed around the nucleus and what are the energies of these electrons. Therefore, this model failed to explain the existence of certain definite lines in the hydrogen spectrum.

1.3 Developments Leading to the Bohr's Model of Atom

Historically, results observed from the studies of interactions of radiations with matter have provided immense information regarding the structure of atoms and molecules. Neils Bohr utilised these results to improve upon the model proposed by Rutherford. Two developments played a major role in the formulation of Bohr's model of atom. These were:

(i) Dual character of the electromagnetic radiation which means that radiations possess both wave like and particle like properties, and

(ii) Experimental results regarding atomic spectra which can be explained only by assuming quantized electronic energy levels in atoms.

1.3.1 Wave Nature of Electromagnetic Radiation

James Maxwell (1870) was the first to give a comprehensive explanation about the interaction between the charged bodies and the behaviour of electrical and magnetic fields on macroscopic level. He suggested that when electrically charged particle moves under acceleration, alternating electrical and magnetic fields are produced and transmitted. These fields are transmitted in the form of waves called electromagnetic waves or electromagnetic radiations.

Light is the form of radiation known from early days and speculation about its nature dates back to remote ancient times. In earlier days (Newton) light was supposed to be made of particles. It was only in the 19th century the wave nature of light was established. Maxwell was again the first to reveal that light waves are associated with oscillating electric and magnetic characters (Fig. 1.3). Although electromagnetic wave motion is complex in nature, we will consider here only a few simple properties.

I. The oscillating electric and magnetic fields produced by oscillating charged particles are perpendicular to each other and both are perpendicular to the direction of propagation of the wave. Simplified picture of electromagnetic wave is shown in Fig. 1.3.

II. Unlike sound waves or water waves, electromagnetic waves do not require medium and can move in vacuum.

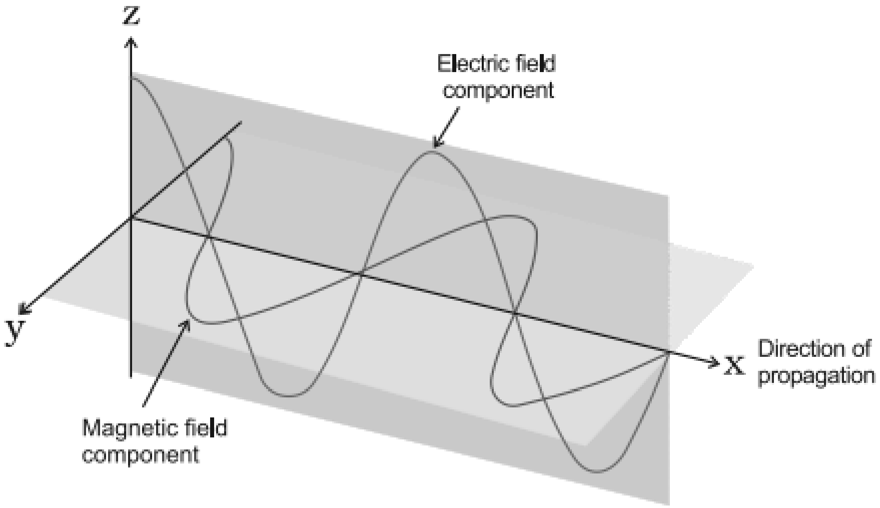


Fig.l.3 The electric and magnetic field components of an electromagnetic wave. These components have the same wavelength, frequency, speed and amplitude, but they vibrate in two mutually perpendicular planes.

III. It is now well established that there are many types of electromagnetic radiations, which differ from one another in wavelength (or frequency). These constitute what is called electromagnetic spectrum (Fig. 1.4). Different regions of the spectrum are identified by different names. Some examples are: radio frequency region around 10^6 Hz, used for broadcasting; microwave region around 10^{10} Hz used for radar; infrared region around 10^{13} Hz used for heating; ultraviolet region around 10^{16} Hz a component of sun's radiation. The small portion around 10^{15} Hz, is what is ordinarily called visible light. It is only this part which our eyes can see (or detect). Special instruments are required to detect non-visible radiation.

IV. Different kinds of units are used to represent electromagnetic radiation.

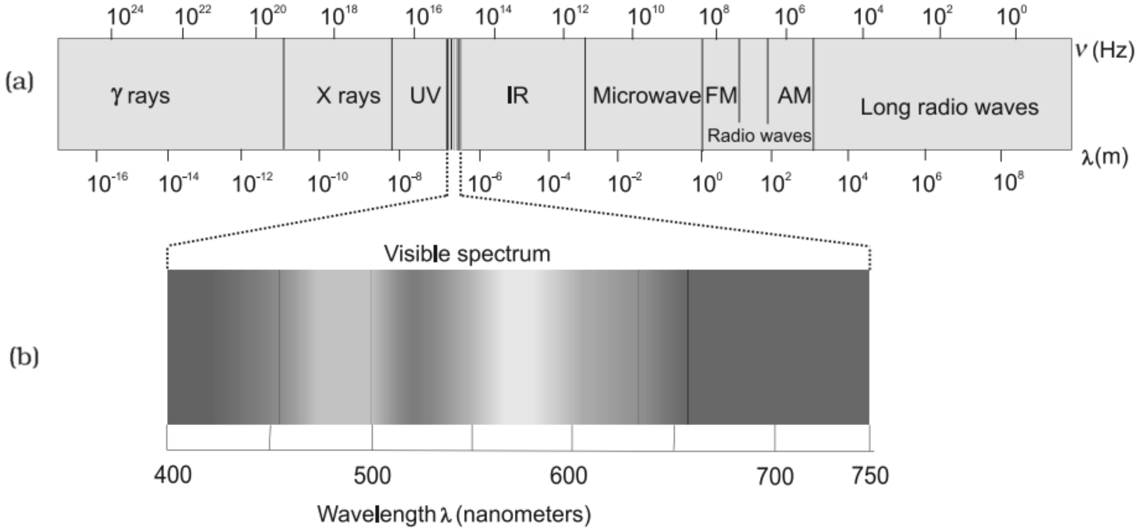


Fig.1.4 (a) The spectrum of electromagnetic radiation. (b) Visible spectrum. The visible region

is only a small part of the entire spectrum

These radiations are characterized by the properties, namely, frequency (ν) and wavelength (λ).The SI unit for frequency (ν) is hertz (Hz, S^{-1}), after Heinrich Hertz. It is defined as the number of waves that pass a given point in one second.

Wavelength should have the units of length and as you know that the SI units of length is meter (m). Since electromagnetic radiation consists of different kinds of waves of much smaller wavelengths, smaller units are used. Fig.1.4 shows various types of electro-magnetic radiations which differ from one another in wavelengths and frequencies.

In vaccum all types of electromagnetic radiations, regardless of wavelength, travel at the same speed, i.e., 3.0 x 10^8 m S^{-1} (2.997925 x 10^8 m S^{-I}, to be precise). This is called speed of light and is given the symbol 'c'. The frequency (ν), wavelength (λ) and velocity of light (c) are related by the equation (1.2).

$$C = \nu\ \lambda \qquad (1.2)$$

The other commonly used quantity especially in spectroscopy, is the wave number ($\bar{\nu}$). It is defined as the number of wavelengths per unit Length. Its units are reciprocal of wavelength unit, i.e., m^{-1}. However commonly used unit is cm^{-1}.

1.3.2 Particle Nature of Electromagnetic Radiation: Planck's Quantum Theory

Some of the experimental phenomenon such as diffraction and interference can be explained by the wave nature of the electromagnetic radiation. However, following are some of the observations which could not be explained with the help of even the electromagentic theory of 19th century physics (known as classical physics):

(i) the nature of emission of radiation from hot bodies (black -body radiation)

(ii) ejection of electrons from metal surface when radiation strikes it (photoelectric effect)

(iii) variation of heat capacity of solids as a function of temperature

(iv) line spectra of atoms with special reference to hydrogen

It is noteworthy that the first concrete explanation for the phenomenon of the black body radiation was given by Max Planck in 1900. This phenomenon is given below:

When solids are heated, they emit radiation over a wide range of wavelengths. For example, when an iron rod is heated in a furnace, it first turns to dull red and then the temperature increases. As this is heated further, the radiation emitted becomes white and then becomes blue as the temperature becomes very high. In terms of frequency, it means that the radiation emitted goes from a lower frequency to a higher frequency as the temperature increases. The red colour lies in the lower frequency region while blue colour belongs to the higher frequency region of the electromagnetic spectrum. The ideal body, which emits and absorbs all frequencies, is called a black body and the radiation emitted by such a body is called black body radiation. The exact frequency distribution of the emitted radiation (i.e., intensity versus frequency curve of the radiation) from a black body depends only on its temperature. At a given temperature, intensity of radiation emitted increases with decrease of wavelength, reaches a maximum value at a given wavelength and then starts decreasing with further decrease of wavelength, as shown in Fig. 1.5.

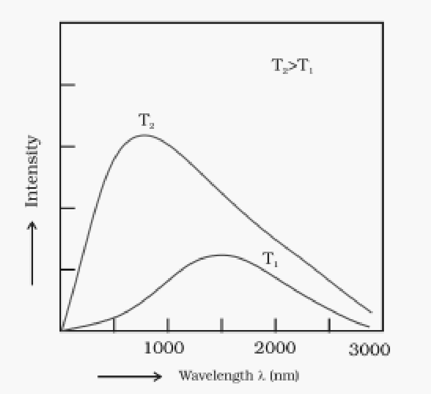


Fig.1.5 Wavelength-intensity relationship

The above experimental results cannot be explained satisfactorily on the basis of the wave theory of light. Planck suggested that atoms and molecules could emit (or absorb) energy only in discrete quantities and not in a continuous manner, a belief popular at that time. Planck gave the name quantum to the smallest quantity of energy that can be emitted or absorbed in the form of electromagnetic radiation. The energy (E) of a quantum of radiation is proportional to its frequency (ν) and is expressed by equation (1.3).

$$E = h\nu \qquad (1.3)$$

The proportionality constant, 'h' is known as Planck's constant and has the value 6.626×10^{-34} J s.

With this theory, Planck was able to explain the distribution of intensity in the radiation from black body as a function of frequency or wavelength at different temperatures.

Photoelectric Effect

In 1887, H. Hertz performed a very interesting experiment in which electrons (or electric current) were ejected when certain metals (for example potassium, rubidium, cesium etc.) were exposed to a beam of light as shown in Fig. 1.6. The phenomenon is called Photoelectric effect.

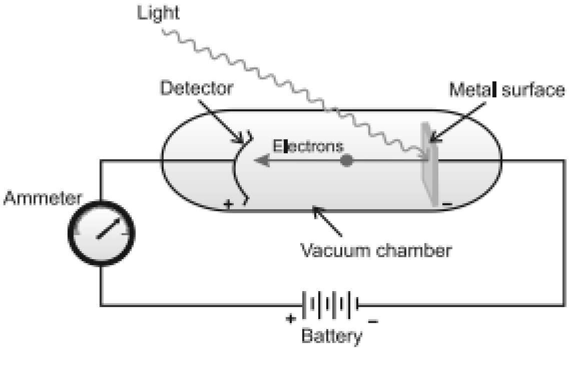


Fig.1.6 Equipment for studying the photoelectric effect, Light of a particular frequency strikes a clean metal surface inside a vacuum chamber. Electrons are ejected from the metal and are counted by a detector that measures their kinetic energy.

The results observed in this experiment were:

(i) The electrons are ejected from the metal surface as soon as the beam of light strikes the surface, i.e., there is no timelag between the striking of light beam and the ejection of electrons from the metal surface.

(ii) The number of electrons ejected is proportional to the intensity or brightness of light.

(iii) For each metal, there is a characteristic minimum frequency, ν (also known as threshold frequency) below which photoelectric effect is not observed. At a frequency $\nu > \nu_0$, the ejected electrons come out with certain kinetic energy. The kinetic energies of these electrons increase with the increase of frequency of the light used.

All the above results could not be explained on the basis of laws of classical physics. According to latter, the energy content of the beam of light depend s upon the brightness of the light. In other words, number of electrons ejected and kinetic energy associated with them should depend on the brightness of light. It has been observed that though the number of electrons ejected does depend upon the brightness of light, the kinetic energy of the ejected electrons does not. For example, red light [ν = (4.3 to 4.6) x10^{14} Hz] of any brightness (intensity) may shine on a piece of potassium metal for hours but no photoelectrons are ejected. But, as soon as even a very weak yellow light [ν = (5.1-5.2) 10^{14} Hz] shines on the potassium metal, the photoelectric effect is observed. The threshold frequency (ν) for potassium metal is 5.0 x 10^{14} Hz. Einstein (1905) was able to explain the photoelectric effect using Planck's quantum theory of electromagnetic radiation as a starting point.

Shining a beam of light on to a metal surface can, therefore, be viewed as shooting a beam of particles, the photons. When a photon of sufficient energy strikes an electron in the atom of the metal, it transfers its energy instantaneously to, the electron during the collision and the electron is ejected without any time lag or delay. Greater the energy possessed by the photon, greater will be transfer of energy to the electron and greater the kinetic energy of the ejected-electron. In other words, kinetic energy of the ejected' electron is proportional to the frequency of the electromagnetic radiation. Since the striking photon has energy equal to $h\nu$ and the minimum energy required to eject the electron is $h\nu_0$ (also called work function, W_o; Table 1.2), then the difference in energy

Table 1.2 Definitions of SI base units

Unit of length	Metre	The *metre* is the length of the path travelled by light in vacuum during a time interval of1/299 792 458 of a second.
Unit of mass	kilogram	The *kilogram* is the unit of mass; it is equal to the mass of the international prototype of the kilogram.
Unit of time	Second	The second duration of 9192 631770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the caesium-133 atom.
Unit of electric current	Ampere	The ampere is at that constant current which, if maintained in two straight parallel conductors of infinite length, of negligible circular cross-section, and placed 1 metre apart in vacuum, would produce between these conductors a force equal to 2 × 10–7newton per metre of length.

Unit of thermodynamic Temperature	kelvin	The *Kelvin*, unit of thermodynamic temperature, is the fraction 1/273.16 of the thermodynamic temperature of the triple point of water.
Unit of amount of substance.	mole	1. The *mole* is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12; its symbol is "mol." 2. When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles.
Unit of luminous intensity	Candela	The *candela* is the luminous intensity, in agiven direction, of a source that emitsmonochromatic radiation of frequency 540 × 1012 hertz and that has a radiant intensity in that direction of 1/683 watt per steradian.

($h\nu - h\nu_0$) is transferred as the kinetic energy of the photoelectron. Following the conservation of energy principle, the kinetic energy of the ejected electron is given by the equation 1.4.

$$h\nu = h\nu_0 + \frac{1}{2} m_e \mathrm{V}^2 \qquad (1.4\ )$$

where m_e is the mass of the electron and V is the velocity associated with the ejected electron. Lastly, a more intense beam of light consists of larger number of photons, consequently the number of electrons ejected is also larger as compared to that in an experiment in which a beam of weaker intensity of light is employed.

Dual Behaviour of Electromagnetic Radiation:

The particle nature of light posed a dilemma for scientists. On the one hand, it could explain the black body radiation and photoelectric effect satisfactorily but on the other hand, it was not consistent with the known wave behaviour of light which could account for the phenomena of interference and diffraction. The only way to resolve the dilemma was to accept the idea that light possesses both particle and wave-like properties, i.e., light has dual behaviour. Depending on the experiment, we find that light behaves either as a wave or as a stream of particles. Whenever radiation interacts with matter, it displays particle like properties in contrast to the wave like properties (interference and diffraction) which it exhibits when it propagates. This concept was totally alien to the way the scientists thought about matter and radiation and it took them a long time to become convinced of its validity. It turns out as you shall see later, that some microscopic particles like electrons also exhibit this wave-particle duality.

Evidence for the quantized Electronic Energy Levels: Atomic spectra

The speed of light depends upon the nature of the medium through which it passes. As a result, the beam of light is deviated or refracted from its original path as it passes from one medium to another. It is observed that when a ray of white light is passed through a prism, the wave with shorter wavelength bends more than the one with a longer wavelength. Since ordinary white light consists of waves with all the wavelengths in the visible range, a ray of white light is spread out into a series of coloured bands called spectrum. The light of red colour which has longest wavelength is deviated the least while the violet light, which has shortest wavelength is deviated the most. The spectrum of white light, that we can see, ranges from violet at 7.50×10^{14} Hz to red at 4×10^{14} Hz. Such a spectrum is called continuous spectrum. Continuous because violet merges into blue, blue into green and so on. A similar spectrum is produced when a rainbow forms in the sky. Remember that visible light is just a small portion of the electromagnetic radiation (Fig.1.4). When electromagnetic radiation interacts with matter, atoms and molecules may absorb energy and reach to a higher energy state. With higher energy, these are in an unstable state. For returning to their normal (more stable. lower energy states) energy state, the atoms and molecules emit radiations in various regions of the electromagnetic spectrum.

Emission and Absorption Spectra

The spectrum of radiation emitted by a substance that has absorbed energy is called an emission spectrum. Atoms, molecules or ions that have absorbed radiation are said to be "excited". To produce an emission spectrum, energy is supplied to a sample by heating it or irradiating it and the wavelength (or frequency) of the radiation emitted, as the sample gives up the absorbed energy, is recorded.

An absorption spectrum is like the photographic negative of an emission spectrum. A continuum of radiation is passed through a sample which absorbs radiation of certain wavelengths .The missing wavelength which corresponds to the radiation absorbed by the matter, leave dark spaces in the bright continuous spectrum.

The study of emission or absorption spectra is referred to as spectroscopy. The spectrum of the visible light, as discussed above, was continuous as all wavelengths (red to violet) of the visible light are represented in the spectra. The emission spectra of atoms in the gas phase, on the other hand, do not show a continuous spread of wavelength from red to violet, rather they emit light only at specific wavelengths with dark spaces between them. Such spectra are called line spectra or atomic spectra because the emitted radiation is identified by the appearance of bright lines in the spectra (Fig, 1.7)

Line emission spectra are of great interest in the study of electronic structure. Each element has a unique line emission spectrum. The characteristic lines in atomic spectra can be used in chemical analysis to identify unknown atoms in the same way as finger prints are used to identify people. The exact matching of lines of the emission spectrum of the atoms of a known element with the lines from an unknown sample quickly establishes the identity of the latter, German chemist, Robert Bunsen (1811-1899) was one of the first investigators to use line spectra to identify elements.

Elements like rubidium (Rb), caesium (Cs) thallium (Tl), indium (In), gallium (Ga) and scandium (Sc) were discovered when their minerals were analysed by spectroscopic methods. The element helium (He) was discovered in the sun by spectroscopic method.

Line Spectrum of Hydrogen

When an electric discharge is passed through gaseous hydrogen, the H_2 molecules dissociate and the energetically excited hydrogen atoms produced emit electromagnetic radiation of discrete frequencies. The hydrogen spectrum consists of several series of lines named after their discoverers. Balmer showed in 1885 on the basis of experimental observations that if spectral lines are expressed in terms of wave number ($\bar{\nu}$), then the visible lines of the hydrogen spectrum obey the following formula

$$\bar{\nu} = 109{,}677\left(\frac{1}{2^2} - \frac{1}{n^2}\right) cm^{-1} \qquad (1.5)$$

where n is an integer equal to or greater than 3 (i.e., n = 3,4,5,....)

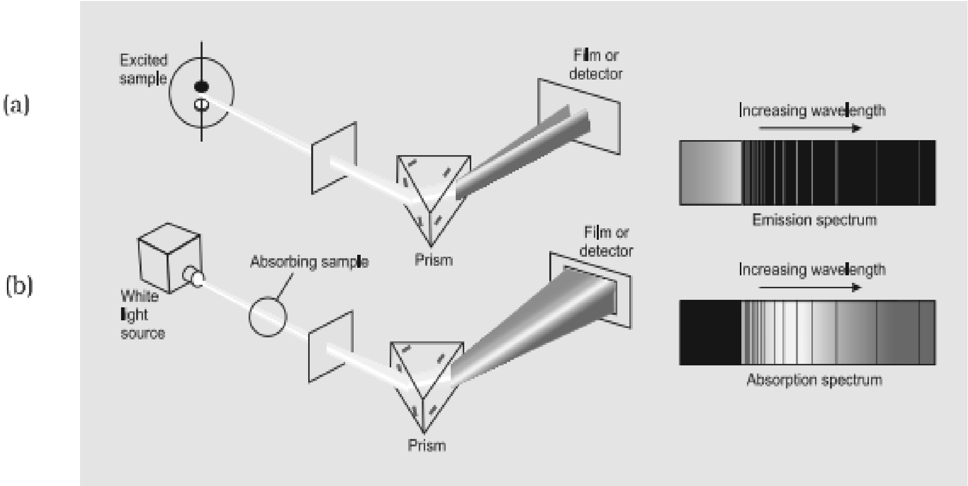


Fig. 1.7 (a} Atomic emission. The light emitted by a sample of excited hydrogen atoms (or any other element) can be passed through a prism and separated into certain discrete wavelengths. Thus an emission spectrum, which is a photographic recording of the separated wavelengths is called as line spectrum. Any sample of reasonable size contains an enormous number of atoms. Although a single atom can be in only one excited state at a time, the collection of atoms contains all possible excited states. The light emitted as these atoms fall to lower energy states is responsible for the spectrum. **(b) Atomic absorption.** When white light is passed through unexcited atomic hydrogen and then through a slit and prism, the transmitted light is lacking in intensity at the same wavelengths as are emitted in (a) The recorded absorption spectrum is also a line spectrum and the photographic negative of the emission spectrum.

The series of lines described by this formula are called the Balmer series. The Balmer series of lines are the only lines in the hydrogen spectrum which appear in the visible region of the electromagnetic spectrum. The Swedish spectroscopist, Johannes Rydberg noted that all series of lines in the hydrogen spectrum could be described by the following expression:

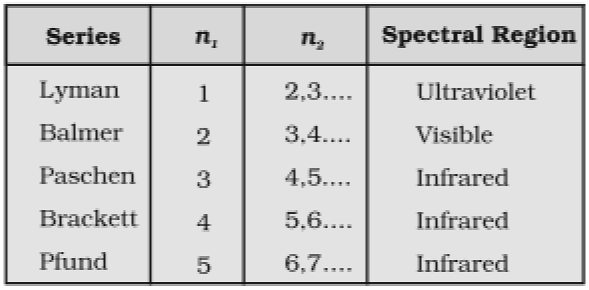
$$\bar{\nu} = 109,677\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\text{cm}^{-1} \qquad (1.\ 6)$$

Where n_1= 1,2,………

n_2= n_1+1, n_1+2, …….

The value 1,09,677 cm^{-1} is called the Rydberg constant for hydrogen. The first five series of lines that correspond to n = 1. 2. 3, 4, 5 are known as Lyman, Balmer, Paschen, Bracket and Pfund series respectively. Table 1.3 shows these series of transitions in the hydrogen spectrum. Fig.1.8 shows the Lyman, Balmer and Paschen series of transitions for hydrogen atom.

Table 1.3 The Spectral Lines for Atomic Hydrogen



Series	n_1	n_2	Spectral Region
Lyman	1	2,3....	Ultraviolet
Balmer	2	3,4....	Visible
Paschen	3	4,5....	Infrared
Brackett	4	5,6....	Infrared
Pfund	5	6,7....	Infrared

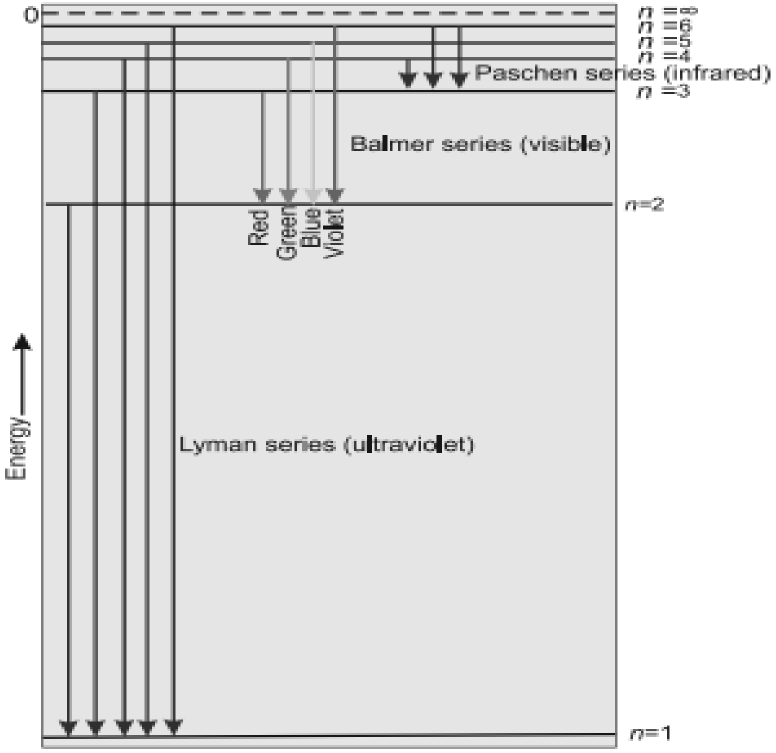


Fig.1.8 Transitions of the electron in the hydrogen atom (The diagram shows the Lyman Balmer and Paschen series of transitions)

Of all the elements, hydrogen atom has the simplest line spectrum. Line spectrum becomes more and more complex for heavier atom. There are however certain features which are common to all line spectra, i.e.,

(i) line spectrum of element is unique and

(ii) there is regularity in the line spectrum of each element.

The questions which arise are: What are the reasons for these similarities?

Is it something to do with the electronic structure of atoms'?

These are the questions need to be answered. We shall find later that the answers to these questions provide the key in understanding electronic structure of these elements.

1.4 Bohr's Model for Hydrogen Atom

Neils Bohr (1913) was the first to explain quantitatively the general features of hydrogen atom structure and its spectrum. Though the theory is not the modern quantum mechanics, it can still be used to rationalize many points in the atomic structure and spectra. Bohr's model for hydrogen atom is based on the following postulates:

i) The electron in the hydrogen atom can move around the nucleus in a circular path of fixed radius and energy. These paths are called orbits, stationary states or allowed energy states. These orbits are arranged concentrically around the nucleus.

ii) The energy of an electron in the orbit does not change with time. However the electron will move from a lower stationary state to a higher stationary state when required amount of energy is absorbed by the electron or energy is emitted when electron moves from higher stationary state to lower stationary state (equation 1.13). The energy change does not take place in a continuous manner.

iii) The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by ΔE, is given by:

$$\nu = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h} \qquad (1.7)$$

where E_1 and E_2 are the energies of the lower and higher allowed energy states respectively. This expression is commonly known as Bohr's frequency rule.

iv) The angular momentum of an electron in a given stationary state can be expressed as in equation (1.8)

$$m_e vr = n.\frac{h}{2\pi} \qquad n=1,2,3....... \qquad (1.8)$$

Thus an electron can move only in those orbits for which its angular momentum is integral multiple of $h/2\pi$ that is why only certain fixed orbits are allowed.

The details regarding the derivation of energies of the stationary states used by Bohr, are quite complicated and will be discussed in higher classes. However, according to Bohr's theory for hydrogen atom:

a) The stationary states for electron are numbered n = 1,2,3..........These integral numbers (Section 1.6.2) are known as Principal quantum numbers.

b) The radii of the stationary states are expressed as:

$$r_n = n^2 a_0 \qquad (1.9)$$

where $a_0 = 52.9$ pm. Thus the radius of the first stationary state, called the Bohr radius, is 52.9 pm. Normally the electron in the hydrogen atom is found in this orbit (that is n= l) . As n increases the value of r will increase. In other words, the electron will be present away from the nucleus.

c) The most important property associated with the electron, is the energy of its stationary state. It is given by the expression.

$$E_n = - R_H \left[\frac{1}{n^2} \right] \qquad n=1,2,3,---------- \qquad (1.10)$$

where R_H is called Rydberg constant and its value is 2.l8 x 10^{-18} J. The energy of the lowest state, also called as the ground state, is

$$E_1 = - 2.18 \text{ x } 10^{-18} \left[\frac{1}{1^2} \right] = - 2.18 \text{ x } 10^{-18} \text{ J}$$

The energy of the stationary state for n = 2, will be :

$$E_2 = - 2.18 \text{ x } 10^{-18} \left[\frac{1}{2^2} \right] = - 0545 \text{ x } 10^{-18} \text{ J}$$

Fig.1.8 depicts the energies of different stationary states or energy levels of hydrogen atom. This representation is called an energy level diagram. When the electron is free from the influence of nucleus, the energy is taken as zero. The electron in this situation is associated with the stationary state of Principal Quantum number =$n = \infty$ and is called as ionized hydrogen atom. When the electron is attracted by the nucleus and is present in orbit n, the energy is emitted and its energy is lowered. That is the reason for the presence of negative sign in equation (1.10) and depicts its stability relative to the reference state of zero energy and $n = \infty$.

d) Bohr's theory can also be applied to the ions containing only one electron, similar to that present in hydrogen atom. For example, He^+, Li^{2+}, Be^{3+} and so on. The energies of the stationary states associated with these kinds of ions (also known as hydrogen like species) are given by the expression.

$$E_n = - 2.18 \text{ x } 10^{-18} \left[\frac{Z^2}{n^2} \right] \text{J} \qquad (1.11)$$

and radii by the expression

$$r_n = \frac{52.9(n^2)}{Z}\,\text{pm} \qquad (1.12)$$

where Z is the atomic number and has values 2, 3 for the helium and lithium atoms respectively. From the above equations, it is evident that the value of energy becomes more negative and that of radius becomes smaller with increase of Z. This means that electron will be tightly bound to the nucleus.

e) It is also possible to calculate the velocities of electrons moving in these orbits. Although the precise equation is not given here, qualitatively the magnitude of velocity of electron increases with increase of positive charge on the nucleus and decreases with increase of principal quantum number.

1.4.1. Explanation of Line Spectrum of Hydrogen

Line spectrum observed in case of hydrogen atom, as mentioned in section 1.3.3, can be explained quantitatively using Bohr's model. According to assumption 2, radiation (energy) is absorbed if the electron moves from the orbit of smaller Principal quantum number to the orbit of higher Principal quantum number, whereas the radiation (energy) is emitted if the electron moves from higher orbit to lower orbit. The energy gap between the two orbits is given by equation (1.13)

$$\Delta E = E_f - E_i \qquad (1.13)$$

$$\Delta E = \left(\frac{-R_H}{n_f^2}\right) - \left(\frac{-R_H}{n_i^2}\right)$$ where n_1 and n_f stand for initial and final orbits

$$\Delta E = R_H\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) = 2.18 \text{ x } 10^{-18}\text{ J}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \qquad (1.14)$$

The frequency (ν) associated with the absorption and emission of the photon can be evaluated by using equation (1.15)

$$\nu = \frac{\Delta E}{h} = \frac{R_H}{h}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) = \left(\frac{2.18 \text{ x } 10^{-18}\text{J}}{6.626 \text{ x } 10^{-34}\text{Js}}\right)\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \qquad (1.15)$$

$$= 3.29\ x\ 10^{15}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)Hz \qquad (1.16)$$

and in terms of wavenumbers ($\bar{\nu}$)

$$\bar{\nu} = \frac{\nu}{c} = \frac{R_H}{hc}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \qquad (1.17)$$

$$= \frac{3.29\ x\ 10^{15} s^{-1}}{3\ x\ 10^{8} m\ s^{-1}}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) = 1.09677\ x\ 10^{7}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)m^{-1} \qquad (1.18)$$

In case of absorption spectru1n, $n_f > n_i$ and the ter1n in the parenthesis is positive and energy is absorbed. On the other hand in case of emission spectrum $n_1 > n_f$, ΔE is negative and energy is released.

The expression (1.14) is similar to that used by Rydberg (1.6) derived empirically using the experimental data available at that time. Further, each spectral line, whether in absorption or emission spectrum, can be associated to the particular transition in hydrogen atom. In case of large number of hydrogen atoms, different possible transitions can be observed and thus leading to large number of spectral lines. The brightness or intensity of spectral lines depends upon the number of photons of same wavelength or frequency absorbed or emitted.

1.4.2 Limitations of Bohr's Model

Bohr's model of the hydrogen atom was no doubt an improvement over Rutherford's nuclear model, as it could account for the stability and line spectra of hydrogen atom and hydrogen like ions (for example He^+, Li^{2+}, Be^{3+}, and so on). However, Bohr's model was too simple to account for the following points.

i) It fails to account for the finer details (doublet. that is two closely spaced lines) of the hydrogen atom spectrum observed by using sophisticated spectroscopic techniques. This model is also unable to explain the spectrum of atoms other than hydrogen, for example, helium atom which possesses only two electrons. Further, Bohr's theory was also unable to explain the splitting of spectral lines in the presence of magnetic field (Zeeman effect) or an electric field (Stark effect).

ii) It could not explain the ability of atoms to form molecules by chemical bonds.

In other words, taking into account the points mentioned above, one needs a better theory which can explain the salient features of the structure of complex atoms.

1.5 Towards Quantum Mechanical Model of the Atom

In view of the shortcoming of the Bohr's model, attempts were made to develop a more suitable and general model for atoms. Two important developments which contributed significantly in the formulation of such a model were:

1. Dual behaviour of matter,

2. Heisenberg uncertainty principle.

1.5.1 Dual Behaviour of Matter

The French physicist, de Broglie in 1924 proposed that matter, like radiation, should also exhibit dual behaviour i.e., both particle and wavelike properties. This means that just as the photon has momentum as well as wavelength, electrons should also have momentum as well as wavelength, de Broglie, from this analogy, gave the following relation between wavelength (λ) and momentum (p) of a material particle.

$$\lambda = \frac{h}{mv} = \frac{h}{p} \qquad (1.19)$$

where ‘m’ is the mass of the particle, ‘v’ its velocity and ‘p’ its momentum. de Broglie's prediction was confirmed experimentally when it was found that an electron beam undergoes diffraction , a phenomenon characteristic of waves. This fact has been put to use in making an electron microscope, which is based on the wave like behaviour of electrons just as an ordinary microscope utilises the wave nature of light. An electron microscope is a powerful tool in modern scientific research because it achieves a magnification of about 15 million times.

It needs to be noted that according to de Broglie, every object in motion has a wave character. The wavelengths associated with ordinary objects are so short (because of their large masses) that their wave properties cannot be detected. The wavelengths associated with electrons and other subatomic particles (with very small mass) can however be detected experimentally. Results obtained from the following problem s prove these points qualitatively.

1.5.2 Heisenberg's Uncertainty Principle

Werner Heisenberg a German physicist in 1927, stated uncertainty principle which is the consequence of dual behaviour of matter and radiation. **It states that it is impossible to determine simultaneously, the exact position and exact momentum (or velocity) of an electron.**

Mathematically, it can be given as in equation (1.20).

$$\Delta x . \Delta p \geq \frac{h}{4\pi} \tag{1.20}$$

$$\text{or} \quad \Delta x . \Delta (m.\mathrm{V}_x) \geq \frac{h}{4\pi}$$

$$\text{or} \quad \Delta x . \Delta \mathrm{V}_x \geq \frac{h}{4\pi m}$$

Where Δx is the uncertainty in position and Δp (or $\Delta \mathrm{V}_x$) is the uncertainty in momentum (or velocity) of the particle. If the position of the electron is known with high degree of accuracy Δx is small) , then the velocity of the electron will be uncertain [$\Delta \mathrm{V}_x$ is large]. On the other hand, if the velocity of the electron is known precisely ($\Delta \mathrm{V}_x$ is s1nall), then the position of the electron will be uncertain (Δx will be large) . Thus, if we carry out some physical measurements on the electron's position or velocity, the outcome will always depict a fuzzy or blur picture.

The uncertainty principle can be best understood with the help of an example. Suppose you are asked to measure the thickness of a sheet of paper with an unmarked metrestick. Obviously, the results obtained would be extremely inaccurate and meaningless. In order to obtain any accuracy, you should use an instrument graduated in units smaller than the thickness of a sheet of the paper. Analogously, in order to determine the position of an electron, we must use a meterstick calibrated in units of smaller than the dimensions of electron (keep in mind that an electron is considered as a point charge and is therefore, dimensionless). To observe an electron, we can illuminate it with "light" or electromagnetic radiation. The "light" used must have a wavelength smaller than the dimensions of an electron. The high momentum photons of such light would change the energy of electrons by collisions. In this process we, no doubt, would be able to calculate the position of the electron, but we would know very little about the velocity of the electron after the collision.

1.5.3 Significance of Uncertainty Principle

One of the important implications of the Heisenberg Uncertainty Principle is that it rules out existence of definite paths or trajectories of electrons and other similar particles. The trajectory of an object is determined by its location and velocity at various moments. If we know where a body is at a particular instant and if we also know its velocity and the forces acting on it at that instant, we can tell where the body would be sometime later. We, therefore, conclude that the position of an object and its velocity fix its trajectory. Since for a sub-atomic object such as an electron, it is not possible simultaneously to determine the position and velocity at any given instant to an arbitrary degree of precision, it is not possible to talk of the trajectory of an electron.

The effect of Heisenberg Uncertainty Principle is significant only for motion of microscopic objects and is negligible for that of macroscopic objects.

1.6 Quantum Mechanical Model of Atom

Classical mechanics, based on Newton's laws of motion, successfully describes the motion of all macroscopic objects such as a falling stone, orbiting planets etc., which have essentially a particle-like behaviour as shown in the previous section. However it fails when applied to microscopic objects like electrons, atoms, molecules etc. This is mainly because of the fact that classical mechanics ignores the concept of dual behaviour of matter especially for sub-atomic particles and the uncertainty principle. The branch of science that takes into account this dual behaviour of matter is called quantum mechanics.

Quantum mechanics is a theoretical science that deals with the study of the motions of the microscopic objects that have both observable wave like and particle like properties. It specifies the laws of motion that these objects obey, When quantum mechanics is applied to macroscopic objects (for which wave like properties are insignificant) the results are the same as those from the classical mechanics.

Quantum mechanics was developed independently in 1926 by Werner Heisenberg and Erwin Schrodinger. Here, however, we shall be discussing the quantum mechanics which is based on the ideas of wave motion. The fundamental equation of quantum mechanics was developed by Schrodinger and it won him the Nobel Prize in Physics in 1933. This equation which incorporates wave-particle duality of matter as proposed by de Broglie is quite co1nplex and knowledge of higher mathematics is needed to solve it. You will learn its solutions for different systems in higher classes.

For a system (such as an atom or a molecule whose energy does not change with time) the Schrodinger equation is written as

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi=0$$

which is written as $H\psi = E\psi$

$$H=-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V$$

where H is a mathematical operator called Hamiltonian. Schrodinger gave a recipe of constructing this operator from the expression for the total energy of the system. The total energy of the system takes into account the kinetic energies of all the sub-atomic particles (electrons, nuclei), attractive potential between the electrons and nuclei and repulsive potential among the electrons and nuclei individually. Solution of this equation gives E and ψ.

Hydrogen Atom and the Schrodinger Equation

When Schrodinger equation is solved for hydrogen atom, the solution gives the possible energy levels the electron can occupy and the corresponding wave function(s) (ψ) of the electron associated with each energy level. These quantized energy states and corresponding wave functions which are characterized by a set of three quantum numbers (principal quantum number n, azimuthal quantum number l and magnetic quantum number m_1) arise as a natural consequence in the solution of the Schrodinger equation. When an electron is in any energy state, the wave function corresponding to that energy state contains all information about the electron. The wave function is a mathematical function whose value depends upon the coordinates of the electron in the atom and does not carry any physical meaning. Such wave functions of hydrogen or hydrogen like species with one electron are called atomic orbitals. Such wave functions pertaining to one-electron species are called one-electron systems. The probability of finding an electron at a point within an atom is proportional to the $|\psi^2|$ at that point. The quantum mechanical results of the hydrogen atom successfully predict all aspects of the hydrogen atom spectrum including some phenomena that could not be explained by the Bohr model.

Application of Schrodinger equation to multi-electron atoms presents a difficulty: the Schrodinger equation cannot be solved exactly for a multi- electron atom. This difficulty can be overcome by using approximate methods. Such calculations with the aid of modern computers show that orbitals in atoms other than hydrogen do not differ in any radical way from the hydrogen orbitals discussed above. The principal difference lies in the consequence of increased nuclear charge. Because of this all the orbitals are somewhat contracted. Further, as you shall see later (in subsections 1.6.3 and 1.6.4) , unlike orbitals of hydrogen or hydrogen like species, whose energies depend only on the quantum number n, the energies of the orbitals in multi-electron atoms depend on quantum numbers n and l.

1.6.1 Orbitals and Quantum Numbers

A large number of orbitals are possible in an atom. Qualitatively these orbitals can be distinguished by their size, shape and orientation. An orbital of smaller size means there is more chance of finding the electron near the nucleus. Similarly shape and orientation mean that there is more probability of finding the electron along certain directions than along others. Atomic orbitals are precisely distinguished by what are known as quantum numbers. Each orbital is designated by three quantum numbers labelled as n, *l* and m_l.

The principal quantum number 'n' is a positive integer with value of n= 1,2,3........ The principal quantum number determines the size and to large extent the energy of the orbital. For hydrogen atom and hydrogen like species (He^+, Li^{2+}, ... etc.) energy and size of the orbital depends only on ' n'.

The principal quantum number also identifies the shell. With the increase in the value of 'n', the number of allowed orbital increases and are given by 'n^2 '. All the orbitals of a given value of 'n' constitute a single shell of atom and are represented by the following letters

n =	1	2	3	4	....
Shell =	K	L	M	N	....

Size of an orbital increases with increase of principal quantum number ' n'. In other words the electron will be located away from the nucleus. Since energy is required in shifting away the negatively charged electron from the positively charged nucleus, the energy of the orbital will increase with increase of 'n'.

Azimuthal quantum number '*l*' is also known as **orbital angular momentum** or **subsidiary quantum number**. It defines the three dimensional shape of the orbital. For a given value of n, *l* can have n values ranging from 0 to n - 1, that is, for a given value of n,

the possible value of *l* are : *l* = 0, 1, 2, ... (n-1)

For example, when n = 1, value of *l* is only 0.

For n = 2, the possible value of *l* can be 0 and 1. For n = 3, the possible *l* values are 0, 1 and 2.

Each shell consists of one or more sub- shells or sub-levels. The number of sub-shells in a principal shell is equal to the value of n. For example in the first shell (n = 1), there is only one sub-shell which corresponds to *l* = 0. There are two sub-shells (*l* = 0, 1) in the second shell (n = 2), three (*l* = 0, 1, 2) in third shell (n = 3) and so on. Each sub-shell is assigned an azimuthal quantum number (*l*). Sub-shells corresponding to different values of '*l*' are represented by the following symbols.

Value for *l* :	0	1	2	3	4	5	• • • • • • • • • • • •
notation for sub-shell	s	p	d	f	g	h	• • • • • • • • • • • •

Table 1.4 shows the permissible values of '*l*' for a given principal quantum number and the corresponding sub-shell notation.

Magnetic orbital quantum number 'm_l' gives information about the **spatial orientation of the orbital with respect to standard set of co-ordinate axis**. For any sub-shell (defined by '*l*' value) 2*l*+ 1 values of 'm' are possible and these values are given by

$m_l = -l, -(l-1), -(l-2) \ldots 0, 1 \ldots (l-2), (l-1), l$

Thus for *l* = 0, the only permitted value of m = 0, [2(0)+1= 1, one s orbital]. For *l* = 1, m can be -1, 0 and + l [2(1)+1 = 3, three p orbitals]. For *l* = 2, m = -2, -1, 0, +1and +2, [2(2)+1 = 5, five d orbitals]. It should be noted that the values of are derived from *l* and that the value of *l* are derived from n.

Each orbital in an atom, therefore, is defined by a set of values for n, *l* and m_l An orbital described by the quantum numbers n = 2, *l* = 1, m = 0 is an orbital in the p sub-shell of the second shell. The following chart gives the relation between the sub-shell and the number of orbitals associated with it.

Table 1.4 Subshell Notations

n	*l*	Subshell notation
1	0	1*s*
2	0	2*s*
2	1	2*p*
3	0	3*s*
3	1	3*p*
3	2	3*d*
4	0	4*s*
4	1	4*p*
4	2	4*d*
4	3	4*f*

Value of *l*	0	1	2	3	4	5
Subshell notation	*s*	*p*	*d*	*f*	*g*	*h*
number of orbitals	1	3	5	7	9	11

Electron spin 's': The three quantum numbers labelling an atomic orbital can be used equally well to define its energy, shape and orientation. But all these quantum numbers are not enough to explain the line spectra observed in the case of multi-electron atoms, that is, some of the lines actually occur in doublets (two lines closely spaced), triplets (three lines, closely spaced) etc. This suggests the presence of a few more energy levels than predicted by the three quantum numbers.

In 1925, George Uhlenbeck and Samuel Goudsmit proposed the presence of the fourth quantum number known as the **electron spin quantum number (m_s)**. An electron spins around its own axis, much in a similar way as earth spins around its own axis while revolving around the sun. In other words, an electron has, besides charge and mass intrinsic spin angular quantum number. Spin angular momentum of the electron - a vector quantity, can have two orientations relative to the chosen axis. These two orientations are distinguished by the spin quantum nu1nbers m which can take the values of +1/2 or - l/2. These are called the **two spin states of the electron** and are normally represented by two arrows, ↑(spin up) and ↓, (spin down). Two electrons that have different ms values (one + 1/2 and the other -1/2) are said to have opposite spins. An orbital cannot hold more than two electrons and these two electrons should have opposite spins.

To sum up the four quantum numbers provide the following information :

i) 'n' defines the shell, determines the size of the orbital and also to a large extent the energy of the orbital.

ii) There are n sub-shells in the nth shell. '*l*' identifies the sub-shell and determines the shape of the orbital (see section 1.6.2) . There are (2*l*+ 1) orbitals of each type in a sub-shell, that is, one s orbital (*l* = 0) , three 'p' orbitals (*l* = 1) and five d orbitals (*l* = 2) per sub-shell. To some extent l also determines the energy of the orbital in a multi-electron atom.

iii) m_l designates the orientation of the orbital. For a given value of *l*, have (2*l*+ 1) values, the same as the number of orbitals per sub-shell. It means that the number of orbitals is equal to the number of ways in which they are oriented.

iv) m_s refers to orientation of the spin of the electron.

1.6.2 Shapes of Atomic Orbitals

The orbital wave function or ψ for an electron in an atom has no physical meaning. It is simply a mathematical function of the coordinates of the electron. However, for different orbitals the plots of corresponding wave functions as a function of 'r' (the distance from the nucleus) are different. Fig. 1.9(a), gives such plots for 1s (n = 1, *l* = 0) and 2s (n = 2, *l* = 0) orbitals.

According to the German physicist, Max Born, the square of the wave function (i.e. ψ^2) at a point gives the probability density of the electron at that point. The variation of ψ^2 as a function of 'r' for 1s and 2s orbitals is given in Fig. 1.9(b). Here again, you may note that the curves for ls and 2s orbitals are different.

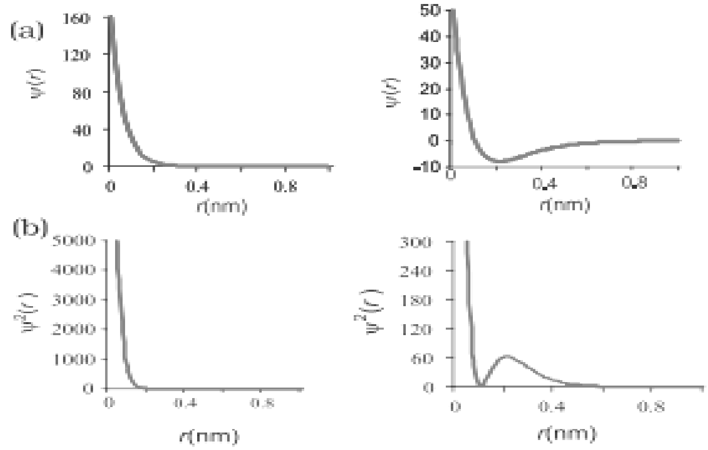


Fig.1.9 The plots of (a) the orbital wave function ψ (r); (b) the variation of probability density ψ^2 (r) as a junction of distance r of the electron from the nucleus for ls and 2s orbitals.

It may be noted that for ls orbital the probability density is maximum at the nucleus and it decreases sharply as we move away from it. On the other hand, for 2s orbital, the probability density first decreases sharply to zero and again starts increasing. After reaching small maxima, it decreases again and approaches zero as the value of 'r' increases further. The region where this probability density function reduces to zero is called nodal surfaces or simply nodes. In general, it has been found that ns-orbital has (n - 1) nodes, that is, number of nodes increases with increase of principal quantum number n. In other words, number of nodes for 2s orbital is one, two for 3s and so on.

These probability density variations can be visualised in terms of charge cloud diagrams [Fig. 1.10(a)]. In these diagrams, the density of the dots in a region represents electron probability density in that region.

Boundary surface diagrams of constant probability density for different orbitals give a fairly good representation of the shapes of the orbitals. In this representation, a boundary surface or contour surface is drawn in space for an orbital on which the value of probability density $|\varphi^2|$ is constant. In principle many such boundary surfaces may be possible. However, for a given orbital, only that boundary surface diagram of constant probability density is taken to be good representation of the shape of the orbital which encloses a region or volume in which the probability of finding the electron is very high, say, 90%. The boundary surface diagram for l s and 2s orbitals are given in Fig. 1.10(b) . One may ask a question: Why do we not draw a boundary surface diagram, which bounds a region in which the probability of finding the electron is, 100 %?.

The answer to this question is that the probability density $|\varphi^2|$ as always some value, howsoever small it may be, at any finite distance from the nucleus. It is therefore, not possible to draw a boundary surface diagram of a rigid size in which the probability of finding the electron is 100%. Boundary surface diagram for a s orbital is actually a sphere centered on the nucleus. In two dimensions, this sphere looks like a circle. It encloses a region in which probability of finding the electron is about 90%.

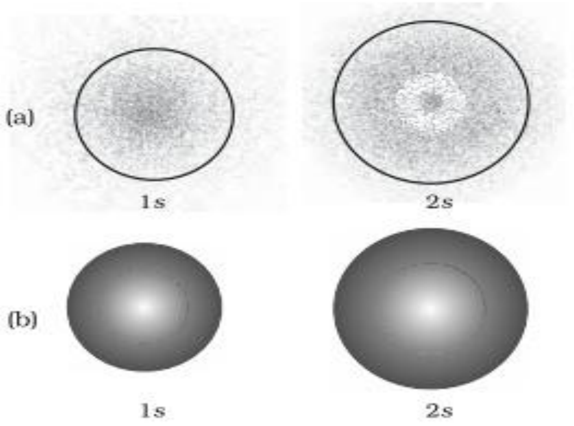


Fig. 1.10 (a) Probability density plots of ls and 2s atomic orbitals. The density of the dots represents the probability density of finding the electron in that region. (b) Boundary surface diagram for 1s and 2s orbitals

Thus we see that 1s and 2s orbitals are spherical in shape. In reality all the s-orbitals are spherically symmetric, that is, the probability of finding the electron at a given distance is equal in all the directions. It is also observed that the size of the s orbital increases with increase in n, that is, 4s > 3s> 2s > 1s and the electron is located further away from the nucleus as the principal quantum number increases.

Boundary surface diagrams for three 2p orbitals ($l = 1$) are shown in Fig. 1.11. In these diagrams, the nucleus is at the origin. Here, unlike s-orbitals, the boundary surface diagrams are not spherical. Instead each p orbital consists of two sections called lobes that are on either side of the plane that passes through the nucleus. The probability density function is zero on the plane where the two lobes touch each other. The size, shape and energy of the three orbitals are identical. They differ however, in the way the lobes are oriented. Since the lobes may be considered to lie along the x. y or z axis, they are given the designations $2p_x$, $2p_Y$, and $2p_z$. It should be understood, however, that there is no simple relation between the values of (-1, 0 and + 1) and the x. y and z directions. For our purpose, it is sufficient to remember that, because there are three possible values of m_l, there are, therefore, three p orbitals whose axes are mutually perpendicular. Like s orbitals, p orbitals increase in size and energy with increase in the principal quantum number and hence the order of the energy and size of various p orbitals is 4p > 3p > 2p. Further, like s orbitals, the probability density functions for p-orbital also pass through value zero, besides at zero and infinite distance, as the distance from the nucleus increases. The number of nodes is given by the n -2, that is number of radial node is 1 for 3p orbital, two for 4p orbital and so on.

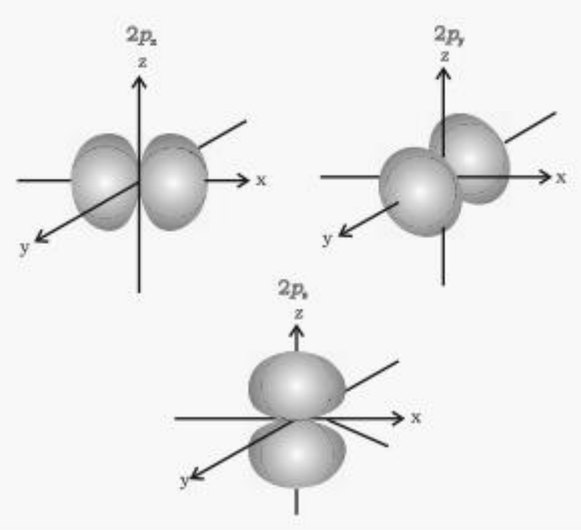


Fig.1.11 Boundary surface diagrams of the three 2p orbitals.

For *l* = 2, the orbital is known as d-orbital and the minimum value of principal quantum number (n) has to be 3 as the value of *l* cannot be greater than n-1. There are five m_l values (-2, -1, 0, + 1 and +2) for *l* = 2 and thus there are five d orbitals. The boundary surface diagram of d orbitals are shown in Fig. 1.12.

The five d-orbitals are designated as $d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}, and\ d_{z^2}$. The shapes of the first four d-orbitals are similar to each other, where as that of the fifth one, d_{z^2} is different from others, but all five 3d orbitals are equivalent in energy. The d orbitals for which n is greater than 3 (4d, 5d...) also have shapes similar to 3d orbital, but differ in energy and size.

Besides the radial nodes (i.e.. probability density function is zero), the probability density functions for the np and nd orbitals are zero at the plane (s) , passing through the nucleus (origin). For example, in case of P_z orbital, xy-plane is a nodal plane, in case of d_{xy} orbital, there are two nodal planes passing through the origin and bisecting the xy plane containing z-axis. These are called angular nodes and number of angular nodes is given by '*l*'. i.e.. one angular node for p orbitals, two angular nodes for 'd' orbitals and so on. The total number of nodes is given by (n-1), i.e., sum of *l* angular nodes and (*n* - *l* - 1) radial nodes.

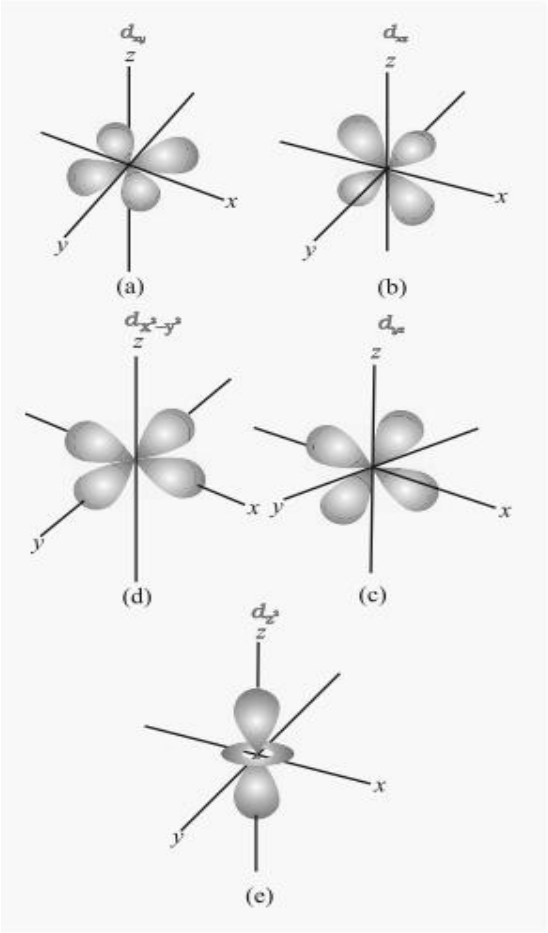


Fig.1.12 Boundary surface diagrams of the five 3d orbitals.

1.6.3 Energies of Orbitals

The energy of an electron in a hydrogen atom is determined solely by the principal quantum number. Thus the energy of the orbitals increases as follows:

Is < 2s = 2p < 3s = 3p = 3d <45 = 4p = 4d= 4J< (1.23)

and is depicted in Fig. 1.13. Although the shapes of 2s and 2p orbitals are different, an electron has the same energy when it is in the 2s orbital as when it is present 2p orbital. The orbitals having the same energy are called degenerate. The 1s orbital in a hydrogen atom, as said earlier, corresponds to the most stable condition and is called the ground state and an electron residing in this orbital is most strongly held by the nucleus. An electron in the 2s, 2p or higher orbitals in a hydrogen atom is in excited state.

The energy of an electron in a multi-electron atom, unlike that of the hydrogen atom depends not only on its principal quantum number (shell), but also on its azimuthal quantum number (subshell). That is, for a given principal quantum number, s,p, d,f ...all have different energies. The main reason for having different energies of the subshells is the mutual repulsion among the electrons in a multi-electron atom. The only electrical interaction present in hydrogen atom is the attraction between the negatively charged electron and the positively charged nucleus. In multi-electron atoms, besides the presence of attraction between the electron and nucleus, there are repulsion terms between every electron and other electrons present in the atom. Thus the stability of an electron in multi-electron atom is because total attractive interactions are more than the repulsive interactions. In general, the repulsive interaction of the electrons in the outer shell with the electrons in the inner shell is more important. On the other hand, the attractive interactions of an electron increase with increase of positive charge (Ze) on the nucleus. Due to the presence of electrons in the inner shells, the electron in the outer shell will not experience the full positive charge of the nucleus (Ze). The effect will be lowered due to the partial screening of positive charge on the nucleus by the inner shell electrons. This is known as the shielding of the outer shell electrons from the nucleus by the inner shell electrons, and the net positive charge experienced by the outer electrons is known as effective nuclear charge (Z_{eff} e). Despite the shielding of the outer electrons from the nucleus by the inner shell electrons, the attractive force experienced by the outer shell electrons increases with increase of nuclear charge. In other words, the energy of interaction between, the nucleus and electron (that is orbital energy) decreases (that is more negative) with the increase of atomic number (Z).

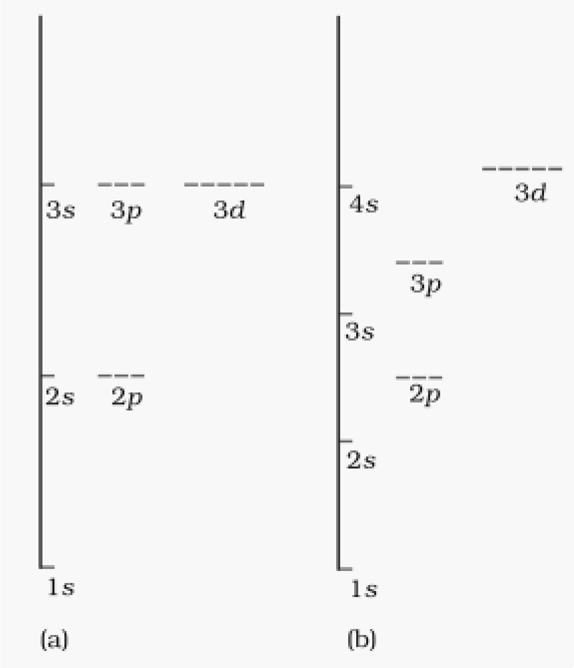
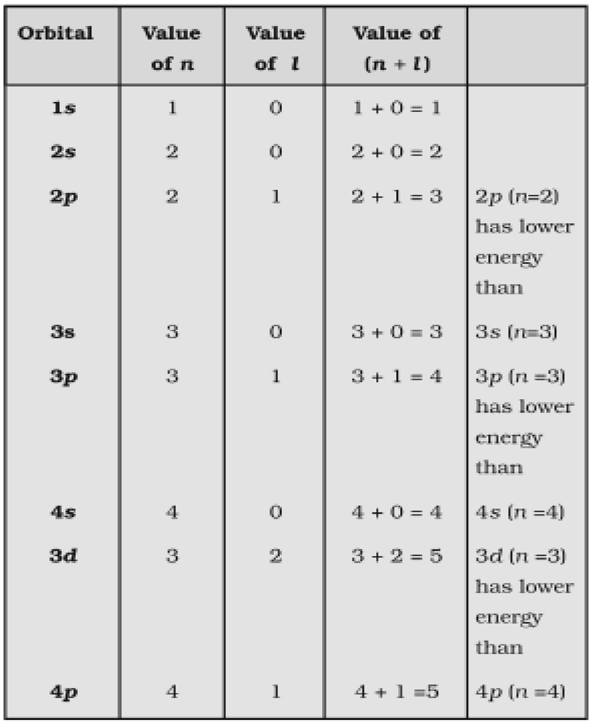


Fig.1.13 Energy level diagrams for the few electronic shells of (a) hydrogen atom and (b) multi-electronic atoms. Note that orbitals for the same value of principal quantum number, have the same energies even for different azimuthal quantum number for hydrogen atom. In case of multi-electron atoms, orbitals with same principal quantum number possess different energies for different azimuthal quantum numbers.

Both the attractive and repulsive interactions depend upon the shell and shape of the orbital in which the electron is present. For example electrons present in spherical shaped, s orbital shields the outer electrons from the nucleus more effectively as compared to electrons present in p orbital. Similarly electrons present in p orbitals shield the outer electrons from the nucleus more than the electrons present in d orbitals, even though all these orbitals are present in the same shell. Further within a shell, due to spherical shape of s orbital, the s orbital electron spends more time close to the nucleus in comparison to p orbital electron which spends more time in the vicinity of nucleus in comparison to d orbital electron. In other words, for a given shell (principal quantum number), the Z_{eff} experienced by the electron decreases with increase of azimuthal quantum number (0, that is, the s orbital electron will be more tightly bound to the nucleus than p orbital electron which in turn will be better tightly bound than the d orbital electron. The energy of electrons in s orbital will be lower (more negative) than that of p orbital electron which will have less energy than that of d orbital electron and so on. Since the extent of shielding from the nucleus is different for electrons in different orbitals, it leads to the splitting of energy levels within the same shell (or same principal quantum number), that is, energy of electron in an orbital, as mentioned earlier, depends upon the values of n and l. Mathematically, the dependence of energies of the orbitals on n and l are quite complicated but one simple rule is that, the lower the value of (n + *l*) for an orbital, the lower is its energy. If two orbitals have the same value of (n + *l*), the orbital with lower value of n will have the lower energy. The Table 1.5 illustrates the (n + *l*) rule and Fig. 1.16 depicts the energy levels of multi-electrons atoms. It may be noted that different subshells of a particular shell have different energies in case of multi- electrons atoms. However, in hydrogen atom, these have the same energy. Lastly it may be mentioned here that energies of the orbitals in the same subshell decrease with increase in the atomic number (Z_{eff}). For example, energy of 2s orbital of hydrogen atom is greater than that of 2s orbital of lithium and that of lithium is greater than that of sodium and so on, that is, $E_{2S}(H) > E_{2S}(Li) > E_{2S}(Na) > E_{2S}(K)$.

Table 1.5 Arrangement of Orbitals with Increasing Energy on the Basis of (n+l) rule.



Orbital	Value of *n*	Value of *l*	Value of (*n* + *l*)	
1*s*	1	0	1 + 0 = 1	
2*s*	2	0	2 + 0 = 2	
2*p*	2	1	2 + 1 = 3	2*p* (*n*=2) has lower energy than
3*s*	3	0	3 + 0 = 3	3*s* (*n*=3)
3*p*	3	1	3 + 1 = 4	3*p* (*n* =3) has lower energy than
4*s*	4	0	4 + 0 = 4	4*s* (*n* =4)
3*d*	3	2	3 + 2 = 5	3*d* (*n* =3) has lower energy than
4*p*	4	1	4 + 1 =5	4*p* (*n* =4)

1.6.4 Filling of Orbitals in Atom

The filling of electrons into the orbitals of different atoms takes place according to the Aufbau principle which is based on the Pauli's exclusion principle, the Hund's rule of maximum multipli city and the relative energies of the orbitals.

- **Aufbau Principle:**

The word ‘aufbau’ in German means 'building up'. The building up of orbitals means the filling up of orbitals with electrons. The principle states: In the ground state of the atoms, the orbitals are filled in order of their increasing energies. In other words, electrons first occupy the lowest energy orbital available to them and enter into higher energy orbitals only after the lower energy orbitals are filled.

The order in which the energies of the orbitals increase and hence the order in which the orbitals are filled is as follows:

ls, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 4J, 5d, 6p, 7s...

The order may be remembered by using the method given in Fig. 1.14. Starting from the top, the direction of the arrows gives the order of filling of orbitals that is starting from right top to bottom left.

- **Pauli Exclusion Principle:**

The number of electrons to be filled in various orbitals is restricted by the exclusion principle, given by the Austria n scientist Wolfgang Pauli (1926). According to this principle: No two electrons in an atom can have the same set of four quantum numbers. Pauli exclusion principle can also be stated as: "Only two electrons may exist in the same orbital and these electrons must have opposite spin." This means that the two electrons can have the same value of three quantum numbers n, l and m_l, but must have the opposite spin quantum number. The restriction imposed by Pauli's exclusion principle on the number of electrons in an orbital helps in calculating the capacity of electrons to be present in any subshell. For example, subshell ls comprises of one orbital and thus the maximum number of electrons present in 1s subshell can be two, in p and d subshells, the maximum number of electrons can be 6 and 10 and so on. This can be summed up as: the maximum number of electrons in the shell with principal quantum number n is equal to $2n^2$.

- **Hund's Rule of Maximum Multiplicity:**

This rule deals with the filling of electrons into the orbitals belonging to the same subshell (that is, orbitals of equalenergy, called degenerate orbitals). It states pairing of electrons in the orbitals belonging to the same subshell (p, d or f) does not take place until each orbital belonging to that subshell has got one electron each i.e., it is singly occupied.

Since there are three p, five d and seven f orbitals, therefore, the pairing of electrons will start in the p, d and f orbitals with the entry of 4th, 6th and 8th electron, respectively. It has been observed that half filled and fully filled degenerate set of orbitals acquire extra stability due to their symmetry.

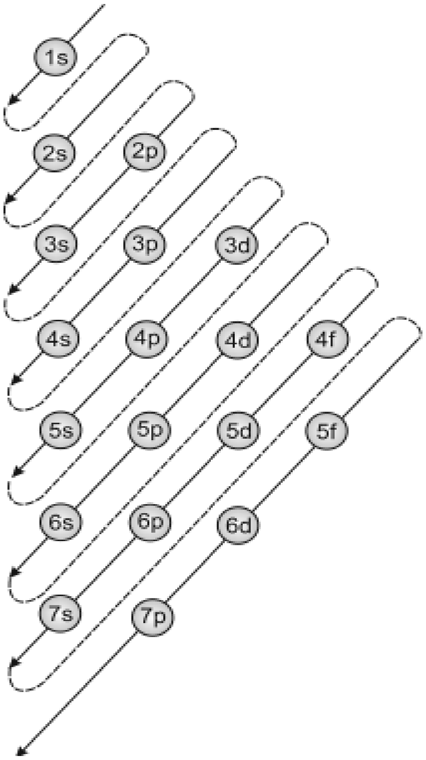


Fig.1.14Order of filling of orbitals

1.6.5 Electronic Configuration of Atoms

The distribution of electrons into orbitals of an atom is called its electronic configuration. If one keeps in mind the basic rules which govern the filling of different atomic orbitals, the electronic configurations of different atoms can be written very easily.

The electronic configuration of different atoms can be represented in two ways. For example:

i) $s^a p^b d^c$ ……… notation

ii) Orbital diagram

In the first notation, the subshell is represented by the respective letter symbol and the number of electrons present in the subshell is depicted, as the super script, like a, b, c,... etc. The similar subshell represented for different shells is differentiated by writing the principal quantum number before the respective subshell. In the second notation each orbital of the subshell is represented by a box and the electron is represented by an arrow (↑) a positive spin or an arrow (↓) a negative spin. The advantage of second notation over the first is that it represents all the four quantum numbers.

The hydrogen atom has only one electron which goes in the orbital with the lowest energy, namely 1s. The electronic configuration of the hydrogen atom is $1s^1$ meaning that it has one electron in the 1s orbital. The second electron in helium (He) can also occupy the 1s orbital. Its configuration is, therefore, l s^2. As mentioned above, the two electrons differ from each other with opposite spin, as can be seen from the orbital diagram.

The third electron of lithium (Li) is not allowed in the 1s orbital because of Pauli exclusion principle. It, therefore, takes the next available choice, namely the 2s orbital. The electronic configuration of Li is $1s^2 2s^1$. The 2s orbital can accommodate one more electron. The configuration of Beryllium (Be) atom is therefore, $ls^2\ 2s^2$.

In the next six elements boron (B, $1s^2 2s^2 2p^1$), carbon (C, $1s^2 2s^2\ 2p^2$), nitrogen (N, $ls^2 2s^2 2p^3$), oxygen (O, $ls^2 2s^2 2p^4$), fluorine (F, $ls^2 2s^2 2p^5$) and neon (Ne, $ls^2 2s^2 2p^6$), the 2p orbitals get progressively filled. This process is completed with the neon atom. The orbital picture of these elements can be represented as follows:

The electronic configuration of the elements sodium (Na, $1s^2 2s^2 2p^6 3s^1$) to argon (Ar, $1s^2 2s^2 2p^6 3s^2 3p^6$), follow exactly the same pattern as the elements from lithium to neon with the difference that the 3s and 3p orbitals are getting filled now. This process can be simplified if we represent the total number of electrons in the first two shells by the name of element neon (Ne). The electronic configuration of the elements from sodium to argon can be written as (Na,[Ne]$3s^1$) to (Ar, [Ne] $3s^2 3p^6$). The electrons in the completely filled shells are known as core electrons and the electrons that are added to the electronic shell with the highest principal quantum number are called valence electrons. For example, the electrons in Ne are the core electrons and the electrons from Na to Ar are the valence electrons. In potassium (K) and calcium (Ca), the 4s orbital, being lower in energy than the 3d orbitals, is occupied by one and two electrons respectively.

A new pattern is followed beginning with scandium (Sc). The 3d orbital, being lower in energy than the 4p orbital is filled first. Consequently, in the next ten elements, scandium (Sc), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu) and zinc (Zn) , the five 3d orbitals are progressively occupied. We may be puzzled by the fact that chromium and copper have five and ten electrons in 3d orbitals rather than four and nine as their position would have indicated with two electrons in the 4s orbital. The reason is that fully filled orbitals and half- filled orbitals have extra stability (that is, lower energy). Thus p^3, p^6, d^5, d^{10}, f^7, f^{14} etc. configurations, which are either half-filled or fully filled, are more stable. Chromium and copper therefore adopt the d^5 and d^{10} configuration.

With the saturation of the 3d orbitals, the filling of the 4p orbital starts at gallium (Ga) and is complete at krypton (Kr). In the next eighteen elements from rubidium (Rb) to xenon (Xe), the pattern of filling the 5s, 4d and 5p orbitals are similar to that of 4s, 3d and 4p orbitals as discussed above. Then comes the turn of the 6s orbital. In caesium (Cs) and the barium (Ba), this orbital contains one and two electrons, respectively. Then from lanthanum (La) to mercury (Hg), the filling up of electrons takes place in 4f and 5d orbitals. After this filling of 6p then 7s and finally 5f and 6d orbitals takes place. The elements after uranium (U) are all short-lived and all of them are produced artificially. The electronic configurations of the known ele1nents (as determined by spectroscopic methods) are tabulated in Table 1.6.

One may ask what is the utility of knowing the electron configuration?. The modern approach to the chemistry, infact, depends almost entirely on electronic distribution to understand and explain chemical behaviour. For example, questions like why two or more atoms combine to form molecules, why some elements are metals while others are non- metals, why elements like helium and argon are not reactive but elements like the halogens are reactive, find simple explanation from the electronic configuration. These questions have no answer in the Daltonian model of atom. A detailed understanding of the electronic structure of atom is, therefore, very essential for getting an insight into the various aspects of modern che1nical knowledge.

1.6.6 Stability of Completely Filled and Half Filled Subshells

The ground state electronic configuration of the atom of an element always correspond s to the state of the lowest total electronic energy. The electronic configurations of most of the atoms follow the basic rules given in Section 1.6.5. However, in certain elements such as Cu, or Cr, where the two subshells (4s and 3d) differ slightly in their energies, an electron shifts from a subshell of lower energy (4s) to a subshell of higher energy (3d), provided such a shift results in all orbitals of the subshell of higher energy getting either completely filled or half filled. The valence electronic configurations of Cr and Cu, therefore, are $3d^5 4s^1$ and $3d^{10} 4s^1$ respectively and not $3d^4 4s^2$ and $3d^9 4s^2$. It has been found that there is extra stability associated with these electronic configurations.

Causes of Stability of Completely Filled and Half Filled Sub-shells

The completely filled and completely half filled sub-shells are stable due to the following reasons:

l. Symmetrical distribution of electrons: It is well known that symmetry leads to stability. The completely filled or half filled subbshells have symmetrical distribution of electrons in them and are therefore more stable. Electrons in the same subshell (here 3d) have equal energy but different spatial distribution. Consequently, their shielding of one another is relatively small and the electrons are more strongly attracted by the nucleus.

2. Exchange Energy: The stabilizing effect arises whenever two or more electrons with the same spin are present in the degenerate orbitals of a subshell. These electrons tend to exchange their

positions and the energy released due to this exchange is called exchange energy. The number of exchanges that can take place is maximum when the subshell is either half filled or completely filled (Fig. 1. 15) . As a result the exchange energy is maximum and so is the stability.

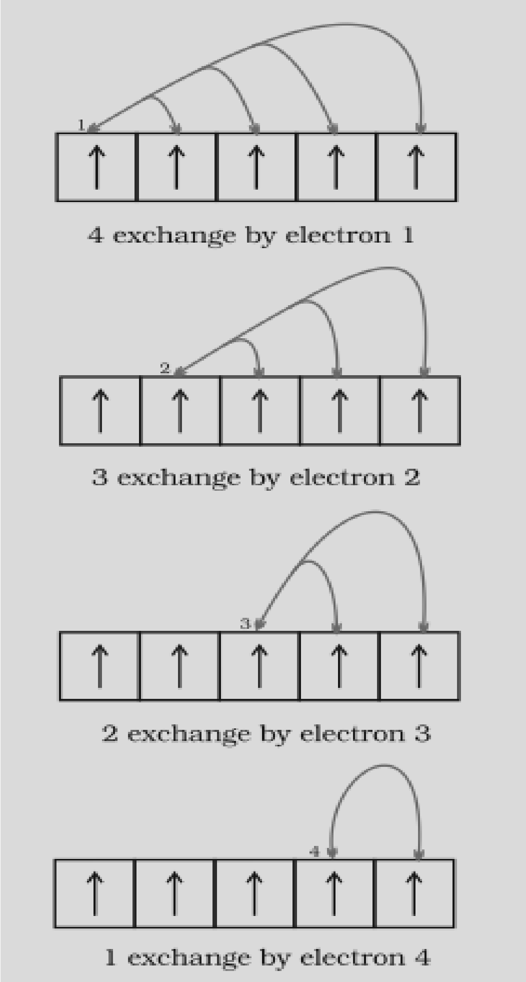
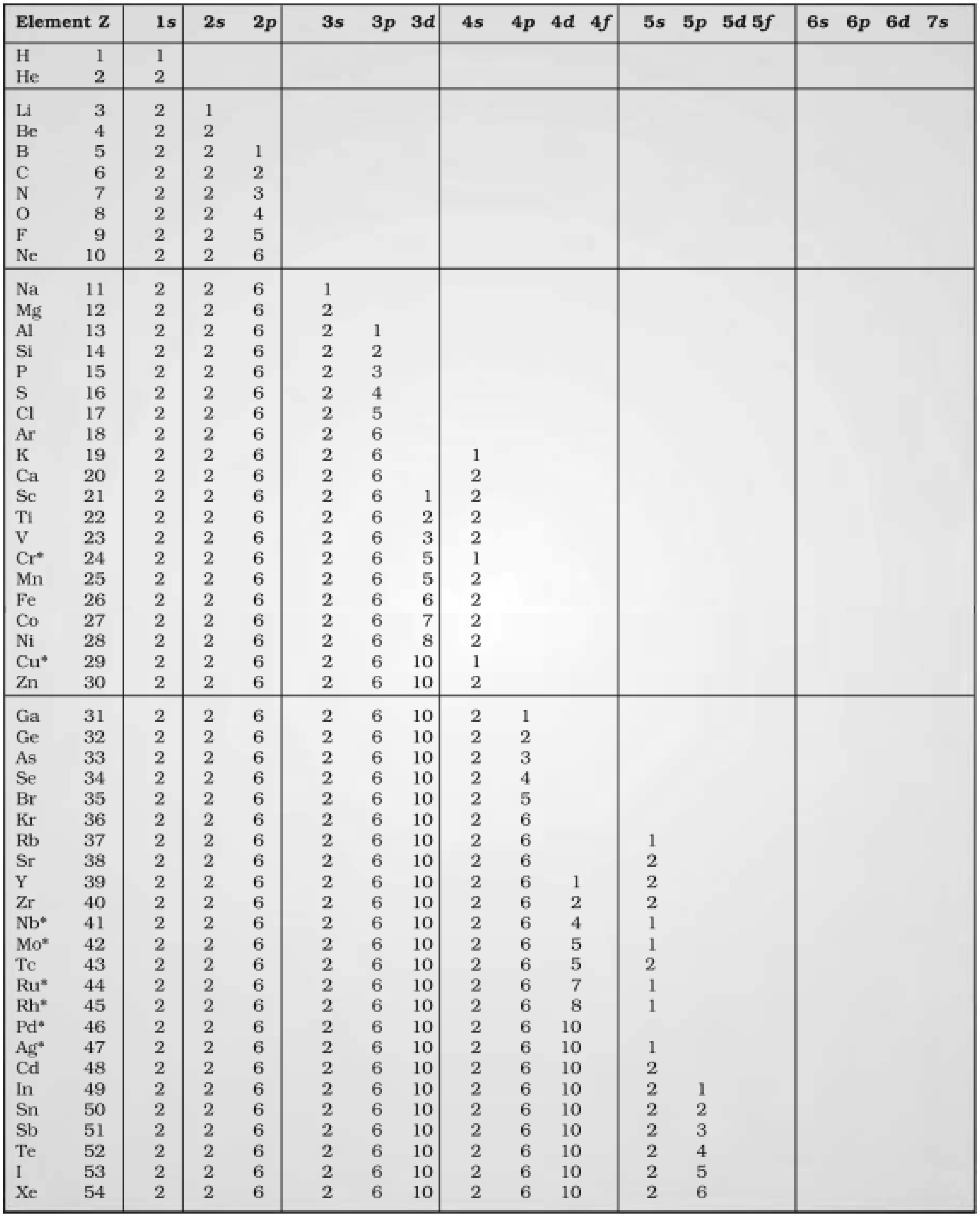


Fig.1.15 Possible exchange for a d^5 configuration

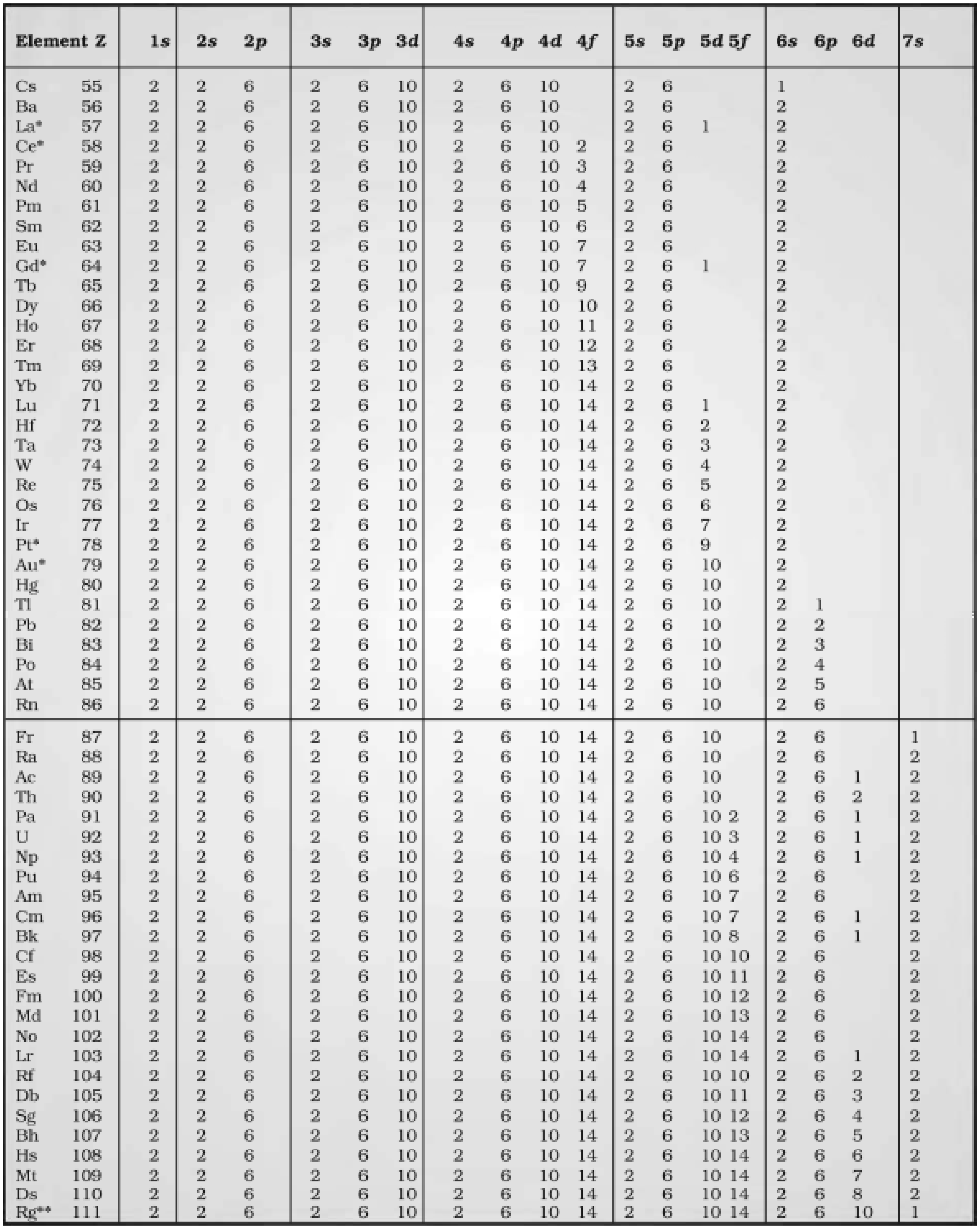
You may note that the exchange energy is at the basis of Hund's rule that electrons which enter orbitals of equal energy have parallel spins as far as possible. In other words, the extra stability of half-filled and completely filled subshell is due to: (i) relatively small shielding, (ii) smaller columbic repulsion energy, and (iii) larger exchange energy. Details about the exchange energy will be dealt with in higher classes.

Table 1.6 Electronic Configuration of the Elements



Element	Z	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
H	1	1																	
He	2	2																	
Li	3	2	1																
Be	4	2	2																
B	5	2	2	1															
C	6	2	2	2															
N	7	2	2	3															
O	8	2	2	4															
F	9	2	2	5															
Ne	10	2	2	6															
Na	11	2	2	6	1														
Mg	12	2	2	6	2														
Al	13	2	2	6	2	1													
Si	14	2	2	6	2	2													
P	15	2	2	6	2	3													
S	16	2	2	6	2	4													
Cl	17	2	2	6	2	5													
Ar	18	2	2	6	2	6													
K	19	2	2	6	2	6		1											
Ca	20	2	2	6	2	6		2											
Sc	21	2	2	6	2	6	1	2											
Ti	22	2	2	6	2	6	2	2											
V	23	2	2	6	2	6	3	2											
Cr*	24	2	2	6	2	6	5	1											
Mn	25	2	2	6	2	6	5	2											
Fe	26	2	2	6	2	6	6	2											
Co	27	2	2	6	2	6	7	2											
Ni	28	2	2	6	2	6	8	2											
Cu*	29	2	2	6	2	6	10	1											
Zn	30	2	2	6	2	6	10	2											
Ga	31	2	2	6	2	6	10	2	1										
Ge	32	2	2	6	2	6	10	2	2										
As	33	2	2	6	2	6	10	2	3										
Se	34	2	2	6	2	6	10	2	4										
Br	35	2	2	6	2	6	10	2	5										
Kr	36	2	2	6	2	6	10	2	6										
Rb	37	2	2	6	2	6	10	2	6			1							
Sr	38	2	2	6	2	6	10	2	6			2							
Y	39	2	2	6	2	6	10	2	6	1		2							
Zr	40	2	2	6	2	6	10	2	6	2		2							
Nb*	41	2	2	6	2	6	10	2	6	4		1							
Mo*	42	2	2	6	2	6	10	2	6	5		1							
Tc	43	2	2	6	2	6	10	2	6	5		2							
Ru*	44	2	2	6	2	6	10	2	6	7		1							
Rh*	45	2	2	6	2	6	10	2	6	8		1							
Pd*	46	2	2	6	2	6	10	2	6	10									
Ag*	47	2	2	6	2	6	10	2	6	10		1							
Cd	48	2	2	6	2	6	10	2	6	10		2							
In	49	2	2	6	2	6	10	2	6	10		2	1						
Sn	50	2	2	6	2	6	10	2	6	10		2	2						
Sb	51	2	2	6	2	6	10	2	6	10		2	3						
Te	52	2	2	6	2	6	10	2	6	10		2	4						
I	53	2	2	6	2	6	10	2	6	10		2	5						
Xe	54	2	2	6	2	6	10	2	6	10		2	6						

** Elements with exceptional electronic configurations*



Element	Z	1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	5*f*	6*s*	6*p*	6*d*	7*s*
Cs	55	2	2	6	2	6	10	2	6	10		2	6			1			
Ba	56	2	2	6	2	6	10	2	6	10		2	6			2			
La*	57	2	2	6	2	6	10	2	6	10		2	6	1		2			
Ce*	58	2	2	6	2	6	10	2	6	10	2	2	6			2			
Pr	59	2	2	6	2	6	10	2	6	10	3	2	6			2			
Nd	60	2	2	6	2	6	10	2	6	10	4	2	6			2			
Pm	61	2	2	6	2	6	10	2	6	10	5	2	6			2			
Sm	62	2	2	6	2	6	10	2	6	10	6	2	6			2			
Eu	63	2	2	6	2	6	10	2	6	10	7	2	6			2			
Gd*	64	2	2	6	2	6	10	2	6	10	7	2	6	1		2			
Tb	65	2	2	6	2	6	10	2	6	10	9	2	6			2			
Dy	66	2	2	6	2	6	10	2	6	10	10	2	6			2			
Ho	67	2	2	6	2	6	10	2	6	10	11	2	6			2			
Er	68	2	2	6	2	6	10	2	6	10	12	2	6			2			
Tm	69	2	2	6	2	6	10	2	6	10	13	2	6			2			
Yb	70	2	2	6	2	6	10	2	6	10	14	2	6			2			
Lu	71	2	2	6	2	6	10	2	6	10	14	2	6	1		2			
Hf	72	2	2	6	2	6	10	2	6	10	14	2	6	2		2			
Ta	73	2	2	6	2	6	10	2	6	10	14	2	6	3		2			
W	74	2	2	6	2	6	10	2	6	10	14	2	6	4		2			
Re	75	2	2	6	2	6	10	2	6	10	14	2	6	5		2			
Os	76	2	2	6	2	6	10	2	6	10	14	2	6	6		2			
Ir	77	2	2	6	2	6	10	2	6	10	14	2	6	7		2			
Pt*	78	2	2	6	2	6	10	2	6	10	14	2	6	9		2			
Au*	79	2	2	6	2	6	10	2	6	10	14	2	6	10		2			
Hg	80	2	2	6	2	6	10	2	6	10	14	2	6	10		2			
Tl	81	2	2	6	2	6	10	2	6	10	14	2	6	10		2	1		
Pb	82	2	2	6	2	6	10	2	6	10	14	2	6	10		2	2		
Bi	83	2	2	6	2	6	10	2	6	10	14	2	6	10		2	3		
Po	84	2	2	6	2	6	10	2	6	10	14	2	6	10		2	4		
At	85	2	2	6	2	6	10	2	6	10	14	2	6	10		2	5		
Rn	86	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		
Fr	87	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		1
Ra	88	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		2
Ac	89	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	1	2
Th	90	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	2	2
Pa	91	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2	6	1	2
U	92	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1	2
Np	93	2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6	1	2
Pu	94	2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6		2
Am	95	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6		2
Cm	96	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1	2
Bk	97	2	2	6	2	6	10	2	6	10	14	2	6	10	8	2	6	1	2
Cf	98	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6		2
Es	99	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6		2
Fm	100	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6		2
Md	101	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6		2
No	102	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6		2
Lr	103	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	1	2
Rf	104	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6	2	2
Db	105	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6	3	2
Sg	106	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6	4	2
Bh	107	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6	5	2
Hs	108	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	6	2
Mt	109	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	7	2
Ds	110	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	8	2
Rg**	111	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	10	1

** *Elements with atomic number 112 and above have been reported but not yet fully authenticated and named.*

SUMMARY

Atoms are the building blocks of elements. They are the smallest parts of an element that chemically react. The first atomic theory, proposed by John Dalton in 1808, regarded atom as the ultimate indivisible particle of matter. Towards the end of the nineteenth century, it was proved experimentally that atoms are divisible and consist of three fundamental particles: electrons, protons and neutrons. The discovery of sub-atomic particles led to the proposal of various atomic models to explain the structure of atom.

Thomson in 1898 proposed that an atom consists of uniform sphere of positive electricity with electrons embedded into it. This model in which mass of the atom is considered to be evenly spread over the atom was proved wrong by Rutherford's famous alpha-particle scattering experiment in 1909. Rutherford concluded that atom is made of a tiny positively charged nucleus, at its centre with electrons revolving around it in circular orbits. Rutherford model, which resembles the solar system, was no doubt an improvement over Thomson model but it could not account for the stability of the atom i.e., why the electron does not fall into the nucleus. Further, it was also silent about the electronic structure of atoms i.e., about the distribution and relative energies of electrons around the nucleus. The difficu1ties of the Rutherford model were overcome by Niels Bohr in 1913 in his model of the hydrogen atom. Bohr postulated that electron moves around the nucleus in circular orbits. Only certain orbits can exist and each orbit corresponds to a specific energy. Bohr calculated the energy of electron in various orbits and for each orbit predicted the distance between the electron and nucleus. Bohr model, though offering a satisfactory model for explaining the spectra of the hydrogen atom, could not explain the spectra of multi-electron atoms. The reason for this was soon discovered. In Bohr model, an electron is regarded as a charged particle moving in a well defined circular orbit about the nucleus. The wave character of the electron is ignored in Bohr's theory. An orbit is a clearly defined path and this path can completely be defined only if both the exact position and the exact velocity of the electron at the same time are known. This is not possible according to the Heisenberg uncertainty principle. Bohr model of the hydrogen atom, therefore, not only ignores the dual behaviour of electron but also contradicts Heisenberg uncertainty principle.

Erwin Schrodinger, in 1926, proposed an equation called Schrodinger equation to describe the electron distributions in space and the allowed energy levels in atoms. This eqL1ation incorporates de Broglie's concept of wave-particle duality and is consistent with Heisenberg uncertainty principle. When Schrodinger equation is solved for the electron in a hydrogen atom, the solution gives the possible energy states the electron can occupy [and the corresponding wave function(s) (ψ) (which in fact are the mathematical functions) of the electron associated with each energy state). These quantized energy states and corresponding wave functions which are characterized by a set of three quantum numbers (principal quantum number n, azimuthal quantum number l and magnetic quantum number m_l) arise as a natural consequence in the solution of the Schrodinger equation. The restrictions on the values of these three quantum numbers also come naturally from this solution. The quantum mechanical model of the hydrogen atom Successfully predicts all aspects of the hydrogen atom spectrum including some phenomena that could not be explained by the Bohr model.

According to the quantum mechanical model of the atom, the electron distribution of an atom containing a number of electrons is divided into shells. The shells, in turn, are thought to consist of one or more subshells and subshells are assumed to be composed of one or more orbitals, which the electrons occupy. While for hydrogen and hydrogen like systems (such as He^+, Li^{2+} etc.) all the orbitals within a given shell have same energy, the energy of the orbitals in a multi-electron atom depends upon the values of n and *l*: The lower the value of (n + *l*) for an orbital, the lower is its energy. If two orbitals have the same (n + *l*) value, the orbital with lower value of n has the lower energy. In an atom many such orbitals are possible and electrons are filled in those orbitals in order of increasing energy in accordance with Pauli exclusion principle (no two electrons inan atom can have the same set of four quantum numbers) and Hund's rule of maximum multiplicity (pairing of electrons in the orbitals belonging to the same subshell does not take place until each orbital belonging to that subshell has got one electron each, i.e., is singly occupied) u. This forms the basis of the electronic structure of atoms.

QUESTION BANK

CHAPTER 1: ATOMIC STURCTURE

Short Answer Questions **(4 Marks)**

1. What are the postulates of Bohr's model of hydrogen atom?
2. Explain various series of line spectra in hydrogen atom?
3. What are the evidences in favour of dual behavior of electron?
4. Explain the significance of n, *l*, m_l and m_s quantum numbers?
5. Define atomic orbitals, write the shapes of s, p, and d orbitals?
6. Define Aufbau Principle, Pauli's exclusion principle and Hund's rule of maximum multiplicity?

CHAPTER-2

CLASSIFICATION OF ELEMENTS AND PERIODIC PROPERTIES

In this unit, we will study the historical development of the periodic table as it stands today and the modern periodic law. We will also learn how the periodic classification follows as a logical consequence of the electronic configuration of atoms. Finally, we shall inspect some of the periodic trends in the physical and chemical properties of the elements.

2.1 Why do we need to classify elements?

We know by now that the elements are the basic units of all types of matter. In 1800, only 31 elements were known. By 1865, the number of identified elements had more than doubled to 63. At present 114 elements are known. Of them, the recently discovered elements are man-made. Efforts to synthesize new elements are continuing. With such a large number of elements it is very difficult to study individually the chemistry of all these elements and their innumerable compounds individually. To ease out this problem, scientists searched for a systematic way to organize their knowledge by classifying the elements. Not only that it would rationalize known chemical facts about elements, but even predict new ones for undertaking further study.

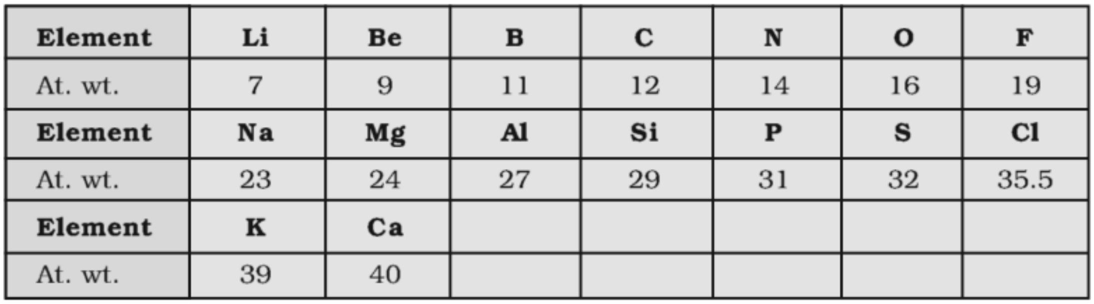
2.2 Genesis of Periodic Classification

Classification of elements into groups and development of periodic law and periodic table are the consequences of systematizing the knowledge gained by a number of scientists through their observations and experiments. The German chemist, Johann Dobereiner in early 1800's was the first to consider the idea of trends among properties of elements. By 1829 he noted a similarity among the physical and chemical properties of several groups of three elements (**Triads**). In each case, he noticed that the middle element of each of the **triads** had an atomic weight about half way between the atomic weights of the other two (Table 2.1). Also the properties of the middle element were in between those of the other two members. Since Dobereiner's relationship, referred to as the law of triads, seemed to work only for a few elements, it was dismissed as coincidence. The next reported attempt to classify elements was made by a French geologist. A.E.B.de Chancourtois in 1862. He arranged the then known elements in order of increasing atomic weights and made a cylindrical table of elements to display the periodic recurrence of properties. This also did not attract much attention. The English chemist, John Alexander Newlands in 1865 profounded the **law of Octaves**. He arranged the elements in increasing order of their atomic weights and noted that every eighth element had properties similar to the first element (Table 2.2). The relationship was just like every eighth note that resembles the first in octaves of music. Newlands's law of Octaves seemed to be true only for elements up to calcium. Although his idea was not widely accepted at that time, he, for his work, was later awarded Davy Medal in 1887 by the Royal Society, London.

Table 2.1 Dobereiner's Triads

Element	Atomic weight	Element	Atomic weight	Element	Atomic weight
Li	7	Ca	40	Cl	35.5
Na	23	Sr	88	Br	80
K	39	Ba	137	I	127

Table 2.2 Newlands's Octaves



Element	**Li**	**Be**	**B**	**C**	**N**	**O**	**F**
At. wt.	7	9	11	12	14	16	19
Element	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
At. wt.	23	24	27	29	31	32	35.5
Element	**K**	**Ca**					
At. wt.	39	40					

The Periodic Law, as we know it today owes its development to the Russian chemist, Dmitri Mendeleev (1834- 1907) and the German chemist, Lothar Meyer (1830- 1895). Working independently, both the chemists in 1869 proposed that on arranging elements in the increasing order of their atomic weights, similarities appear in physical and chemical properties at regular intervals. Lothar Meyer plotted the physical properties such as atomic volume, melting point and boiling point against atomic weight and obtained a periodically repeated pattern. Unlike Newlands, Lothar Meyer observed a change in length of that repeating pattern. By 1868, Lothar Meyer had developed a table of the elements that closely resembles the modern periodic table. However, his work was not published until after the work of Dmitri Mendeleev, the scientist who is generally credited with the development of the modern periodic table.

While Dobereiner initiated the study of periodic relationship, it was Mendeleev who was responsible for publishing the periodic law for the first time. It states as follows:

The properties of elements are periodic functions of their atomic weights.

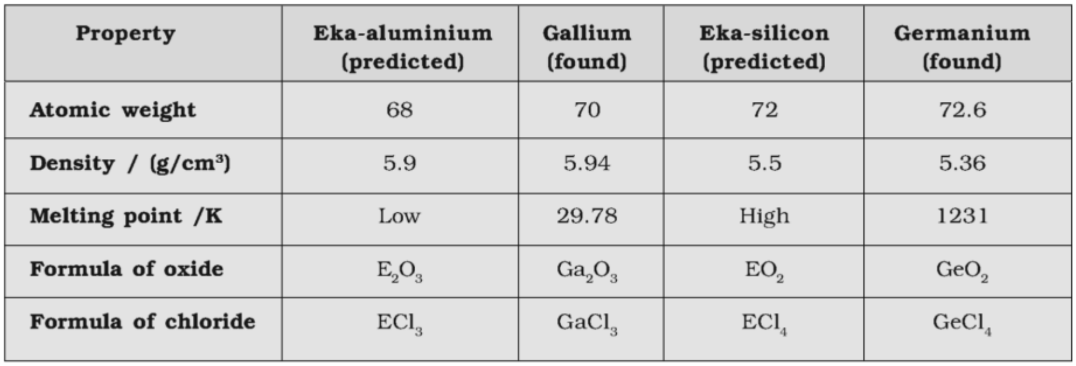
Mendeleev arranged elements in horizontal rows and vertical columns of a table in order of their increasing atomic weights in such a way that the elements with similar properties occupied the same vertical column or group. Mendeleev's system of classifying elements was more elaborate than that of Lothar Meyer's. He fully recognized the significance of periodicity and used broader range of physical and chemical properties to classify the elements. In particular, Mendeleev relied on the similarities in the empirical formulas and properties of the compounds formed by the elements. He realized that some of the elements did not fit in with his scheme of classification if the order of atomic weight was strictly followed. He ignored the order of atomic weights, thinking that the atomic measurements might be incorrect, and placed the elements with similar properties together. For example, iodine with lower atomic weight than that of tellurium (Group VI) was placed in Group VII along with fluorine, chlorine, bromine because of similarities in properties (Fig. 2. 1). At the same time, keeping his primary aim of arranging the elements of similar properties in the same group, he proposed that some of the elements were still undiscovered and therefore, left several gaps in the table. For example, both gallium and germanium were unknown at the time Mendeleev published his periodic table. He left the gap under aluminium and a gap under silicon, and called these elements Eka-aluminium and Eka-Silicon. Mendeleev predicted not only the existence of gallium and germanium, but also described some of their general physical properties. These elements were discovered later. Some of the properties predicted by Mendeleev for these elements and those found experimentally are listed in Table 2.3.

The boldness of Mendeleev's quantitative predictions and their eventual success made him and his periodic table famous. Mendeleev's periodic table published in 1905 is shown in Fig. 2. 1.

SERIES	GROUPS OF ELEMENTS								
	0	I	II	III	IV	V	VI	VII	VIII
1	-	Hydrogen H 1.008	-	-					
2	Helium He 4.0	Lithium Li 7.03	Beryllium Be 9.1	Boron B 11.0	Carbon C 12.0	Nitrogen N 14.04	Oxygen O 16.00	Fluorine F 19.0	
3	Neon Ne 19.9	Sodium Na 23.5	Magnesium Mg 24.3	Aluminium Al 27.0	Silicon Si 28.4	Phosphorus P 31.0	Sulphur S 32.06	Chlorine Cl 35.45	
4	Argon Ar 38	Potassium K 39.1	Calcium Ca 40.1	Scandium Sc 44.1	Titanium Ti 48.1	Vanadium V 51.4	Chromium Cr 52.1	Manganese Mn 55.0	Iron Fe 55.9 Cobalt Co 59 Nickel Ni 59 (Cu)
5		Copper Cu 63.6	Zinc Zn 65.4	Gallium Ga 70.0	Germanium Ge 72.3	Arsenic As 75	Selenium Se 79	Bromine Br 79.95	
6	Krypton Kr 81.8	Rubidium Rb 85.4	Strontium Sr 87.6	Yttrium Y 89.0	Zirconium Zr 90.6	Niobium Nb 94.0	Molybdenum Mo 96.0	-	Ruthenium Ru 101.7 Rhodium Rh 103.0 Palladium Pd 106.5 (Ag)
7		Silver Ag 107.9	Cadmium Cd 112.4	Indium In 114.0	Tin Sn 119.0	Antimony Sb 120.0	Tellurium Te 127.6	Iodine I 126.9	
8	Xenon Xe 128	Caesium Cs 132.9	Barium Ba 137.4	Lanthanum La 139	Cerium Ce 140	-	-	-	
9		-	-	-	-	-	-	-	
10	-	-	-	Ytterbium Yb 173	-	Tantalum Ta 183	Tungsten W 184	-	Osmium Os 191 Iridium Ir 193 Platinum Pt 194.9 (Au)
11		Gold Au 197.2	Mercury Hg 200.0	Thallium Tl 204.1	Lead Pb 206.9	Bismuth Bi 208	-	-	
12	-	-	Radium Ra 224	-	Thorium Th 232	-	Uranium U 239		
					HIGHER SALINE OXIDES				
	R	R_2O	RO	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7	RO_4
					HIGHER GASEOUS HYDROGEN COMPOUNDS				
					RH_4	RH_3	RH_2	RH	

Fig.2.1 Mendeleev's periodic table published earlier

Table 2.3 Mendeleev's Predictions for the Elements Ekaaluminium (Gallium) and Ekasilicon (Germanium)



Property	Eka-aluminium (predicted)	Gallium (found)	Eka-silicon (predicted)	Germanium (found)
Atomic weight	68	70	72	72.6
Density / (g/cm³)	5.9	5.94	5.5	5.36
Melting point /K	Low	29.78	High	1231
Formula of oxide	E_2O_3	Ga_2O_3	EO_2	GeO_2
Formula of chloride	ECl_3	$GaCl_3$	ECl_4	$GeCl_4$

2.3 Modern periodic law and the present from of the periodic table

We must bear in mind that when Mendeleev developed his **periodic table**, chemists knew nothing about the internal structure of atom. However, the beginning of the 20th century witnessed profound developments in theories about sub-atomic particles. In1913, the English physicist, Henry Moseley observed regularities in the characteristic X-ray spectra of the elements. A plot of $\sqrt{\nu}$ where ν is frequency of X-rays emitted) against atomic number (Z) gave a straight line and not the plot of $\sqrt{\nu}$ Vs atomic mass. He there by showed that the atomic number is a more fundamental property of an element than its atomic mass. Mendeleev's periodic law was, therefore, accordingly modified. This is known as the Modern periodic law and can be stated as:

'The physical and chemical properties of elements are the periodic functions of their atomic numbers.'

The periodic law revealed important analogies among the 94 naturally occurring elements (neptunium and plutonium like actinium and protactinium are also found in pitch blend, an ore of uranium). It stimulated renewed interest in Inorganic Chemistry and has carried into the present with the creation of artificially produced short-lived elements.

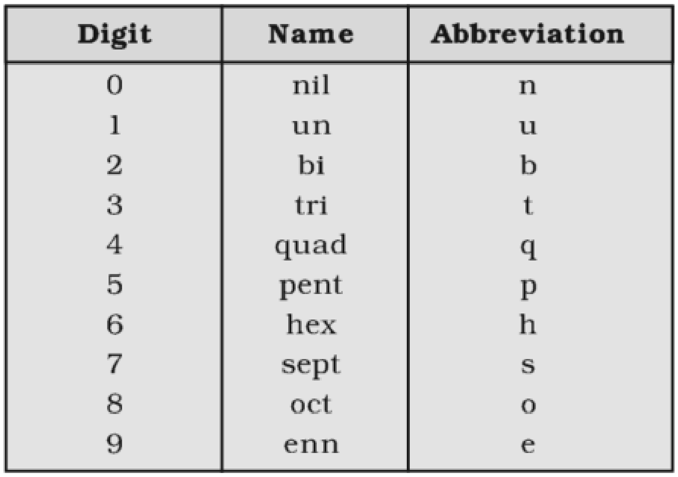
You may recall that the atomic number is equal to the nuclear charge (i.e., number of protons) or the number of electrons in a neutral atom. It is then easy to visualize the significance of quantum numbers and electronic configurations in periodicity of elements. In fact, it is now recognized that the periodic law is essentially the consequence of the periodic variation in electronic configurations, which indeed determine the physical and chemical properties of elements and their compounds.

Numerous forms of periodic table have been devised from time to time. Some forms emphasize chemical reactions and valence, whereas others stress the electronic configuration of elements. A modern version, the so-called "long form" of the periodic table of the elements (Fig.2.2), is the most convenient and widely used. The horizontal rows (which Mendeleev called series) are called periods and the vertical columns, groups. Elements having similar outer electronic configurations in their atoms are arranged in vertical columns, referred to as groups or families. According to the recommendation of International Union of Pure and Applied Chemistry (IUPAC), the groups are numbered from 1 to 18 replacing the older notation of groups IA ... VIIA, VIII, IB... VIIB and 0.

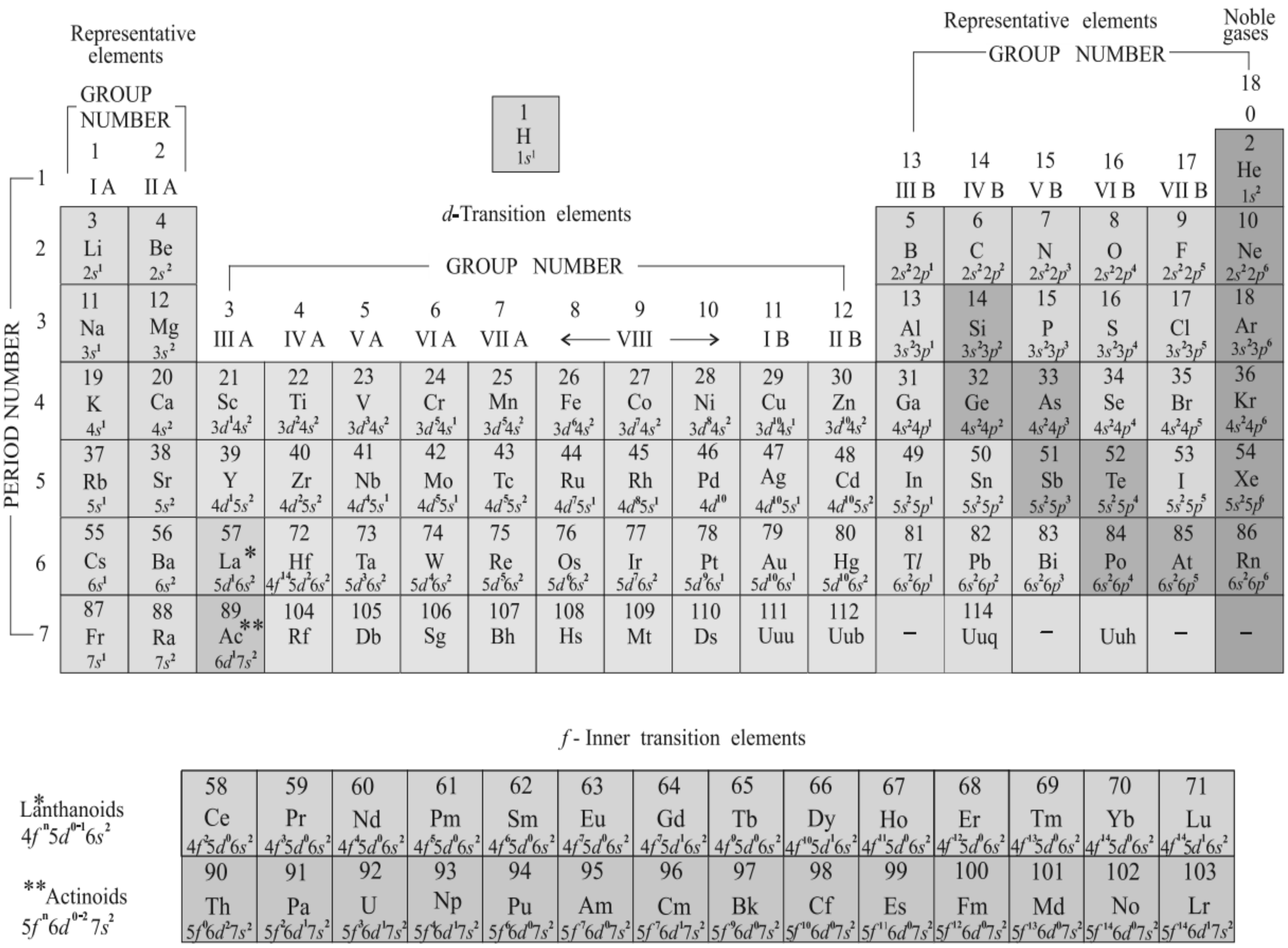
2.4 Nomenclature of elements with atomic number > 100

The naming of the new elements had been traditionally the privilege of the discoverer (or discoverers) and the suggested name was ratified by the IUPAC. In recent years this has led to some controversy. The new elements with very high atomic numbers are so unstable that only minute quantities, sometimes only a few atoms of them are obtained. Their synthesis and characterization, therefore, require highly sophisticated costly equipment and laboratory. Such work is carried out with competitive spirit only in some laboratories in the world. Scientists, before collecting the reliable data on the new element, at times get tempted to claim for its discovery. For example, both American and Soviet scientists claimed credit for discovering element 104. The Americans named it Rutherfordium whereas Soviets named it Kurchatovium. To avoid such problems, the IUPAC has made recommendation that until a new element's discovery is proved, and its name is officially recognized, a systematic nomenclature be derived directly from the atomic number of the element using the numerical roots for 0 and numbers 1-9. These are shown in Table 2.4. The roots are put together in order of digits which make up the atomic number and "ium" is added at the end. The IUPAC names for elements with Z above 100 are shown in Table 2.5.

Table 2.4 Notation for IUPAC Nomenclature of Elements



Digit	Name	Abbreviation
0	nil	n
1	un	u
2	bi	b
3	tri	t
4	quad	q
5	pent	p
6	hex	h
7	sept	s
8	oct	o
9	enn	e



Representative elements GROUP NUMBER 1 2

d-Transition elements GROUP NUMBER 3–12

Representative elements GROUP NUMBER 13–17

Noble gases 18 0

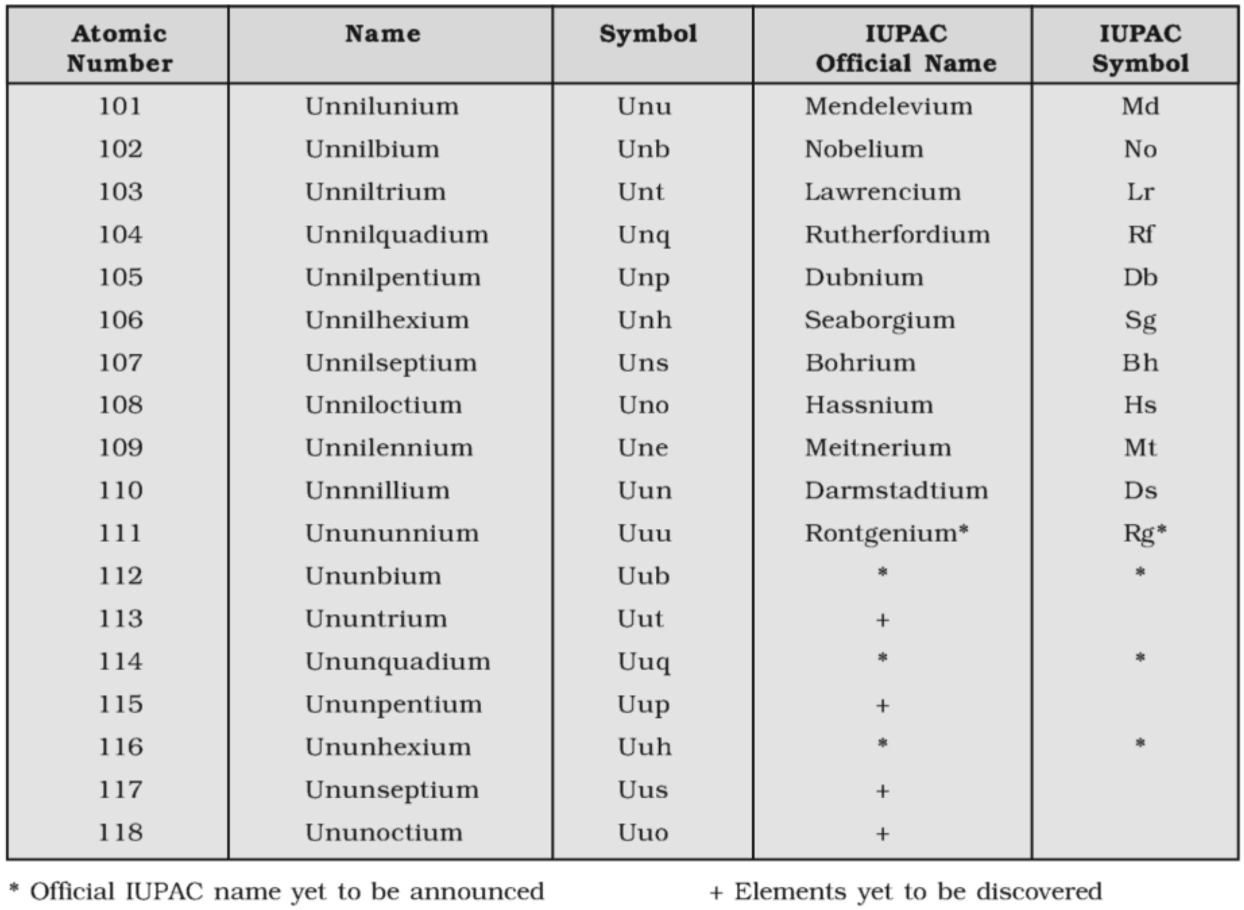
PERIOD NUMBER	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	IA	IIA	IIIA	IVA	VA	VIA	VIIA	← VIII →			IB	IIB	IIIB	IVB	VB	VIB	VIIB	0
1	1 H $1s^1$																	2 He $1s^2$
2	3 Li $2s^1$	4 Be $2s^2$											5 B $2s^22p^1$	6 C $2s^22p^2$	7 N $2s^22p^3$	8 O $2s^22p^4$	9 F $2s^22p^5$	10 Ne $2s^22p^6$
3	11 Na $3s^1$	12 Mg $3s^2$											13 Al $3s^23p^1$	14 Si $3s^23p^2$	15 P $3s^23p^3$	16 S $3s^23p^4$	17 Cl $3s^23p^5$	18 Ar $3s^23p^6$
4	19 K $4s^1$	20 Ca $4s^2$	21 Sc $3d^14s^2$	22 Ti $3d^24s^2$	23 V $3d^34s^2$	24 Cr $3d^54s^1$	25 Mn $3d^54s^2$	26 Fe $3d^64s^2$	27 Co $3d^74s^2$	28 Ni $3d^84s^2$	29 Cu $3d^{10}4s^1$	30 Zn $3d^{10}4s^2$	31 Ga $4s^24p^1$	32 Ge $4s^24p^2$	33 As $4s^24p^3$	34 Se $4s^24p^4$	35 Br $4s^24p^5$	36 Kr $4s^24p^6$
5	37 Rb $5s^1$	38 Sr $5s^2$	39 Y $4d^15s^2$	40 Zr $4d^25s^2$	41 Nb $4d^45s^1$	42 Mo $4d^55s^1$	43 Tc $4d^55s^2$	44 Ru $4d^75s^1$	45 Rh $4d^85s^1$	46 Pd $4d^{10}$	47 Ag $4d^{10}5s^1$	48 Cd $4d^{10}5s^2$	49 In $5s^25p^1$	50 Sn $5s^25p^2$	51 Sb $5s^25p^3$	52 Te $5s^25p^4$	53 I $5s^25p^5$	54 Xe $5s^25p^6$
6	55 Cs $6s^1$	56 Ba $6s^2$	57 La* $5d^16s^2$	72 Hf $4f^{14}5d^26s^2$	73 Ta $5d^36s^2$	74 W $5d^46s^2$	75 Re $5d^56s^2$	76 Os $5d^66s^2$	77 Ir $5d^76s^2$	78 Pt $5d^96s^1$	79 Au $5d^{10}6s^1$	80 Hg $5d^{10}6s^2$	81 Tl $6s^26p^1$	82 Pb $6s^26p^2$	83 Bi $6s^26p^3$	84 Po $6s^26p^4$	85 At $6s^26p^5$	86 Rn $6s^26p^6$
7	87 Fr $7s^1$	88 Ra $7s^2$	89 Ac** $6d^17s^2$	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Uuu	112 Uub	–	114 Uuq	–	Uuh	–	–

f - Inner transition elements

*Lanthanoids $4f^n5d^{0-1}6s^2$	58 Ce $4f^25d^06s^2$	59 Pr $4f^35d^06s^2$	60 Nd $4f^45d^06s^2$	61 Pm $4f^55d^06s^2$	62 Sm $4f^65d^06s^2$	63 Eu $4f^75d^06s^2$	64 Gd $4f^75d^16s^2$	65 Tb $4f^95d^06s^2$	66 Dy $4f^{10}5d^16s^2$	67 Ho $4f^{11}5d^06s^2$	68 Er $4f^{12}5d^06s^2$	69 Tm $4f^{13}5d^06s^2$	70 Yb $4f^{14}5d^06s^2$	71 Lu $4f^{14}5d^16s^2$
**Actinoids $5f^n6d^{0-2}7s^2$	90 Th $5f^06d^27s^2$	91 Pa $5f^26d^17s^2$	92 U $5f^36d^17s^2$	93 Np $5f^46d^17s^2$	94 Pu $5f^66d^07s^2$	95 Am $5f^76d^07s^2$	96 Cm $5f^76d^17s^2$	97 Bk $5f^96d^07s^2$	98 Cf $5f^{10}6d^07s^2$	99 Es $5f^{11}6d^07s^2$	100 Fm $5f^{12}6d^07s^2$	101 Md $5f^{13}6d^07s^2$	102 No $5f^{14}6d^07s^2$	103 Lr $5f^{14}6d^17s^2$

Fig.2. 2 Long form of the periodic table of the elements with their atomic numbers and ground state outer electronic configurations. The groups are numbered 1-18 in accordance with the 1984 IUPAC recommendations. This notation replaces the old numbering scheme of IA-VITA, VIII, IB-VIIB and 0 for the elements.

Table 2.5 Nomenclature of Elements with Atomic Number Above 100



Atomic Number	Name	Symbol	IUPAC Official Name	IUPAC Symbol
101	Unnilunium	Unu	Mendelevium	Md
102	Unnilbium	Unb	Nobelium	No
103	Unniltrium	Unt	Lawrencium	Lr
104	Unnilquadium	Unq	Rutherfordium	Rf
105	Unnilpentium	Unp	Dubnium	Db
106	Unnilhexium	Unh	Seaborgium	Sg
107	Unnilseptium	Uns	Bohrium	Bh
108	Unniloctium	Uno	Hassnium	Hs
109	Unnilennium	Une	Meitnerium	Mt
110	Unnnillium	Uun	Darmstadtium	Ds
111	Unununnium	Uuu	Rontgenium*	Rg*
112	Ununbium	Uub	*	*
113	Ununtrium	Uut	+	
114	Ununquadium	Uuq	*	*
115	Ununpentium	Uup	+	
116	Ununhexium	Uuh	*	*
117	Ununseptium	Uus	+	
118	Ununoctium	Uuo	+	

* Official IUPAC name yet to be announced + Elements yet to be discovered

Thus, the new element first gets a temporary name, with symbol consisting of three letters. Later permanent name and symbol are given by a vote of IUPAC representatives from each country. The permanent name might reflect the country (or state of the country) in which the element was discovered, or pay tribute to a notable scientist. As of now, elements with atomic numbers up to 112, 114 and 116 have been discovered. Elements with atomic numbers 113, l l5, 117 and 118 are not yet known.

2.5 Electronic Configurations of Elements and the Periodic Table

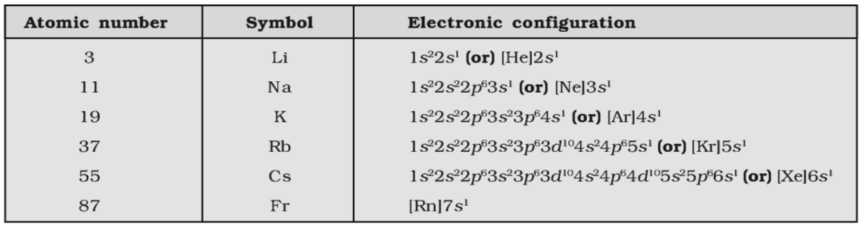
In the preceding unit we have learnt that an electron in an atom is characterized by a set of four quantum numbers and the principal quantum number (n) defines the main energy level known as shell. We have also studied about the filling of electrons into different sub shells, also referred to as orbital’s (s, p, d, f) in an atom. The distribution of electrons into orbital’s of an atom is called its electronic configuration. An element's location in the periodic table reflects the quantum numbers of the last orbital filled. In this section we will observe a direct connection between the electronic configurations of the elements and the long form of the periodic table.

(a) Electronic Configurations in Periods

The period indicates the value of n for the outermost or valence shell. In other words, successive period in the periodic table is associated with the filling of the next higher principal energy level (n = 1, n = 2, etc.). It can be readily seen that the number of elements in each period is twice the number of atomic orbital's available in the energy level that is being filled. The first period (n = 1) starts with the filling of the lowest level (1s) and therefore has two elements -hydrogen (ls^1) and helium (ls^2) when the first shell (K) is completed. The second period (n = 2) starts with lithium and the third electron enters the 2s orbital. The next element, beryllium has four electrons and has the electronic configuration $1s^2 2s^2$. Starting from the next element boron, the 2p orbital's are filled with electrons when the L shell is completed at neon ($2s^2 2p^6$). Thus there are 8 elements in the second period. The third period (n = 3) begins at sodium, and the added electron enters a 3s orbital. Successive filling of 3s and 3p orbital's gives rise to the third period of 8 elements from sodium to argon. The fourth period (n = 4) starts at potassium, and the added electrons fill up the 4s orbital. Now you may note that before the 4p orbital is filled, filling up of 3d orbital's becomes energetically favorable and we come across the so called 3d transition series of elements. This starts from scandium (Z= 21) which has the electronic configuration $3d^1 4s^2$. The 3d orbital's are filled at zinc (Z=30) with electronic configuration $3d^{10} 4s^2$. The fourth period ends at krypton with the filling up of the 4p orbital's. Altogether we have 18 elements in this fourth period. The fifth period (n = 5) beginning with rubidium is similar to the fourth period and contains the 4d transition series starting at yttrium (Z = 39) . This period ends at xenon with the filling up of the 5p orbital's. The sixth period (n = 6) contains 32 elements and successive electrons enter 6s, 4f, 5d and 6p orbital's, in the order filling up of the 4f orbital's begins with cerium (Z = 58) and ends at lutetium (Z= 71) to give the 4f-inner transition series which is called the lanthanide series. The seventh period (n = 7) is similar to the sixth period with the successive filling up of the 7s, 5f, 6d and 7p orbital's and includes most of the man- made radioactive elements. This period will end at the element with atomic number 118 which would belong to the noble gas family. Filling up of the 5f orbital's after actinium (Z= 89) gives the 5f-inner transition series known as the actinide series. The 4f- and 5f-inner transition series of elements are placed separately in the periodic table to maintain its structure and to preserve the principle of classification by keeping elements with similar properties in a single column.

(b) Groupwise Electronic Configurations

Elements in the same vertical column or group have similar valence shell electronic configurations, the same number of electrons in the outer orbital's, and similar properties. For example, the Group 1 elements (alkali metals) all have ns valence shell electronic configuration as shown below.



Atomic number	Symbol	Electronic configuration
3	Li	$1s^2 2s^1$ **(or)** $[He] 2s^1$
11	Na	$1s^2 2s^2 2p^6 3s^1$ **(or)** $[Ne] 3s^1$
19	K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ **(or)** $[Ar] 4s^1$
37	Rb	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$ **(or)** $[Kr] 5s^1$
55	Cs	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^1$ **(or)** $[Xe] 6s^1$
87	Fr	$[Rn] 7s^1$

Thus it can be seen that the properties of an element have periodic dependence upon its atomic number and not on relative atomic mass.

2.6 Electronic configuration and types of elements: s-, p-, d-, f- Blocks

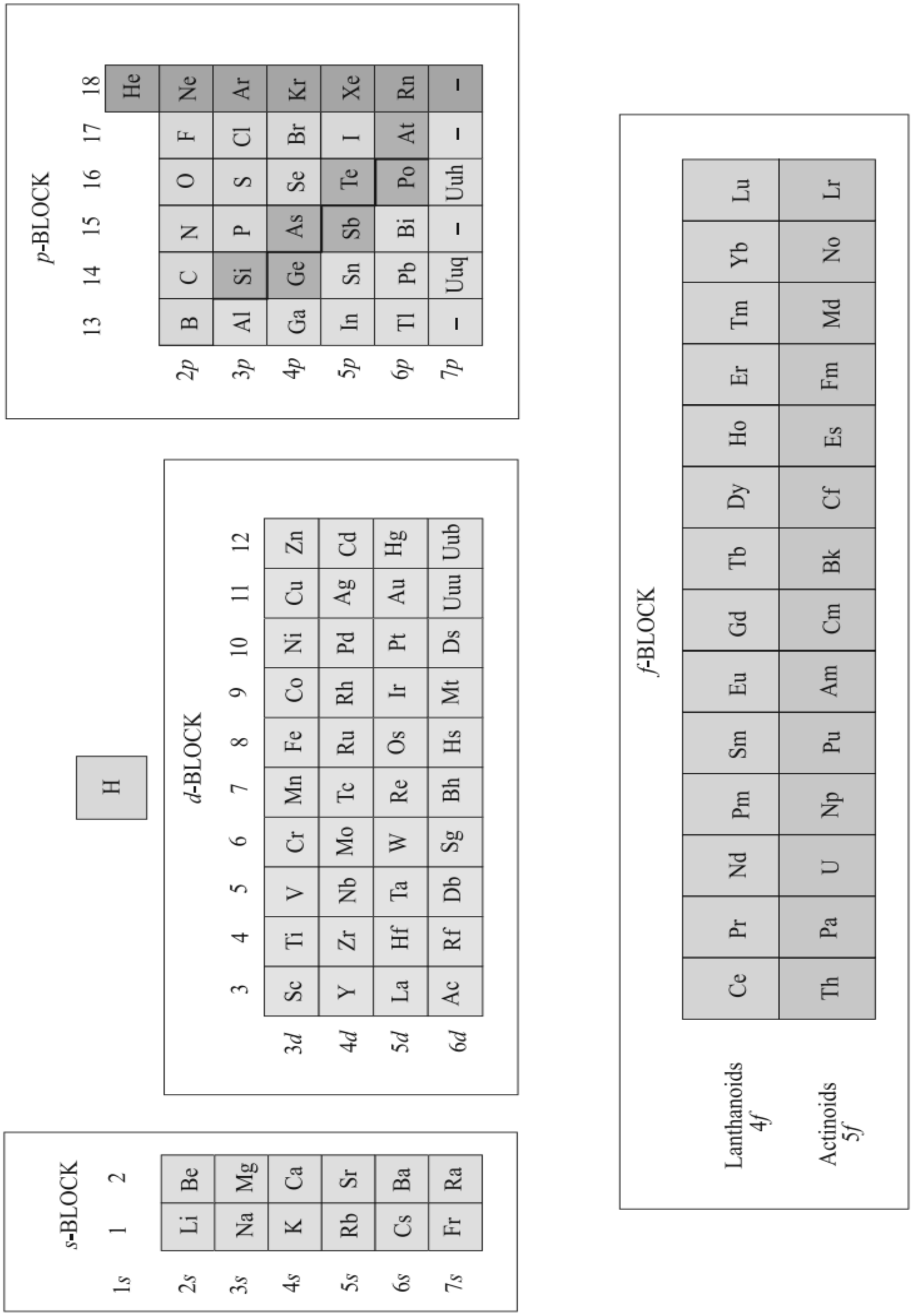
The Aufbau (build up) principle and the electronic configuration of atoms provide a theoretical foundation for the periodic classification. The elements in a vertical column of the periodic table constitute a group or family and exhibit similar chemical behavior. This similarity arises because these elements have the same number and same distribution of electrons in their outermost orbital. We can classify the elements into four blocks viz., s-block, p-block, d-block and f-block depending on the type of atomic orbital's that are being filled with electrons. This is illustrated in Fig. 2.3. We notice two exceptions to this categorization. Strictly, helium belongs to the s-block but its positioning in the p-block along with other group 18 elements is justified because it has a completely filled valence shell (1s) and as a result, exhibits properties characteristic of other noble gases. The other exception is hydrogen. It has a lone s-electron and hence can be placed in group 1 (alkali metals). It can also gain an electron to achieve a noble gas arrangement and hence it can behave similar to a group 17 (halogen family) elements. Because it is a special case, we shall place hydrogen separately at the top of the Periodic Table as shown in Fig. 2.2 and Fig. 2.3. We will briefly discuss the salient features of the four types of elements marked in the Periodic Table. More about these elements will be discussed later. During the description of their features certain terminology has been used which has been classified in section 2.7.

2.6.1 The s-Block Elements

The elements of Group 1 (alkali metals) and Group 2 (alkaline earth metals) which have ns^1 and ns^2 outermost electronic configuration belong to the s-Block Elements. They are all reactive metals with low ionization enthalpies. They lose the outermost electron (s) readily to form 1+ ion (in the case of alkali metals) or 2+ ion (in the case of alkaline earth metals). The metallic character and the reactivity increase as we go down the group. Because of high reactivity they are never found pure in nature. The compounds of the s-block elements, with the exception of those of lithium and beryllium are predominantly ionic.

2.6.2 The p-Block Elements

The p-Block Elements comprise those belonging to Group 13 to 18 and these together with the s-Block Elements are called the Representative Elements or Main Group Elements. The outermost electronic configuration varies from $ns^2\ np^1$ to ns^2np^6 in each period. At the end of each period is a noble gas element with a closed valence shell ns^2np^6 configuration. All the orbitals in the valence shell of the noble gases are completely filled by electrons and it is very difficult to alter this stable arrangement by the addition or removal of electrons. The noble gases thus exhibit very low chemical reactivity. Preceding the noble gas family are two chemically important groups of non-metals. They are the halogens (Group 17) and the chalcogens (Group 16). These two groups of elements have high negative electron gain enthalpies and readily add one or two electrons respectively to attain the stable noble gas configuration. The non-metallic character increases as we move from left to right across a period and metallic character increases as we go down the group.



s-BLOCK

	1	2
1*s*	H	
2*s*	Li	Be
3*s*	Na	Mg
4*s*	K	Ca
5*s*	Rb	Sr
6*s*	Cs	Ba
7*s*	Fr	Ra

d-BLOCK

	3	4	5	6	7	8	9	10	11	12
3*d*	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
4*d*	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
5*d*	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
6*d*	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Uuu	Uub

p-BLOCK

	13	14	15	16	17	18
						He
2*p*	B	C	N	O	F	Ne
3*p*	Al	Si	P	S	Cl	Ar
4*p*	Ga	Ge	As	Se	Br	Kr
5*p*	In	Sn	Sb	Te	I	Xe
6*p*	Tl	Pb	Bi	Po	At	Rn
7*p*	–	Uuq	–	Uuh	–	–

f-BLOCK

Lanthanoids 4*f*	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Actinoids 5*f*	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Fig. 2.3 The types of elements in the Periodic Table based on the orbitals that are being filled

2.6.3 The d-Block Elements (Transition Elements)

These are the elements of Group 3 to 12 in the centre of the Periodic Table. These are characterized by the filling of inner d orbitals by electrons and are therefore referred to as d-Block Elements. These elements have the general outermost electronic configuration $(n-1)d^{1-10}\,ns^{0-2}$. They are all metals. They mostly form coloured ions, exhibit variable valence (oxidation states), paramagnetic and oftenly used as catalysts. However, Zn, Cd and Hg which have the electronic configuration, $(n-1)\,d^{10}ns^2$ do not show most of the properties of transition elements. In a way, transition metals form a bridge between the chemically active metals of s-block elements and the less active elements of Groups 13 and 14 and thus take their familiar name "Transition Elements".

2.6.4 The f-Block Elements (Inner-Transition Elements)

The two rows of elements at the bottom of the Periodic Table, called the Lanthanides, Ce(Z = 58) - Lu (Z = 71) and Actinoids, Th (Z = 90) - Lr (Z = 103) are characterised by the outer electronic configuration $(n-2)f^{1-14}\,(n-l)d^{0-1}\,ns^2$. The last electron added to each element is filled in f orbital. These two series of elements are hence called the Inner- Transition Elements (f-Block Elements). They are all metals.

2.6.5 Metals, Non-metals and Metalloids

In addition to displaying the classification of elements into s-, p-, d-, and f-blocks, Fig. 2.3 shows another broad classification of elements based on their properties. The elements can be divided into Metals and Non-Metals. Metals comprise more than 78% of all known elements and appear on the left side of the Periodic Table. Metals are usually solids at room temperature [Mercury is an exception; gallium and cesium also have very low melting points (303K and 302K, respectively). Metals usually have high melting and boiling points. They are good conductors of heat and electricity. They are malleable (can be flattened into thin sheets by hammering) and ductile (can be drawn into wires). In contrast, non-metals are located at the top right hand side of the Periodic Table. In fact, in a horizontal row, the property of elements changes from metallic on the left to non-metallic on the right. Non- metals are usually solids or gases at room temperature with low melting and boiling points (boron and carbon are exceptions) . They are poor conductors of heat and electricity. Most non- metallic solids are brittle and are neither malleable nor ductile. The elements become more metallic as we go down a group; the non-metallic character increases as one goes from left to right across the Periodic Table. The change from metallic to non-metallic character is not abrupt as shown by the thick zig-zag line in Fig. 2.3. The elements (e.g., silicon, germanium, arsenic, antimony and tellurium) bordering this line and running diagonally across the Periodic Table show properties that are characteristic of both metals and non-metals. These elements are called Semi-metals or Metalloids.

2.7 Periodic Trends in Properties of Elements

There are many observable patterns in the physical and chemical properties of elements as we descend in a group or move across a period in the Periodic Table. For example, within a period, chemical reactivity tends to be high in Group 1 metals, lower in elements towards the middle of the table, and increases to a maximum in the Group 17 non-metals. Likewise within a group of representative metals (say alkali metals) reactivity increases on moving down the group, whereas within a group of non-metals (say halogens), reactivity decreases down the group. But why do the properties of elements follow these trends? And how can we explain periodicity? To answer these questions, we must look into the theories of atomic structure and properties of the atom. In this section we shall discuss the periodic trends in certain physical and chemical properties and try to explain them in terms of number of electrons and energy levels.

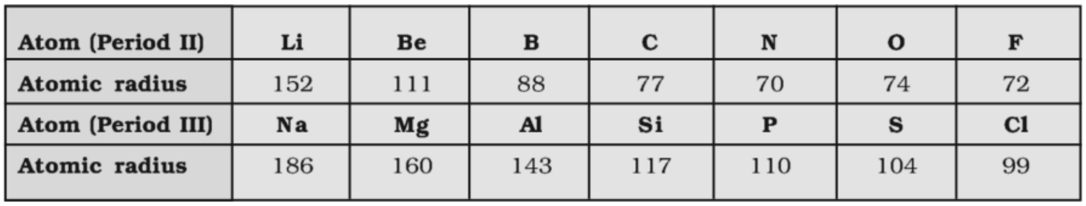
2.7.1 Trends in Physical Properties

There are numerous physical properties of elements such as melting and boiling points, heats of fusion and vaporization, energy of atomization, etc. which show periodic variations. However, we shall discuss the periodic trends with respect to atomic and ionic radii, ionization enthalpy, electron gain enthalpy and electronegativity.

(a) Atomic Radius

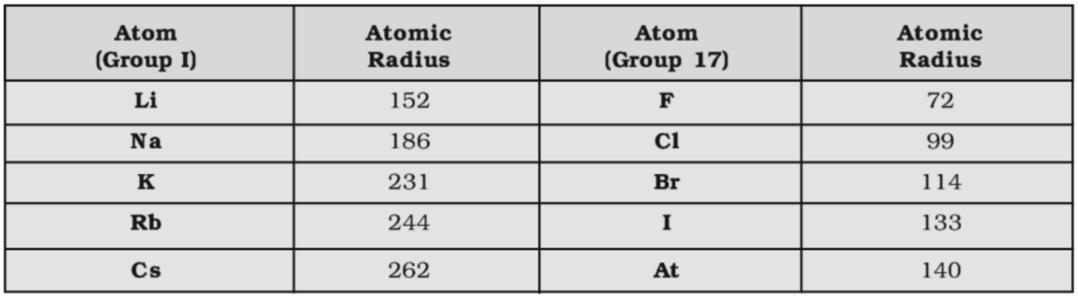
You can very well imagine that finding the size of an atom is a lot more complicated than measuring the radius of a ball. Do you know why? Firstly, because the size of an atom (1.2 A i.e.,1.2xl0^{-10} m in radius) is very small. Secondly, since the electron cloud surrounding the atom does not have a sharp boundary, the determination of the atomic size cannot be precise. In other words, there is no practical way by which the size of an individual atom can be measured. However, an estimate of the atomic size can be made by knowing the distance between the atoms in the combined state. One practical approach to estimate the size of an atom of a non -metallic element is to measure the distance between two atoms when they are bound together by a single bond in a covalent molecule and from this value, the "Covalent Radius" of the element can be calculated. For example, the bond distance in the chlorine molecule (Cl_2) is 198 pm and half this distance (99 pm). is taken as the atomic radius of chlorine. For metals, we define the term "Metallic Radius" which is taken as half the inter nuclear distance separating the metal cores in the metallic crystal. For example, the distance between two adjacent copper atoms in solid copper is 256 pm; hence the metallic radius of copper is assigned a value of 128pm. For simplicity, in this book, we use the term Atomic Radius to refer to both covalent and metallic radius depending on whether the element is a non-metal or a metal. Atomic radii can be measured by X- ray or other spectroscopic methods. The atomic radii of a few elements are listed in Table 2.6. Two trends are obvious. We can explain these trends in terms of nuclear charge and energy level. The atomic size generally decreases across a period as illustrated in Fig. 2.4(a) for the elements of the second period. It is because within the period the outer electron s are in the same valence shell and the effective nuclear charge increases as the atomic number increases resulting in the increased attraction of electrons to the nucleus. Within a family or vertical column of the periodic table, the atomic radius increases regularly with atomic number as illustrated in Fig. 2.4(b). For alkali metals and halogens, as we descend the groups, the principal quantum number (n) increases and the valence electrons are farther from the nucleus. This happens because the inner energy levels are filled with electrons, which serve to shield the outer electrons from the pull of the nucleus. Consequently the size of the atom increases as reflected in the atomic radii.

Table 2.6(a) Atomic Radii/pmAcross the Periods



Atom (Period II)	**Li**	**Be**	**B**	**C**	**N**	**O**	**F**
Atomic radius	152	111	88	77	70	74	72
Atom (Period III)	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
Atomic radius	186	160	143	117	110	104	99

Table 2.6(b) Atomic Radii/pm Down a Family



Atom (Group I)	Atomic Radius	Atom (Group 17)	Atomic Radius
Li	152	**F**	72
Na	186	**Cl**	99
K	231	**Br**	114
Rb	244	**I**	133
Cs	262	**At**	140

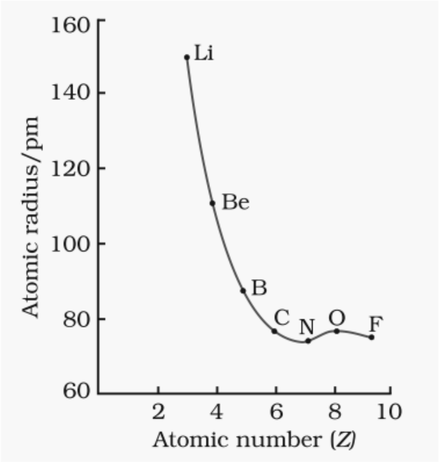


Fig.2.4 (a) Variation of atomic radius with atomic number across the second period

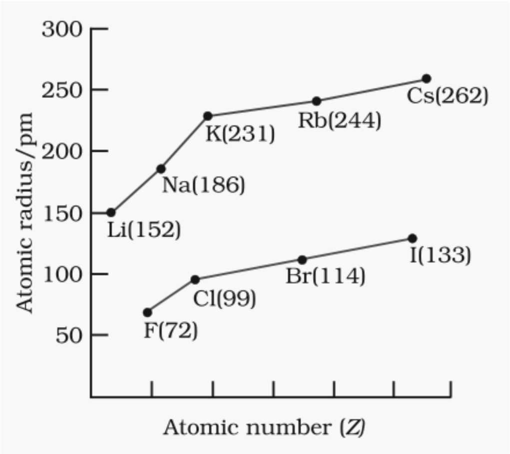


Fig. 2.4(b) Variation of atomic radius with atomic number for alkali metals and halogens

Note that the atomic radii of noble gases are not considered here. Being mono atomic, their (non-bonded radii) values are very large. In fact radii of noble gases should be compared not with the covalent radii but with the Vander Waals radii of other elements.

(b) Ionic Radius

The removal of an electron from an atom results in the formation of a cation, whereas gain of an electron leads to an anion. The ionic radii can be estimated by measuring the distances between cation and anion in ionic crystals. In general, the ionic radii of elements exhibit the same trend as the atomic radii. A cation is smaller than its parent atom because it has fewer electrons while its nuclear charge remains the same. The size of an anion will be larger than that of the parent atom because the addition of one or more electrons would result in increased repulsion among the electrons and a decrease in effective nuclear charge. For example, the ionic radius of fluoride ion (F^-) is 136 pm whereas the atomic radius of fluorine is only 72 pm. On the other hand, the atomic radius of sodium is 186 pm compared to the ionic radius of 95 pm for Na^+.

When we find some atoms and ions which contain the same number of electrons, we call them isoelectronic species. For example, 0^{2-},F^-,Na^+ and Mg^{2+} have the same number of electrons (10). Their radii would be different because of their different nuclear charges. The cation with the greater positive charge will have a smaller radius because of the greater attraction of the electrons to the nucleus. Anion with the greater negative charge will have the larger radius. In this case, the net repulsion of the electrons will outweigh the nuclear charge and the ion will expand in size.

(c) Ionization Enthalpy

A quantitative measure of the tendency of an element to lose electron is given by its Ionization Enthalpy. It represents the energy required to remove an electron from an isolated gaseous atom (X) in its ground state. In other words, the first ionization enthalpy for an element X is the enthalpy change ($\Delta_i H$) for the reaction depicted in equation 2.1.

$$X_{(g)} \rightarrow X^{+}_{(g)} + e^{-} \qquad (2.1)$$

The ionization enthalpy is expressed in units of kJ mol^{-1}. We can define the second ionization enthalpy as the energy required to remove the second most loosely bound electron; it is the energy required to carry out the reaction shown in equation 2.2.

$$X^{+}_{(g)} \rightarrow X^{2+}_{(g)} + e^{-} \qquad (2.2)$$

Energy is always required to remove electrons from an atom and hence ionization enthalpies are always positive. The second ionization enthalpy will be higher than the first ionization enthalpy because it is more difficult to remove an electron from a positively charged ion than from a neutral atom. In the same way the third ionization enthalpy will be higher than the second and so on. The term "ionization enthalpy", if not qualified is taken as the first ionization enthalpy.

The first ionization enthalpies of elements having atomic numbers up to 60 are plotted in Fig. 2.5. The periodicity of the graph is quite striking. You will find maxima at the noble gases which have closed electron shells and very stable electron configurations. On the other hand, minima occur at the alkali metals and their low ionization enthalpies can be correlated with their high reactivity. In addition, you will notice two trends the first ionization enthalpy generally increases as we go across a period and decreases as we descend in a group. These trends are illustrated in Figs. 2.6(a) and 2.6(b) respectively for the elements of the second period and the first group of the periodic table. You will appreciate that the ionization enthalpy and atomic radius are closely related properties. To understand these trends, we have to consider two factors: (i) the attraction of electrons towards the nucleus, and (ii) the repulsion of electrons from each other. The effective nuclear charge experienced by a valence electron in an atom will be less than the actual charge on the nucleus because of "shielding" or "screening" of the valence electron from the nucleus by the intervening core electrons. For example, the 2s electron in lithium is shielded from the nucleus by the inner core of ls electrons. As a result, the valence electron experiences a net positive charge which is less than the actual charge of +3. In general, shielding is effective when the orbitals in the inner shells are completely filled. This situation occurs in the case of alkali metals which have a lone ns-outermost electron preceded by a noble gas electronic configuration.

When we move from lithium to fluorine across the second period, successive electrons are added to orbital’s in the same principal quantum level and the shielding of the nuclear charge by the inner core of electrons does not increase very much to compensate for the increased attraction of the electron to the nucleus. Thus, across a period, increasing nuclear charge outweighs the shielding. Consequently, the outermost electrons are held more and more tightly and the ionization enthalpy increases across a period.

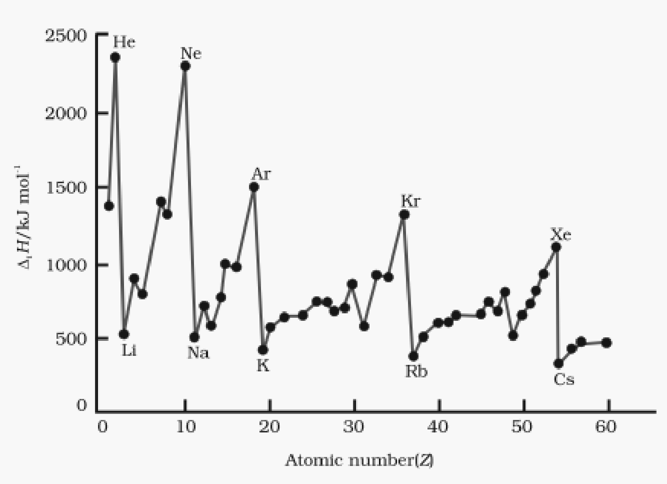


Fig.2.5 Variation of first ionization enthalpies ($\Delta_i H$) with atomic number for elements with Z = 1 to 60

As we go down a group, the outermost electron being increasingly farther from the nucleus, there is an increased shielding of the nuclear charge by the electrons in the inner levels. In this case, increase in shielding outweighs the increasing nuclear charge and the removal of the outermost electron requires less energy down a group.

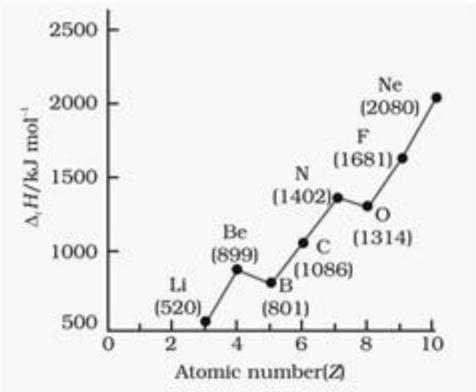


Fig. 2.6 (a)

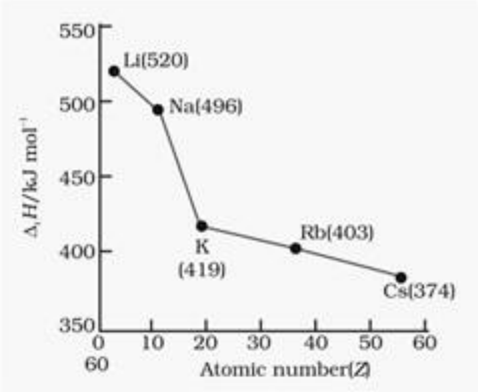


Fig. 2.6 (b)

Fig.2.6(a) First ionization enthalpies ($\Delta_i H$) of elements of the second period as a function of atomic number (Z) and Fig. 2.6(b) $\Delta_i H$ of alkali metals as a function of Z.

From Fig. 3.6(a), you will also notice that the first ionization enthalpy of boron (Z= 5) is slightly less than that of beryllium (Z = 4) even though the former has a greater nuclear charge. When we consider the same principal quantum level, an s-electron is attracted to the nucleus more than a p-electron. In beryllium, the electron removed during the ionization is an s-electron whereas the electron removed during ionization of boron is a p-electron. The penetration of a 2s electron to the nucleus is more than that of a 2p electron; hence the 2p electron of boron is more shielded from the nucleus by the inner core of electrons than the 2s electrons of beryllium. Therefore, it is easier to remove the 2p-electron from boron compared to the removal of a 2s electron from beryllium. Thus, boron has a smaller first ionization enthalpy than beryllium. Another "anomaly" is the smaller first ionization enthalpy of oxygen compared to nitrogen. This arises because in the nitrogen atom, three 2p electrons reside in different atomic orbitals (Hund's rule) whereas in the oxygen atom, two of the four 2p electrons must occupy the same 2p orbital resulting in increased electron-electron repulsion. Consequently, it is easier to remove the fourth 2p-electron from oxygen than it is, to remove one of the three 2p-electrons from nitrogen.

(d) Electron Gain Enthalpy

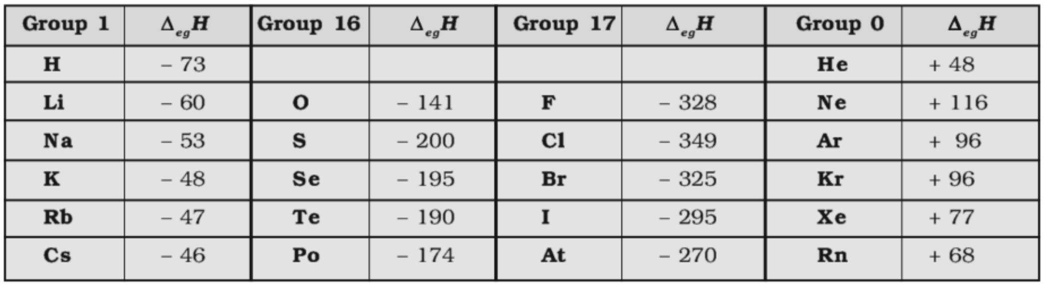
When an electron is added to a neutral gaseous atom (X) to convert it into a negative ion , the enthalpy change accompanying the process is defined as the Electron Gain Enthalpy ($\Delta_{eg}\mathrm{H}$). Electron gain enthalpy provides a measure of the ease with which an atom adds an electron

to form anion as represented by equation 2.3.

$$X_{(g)} + e^{-} \rightarrow X^{-}_{(g)} \qquad (2.3)$$

Depending on the element, the process of adding an electron to the atom can be either endothermic or exothermic. For many elements energy is released when an electron is added to the atom and the electron gain enthalpy is negative. For example, group 17 elements (the halogens) have very high negative electron gain enthalpies because they can attain stable noble gas electronic configurations by picking up an electron. On the other hand, noble gases have large positive electron gain enthalpies because the electron has to enter the next higher principal quantum level leading to a very unstable electronic configuration. It may be noted that electron gain enthalpies have large negative values toward the upper right of the periodic table preceding the noble gases.

Table 2.7 Electron Gain Enthalpies / (kJ mol^{-1} of Some Main Group Elements



Group 1	$\Delta_{eg}H$	Group 16	$\Delta_{eg}H$	Group 17	$\Delta_{eg}H$	Group 0	$\Delta_{eg}H$
H	– 73					**He**	+ 48
Li	– 60	**O**	– 141	**F**	– 328	**Ne**	+ 116
Na	– 53	**S**	– 200	**Cl**	– 349	**Ar**	+ 96
K	– 48	**Se**	– 195	**Br**	– 325	**Kr**	+ 96
Rb	– 47	**Te**	– 190	**I**	– 295	**Xe**	+ 77
Cs	– 46	**Po**	– 174	**At**	– 270	**Rn**	+ 68

The variation in electron gain enthalpies of elements is less systematic than for ionization enthalpies. As a general rule, electron gain enthalpy becomes more negative with increase in the atomic number across a period. The effective nuclear charge increases from left to right across a period and consequently it will be easier to add an electron to a smaller atom since the added electron on an average would be closer to the positively charged nucleus. We should also expect electron gain enthalpy to become less negative as we go down a group because the size of the atom increases and the added electron would be farther from the nucleus. This is generally the case (Table 2.7). However, electron gain enthalpy of O or F is less than that of the succeeding element. This is because when an electron is added to O or F, the added electron goes to the smaller n = 2 quantum level and suffers significant repulsion from the other electrons present in this level. For the n = 3 quantum level (S or CI), the added electron occupies a larger region of space and the electron-electron repulsion is much less.

(e) Electronegativity

A qualitative measure of the ability of an atom in a chemical compound to attract shared electrons to itself is called electronegativity. Unlike ionization enthalpy and electron gain enthalpy, it is not a measureable quantity. However, a number of numerical scales of electronegativity of elements viz., Pauling scale, Mulliken-Jaffe scale, Allred-Rochow scale have been developed. The one which is the most widely used is the Pauling scale. Linus Pauling, an American scientist, in 1922 assigned arbitrarily a value of 4.0 to fluorine, the element considered to have the greatest ability to attract electrons. Approximate values for the electronegativity of a few elements are given in Table 2.8(a)

The electronegativity of any given element is not constant; it varies depending on the element to which it is bound. Though it is not a measurable quantity, it does provide a means of predicting the nature of force that holds a pair of atoms together - a relationship that you will explore later.

Electronegativity generally increases across a period from left to right (say from lithium to fluorine) and decrease down a group (say from fluorine to astatine) in the periodic table. How can these trends to be explained? Can the electronegativity be related to atomic radii, which tend to decrease across each period from left to right, but increase down each group? The attraction between the outer (or valence) electrons and the nucleus increases as the atomic radius decreases in a period. The electronegativity also increases. On the same account electronegativity values decrease with the increase in atomic radii down a group. The trend is similar to that of ionization enthalpy.

Knowing the relationship between electronegativity and atomic radius, can you now visualize the relationship between electronegativity and non-metallic properties. Non-metallic elements have strong tendency to gain electrons. Therefore, electronegativity is directly related to those non-metallic properties of elements. It can be further extended to say that the electronegativity is inversely related to the metallic properties of elements. Thus, the increase in electronegativities across a period is accompanied by an increase in non-metallic properties (or decrease in metallic properties) of elements. Similarly, the decrease in electronegativity down a group is accompanied by a decrease in non-metallic properties (or increase in metallic properties) of elements. All these periodic trends are summarised in figure 2.7.

Table 2.8(a) Electronegativity Values (on Pauling scale) Across the Periods

Atom (Period II)	**Li**	**Be**	**B**	**C**	**N**	**O**	**F**
Electronegativity	1.0	1.5	2.0	2.5	3.0	3.5	4.0
Atom (Period III)	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
Electronegativity	0.9	1.2	1.5	1.8	2.1	2.5	3.0

Table 2.8(b) Electronegativity Values (on Pauling scale) Down a Family

Atom (Group I)	**Electronegativity Value**	**Atom (Group 17)**	**Electronegativity Value**
Li	1.0	**F**	4.0
Na	0.9	**Cl**	3.0
K	0.8	**Br**	2.8
Rb	0.8	**I**	2.5
Cs	0.7	**At**	2.2

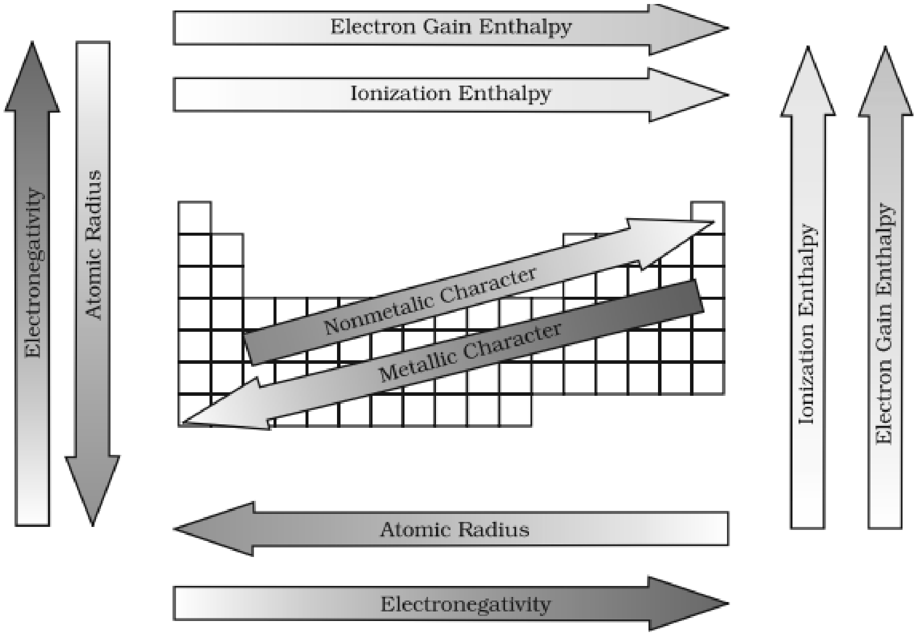


Fig. 2.7 The periodic trends of elements in the periodic table

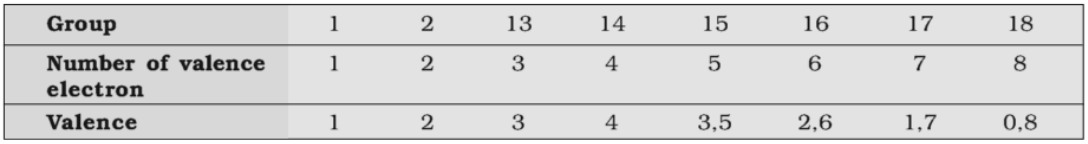
2.7.2 Periodic Trends in Chemical Properties

Most of the trends in chemical properties of elements, such as diagonal relationships, inert pair effect, effects of lanthanide contraction etc. will be dealt with along the discussion of each group in later units. In this section we shall study the periodicity of the valence state shown by elements and the anomalous properties of the second period elements (from lithium to fluorine).

(a) Periodicity of Valence or Oxidation States

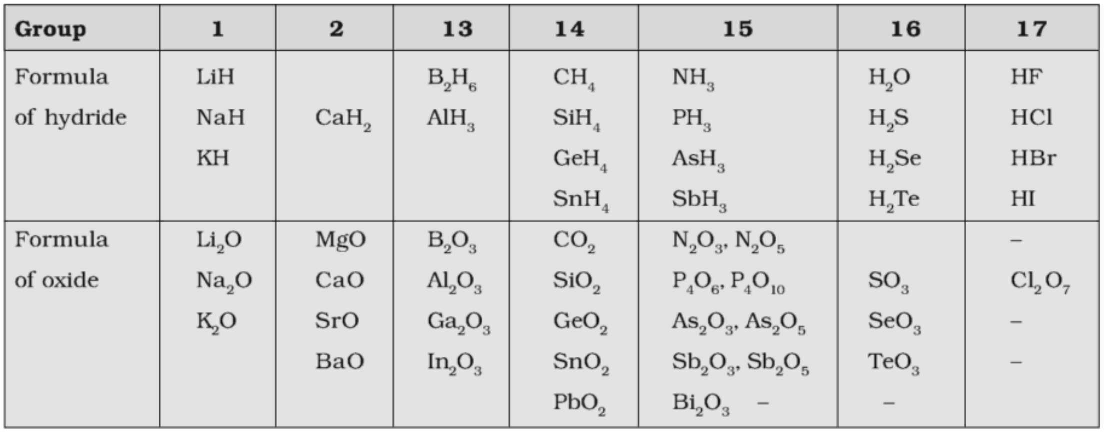
The valence is the most characteristic property of the elements and can be understood in terms of their electronic configurations. The valence of representative elements is usually (though not necessarily) equal to the number of electrons in the outermost orbital's and / or equal to eight minus the number of outermost electrons as shown below.

Nowadays the term oxidation state is frequently used for valence. Consider the two oxygen containing compounds: OF_2 and Na_2O. The order of electronegativity of the three elements involved in these compounds is F > O > Na. Each of the atoms of fluorine, with outer electronic configuration $2s^2 2p^5$, shares one electron with oxygen in the OF_2 molecule. Being highest electronegative element, fluorine is given oxidation state -1. Since there are two fluorine atoms in this molecule, oxygen with outer electronic configuration $2s^2 2p^4$ shares two electrons with fluorine atoms and thereby exhibits oxidation state +2. In Na_2O, oxygen being more electronegative accepts two electrons, one from each of the two sodium atoms and, thus, shows oxidation state -2. On the other hand sodium with electronic configuration $3s^1$ loses one electron to oxygen and is given oxidation state + l. Thus, the oxidation state of an element in a particular compound can be defined as the charge acquired by its atom on the basis of electronegative consideration from other atoms in the molecule.



Group	1	2	13	14	15	16	17	18
Number of valence electron	1	2	3	4	5	6	7	8
Valence	1	2	3	4	3,5	2,6	1,7	0,8

Table 2.9 Periodic Trends in Valence of Elements as shown by the Formulas of Their Compounds

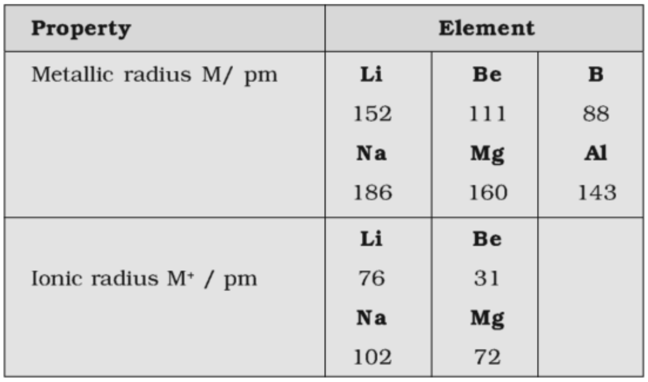


Group	1	2	13	14	15	16	17
Formula of hydride	LiH		B_2H_6	CH_4	NH_3	H_2O	HF
	NaH	CaH_2	AlH_3	SiH_4	PH_3	H_2S	HCl
	KH			GeH_4	AsH_3	H_2Se	HBr
				SnH_4	SbH_3	H_2Te	HI
Formula of oxide	Li_2O	MgO	B_2O_3	CO_2	N_2O_3, N_2O_5		–
	Na_2O	CaO	Al_2O_3	SiO_2	P_4O_6, P_4O_{10}	SO_3	Cl_2O_7
	K_2O	SrO	Ga_2O_3	GeO_2	As_2O_3, As_2O_5	SeO_3	–
		BaO	In_2O_3	SnO_2	Sb_2O_3, Sb_2O_5	TeO_3	–
				PbO_2	Bi_2O_3 –	–	

Some periodic trends observed in the valence of elements (hydrides and oxides) are shown in Table 2.9. Other such periodic trends which occur in the chemical behaviour of the elements are discussed elsewhere in this book. There are many elements which exhibit variable valence. This is particularly characteristic of transition elements and actinoids', which we shall study later.

(b) Anomalous Properties of Second Period Elements

The first element of each of the groups 1 (lithium) and 2 (beryllium) and groups 13- 17 (boron to fluorine) differs in many respects from the other members of their respective group. For example, lithium unlike other alkali metals and beryllium unlike other alkaline earth metals form compounds with pronounced covalent character; the other members of these groups predominantly form ionic compounds. In fact the behavior of lithium and beryllium is more similar with the second element of the following group i.e., magnesium and aluminum respectively. This sort of similarity is commonly referred to as diagonal relationship in the periodic properties.



Property	Element		
Metallic radius M/ pm	**Li**	**Be**	**B**
	152	111	88
	Na	**Mg**	**Al**
	186	160	143
Ionic radius M^+ / pm	**Li**	**Be**	
	76	31	
	Na	**Mg**	
	102	72	

What are the reasons for the different chemical behavior of the first member of a group of elements in the s- and p-blocks compared to that of the subsequent members in the same group? The anomalous behavior is attributed to their small size, large charge/ radius ratio and high electronegativity of the elements. In addition, the first member of group has only four valence orbitals (2s and 2p) available for bonding, whereas the second member of the groups have nine valence orbitals (3s. 3p. 3d). As a consequence of this, the maximum covalency of the first member of each group is 4 (e.g., boron can only form $[BF_4]^-$, whereas the other members of the groups can expand their valence shell to accommodate more than four pairs of electrons e.g., aluminum forms $[AlF_6]^{3-}$. Furthermore, the first member of p-block elements displays greater ability to form p_{π} -p_{π} multiple bonds to itself (e.g. C = C, C ≡ C, N = N, N ≡ N) and to other second period elements (e.g., C = 0, C ≡ N, C = N, N = O) compared to subsequent members of the same group.

2.7.3 Periodic Trends and Chemical Reactivity

We have observed the periodic trends in certain fundamental properties such as atomic and ionic radii, ionization enthalpy, electron gain enthalpy and valence. We know by now that the periodicity is related to electronic configuration. That is, all chemical and physical properties are a manifestation of the electronic configuration of elements. We shall now try to explore relationships between these fundamental properties of elements with their chemical reactivity.

The atomic and ionic radii, as we know generally decrease in a period from left to right. As a consequence, the ionization enthalpies generally increase (with some exceptions as outlined in section 2.7.1(a)) and electron gain enthalpies become more negative across a period. In other words, the ionization enthalpy of the extreme left element in a period is the least and the electron gain enthalpy of the element on the extreme right is the highest negative (note: noble gases having completely filled shells have rather positive electron gain enthalpy values). This results into high chemical reactivity at the two extremes and the lowest in the centre. Thus, the maximum chemical reactivity at the extreme left (among alkali metals) is exhibited by the loss of an electron leading to the formation of a cation and at the extreme right (among halogens) shown by the gain of an electron forming an anion. This property can be related with the reducing and oxidizing behaviour of the elements which you will learn later. However, here it can be directly related to the metallic and non-metallic character of elements. Thus, the metallic character of an element, which is highest at the extremely left decreases and the non-metallic character increases while moving from left to right across the period. The chemical reactivity of an element can be best shown by its reactions with oxygen and halogens. Here, we shall consider the reaction of the elements with oxygen only. Elements on two extremes of a period easily combine with oxygen to form oxides. The normal oxide formed by the element on extreme left is the most basic (e.g., Na_2O), whereas that formed by the element on extreme right is the most acidic (e.g., Cl_2O_7). Oxides of elements in the centre are amphoteric (e.g., Al_2O_3, As_2O_3) or neutral (e.g.. CO,NO, N_2O). Amphoteric oxides behave as acidic with bases and as basic with acids, whereas neutral oxides have no acidic or basic properties.

Among transition metals (3d series), the change in atomic radii is much smaller as compared to those of representative elements across the period. The change in atomic radii is still smaller among inner-transition metals (4f series). The ionization enthalpies are intermediate between those of s and p blocks. As a consequence, they are less electropositive than group 1 and 2 metals.

In a group, the increase in atomic and ionic radii with increase in atomic number generally results in a gradual decrease in ionization enthalpies and a regular decrease (with exception in some third period elements as shown in section 2.7. l(d)) in electron gain enthalpies in the case of main group elements. Thus, the metallic character increases down the group and non -metallic character decreases. This trend can be related with their reducing and oxidizing property which you will learn later. In the case of transition elements, however, a reverse trend is observed. This can be explained in terms of atomic size and ionization enthalpy.

SUMMARY

In this Unit, you have studied the development of the Periodic Law and the Periodic Table. Mendeleev's Periodic Table was based on atomic masses. Modern Periodic Table arranges the elements in the order of their atomic numbers in seven horizontal rows (periods) and eighteen vertical columns (groups or families). Atomic numbers in a period are consecutive, whereas in a group they increase in a pattern. Elements of the same group have similar valence shell electronic configuration and, therefore, exhibit similar chemical properties. However, the elements of the same period have incrementally increasing number of electrons from left to right, and, therefore, have different valences. Four types of elements can be recognized in the periodic table on the basis of their electronic configurations. These are s-block, p-block, d-block and f-block elements. Hydrogen with one electron in the ls orbital occupies a unique position in the periodic table. Metals comprise more than seventy eight percent of the known elements. Non- metals, which are located at the top of the periodic table, are less than twenty in number. Elements which lie at the border line between metals and non-metals (e.g., Si, Ge, As) are called metalloids or semi-metals. Metallic character increases with increasing atomic number in a group whereas decreases from left to right in a period. The physical and chemical properties of elements vary periodically with their atomic numbers.

Periodic trends are observed in atomic sizes, ionization enthalpies, electron gain enthalpies, electronegativity and valence. The atomic radii decrease while going from left to right in a period and increase with atomic number in a group. Ionization enthalpies generally increase across a period and decrease down a group. Electronegativity also shows a similar trend. Electron gain enthalpies, in general, become more negative across a period and less negative down a group. There is some periodicity in valence, for example, among representative elements; the valence is either equal to the number of electrons in the outermost orbitals or eight minus this number. Chemical reactivity is highest at the two extremes of a period and is lowest in the centre. The reactivity on the left extreme of a period is because of the ease of electron loss (or low ionization enthalpy). Highly reactive elements do not occur in nature in free state; they usually occur in the combined form. Oxides formed of the elements on the left are basic and of the elements on the right are acidic in nature. Oxides of elements in the centre are amphoteric or neutral.

QUESTION BANK

CHAPTER 2:CLASSIFICATION OF ELEMENTS AND PERIODIC PROPERTIES

Short Answer Questions **(4 Marks)**

1. State modern periodic law? How many groups and periods are present in the long form of the periodic table?
2. Write an essay on s, p, d and f block elements?
3. What is periodic property? How the following properties vary in a group and in a period, explain?

   a) Atomic radius b) Electron gain enthalpy?
4. What is periodic property? How the following properties vary in a group and in a period?

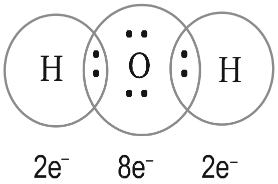
   a) Ionization Enthalpy b) Electro negativity.
5. Why secondary Ionization Enthalpy is greater than primary Ionization enthalpy, explain it?

CHAPTER-3

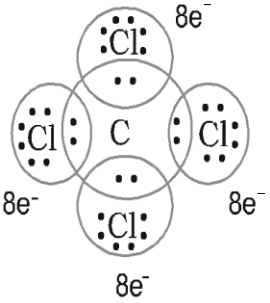
CHEMICAL BONDING AND MOLECULAR STRUCTURE

3. 1.1Covalent Bond

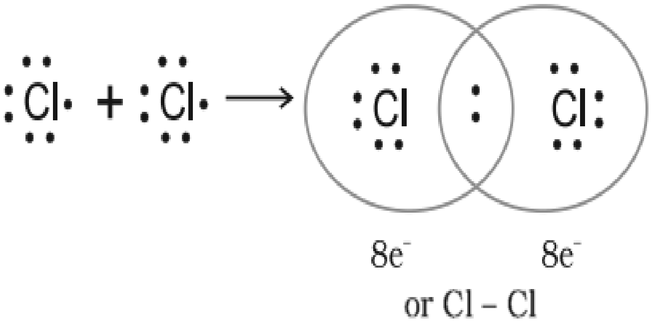
Langmuir (1919) refined the Lewis postulations by abandoning the idea of the stationary cubical arrangement of the octet, and by introducing the term covalent bond. The Lewis- Langmuir theory can be understood by considering the formation of the chlorine molecule, Cl_2. The Cl atom with electronic configuration, [Ne] $3s^23p^5$, is one electron short of the argon configuration. The formation of the Cl_2 molecule can be understood in terms of the sharing of a pair of electrons between the two chlorine atoms, each chlorine atom contributing one electron to the shared pair. In the process both chlorine atoms attain the outer shell octet of the nearest noble gas (i.e., argon).



H atoms attain a duplet of electrons and O, the octet



Each of the four Cl atoms along with the C atom attains octet of electrons

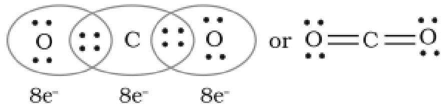


Covalent bond between two Cl atoms

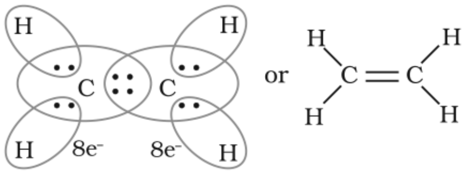
The dots represent electrons. Such structures are referred to as Lewis dot structures. The Lewis dot structures can be written for other molecules also, in which the combining atoms may be identical or different. The important conditions being that:

- Each bond is formed as a result of sharing of an electron pair between the atoms.
- Each combining atom contributes at least one electron to the shared pair.
- The combining atoms attain the outer- shell noble gas configurations as a result of the sharing of electrons.
- Thus in water and carbon tetrachloride molecules, formation of covalent bonds can be represented as:

  Thus, when two atoms share one electron pair they are said to be joined by a single covalent bond. In many compounds we have multiple bonds between atoms. The formation of multiple bonds envisages sharing of more than one electron pair between two atoms. If two atoms share two pairs of electrons, the covalent bond between them is called a double bond. For example, in the carbon dioxide molecule, we have two double bonds between the carbon and oxygen atoms. Similarly in ethene molecule the two carbon atoms are joined by a double bond.

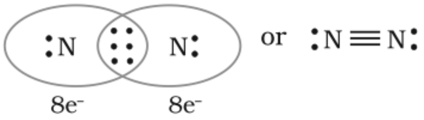


Double bonds in CO_2 molecule

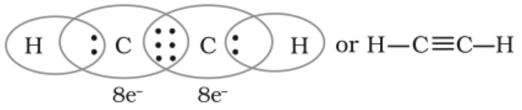


C_2H_4 molecule

When combining atoms share three electron pairs as in the case of two nitrogen atoms in the N_2 molecule and the two carbon atoms in the ethyne molecule, a triple bond is formed.



N_2 molecule



C_2H_2 molecule

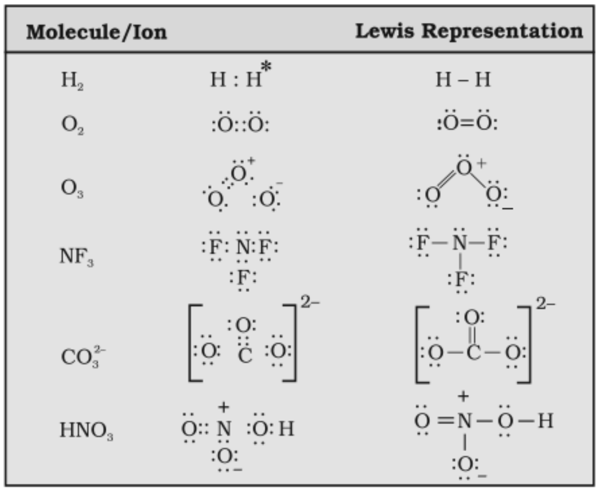
Lewis Representation of Simple Molecules (the Lewis Structures)

The Lewis dot structures provide a picture of bonding in molecules and ions in terms of the shared pairs of electrons and the octet rule. While such a picture may not explain the bonding and behaviour of a molecule completely, it does help in understanding the formation and properties of a molecule to a large extent. Writing of Lewis dot structures of molecules is, therefore, very useful. The Lewis dot structures can be written by adopting the fallowing steps:

- The total number of electrons required for writing the structures is obtained by adding the valence electrons of the combining atoms. For example, in the CH_4 molecule there are eight valence electrons available for bonding (4 from carbon and 4 from the four hydrogen atoms).
- For anions, each negative charge would mean addition of one electron. For cations, each positive charge would result in subtraction of one electron from the total number of valence electrons. For example, for the CO_3^{2-} ion, the two negative charges indicate that there are two additional electrons than those provided by the neutral atoms. For NH_4^+ ion, one positive charge indicates the loss of one electron from the group of neutral atoms.
- Knowing the chemical symbols of the combining atoms and having knowledge of the skeletal structure of the compound (known or guessed intelligently), it is easy to distribute the total number of electrons as bonding shared pairs between the atoms in proportion to the total bonds.
- In general the least electronegative atom occupies the central position in the molecule/ ion. For example in the NF_3 and CO_3^{2-}, nitrogen and carbon are the central atoms whereas fluorine and oxygen occupy the terminal positions.
- After accounting for the shared pairs of electrons for single bonds, the remaining electron pairs are either utilized for multiple bonding or remain as the lone pairs. The basic requirement being that each bonded atom gets an octet of electrons.

Lewis representations of a few molecules/ ions are given in Table 3. 1.

Table 3.1 The Lewis Representation of Some Molecules



** Each H atom attains the configuration of helium (a duplet of electrons)*

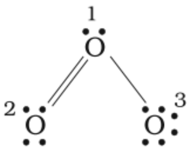
3.1.2 Formal Charge

Lewis dot structures, in general, do not represent the actual shapes of the molecules. In case of polyatomic ions, the net charge is possessed by the ion as a whole and not by a particular atom. It is, however, feasible to assign a formal charge on each atom. The formal charge of an atom in a polyatomic molecule or ion may be defined as the difference between the number of valence electrons of that atom in an isolated or free state and the number of electrons assigned to that atom in the Lewis structure. It is expressed as:

$$\boxed{\text{Formal charge (F.C.) on an atom in a Lewis structure}} =$$

$$\boxed{\begin{array}{l}\left[\text{total number of valence electrons in the free atom}\right] - \left[\text{total number of non bonding (lone pair) electrons}\right] \\ \qquad - (1/2)\left[\text{total number of bonding(shared) electrons}\right]\end{array}}$$

The counting is based on the assumption that the atom in the molecule owns one electron of each shared pair and both the electrons of a lone pair. Let us consider the ozone molecule (O_3). The Lewis structure of O_3 may be drawn as:



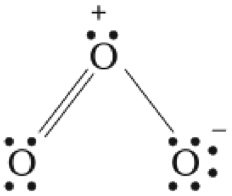
The atoms have been numbered as 1, 2 and 3.

The central O atom marked 1= 6 – 2 - (1/2) 6 = +1

The end O atom marked 2 = 6 – 4 - (1/2) 4 = 0

The end O atom marked 3 = 6 – 6 - (1/2) 2 = -1

Hence, we represent O_3 along with the formal charges as follows:



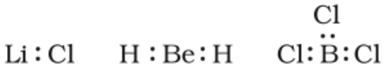
We must understand that formal charges do not indicate real charge separation within the molecule. Indicating the charges on the atoms in the Lewis structure only helps in keeping track of the valence electrons in the molecule. Formal charges help in the selection of the lowest energy structure from a number of possible Lewis structures for a given species. Generally the lowest energy structure is the one with the smallest formal charges on the atoms. The formal charge is a factor based on a pure covalent view of bonding in which electron pairs are shared equally by neighbouring atoms.

3.1.3 Limitations of the Octet Rule

The octet rule, though useful, is not universal. It is quite useful for understanding the structures of most of the organic compounds and it applies mainly to the second period elements of the periodic table. There are three types of exceptions to the octet rule.

The incomplete octet of the central atom

In some compounds, the number of electrons surrounding the central atom is less than eight. This is especially the case with elements having less than four valence electrons. Examples are LiCl, BeH_2 and $BC1_3$.

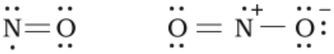


$$\mathrm{Li}:\mathrm{Cl} \qquad \mathrm{H}:\mathrm{Be}:\mathrm{H} \qquad \mathrm{Cl}:\overset{\mathrm{Cl}}{\ddot{\mathrm{B}}}:\mathrm{Cl}$$

Li, Be and B have 1, 2 and 3 valence electrons only. Some other such compounds are $AICl_3$ and BF_3.

Odd-electron molecules

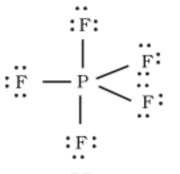
In molecules with an odd number of electrons like nitric oxide, NO and nitrogen dioxide, $N0_2$, the octet rule is not satisfied for all the atoms.



$$\ddot{\mathrm{N}}=\ddot{\mathrm{O}} \qquad \ddot{\mathrm{O}}=\overset{+}{\mathrm{N}}-\ddot{\mathrm{O}}:^{-}$$

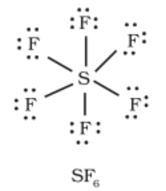
The expanded octet

Elements in and beyond the third period of the periodic table have apart from 3s,3p and 3d orbitals also available for bonding. In a number of compounds of these elements there are more than eight valence electrons around the central atom. This is termed as the expanded octet. Obviously the octet rule does not apply in such cases. Some of the examples of such compounds are: PF_5, SF_6, H_2SO_4 and a number of coordination compounds.



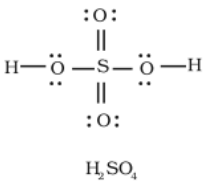
PF_5

10 electrons around the P atom



SF_6

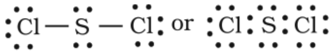
12 electrons around the S atom



H_2SO_4

12 electrons around the S atom

Interestingly, sulphur also forms many compounds in which the octet rule is obeyed. In sulphur dichloride, the S atom has an octet of electrons around it.



Other drawbacks of the octet theory

- It is clear that octet rule is based upon the chemical inertness of noble gases. However, some noble gases (for example xenon and krypton) also combine with oxygen and fluorine to form a number of compounds like XeF_2, KrF_2, $XeOF_2$ etc.,
- This theory does not account for the shape of molecules.
- It does not explain the relative stability of the molecules being totally silent about the energy of a molecule.

3.2 Ionic or Electrovalent bond

The electrostatic attraction force existing between the cation and the anion produced by the electron transfer from one atom to the other is known as the ionic (or) electrovalent bond. The compounds containing such a bond are referred to as ionic (or) electrovalent compounds.

The formation of ionic compounds would primarily depend upon:

- The ease of formation of the positive and negative ions from the respective neutral atoms;
- The arrangement of the positive and negative ions in the solid, that is, the lattice of the crystalline compound.

The formation of a positive ion involves ionization, i.e., removal of electron (s) from the neutral atom and that of the negative ion involves the addition of electron(s) to the neutral atom.

$M_{(g)} \rightarrow M^{+}_{(g)} + e^{-}$ Ionization enthalpy

$X_{(g)} + e^{-} \rightarrow X^{-}_{(g)}$ Electron gain enthalpy

$M^{+}_{(g)} + X^{-}_{(g)} \rightarrow MX_{(S)}$

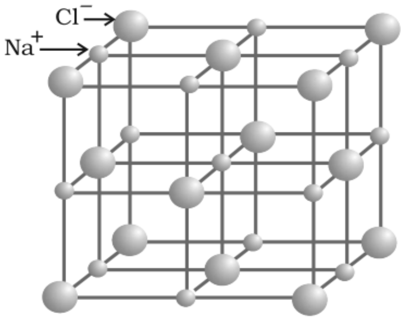
The electron gain enthalpy, $\Delta_{eg}H$, is the enthalpy change (Unit 2), when a gas phase atom in its ground state gains an electron. The electron gain process may be exothermic or endothermic. The ionization, on the other hand, is always endothermic. Electron affinity is the negative of the energy change accompanying electron gain.

Obviously ionic bonds will be formed more easily between elements with comparatively low ionization enthalpies and elements with comparatively high negative value of electron gain enthalpy.

Most ionic compounds have cations derived from metallic elements and anions from non-metallic elements. The ammonium ion, NH_4^+ (made up of two non-metallic elements) is an exception. It forms the cation of a number of ionic compounds.

Ionic compounds in the crystalline state consist of orderly three- dimensional arrangements of cations and anions held together by columbic interaction energies. These compounds crystallise in different crystal structures determined by the size of the ions, their packing arrangements and other factors. The crystal structure of sodium chloride, NaCl (rock salt), for example is shown below.

In ionic solids, the sum of the electron gain enthalpy and the ionization enthalpy may be positive but still the crystal structure gets stabilized due to the energy released in the formation of the crystal lattice. For example: the ionization enthalpy for $Na^+(g)$ formation from Na(g) is 495.8 kJ mol^{-1}: while the electron gain enthalpy for the change $Cl(g) + e^- \rightarrow Cl^-(g)$ is, - 348.7 kJ mol^{-1} only. The sum of the two, 147.1 kJ $mol^{-1}$is more than compensated for by the enthalpy of lattice formation of NaCl (s) (-788 kJ mol^{-1}). Therefore, the energy released in the processes is more than the energy absorbed. Thus a qualitative measure of the stability of an ionic compound is provided by its enthalpy of lattice formation and not simply by achieving octet of electrons around the ionic species in gaseous state.



Rock salt structure

Since lattice enthalpy plays a key role in the formation of ionic compounds, it is important that we learn more about it.

3.2.1 Lattice Enthalpy

The Lattice Enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions. For example, the lattice enthalpy of NaCl is 788 $kJmol^{-1}$. This means that 788 kJ of energy is required to separate one mole of solid NaCl into one mole of $Na^+(g)$ and one mole of $Cl^-(g)$ to an infinite distance.

This process involves both the attractive forces between ions of opposite charges and the repulsive forces between ions of like charge. The solid crystal being three- dimensional; it is not possible to calculate lattice enthalpy directly from the interaction of forces of attraction and repulsion only. Factors associated with the crystal geometry have to be included.

3.3 BOND PARAMETERS

3.3.1 Bond Length

Bond length is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule. Bond lengths are measured by spectroscopic, X-ray diffraction and electron-diffraction techniques about which you will learn in higher classes. Each atom of the bonded pair contributes to the bond length (Fig. 3.1). In the case of a covalent bond, the contribution from each atom is called the covalent radius of that atom.

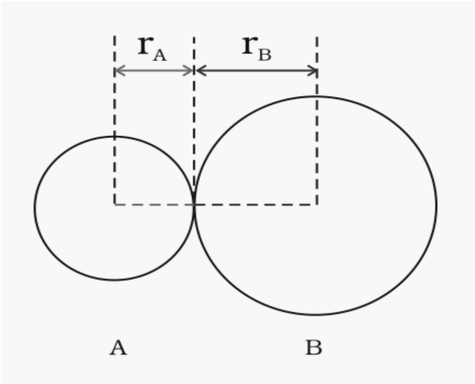


Fig. 3.1 The bond length in a covalent molecule AB. R = $r_A + r_B$ (R is the bond length and r_A and r_B are the covalent radii of atoms A and B respectively)

The covalent radius is measured approximately as the radius of an atom's core which is in contact with the core of an adjacent atom in a bonded situation. The covalent radius is half of the distance between two similar atoms joined by a covalent bond in the same molecule. The Vander Waals radius represents the overall size of the atom which includes its valence shell in a non-bonded situation. Further, the Vander Waals radius is half of the distance between two similar atoms in separate molecules in a solid. Covalent and Vander Waals radii of chlorine are depicted in Fig.3.2.

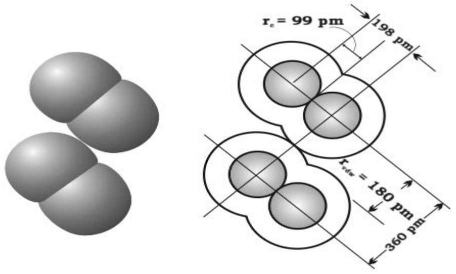
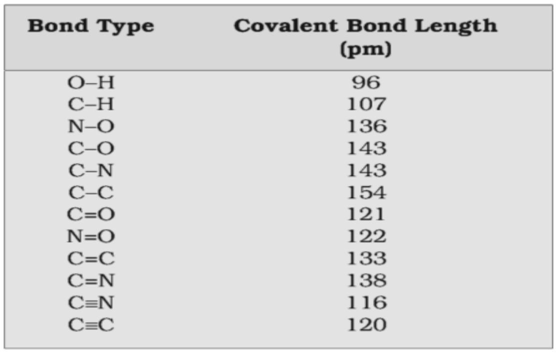


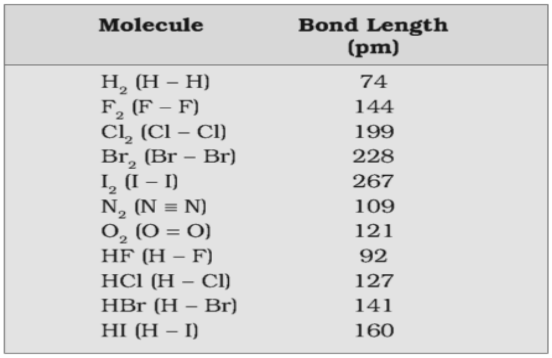
Fig. 3.2 Covalent and Vander Waals radii in a chlorine molecule. The inner circles correspond to the size of the chlorine atom (r_{vdw} and r_c are Vander Waals and covalent radii respectively).

Table 3.2 Average Bond Lengths for Some Single, Double and Triple Bonds



Bond Type	Covalent Bond Length (pm)
O–H	96
C–H	107
N–O	136
C–O	143
C–N	143
C–C	154
C=O	121
N=O	122
C=C	133
C=N	138
C≡N	116
C≡C	120

Table 3.3 Bond Lengths in Some molecules. Common

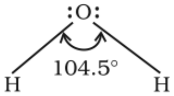


Molecule	Bond Length (pm)
H_2 (H – H)	74
F_2 (F – F)	144
Cl_2 (Cl – Cl)	199
Br_2 (Br – Br)	228
I_2 (I – I)	267
N_2 (N ≡ N)	109
O_2 (O = O)	121
HF (H – F)	92
HCl (H – Cl)	127
HBr (H – Br)	141
HI (H – I)	160

Some typical average bond lengths for single, double and triple bonds are shown in Table 3.2. Bond lengths for some common molecules are given in Table 3.3.

3.3.2 Bond Angle

It is defined as the angle between the orbitals containing bonding electron pairs around the central atom in a molecule/complex ion. Bond angle is expressed in degree which can be experimentally determined by spectroscopic methods. It gives some idea regarding the distribution of orbitals around the central atom in a molecule/ complex ion and hence it helps us in determining its shape. For example H-O-H bond angle in water can be represented as under:



3.3.3 Bond Enthalpy

It is defined as the amount of energy required to break one mole of bonds of a particular type between two atoms in a gaseous state. The unit of bond enthalpy is kJ mol^{-1}. For example, the H - H bond enthalpy in hydrogen molecule is 435.8 kJ $mo1^{-1}$.

$$H_2\ g\ \rightarrow H\ g\ + H\ g\ ;\ \Delta_a H = \ 435.8\ \text{kJ mo1}^{-1}$$

Similarly the bond enthalpy for molecules containing multiple bonds, for example O_2 and N_2 will be as under:

$$O_2(O{=}O)\ g\ \rightarrow O\ g\ + O\ g\ ;\ \Delta_a H = \ 498\ \text{kJ mo1}^{-1}$$

$$N_2(N{\equiv}N)\ g\ \rightarrow N\ g\ + N\ g\ ;\ \Delta_a H = \ 946.0\ \text{kJ mo1}^{-1}$$

It is important that larger the bond dissociation enthalpy, stronger will be the bond in the molecule. For hetero nuclear diatomic molecules like HCl, we have

$$HCl\ g\ \rightarrow H\ g\ + Cl\ g\ ;\ \Delta_a H = \ 431.0\ \text{kJ mo1}^{-1}$$

In case of polyatomic molecules, the measurement of bond strength is more complicated. For example in case of H_2O molecule, the enthalpy needed to break the two O - H bonds is not the same.

$$H_2O\ g \rightarrow H\ g\ + OH\ g\ ;\ \Delta_a H_1 = 502\ \text{kJ mo1}^{-1}$$

$$OH\ g \rightarrow H\ g\ + O\ g\ ;\ \Delta_a H_2 = 427\ \text{kJ mo1}^{-1}$$

The difference in the $\Delta_a H$ value shows that the second O - H bond undergoes some change because of changed chemical environment. This is the reason for some difference in energy of the same O - H bond in different molecules like C_2H_5OH (ethanol) and water. Therefore in polyatomic molecules, the term mean or average bond enthalpy is used. It is obtained by dividing total bond dissociation enthalpy by the number of bonds broken as explained below in case of water molecule,

The average bond enthalpy = (502 + 427)/2 = 464.5 kJ mo1^{-1}

3.3.4 Bond Order

In the Lewis description of covalent bond, the Bond Order is given by the number of bonds between the two atoms in a molecule. The bond order, for example in H_2 (with a single shared electron pair), in O_2 (with two shared electron pairs) and in N_2 (with three shared electron pairs) is 1, 2, 3 respectively. Similarly in CO (three shared electron pairs between C and O) the bond order is 3. For N_2, bond order is 3 and its $\Delta_a H$ is 946 kJ mol $^{-1}$; being one of the highest for a diatomic molecule.

Isoelectronic molecules and ions have identical bond orders; for example, F_2 and O_2^{2-} have bond order 1. N_2, CO and NO^+ have bond order 3.

A general correlation useful for understanding the stabilities of molecules is that: with increase in bond order, bond enthalpy increases and bond length decreases.

3.3.5 Resonance Structures

It is often observed that a single Lewis structure is inadequate for the representation of a molecule in conformity with its experimentally determined parameters. For example, the ozone, O_3 molecule can be equally represented by the structures I and II shown below:

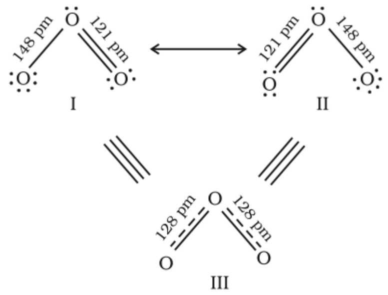


Fig. 3.3 Resonance in O_3 molecule

In both structures we have a O-O single bond and a O=O double bond. The normal O-O and O=O bond lengths are 148 pm and 121 pm respectively. Experimentally determined oxygen-oxygen bond lengths in the O_3 molecule are same (128 pm). Thus the oxygen-oxygen bonds in the O_3 molecule are intermediate between a double and a single bond. Obviously, this cannot be represented by either of the two Lewis structures shown above.

The concept of resonance was introduced to deal with the type of difficulty experienced in the depiction of accurate structures of molecules like O_3. According to the concept of resonance, whenever a single Lewis structure cannot describe a molecule accurately, a number of structures with similar energy, positions of nuclei, bonding and non-bonding pairs of electrons are taken as the canonical structures of the hybrid which describes the molecule accurately. Thus for O_3, the two structures shown above constitute the canonical structures or resonance structures and their hybrid i.e., the III structure represents the structure of O_3 more accurately. This is also called resonance hybrid. Resonance is represented by a double headed arrow (↔).

In general, it may be stated that

- Resonance stabilizes the molecule as the energy of the resonance hybrid is less than the energy of any single canonical structure; and,
- Resonance averages the bond characteristics as a whole. Thus the energy of the O_3 resonance hybrid is lower than either of the two canonical forms I and II (Fig 3.3).

3.3.6 Polarity of Bonds

The existence of a hundred percent ionic or covalent bond represents an ideal situation. In reality no bond or a compound is either completely covalent or ionic. Even in case of covalent bond between two hydrogen atoms, there is some ionic character.

When covalent bond is formed between two similar atoms, for example in H_2, O_2, Cl_2, N_2 or F_2, the shared pair of electrons is equally attracted by the two atoms. As a result electron pair is situated exactly between the two identical nuclei. The bond so formed is called non-polar covalent bond. Contrary to this in case of a hetero nuclear molecule like HF, the shared electron pair between the two atoms gets displaced more towards fluorine since the electro negativity of fluorine (Unit 2) is far greater than that of hydrogen. The resultant covalent bond is a polar covalent bond.

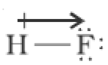
As a result of polarisation, the molecule possesses the dipole moment (depicted below) which can be defined as the product of the magnitude of the charge and the distance between the centres of positive and negative charge. It is usually designated by a Greek letter 'μ'. Mathematically, it is expressed as follows:

Dipole moment (μ) = charge (Q) x distance of separation (r)

Dipole moment is usually expressed in Debye units (D). The conversion factor is

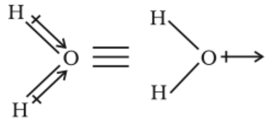
1 D = 3.33564×10^{-30} C m   where C is coulomb and m is meter.

Further dipole moment is a vector quantity and is depicted by a small arrow with tail on the positive centre and head pointing towards the negative centre. For example the dipole moment of HF may be represented as:



The shift in electron density is symbolized by crossed arrow (+⟶) above the Lewis structure to indicate the direction of the shift.

In case of polyatomic molecules the dipole moment not only depends upon the individual dipole moments of bonds known as bond dipoles but also on the spatial arrangement of various bonds in the molecule. In such case, the dipole moment of a molecule is the vector sum of the dipole moments of various bonds. For example in H_2O molecule, which has a bent structure, the two O-H bonds are oriented at an angle of 104.5°. Net dipole moment of 6.17×10^{-30} C m is the resultant of the dipole moments of two O-H bonds.



(a)
Bond dipole

(b)
Resultant
dipole moment

Net Dipole moment, μ =1.85 D

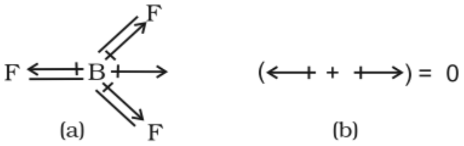
$$= 1.85 \times 3.33564 \times 10^{-30} \text{ C m} = 6.17 \times 10^{-30} \text{ C m}$$

The dipole moment in case of BeF_2 is zero. This is because the two equal bond dipoles point in opposite directions and cancel the effect of each other.

Bond dipoles in BeF_2

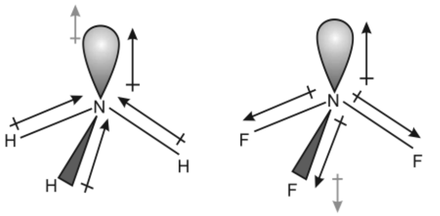
Total dipole moment in BeF_2

In tetra-atomic molecule, for example in BF_3, the dipole moment is zero although the B - F bonds are oriented at an angle of 120° to one another, the three bond moments give a net sum of zero as the resultant of any two is equal and opposite to the third.



BF_3 molecule; representation of
(a) bond dipoles and (b) total dipole moment

Let us study an interesting case of NH_3 and NF_3 molecule. Both the molecules have pyramidal shape with a lone pair of electrons on nitrogen atom. Although fluorine is more electronegative than nitrogen, the resultant dipole moment of NH_3 is greater than that of NF_3. This is because, in case of NH_3 the orbital dipole due to lone pair is in the same direction as the resultant dipole moment of the N - H bonds, whereas in NF_3 the orbital dipole is in the direction opposite to the resultant dipole moment of the three N-F bonds. The orbital dipole because of lone pair decreases the effect of the resultant N - F bond moments, which results in the low dipole moment of NF_3 as represented below:

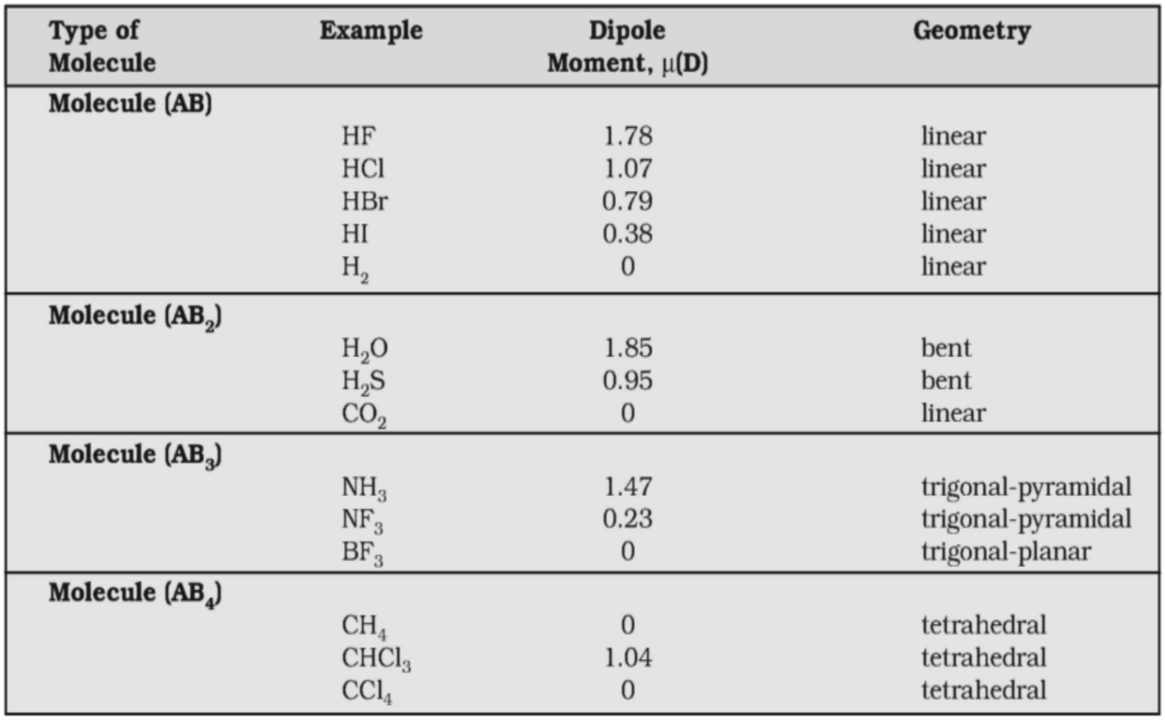


Resultant dipole moment in $NH_3 = 4.90 \times 10^{-30}$ C m

Resultant dipole moment in $NF_3 = 0.80 \times 10^{-30}$ C m

Dipole moments of some molecules are shown in Table 3.4.

Table 3.4 Dipole Moments of Selected Molecules



Type of Molecule	Example	Dipole Moment, μ(D)	Geometry
Molecule (AB)			
	HF	1.78	linear
	HCl	1.07	linear
	HBr	0.79	linear
	HI	0.38	linear
	H_2	0	linear
Molecule (AB_2)			
	H_2O	1.85	bent
	H_2S	0.95	bent
	CO_2	0	linear
Molecule (AB_3)			
	NH_3	1.47	trigonal-pyramidal
	NF_3	0.23	trigonal-pyramidal
	BF_3	0	trigonal-planar
Molecule (AB_4)			
	CH_4	0	tetrahedral
	$CHCl_3$	1.04	tetrahedral
	CCl_4	0	tetrahedral

3.4 The Valence Shell Electron Pair Repulsion (V_{SEPR}) Theory

As already explained, Lewis concept is unable to explain the shapes of molecules. This theory provides a simple procedure to predict the shapes of covalent molecules. Nevil Sidgwick and Herbert Powell in 1940, proposed a simple theory based on the repulsive interactions of the electron pairs in the valence shell of the atoms. It was further developed and redefined by Ronald Sydney Nyholm and Ronald James Gillespie (1957).

The main postulates of V_{SEPR} theory are as follows:

- The shape of a molecule depends upon the number of valence shell electron pairs (bonded or non-bonded) around the central atom.
- Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.
- These pairs of electrons tend to occupy such positions in space that minimize repulsion and thus maximize distance between them.
- The valence shell is taken as a sphere with the electron pairs localizing on the spherical surface at maximum distance from one another.
- A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.
- Where two or more resonance structures can represent a molecule, the V_{SEPR} model is applicable to any such structure.

The repulsive interaction of electron pairs decrease in the order:

Lone pair (lp) - Lone pair (lp) > Lone pair (lp) - Bond pair (bp) >Bond pair (bp) - Bond pair (bp)

Nyholm and Gillespie (1957) refined the VSEPR model by explaining the important difference between the lone pairs and bonding pairs of electrons. While the lone pairs are localised on the central atom, each bonded pair is shared between two atoms. As a result, the lone pair electrons in a molecule occupy more space as compared to the bonding pairs of electrons. These results in greater repulsion between lone pairs of electrons as compared to the lone pair - bond pair and bond pair - bond pair repulsions. These repulsion effects result in deviations from idealized shapes and alterations in bond angles in molecules.

For the prediction of geometrical shapes of molecules with the help of VSEPR theory, it is convenient to divide molecules into two categories as (i) molecules in which the central atom has no lone pair and (ii) molecules in which the central atom has one or more lone pairs.

Table 3.5 shows the arrangement of electron pairs about a central atom A (without any lone pairs) and geometries of some molecules/ions of the type AB. Table 3.6 shows shapes of some simple molecules and ions in which the central atom has one or more lone pairs. Table 3.7 explains the reasons for the distortions in the geometry of the molecule.

As depicted in Table 3.5, in the compounds of AB_2, AB_3, AB_4, AB_5 and AB_6,), the arrangement of electron pairs and the B atoms around central atom A are: linear, trigonal planar, tetrahedral, trigonal bipyramidal and octahedral respectively. Such arrangement can be seen in the molecules like BF_3 (AB_3), CH_4 (AB_4) and $PC1_5$ (AB_5) as depicted below by their ball and stick models.

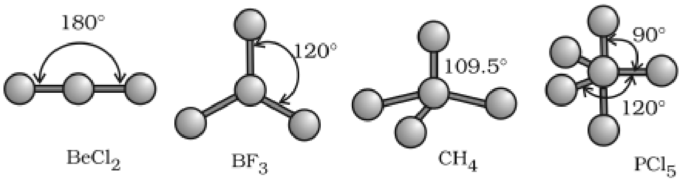


Fig. 3.4 The shapes of molecules in which central atom has no lone pair.

Table 3.5 Geometry of molecules in which the central atom has no lone pair of electrons

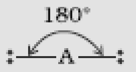
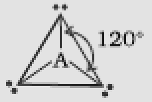
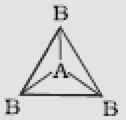
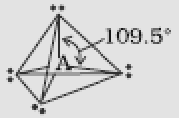
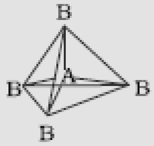
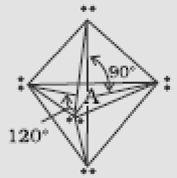
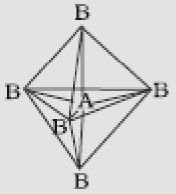
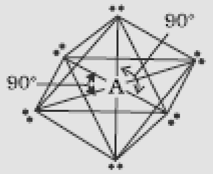
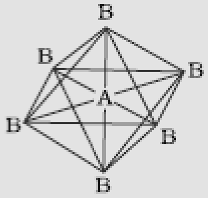
Number of electron pairs	Arrangement of electron pairs	Molecular geometry	Examples
2	 Linear	B—A—B Linear	$BeCl_2$, $HgCl_2$
3	 Trigonal planar	 Trigonal planar	BF_3
4	 Tetrahedral	 Tetrahedral	CH_4, NH_4^+
5	 Trigonal bipyramidal	 Trigonal bipyramidal	PCl_5
6	 Octahedral	 Octahedral	SF_6

Table 3.6 Shape (Geometry) of some simple Molecules/Ions with Central Ions having one or more Lone Pair of Electrons (E)

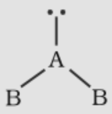
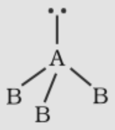
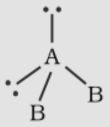
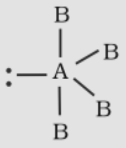
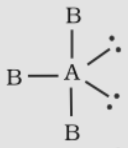
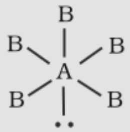
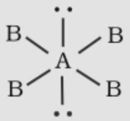
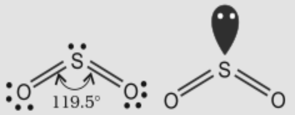
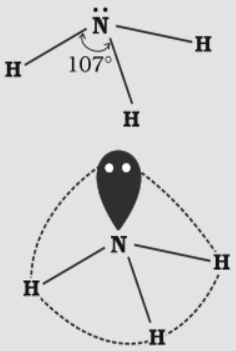
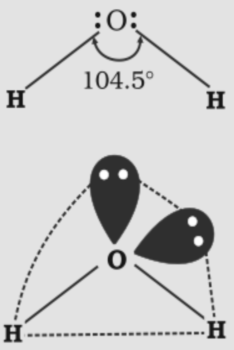
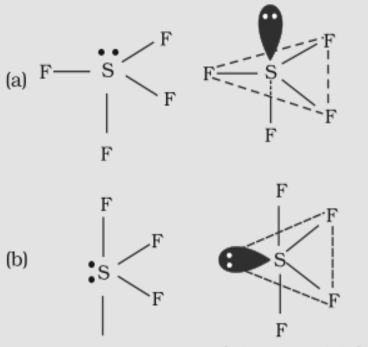
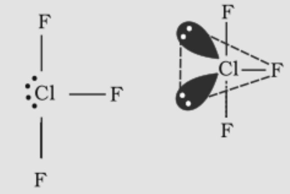
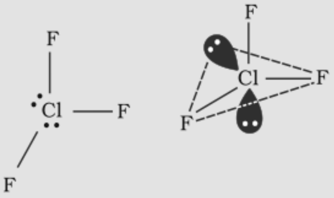
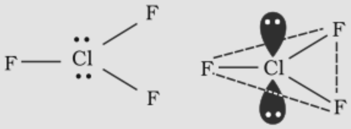
Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electron pairs	Shape	Examples
AB_2E	2	1	 Trigonal planar	Bent	SO_2, O_3
AB_3E	3	1	 Tetrahedral	Trogonal pyramidal	NH_3
AB_2E_2	2	2	 Tetrahedral	Bent	H_2O
AB_4E	4	1	 Trigonal bi-pyramidal	See saw	SF_4
AB_3E_2	3	2	 Trigonal bi-pyramidal	T-shape	ClF_3
AB_5E	5	1	 Octahedral	Square pyramid	BrF_5
AB_4E_2	4	2	 Octahedral	Square planar	XeF_4

Table 3.7 Shapes of Molecules containing Lone Pair and Bond Pair

Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electrons	Shape	Reason for the shape acquired
AB_2E	4	1		Bent	Theoretically the shape should have been triangular planar but actually it is found to be bent or v-shaped. The reason being the lone pair-bond pair repulsion is much more as compared to the bond pair-bond pair repulsion. So the angle is reduced to 119.5 from 120 .
AB_3E	3	1		Trigonal pyramidal	Had there been a bp in place of lp the shape would have been tetrahedral but one lone pair is present and due to the repulsion between lp-bp (which is more than bp-bp repulsion) the angle between bond pairs is reduced to 107 from 109.5 .
AB_2E_2	2	2		Bent	The shape should have been tetrahedral if there were all bp but two lp are present so the shape is distorted tetrahedral or angular. The reason is lp-lp repulsion is more than lp-bp repulsion which is more than bp-bp repulsion. Thus, the angle is reduced to 104.5 from 109.5 .
AB_4E	4	1	 (More stable)	See-saw	In (a) the lp is present at axial position so there are three lp—bp repulsions at 90 . In(b) the lp is in an equatorial position, and there are two lp—bp repulsions. Hence, arrangement (b) is more stable. The shape shown in (b) is described as a distorted tetrahedron, a folded square or a see-saw.

Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electrons	Shape	Reason for the shape acquired
AB_3E_2	3	2	(a)  (b)  (c) 	T-shape	In (a) the lp are at equatorial position so there are less lp-bp repulsions as compared to others in which the lp are at axial positions. So structure (a) is most stable. (T-shaped).

The VSEPR Theory is able to predict geometry of a large number of molecules, especially the compounds of p-block elements accurately. It is also quite successful in determining the geometry quite-accurately even when the energy difference between possible structures is very small. The theoretical basis of the VSEPR theory regarding the effects of electron pair repulsions on molecular shapes is not clear and continues to be a subject of doubt and discussion.

3.5 Valence Bond Theory

As we know that Lewis approach helps in writing the structure of molecules but it fails to explain the formation of chemical bond. It also does not give any reason for the difference in bond dissociation enthalpies and bond lengths in molecules like H_2 (435.8 kJ mol^{-1}, 74 pm) and F_2 (150.6 $kJmo1^{-1}$, 42 pm) , although in both the cases a single covalent bond is formed by the sharing of an electron pair between the respective atoms. It also gives no idea about the shapes of polyatomic molecules.

Similarly the VSEPR theory gives the geometry of simple molecules but theoretically, it does not explain them and also it has limited applications. To overcome these limitations the two important theories based on quantum mechanical principles are introduced. These are valence bond (VB) theory and molecular orbital (MO) theory.

Valence bond theory was introduced by Walter Heitler and Fritz London (1927) and developed further by Pauling and others. A discussion of the valence bond theory is based on the knowledge of atomic orbitals, electronic configurations of elements, the overlap criteria of atomic orbitals, the hybridization of atomic orbitals and the principles of variation and superposition. A rigorous treatment of the VB theory in terms of these aspects is beyond the scope of this book. Therefore, for the sake of convenience valence bond theory has been discussed in terms of qualitative and non-mathematical treatment only. To start with, let us consider the formation of hydrogen molecule which is the simplest of all molecules.

Consider two hydrogen atoms A and B approaching each other having nuclei N_A and N_B and electrons present in them are represented by e_A and e_B. When the two atoms are at large distance from each other, there is no interaction between them. As these two atoms approach each other, new attractive and repulsive forces begin to operate.

Attractive forces arise between:

(i) Nucleus of one atom and its own electron that is N_A - e_A and N_B - e_B

(ii)Nucleus of one atom and electron of other atom i.e., N_A- e_B, N_B- e_A.

Similarly repulsive forces arise between:

(i) Electrons of two atoms like e_A - e_B,

(ii)Nuclei of two atoms N_A - N_B.

Attractive forces tend to bring the two atoms close to each other whereas repulsive forces tend to push them apart (Fig. 3.5).

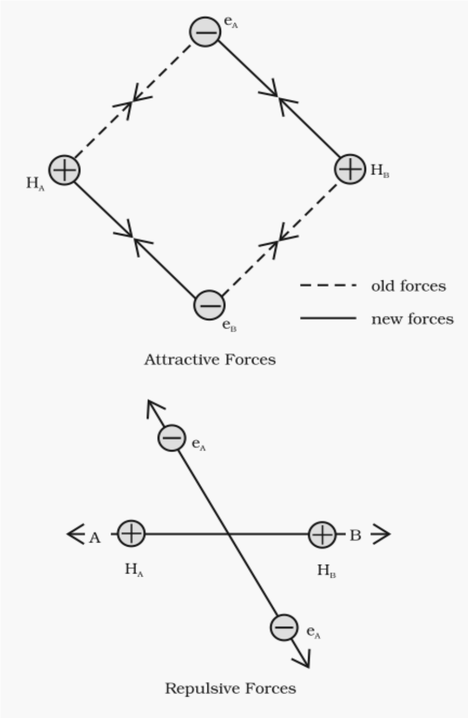


Fig. 3.5 Forces of attraction and repulsion during the formation of H_2 molecule

Experimentally, it has been found that the magnitude of new attractive force is more than the new repulsive forces. As a result, two atoms approach each other and potential energy decreases. Ultimately a stage is reached where the net force of attraction balances the force of repulsion and system acquires minimum energy. At this stage two hydrogen atoms are said to be bonded together to form a stable molecule having the bond length of 74 pm.

Since the energy gets released when the bond is formed between two hydrogen atoms, the hydrogen molecule is more stable than that of isolated hydrogen atoms. The energy so released is called as bond enthalpy, which is corresponding to minimum in the curve depicted in Fig. 3.6. Conversely, 435.8 kJ of energy is required to dissociate one mole of H_2 molecule.

$$H_2\ \ g\ \ +435.8\ \text{kJ mo1}^{-1} \rightarrow H\ \ g\ \ + H\ \ g$$

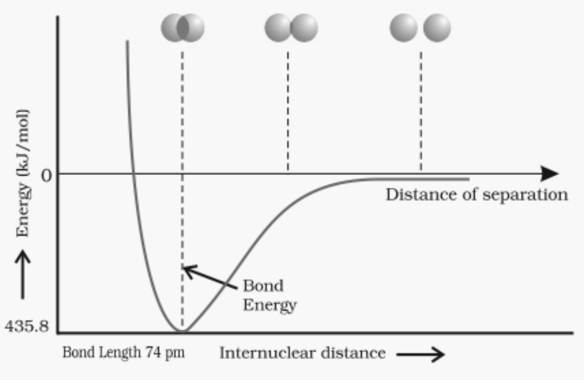


Fig. 3.6 The potential energy curve for the formation of H_2 molecule as a function of inter-nuclear distance of the H atoms. The minimum in the curve corresponds to the most stable state of H_2.

3.5. 1 Orbital Overlap Concept

In the formation of hydrogen molecule, there is a minimum energy state when two hydrogen atoms are so near that their atomic orbitals undergo partial interpenetration. This partial merging of atomic orbitals is called overlapping of atomic orbitals which results in the pairing of electrons. The extent of overlap decides the strength of a covalent bond. In general, greater the overlap the stronger is the bond farmed between two atoms. Therefore, according to orbital overlap concept, the formation of a covalent bond between two atoms results by pairing of electrons present in the valence shell having opposite spins.

3.5.2 Directional Properties of Bonds

As we have already seen the formation of covalent bond depends on the overlapping of atomic orbitals. The molecule of hydrogen is formed due to the overlap of 1s-orbitals of two H atoms, when they combine with each other.

In case of polyatomic molecules like CH_4, NH_3 and H_2O, the geometry of the molecules is also important in addition to the bond formation. For example why is it so that CH_4 molecule has tetrahedral shape and HCH bond angles are 109.5? Why is the shape of NH_3 molecule pyramidal?

The valence bond theory explains the formation and directional properties of bonds in polyatomic molecules like CH_4, NH_3 and H_2O, etc. in terms of overlap and hybridisation of atomic orbitals.

3.5.3 Overlapping of Atomic Orbital's

When two atoms come close to each other, there is overlapping of atomic orbitals. This overlap may be positive, negative or zero depending upon the properties of overlapping of atomic orbitals. The various arrangements of s and p orbitals resulting in positive, negative and zero overlap are depicted in Fig. 3.7.

The criterion of overlap, as the main factor for the formation of covalent bonds applies uniformly to the homonuclear/heteronuclear diatomic molecules and polyatomic molecules. In the case of polyatomic molecules like CH_4, NH_3 and H_2O, the VB theory has to account for their characteristic shapes as well. We know that the shapes of CH_4, NH_3, and H_2O molecules are tetrahedral, pyramidal and bent respectively. It would be therefore interesting to find out if these geometrical shapes can be explained in terms of the orbital overlaps.

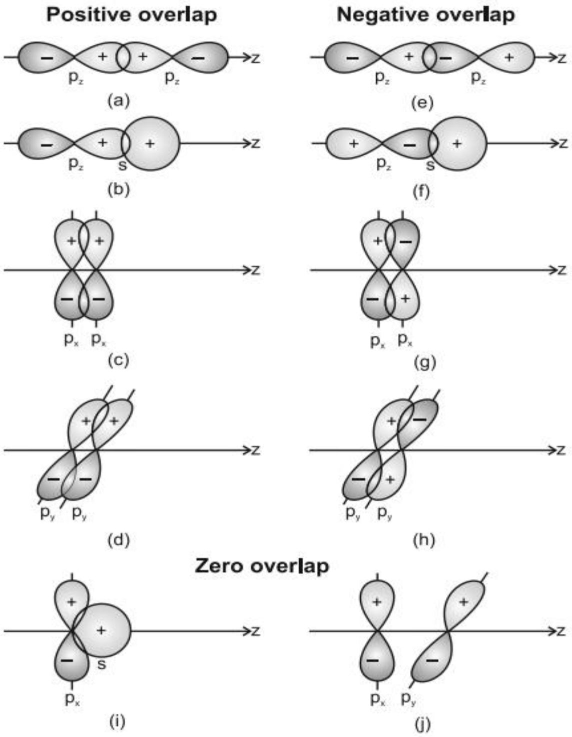


Fig. 3.7 Positive, negative and zero overlaps of s and p atomic orbitals

Let us first consider the CH_4 (methane) molecule. The electronic configuration of carbon in its ground state is [He] $2s^2\ 2p^2$ which in the excited state becomes [He] $2s^1 2p_x^1\ 2p_y^1 2p_z^1$. The energy required for this excitation is compensated by the release of energy due to overlap between the orbitals of carbon and the hydrogen. The four atomic orbitals of carbon, each with an unpaired electron can overlap with the 1s orbitals of the four H atoms which are also singly occupied. This will result in the formation of four C-H bonds. It will however, be observed that while the three p orbitals of carbon are at 90 to one another. the HCH angle for these will also be 90. That is three C-H bonds will be oriented at 90 to one another. The 2s orbital of carbon and the 1s orbital of H are spherically symmetrical and they can overlap in any direction. Therefore the direction of the fourth C-H bond cannot be ascertained. This description does not fit in with the tetrahedral HCH angles of 109.5. Clearly, it follows that simple atomic orbital overlap does not account for the directional characteristics of bonds in CH_4. Using similar procedure and arguments, it can be seen that in the case of NH_3 and H_2O molecules, the HNH and HOH angles should be 90. This is in disagreement with the actual bond angles of 107 and 104.5 in the NH_3 and H_2O molecules respectively.

3.5.4 Types of Overlapping and Nature of Covalent Bonds

The covalent bond may be classified into two types depending upon the types of overlapping:

(i) Sigma (σ) bond, and (ii) pi(π) bond

(i) **Sigma (σ) bond**: This type of covalent bond is formed by the end to end (hand-on) overlap of bonding orbitals along the internuclear axis. This is called as head on overlap or axial overlap. This can be formed by any one of the following types of combinations of atomic orbitals.

- **S-S overlapping**: In this case, there is overlap of two half filled s-orbitals along the internuclear axis as shown below :
- **S-P overlapping**: This type of overlap occurs between half filled s-orbitals of one atom and half filled p-orbitals of another atom.
- **P-P overlapping**: This type of overlap takes place between half filled p-orbitals of the two approaching atoms.

(ii) **pi (π) bond** : In the formation of π bond the atomic orbitals overlap in such a way that their axes remain parallel to each other and perpendicular to the internuclear axis. The orbitals formed due to sidewise overlapping consists of two saucer type charged clouds above and below the plane of the participating atoms.

3.5.5 Strength of Sigma and pi Bonds

Basically the strength of a bond depends upon the extent of overlapping. In case of sigma bond, the overlapping of orbitals takes place to a larger extent. Hence, it is stronger as compared to the pi bond where the extent of overlapping occurs to a smaller extent. Further, it is important to note that pi bond between two atoms is formed in addition to a sigma bond. It is always present in the molecules containing multiple bond (double or triple bonds).

3.6 Hybridisation

In order to explain the characteristic geometrical shapes of polyatomic molecules like CH_4, NH_3 and H_2O etc., Pauling introduced the concept of hybridisation. According to him the atomic orbitals combine to form new set of equivalent orbitals known as hybrid orbitals. Unlike pure orbitals, the hybrid orbitals are used in bond formation. The phenomenon is known as hybridisation which can be defined as the process of intermixing of the orbitals of slightly different energies so as to redistribute their energies, resulting in the formation of new set of orbitals of equivalent energies and shape. For example when one 2s and three 2p-orbitals of carbon hybridise, there is the formation of four new sp^3 hybrid orbitals.

Salient features of hybridisation: The main features of hybridisation are as under:

1. The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
2. The hybridised orbitals are always equivalent in energy and shape.
3. The hybrid orbitals are more effective in fanning stable bonds than the pure atomic orbitals.
4. These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement. Therefore, the type of hybridisation indicates the geometry of the molecules.

Important conditions for hybridisation

(i) The orbitals present in the valence shell of the atom are hybridised.

(ii)The orbitals undergoing hybridisation should have almost equal energy.

(iii) Promotion of electron is not essential condition prior to hybridisation.

(iv) It is not necessary that only half filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridisation.

3.6.1 Types of Hybridisation

There are various types of hybridisation involving s, p and d orbitals. The different types of hybridisation are as under:

(I) sp hybridisation: This type of hybridisation involves the mixing of one s and one p orbital resulting in the formation of two equivalent sp hybrid orbitals. The suitable orbitals for sp hybridisation are s and p_z, if the hybrid orbitals are to lie along the z-axis. Each sp hybrid orbitals has 50% s-character and 50% p-character. Such a molecule in which the central atom is sp-hybridised and linked directly to two other central atoms possesses linear geometry. This type of hybridisation is also known as diagonal hybridisation.

The two sp hybrids point in the opposite direction along the z-axis with projecting positive lobes and very small negative lobes, which provides more effective overlapping resulting in the formation of stronger bonds.

Example of molecule having sp hybridization:

$BeCl_2$: The ground state electronic configuration of Be is $1s^2 2s^2$. In the exited state one of the 2s-electrons is promoted to vacant 2p orbital to account for its bivalency. One 2s and one 2p-orbitals get hybridized to form two sp hybridized orbitals. These two sp hybrid orbitals are oriented in opposite direction forming an angle of 180. Each of the sp hybridized orbital overlaps with the 2p-orbital of chlorine axially and form two Be- Cl sigma bonds. This is shown in Fig. 3.8.

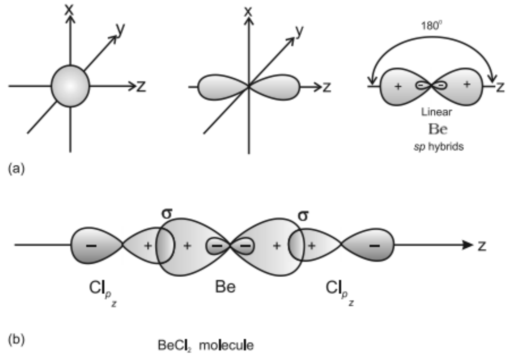


Fig.3.8 (a) Formation of sp hybridization s and p orbitals; (b) Formation of the linear $BeCl_2$ molecule

(II) sp^2 hybridization: In this hybridization there is involvement of one s and two p-orbitals in order to form three equivalent sp^2 hybridised orbitals. For example, in $BC1_3$ molecule, the ground state electronic configuration of central boron atom is $ls^2 2s^2 2p^1$. In the excited state, one of the 2s electrons is promoted to vacant 2p orbital as a result boron has three unpaired electrons. These three orbitals (one 2s and two 2p) hybridise to form three sp^2 hybrid orbitals. The three hybrid orbitals so formed are oriented in a trigonal planar arrangement and overlap with 2p orbitals of chlorine to form three B-Cl bonds. Therefore, in $BC1_3$ (Fig. 3.9), the geometry is trigonal planar with Cl-B-Cl bond angle of 120.

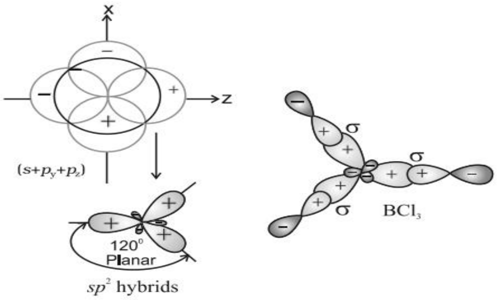


Fig.3.9 (a) Formation of sp^2 hyrids and BCl_3 molecule

(III) sp^3 hybridization: This type of hybridization can be explained by taking the example of CH_4 molecule in which there is mixing of one s-orbital and three p-orbitals of the valence shell to form four sp^3 hybrid orbital of equivalent energies and shape. There is 25% s- character and 75% p - character in each sp3 hybrid orbital. The four sp^3 hybrid orbitals so formed are directed towards the four corners of the tetrahedron. The angle between sp3 hybrid orbital is 109.5 as shown in Fig. 3.10.

The structure of NH_3 and H_2O molecules can also be explained with the help of sp^3 hybridization. In NH_3, the valence shell (outer) electronic configuration of nitrogen in the ground state is $2s^2\ 2P_x^1 2p_y^1\ 2p_z^1$; having three unpaired electrons in the sp^3 hybrid orbitals and a lone pair of electrons is present in the fourth one. These three hybrid orbitals overlap with 1s orbitals of hydrogen atoms to form three N-H sigma bonds. We know that the force of repulsion between a lone pair and a bond pair is more than the force of repulsion between two bond pairs of electrons. The molecule thus gets distorted and the bond angle is reduced to 107 from 109. The geometry of such a molecule will be pyramidal as shown in Fig. 3.11.

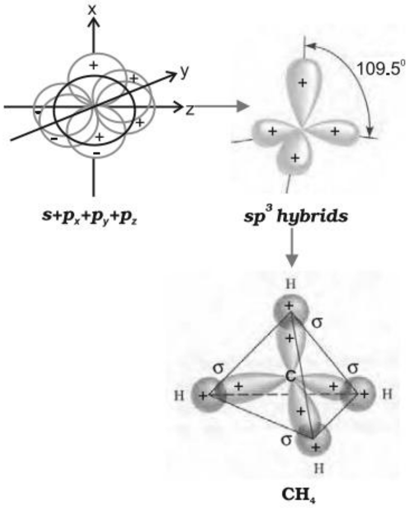


Fig.3.10 Formation of sp^3 hyrid by the combination of s, p_x, p_y and p_z atomic orbitals of carbon and the formation of CH_4 molecule.

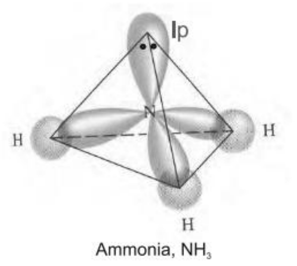


Fig.3.11 Formation of NH_3 molecule.

In case of H_2O molecule, the four oxygen orbitals (one 2s and three 2p) undergo sp^3 hybridization forming four sp^3 hybrid orbitals out of which two contain one electron each and the other two contain a pair of electrons. These four sp^3 hybrid orbitals acquire a tetrahedral geometry, with two corners occupied by hydrogen atoms while the other two by the lone pairs. The bond angle in this case is reduced to 104.5 from 109.5 (Fig. 3.12) and the molecule thus acquires a V-shape or angular geometry.

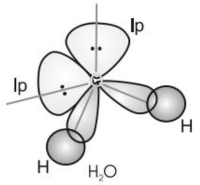


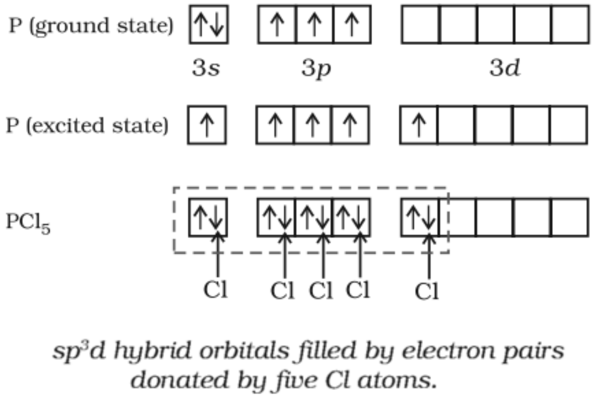
Fig.3.12 Formation of H_2O molecule.

3.6.2 Hybridization of Elements involving d Orbitals: The elements present in the third period contain d orbitals in addition to s and p orbitals. The energy of the 3d orbitals is comparable to the energy of the 3s and 3p orbitals. The energy of 3d orbitals is also comparable to those of 4s and 4p orbitals. As a consequence the hybridization involving either 3s, 3p and 3d or 3d, 4s and 4p is possible. However, since the difference in energies of 3p and 4s orbitals is significant, no hybridization involving 3p, 3d and 4s orbitals is possible. The important hybridization schemes involving s, p and d orbitals are summarized below:

Shape of molecules/ ions	Hybridisation type	Atomic orbitals	Examples
Square planar	dsp^2	$d+s+p(2)$	$[Ni(CN)_4]^{2-}$, $[Pt(Cl)_4]^{2-}$
Trigonal bipyramidal	sp^3d	$s+p(3)+d$	PF_5, PCl_5
Square pyramidal	dsp^3	$d+s+p(3)$	BrF_5, $XeOF_4$
Octahedral	sp^3d^2 d^2sp^3	$s+p(3)+d(2)$ $d(2)+s+p(3)$	SF_6, $[CrF_6]^{3-}$ $[Co(NH_3)_6]^{3+}$

(i) Formation of PCl_5 (sp^3d hybridization):

The ground state and the excited state outer most electronic configurations of phosphorus (Z= 15) are represented below.



Now the five orbitals (i.e., one s, three p and one d orbitals) are available for hybridization to yield a set of five sp^3d hybrid orbitals which are directed towards the five corners of a trigonal bipyramidal as depicted in the Fig. 3.13.

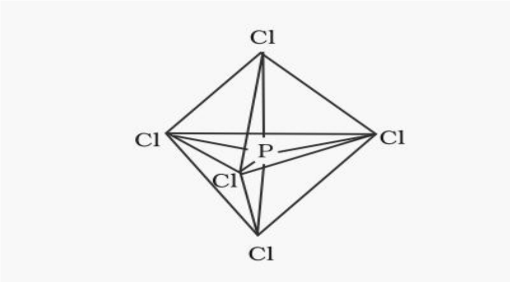


Fig.3.13 Trigonal bipyramidal shape of PCl_5 molecule.

It should be noted that all the bond angles in trigonal bipyramidal geometry are not equivalent. In $PC1_5$ the five sp^3d orbitals of phosphorus overlap with the singly occupied p orbitals of chlorine atoms to form five P-Cl sigma bonds. Three P-Cl bond lie in one plane and make an angle of 120 with each other; these bonds are termed as equatorial bonds. The remaining two P-Cl bonds lying above and the other lying below the equatorial plane, make an angle of 90 with the plane. These bonds are called axial bonds. As the axial bond pairs suffer in ore repulsive interaction from the equatorial bond pairs, therefore axial bonds have been found to be slightly longer and hence slightly weaker than the equatorial bonds; which makes $PC1_5$ molecule more reactive.

(ii) Formation of SF_6 (sp^3d^2 hybridization): In SF_6, the central sulphur atom has the ground state outer electronic configuration $3s^2 3p^4$. In the exited state, the available six orbitals i.e., one s, three p and two d are singly occupied by electrons. These orbitals hybridise to form six new sp^3d^2 hybrid orbitals, which are projected towards the six corners of a regular octahedron in SF_6. These six sp^3d^2 hybrid orbitals overlap with singly occupied orbitals of fluorine atoms to form six S-F sigma bonds. Thus SF_6 molecule has a regular octahedral geometry as shown in Fig. 3.14.

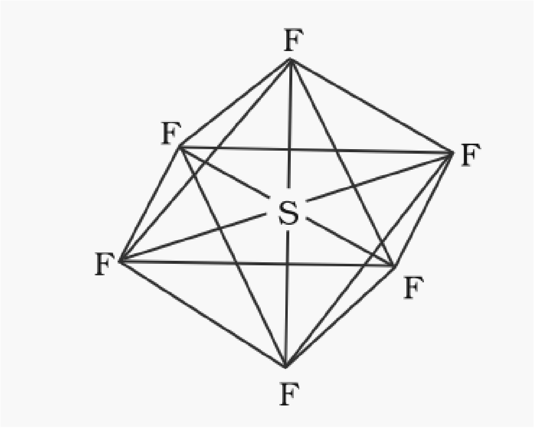


Fig.3.14 Octahedral shape of SF_6 molecule.

3.7 Co-ordinate-covalent bonding or Dative bonding

The electron contributions of combining atoms in a covalent bond are generally equal. In each shared pair of electrons one electron is contributed from each atom of the bond. However in some bond formation, the whole of the shared pair of electrons comes from only one of the combining atoms of the bond, which is referred as the donor atom. The other atom which does not contribute the electron to the shared pair but tries to pull the pair of electron towards itself is called as the acceptor atom. The bond thus formed is between the donor and acceptor atom is called as the co-ordinate or co-ordinate - covalent or dative bond.

A coordinate bond is showed as an arrow which points from the donor to the acceptor atom. In some cases, the donated pair of electron comes from a molecule as a whole which is already formed to an already formed acceptor molecule as a whole.

For Example, coordination bond between H_3N: and BF_3 molecules. The molecule, ammonia (donor) which gives a pair of electrons (lone pair) to BF_3 molecule which is electron deficient (acceptor), which has an empty orbital to accommodate the pair of electrons. Thus a dative bond is formed and the molecule as a whole is represented as $H_3N \rightarrow BF_3$.

When Proton is added to ammonia, a pair of electron is donated by nitrogen to proton and then proton shares the electron pair to form coordinate covalent bond.

3.8 Hydrogen Bonding

Nitrogen, oxygen and fluorine are the highly electronegative elements. When they are attached to a hydrogen atom to form covalent bond, the electrons of the covalent bond are shifted towards the more electronegative atom. This partially positively charged hydrogen atom forms a bond with the other more electronegative atom. This bond is known as hydrogen bond and is weaker than the covalent bond. For example, in HF molecule, the hydrogen bond exists between hydrogen atom of one molecule and fluorine atom of another molecule as depicted below:

Here, hydrogen bond acts as a bridge between two atoms which holds one atom by covalent bond and the other by hydrogen bond. Hydrogen bond is represented by a dotted line (---) while a solid line represents the covalent bond. Thus, hydrogen bond can be defined as the attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O or N) of another molecule.

3.8.1 Cause of Formation of Hydrogen Bond

When hydrogen is bonded to strongly electronegative element 'X', the electron pair shared between the two atoms moves far away from hydrogen atom. As a result the hydrogen atom becomes highly electropositive with respect to the other atom 'X'. Since there is displacement of electrons towards X, the hydrogen acquires fractional positive charge ($\delta+$) while 'X' attain fractional negative charge ($\delta-$). This results in the formation of a polar molecule having electrostatic force of attraction which can be represented as:

The magnitude of H-bonding depends on the physical state of the compound. It is maximum in the solid state and minimum in the gaseous state. Thus, the hydrogen bonds have strong influence on the structure and properties of the compounds.

3.8.2 Types of H-Bonds

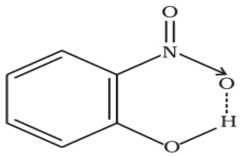
There are two types of H-bonds

(1) Intermolecular hydrogen bond

(2) Intramolecular hydrogen bond

(1) Intermolecular hydrogen bond: It is formed between two different molecules of the same or different compounds. For example, H-bond in case of HF molecule, alcohol or water molecules, etc.

(2) Intramolecular hydrogen bond: It is formed when hydrogen atom is in between the two highly electronegative (F, O, N) atoms present within the same molecule. For example, in o-nitrophenol the hydrogen is in between the two oxygen atoms.



SUMMARY

The first description of **covalent bonding** was provided by Lewis in terms of the sharing of electron pairs between atoms and he related the process to the attainment of noble gas configurations by reacting atoms as a result of sharing of electrons. The Lewis dot symbols show the number of valence electrons of the atoms of a given element and Lewis dot structures show pictorial representations of bonding in molecules.

An ionic compound is pictured as a three-dimensional aggregation of positive and negative ions in an ordered arrangement called the crystal lattice. In a crystalline solid there is a charge balance between the positive and negative ions. The crystal lattice is stabilized by the **enthalpy of lattice formation**.

While a single covalent bond is formed by sharing of an electron pair between two atoms, multiple bonds result from the sharing of two or three electron pairs. Some bonded atoms have additional pairs of electrons not involved in bonding. These are called lone- pairs of electrons. A Lewis dot structure shows the arrangement of bonded pairs and lone pairs around each atom in a molecule. Important parameters, associated with chemical bonds, like: bond length, bond angle, bond enthalpy, bond order and bond polarity have significant effect on the properties of compounds.

A number of molecules and polyatomic ions cannot be described accurately by a single Lewis structure and a number of descriptions (representations) based on the same skeletal structure are written and these taken together represent the molecule or ion. This is a very important and extremely useful concept called resonance. The contributing structures or canonical forms taken together constitute the resonance hybrid which represents the molecule or ion.

The VSEPR model used for predicting the geometrical shapes of molecules is based on the assumption that electron pairs repel each other and, therefore, tend to remain as far apart as possible. According to this model, molecular geometry is determined by repulsions between lone pairs and lone pairs; lone pairs and bonding pairs and bonding pairs and bonding pairs. The order of these repulsions being: lp-lp > lp-bp > bp-bp

The valence bond (VB) approach to covalent bonding is basically concerned with the energetics of covalent bond formation about which the Lewis and VSEPR models are silent. Basically the VB theory discusses bond formation in terms of overlap of orbitals. For example the formation of the H_2 molecule from two hydrogen atoms involves the overlap of the ls orbitals of the two H atoms which are singly occupied. It is seen that the potential energy of the system gets lowered as the two H atoms come near to each other. At the equilibrium inter-nuclear distance (bond distance) the energy touches a minimum. Any attempt to bring the nuclei still closer results in a sudden increase in energy and consequent destabilization of the molecule. Because of orbital overlap the electron density between the nuclei increases which helps in bringing them closer. It is however seen that the actual bond enthalpy and bond length values are not obtained by overlap alone and other variables have to be taken into account.

For explaining the characteristic shapes of polyatomic molecules Pauling introduced the concept of hybridization of atomic orbitals. sp, sp^2, sp^3 hybridizations of atomic orbitals of Be, B, C, N and O are used to explain the formation and geometrical shapes of molecules like $BeC1_2$, $BC1_3$, CH_4, NH_3 and H_2O.

Hydrogen bond is formed when a hydrogen atom finds itself between two highly electronegative atoms such as F, O and N. It may be intermolecular (existing between two or more molecules of the same or different substances) or intra-molecular (present within the same molecule). Hydrogen bonds have a powerful effect on the structure and properties of many compounds.

QUESTION BANK

CHAPTER 3: CHEMICAL BONDING AND MOLECULAR STRUCTURE

***Short Answer Questions* (4 Marks)**

1. Explain the formation of Ionic bond?
2. What are the factors favorable for the formation of Ionic bond?
3. How do you predict the shapes of the following molecules making use of V_{SEPR} theory?

   a) XeF_2 b) BrF_5 c) ClF_3 d) SF_4
4. Explain the structure of CH_4 molecule.
5. Explain the hybridization involved in PCl_5 molecule.
6. Explain the hybridization involved in SF_6 molecule.
7. What is Hydrogen bond? What are the different types of hydrogen bonds? Give example.

CHAPTER - 4

STATES OF MATTER

INTRODUCTION

In previous units we have learnt about the properties related to single particle of matter, such as atomic size, ionization enthalpy, electronic charge density, molecular shape and polarity. etc. Most of the observable characteristics of chemical systems with which we are familiar represent bulk properties of matter, i.e., the properties associated with a collection of a large number of atoms, ions or molecules. For example, an individual molecule of a liquid does not boil but the bulk boils. Collection of water molecules has wetting properties; individual molecules do not wet. Water can exist as ice, which is a solid; it can exist as liquid; or it can exist in the gaseous state as water vapour or steam. Physical properties of ice, water and steam are very different. In all the three states of water chemical composition of water remains the same i.e., H_2O. Characteristics of the three states of water depend on the energies of molecules and on the manner in which water molecules aggregate. Same is true for other substances also.

Chemical properties of a substance do not change with the change of its physical state; but rate of chemical reactions do depend upon the physical state. Many times in calculations while dealing with data of experiments we require knowledge of the state of matter. Therefore, it becomes necessary for a chemist to know the physical laws which govern the behaviour of matter in different states. In this unit, we will learn more about these three physical states of matter particularly liquid and gaseous states. To begin with, it is necessary to understand the nature of intermolecular forces, molecular interactions and effect of thermal energy on the motion of particles because a balance between these determines the state of a substance.

4. 1 Inter molecular Forces

Intermolecular forces are the forces of attraction and repulsion between interacting particles (atoms and molecules). This term does not include the electrostatic forces that exist between the two oppositely charged ions and the forces that hold atoms of a molecule together i.e., covalent bonds.

Attractive intermolecular forces are known as Van der Waals forces, in honour of Dutch scientist Johannes Van der Waals (1837- 1923), who explained the deviation of real gases from the ideal behaviour through these forces. We will learn about this later in this unit. Van der Waals forces vary considerably in magnitude and include dispersion forces or London forces, dipole-dipole forces, and dipole-induced dipole forces. A particularly strong type of dipole-dipole interaction is hydrogen bonding. Only a few elements can participate in hydrogen bond formation, therefore it is treated as a separate category.

4.2 Thermal Energy

Thermal energy is the energy of a body arising from motion of its atoms or molecules. It is directly proportional to the temperature of the substance. It is the measure of average kinetic energy of the particles of the matter and is thus responsible for movement of particles. This movement of particles is called thermal motion.

4.3 Intermolecular Forces Vs Thermal Interactions

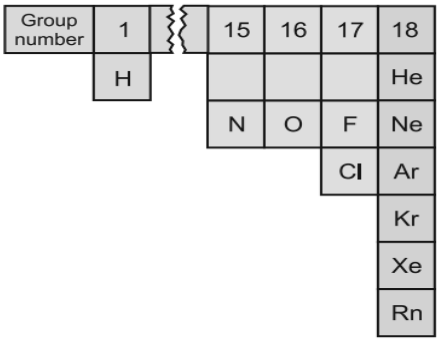
We have already learnt that intermolecular forces tend to keep the molecules together but thermal energy of the molecules tends to keep them apart. Three states of matter are the result of balance between intermolecular forces and the thermal energy of the molecules. When molecular interactions are very weak, molecules do not cling together to make liquid or solid unless thermal energy is reduced by lowering the temperature. Gases do not liquify on compression only, although molecules come very close to each other and intermolecular forces operate to the maximum. However, when thermal energy of molecules is reduced by lowering the temperature; the gases can be very easily liquified. Predominance of thermal energy and the molecular interaction energy of a substance in three states is depicted as follows:

We have already learnt the cause for the existence of the three states of matter. Now we will learn more about gaseous and liquid states and the laws which govern the behaviour of matter in these states. We shall deal with the solid state in class XII.

4.4 The Gaseous State

This is the simplest state of matter. Throughout our life we remain immersed in the ocean of air which is a mixture of gases. We spend our life in the lowermost layer of the atmosphere called troposphere, which is held to the surface of the earth by gravitational force. The thin layer of atmosphere is vital to our life. It shields us from harmful radiations and contains substances like dioxygen, dinitrogen, carbon dioxide, water vapour, etc.

Let us now focus our attention on the behaviour of substances which exist in the gaseous state under normal conditions of temperature and pressure. A look at the periodic table shows that only eleven ele1nentsexistasgases under normal conditions (Fig 4.1).



Group number	1	15	16	17	18
	H				He
		N	O	F	Ne
				Cl	Ar
					Kr
					Xe
					Rn

Fig.4.1 Eleven elements that exist as gases

The gaseous state is characterized by the following physical properties.

- Gases are highly compressible.
- Gases exert pressure equally in all directions.
- Gases have much lower density than the solids and liquids.
- The volume and the shape of gases are not fixed. These assume volume and shape of the container.
- Gases mix evenly and completely in all proportions without any mechanical aid.

Simplicity of gases is due to the fact that the forces of interaction between their molecules are negligible. Their behaviour is governed by same general laws, which were discovered as a result of their experimental studies. These laws are relationships between measurable properties of gases. Some of these properties like pressure, volume, temperature and mass are very important because relationships between these variables describe state of the gas. Interdependence of these variables leads to the formulation of gas laws. In the next section we will learn about gas laws.

4.5 The Gas Laws

The gas laws which we will study now are the result of research carried on for several centuries on the physical properties of gases. The first reliable measurement on properties of gases was made by Anglo-Irish scientist Robert Boyle in 1662. The law which he formulated is known as Boyle's Law. Later on attempts to fly in air with the help of hot air balloons motivated Jaccques Charles and Joseph Lewis Gay Lussac to discover additional gas laws. Contribution from Avogadro and others provided lot of information about gaseous state.

4.5.1 Boyle's Law (Pressure-Volume Relationship)

On the basis of his experiments, Robert Boyle reached to the conclusion that at constant temperature, the pressure of a fixed amount (i.e., number of moles n) of gas varies inversely with its volume. This is known as Boyle's law. Mathematically, it can be written as

$$p \propto \frac{1}{V} \quad \text{(at constant T and n)} \qquad (4.1)$$

$$\Rightarrow p = k_1 \frac{1}{V} \qquad (4.2)$$

where k is the proportionality constant. The value of constant k depends upon the a1nount of the gas, temperature of the gas and the units in which p and V are expressed.

On rearranging equation (4.2) we obtain

$$pV = k_1 \qquad (4.3)$$

It means that at constant temperature, product of pressure and volume of a fixed amount of gas is constant. If a fixed amount of gas at constant temperature T occupying volume V at pressure p_1 undergoes expansion, so that volume becomes V_2 and pressure becomes p_2, then according to Boyle's law:

$$p_1V_1 = p_2V_2 = \text{constant} \qquad (4.4)$$

$$\Rightarrow \frac{p_1}{p_2} = \frac{V_2}{V_1} \qquad (4.5)$$

Figure 4.5 shows two conventional ways of graphically presenting Boyle's law. Fig. 4.2 (a) is the graph of equation (4.3) at different temperatures. The value of k for each curve is different because for a given mass of gas, it varies only with temperature. Each curve corresponds to a different constant temperature and is known as an isotherm (constant temperature plot). Higher curves correspond to higher temperature. It should be noted that volume of the gas doubles if pressure is halved. Table 4.1 gives effect of pressure on volume of 0.09 mol of CO at 300 K.

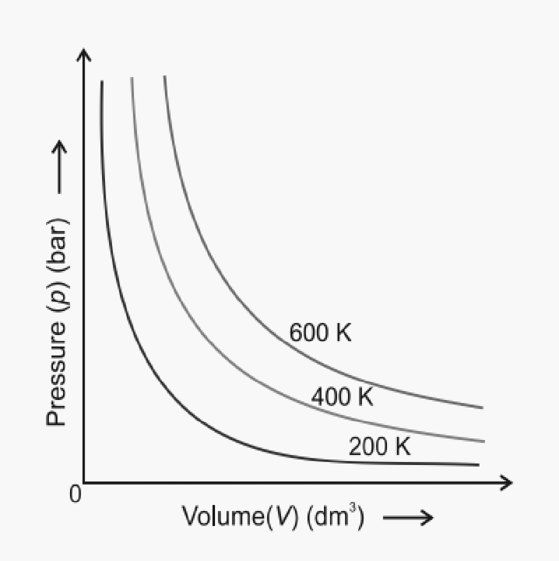


Fig. 4.2(a) Graph of pressure, P Vs Volume, V

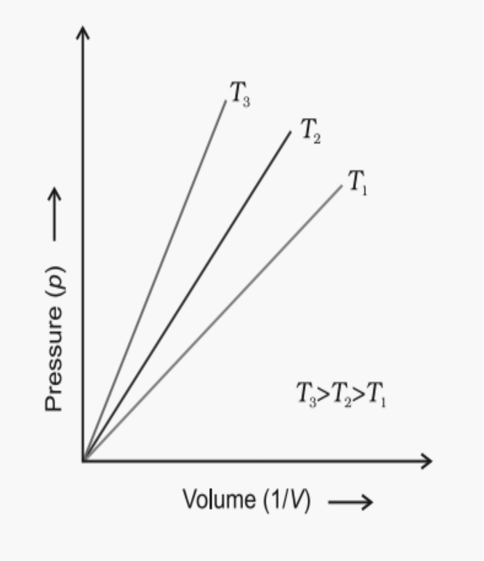


Fig. 4.5(b) Graph of pressure of a gas P Vs. 1/V of a gas at different temperatures.

Fig 4.2 (b) represents the graph between p and 1/V. It is a straight line passing through origin. However, at high pressures, gases deviate from Boyle's law and under such conditions a straight line is not obtained in the graph.

Table 4.1 Effect of pressure on the volume of 0.09 mol of CO at 300 K.

Pressure/10^4 Pa	**Volume/10^{-3} m^3**	**$(1/V)/m^{-3}$**	**$pV/10^2$ Pa m^3**
2.0	112.0	8.90	22.40
2.5	89.2	11.2	22.30
3.5	64.2	15.6	22.47
4.0	56.3	17.7	22.50
6.0	37.4	26.7	22.44
8.0	28.1	35.6	22.48
10.0	22.4	44.6	22.40

Experiments of Boyle, in a quantitative manner prove that gases are highly compressible because when a given mass of a gas is compressed, the same number of molecules occupies a smaller space. This means that gases become denser at high pressure. A relationship can be obtained between density and pressure of a gas by using Boyle's law:

By definition, density'd' is related to the mass 'm' and the volume 'V by the relation $d = \frac{m}{v}$. If we put value of V in this equation from Boyle's law equation, we obtain the relationship.

$$d = \left(\frac{m}{k_1}\right)p = k^1 p$$

This shows that at a constant temperature, pressure is directly proportional to the density of a fixed mass of the gas.

4.5.2 Charles' Law (Temperature-Volume Relationship)

Charles and Gay Lussac performed several experiments on gases independently to improve upon hot air balloon technology. Their investigations showed that for a fixed mass of a gas at constant pressure, volu1ne of a gas increases on increasing temperature and decreases on cooling. They found that for each degree rise in temperature, volume of a gas increases by 1/273.15 of the original volume of the gas at 0^0 C. Thus if volumes of the gas at 0^0 C and at t^0 C are V_0 and V_t respectively, then

$$V_t = V_0 + \frac{t}{273.15} V_0$$

$$\Rightarrow V_t = V_0 \left(1 + \frac{t}{273.15}\right)$$

$$\Rightarrow V_t = V_0 \left(\frac{273.15 + t}{273.15}\right) \qquad (4.6)$$

At this stage, we define a new scale of temperature such that t^0 C on new scale is given by T = 273.15 + t and O^0C will be given by T= 273.15. This new temperature scale is called the Kelvin temperature scale or Absolute temperature scale.

Thus 0^0C on the celsius scale is equal to 273.15 K at the absolute scale. Note that degree sign is not used while writing the temperature in absolute temperature scale. i.e., Kelvin scale. Kelvin scale of temperature is also called Thermodynamic scale of temperature and is used in all scientific works.

Thus we add 273 (more precisely 273.15) to the Celsius temperature to obtain temperature at Kelvin scale.

If we write T_t = 273.15 + t and T_0= 273.15 in the equation (4.6), we obtain the relationship

$$V_t = V_0 \left(\frac{T_t}{T_0}\right)$$

$$\Rightarrow \frac{V_t}{V_0} = \frac{T_t}{T_0} \qquad (4.7)$$

Thus we can write a general equation as follows

$$\frac{V_2}{V_1} = \frac{T_2}{T_1} \qquad (4.8)$$

$$\Rightarrow \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\Rightarrow \frac{V}{T} = \text{constant} = k_2 \qquad (4.9)$$

$$\text{Thus } V = k_2 T \qquad (4.10)$$

The value of constant k_2 (4. 10) is determined by the pressure of the gas, its amount and the units in which volume V is expressed.

Equation (4.10) is the mathematical expression for Charles' law, which states that pressure remaining constant, the volume of a fixed mass of a gas is directly proportional to its absolute temperature. Charles found that for all gases, at any given pressure, graph of volume Vs temperature (in celsius) is a straight line and on extending to zero volume, each line intercepts the temperature axis at - 273. 15 C. Slopes of lines obtained at different pressure are different but at zero volume all the lines meet the temperature axis at - 273. 15^0 C (Fig. 4.3).

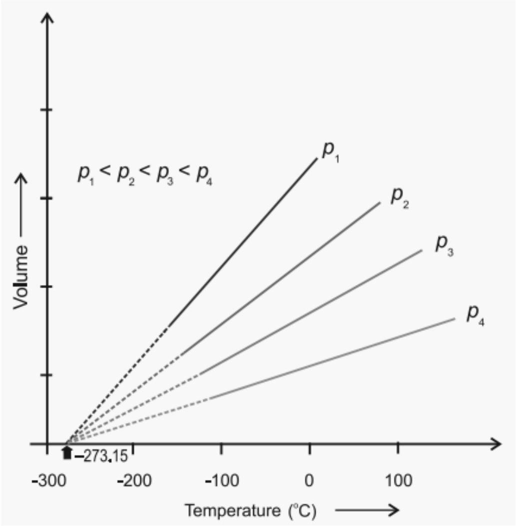


Fig. 4.3 Volume Vs Temperature graph

Each line of the volume Vs temperature graph is called isobar. Observations of Charles can be interpreted if we put the value of ‘t’ in equation (4.3) as - 273.15C. We can see that the volume of the gas at - 273.15 C will be zero. This means that gas will not exist. In fact all the gases get liquified before this temperature is reached. The lowest hypothetical or imaginary temperature at which gases are supposed to occupy zero volume is called Absolute zero.

All gases obey Charles' law at very low pressures and high temperatures.

4.5.3 Gay Lussac's Law (Pressure-Temperature Relationship)

Pressure in well inflated tyres of automobiles is al1nost constant, but on a hot summer day this increases considerably and tyre may burst if pressure is not adjusted properly. During winters, on a cold morning one may find the pressure in the tyres of a vehicle decreased considerably. The mathematical relationship between pressure and temperature was given by Joseph Gay Lussac and is known as Gay Lussac's law. It states that at constant volume, pressure of a fixed amount of a gas varies directly with the temperature. Mathematically,

$$p \propto T$$

$$\frac{p}{T} = \text{constant}$$

This relationship can be derived from Boyle's law and Charles' Law. Pressure vs temperature (Kelvin) graph at constant molar volume is shown in Fig. 4.4. Each line of this graph is called isochore.

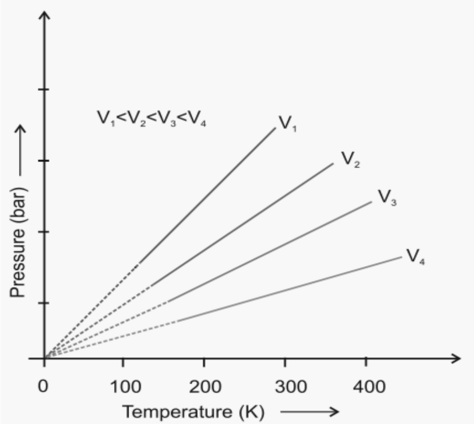


Fig 4.4 Pressure Vs temperature graph (isochors) of a graph

4.5.4 Avogadro Law (Volume- Amount Relationship)

In 1811 Italian scientist Amedeo Avogadro tried to combine conclusions of Dalton's atomic theory and Gay Lussac's law of combining volumes which is now known as Avogadro law. It states that equal volumes of all gases under the same conditions of temperature and pressure contain equal number of molecules. This means that as long as the temperature and pressure remain constant, the volume depends upon number of molecules of the gas or in other words amount of the gas. Mathematically we can write

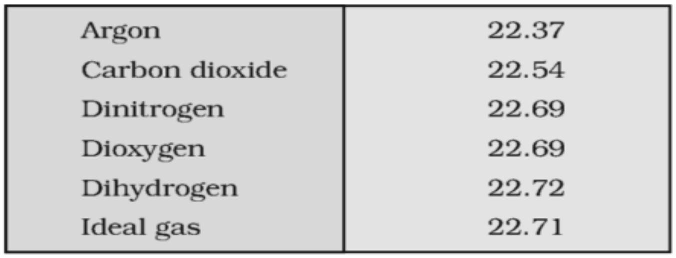
$V \propto n$ where n is the number of moles of the gas.

$$\Rightarrow V = k_4 n \qquad (4.11)$$

The number of molecules in one mole of a gas has been determined to be 6.022 x 10^{23} and is known as Avogadro constant. You will find that this is the same number which we came across while discussing definition of a 'mole'.

Since volume of a gas is directly proportional to the number of moles; one mole of each gas at standard temperature and pressure (STP) will have same volume. Standard temperature and pressure means, 273.15 K (0°C) temperature and 1 bar (i.e., exactly 105 Pascal) pressure. These values approximate freezing temperature of water and atmospheric pressure at sea level. At STP molar volume of an ideal gas or a combination of ideal gases is 22.71098 L mo1^{-1}. Molar volume of some gases is given in Table 4.2.

Table 4.2 Molar volume in liters per mole of some gases at 273.15 K and 1 bar (STP)



Argon	22.37
Carbon dioxide	22.54
Dinitrogen	22.69
Dioxygen	22.69
Dihydrogen	22.72
Ideal gas	22.71

Number of moles of a gas can be calculated as follows

$$n=\frac{m}{M} \tag{4.12}$$

Where m = mass of the gas under investigation and M = molar mass. Thus,

$$V=k_4\frac{m}{M} \tag{4. 13}$$

Equation (4.13) can be rearranged as follows :

$$M=k_4\frac{m}{V}=k_4d \tag{4. 14}$$

Here 'd' is the density of the gas. We can conclude from equation (4.14) that the density of a gas is directly proportional to its molar mass.

A gas that follows Boyle's law, Charles' law and Avogadro law strictly is called an ideal gas. Such a gas is hypothetical. It is assumed that intermolecular forces are not present between the molecules of an ideal gas. Real gases follow these laws only under certain specific conditions when forces of interaction are practically negligible. In all other situations these deviate from ideal behaviour. You will learn about the deviations later in this unit.

Ideal Gas Equation

The three laws which we have learnt till now can be combined together in a single equation which is known as ideal gas equation.

At constant T and n; $V \propto \frac{1}{p}$ Boyle's Law

At constant p and n; $V \propto T$ Charles' Law

At constant p and T ; $V \propto n$ Avogadro Law

Thus, $$V \propto \frac{nT}{p} \tag{4. 15}$$

$$\Rightarrow V = R\frac{nT}{p} \tag{4. 16}$$

where R is proportionality constant. On rearranging the equation (4.16) we obtain

$$pV = nRT \tag{4. 17}$$

$$\Rightarrow R=\frac{pV}{nT} \tag{4. 18}$$

R is called gas constant. It is same for all gases. Therefore, it is also called Universal Gas Constant. Equation (4.17) is called ideal gas equation.

Equation (4.18) shows that the value of R depends upon units in which p, V and T are measured. If three variables in this equation are known fourth can be calculated. From this equation we can see that at constant temperature and pressure n moles of any gas will have the same volume because $V=\frac{nRT}{p}$ and n, R, T and p are constant. This equation will be applicable to any gas, under those conditions when behaviour of the gas approaches ideal behaviour. Volume of one mole of an ideal gas under STP conditions (273.15 K and 1 bar pressure) is 22.710981 L mol^{-1}. Value of R is 8.20578 x 10^{-2} L.atm K^{-1} $mo1^{-1}$.

Ideal gas equation is a relation between four variables and it describes the state of any gas, therefore, it is also called equation of state.

Let us now go back to the ideal gas equation. This is the relationship for the simultaneous variation of the variables. If temperature, volume and pressure of a fixed amount of gas vary from T_1, V_1 and p_1 to V_2, T_2, and p_2 then we can write

$$\frac{p_1V_1}{T_1} = nR \quad \text{and} \quad \frac{p_2V_2}{T_2} = nR$$

$$\Rightarrow \frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2} \tag{4. 19}$$

Equation (4. 19) is a very useful equation. If out of six, values of five variables are known, the value of unknown variable can be calculated from the equation (4.19). This equation is also known as Combined gas law.

4.6 Graham's Law of Diffusion

When two gases are placed in contact, they mix spontaneously. This is due to the movement of molecule of one gas into the other gas. This process of mixing of gases by random motion of the molecules is called as **diffusion.**

In 1829, Graham formulated what is now known as Graham's law of diffusion. It states that,

"Under the same conditions of temperature and pressure, the rates of diffusion of different gases are inversely proportional to the square roots of their densities". Mathematically the law can be expressed as

$$r \propto \frac{1}{\sqrt{d}} \tag{4. 20}$$

where ‘r’ is the rate of diffusion and ‘d’ is the density of the gas. The rate of diffusion of a gas is the volume of the gas that diffuses in unit time.

$$r = \frac{\text{volume of the gas diffused (v)}}{\text{Time of diffusion (t)}}$$

Under similar conditions of temperature and pressure, let r_1 and r_2 be the rates of diffusion and d_1 and d_2 be the densities of two gases respectively. Then according to Graham’s law of diffusion

$$r_1 \propto \frac{1}{\sqrt{d_1}}; r_2 \propto \frac{1}{\sqrt{d_2}}$$

$$\frac{r_1}{r_2}=\sqrt{\frac{d_2}{d_1}} \qquad (4.\ 21)$$

Since the molar mass of a gas is directly proportional to its density

$$M \propto d$$

$$r \propto \frac{1}{\sqrt{M}}$$

$$\frac{r_1}{r_2}=\sqrt{\frac{M_2}{M_1}} \qquad (4.\ 22)$$

where M_1 and M_2 are molar masses of the gases

Thus, the rate of diffusion of a gas is inversely proportional to the square root of its molar mass. But, the molar mass of a gas is proportional to its vapour density,

$$M \propto V_d \ \text{ or } (M = 2 \text{ X } V_d)$$

$$\frac{r_1}{r_2}=\sqrt{\frac{d_2}{d_1}}=\sqrt{\frac{M_2}{M_1}}=\sqrt{\frac{V_{d_2}}{V_{d_1}}} \qquad (4.\ 23)$$

4.6.1 Dalton's Law of Partial Pressures

The law was formulated by John Dalton in 1801. It states that the total pressure exerted by the mixture of non-reactive gases is equal to the sum of the partial pressures of individual gases i .e.. the pressures which these gases would exert if they were enclosed separately in the same volume and under the same conditions of temperature. In a mixture of gases, the pressure exerted by the individual gas is called partial pressure. Mathematically,

$$p_{Total} = p_1 + p_2 + p_3 + ...(\text{at constant T,V}) \qquad (4.\ 24)$$

where p_{Total} is the total pressure exerted by the mixture of gases and p_1, p_2, p_3 etc. are partial pressures of gases.

Gases are generally collected over water and therefore are moist. Pressure of dry gas can be calculated by subtracting vapour pressure of water from the total pressure of the moist gas which contains water vapours also. Pressure exerted by saturated water vapour is called aqueous tension.

$$p_{Dry\ gas} = p_{Total} - \text{Aqueous tension} \qquad (4.25)$$

Partial pressure in terms of mole fraction

Suppose at the temperature T, three gases, enclosed in the volume V, exert partial pressure p_1, p_2 and p_3 respectively, then,

$$p_1 = \frac{n_1RT}{V} \qquad (4.\ 26)$$

$$p_2 = \frac{n_2RT}{V} \tag{4. 27}$$

$$p_3 = \frac{n_3RT}{V} \tag{4. 28}$$

where n_1, n_2 and n_3 are number of moles of these gases. Thus, expression for total pressure will be

$$\begin{aligned} p_{Total} &= p_1 + p_2 + p_3 \\ &= \frac{n_1RT}{V} + \frac{n_2RT}{V} + \frac{n_3RT}{V} \\ &= (n_1 + n_2 + n_3)\frac{RT}{V} \end{aligned} \tag{4. 29}$$

On dividing p_1 by p_{Total} we get

$$\frac{p_1}{p_{Total}} = \left(\frac{n_1}{n_1 + n_2 + n_3}\right) = \frac{n_1}{n} = x_1 \tag{4. 30}$$

where $n = n_1 + n_2 + n_3$, x_1 is called mole fraction of the first gas.

Thus, $p_2 = x_1\ p_{Total}$ (4. 31)

Similarly for other two gases we can write

$$p_2 = x_2\ p_{Total} \quad p_3 = x_3\ p_{Total} \tag{4. 32}$$

Thus a general equation can be written as

$$p_i = x_i\ p_{Total} \tag{4. 33}$$

Where p_i and x_i are partial pressure and mole fraction of i^{th} gas respectively. If total pressure of a mixture of gases is known, the equation (4.33) can be used to find out pressure exerted by individual gases.

4.7 Kinetic Molecular Theory of Gases

So far we have learnt the laws (e.g., Boyle's law, Charles' law etc.) which are concise statements of experimental facts observed in the laboratory by the scientists. Conducting careful experiments is an important aspect of scientific method and it tells us how the particular system is behaving under different conditions. However, once the experimental facts are established, a scientist is curious to know why the system is behaving in that way. For example, gas laws help us to predict that pressure increases when we compress gases but we would like to know what happens at molecular level when a gas is compressed. A theory is constructed to answer such questions. A theory is a model (i.e., a mental picture) that enables us to better understand our observations. The theory that attempts to elucidate the behaviour of gases is known as kinetic molecular theory.

Assumptions or postulates of the kinetic- molecular theory of gases are given below. These postulates are related to atoms and molecules which cannot be seen, hence it is said to provide a microscopic model of gases.

- Gases consist of large number of identical particles (atoms or molecules) that are so small and so far apart on the average that the actual volume of the molecules is negligible in comparison to the empty space between them. They are considered as point masses. This assumption explains the great compressibility of gases.
- There is no force of attraction between the particles of a gas at ordinary temperature and pressure. The support for this assumption comes from the fact that gases expand and occupy all the space available to them.
- Particles of a gas are always in constant and random motion. If the particles were at rest and occupied fixed positions, then a gas would have had a fixed shape which is not observed.
- Particles of a gas move in all possible directions in straight lines. During their random motion, they collide with each other and with the walls of the container. Pressure is exerted by the gas as a result of collision of the particles with the walls of the container.
- Collisions of gas molecules are perfectly elastic. This means that total energy of molecules before and after the collision remains same. There may be exchange of energy between colliding molecules, their individual energies may change, but the sum of their energies remains constant. If there were loss of kinetic energy, the motion of molecules will stop and gases will settle down. This is contrary to what is actually observed.
- At any particular time, different particles in the gas have different speeds and hence different kinetic energies. This assumption is reasonable because as the particles collide, we expect their speed to change. Even if initial speed of all the particles was same, the molecular collisions will disrupt this uniformity. Consequently the particles mu st have different speeds, which go on changing constantly. It is possible to show that though the individual speeds are changing, the distribution of speeds remains constant at a particular temperature.
- If a molecule has variable speed, then it must have a variable kinetic energy. Under these circumstances, we can talk only about average kinetic energy. In kinetic theory it is assumed that average kinetic energy of the gas molecules is directly proportional to the absolute temperature. It is seen that on heating a gas at constant volume, the pressure increases. On heating the gas, kinetic energy of the particles increases and these strike the walls of the container more frequently thus exerting more pressure.

Kinetic theory of gases allows us to derive theoretically, all the gas laws studied in the previous sections. Calculations and predictions based on kinetic theory of gases agree very well with the experimental observations and thus establish the correctness of this model.

4.8 Kinetic Gas Equation of an Ideal Gas

We can use this equation to calculate the root mean square velocity of gas molecules at any given temperature and pressure.

$$pV = \frac{1}{3} mnu_{rms}^{2} \qquad (4.34)$$

where p = Pressure of the gas, V = Volume of the gas, m = mass of one molecule of the gas

n = no of molecules of the gas, u_{rms} = RMS speed of the gas molecules.

4.9 Distribution of Molecular Speeds

In 1860 James Clerk Maxwell (1831–1879) developed an expression that describes the distribution of molecular speeds in a very definite manner. His work and subsequent developments by other scientists were highly controversial because direct detection of molecules could not be achieved experimentally at that time. However, about 60 years later, experiments were conceived that confirmed Maxwell's predictions.

At a particular temperature, different molecules of a gas possess different speeds. Due to continuous collision among the molecules themselves and against the walls of the container, their speed keeps on changing. As a result of collision, some others are speeded up, some others are slowed down and hence the fashions of molecules possessing particular speed remain constant at constant temperature.

If fractions of molecules possessing particular speed are plotted against their corresponding speeds at a particular temperature, a curve is obtained. This distribution of speed is called Maxwell-Boltzmann distribution.

Fig 4.5 Maxwell – Boltzmann distribution curve for a gas at three different temperatures

From this curve, it may observed that,

1) Fraction of molecules having too low or too high-speed are very small.
2) The peak of the curve corresponds to a speed possessed by the maximum fraction or maximum number of molecules. This speed is called most probable speed.

Maxwell – Boltzmann distribution curve for a gas at three different temperatures is

- The peak shift forward showing that the most probable velocity increases.
- The peak shift downwards showing that fraction of molecules or number of molecules possessing most probable velocity decreases.
- The curve is flattened in the middle showing that more molecules have speeds near to the most probable speed.
- The fraction of molecules having higher speed increases.

- The fraction of molecules having lower speed decreases.

Molecular Velocities

In kinetic theory of gas the velocity of molecules is expressed in the following three terms.

(i) **Root-mean square velocity or R.M.S. Velocity (u_{rms})** may be defined as, “The square root of the mean value of the squares of the velocities of all molecules”. It is denoted by u. If $u_1, u_2, \ldots.., u_n$ are the velocities for N molecules, then

$$u_{rms} = \sqrt{\frac{u_1^2 + u_2^2 + \ldots.. + u_n^2}{N}} \qquad (4.35)$$

(ii*)* **The average velocity (u_{av})** is the arithmetic mean of the velocities of all molecules. It is denoted by v and is given by the following equation:

$$u_{av} = \frac{u_1 + u_2 + \ldots.. + u_n}{N} \qquad (4.36)$$

Average velocity (u_{av}) = 0.9213 x R. M. S. velocity (u_{rms})

(ii) **The most probable velocity (u_{mp})** is the velocity possessed by maximum number of

molecules of the gas at a given temperature. It is denoted by α and is given by the following equation:

$$u_{mp} = \sqrt{\frac{2RT}{M}} \qquad (4.37)$$

R= Gas constant, M= molar mass of the gas

These three velocities are related to each other as:

$$u_{rms} > u_{av} > u_{mp}$$

$$u_{mp} : u_{av} : u_{rms} = \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}}$$

$$= \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3} \qquad (4.38)$$

$$= 1.000 : 1.128 : 1.224$$

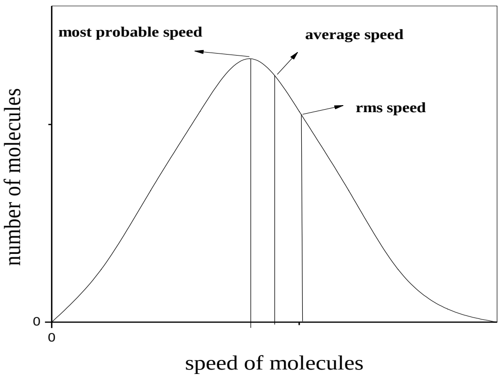


Fig 4.6 Maxwell's distribution of three types of velocities

4.10 Kinetic Energy

Kinetic gas equation $pV = \frac{1}{3} mnu_{rms}^2$

For one mole of a gas 'n' the number of molecules is equal to Avogadro's number 'N'. Then 'mN' represents the molar mass 'M' of the gas.

$$pV = \frac{1}{3} Mu_{rms}^2 = \frac{2}{3}\left(\frac{1}{2} Mu_{rms}^2\right) = \frac{2}{3} E_k \qquad (4.39)$$

where E_k is the kinetic energy of one mole of gas. For one mole of gas, the ideal gas equation is

$$pV = RT \qquad (4.40)$$

From equations (4.39) and (4.40) we have

$$\frac{2}{3} E_k = RT \text{ or } E_k = \frac{3}{2} RT \qquad (4.41)$$

For 'n' moles of a gas $E_k = \frac{3}{2} nRT$ (4.42)

Kinetic energy is directly proportional to the temperature in Kelvin scale $E_k \propto T$

It means that one mole of any gas has the same kinetic energy at a given temperature. The kinetic energy for one molecule of a gas

$$\frac{E_k}{N} = \frac{3}{2}\left(\frac{R}{N}\right)T = \frac{3}{2} kT \qquad (4.43)$$

where 'k' is called Boltzmann constant k= 1.38 x 10^{-16} erg K^{-1} molecule^{-1} = 1.38 x 10^{-23} J K^{-1} molecule^{-1}

4.11 Behaviour of Real Gases: Deviation From Ideal Gas Behaviour

Our theoretical model of gases corresponds very well with the experimental observations. Difficulty arises when we try to test how far the relation pV= nRT reproduce actual pressure-volume-temperature relationship of gases. To test this point we plot pV vs p plot of gases because at constant temperature, pV will be constant (Boyle's law) and pV vs p graph at all pressures will be a straight line parallel to x-axis. Fig. 4.7 shows such a plot constructed from actual data for several gases at 273 K.

It can be seen easily that at constant temperature pV vs p plot for real gases is not a straight line. There is a significant deviation from ideal behaviour. Two types of curves are seen. In the curves for dihydrogen and helium, as the pressure increases the value of pV also increases. The second type of plot is seen in the case of other gases like carbon monoxide and methane. In these plots first there is a negative deviation from ideal behavior, the pV value decreases with increase in pressure and reaches to a minimum value characteristic of a gas. After that pV value starts increasing. The curve then crosses the line for ideal gas and after that shows positive deviation continuously. It is thus; found that real gases do not follow ideal gas equation perfectly under all conditions.

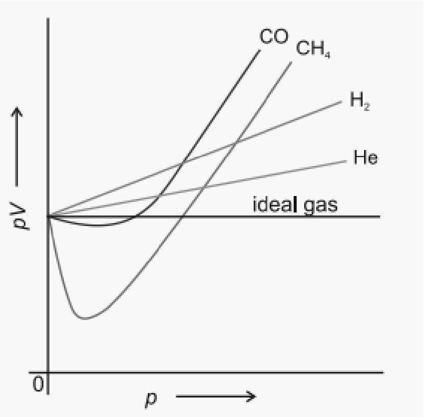


Fig. 4.7 plots of pV vs p for real gas and ideal gas

Deviation from ideal behaviour also becomes apparent when pressure vs volume plot is drawn. The pressure vs volume plot of experimental data (real gas) and that theoretically calculated from Boyle's law (ideal gas) should coincide. Fig. 4.8 shows these plots. It is apparent that at very high pressure the measured volume is more than the calculated volume. At low pressures, measured and calculated volumes approach each other.

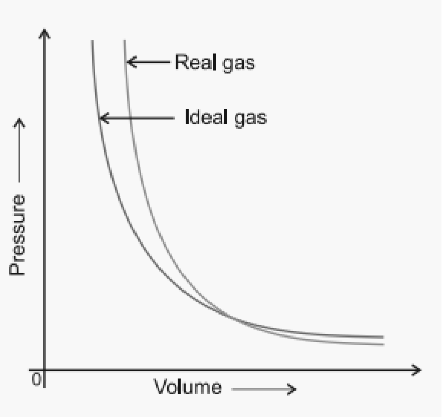


Fig. 4.8 plots of pressure vs volume for real gas and ideal gas

It is found that real gases do not follow, Boyle's law. Charles law and Avogadro law perfectly under all conditions. Now two questions arise.

(i) Why do gases deviate from the ideal behaviour?

(ii) What are the conditions under which gases deviate from ideality?

We get the answer of the first question if we look into postulates of kinetic theory once again. We find that two assumptions of the kinetic theory do not hold good. These are

(a) There is no force of attraction between the molecules of a gas.

(b) Volume of the molecules of a gas is negligibly small in comparison to the space occupied by the gas.

If assumption (a) is correct, the gas will never liquefy. However, we know that gases do liquefy when cooled and compressed. Also, liquid s formed is very difficult to compress.

This means that forces of repulsion are powerful enough and prevent squashing of molecules in tiny volu1ne. If assumption (b) is correct, the pressure vs volume graph of experimental data (real gas) and that theoretically calculated from Boyles law (ideal gas) should coincide.

Real gases show deviations from ideal gas law because molecules interact with each other. At high pressures molecules of gases are very close to each other. Molecular interactions start operating. At high pressure, molecules do not strike the walls of the container with full i1npact because these are dragged back by other molecules due to molecular attractive forces. This affects the pressure exerted by the molecules on the walls of the container. Thus, the pressure exerted by the gas is lower than the pressure exerted by the ideal gas.

$$p_{\text{ideal}} = \underset{\text{observed pressure}}{p_{\text{real}}} + \underset{\text{correction term}}{\frac{an^2}{V^2}} \qquad (4.44)$$

Here ‘a’ is constant.

Repulsive forces also become significant. Repulsive interactions are short-range interactions and are significant when molecules are almost in contact. This is the situation at high pressure. The repulsive forces cause the molecules to behave as small but impenetrable spheres. The volume occupied by the molecules also becomes significant because instead of moving in volume V, these are now restricted to volume (V-nb) where nb is approximately the total volume occupied by the molecules themselves. Here, ‘b’ is a constant. Having taken into account the corrections for pressure and volume, we can rewrite equation (4.44) as

$$\left(p+\frac{an^2}{V^2}\right) V - nb = nRT \qquad (4.45)$$

Equation (4.45) is known as van der Waals equation. In this equation n is number of moles of the gas. Constants ‘a’ and ‘b’ are called van der Waals constants and their value depends on the characteristic of a gas. Value of 'a' is measure of magnitude of intermolecular attractive forces within the gas and is independent of temperature and pressure.

Also, at very low temperature, intermolecular forces become significant. As the molecules travel with low average speed, these can be captured by one another due to attractive forces. Real gases show ideal behaviour when conditions of temperature and pressure are such that the intermolecular forces are practically negligible. The real gases show ideal behaviour when pressure approaches zero.

The deviation from ideal behaviour can be measured in terms of compressibility factor Z, which is the ratio of product p V and nRT. Mathematically

$$Z = \frac{\mathrm{pV}}{\mathrm{nRT}} \tag{4.46}$$

For ideal gas Z = 1 at all temperatures and pressures because pV = n RT. The graph of Z vs p will be a straight line parallel to pressure axis (Fig. 4.9). For gases which deviate from ideality, value of Z deviates from unity. At very low pressures all gases shown have $Z \approx 1$ and behave as ideal gas. At high pressure all the gases have Z > 1. These are more difficult to co1npress. At inter1nedia te pressures, most gases have Z < 1. Thus gases show ideal behaviour when the volume occupied is large so that the volume of the molecules can be neglected in comparison to it. In other words, the behaviour of the gas becomes more ideal when pressure is very low. Up to what pressure a gas will follow the ideal gas law depends upon nature of the gas and its temperature. The temperature at which a real gas obeys ideal gas law over an appreciable range of pressure is called Boyle temperature or Boyle point. Boyle point of a gas depends upon its nature. Above their Boyle point, real gases show positive deviations from ideality and Z values are greater than one. The forces of attraction between the molecules are very feeble. Below Boyle temperature real gases first show decrease in Z value with increasing pressure, which reaches a minimum value. On further increase in pressure, the value of Z increases continuously. Above explanation shows that at low pressure and high temperature gases show ideal behaviour. These conditions are different for different gases.

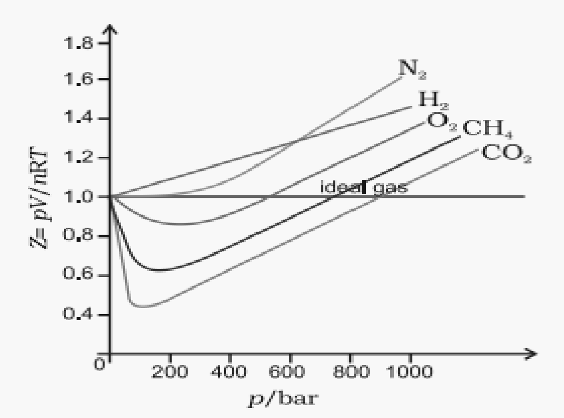


Fig. 4.9 variation of compressibility factor for some gases

More in sight is obtained in the significance of Z if we note the following derivation

$$Z = \frac{\mathrm{pV_{real}}}{\mathrm{nRT}} \tag{4.47}$$

If the gas shows ideal behaviour then $V_{real} = \frac{nRT}{p}$. On putting this value of $\frac{nRT}{p}$ in equation (4.47)

we have $$Z = \frac{V_{real}}{V_{ideal}} \tag{4.48}$$

From equation (4.48) we can see that compressibility factor is the ratio of actual molar volume of a gas to the molar volume of it, if it were an ideal gas at that temperature and pressure.

4.12 Liquid State

Intermolecular forces are stronger in liquid state than in gaseous state. Molecules in liquids are so close that there is very little empty space between the1n and under normal conditions liquids are denser than gases. Molecules of liquids are held together by attractive intermolecular forces. Liquids have definite volume because molecules do not separate from each other. However, molecules of liquids can move past one another freely, therefore, liquids can flow, can be poured and can assume the shape of the container in which these are stored. In the following sections we will look into some of the physical properties of the liquids such as vapour pressure, surface tension and viscosity.

4.12.1 Vapour Pressure

If an evacuated container is partially filled with a liquid, a portion of liquid evaporates to fill the remaining volume of the container with vapour. Initially the liquid evaporates and pressure exerted by vapours on the walls of the container (vapour pressure) increases. After some time it becomes constant, an equilibrium is established between liquid phase and vapour phase. Vapour pressure at this stage is known as equilibrium vapour pressure or saturated vapour pressure. Since process of vapourisation is temperature dependent; the temperature must be mentioned while reporting the vapour pressure of a liquid .

When a liquid is heated in an open vessel, the liquid vapourises from the surface. At the temperature at which vapour pressure of the liquid becomes equal to the external pressure, vapourisation can occur throughout the bulk of the liquid and vapours expand freely into the surroundings. The condition of free vapourisation throughout the liquid is called boiling. The temperature at which vapour pressure of liquid is equal to the external pressure is called boiling temperature at that pressure. Vapour pressure of some common liquids at various temperatures is given in (Fig. 4.10). At 1 atm pressure boiling temperature is called normal boiling point. If pressure is 1 bar then the boiling point is called standard boiling point of the liquid. Standard boiling point of the liquid is slightly lower than the normal boiling point because 1 bar pressure is slightly less than 1 atm pressure. The normal boiling point of water is 100^0 C (373 K), its standard boiling point is 99.6^0 C (372.6 K).

At high altitudes atmospheric pressure is low. Therefore liquids at high altitudes boil at lower temperatures in comparison to that at sea level. Since water boils at low temperature on hills, the pressure cooker is used for cooking food. In hospitals surgical instruments are sterilized in autoclaves in which boiling point of water is increased by increasing the pressure above the atmospheric pressure by using a weight covering the vent.

Boiling does not occur when liquid is heated in a closed vessel. On heating continuously vapour pressure increases. At first a clear boundary is visible between liquid and vapour phase because liquid is more dense than vapour. As the temperature increases more and more molecules go to vapour phase and density of vapours rises. At the same time liquid becomes less dense. It expands because molecules move apart. When density of liquid and vapours becomes the same; the clear boundary between liquid and vapours disappears. This temperature is called critical temperature about which we have already discussed.

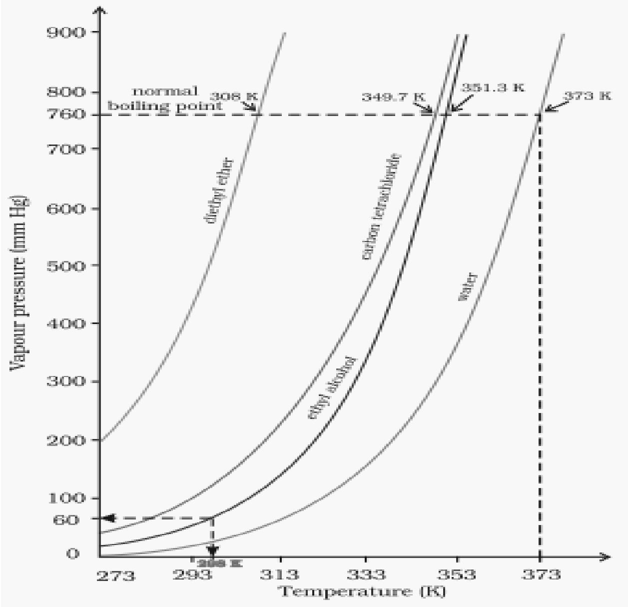


Fig. 4.10 vapor pressure vs temperature curve of some common liquids

4.12.2 Surface Tension

It is well known fact that liquids assume the shape of the container. Why is it then small drops of mercury form spherical bead instead of spreading on the surface? Why do particles of soil at the bottom of river remain separated but they stick together when taken out? Why does a liquid rise (or fall) in a thin capillary as soon as the capillary touches the surface of the liquid? All these phenomena are caused due to the characteristic property of liquids, called surface tension. A molecule in the bulk of liquid experiences equal intermolecular forces from all sides. The molecule therefore does not experience any net force. But for the molecule on the surface of liquid, net attractive force is towards the interior of the liquid (Fig. 4. 11), due to the molecules below it. Since there are no molecules above it.

Liquids tend to minimize their surface area. The molecules on the surface experience a net downward force and have more energy than the molecules in the bulk, which do not experience any net force. Therefore, liquids tend to have minimum number of molecules at their surface. If surface of the liquid is increased by pulling a molecule from the bulk, attractive forces will have to be overcome. This will require expenditure of energy. The energy required to increase the surface area of the liquid by one unit is defined as surface energy. Its dimensions are J m^{-2}. Surface tension is defined as the force acting per unit length perpendicular to the line drawn on the surface of liquid. It is denoted by Greek letter 'γ' (Gamma). It has dimensions of kg s^{-2} and in SI unit it is expressed as N m^{-1}. The lowest energy state of the liquid will be when surface area is minimum. Spherical shape satisfies this condition that is why mercury drops are spherical in shape. This is the reason that sharp glass edges are heated for making them smooth. On heating, the glass melts and the surface of the liquid tends to take the rounded shape at the edges, which makes the edges smooth. This is called fire polishing of glass.

Liquid tends to rise (or fall) in the capillary because of surface tension. Liquids wet the things because they spread across their surfaces as thin film. Moist soil grains are pulled together because surface area of thin film of water is reduced. It is surface tension which gives stretching property to the surface of a liquid. On flat surface, droplets are slightly flattened by the effect of gravity; but in the gravity free environments drops are perfectly spherical.

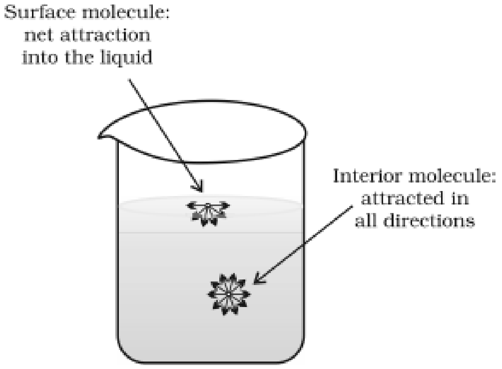


Fig. 4.11 Forces acting on a molecule on liquid surface and on a molecule inside the liquid

The magnitude of surface tension of a liquid depends on the attractive forces between the molecules. When the attractive forces are large, the surface tension is large. Increase in temperature increases the kinetic energy of the molecules and effectiveness of intermolecular attraction decreases, so surface tension decreases as the temperature is raised.

4.12.3 Viscosity

It is one of the characteristic properties of liquids. Viscosity is a measure of resistance to flow which arises due to the internal friction between layers of fluid as they slip past one another while liquid flows. Strong intermolecular forces between molecules hold them together and resist movement of layers past one another.

When a liquid flows over a fixed surface, the layer of molecules in the immediate contact of surface is stationary. The velocity of upper layers increases as the distance of layers from the fixed layer increases. This type of flow in which there is a regular gradation of velocity in passing from one layer to the next is called laminar flow. If we choose any layer in the flowing liquid (Fig.4.12), the layer above it accelerates its flow and the layer below this retards its flow.

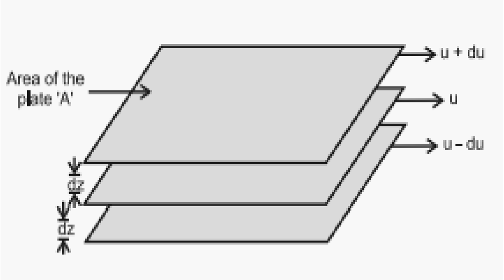


Fig. 4.12 Gradation of velocity in the laminar flow

If the velocity of the layer at a distance ‘dz’ is changed by a value ‘du’ then velocity gradient is given by the amount $\frac{du}{dz}$. A force is required to maintain the flow of layers. This force is proportional to the area of contact of layers and velocity gradient i.e.

$F \propto A$ (‘A’ is the area of contact.)

$F \propto \frac{du}{dz}$ (where $\frac{du}{dz}$ is velocity gradient; the change in velocity with distance)

$$F \propto A.\frac{du}{dz} \Rightarrow F = \eta A.\frac{du}{dz}$$

$'\eta'$ is proportionality constant and is called coefficient of viscosity. Viscosity coefficient is the force when velocity gradient is unity and the area of contact is unit area. Thus $'\eta'$ is measure of viscosity. SI unit of viscosity coefficient is 1 newton second per square meter ($N\ s\ m^{-2}$) = Pascal second ($Pa\ s = lkg\ m^{-1}s^{-1}$). In cgs system the unit of coefficient of viscosity is poise (named after great scientist Jean Louise Poiseuille).

1 poise =1 $g\ cm^{-1}s^{-1} = 10^{-1}\ kg\ m^{-1}s^{-1}$

Greater the viscosity, the more slowly the liquid flows. Hydrogen bonding and van der Waals forces are strong enough to cause high viscosity. Glass is an extremely viscous liquid. It is so viscous that many of its properties resemble solids. However, property of flow of glass can be experienced by measuring the thickness of windowpanes of old buildings. These become thicker at the bottom than at the top.

Viscosity of liquids decreases as the temperature rises because at high temperature molecules have high kinetic energy and can overco1ne the intermolecular forces to slip past one another between the layers.

SUMMARY

Intermolecular forces operate between the particles of matter. These forces differ from pure electrostatic forces that exist between two oppositely charged ions. Also, these do not include forces that hold atoms of a covalent molecule together through covalent bond. Competition between thermal energy and intermolecular interactions determines the state of matter. "Bulk" properties of matter such as behaviour of gases, characteristics of solids and liquids and change of state depend upon energy of constituent particles and the type of interaction between them. Chemical properties of a substance do not change with change of state, bt.1t the reactivity depends upon the physical state.

Forces of interaction between gas molecules are negligible and are almost independent of their chemical nature. Interdependence of some observable properties namely pressure, volume, temperature and mass leads to different gas laws obtained from experimental stt.1dies on gases. Boyle's law states that under isothermal condition, pressure of a fixed amount of a gas is inversely proportional to its volume. Charles' law is a relationship between volt.1me and absolt.1te temperature under isobaric condition. It states that volume of a fixed amount of gas is directly proportional to its absolute temperature ($V \propto T$). If state of a gas is represented by p_1, V_1 and T_1 and it changes to state at p_2, V_2 and T_2, then relationship between these two states is given by combined gas law according to which $\frac{p_1V_1}{T_1}=\frac{p_2V_2}{T_2}$. Any one of the variables of this gas can be found out if other five variables are known. Avogadro law states that equal volumes of all gases under same conditions of temperature and pressure contain equal number of molecules. Graham's law of diffusion states that under the same conditions of temperature and pressure, the rates of diffusion of different gases are inversely proportional to the square roots of their densities. Thus $r \propto \frac{1}{\sqrt{d}}$. Dalton's law of partial pressure states that total pressure exerted by a mixture of non-reacting gases is equal to the sum of partial pressures exerted by them. Thus $p = p_1+p_2+p_3+ \ldots$. Relationship between pressure, volume, temperature and number of moles of a gas describes its state and is called equation of state of the gas. Equation of state for ideal gas is pV = nRT, where R is a gas constant and its value depends upon units chosen for pressure, volume and temperature. According to kinetic molecular theory, gases consist of small and tiny particles called molecules. The molecules possess different types of speeds like rms, average and most probable speeds. Kinetic energy of gas molecules is given by $E_k=\frac{3}{2}nRT$.

At high pressure and low temperature intermolecular forces start operating strongly between the molecules of gases because they come close to each other. Under suitable temperature and pressure conditions gases can be liquified. Liquids may be considered as continuation of gas phase into a region of small volt.rme and very strong molecular attractions. Some properties of liquids e.g., surface tension and viscosity are due to strong intermolecular attractive forces.

EXERCISES

4.1 What will be the minimum pressure required to compress 500 dm^3 of air at 1 bar to 200 dm^3 at 30 C?

4.2 A vessel of 120 mL capacity contains a certain amount of gas at 35 C and 1.2 bar pressure. The gas is transferred to another vessel of volume 180 mL at 35 C. What would be its pressure?

4.3 At 0 C, the density of a certain oxide of a gas at 2 bar is same as that of dinitrogen at 5 bar. What is the molecular mass of the oxide?

4.4 Pressure of 1 g of an ideal gas A at 27 C is found to be 2 bar. When 2 g of another ideal gas B is introduced in the same flask at same temperature the pressure becomes 3 bar. Find a relationship between their molecular masses.

4.5 What will be the pressure exerted by a mixture of 3.2 g of methane and 4.4 g of carbon dioxide contained in a 9 dm^3 flask at 27 C ?

4.6 What will be the pressure of the gaseous mixture when 0.5 L of H_2 at 0.8 bar and 2.0 L of dioxygen at 0.7 bar are introduced in a IL vessel at 27 C?

4.7 Density of a gas is found to be 5.46 g/dm3 at 27 C at 2 bar pressure. What will be its density at STP?

4.8 34.05 mL of phosphorus vapour weighs 0.0625 g at 546 C and 0.1 bar pressure. What is the molar mass of phosphorus?

4.9 Calculate the temperature of 4.0 mol of a gas occupying 5 dm^3 at 3.32 bar. ($R = 0.083$ bar dm^3K^{-1} mol^{-1}).

4.10 Calculate the total pressure in a mixture of 8 g of dioxygen and 4 g of dihydrogen confined in a vessel of 1 dm^3 at 27 C. R = 0.083 bar dm^3 K^{-1} mol^{-1}.
4.11 Calculate the volume occupied by 8.8 g of CO_2 at 31.1 C and 1 bar pressure. R = 0.083 bar dm^3 K^{-1} mol^{-1}.
4.12 A mixture of dihydrogen and dioxygen at one bar pressure contains 20°/o by weight of dihydrogen. Calculate the partial pressure of dihydrogen.
4.13 In terms of Charles' law explain why -273 C is the lowest possible temperature.
4.14 Explain the physical significance of van der Waals parameters.

QUESTION BANK

CHAPTER 4: STATES OF MATTER: GASES AND LIQUIDS

Very Short Answer Questions **(01 Mark)**

1. What is Ideal gas?
2. Give the values of gas constant in different units?
3. Sate Graham’s law of diffusion?
4. How many times methane diffuse faster than sulphar dioxide
5. State Dolton’s law of Partial Pressure?
6. Give the relation between the Partial Pressure of a gas and its mole fraction?
7. Give an equation to calculate the kinetic energy of gas molecules?
8. What is Boltzman’s constant? Give its value?
9. What is Rms speed?
10. What is Average speed?
11. What most probable speed?
12. What is surface tension.
13. Write the postulates of the kinetic molecular theory. (04 Marks)

CHAPTER-5
STOICHIOMETRY

Introduction

Chemical equations provide us with information about the types of particles that react to form products. Chemical equations also provide us with the relative number of particles and moles that react to form products. Stoichiometry involved estimating the quantities of reactants or products in a chemical reaction using the relationships found in the balanced chemical equation. The word stoichiometry actually comes from two Greek words: stoikheion, which means element, and metron, which means measure.

In this chapter, you will explore the quantitative relationships that exist between the reactants and products in addition to mole concept, equivalent weight, and calculations of empirical and molecular formulae of compounds.

5.1 Atomic Mass and Molecular Mass

Atomic Mass:

Every particle of matter has some amount of mass associated with it whether small or large. Everything is made up of atoms. Mass of an atomic particle is known as atomic mass. This is commonly expressed as per the international agreement in terms of a unified atomic mass unit (1 amu = 1.66×10^{-24} g.). It can be best defined as 1/12 of the mass of a carbon-12 atom in its ground state. The mass of an atom can be accounted by the sum of mass of protons and neutrons which is almost equal to the atomic mass. This small variation is due to the binding energy mass loss.

The atomic weight of an atom is a dimensionless number when it is divided by unified atomic weight. This is called the relative isotropic mass. The atomic masses of elements vary from 1.008 amu for hydrogen up to 250 amu for elements which have a very high atomic number. Mass of molecules can be determined by adding the average atomic mass of each atom in the molecule.

Gram Atomic Mass:

The quantity of an element whose mass in grams is numerically equal to its atomic mass. In simple terms, atomic mass of an element expressed in grams is the gram atomic mass or gram atom.

For example, the atomic mass of oxygen = 16 amu
Therefore gram atomic mass of oxygen = 16 g

Molecular mass:

Molecular mass is the amount of mass associated with a molecule. It is also known as molecular weight. It can be calculated by adding the mass of each atom multiplied by the number of atoms of the element existing in the molecule. For example, water is made up of 1 oxygen atom and 2 hydrogen atoms. Mass of water molecule is equal to the average atomic mass of hydrogen multiplied by two plus the atomic mass of oxygen. Molecular mass of elements depends upon the constituent atoms of the molecule.

Gram Molecular Mass:

A quantity of substance whose mass in grams is numerically equal to its molecular mass is called gram molecular mass. In simple terms, molecular mass of a substance expressed in grams is called gram molecular mass.
e.g., the molecular mass of oxygen = 32 amu

Therefore, gram molecular mass of oxygen = 32 g

5.2 Mole Concept

While carrying out reaction we are often interested in knowing the number of atoms and molecules. Sometimes, we have to take the atoms or molecules of different reactants in a definite ratio. In order to overcome these difficulties, the concept of mole was introduced. According to this concept number of particles of the substance is related to the mass of the substance.

Definition

"The mole may be defined as the amount of the substance that contains as many specified elementary particles as the number of atoms in 12g of carbon - 12 isotope".

(i.e) one mole of an atom consists of Avogadro number of particles.

One mole = 6.023×10^{23} particles

One mole of oxygen molecule = 6.023×10^{23} oxygen molecules

One mole of oxygen atom = 6.023×10^{23} oxygen atoms

One mole of ethanol = 6.023×10^{23} ethanol molecules

In using the term mole for ionic substances, we mean the number of formula units of the substance. For example, a mole of sodium carbonate, Na_2CO_3 is a quantity containing 6.023×10^{23} Na_2CO_3 units. But each formula unit of Na_2CO_3 contains $2 \times 6.023 \times 10^{23}$ Na^+ ions and one and $1 \times 6.023 \times 10^{23}$ CO_3^{2-} ions.

When using the term mole, it is important to specify the formula of the unit to avoid any misunderstanding.

Eg. A mole of oxygen atom (with the formula O) contains 6.023×10^{23} Oxygen atoms. A mole of Oxygen molecule (formula O_2) contains 6.023×10^{23} O_2 molecules (i.e) $2 \times 6.023 \times 10^{23}$ Oxygen.

The volume of 1 mole of any gas is called its molar volume and is equal to 22.4 L at standard temperature and pressure. Molar volume allows conversions to be made between moles and volume of gases at STP.

There are three mole equalities. They are:

1 mol = 6.02×10^{23} particles

1 mol = g-formula-mass

1 mol = 22.4 L for a gas at STP

Solved Problem 5.1:

How many moles of magnesium is 3.01×10^{22} atoms of magnesium?

Solution:

$$3.01 \times 10^{22} \text{ atoms} \left(\frac{1\,mole}{6.02x10^{23} atoms} \right) = 5 \times 10^{-2} \text{ moles}$$

Solved Problem 5.2:

How many molecules are there in 4.00 moles of glucose, $C_6H_{12}O_6$?

Solution:

$$4.00 \text{ moles} \left(\frac{6.02x10^{23}\ molecules}{1\,mole}\right) = 2.41 \text{ x } 10^{24} \text{ molecules}$$

Solved Problem 5.3:

How many moles in 28 grams of CO_2?

Solution:

Gram-formula-mass of CO_2 1 C = 1 x 12.01 g = 12.01 g

2 O = 2 x 16.00 g = <u>32.00 g</u>

64.00 g/mol

$$28 \text{ g } CO_2 \left(\frac{1\,mole}{44.00\ g}\right) = 0.64 \text{ moles } CO_2$$

Solved Problem 5.4:

What is the mass of 5 moles of Fe_2O_3?

Solution:

Gram-formula-mass Fe_2O_3 2 Fe = 2 x 55.6 g = 111.2 g

3 O = 3 x 16.0 g = <u>48.0 g</u>

159.2 g/mol

$$5 \text{ moles } Fe_2O_3\left(\frac{159.2\ g}{1\,mole}\right) = 800 \text{ grams } Fe_2O_3$$

Solved Problem 5.5:

Determine the volume, in liters, occupied by 0.030 moles of a gas at STP.

Solution:

$$0.030 \text{ mol} \left(\frac{22.4\ L}{1\,mole}\right) = 0.67 \text{ L}$$

Solved Problem 5.6:

How many moles of argon atoms are present in 11.2 L of argon gas at STP?

Solution:

$$11.2\text{ L}\left(\frac{1\,mole}{22.4\,L}\right) = 0.500\text{ moles}$$

5.3 Equivalent weight

Elements combine with other elements to from compounds. Each element combines with another element with a definite weight. This combining weight of element to another metal is called the equivalent weight of the element. If we take certain weight of any element as standard, we can find equivalent weight of corresponding other element on regard of the standard element.

Equivalent weight is defined *as "The number of parts by weight of any element that combine with (or displace) directly or indirectly, 1.008 parts by weight of Hydrogen or 8 parts by weight of oxygen or 35.5 parts by weight of chlorine".*

Example 1:

$$C + O_2 \rightarrow CO_2$$

As the definition says, the weight of element that combines with 8 parts by weight of oxygen is the equivalent weight of that element. So let's find the weight of carbon that combine with 8 parts by weight of oxygen in the above reaction. In the above reaction, one mole of carbon reacts with one mole of oxygen to give one mole of carbon dioxide.

i.e. 32 parts by weight of oxygen is combining with 12 parts by weight of carbon.

1 part by weight of oxygen is combining with (12/32) parts by weight of carbon.

8 parts by weight of oxygen is combining with [(12/32) x 8] 3 parts by weight of carbon

Therefore, equivalent weight of carbon is 3 gm.

Example 2:

$$2Na + 2HCl \rightarrow 2NaCl + H_2$$

Here, 2 mole of Na reacts with 2 moles of HCl to give 2 moles of NaCl and one mole of H_2.

In this reaction, Na has displaced hydrogen from HCl.

2 Parts by weight of hydrogen is replaced by (23 x 2) 46 parts by weight of Na.

1 part by weight of hydrogen is replaced by 46/2 parts by weight of Na. =23

Therefore, equivalent weight of Na is 23.

Equivalent weight of Acid, Base, salt and oxidizing/Reducing agents:

5.3.1 Equivalent weight of Acid:

For an acid, equivalent weight is the molecular weight divided by its basicity.

$$\text{Equivalent weight of acid} = \frac{\text{Molecular weight of the acid}}{\text{basicity}}$$

Basicity of an acid is the number of replaceable hydrogen of an acid. In HCl, there is one replaceable hydrogen, so its basicity is one. In H_2SO_4 there are 2 replaceable hydrogens so its basicity is two.

Lets calculate equivalent weight of HCl and H_2SO_4?
For HCl:
The molecular formula is HCl is (1.008 + 35.6) =36.451 gm.
Basicity =1

$$\text{Equivalent weight} = \frac{\text{Molecular weight}}{\text{basicity}}$$

$$= 36.451/1$$

$$= 36.451 \text{ gm}$$

For H_2SO_4:
The molecular formula is (2 x 1.008 + 32 + 4 x 16) = 98gm.
Basicity =2
Equivalent weight = 98gm/2= 49 gm.

5.3.2 Equivalent weight of Base:

$$\text{Equivalent weight of base} = \frac{\text{Molecular weight of the base}}{\text{Acidity}}$$

Acidity of base is the number of replaceable hydroxyl ion which is generated when dissolved in water. The number of replaceable hydroxyl ion for NaOH is 1, so its acidity is 1. For $Ca(OH)_2$, there is two replaceable hydroxyl ions, so its acidity is 2.

Lets calculate equivalent weight of NaOH:

Molecular formula of NaOH is (23+ 16+ 1.008) = 40g.

Acidity =1

Equivalent weight = 40/1

= 40 g.

5.3.3 Equivalent weight of Salt:

$$\text{Equivalent weight of salt} = \frac{\text{Molecular weight of the salt}}{\text{Total charge of cation or anion in the salt}}$$

For NaCl:
Molecular weight of NaCl= 23+35.5 =58.5g
Total charge on cation or anion of NaCl =1

$$\text{Equivalent weight of NaCl} = \frac{\text{Molecular weight of NaCl}}{\text{Total charge of cation or anion in NaCl}} = \frac{58.5}{1} = 58.5\text{g}$$

For NaCl:
Molecular weight of Na_2CO_3= 2x23+12+3x16 =106g
Total charge on cation or anion of Na_2CO_3 =2

$$\text{Equivalent weight of } Na_2CO_3 = \frac{\text{Molecular weight of } Na_2CO_3}{\text{Total charge of cation or anion in } Na_2CO_3} = \frac{106}{2} = 53\text{g}$$

5.3.4 Equivalent weight of Oxidant and Reductant:

$$\text{Equivalent weight of oxidant or reductant} = \frac{\text{Molecular weight of the salt}}{\text{Total change in the oxidation state of oxidant or reductant}}$$

For example,

When $KMnO_4$ changes to $MnSO_4$, the oxidation number of Mn changes from +7 to +2 state. The total change in oxidation number is 5. So,

Equivalent weight of $KMnO_4$ in acidic medium = molecular weight of $KMnO_4$/5 = 161/5 = 32.2 gm

5.4 Percent Composition

The elemental composition of a compound defines its chemical identity, and chemical formulas are the most suitable way of representing this elemental composition. When a compound’s formula is unknown, measuring the mass of each of its constituent elements is often the first step in the process of determining the formula experimentally. The results of these measurements allow the calculation of the compound’s percent composition, defined as the percentage by mass of each element in the compound. For example, consider a gaseous compound composed exclusively of carbon and hydrogen. The percent composition of this compound could be represented as follows:

$$\%\,\text{H} = \frac{\text{mass H}}{\text{mass compound}} \times 100\%$$

$$\%\,\text{C} = \frac{\text{mass C}}{\text{mass compound}} \times 100\%$$

Solved problem 5.7:

Analysis of a 12.04 g sample of a liquid compound composed of carbon, hydrogen, and nitrogen showed it to contain 7.34 g C, 1.85 g H, and 2.85 g N. What is the percent composition of this compound?

Solution:

To calculate percent composition, we divide the experimentally derived mass of each element by the overall mass of the compound, and then convert to a percentage:

$$\%\,\mathrm{C} = \frac{7.34\ \mathrm{g\ C}}{12.04\ \mathrm{g\ compound}} \times 100\% = 61.0\%$$

$$\%\,\mathrm{H} = \frac{1.85\ \mathrm{g\ H}}{12.04\ \mathrm{g\ compound}} \times 100\% = 15.4\%$$

$$\%\,\mathrm{N} = \frac{2.85\ \mathrm{g\ N}}{12.04\ \mathrm{g\ compound}} \times 100\% = 23.7\%$$

The analysis results indicate that the compound is 61.0% C, 15.4% H, and 23.7% N by mass.

5.5 Empirical Formula

"An empirical formula (or) simplest formula for a compound is the formula of a substance written with the smallest integer subscripts".

For most ionic substances, the empirical formula is the formula of the compound. This is often not the case for molecular substances. For example, the formula of sodium peroxide, an ionic compound of Na+ and O_2^{2-}, is Na_2O_2. Its empirical formula is NaO. Thus empirical formula tells you the ratio of numbers of atoms in the compound.

Steps for writing the Empirical formula:

The percentage of the elements in the compound is determined by suitable methods and from the data collected, the empirical formula is determined by the following steps.

i. Divide the percentage of each element by its atomic mass. This will give the relative number of moles of various elements present in the compound.
ii. Divide the quotients obtained in the above step by the smallest of them so as to get a simple ratio of moles of various elements.
iii. Multiply the figures, so obtained by a suitable integer of necessary in order to obtain whole number ratio.
iv. Finally write down the symbols of the various elements side by side and put the above numbers as the subscripts to the lower right hand of each symbol. This will represent the empirical formula of the compound.

5.6 Molecular Formula from Empirical Formula

A chemical formula that shows the total number and kinds of atoms in a molecule is known as molecular formula

Molecular formulas are derived by comparing the compound’s molecular or molar mass to its empirical formula mass. As the name suggests, an empirical formula mass is the sum of the average atomic masses of all the atoms represented in an empirical formula.

Example:

The molecular formula of acetylene, C_2H_2 is equivalent to $(CH)_2$, and the molecular formula of benzene, C_6H_6 is equivalent to $(CH)_6$. In both the cases, the empirical formula is CH. Therefore, the molecular weight is some multiple of the empirical formula weight, which is obtained by summing the atomic Weights from the empirical formula. For any molecular compound

Molecular Weight = n x empirical formula weight.

Where `n' is the whole number of empirical formula units in the molecule. The molecular formula can be obtained by multiplying the subscripts of the empirical formula by `n' which can be calculated by the following equation

$$n = \frac{\text{Molecular Weight}}{\text{Empirical formula Weight}}$$

Steps for writing the molecular formula

i. Calculate the empirical formula
ii. Find out the empirical formula mass by adding the atomic mass of all the atoms present in the empirical formula of the compound.
iii. Divide the molecular mass (determined experimentally by some suitable method) by the empirical formula mass and find out the value of n which is a whole number.
iv. Multiply the empirical formula of the compound with n, so as to find out the molecular formula of the compound.

Solved Problem 5.8:

1. A compound on analysis gave the following percentage composition C = 54.54%, H, 9.09% 0 = 36.36. The vapour density of the compound was found to be 44. Find out the molecular formula of the compound.

Solution:

Calculation of empirical formula:

Element	%	Relative No.	Simple	Simplest whole
C	54.54	54.54/12=4.53	4.53/2.27 =2	2
H	9.09	9.09/1 = 9.09	9.09/2.27 =4	4
O	36.36	36.36/16 = 2.27	2.27/2.27=1	1

Empirical formula is $C_2 H_4 O$.

Calculation of Molecular formula:

Empirical formula mass = 12 x 2 + 1 x 4 + 16 x 1 = 44

Molecular mass = 2 x Vapour density

= 2 x 44 = 88

$$n = \frac{\text{Molecular Weight}}{\text{Empirical formula Weight}} = \frac{88}{44} = 2$$

Molecular formula = Empirical formula x n

$= C_2 H_4 O \times 2$

$= C_4 H_8 O_2$

5.7 Methods of expressing the concentration of solution

The concentration of a solution refers to the amount of solute present in the given quantity of solution or solvent. The concentration of a solution may be expressed quantitatively in any of the following ways.

Mass Percentage:

Percentages are also commonly used to express the composition of mixtures, including solutions. The mass percentage of a solution component is defined as the ratio of the component's mass to the solution's mass, expressed as a percentage:

$$\text{mass percentage} = \frac{\text{mass of component (solute)}}{\text{mass of solution}} \times 100\%$$

Mass percentage is also referred to by similar names such as percent mass, percent weight, weight/weight percent, and other variations on this theme. The most common symbol for mass percentage is (w/w)%.

Solved Problem 5.9:

What is the weight percent of glucose in a solution made by dissolving 4.6 g of glucose in 145.2 g of water?

solution:

To get weight percent we need the weight of the solute and the total weight of the solution.

determine total weight of solution:

weight of glucose = 4.6 g (solute)

weight of water = 145.2 g (solvent)

total weight of the solution = solute + solvent = 4.6 g + 145.2 g = 149.8 g

$$\text{mass percentage of glucose} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\% = \frac{4.6\text{g}}{149.8} \times 100\% = 3.1\%$$

Mole Fraction:

Mole fraction is the ratio of number of moles of one component (Solute or Solvent) to the total number of moles of all the components (Solute and Solvent) present in the Solution. It is denoted by X. Let us suppose that a solution contains 2 components A&B and suppose that n_A moles of A and n_B moles of B are present in the solution. Then,

$$\text{Molefraction of A, } X_A = \frac{n_A}{n_A + n_B}$$

$$\text{Molefraction of B, } X_B = \frac{n_B}{n_A + n_B}$$

Adding mole fractions of A and B we get,

$$X_A + X_B = \frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} = \frac{n_A + n_B}{n_A + n_B} = 1$$

Thus, sum of the two mole fractions is one. Therefore, if mole fraction of one component in a binary solution is known, that of the other can be calculated.

Solved Problem 5.10:

A solution is prepared by mixing 25.0 g of water, H_2O, and 25.0 g of ethanol, C_2H_5OH. Determine the mole fractions of each substance.

Solution:

Determine the moles of each substance:

$$\text{Moles of water} = \frac{\text{Mass}}{\text{Molar Mass}} = \frac{25.0\text{ g}}{18\text{ g mol}^{-1}} = 1.39\text{ mol}$$

$$\text{Moles of } C_2H_5OH = \frac{\text{Mass}}{\text{Molar Mass}} = \frac{25.0\text{ g}}{46.07\text{ g mol}^{-1}} = 0.54\text{ mol}$$

Determine mole fractions:

$$\text{Molefraction of } H_2O,\ X_{H_2O} = \frac{n_{H_2O}}{n_{H_2O} + n_{C_2H_5OH}} = \frac{1.39}{1.39 + 0.54} = 0.72$$

$$\text{Molefraction of } C_2H_5OH,\ X_{C_2H_5OH} = 1 - 0.72 = 0.28$$

Molarity (M):

Molarity of a solution is defined as the number of gram-moles of solute dissolved in 1 litre of a solution. **Molarity (**M**)** is a useful concentration unit for many applications in chemistry.

$$\text{molarity, M} = \frac{\text{No.of moles of solute}}{\text{Volume of Solution in litres}}$$

If `X' grams of the solute is present in V cm^3 of a given solution, then,

$$\text{molarity, M} = \frac{X}{\text{molar mass}} \text{ x } \frac{1000}{V}$$

Solved Problem 5.11:

4.5 g of urea (molar mass = 60 g mol^{-1}) are dissolved in water and solution is made to 100 ml in a volumetric flask. Calculate the molarity of solution.

Solution:

Mass of Urea = 4.5g

$$\text{moles of urea} = \frac{\text{Mass of urea}}{\text{Molar Mass of urea}} = \frac{4.5\text{ g}}{60\text{ g mol}^{-1}} = 0.075\text{ mol}$$

Volume of solution = 100 ml = 0.1 lit

$$\text{molarity, M} = \frac{\text{No.of moles of urea}}{\text{volume of solution in litres}} = \frac{0.075}{0.1} = 0.75\text{M}$$

Normality:

Normality of a solution is defined as the number of gram equivalents of the solute dissolved per litre of the given solution. The solute's role in the reaction determines the solution's normality. Normality is also known as the equivalent concentration of a solution.

$$\text{normality, N} = \frac{\text{No.of gram equivalent of solute}}{\text{Volume of Solution in litres}}$$

If `X' grams of the solute is present in V cm^3 of a given solution, then,

$$\text{normality, N} = \frac{\text{X}}{\text{equivalent mass}} \text{ x } \frac{1000}{\text{V}}$$

Normality is represented by the symbol N. Normality can also be calculated from strength as follows

Solved Problem 5.12:

Calculate the normality of solution containing 3.15g of hydrated oxalic acid ($H_2C_2O_4.2H_2O$) in 250 ml of solution (Mol. mass = 126).

Solution:

Mass of oxalic acid = 3.15g

Molar mass of oxalic acid = 126 g

$$\text{Equivalent mass of oxalic acid} = \frac{\text{Mol.mass}}{\text{Basicity}} = \frac{126}{2} = 63$$

Volume of the solution = 250 ml

$$\text{normality, N} = \frac{\text{mass of oxalic acid}}{\text{equivalent mass}} \text{ x } \frac{1000}{\text{vol in ml}} = \frac{3.15\text{g}}{63\text{g}} \text{ x } \frac{1000}{250 \text{ ml}} = 0.2\text{N}$$

Molality (m):

Molality of a solution is defined as the number of gram-moles of solute dissolved in 1000 grams (or 1 kg) of a Solvent. Mathematically,

$$\text{molality, m} = \frac{\text{No.of moles of solute}}{\text{Mass of solvent in kilo grams}}$$

If `X' grams of the solute is present in b grams of the solvent, then,

$$\text{molality, m} = \frac{\text{X}}{\text{molar mass}} \text{ x } \frac{1000}{\text{b g}}$$

Molality is represented by the symbol ‘m’.

Solved Problem 5.13:

Calculate the molality of an aqueous solution containing 3.0g of urea (mol. mass=60) in 250g of water.

Solution:

Mass of solute (urea) = 3.0g

Molar mass of urea = 60 g mol^{-1}

Mass of solvent (water) = 250 g

$$\text{molality, m} = \frac{\text{mass of solute}}{\text{molar mass}} \text{ x } \frac{1000}{\text{mass of solvent in g}} = \frac{3\text{g}}{60\text{g mol}^{-1}} \text{ x } \frac{1000}{250 \text{ g}} = 0.2\text{m}$$

5.8 Oxidation Number (or) Oxidation State

Oxidation number of the element is defined as the residual charge which its atom has (or) appears to have when all other atoms from the molecule are removed as ions. Atoms can have positive, zero or negative values of oxidation numbers depending upon their state of combination.

General Rules for assigning Oxidation Number to an atom

The following rules are employed for determining oxidation number of the atoms.

1. The oxidation number of the element in the free (or) elementary state is always Zero.
   Oxidation number of Helium in He = 0
   Oxidation number of chlorine in Cl_2 = 0
2. The oxidation number of the element in monoatomic ion is equal to the charge on the ion.
3. The oxidation number of fluorine is always - 1 in all its compounds.
4. Hydrogen is assigned oxidation number +1 in all its compounds except in metal hydrides. In metal hydrides like NaH, MgH_2, CaH_2, LiH, etc., the oxidation number of hydrogen is -1.
5. Oxygen is assigned oxidation number -2 in most of its compounds, however in peroxides like H_2O_2, BaO_2, Na_2O_2, etc its oxidation number is -1, Similarly the exception also occurs in compounds of Fluorine and oxygen like OF_2 and O_2F_2 in which the oxidation number of oxygen is +2 and +1

respectively.

6. The oxidation numbers of all the atoms in neutral molecule is Zero. In case of polyatomic ion the sum of oxidation numbers of all its atoms is equal to the charge on the ion.
7. In binary compounds of metal and non-metal the metal atom has positive oxidation number while the non-metal atom has negative oxidation number. Example. Oxidation number of K in KI is +1 but oxidation number of I is - 1.
8. In binary compounds of non-metals, the more electronegative atom has negative oxidation number, but less electronegative atom has positive oxidation number.

   Example : Oxidation number of Cl in ClF_3 is positive (+3) while that in ICl is negative (-1).

Solved Problem 5.14:

Calculate the oxidation number of underlined elements in the following species.

$$\underline{C}O_2,\ \underline{Cr}_2O_7^{2-},\ \underline{Al}_2O_3,\ \underline{P}O_4^{3-}$$

Solution:

1. C in CO_2.

   Let oxidation number of C be x. Oxidation number of each O atom = -2.
   Sum of oxidation number of all atoms = $x+2(-2) = x - 4$.

   As it is neutral molecule, the sum must be equal to zero.

   $x - 4 = 0$ (or) $x = +4$

2. Cr in $Cr_2O_7^{2-}$

   Let oxidation number of Cr = x.
   Oxidation number of each oxygen atom = -2
   Sum of oxidation number of all atoms = $2x + 7(-2) = 2x - 14$
   Sum of oxidation number must be equal to the charge on the ion.
   Thus, $2x - 14 = -2$
   $2x = -2 + 14 = +12$
   $x = 12/2 = +6$

3. Al in Al_2O_3

   Let oxidation number of Al = x.
   Oxidation number of each oxygen atom = -2
   Sum of oxidation number of all atoms = $2x + 3(-2) = 2x - 6$
   As it is neutral molecule, the sum must be equal to zero.
   Thus, $2x - 6 = 0$
   $2x = +6$
   $x = 6/2 = +3$

4. P in PO_4^{3-}

   Let oxidation number of P = x.
   Oxidation number of each oxygen atom = -2
   Sum of oxidation number of all atoms = $x + 4(-2) = x - 8$

Sum of oxidation number must be equal to the charge on the ion.

Thus, $x - 8 = -3$

$x = -3 + 8 = +5$

5.8.1 Oxidation and Reduction in Terms of Oxidation Number

Oxidation

"A chemical process in which oxidation number of the element increases".

Reduction

"A chemical process in which oxidation number of the element decreases".

Eg. Reaction between H_2S and Br_2 to give HBr and Sulphur.

In the above example, the oxidation number of bromine decreases from 0 to -1, thus, it is reduced. The oxidation number of S increases from – 2 to 0. Hence, S is oxidised.

Let us now define oxidising and reducing agents in the light of the concept of oxidation number: Oxidising agent is a substance which undergoes decrease in the oxidation number of one or more of its elements. Reducing agent is a substance which undergoes increase in the oxidation number of one or more of its elements. In the above example, H_2S is reducing agent while Br_2 is oxidising agent.

5.9 Balancing of redox reactions:

A reaction which has an equal number of atoms of all the elements on both sides of the chemical equation is called a balanced chemical equation. The law of conservation of mass states that mass can neither be created nor destroyed. Hence, it is for this reason that chemical equations should be balanced. Balancing redox reactions is slightly more complex than balancing standard reactions. To maintain charge neutrality in the sample, the redox reaction will entail both a reduction component and an oxidation components and is often separated into independent two hypothetical half-reactions to aid in understanding the reaction.

5.9.1 Ion-Electron Method:

This method involves the following steps:

1. Divide the complete equation into two half reactions, one representing oxidation and the other reduction.
2. Balance the atoms in each half reaction separately according to the following steps:
    a. First of all balance the atoms other than H and O.

b. In a reaction taking place in acidic or neutral medium, oxygen atoms are balanced by adding molecules of water to the side deficient in oxygen atoms while hydrogen atoms are balanced by adding H^+ ions to the other side deficient in hydrogen atoms.

c. On the other hand, in alkaline medium (OH_-), every excess of oxygen atom on one side is balanced by adding one H_2O to the same side and $2OH^-$ to the other side. In case hydrogen is still unbalanced, then balance by adding one OH-, for every excess of H atom on the same side as the excess and one H_2O on the other side.

3. Equalize the charge on both sides by adding a suitable number of electrons to the side deficient in negative charge.
4. Multiply the two half reactions by suitable integers so that the total number of electrons gained in one half reaction is equal to the number of electrons lost in the other half reaction.

Solved problem 5.15:

Balance the redox reaction $Al + NO_3^- \rightarrow Al\ \ OH_4^- + NH_3$ in alkaline medium.

Solution:

Step	Oxidation half	Reduction half
Dividing the equation in two half reactions	$NO_3^- \rightarrow NH_3$	$Al + OH^- \rightarrow Al\ \ OH_4^-$
All the atoms other than O & H are balanced	$NO_3^- \rightarrow NH_3$	$Al + OH^- \rightarrow Al\ \ OH_4^-$
Then O and H are balanced using OH^- and H_2O (alkaline medium)	$NO_3^- + 6H_2O \rightarrow NH_3 + 9OH^-$	$Al + 4OH^- \rightarrow Al\ \ OH_4^-$
Electrons need to be added in order to balance the charge	$8\ e^- + NO_3^- + 6\ H_2O \rightarrow NH_3 + 9\ OH^-$	$Al + 4\ OH^- \rightarrow Al\ \ OH_4^- + 3\ e^-$
Loss and gain of electrons need to be made equal: For this, we need to multiply first equation by 3 and second equation by 8.	$3\ x\ (8\ e^- + NO_3^- + 6\ H_2O \rightarrow NH_3 + 9\ OH^-)$	$8\ x\ (Al + 4\ OH^- \rightarrow Al\ \ OH_4^- + 3\ e^-)$

Adding both equations we get the balanced redox equation

$$3NO_3^- + 18H_2O + 8Al + 5\ OH^- \rightarrow 8Al\ \ OH_4^- + 3NH_3$$

Solved problem 5.16:

Balance the redox reaction $Cr_2O_7^{2-} + SO_2 \rightarrow Cr^{3+} + SO_4^{2}$ in acidic medium.

Solution:

Step	Oxidation half	Reduction half
Dividing the equation in two half reactions	$SO_2 \rightarrow SO_4^{2-}$	$Cr_2O_7^{2-} \rightarrow Cr^{3+}$
All the atoms other than O & H are balanced	$SO_2 \rightarrow SO_4^{2-}$	$Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$
Then O and H are balanced using OH^- and H_2O (acidic medium)	$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+$	$Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$
Electrons need to be added in order to balance the charge	$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

Loss and gain of electrons need to be made equal: For this, we need to multiply first equation by 3.	3 x ($SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$)	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

Adding both equations we get the balanced redox equation

$$Cr_2O_7^{2-} + 2\,H^+ + 3\,SO_2 \rightarrow 2Cr^{3+} + 3\,SO_4^{2-} + 7H_2O$$

SUMMARY

Isotope carbon-12 (^{12}C) is assigned a relative mass of exactly 12 u (atomic mass unit); the masses of other atoms are assigned values relative to this carbon-12. The molar mass of a compound is the mass of 1 mole of the compound in grams. A mole is a quantity that contains the same number of items (atoms, molecules, ions, etc.) equal to the number of carbon atoms in exactly 12 grams of ^{12}C.

To determine the formula of a compound we first have to know its elemental composition and their mass percentages. This information can be obtained by performing elemental analyses on a sample of the compound. Knowledge of the elemental composition will yield the empirical formula, and if the molar mass (or molecular mass) is also known, the molecular formula can be deduced. The empirical formula is a formula that shows the simplest mole ratio of elements in the compound. The molecular formula of a compound is the true formula that indicates the actual number of atoms of each type in a molecule (or the number of moles of each type of element in 1 mole of the compound). But it does not tell how atoms are connected in the molecule.

The concentration of a solution refers to the amount of solute present in the given quantity of solution or solvent. Percentages are also commonly used to express the composition of mixtures, including solutions. The mass percentage of a solution component is defined as the ratio of the component's mass to the solution's mass, expressed as a percentage. Mole fraction is the ratio of number of moles of one component (Solute or Solvent) to the total number of moles of all the components (Solute and Solvent) present in the Solution. Molarity of a solution is defined as the number of gram-moles of solute dissolved in 1 litre of a solution. Normality of a solution is defined as the number of gram equivalents of the solute dissolved per litre of the given solution. Molality of a solution is defined as the number of gram-moles of solute dissolved in 1000 grams (or 1 kg) of a Solvent.

In chemical reactions atoms are not created or destroyed, and this is indicated in the balanced equation. Balancing equation is done by introducing the smallest integer coefficients to one or more of the reactants and/or products involved in the reaction without changing their formula. Thus, the formula of each substance in an equation must be written correctly first before any attempt to balance the equation is made. Oxidation number of the element is defined as the residual charge which its atom has (or) appears to have when all other atoms from the molecule are removed as ions. Balancing redox reactions is slightly more complex than balancing standard reactions. To maintain charge neutrality in the sample, the redox reaction will entail both a reduction component and oxidation components and is often separated into independent two hypothetical half-reactions to aid in understanding the reaction.

EXERCISE

5.1 How many moles are 1.20 x 10^{25} atoms of phosphorous?
5.2 How many molecules are in 0.400 moles of N_2O_5?
5.3 Find the grams in 1.26 x 10^{-4} mol of $HC_2H_3O_2$.
5.4 Find the mass in 2.6 mol of lithium bromide.
5.5 What is the volume of 0.05 mol of neon gas at STP?
5.6 How many moles are there in 25.0 g of sodium?
5.7 What is the mass of 4.2 x 10^{22} atoms of phosphorus?
5.8 What is the mass of 0.675 mole of copper?
5.9 How many atoms are in 1.50 moles of carbon?
5.10 How many moles are there in 7.50 x 10^{21} atoms of iron?
5.11 A sample of $Ba(ClO_3)_2$ has a mass of 15.5 g. How many atoms are in the sample?
5.12 How many moles of oxygen molecules are present in 64.0 g of oxygen?
5.13 What is the volume of 34 g of ammonia, NH_3 at STP?
5.14 How many molecules of sulfur dioxide, SO_2, are in 40 L of sulfuric dioxide at STP?
5.15 How many oxygen molecules are in a box that contains 0.8 mole of oxygen?
5.16 A box contains 4 moles of sulfur trioxide. How many molecules are in the box?
5.17 If 10 L of nitrogen is in a container at STP, how many moles are in the container?
5.18 What is the molecular weight of hydrogen peroxide?
5.19 What is the mass of 3 moles of carbon?
5.20 Analysis of a certain compound showed that 39.348 grams of it contained 0.883 grams of hydrogen, 10.497 grams of Carbon, and 27.968 grams of Oxygen. Calculate the empirical formula of the compound.
5.21 A certain compound contains 7.3%Carbon, 4.5 % hydrogen, 36.4% oxygen, and 31.8% nitrogen. Its relative molecular mass is 176.0. Find its empirical and molecular formulas.
5.22 Assign oxidation numbers to the underline elements in each of the following species
$NaH_2\underline{P}O_4$, $H_4\underline{P}_2O_7$, $K_2\underline{Mn}O_4$, $Na\underline{B}H_4$,
5.23 Balance the Redox equations using ion electron method
$MnO_4^-{}_{(aq)} + Fe^{2+}{}_{(aq)} \rightarrow Mn^{2+}{}_{(aq)} + Fe^{3+}{}_{(aq)}$ in an acidic solution.
5.24 Balance in basic solution using ion electron method
$MnO_4^- + H_2S \rightarrow S + MnO$

QUESTION BANK

Chapter 5: STOICHEMISTRY

Very Short Answer Questions **(2 Marks)**

1. How many number of moles of glucose present in 540 gms of glucose.
2. The empirical formula of a compound is CH_2O its molecular weight is 90. Calculate the molecular formula of the compound.
3. Define the molar mass.
4. Define normality?
5. Write formulas for the following compounds.
   a) Mercury (II) Chloride b) Nickel (II) Sulphate c) Tin (IV) orise
   b) d) Thallium (I) Sulpate e) Iron (III) Sulphate f) Chromium (III) Oxide.
6. Assign oxidation number to the underlined elements in each of the following species.
   a) $NaH_2\underline{P}O_4$ b) $NaH\underline{S}O_4$ c) $H_4\underline{P}_2O_7$ d) $K_2\underline{Mn}O_4$ e) CaO2 f) $Na\underline{B}H_4$ g) $H_2\underline{S}_2O_7$

Chapter-6

THERMODYNAMICS

Chemical energy stored by molecules can be released as heat during chemical reactions when a fuel like methane, cooking gas or coal burns in air. The chemical energy may also be used to do mechanical work when a fuel burns in an engine or to provide electrical energy through a galvanic cell like dry cell. Thus, various forms of energy are interrelated and under certain conditions. these may be transformed from one form into another. The study of these energy transformations forms the subject matter of thermodynamics. The laws of thermodynamics deal with energy changes of macroscopic systems involving a large number of molecules rather than microscopic systems containing a few molecules. Thermodynamics is not concerned about how and at what rate these energy transformations are carried out, but is based on initial and final states of a system undergoing the change. Laws of thermodynamics apply only when a syste1n is in equilibrium or moves from one equilibrium state to another equilibrium state. Macroscopic properties like pressure and temperature do not change with time for a system in equilibrium state. In this unit, we would like to answer some of the important questions through thermodynamics, like:

How do we determine the energy changes involved in a chemical reaction/ process? Will it occur or not?

What drives a chemical reaction/ process?

To what extent do the chemical reactions proceed?

6.1 Thermodynamic State

We are interested in chemical reactions and the energy changes accompanying them. In order to quantify these energy changes, we need to separate the system which is under observations, from remaining part of the universe.

6.1.1 The System and the Surroundings

A system in thermodynamics refers to that part of universe in which observations are made and remaining universe constitutes the surroundings. The surroundings include everything other than the system. System and the surroundings together constitute the universe.

The universe = The system + The surroundings

However, the entire universe other than the system is not affected by the changes taking place in the system. Therefore, for all practical purposes, the surroundings are that portion of the remaining universe which can interact with the system. Usually, the region of space in the neighborhood of the system constitutes its surroundings.

For example, if we are studying the reaction between two substances A and B kept in a beaker, the beaker containing the reaction mixture is the system and the room where the beaker is kept is the surroundings (Fig. 6.1).

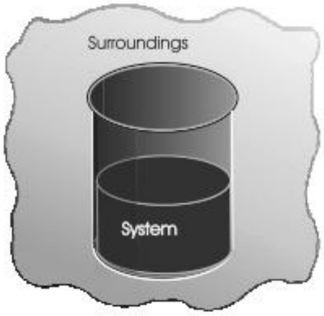


Fig. 6.1 System and surroundings

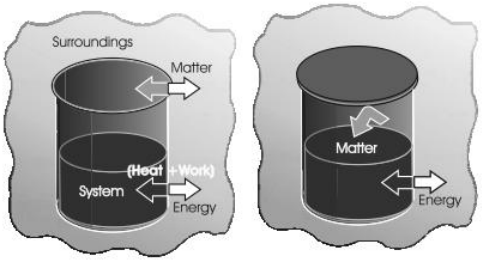
Note that the system may be defined by physical boundaries, like beaker or test tube, or the system may simply be defined by a set of Cartesian coordinates specifying a particular volume in space. It is necessary to think of the syste1n as separated from the surround ings by some sort of wall which may be real or imaginary. The wall that separates the system from the surroundings is called boundary. This is designed to allow us to control and keep track of all inove1nents of matter and energy in or out of the system.

6.1.2 Types of the System

We, further classify the systems according to the movements of matter and energy in or out of the system.

1. Open System

In an open system, there is exchange of energy and matter between system and surroundings [Fig. 6.2 (a)]. The presence of reactants in an open beaker is an example of an open system. Here the boundary is an imaginary surface enclosing the beaker and reactants.



(a) Open System (b) Closed System

(c) Isolated System

Fig. 6.2 Open, closed and isolated systems

2. Closed System

In a closed system, there is no exchange of matter, but exchange of energy is possible between system and the surroundings [Fig. 6.2 (b)]. The presence of reactants in a closed vessel made of conducting material e.g., copper or steel is an example of a closed system.

3. Isolated System

In an isolated system, there is no exchange of energy or matter between the system and the surroundings [Fig. 6.2 (c)]. The presence of reactants in a thermos flask or any other closed insulated vessel is an example of an isolated system.

6.1.3 The State of the System

The system must be described in order to make any useful calculations by specifying quantitatively each of the properties such as its pressure (p), volume (V) , and temperature (T) as well as the composition of the system. We need to describe the system by specifying it before and after the change. You would recall from your Physics course that the state of a system in mechanics is completely specified at a given instant of time, by the position and velocity of each mass point of the system. In thermodynamics, a different and much simpler concept of the state of a system is introduced. It does not need detailed knowledge of motion of each particle because; we deal with average measurable properties of the system. We specify the state of the system by state functions or state variables.

The state of a thermodynamic system is described by its measurable or macroscopic (bulk) properties. We can describe the state of a gas by quoting its pressure (p), volu1ne (V) , temperature (T), amount (n) etc. Variables like p, V, T are called state variables or state functions because their values depend only on the state of the system and not on how it is reached. In order to completely define the state of a system it is not necessary to define all the properties of the system; as only a certain number of properties can be varied independently. This number depends on the nature of the system. Once these minimum numbers of macroscopic properties are fixed, others automatically have definite values.

The state of the surroundings can never be completely specified; fortunately it is not necessary to do so.

6.1.4 The Internal Energy as a State Function

When we talk about our chemical system losing or gaining energy, we need to introduce a quantity which represents the total energy of the system. It may be chemical, electrical, mechanical or any other type of energy you may think of, the sum of all these is the energy of the system. In thermodynamics, we call it the internal energy, U of the system, which may change, when

- heat passes into or out of the system,
- work is done on or by the system,
- matter enters or leaves the system.

(a) Work

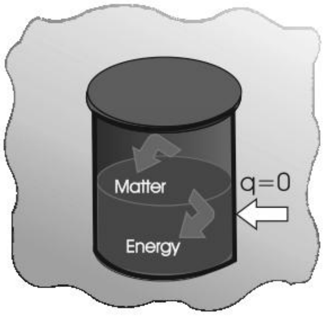


Fig. 6.3 An adiabatic system which does not permit the transfer of heat through its boundary

Let us first examine a change in internal energy by doing work. We take a system containing some quantity of water in a thermos flask or in an insulated beaker. This would not allow exchange of heat between the system and surroundings through its boundary and we call this type of system as adiabatic. The manner in which the state of such a system may be changed will be called adiabatic process. Adiabatic process is a process in which there is no transfer of heat between the system and surroundings. Here, the wall separating the system and the surroundings is called the adiabatic wall (Fig 6.3).

Let us bring the change in the internal energy of the system by doing some work on it. Let us call the initial state of the system as state A and its temperature as T_A. Let the internal energy of the system in state A be called U_A. We can change the state of the system in two different ways.

One way: We do some mechanical work, say 1 kJ, by rotating a set of small paddles and thereby churning water. Let the new state be called B state and its temperature, as T_B. It is found that $T_B > T_A$ and the change in temperature, $\Delta T = T_B - T_A$. Let the internal energy of the system in state B be U_B and the change in internal energy, $\Delta U = U_B - U_A$

Second way: We now do an equal amount (i.e., l kJ) electrical work with the help of an immersion rod and note down the temperature change. We find that the change in temperature is same as in the earlier case, say, $T_B - T_A$.

In fact, the experiments in the above manner were done by J. P. Joule between 1840-50 and he was able to show that a given amount of work done on the system, no matter how it was done (irrespective of path) produced the same change of state, as measured by the change in the temperature of the system.

So , it seems appropriate to define a quantity, the internal energy U, whose value is characteristic of the state of a system, whereby the adiabatic work, w_{ad} required to bring about a change of state is equal to the difference between the value of U in one state and that in another state, ΔU i.e,

$$\Delta U = U_2 - U_1 = W_{ad}$$

Therefore, internal energy, U, of the syste1n is a state function.

The positive sign expresses that W_{ad} is positive when work is done on the system. Similarly, if the work is done by the system W_{ad} will be negative.

Can you name some other familiar state functions? Some of other familiar state functions are V, p, and T. For example, if we bring a change in temperature of the system from 25°C to 35°C, the change in temperature is 35°C - 25°C = + 10°C, whether we go straight up to 35°C or we cool the system for a few degrees, then take the system to the final temperature. Thus, T is a state function and the change in temperature is independent of the route taken. Volume of water in a pond, for example, is a state function, because change in volume of its water is independent of the route by which water is filled in the pond, either by rain or by tube well or by both.

(b) Heat

We can also change the internal energy of a system by transfer of heat from the surroundings to the system or vice-versa without expenditure of work. This exchange of energy, which is a result of temperature difference is called heat, q. Let us consider bringing about the same change in temperature (the same initial and final states as before in section 6.1.4 (a) by transfer of heat through thermally conducting walls instead of adiabatic walls (Fig. 6.4).

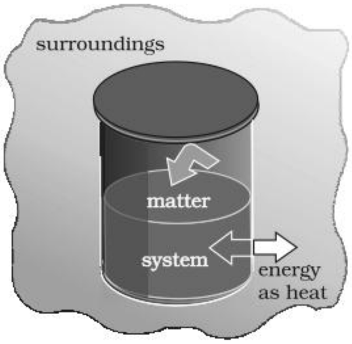


Fig. 6.4 A system which allows heat transfer through its boundary

We take water at temperature, T_A in a container having thermally conducting walls, say made up of copper and enclose it in a huge heat reservoir at temperature, T_B. The heat absorbed by the system (water), q can be measured in terms of temperature difference, $T_B - T_A$. In this case change in internal energy, $\Delta U = q$, when no work is done at constant volume.

The q is positive, when heat is transferred from the surroundings to the system and q is negative when heat is transferred from system to the surroundings.

(c) The general case

Let us consider the general case in which a change of state is brought about both by doing work and by transfer of heat. We write change in internal energy for this case as:

$$\Delta U = q + w \quad (6.1)$$

For a given change in state, q and w can vary depending on how the change is carried out. However, $q + w = \Delta U$ will depend only on initial and final state. It will be independent of the way the change is carried out. If there is no transfer of energy as heat or as work (isolated system) i.e., if w = 0 and q = 0, then $\Delta U = 0$.

The equation 6.1 i .e ., $\Delta U = q + w$ is mathematical statement of the first law of thermodynamics, which states that

The energy of an isolated system is constant.

It is commonly stated as the law of conservation of energy i.e., *energy can neither be created nor be destroyed.*

Note: There is considerable difference between the character of the thermodynamic property energy and that of a mechanical property such as volume. We can specify an unambiguous (absolute) value for volume of a system in a particular state, but not the absolute value of the internal energy. However, we can measure only the changes in the internal energy, ΔU of the system.

6.2.1 Enthalpy, H

We know that the heat absorbed at constant volume is equal to change in the internal energy i.e., $\Delta U = q_v$. But most of chemical reactions are carried out not at constant volume, but in flasks or test tubes under constant atmospheric pressure. We need to define another state function which may be suitable under these conditions.

We may write equation (6. 1) as $\Delta U = q_p - p\,\Delta V$ at constant pressure, where q_p is heat absorbed by the system and $-p\,\Delta V$ represent expansion work done by the system.

Let us represent the initial state by subscript 1 and final state by 2

We can rewrite the above equation as

$U_2 - U_1 = q_p - p\,(V_2 - V_1)$

On rearranging, we get

$$q_p = U_2 + p\,V_2 - U_1 + p\,V_1 \tag{6.2}$$

Now we can define another thermodynamic function, the enthalpy H [Greek word enthalpien, to warm or heat content] as:

$$H = U + pV \tag{6.3}$$

so, equation (6.2) becomes $q_p = H_2 - H_1 = \Delta H$

Although q is a path dependent function, H is a state function because it depends on U, p and V, all of which are state functions. Therefore, ΔH is independent of path. Hence, q_p is also independent of path.

For finite changes at constant pressure, we can write equation 6.3 as

$$\Delta H = \Delta U + p\,\Delta V \tag{6.4}$$

It is important to note that when heat is absorbed by the system at constant pressure, we are actually measuring changes in the enthalpy.

Remember $\Delta H = q_p$, heat absorbed by the system at constant pressure.

ΔH is negative for exothermic reactions which evolve heat during the reaction and ΔH is positive for endothermic reactions which absorb heat from the surroundings.

6.2.2 Extensive and Intensive Properties

In thermodynamics, a distinction is made between extensive properties and intensive properties. An extensive property is a property whose value depends on the quantity or size of matter present in the system. For example, mass, volume, internal energy, enthalpy, heat capacity, etc. are extensive properties.

Those properties which do not depend on the quantity or size of matter present are known as intensive properties. For example temperature, density, pressure etc. are intensive properties.

6.2.3 Heat Capacity

In this sub-section, let us see how to measure heat transferred to a system. This heat appears as a rise in temperature of the system in case of heat absorbed by the system.

The increase of temperature is proportional to the heat transferred

$$q = \text{coeff} \times \Delta T$$

The magnitude of the coefficient depends on the size, composition and nature of the system. We can also write it as $q = C\,\Delta T$

The coefficient, C is called the heat capacity.

Thus, we can measure the heat supplied by monitoring the temperature rise, provided we know the heat capacity.

When C is large, a given amount of heat results in only a small temperature rise. Water has a large heat capacity i.e., a lot of energy is needed to raise its temperature.

C is directly proportional to amount of substance. The molar heat capacity of a substance, $C_m = \left(\frac{C}{n}\right)$ is the heat capacity for one mole of the substance and is the quantity of heat needed to raise the temperature of one mole by one degree celsius (or one kelvin). Specific heat, also called specific heat capacity is the quantity of heat required to raise the temperature of one unit mass of a substance by one degree celsius (or one kelvin). For finding out the heat, q required to raise the temperatures of a sample, we multiply the specific heat of the substance, c, by the mass m, and temperatures change, ΔT as

$$q = c \times m \times \Delta T \qquad (6.5)$$

6.3 Enthalpy Change, $\Delta_r H$ Of A Reaction - Reaction Enthalpy

In a chemical reaction, reactants are converted into products and is represented by,

$$\text{Reactants} \rightarrow \text{Products}$$

The enthalpy change accompanying a reaction is called the reaction enthalpy. The enthalpy change of a chemical reaction is given by the symbol $\Delta_r H$.

$\Delta_r H$ = (sum of enthalpies of products) - (sum of enthalpies of reactants)

$$\Delta_r H = \sum_i a_i H_{\text{products}} - \sum_i b_i H_{reactants} \qquad (6.6)$$

a_i and b_i are the stoichiometric coefficients of the products and reactants respectively in the balanced chemical equation.

Enthalpy change is a very useful quantity. Knowledge of this quantity is required when one needs to plan the heating or cooling required to maintain an industrial chemical reaction at constant temperature. It is also required to calculate temperature dependence of equilibrium constant.

(a) Standard enthalpy of reactions

Enthalpy of a reaction depends on the conditions under which a reaction is carried out. It is, therefore, necessary that we must specify some standard conditions. The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states.

The standard state of a substance at a specified temperature is its pure form at 1bar. For example, the standard state of liquid ethanol at 298 K is pure liquid ethanol at 1bar; Usually data are taken at 298 K.

Standard conditions are denoted by adding the superscript to the symbol ΔH, e.g.,

(b) Standard enthalpy of formation

The standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states of aggregation (also known as reference states) is called Standard Molar Enthalpy of Formation. Its symbol is $\Delta_f H^{\square}$, where the subscript 'f ' indicates that one mole of the compound in question has been formed in its standard state from its elements in their most stable states of aggregation. The reference state of an element is its most stable state of aggregation at 25^0 C and 1 bar pressure. For example, the reference state of hydrogen is H_2 gas and those of oxygen, carbon and sulphur are O_2 gas, $C_{graphlte}$ and $S_{rhombic}$ respectively. Some reactions with standard molar enthalpies of fomation are given below.

$$H_2(g) + \frac{1}{2} O_2 (g) \rightarrow H_2O (l) \qquad \Delta_f H^{\circ} = -285.8 \text{ kJ mol}^{-1}$$

$$C \text{ (graphite, s)} + 2H_2 (g) \rightarrow CH_4 (g) \qquad \Delta_f H^{\circ} = -74.81 \text{ kJ mol}^{-1}$$

$$2\ C \text{ (graphite, s)} + 3H_2 (g) + \frac{1}{2} O_2 (g) \rightarrow C_2H_5OH(l) \qquad \Delta_f H^{\circ} = -277.7 \text{ kJ mol}^{-1}$$

It is important to understand that a standard molar enthalpy of formation, $\Delta_f H^{\circ}$ is just a special case of $\Delta_r H^{\circ}$, where one mole of a compound is formed from its constituent elements, as in the above three equations, where 1 mol of each, water, methane and ethanol is formed. In contrast, the enthalpy changes for an exothermic reaction: is not an enthalpy of formation of calcium carbonate, since calcium carbonate has been formed from other compounds, and not from its constituent elements.

$$CaO(s) + CO_2(g) \rightarrow CaCO_3(s) \qquad \Delta_r H^{\circ} = -178.3 \text{ kJ mol}^{-1}$$

Also, for the reaction given below, enthalpy change is not standard enthalpy of formation, $\Delta_f H^0$ for HBr(g) .

$$H_2(g) + Br_2(l) \rightarrow 2HBr (g) \qquad \Delta_f H^{\circ} = -72.8 \text{ kJ mol}^{-1}$$

Here two moles, instead of one mole of the product is formed from the elements, i.e.. $\Delta_rH^0 = 2\Delta_fH^0$. Therefore, by dividing all coefficients in the balanced equation by 2, expression for enthalpy of formation of HBr (g) is written as

$$\frac{1}{2} H_2(g) + \frac{1}{2}Br_2(l) \rightarrow HBr\ (g) \qquad \Delta_fH^\circ = -36.4\ kJ\ mol^{-1}$$

Standard enthalpies of formation of some common substances are given in Table 6.1.

By convention, standard enthalpy for formation, Δ_fH°, of an element in reference state, i.e., its most stable state of aggregation is taken as zero.

Suppose, you are a chemical engineer and want to know how much heat is required to decompose calcium carbonate to lime and carbon dioxide with all the substances in their standard state.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \quad \Delta_rH^\circ =?$$

Here, we can make use of standard enthalpy of formation and calculate the enthalpy change for the reaction. The following general equation can be used for the enthalpy change calculation.

$$\Delta_rH^\circ = \sum_i a_i\, \Delta_f H_0(products) - \sum_i b_i \Delta_f H_0\ (reactants) \qquad (6.\ 7)$$

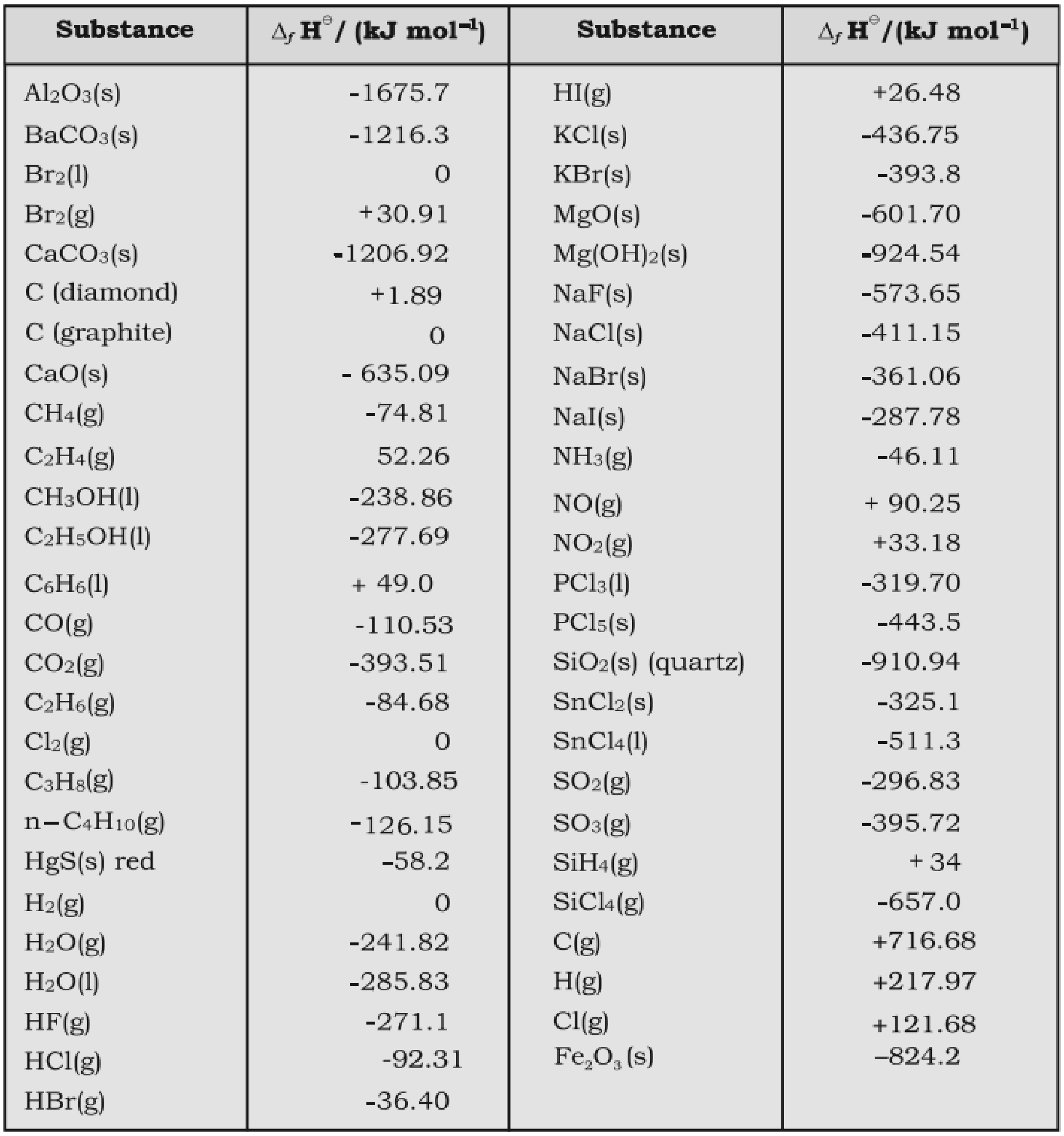
where a and b represent the coefficients of the products and reactants in the balanced equation. Let us apply the above equation for decomposition of calcium carbonate. Here, coefficients 'a' and 'b' are I each. Therefore,

$$\Delta_rH^0 = \sum_i a_i\, \Delta_f H_0[CaO(s)] + \sum_i a_i \Delta_f H_0\ [CO_2(g)] - \sum_i b_i \Delta_f H_0\ [CaCo_3(s)]$$

$$= 1\ (-635.1\ kJ\ mol^{-1}) + 1(-393.5kJ\ mol^{-1})\ -1(1206.9\ kJ\ mol^{-1}) = 178.kJ\ mol^{-1}$$

Thus, the decomposition of $CaCO_3$(s) is an endothermic process and you have to heat it for getting the desired products.

Table 6.1 Standard molar enthalpies of formation at 298 K of a few substances



Substance	$\Delta_f H^\ominus$ / (kJ mol^{-1})	Substance	$\Delta_f H^\ominus$ /(kJ mol^{-1})
$Al_2O_3(s)$	-1675.7	$HI(g)$	+26.48
$BaCO_3(s)$	-1216.3	$KCl(s)$	-436.75
$Br_2(l)$	0	$KBr(s)$	-393.8
$Br_2(g)$	+30.91	$MgO(s)$	-601.70
$CaCO_3(s)$	-1206.92	$Mg(OH)_2(s)$	-924.54
C (diamond)	+1.89	$NaF(s)$	-573.65
C (graphite)	0	$NaCl(s)$	-411.15
$CaO(s)$	- 635.09	$NaBr(s)$	-361.06
$CH_4(g)$	-74.81	$NaI(s)$	-287.78
$C_2H_4(g)$	52.26	$NH_3(g)$	-46.11
$CH_3OH(l)$	-238.86	$NO(g)$	+ 90.25
$C_2H_5OH(l)$	-277.69	$NO_2(g)$	+33.18
$C_6H_6(l)$	+ 49.0	$PCl_3(l)$	-319.70
$CO(g)$	-110.53	$PCl_5(s)$	-443.5
$CO_2(g)$	-393.51	$SiO_2(s)$ (quartz)	-910.94
$C_2H_6(g)$	-84.68	$SnCl_2(s)$	-325.1
$Cl_2(g)$	0	$SnCl_4(l)$	-511.3
$C_3H_8(g)$	-103.85	$SO_2(g)$	-296.83
$n-C_4H_{10}(g)$	-126.15	$SO_3(g)$	-395.72
HgS(s) red	-58.2	$SiH_4(g)$	+ 34
$H_2(g)$	0	$SiCl_4(g)$	-657.0
$H_2O(g)$	-241.82	C(g)	+716.68
$H_2O(l)$	-285.83	H(g)	+217.97
HF(g)	-271.1	Cl(g)	+121.68
HCl(g)	-92.31	$Fe_2O_3(s)$	–824.2
HBr(g)	-36.40		

(c) Hess's Law of Constant Heat Summation

We know that enthalpy is a state function; therefore the change in enthalpy is independent of the path between initial state (reactants) and final state (products). In other words, enthalpy change for a reaction is the same whether it occurs in one step or in a series of steps. This may be stated as follows in the form of Hess's Law.

If a reaction takes place in several steps then its standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions into which the overall reaction may be divided at the same temperature.

Let us understand the importance of this law with the help of an example. Consider the enthalpy change for the reaction

$$\text{C(graphite, s)} + \frac{1}{2}\text{O}_2\text{ (g)} \rightarrow \text{CO (g)} \qquad \Delta_f H^0\,?$$

Although CO(g) is the major product, some CO_2 gas is always produced in this reaction. Therefore, we cannot measure enthalpy change for the above reaction directly. However, if we can find some other reactions involving related species, it is possible to calculate the enthalpy change for the above reaction.

Let us consider the following reactions:

$$\text{C(graphite, s)} + \text{O}_2\text{ (g)} \rightarrow \text{CO}_2\text{ (g)} \qquad \Delta_f H^0 = -393.5 \text{ kJ mol}^{-1} \ldots\ldots\ldots\text{(i)}$$

$$\text{CO} + \frac{1}{2}\text{O}_2\text{ (g)} \rightarrow \text{CO}_2\text{ (g)} \qquad \Delta_f H^0 = -283.0 \text{ kJ mol}^{-1} \ldots\ldots\ldots\text{(ii)}$$

We can combine the above two reactions in such a way so as to obtain the desired reaction. To get one mole of CO(g) on the right, we reverse equation (ii). In this, heat is absorbed instead of being released, so we change sign of $\Delta_f H^{\ominus}$ value

$$\text{CO}_2\text{(g)} \rightarrow \text{CO (g)} + \frac{1}{2}\text{O}_2\text{ (g)} \qquad \Delta_f H^0 = +\,283.0 \text{ kJ mol}^{-1} \ldots\ldots\ldots\text{(iii)}$$

Adding equation (i) and (iii) , we get the desired equation ,

$$\text{C(graphite, s)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{CO(g)}$$

for which $\Delta_r H^0 = -393.5 + 283.0 = -110.5$ kJ mol^{-1}

In general, if enthalpy of an overall reaction $A \rightarrow B$ along one route is $\Delta_r H$ and $\Delta_r H_1$, $\Delta_r H_2$, $\Delta_r H_3$..... representing enthalpies of reactions leading to same product, B along another route, then we have

$$\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 \ldots\ldots\ldots\ldots \qquad (6.8)$$

It can be represented as:

6.4 Spontaneity

The first law of thermodynamics tells us about the relationship between the heat absorbed and the work performed on or by a system. It puts no restrictions on the direction of heat flow. However, the flow of heat is unidirectional from higher temperature to lower temperature. In fact, all naturally occurring processes whether chemical or physical will tend to proceed spontaneously in one direction only. For example a gas expanding to fill the available volume, burning carbon in oxygen giving carbon dioxide.

But heat will not flow from colder body to warmer body on its own, the gas in a container will not spontaneously contract into one corner or carbon dioxide will not form carbon and oxygen spontaneously. These and many other spontaneously occurring changes show unidirectional change. We may ask 'what is the driving force of spontaneously occurring changes? What determines the direction of a spontaneous change? In this section, we shall establish some criterion for these processes whether these will take place or not.

Let us first understand what do we mean by spontaneous reaction or change? You may think by your common observation that spontaneous reaction is one which occurs immediately when contact is made between the reactants. Take the case of combination of hydrogen and oxygen. These gases may be mixed at room temperature and left for many years without observing any perceptible change. Although the reaction is taking place between them, it is at an extremely slow rate. It is still called spontaneous reaction. So spontaneity means 'having the potential to proceed without the assistance of external agency'. However, it does not tell about the rate of the reaction or process. Another aspect of spontaneous reaction or process, as we see is that these cannot reverse their direction on their own. We may summaries it as follows:

A spontaneous process is an irreversible process and may only be reversed by some external agency .

(a) Is decrease in enthalpy a criterion for spontaneity?

If we examine the phenomenon like flow of water down hill or fall of a stone on to the ground, we find that there is a net decrease in potential energy in the direction of change. By analogy, we may be tempted to state that a chemical reaction is spontaneous in a given direction, because decrease in energy has taken place , as in the case of exothermic reactions. For example:

$$\frac{1}{2} N_2 (g) + \frac{1}{2} H_2 (g) \rightarrow NH_3 (g) \quad \Delta_r H^0 = -46.1 \text{ kJ mol}^{-1}$$

$$\frac{1}{2} H_2 (g) + \frac{1}{2} Cl_2 (g) \rightarrow HCl (g) \quad \Delta_r H^0 = -92.32 \text{ kJ mol}^{-1}$$

$$H_2 (g) + \frac{1}{2} O_2 (g) \rightarrow H_2O (l) \quad \Delta_r H^0 = -285.8 \text{ kJ mol}^{-1}$$

The decrease in enthalpy in passing from reactants to products may be shown for any exothermic reaction on an enthalpy diagram as shown in Fig. 6.5.

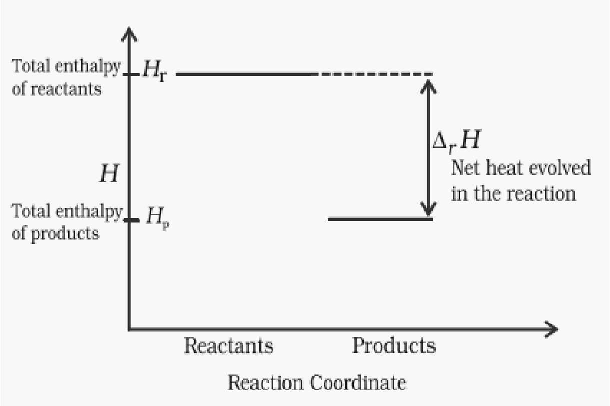


Fig. 6.5 Enthalpy diagram for exothermic reaction

Thus, the postulate that driving force for a chemical reaction may be due to decrease in energy sounds 'reasonable' as the basis of evidence so far!

$$\frac{1}{2} N_2 (g) + O_2 \rightarrow NO_2 (g) \qquad \Delta_r H^0 = = +33.2 \text{ kJ mol}^{-1}$$

$$C \text{ (graphite, s)} + 2 S(l) \rightarrow CS_2 (l) \qquad \Delta_r H^0 = = +128.5 \text{ kJ mol}^{-1}$$

These reactions though endothermic, are spontaneous. The increase in enthalpy may be represented on an enthalpy diagram as shown in Fig. 6.6.

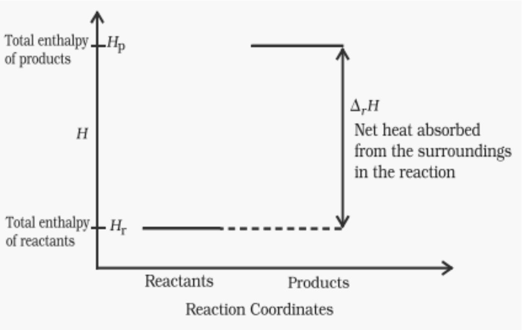


Fig. 6.6 Enthalpy diagram for exothermic reaction

Therefore, it becomes obvious that while decrease in enthalpy may be a contributory factor for spontaneity, but it is not true for all cases.

(b) Entropy and spontaneity

Then, what drives the spontaneous process in a given direction? Let us examine such a case in which $\Delta H = 0$ i.e., there is no change in enthalpy, but still the process is spontaneous.

Let us consider diffusion of two gases into each other in a closed container which is isolated from the surroundings as shown in Fig. 6.7.

The two gases, say, gas A and gas B are represented by black dots and white dots respectively and separated by a movable partition [Fig. 6.7 (a)]. When the partition is withdrawn [Fig.6.7(b)], the gases begin to diffuse into each other and after a period of time, diffusion will be complete.

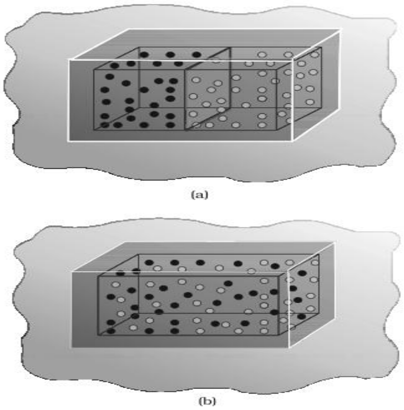


Fig. 6.7 diffusion of two gases

Let us examine the process. Before partition, if we were to pick up the gas molecules from left container, we would be sure that these will be molecules of gas A and similarly if we were to pick up the gas molecules from right container, we would be sure that these will be molecules of gas B. But, if we were to pick up molecules from container when partition is removed, we are not sure whether the molecules picked are of gas A or gas B. We say that the system has become less predictable or more chaotic.

We may now formulate another postulate: in an isolated system, there is always a tendency for the systems' energy to become more disordered or chaotic and this could be a criterion for spontaneous change!

At this point, we introduce another thermodynamic function, entropy denoted as S. The above mentioned disorder is the manifestation of entropy. To form a mental picture, one can think of entropy as a measure of the degree of randomness or disorder in the system. The greater the disorder in an isolated system, the higher is the entropy. As far as a chemical reaction is concerned, this entropy change can be attributed to rearrangement of atoms or ions from one pattern in the reactants to another (in the products) . If the structure of the products is very much disordered than that of the reactants, there will be a resultant increase in entropy. The change in entropy accompanying a chemical reaction may be estimated qualitatively by a consideration of the structures of the species taking part in the reaction. Decrease of regularity in structure would mean increase in entropy. For a given substance, the crystalline solid state is the state of lowest entropy (most ordered), The gaseous state is state of highest entropy.

Now let us try to quantify entropy. One way to calculate the degree of disorder or chaotic distribution of energy among molecules would be through statistical method which is beyond the scope of this treatment. Other way would be to relate this process to the heat involved in a process which would make entropy a thermodynamic concept. Entropy, like any other thermodynamic property such as internal energy U and enthalpy H is a state function and ΔS is independent of path.

Whenever heat is added to the system, it increases molecular motions causing increased randomness in the system. Thus heat (q) has randomising influence on the system. Can we then equate ΔS with q? Wait! Experience suggests us that the distribution of heat also depends on the temperature at which heat is added to the system. A system at higher temperature has greater randomness in it than one at lower temperature. Thus, temperature is the measure of average chaotic motion of particles in the system. Heat added to a system at lower temperature causes greater randomness than when the same quantity of heat is added to it at higher temperature. This suggests that the entropy change is inversely proportional to the temperature. ΔS is related with q and T for a reversible reaction as:

$$\Delta S = \frac{q_{rev}}{T} \tag{6.9}$$

The total entropy change (ΔS_{total}) for the system and surroundings of a spontaneous process is given by

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surr} > 0 \tag{6.10}$$

When a system is in equilibrium, the entropy is maximum, and the change in entropy, $\Delta S=0$.

We can say that entropy for a spontaneous process increases till it reaches maximum and at equilibrium the change in entropy is zero. Since entropy is a state property, we can calculate the change in entropy of a reversible process by

$$\Delta S_{sys} = \frac{q_{sys.rev}}{T}$$

We find that both for reversible and irreversible expansion for an ideal gas, under isothermal conditions, $\Delta U = 0$, but ΔS_{total} i.e., $\Delta S_{system} + \Delta S_{surr}$ is not zero for irreversible process. Thus, ΔU does not discriminate between reversible and irreversible process, whereas ΔS does.

Entropy, Spontaneity and Second Law of Thermodynamics

We know that for an isolated system the change in energy remains constant. Therefore increase in entropy in such systems is the natural direction of a spontaneous change. This, in fact is the second law of Thermodynamics. Second law can also be stated in several ways. The second law of Thermodynamics explains why spontaneous exothermic reactions are so common. In exothermic reactions, heat released by the reaction increases the disorder of the surroundings and overall entropy change is positive which makes the reaction spontaneous.

Statements of the second law of Thermodynamics

1. It is impossible to construct a cyclic heat engine that produces no other effect but the absorption of energy from a hot reservoir and the production of an equal amount of work.
2. It is impossible to construct a cyclic refrigerator whose sole effect is the transfer of energy from a cold reservoir to a warm reservoir without the input of energy by work.
3. The entropy of the Universe never decreases. It either increases (for irreversible processes) or remains the same (for reversible processes).

(c) Gibbs energy and spontaneity

We have seen that for a system, it is the total entropy change, ΔS_{total} which decides the spontaneity of the process. But most of the chemical reactions fall into the category of either closed systems or open systems. Therefore, for most of the chemical reactions there are changes in both enthalpy and entropy. It is clear from the discussion in previous sections that neither decrease in enthalpy nor increase in entropy alone can determine the direction of spontaneous change for these systems.

For this purpose, we define a new thermodynamic function the Gibbs energy or Gibbs function. G, as

$$G = H - TS \qquad (6.11)$$

Gibbs function. G is an extensive property and a state function. The change in Gibbs energy for the system, ΔG_{system} can be written as

$$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys} - S_{sys}\Delta T$$

At constant temperature, $\Delta T = 0$

$\therefore \Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$

Usually the subscript 'system' is dropped and we si1nply write this equation as

$$\Delta G = \Delta H - T\Delta S. \qquad (6.12)$$

Thus, Gibbs energy change = enthalpy change - temperature x entropy change, and is referred to as the Gibbs equation, one of the most important equations in chemistry. Here, we have considered both terms together for spontaneity: energy (in terms of ΔH) and entropy (ΔS, a measure of disorder) as indicated earlier. Dimensionally if we analyses, we find that ΔG has units of energy because, both ΔH and the $T\Delta S$ are energy terms, since $T\Delta S = \text{K} \quad \text{J/K} \quad = \text{J}$.

Now let us consider how ΔG is related to reaction spontaneity.

We know, $\Delta S_{total} = \Delta S_{system} + \Delta S_{surr}$

If the system is in thermal equilibrium with the surrounding, then the temperature of the surrounding is same as that of the system. Also, increase in enthalpy of the surrounding is equal to decrease in the enthalpy of the system.

Therefore, entropy change of surroundings,

$$\Delta S_{surr} = \frac{\Delta H_{surr}}{T} = -\frac{\Delta H_{sys}}{T}$$

$$\Delta S_{total} = \Delta S_{system} + \left(-\frac{\Delta H_{sys}}{T} \right)$$

Rearranging the above equation: $T\Delta S_{total} = T\Delta S_{system} - \Delta H_{sys}$

For spontaneous process, $\Delta S_{total} > 0$, so

$$T\Delta S_{sys} - \Delta H_{sys} > 0 \quad \Rightarrow -(\Delta H_{sys} - T\Delta S_{sys}) > 0$$

Using equation 6.12, the above equation can be written as

$-\Delta G > 0$

$$\therefore \Delta G = \Delta H - T\Delta S < 0 \qquad (6.13)$$

ΔH_{sys} is the enthalpy change of a reaction, $T\Delta S_{sys}$ is the energy which is not available to douseful work. So ΔG is the net energy available to do useful work and is thus a measure of the 'free energy'. For this reason, it is also known as the free energy of the reaction.

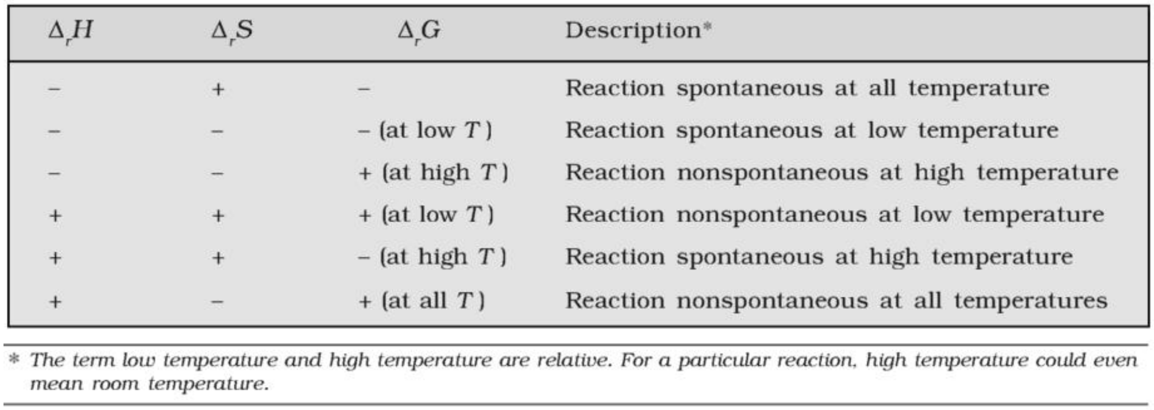
ΔG gives a criteria for spontaneity at constant pressure and temperature.

i. If ΔG is negative (< 0), the process is spontaneous.
ii. If ΔG is positive (> 0), the process is non spontaneous.

Note : If a reaction has a positive enthalpy change and positive entropy change, it can be spontaneous when $T\Delta S$ is large enough to outweigh ΔH . This can happen in two ways;

a) The positive entropy change of the system can be 'small' in which case T must be large.
b) The positive entropy change of the system can be 'large', in which case T may be small. The former is one of the reasons why reactions are often carried out at high temperature. Table 6.2 summarises the effect of temperature on spontaneity of reactions.

Table 6.2 Effect of temperatures on spontaneity of reactions



$\Delta_r H$	$\Delta_r S$	$\Delta_r G$	Description*
–	+	–	Reaction spontaneous at all temperature
–	–	– (at low T)	Reaction spontaneous at low temperature
–	–	+ (at high T)	Reaction nonspontaneous at high temperature
+	+	+ (at low T)	Reaction nonspontaneous at low temperature
+	+	– (at high T)	Reaction spontaneous at high temperature
+	–	+ (at all T)	Reaction nonspontaneous at all temperatures

* *The term low temperature and high temperature are relative. For a particular reaction, high temperature could even mean room temperature.*

6.5 Absolute Entropy and Third Law of Thermodynamics:

Molecules of a substance may move in a straight in any direction, they may spin like a top and bonds in the molecule may stretch and compress. These motions of the molecule are called translational, rotational and vibrational motion respectively. When temperature of the system rises, these motions become more vigorous and entropy increases. On the other hand the temperature is lowered, entropy decreases. *The entropy of pure crystalline substance approaches to zero as the temperature approaches absolute zero. This is called third law of thermodynamics*. This is so because there is a perfect order in a crystal at absolute zero. The statement is confined to pure crystalline solids because theoretical arguments and practical evidences have shown that the entropy of solutions and super cooled liquids is not zero at 0 K. The importance of the third law lies in the fact that it permits the calculation of absolute values of entropy of pure substance from the thermal data alone. For a pure substance, it can be done by summing q_{rev}/T increments from 0 K to 298 K. Standard entropies can be used to calculate standard entropy changes by a Hess's law type of calculation.

SUMMARY

Thermodynamics deals with energy changes in chemical or physical processes and enables us to study these changes quantitatively and to make useful predictions. For these purposes, we divide the universe into the system and the surroundings. Chemical or physical processes lead to evolution or absorption of heat (q), part of which may be converted into work (w). These quantities are related through the first law of thermodynamics via $\Delta U = q + w$. ΔU, change in internal energy, depends on initial and final states only and is a state function, whereas q and w depend on the path and are not the state functions. We follow sign conventions of q and w by giving the positive sign to these quantities when these are added to the system. We can measure the transfer of heat from one system to another which causes the change in temperature.

There are varieties of enthalpy changes. Changes of phase such as melting, vaporization and sublimation usually occur at constant temperature and can be characterized by enthalpy changes which are always positive. Enthalpy of formation, combustion and other enthalpy changes can be calculated using Hess's law. Enthalpy change for chemical reactions can be determined by

First law of thermodynamics does not guide us about the direction of chemical reactions i.e., what is the driving force of a chemical reaction. For isolated systems, $\Delta U = 0$. We define another state function, S, entropy for this purpose. Entropy is a measure of disorder or randomness. For a spontaneous change, total entropy change is positive. Therefore, for an isolated system, $\Delta U = 0, \Delta S > 0$, so entropy change distinguishes a spontaneous change, while energy change does not. Entropy changes can be measured. The second law of Thermodynamics explains why spontaneous exothermic reactions are so common. In exothermic reactions, heat released by the reaction increases the disorder of the surroundings and overall entropy change is positive which makes the reaction spontaneous.

Chemical reactions are generally carried at constant pressure, so we define another state function Gibbs energy, G, which is related to entropy and enthalpy changes of the system by the equation:

$$\Delta G = \Delta H - T\Delta S$$

For a spontaneous change, $\Delta G < 0$ and at equilibrium, $\Delta G = 0$. Temperature is an important factor in the equation. Many reactions which are non-spontaneous at low temperature are made spontaneous at high temperature for systems having positive entropy of reaction. The entropy of pure crystalline substance approaches to zero as the temperature approaches absolute zero. This is called third law of thermodynamics. This is so because there is a perfect order in a crystal at absolute zero. The statement is confined to pure crystalline solids because theoretical arguments and practical evidences have shown that the entropy of solutions and super cooled liquids is not zero at 0 K.

EXERCISE

5.1 In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process?

5.2 Calculate the number of kJ of heat necessary to raise the temperature of 60.0 g of aluminium from 35 ^{0}C to 55^0 C. Molar heat capacity of Al is 24 J mo1^{-1} K$^{-1.}$

5.3 Calculate the ΔH for the following reaction:

$$\mathbf{Sn + 2Cl_2 \rightarrow SnCl_4}$$

a. You are given these two equations:
b. $Sn + Cl_2 \rightarrow SnCl_2 \quad \Delta H = -325$ kJ
c. $SnCl_2 + Cl_2 \rightarrow SnCl_4 \quad \Delta H = -186$ kJ

5.4 Given the following two reactions and enthalpy data:

i. $CH_2CO(g) + 2O_2(g) \rightarrow 2CO_2(g) + H_2O(g) \qquad \Delta H = -981.1$ kJ

ii. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \quad \Delta H = -802.3$ kJ

calculate the enthalpy change for the reaction in which methane and oxygen combine to form ketene, CH_2CO, and water.

$$\mathbf{2CH_4(g) + 2O_2(g) \rightarrow CH_2CO(g) + 3H_2O(g) \quad \Delta H = ?\ kJ/mol}$$

QUESTION BANK

Chapter 6: THERMODINAMICS

***Very Short Answer Questions* (2 Marks)**

1. State the first law of the thermodynamics.
2. What are intensive and extensive properties?
3. Define the Enthalpy of combustion?
4. State Hess’s law of constant Heat summation?
5. Define Entropy, Gibbs energy?
6. State the second law of thermodynamics?
7. State third law of thermo dynamics?

CHAPTER-7

CHEMICAL EQUILIBRIUM AND ACID –BASES

Chemical equilibria are important in numerous biological and environmental processes. For example, equilibria involving O_2molecules and the protein hemoglobin play a crucial role in the transport and delivery of O_2 from our lungs to our muscles. Similar equilibria CO involving molecules and hemoglobin account for the toxicity of CO.

When a liquid evaporates in a closed container, molecules with relatively higher kinetic energy escape the liquid surface into the vapour phase and number of liquid molecules from the vapour phase strike the liquid surface and are retained in the liquid phase. It gives rise to a constant vapour pressure because of an equilibrium in which the number of molecules leaving the liquid equals the number returning to liquid from the vapour. We say that the system has reached equilibrium state at this stage. However, this is not static equilibrium and there is a lot of activity at the boundary between the liquid and the vapour. Thus, at equilibrium, the rate of evaporation is equal to the rate of condensation. It may be represented by

$$H_2O\text{ (liq)} \underset{r_2}{\overset{r_1}{\rightleftharpoons}} H_2O\text{ (vap)} \qquad\qquad r_1 = r_2$$

The double half arrows indicate that the processes in both the directions are going on simultaneously. The mixture of reactants and products in the equilibrium state is called an equilibrium mixture.

Equilibrium can be established for both physical processes and chemical reactions. The reaction may be fast or slow depending on the experimental conditions and the nature of the reactants. When the reactants in a closed vessel at a particular te1nperature react to give products, the concentrations of the reactants keep on decreasing, while those of products keep on increasing for some time after which there is no change in the concentrations of either of the reactants or products. This stage of the system is the dynamic equilibrium and the rates of the forward andreverse reactions become equal. It is due to this dynamic equilibrium stage that there is no change in the concentrations of various species in the reaction mixture. Based on the extent to which the reactions proceed, the state of chemical equilibrium in a chemical reaction may be classified in three groups.

i. The reactions that proceed nearly to completion and only negligible concentrations of the reactants are left. In some cases, it may not be even possible to detect these experimentally.
ii. The reactions in which only small amounts of products are formed and most of the reactants remain unchanged at equilibriu1n stage.
iii. The reactions in which the concentrations of the reactants and products are comparable, when the system is in equilibriu1n.

The extent of a reaction in equilibrium varies with the experimental conditions such as concentrations of reactants, temperature, etc. Optimisation of the operational conditions is very important in industry and laboratory so that equilibrium is favorable in the direction of the desired product. Some important aspects of equilibrium involving physical and chemical processes are dealt in this unit along with the equilibrium involving ions in aqueous solutions which is called as ionic equilibrium.

7.1 Equilibrium Processes

The characteristics of system at equilibrium are better understood if we examine some physical processes. The most familiar examples are phase transformation processes, e.g

$$\text{solid} \rightleftarrows \text{liquid}$$

$$\text{liquid} \rightleftarrows \text{gas}$$

$$\text{solid} \rightleftarrows \text{gas}$$

Ice and water kept in a perfectly insulated thermos flask (no exchange of heat between its contents and the surroundings) at 273K and the atmospheric pressure are in equilibrium state and the system shows interesting characteristic features. We observe that the mass of ice and water do not change with time and the temperature remains constant. However, the equilibrium is not static. The intense activity can be noticed at the boundary between ice and water. Molecules from the liquid water collide against ice and adhere to it and some molecules of ice escape into liquid phase. There is no change of mass of ice and water, as the rates of transfer of molecules from ice into water and of reverse transfer from water into ice are equal at atmospheric pressure and 273 K.

It is obvious that ice and water are in equilibrium only at particular temperature and pressure. For any pure substance at atmospheric pressure, the temperature at which the solid and liquid phases are at equilibrium is called the normal melting point or normal freezing point of the substance. The system here is in dynamic equilibrium and we can infer the following:

i. Both the opposing processes occur simultaneously.
ii. Both the processes occur at the same rate so that the amount of ice and water remains constant.

7.1.1 Liquid-Vapour Equilibrium

This equilibrium can be better understood if we consider the example of a transparent box carrying a U-tube with mercury (manometer). Drying agent like anhydrous calcium chloride (or phosphorus penta-oxide) is placed for a few hours in the box. After removing the drying agent by tilting the box on one side, a watch glass (or petri dish) containing water is quickly placed inside the box. It will be observed that the mercury level in the right limb of the manometer slowly increases and finally attains a constant value, that is, the pressure inside the box increases and reaches a constant value. Also the volume of water in the watch glass decreases (Fig. 7.1). Initially there was no water vapour (or very less) inside the box. As water evaporated the pressure in the box increased due to addition of water molecules into the gaseous phase inside the box. The rate of evaporation is constant. However, the rate of increase in pressure decreases with time due to condensation of vapour into water. Finally it leads to an equilibrium condition when there is no net evaporation. This implies that the number of water molecules from the gaseous state into the liquid state also increases till the equilibrium is attainedi.e., rate of evaporation= rate of condensation.

$$H_2O\ (liq) \rightleftharpoons H_2O\ (vap)$$

At equilibrium the pressure exerted by the water molecules at a given temperature remains constant and is called the equilibrium vapour pressure of water (or just vapour pressure of water); vapour pressure of water increases with temperature. If the above experiment is repeated with methyl alcohol, acetone and ether, it is observed that different liquids have different equilibrium vapour pressures at the same temperature, and the liquid which has a higher vapour pressure is more volatile and has a lower boiling point.

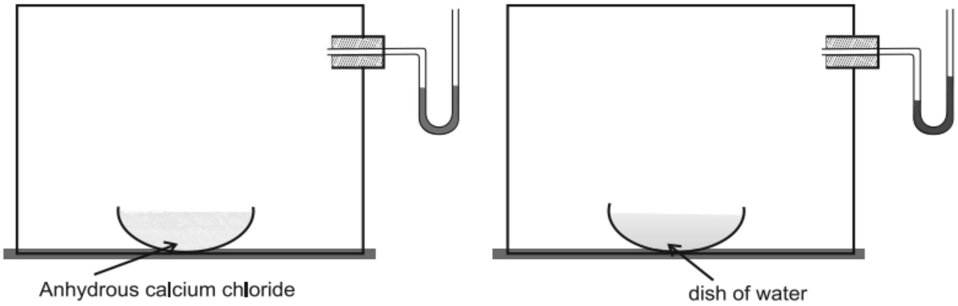


Fig 7.1 Measuring equilibrium vapour pressure of water at a constant temperature

If we expose three watch glasses containing separately lmL each of acetone, ethyl alcohol, and water to atmosphere and repeat the experiment with different volumes of the liquids in a warmer room, it is observed that in all such cases the liquid eventually disappears and the time taken for complete evaporation depends on (i) the nature of the liquid. (ii) The amount of the liquid and (iii) the temperature. When the watch glass is open to the atmosphere, the rate of evaporation remains constant but the molecules are dispersed into large volume of the room. As a consequence the rate of condensation from vapour to liquid state is much less than the rate of evaporation. These are open systems and it is not possible to reach equilibrium in an open system.

Water and water vapour are in equilibrium position at atmospheric pressure (1.013 bar) and at 100 ^{0}C in a closed vessel. The boiling point of water is 100 ^{0}C at 1.013 bar pressure. For any pure liquid at atmospheric pressure(1.013 bar) the temperature at which the liquid and vapours are at equilibrium is calledboiling point of the liquid. It depends on the atmospheric pressure. Boiling point of a liquid depends on the altitude of the place; at high altitude the boiling point decreases.

7.1.2 Solid - Vapour Equilibrium

Let us now consider the systems where solids sublime to vapour phase. If we place solid iodine in a closed vessel, after sometime the vessel gets filled up with violet vapour and the intensity of colour increases with time. After certain time the intensity of colour becomes constant and at this stage equilibrium is attained. Hence solid iodine sublimes to give iodine vapour and the iodine vapour condenses to give solid iodine. The equilibrium can be represented as,

$$I_2\ \text{solid} \rightleftharpoons I_2\ \text{vapour}$$

Other examples showing this kind of equilibrium are,

$$\text{Camphor}\quad\text{solid} \rightleftharpoons \text{Camphor}\quad\text{vapour}$$

$$NH_4Cl\ \ \text{solid} \rightleftharpoons NH_4Cl\quad\text{vapour}$$

7.1.3 Equilibrium Involving Dissolution of Solid or Gases in Liquids

Solids in liquids

We know from our experience that we can dissolve only a limited amount of salt or sugar in a given amount of water at room temperature. If we make a thick sugar syrup solution by dissolving sugar at a higher temperature, sugar crystals separate out if we cool the syrup to the room temperature. We call it a saturated solution when no more of solute can be dissolved in it at a given temperature. The concentration of the solute in a saturated solution depends upon the temperature. In a saturated solution, a dynamic equilibrium exits between the solute molecules in the solid state and in the solution:

$$\text{Sugar}\quad\text{solution} \rightleftharpoons \text{Sugar}\quad\text{solid}$$, andthe

Rateof dissolutionof sugar = rate of crystallisation of sugar.

Equality of the two rates and dynamic nature of equilibrium hasbeen confirmed with the help of radioactive sugar. If we drop some radioactive sugar into saturated solution of non-radioactive sugar, then after some time radioactivity is observed both in the solution and in the solid sugar. Initially there were no radioactive sugar molecules in the solution but due to dynamic nature of equilibrium, there is exchange between the radioactive and non-radioactive sugar molecules between the two phases.The ratio of the radioactive to non-radioactive molecules in the solution increases till it attains a constant value.

Gases in liquids

When a soda water bottle is opened, some of the carbon dioxide gas dissolved in it fizzes out rapidly. The phenomenon arises due to difference in solubility of carbon dioxide at different pressures. There is equilibrium between the molecules in the gaseous state and the molecules dissolved in the liquid under pressure i.e.

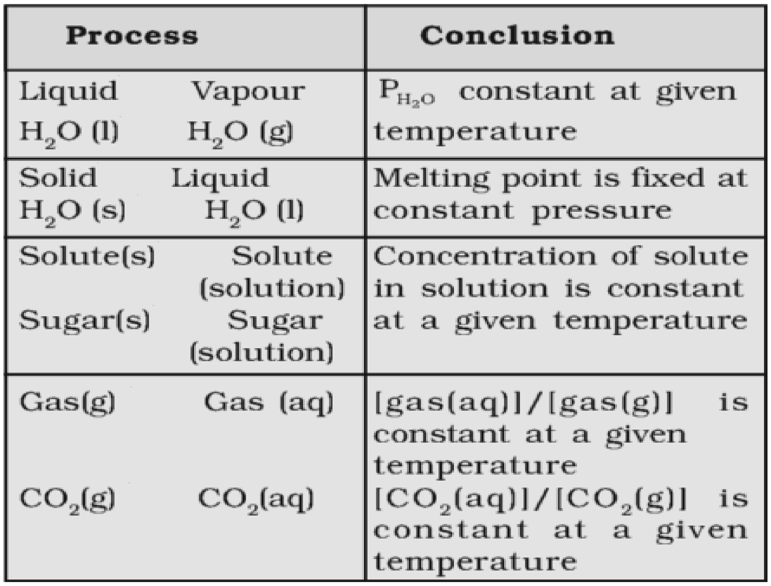
$$CO_2\quad\text{gas} \rightleftharpoons CO_2\quad\text{in solution}$$

This equilibrium is governed by Henry's law, which states that the mass of a gas dissolved in a given mass of a solvent at any temperature is proportional to the pressure of the gas above the solvent. This amount decreases with increase of temperature. The soda water bottle is sealed under pressure of gas when its solubility in water is high. As soon as the bottle is opened, some of the dissolved carbon dioxide gas escapes to reach a new equilibrium condition required for the lower pressure, namely its partial pressure in the atmosphere.This show the soda water in bottle when left open to the air for some time, turns 'flat'. It can be generalised that:

i. For solid liquid equilibrium, there is only one temperature (melting point) at 1atm (1.013bar) at which the two phases can coexist. If there is no exchange of heat with the surroundings, the mass of the two phases remains constant.
ii. For liquid vapour equilibrium, the vapour pressure is constant at a given temperature.
iii. For dissolution of solids in liquids, the solubility is constant at a given temperature.

iv. For dissolution of gases in liquids, the concentration of a gas in liquid is proportional to the pressure(concentration) of the gas over the liquid. These observations are summarised in Table 7.1

Table 7.1 Some Features of Physical Equilibria



Process	Conclusion
Liquid Vapour H_2O (l) H_2O (g)	P_{H_2O} constant at given temperature
Solid Liquid H_2O (s) H_2O (l)	Melting point is fixed at constant pressure
Solute(s) Solute (solution) Sugar(s) Sugar (solution)	Concentration of solute in solution is constant at a given temperature
Gas(g) Gas (aq) CO_2(g) CO_2(aq)	[gas(aq)]/[gas(g)] is constant at a given temperature [CO_2(aq)]/[CO_2(g)] is constant at a given temperature

7.1.4 General Characteristics of Equilibria Involving Physical Processes

For the physical processes discussed above, following characteristics are common to the system at equilibrium:

i. Equilibriu1n is possible only in a closed system at a given temperature.
ii. Both the opposing processes occur at the same rate and there is a dynamic but stable condition.
iii. All measurable properties of the system remain constant.
iv. When equilibrium is attained for a physical process, it is characterised by constant value of one of its parameters at a given temperature. Table 7.1 list s such quantities.
v. The magnitude of such quantities at any stage indicates the extent to which the reaction has proceeded before reaching equilibrium.

7.2 Equilibrium in Chemical Processes - Dynamic Equilibrium

Analogous to the physical systems chemical reactions also attain a state of equilibrium. These reactions can occur both in forward and backward directions. When the rates of the forward and reverse reactions become equal, the concentrations of the reactants and the products remain constant. This is the stage of chemical equilibrium. This equilibrium is dynamic in nature as it consists of forward reaction in which the reactants give product(s) and reverse reaction in which product(s) gives the original reactants.

For a better comprehension, let us consider a general case of a reversible reaction,

$$A + B \rightleftarrows C + D$$

With passage oftime, there is accumulation of the products C and D and depletion of the reactants A and B (Fig. 7.2). This leads to a decrease in the rate of forward reaction and an increase in the rate of the reverse reaction,

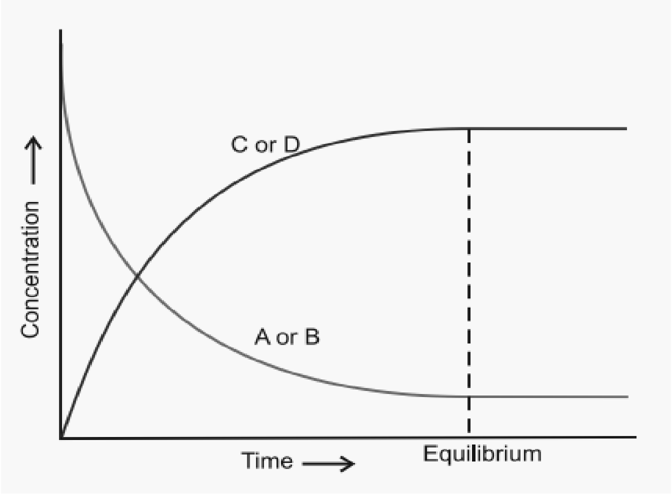


Fig. 7.2 Attainment of chemical equilibrium

Eventually, the two reactions occur at the same rate and the system reaches a state of equilibrium. Similarly, the reaction can reach the state of equilibrium even if we start with only C and D; that is, no A and B being present initially, as the equilibrium can be reached from either direction.

The dynamic nature of chemical equilibrium can be demonstrated in the synthesis of ammonia by Haber's process. In a series of experiments, Haber started with known amounts of nitrogen and hydrogen maintained at high temperature and pressure and at regular intervals determined the amount of ammonia present. He was successful in determining also the concentration of unreacted dihydrogen and dinitrogen. Fig. 7.3 shows that after a certain time the composition of the mixture remains the same even though some of the reactants are still present. This constancy in composition indicates that the reaction has reached equilibrium. In order to understand the dynamic nature of the reaction synthesis of ammonia is carried out with exactly the same starting conditions (of partial pressureand temperature) but using D_2 (deuterium) in place of H_2. The reactionmixtures starting either with H_2or D_2reach equilibrium with the same composition, except that $D_2$and ND_3 are present instead of $H_2$and NH_3. After equilibrium is attained, these two mixtures (H_2, N_2, NH_3 and D_2, N2, ND3) are mixed together and left for a while. Later, when this mixture is analyzed,it is found that the concentration of ammonia isjust the same as before. However, when this mixture is analyzed by a mass spectrometer, it is found that ammonia and all deuterium containing forms of ammonia (NH_3, NH_2D, NHD_2 and ND_3) and hydrogen and its deutrated forms(H_2 , HD and D_2) are present. Thus one can conclude that scrambling of H and D atoms in the molecules must result from a continuation of the forward and reverse reactions in the mixture. If the reaction had simply stopped when they reached equilibrium, then there would have been no mixing of isotopes in this way.

Use of isotope (deuterium) in the formation of ammonia clearly indicates that chemical reactions reach a state of dynamic equilibrium in which the rates of forward and reverse reactions are equal and there is no net change in composition.

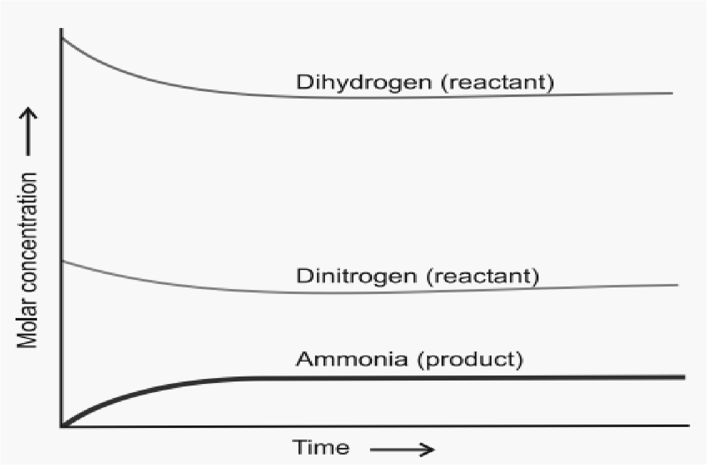


Fig 7.3 Depiction of equilibrium for the reaction $N_2\ g\ +3\,H_2\ g\ \rightleftarrows 2\,NH_3\ g$

Equilibrium can be attained from both sides, whether we start reaction by taking, H_2(g) and N_2(g) and get NH_3(g) or by taking NH_3(g) and decomposing it into N_2(g) and H_2(g).

$$N_2\ g\ +3\,H_2\ g\ \rightleftarrows 2\,NH_3\ g$$

$$H_2\ g\ +I_2\ g\ \rightleftarrows 2HI\ g$$

Similarly let us consider the reaction, $H_2\ g\ +I_2\ g\ \rightleftarrows 2HI\ g$. If we start with equal initial concentration of H_2 and I_2, the reaction proceeds in the forward direction and the concentration of H_2 and I_2 decreases while that of HI increases, until all of these become constant at equilibrium (Fig. 7.4). We can also start with HI alone and make the reaction to proceed in the reverse direction; the concentration of HI will decrease and concentration of H_2 and I_2 will increase until they all become constant when equilibrium is reached (Fig.7.4). If total number of H and I atoms are same in a given volume, the same equilibrium mixture is obtained whether we start it from pure reactants or pure product.

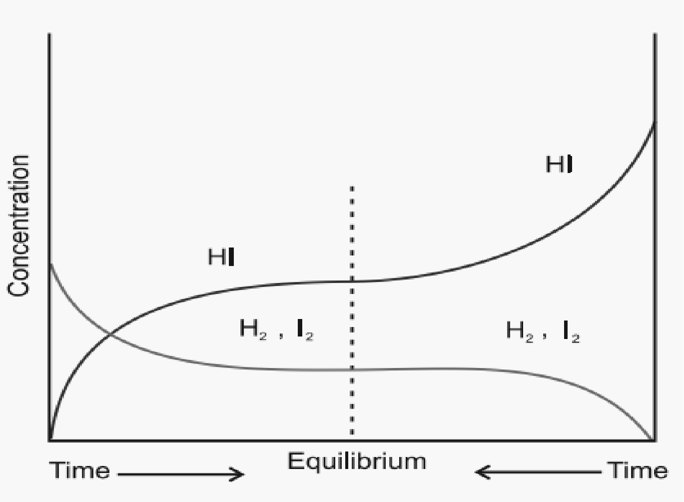


Fig 7.4 Depiction of equilibrium for the reaction $H_2\ g\ +I_2\ g\ \rightleftarrows 2HI\ g$

7.3 Law of Chemical Equilibrium and Equilibrium Constant

A mixture of reactants and products in the equilibrium state is called an equilibrium mixture. In this section we shall address a number of important questions about the composition of equilibrium mixtures: What is the relationship between the concentrations of reactants and products in an equilibrium mixture? How can we determine equilibrium concentrations from initial concentrations?What factors can be exploited to alter the composition of an equilibriu1n mixture? The last question in particular is important when choosing conditions for synthesis of industrial chemicals such as H_2, NH_3, CaO etc.

To answer these questions, let us considera general reversible reaction:

$$A + B \rightleftarrows C + D$$

Where A and B are the reactants, C and D are the products in the balanced chemical equation. On the basis of experimental studies of many reversible reactions, the Norwegian chemists Cato Maximillian Guldberg and Peter Waage proposed in 1864 that the concentrations in an equilibrium mixture are related by the following equilibrium equation,

$$K_c = \frac{[C][D]}{[A][B]} \qquad (7.1)$$

Where K_c is the equilibrium constant and the expression on the right side is called the equilibrium constant express ion.

The equilibrium equation is also known as the law of mass action because in the early days of chemistry, concentration was called "active mass". In order to appreciate their work better, let us consider reaction betweengaseous H_2 and I_2 carried out in a sealed vessel at 731K.

$$H_2\ (g) + I_2(g) \rightleftarrows 2\,HI(g)$$

Six sets of experiments with varying initial conditions were performed, starting with only gaseous H_2 and I_2 in a sealed reaction vessel in first four experiments (1, 2, 3 and 4) and only HI in other two experiments (5 and 6).Experiment 1, 2, 3 and 4 were performed taking different concentrations of H_2 and/or 1_2, and with time it was observed that intensity of the purple colour remained constant and equilibrium was attained. Similarly, for experiments 5 and 6, the equilibrium was attained from the opposite direction.

Data obtained from all six sets of experiments are given in Table 7.2. It is evident from the experiments 1, 2, 3and 4 that number of moles of hydrogen reacted = number of moles of iodine reacted =1/2 (number of moles of HI formed). Also, experiments 5 and 6 indicate that,

$$H_2(g)\ _{eq} = I_2(g)\ _{eq}$$

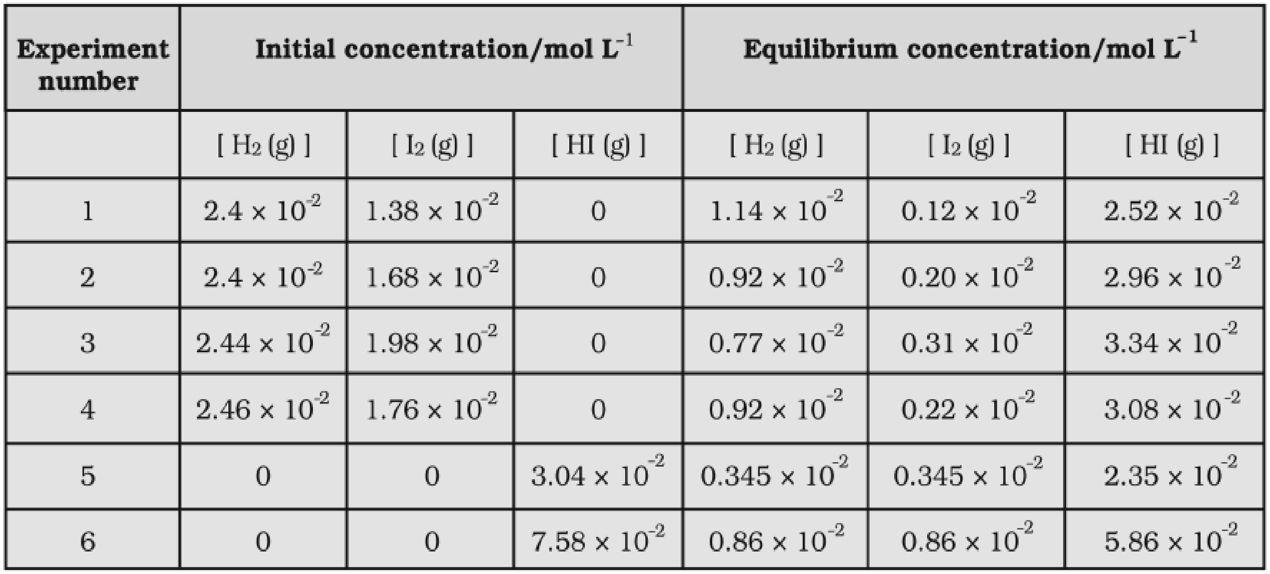
Knowing the above facts, in order to establish a relationship between concentrations of the reactants and products, several combinations can be tried. Let us consider the simple expression,

$$\frac{HI(g)\ _{eq}}{H_2(g)\ _{eq}\ I_2(g)\ _{eq}}$$

It can be seen fro1n Table 7.3 that if we put the equilibrium concentrations of the reactants and products. The above expression is far from constant. However, if we consider the expression

$$\frac{\mathrm{HI(g)}\ {}_{eq}^{2}}{\mathrm{H_2(g)}\ {}_{eq}\ \ \mathrm{I_2(g)}\ {}_{eq}}$$

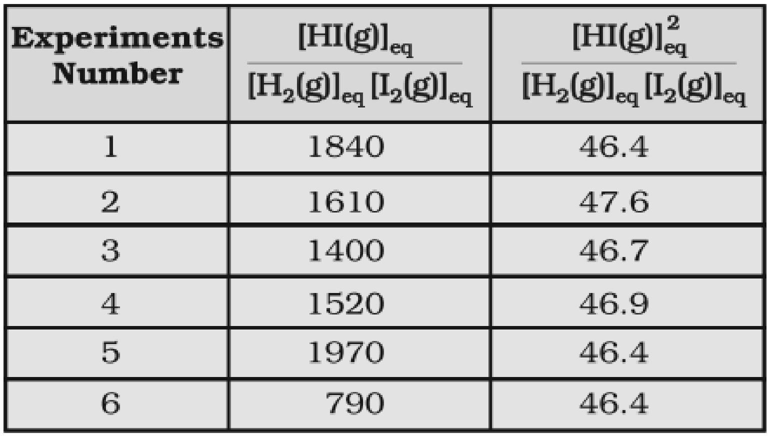
Table 7.2 Initial and equilibrium concentrations of H_2, I_2 and HI



Experiment number	Initial concentration/mol L^{-1}			Equilibrium concentration/mol L^{-1}		
	[H_2 (g)]	[I_2 (g)]	[HI (g)]	[H_2 (g)]	[I_2 (g)]	[HI (g)]
1	2.4×10^{-2}	1.38×10^{-2}	0	1.14×10^{-2}	0.12×10^{-2}	2.52×10^{-2}
2	2.4×10^{-2}	1.68×10^{-2}	0	0.92×10^{-2}	0.20×10^{-2}	2.96×10^{-2}
3	2.44×10^{-2}	1.98×10^{-2}	0	0.77×10^{-2}	0.31×10^{-2}	3.34×10^{-2}
4	2.46×10^{-2}	1.76×10^{-2}	0	0.92×10^{-2}	0.22×10^{-2}	3.08×10^{-2}
5	0	0	3.04×10^{-2}	0.345×10^{-2}	0.345×10^{-2}	2.35×10^{-2}
6	0	0	7.58×10^{-2}	0.86×10^{-2}	0.86×10^{-2}	5.86×10^{-2}

Table 7.3 Expression involving the equilibrium concentration of reactants

$$\mathrm{H_2\ \ g\ +I_2\ \ g} \rightleftharpoons \mathrm{2HI\ \ g}$$



Experiments Number	$\frac{[HI(g)]_{eq}}{[H_2(g)]_{eq}\,[I_2(g)]_{eq}}$	$\frac{[HI(g)]_{eq}^{2}}{[H_2(g)]_{eq}\,[I_2(g)]_{eq}}$
1	1840	46.4
2	1610	47.6
3	1400	46.7
4	1520	46.9
5	1970	46.4
6	790	46.4

We find that this expression gives constant value (as shown in Table 7.3) in all the six cases. It can be seen that in this expression the power of the concentration for reactants and products are actually the stoichiometric coefficients in the equation for the chemical reaction. Thus, for the reaction $H_2\ (g) + I_2(g) \rightleftharpoons 2\ HI(g)$, following equation 7.1, the equilibrium constant K_c is written as,

$$K_c = \frac{HI(g)\ ^{2}_{eq}}{H_2(g)\ _{eq}\ \ I_2(g)\ _{eq}} \qquad (7.2)$$

Generally the subscript 'eq' (used for equilibrium) is omitted from the concentration terms. It is taken for granted that the concentrations in the expression for K_c are equilibrium values. We, therefore, write,

$$K_c = \frac{HI(g)\ ^{2}}{H_2(g)\ \ I_2(g)} \qquad (7.3)$$

The subscript 'c' indicates that K_c is expressed in concentrations of mol L^{-1}.

At a given temperature, the product of concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value. This is known as the Equilibrium Law or Law of Chemical Equilibrium.

The equilibrium constant for a general reaction

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D$$ Is expressed as

$$K_c = \frac{C\ ^{c}\ \ D\ ^{d}}{A\ ^{a}\ \ B\ ^{b}} \qquad (7.4)$$

Where [A], [B], [C] and [D] are equilibrium concentrations of the reactants and products.

Equilibrium constant for the reaction,

$$4\,NH_3(g) + 5\,O_2(g) \rightleftharpoons 4\,NO(g) + 6\,H_2O(g)$$

$$K_c = \ NO\ ^{4}\ \ H_2O\ ^{6}\ /\ \ NH_3\ ^{4}\ \ O_2\ ^{5}$$

Molar concentration of different species isindicated by enclosing these in square bracket and, as mentioned above, it is implied that these are equilibrium concentrations. While writing expression for equilibrium constant, symbol for phases (s, 1, g) are generally ignored.

Let us write equilibrium constant for the reaction,

$$H_2\ \ g\ +I_2\ \ g \rightleftharpoons 2HI\ \ g \qquad (7.5)$$

$$K_c = \ HI\ ^{2}\ /\ \ H_2\ \ \ I_2\ \ = x \qquad (7.6)$$

The equilibrium constant for the reversereaction, $2HI\ \ g \rightleftharpoons H_2\ \ g\ +l_2\ \ g$, at the same temperatureis,

$$K'_c = \ H_2\ \ \ I_2\ \ /\ \ HI\ ^{2} = 1/x = 1/K_c \qquad (7.7)$$

Thus, $K'_c = 1/K_c$ (7.8)

Equilibrium constant for the reverse reaction is the inverse of the equilibrium constant for the reaction in the forward direction. If we change the stoichiometric coefficients in achemical equation by multiplying throughout by a factor then we must make sure that the expression for equilibrium constant also reflects that change. For example, if the reaction (7.5) is written as,

$$1/2\ H_2\ \ g\ + 1/2\ I_2\ \ g \rightleftarrows HI\ \ g \qquad (7.9)$$

The equilibrium constant for the above reaction is given by

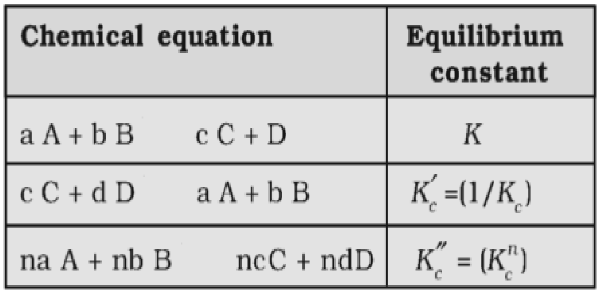
$$K_c'' = HI\ /\ H_2^{\ 1/2}\ I_2^{\ 1/2} = x^{1/2} = K_c^{\ 1/2} \qquad (7.10)$$

On multiplying the equation (7.5) by n. we get

$$n\ H_2\ \ g\ + n\ I_2\ \ g \rightleftarrows 2n\ HI\ \ g \qquad (7.11)$$

Therefore, equilibrium constant for the reaction is equal to $K_c^{\ n}$. These findings are summarised in Table 7.4. It should be noted that because the equilibrium constants K_c and K'_c have different numerical values, it is important to specify the form of the balanced chemical equation when quoting the value of an equilibrium constant.

Table 7.4 Relations between equilibrium constants for a general reaction and its multiples



Chemical equation	Equilibrium constant
a A + b B c C + D	K
c C + d D a A + b B	$K_c' = (1/K_c)$
na A + nb B ncC + ndD	$K_c'' = (K_c^n)$

7.4 Homogeneous Equilibria

In a homogeneous system, all the reactants and products are in the same phase. For example, in the gaseous reaction, $N_2\ (g) + 3\ H_2(g) \rightleftarrows 2\ NH_3(g)$ reactants and products are in the homogeneous phase. Similarly, for the reaction, $CH_3COOC_2H_5\ (aq) + H_2O(l) \rightleftarrows CH_3COOH\ (aq) + C_2H_5OH\ (aq)$ all the reactants and products are in homogeneous solution phase. We shall now consider equilibrium constant for some homogeneous reactions.

7.4.1 Equilibrium Constant in Gaseous Systems

So far we have expressed equilibrium constant of the reactions in term s of molar concentration of the reactants and products, and used symbol, K_c for it. For reactions involving gases, however, it is usually more convenient to express the equilibrium constant in terms of partial pressure.

The ideal gas equation is written as,

$$pV = nRT \Rightarrow p = \frac{n}{V} RT$$

Here, p is the pressure in Pa, n is the number of moles of the gas, V is the volume in m^3 and T is the temperature in Kelvin

Therefore, n/ V is concentration expressed in mol/ m^3. If concentration c, is in mol/L or mol/ dm.^{3}, and p is in bar then, $p = cRT$. We can also write p = [gas]RT. Here, R= 0.0831bar litre/mol K

At constant temperature, the pressure of the gas is proportional to its concentration i.e., $p \propto$ gas

For reaction in equilibrium $H_2\ \ g\ \ +I_2\ \ g \rightleftarrows 2HI\ \ g$

We can write either $K_c = \frac{HI(g)^{\ 2}}{H_2(g)\ \ I_2(g)}$

$$\text{Or}\ \ K_c = \frac{p_{HI}^{\ \ 2}}{p_{H_2}\ \ p_{I_2}} \qquad (7.12)$$

Further, since $p_{HI} =\ HI(g)\ \ RT$, $p_{H_2} =\ H_2(g)\ \ RT$ and $p_{I_2} =\ I_2(g)\ \ RT$

$$\text{Therefore,}\ K_p = \frac{p_{HI}^{\ \ 2}}{p_{H_2}\ \ p_{I_2}} = \frac{HI(g)^{\ 2}[RT]^2}{H_2(g)\ RT.\ I_2(g)\ \ RT} = \frac{HI(g)^{\ 2}}{H_2(g)\ \ I_2(g)} = K_c \qquad (7.13)$$

In this example, $K_p = K_c$ i.e., both equilibrium constants are equal. However, this is not always the case.

For example in reaction $N_2\ \ g\ \ + 3\ H_2\ \ g \rightleftarrows 2\ NH_3\ \ g$

$$K_p = \frac{p_{NH_3}^{\ \ 2}}{p_{N_2}\ \ p_{H_2}^{\ \ 3}} = \frac{NH_3(g)^{\ 2}[RT]^2}{N_2(g)\ RT.\ H_2(g)^{\ 3}[RT]^3} = \frac{NH_3(g)^{\ 2}[RT]^{-2}}{N_2(g)\ \ H_2(g)^{\ 3}} = K_c\ \ RT^{\ -2}$$

$$\text{Or}\ \ K_p = K_c\ \ RT^{\ -2} \qquad (7.14)$$

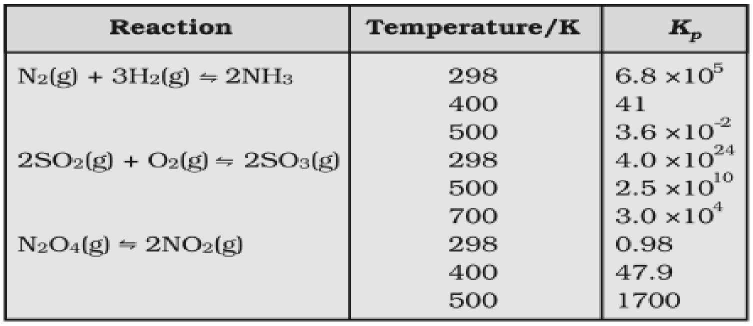
Similarly, for a general reaction $a\,A + b\,B \rightleftarrows c\,C + d\,D$

$$K_p = \frac{p_C^{\ c}\ \ p_D^{\ d}}{p_A^{\ a}\ \ p_B^{\ b}} = \frac{C^{\ c}\ \ D^{\ d}[RT]^{c+d}}{A^{\ a}\ \ B^{\ b}[RT]^{a+b}} = \frac{C^{\ c}\ \ D^{\ d}}{A^{\ a}\ \ B^{\ b}}[RT]^{(c+d)-(a+b)} = K_c\ \ RT^{\ \Delta n} \qquad (7.15)$$

Where Δn = (number of moles of gaseous products) - (number of moles of gaseousreactants) in the balanced chemical equation.

(It is necessary that while calculating the value of $K_P$pressure should be expressed in bar as standard state is 1bar). K_P values for a few selected reactions at different temperatures are given in Table 7.5

Table 7.5 Equilibrium constants K_p for a few selected reactions



Reaction	Temperature/K	K_p
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3$	298	6.8×10^5
	400	41
	500	3.6×10^{-2}
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$	298	4.0×10^{24}
	500	2.5×10^{10}
	700	3.0×10^4
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$	298	0.98
	400	47.9
	500	1700

7.5 Heterogeneous Equilibria

Equilibrium in a system having more than one phase is called heterogeneous equilibrium. The equilibrium between water vapour and liquid water in a closed container is an example of heterogeneous equilibrium.

$$H_2O(liq) \rightleftharpoons H_2O(vap)$$

In this example, there is a gas phase and a liquid phase. In the same way, equilibrium between a solid and its saturated solution is a heterogeneous equilibrium.

$$\mathrm{Ca\ \ OH\ _2\ s\ +\ aq} \rightleftharpoons \mathrm{Ca^{2+}\ \ aq\ \ + 2\,OH^-\ \ aq}$$

Heterogeneous equilibria often involve pure solids or liquids. We can simplify equilibrium expressions for the heterogeneous equilibria involving a pure liquid or a pure solid, as the molar concentration of a pure solid or liquid is constant (i.e., independent of the amount present). In other words if a substance 'X' is involved, then [X(s)] and [X(l)] are constant, whatever the amount of 'X' is taken. Contrary to this, [X(g)] and [X(aq)] will vary as the amount of X in a given volume varies. Let us take thermal dissociation of calcium carbonate which is an interesting and important example of heterogeneous chemical equilibrium.

$$\mathrm{CaCO_3\ \ s} \overset{\Delta}{\rightleftharpoons} \mathrm{CaO\ \ s\ \ + CO_2}\ \ g \qquad (7.16)$$

On the basis of the stoichiometric equation, we can write,

$$K_c = \frac{\left[\mathrm{CaO\ \ s}\right]\left[\mathrm{CO_2}\ \ g\right]}{\left[\mathrm{CaCO_3\ \ s}\right]}$$

Since $\mathrm{CaCO_3\ \ s}$ and $\mathrm{CaO\ \ s}$ are both constant, therefore modified equilibrium constant for the thermal decomposition ofcalcium carbonate will be

$$K_c = \left[\mathrm{CO_2}\ \ g\ \right] \qquad (7.17)$$

$$\mathrm{Or}\ K_p = p_{CO_2} \qquad (7.18)$$

This shows that at a particular temperature, there is a constant concentration or pressure of CO_2in equilibrium with CaO(s) and $CaCO_3$(s). Experimentally it has been found that at 1100 K, the pressure of CO_2 in equilibrium with$CaCO_3$(s)andCaO(s), is 2.0 x 10^5 Pa. Therefore, equilibrium constant at 1100 K for the above reaction is:

$$K_p = p_{CO_2} = 2.0 \times 10^5\ \mathrm{Pa}/10^5\ \mathrm{Pa} = 2.00$$

7.6 Factors Affecting Equilibria

One of the principal goals of chemical synthesis is to maximize the conversion of the reactants to products while minimizing the expenditure of energy. This implies maximum yield of products at mild temperature and pressure conditions. If it does not happen, then the experimental conditions need to be adjusted. For example, in the Haber process for the synthesis of ammonia from N_2 and H_2, the choice of experimental conditions is of real economic importance. Annual world production of ammonia is about hundred million tones, primarily for use as fertilizers.

Equilibrium constant, K_c is independent of initial concentrations. But if a system at equilibrium is subjected to a change in the concentration of one or more of the reacting substances, then the system is no longer at equilibrium; and net reaction takes place in some direction until the system returns to equilibrium once again. Similarly, a change in temperature or pressure of the system may also alter the equilibrium. In order to decide what course the reaction adopts and make a qualitative prediction about the effect of a change in conditions on equilibrium we use Le Chatelier's principle. It states that *a change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to reduce or to counteract the effect of the change*. This is applicable to all physical and chemical equilibria.

We shall now be discussing factors which can influence the equilibrium.

7.6.1 Effect of Concentration Change

In general, when equilibrium is disturbed by the addition / removal of any reactant / products, Le Chatelier's principle predicts that:

- The concentration stress of an added reactant/ product is relieved by net reaction in the direction that consumes the added substance.
- The concentration stress of a removed reactant/product is relieved by net reaction in the direction that replenishes the removed substance.or in other words,

"*When the concentration of any of the reactants or products in a reaction at equilibrium is changed, the composition of the equilibrium mixture changes so as to minimize the effect of concentration changes* ".

Let us take the reaction,

$$H_2\ \ g\ +I_2\ \ g \ \rightleftharpoons\ 2HI\ \ g$$

If $H_2$is added to the reaction mixture at equilibrium, then the equilibrium of the reaction is disturbed. In order to restore it, thereaction proceeds in a direction wherein H is consumed, i.e., more of H_2 and 1_2 react to form HI and finally the equilibrium shifts in right (forward) direction (Fig.7.5). This is in accordance with the Le Chatelier's principle which implies that in case of addition of a reactant /product, a new equilibrium will be set up in which the concentration of the reactant/product should be less than what it was after the addition but more than what it was in the original mixture.
The same point can be explained in terms of the reaction quotient, Q_c,

$$Q_c = \ HI\ ^2 \ /\ \ H_2\ \ \ I_2$$

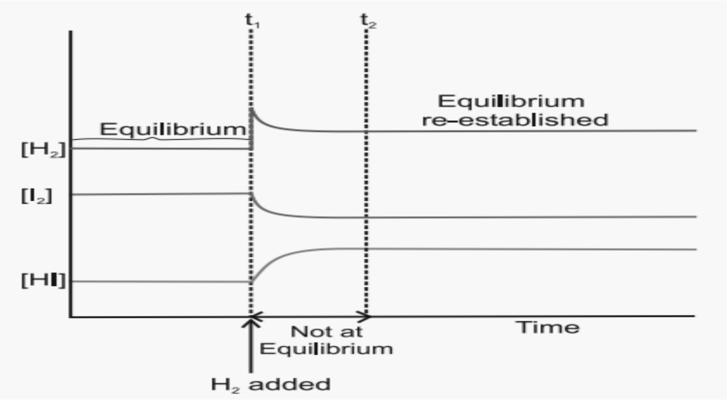


Fig.7.5 Effect of addition of H_2 on change of concentration for the reactants and products in the reaction

$$H_2\ g + I_2\ g \rightleftharpoons 2HI\ g$$

The same point can be explained in terms of the reaction quotient

$$Q_c = [HI]^2/[H_2][I_2]$$

Addition of hydrogen at equilibrium results in value of Q_c being less than K_c.Thus, in order to attain equilibrium again reaction moves in the forward direction. Similarly, we can say that removal of a product also boosts the forward reaction and increases the concentration of the products and this has great commercial application in cases ofreactions, where the product is a gas or avolatile substance. In case of manufacture of ammonia, ammonia is liquified and removed from the reaction mixture so that reaction keeps moving in forward direction. Similarly, in the large scale production of CaO (used as important building material) from $CaCO_3$, constant removal of $CO_2$from the kiln drives the reaction to completion. It should be remembered that continuous removal of a product maintains Q_c at a value less than K_c and reaction continues to move in the forward direction.

7.6.2 Effect of Pressure Change

A pressure change obtained by changing the volume can affect the yield of products in case of a gaseous reaction where the total numberof moles of gaseous reactants and total number of moles of gaseous products are different. In applying Le Chatelier's principle to a heterogeneous equilibrium the effect of pressure changes on solids and liquids can be ignored because the volume (and concentration) of a solution/ liquid is nearlyindependent of pressure.

Consider the reaction,

$$CO\ g + 3\,H_2\ g \rightleftharpoons CH_4\ g + H_2O\ g$$

Here, 4 mol of gaseous reactants ($CO + 3H_2$) become 2 mol of gaseous products ($CH_4 + H_2O$). Suppose equilibrium mixture (for above reaction) kept in a cylinder fitted with a piston at constant temperature is compressed to one half of its original volume. Then, total pressure will be doubled (according to pV = constant). The partial pressure and therefore, concentration of reactants and products have changed and the mixture is no longer at equilibrium. The direction in which the reaction goes to re-establish equilibrium can be predicted by applying the Le Chatelier's principle. Since pressure has doubled, the equilibrium now shifts in the forward direction, a direction in which the number of moles of the gas or pressure decreases (we know pressure is proportional to moles of the gas) . This can also be understood by using reaction quotient, Qc. Let [CO], $[H_2]$,$[CH_4]$ and $[H_2O]$ be the molar concentrations at equilibrium for methanation reaction. When volume of the reaction mixture is halved, the partial pressure and the concentration are doubled. We obtain the reaction quotient by replacing each equilibrium concentration by double its value.

$$Q_c = \frac{[CH_4\ g][H_2O\ g]}{[CO\ g][H_2\ g]^3}$$

As $Q_c < K_c$, the reaction proceeds in the forward direction.

In reaction $C\ s + CO_2\ g \rightleftharpoons 2CO\ g$, when pressure is increased, the reaction goes in the reverse direction because the number of moles of gas increases in the forward direction.

7.6.3 Effect of Inert Gas Addition

If the volume is kept constant and an inert gas such as argon is added which does not take part in the reaction, the equilibrium remains undisturbed. It is because the addition of an inert gas at constant volume does not change the partial pressures or the molar concentrations of the substance involved in the reaction. The reaction quotient changes only if the added gas is a reactant or product involved in the reaction.

7.6.4 Effect of Temperature Change

Whenever equilibrium is disturbed by a change in the concentration, pressure or volume, the composition of the equilibrium mixture changes because the reaction quotient, Q_c no longer equals the equilibrium constant, K_c. However, when a change in temperature occurs, the value of equilibrium constant, K_c is changed. In general, the temperature dependence of the equilibrium constant depends on the sign of ΔH for the reaction.

- The equilibrium constant for an exothermic reaction (negative ΔH) decreases as the temperature increases.
- The equilibrium constant for an endothermic reaction (positive ΔH)increases as the temperature increases. Temperature changesaffect the equilibrium constant and rates of reactions. Production of ammonia according to the reaction,

$$N_2\ g\ + 3\,H_2\ g\ \rightleftharpoons 2\,NH_3\ g \qquad \Delta H = -92.38\ kJ$$

Is an exothermic process. According to Le Chatelier's principle, raising the temperature shifts the equilibrium to left and decreases the equilibrium concentration of ammonia. In other words, low temperature is favorable for high yield of ammonia, but practically very low te1nperatures slow down the reaction and thus a catalyst is used.

7.6.5 Effect of a Catalyst

A catalyst increases the rate of the chemical reaction by making available a new low energy pathway for the conversion of reactants to products. It increases the rate of forward and reverse reactions that pass through the same transition state and does not affect equilibrium. Catalyst lowers the activation energy for the forward and reverse reactions by exactly the same amount. Catalyst does not affect the equilibrium composition of a reaction mixture. It does not appear in the balanced chemical equation or in the equilibrium constant expression.

Let us consider the formation of NH_3 from nitrogen and hydrogen which is highly exothermic reaction and proceeds with decrease in total number of moles formed as compared to the reactants. Equilibrium constant decreases with increase in temperature. At low temperature rate decreases and it takes long time to reach at equilibrium, whereas high temperatures give satisfactory rates but poor yields.

German chemist, Fritz Haber discovered that a catalyst consisting of iron catalyse the reaction to occur at a satisfactory rate at temperatures, where the equilibrium concentration of NH_3 is reasonably favorable. Since the number of moles formed in thereaction is less than those of reactants, the yield of NH_3 can be improved by increasing the pressure.

Optimum conditions of temperature andpressure for the synthesis of NH_3 using catalyst are around 500 ^{0}C and 200 atm.

7.6.6 Applicationof Le Chatlier principle for industrial synthesis

7.6.6.1 Industrial Synthesis of ammonia by Haber's process:

The Haber process is used in the manufacturing of ammonia from nitrogen and hydrogen.

$$N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H=-92.2 \text{ kJ mol}^{-1}$$

For this reversible reaction at equilibrium state at a given temperature

$$K_c = \frac{NH_3{}^{2}}{N_2 \quad H_2{}^{3}} = 3.6 \text{ x}10^5 \quad \text{at } 25^0\text{C}$$

Large value of K_c at low temperature indicates that, all of N_2 and H_2 have to be converted to ammonia. However, the thermodynamic factor K_c does not tell how fast the reaction can occur.

According to the Le Chatlier's principle the forward reaction is favourable for the formation of ammonia at low temperatures since the forward is exothermic. But, at low temperatures, the reactions occur slowly that no measurable amount of ammonia is produced within a reasonable time and attains equilibrium very slowly. Though attempts to increase the rate of reaction by increasing the temperature are counterproductive still some optimum temperature is maintained to increase the reaction rate.

A catalyst may also be used to increase the rate of reaction even at relatively low temperatures. Catalyst used in this process is Fe with Mo as promoter.

There are four moles on the left side of the equation whereas there are only two moles on the right side. It is to say that forward reaction involves a decrease in volume. So, increase in pressure favours the production of ammonia. Hence, Haber's process is carried out at high pressure. The optimum pressure used is 200-500 atm.

The optimum conditions are:

Pressure: 200-500 atm

Temperature: 725-775 K

Catalyst: Fe

Promoter: Mo

7.6.6.2 Industrial Synthesis of SO_3:

The equilibrium chemical equation underlying the synthesis of SO_3 is represented by:

$$2\ SO_2(g)+ O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H= -189 \text{ kJ mol}^{-1}$$

$$K_c = \frac{SO_3{}^{2}}{SO_2{}^{2} \quad O_2} = 1.7 \text{ x}10^{26} \quad \text{at } 25^0\text{C}$$

Large value of K_c at low temperature indicates that the reaction should go to completion. But oxidation of SO_2 to SO_3 is a slow process and it does not give significant amount of SO_3 even after keeping the reactants in contact for a long time.

Though the reaction is exothermic and is favored at low temperature an optimum temperature of 450-500 ^{0}C is maintained to increase the rate of formation of SO_3.

To increase the reaction rate, a catalyst such as platinized asbestos or V_2O_5 is used.

Since the reaction proceeds in the forward direction with decrease in volume i.e., 3 volumes of reactants give 2 volumes of products, a high pressure favors the formation of SO_3. But high pressure leads to the corrosion of reaction chamber. Therefore optimum pressures are used.

The optimum conditions are:Pressure: 1-2 atm., Temperature: 673 K to 723 K and Catalyst: V_2O_5

7.7Acids, Bases and Salts

Acids, bases and salts find widespread occurrence in nature. Hydrochloric acid present in the gastric juice is secreted by the lining of our stomach in a significant amount of 1.2- 1.5 L/ day and is essential for digestive processes.Acetic acid is known to be the main constituent of vinegar. Lemon and orange juices contain citric and ascorbic acids and tartaric acid is found in tamarind paste. As most of the acids taste sour, the word "acid" has been derived from a latin word "acidus" meaning sour. Acids are known to turn blue litmus paper into red and liberate hydrogen on reacting with metals. Similarly, bases are known to turn red litmus paper blue, taste bitter and feel soapy. A common example of a base is washing soda used for washing purposes. When acids and bases are mixed in the right proportion they react with each other to give salts. Some commonly known examples of salts are sodium chloride, barium sulphate, and sodium nitrate. Sodium chloride (common salt) is an important component of our diet and is formed by reaction between hydrochloric acid and sodium hydroxide. It exists in solid state as a cluster of positively charged sodium ions and negatively charged chloride ions which are held together due to electrostatic interactions between oppositely charged species (Fig.7.6). The electrostatic forces between two charges are inversely proportional to dielectric constant of the medium. Water, a universal solvent, possesses a very high dielectric constant of 80. Thus, when sodium chloride is dissolved in water, the electrostatic interactions are reduced by a factor of 80 and this facilitates the ions to move freely in the solution. Also, they are well- separated due to hydration with water molecules.

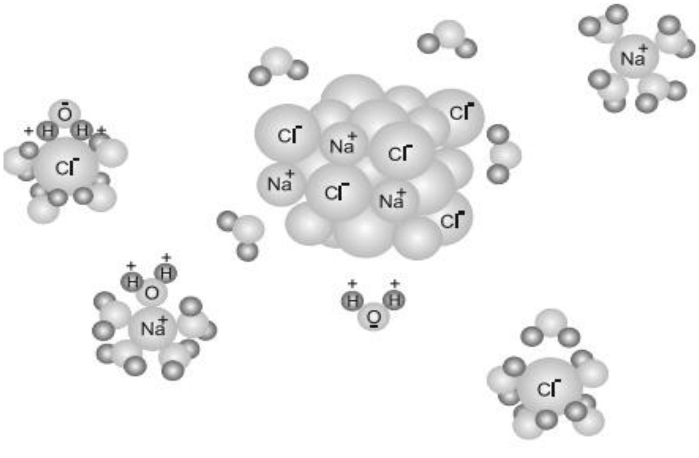


Fig. 7.6 Dissolution of sodium chloride in water

Comparing, the ionization of hydrochloric acid with that of acetic acid in water we find that though both of them are polar covalent molecules, former is co1npletely ionized into its constituent ions, while the latter is only partially ionized (< 5%) . The extent to which ionization occurs depends upon the strength of the bond and the extent of salvation of ions produced. The terms dissociation and ionization have earlier been used with different meaning. Dissociation refers to the process of separation of ions in water already existing as such in the solid state of the solute, as in sodium chloride. On the other hand, ionizationcorresponds to a process in which a neutral molecule splits into charged ions in the between the two anduse the two terms interchangeably.

7.7.1 Arrhenius Concept of Acids and Bases

According to Arrhenius theory, acids are substances that dissociates in water to give hydrogen ions H^+(aq)and bases are and bases are substances that produce hydroxyl ions OH^- (aq). The ionization of an acid HX (aq) canbe represented by the following equations:

$$HX\ \ aq \ \rightarrow H^+\ aq\ + x^-\ aq\ \text{ Or}$$

$$HX\ \ aq\ + H_2O(l) \rightarrow H_3O^+\ aq\ + x^-\ aq$$

A bare proton, H^+ is very reactive and cannot exist freely in aqueous solutions. Thus, it bonds to the oxygen atom of a solvent water molecule to give trigonal pyramidal hydronium ion, H_3O^+ . In this chapter we shall use H^+(aq) and H_3O^+(aq) interchangeably to mean the same i.e., a hydrated proton.

Similarly, a base molecule like MOH ionizes in aqueous solution according to the equation:

$$MOH\ aq \ \rightarrow M^+\ aq\ + OH^-\ aq$$

The hydroxyl ion also exists inthe hydrated form in the aqueous solution. Arrhenius concept of acid and base, however, suffers from the limitation of being applicable only to aqueous solutions and also, does not account for the basicity of substances like, ammonia which do not possess a hydroxyl group.

7.7.2 The Bronsted-Lowry Acids and Bases

The Danish chemist, Johannes Bronsted and the English chemist, Thomas M. Lowry gave a more general definition of acids and bases.According to Bronsted-Lowry theory, acid is a substance that is capable of donating a hydrogen ion H^+ and bases are substances capable of accepting a hydrogen ion, H^+. In short, acids are proton donors and bases are proton acceptors.

Consider the example of dissolution of NH_3 in H_2O represented by the following equation:

The basic solution is formed due to the presence of hydroxyl ions. In this reaction, water molecule acts as proton donor and ammonia molecule acts as proton acceptor and are thus, called Lowry-Bronsted acid and base, respectively. In the reverse reaction, H^+ is transferred from NH_4^+ to OH^-. In this case, NH_4^+ acts as a Bronsted acid while OH^- acted as a Bronsted base. The acid-base pair that differs only by one proton is called a conjugateacid-base pair. Therefore, OH^- is called the conjugate base of an acid H_2O and NH_4^+ is called conjugate acid of the base NH_3. If Bronsted acid is a strong acid then its conjugate base is a weak base and vice- versa. It may be noted that conjugate acid has one extra proton and each conjugate base has one less proton.

Consider the example of ionization of hydrochloric acid in water. HCl(aq) acts as an acid by donating a proton to H_2O which acts as a base.

It can be seen in the above equation, that water acts as a base because it accepts the proton. The species H_3O^+ is produced when water accepts a proton from HCl. Therefore, Cl^- is a conjugate base of HCl and HCl is the conjugate acid of base Cl^-. Similarly, H_2O is a conjugate base of an acid H_3O^+ and H_3O^+ is a conjugate acid of base H_2O.

It is interesting to observe the dual role of water as an acid and a base. In case of reaction with HCl water acts as a base while in case of ammonia it acts as an acid by donating a proton.

7.7.3 Lewis Acids and Bases

G.N. Lewis in 1923 defined an acid as a species which accepts electron pair and base which donates an electron pair. As far as bases are concerned, there is not much difference between Bronsted-Lowry and Lewis concepts, as the base provides a lone pair in both the cases. However, in Lewis concept many acids do not have proton. A typical example is reaction of electron deficient speciesBF_3. with NH_3

BF_3does not have a proton but still acts as an acid and reacts with $NH_3$by accepting its lone pair of electrons. The reaction can be represented by,

$$BF_3 + :NH_3 \rightarrow BF_3:NH_3$$

Electron deficient species like $A1Cl_3$, $Co^{3+,}$, Mg^{2+}, etc. can act as Lewis acids while species like H_2O, NH_3, OH^- etc. which can donate a pair of electrons, can act as Lewis bases.

7.8 Ionization of Acids and Bases

Arrhenius concept of acids and bases becomes useful in case of ionization of acids and bases as mostly ionizations in chemical and biological systems occur in aqueous medium. Strong acids like perchloric acid ($HClO_4$), hydrochloric acid (HCl), hydrobromic acid (HBr), hyrdoiodic acid (HI), nitric acid (HNO_3) and sulphuric acid (H_2SO_4) are termed strong because they are almost completely dissociated into their constituent ions in an aqueous medium, thereby acting as proton (H^+) donors. Similarly, strong bases like lithium hydroxide (LiOH), sodium hydroxide (NaOH), potassium hydroxide (KOH), caesium hydroxide (CsOH) and barium hydroxide $Ba(OH)_2$ are almost completely dissociated into ions in an aqueous medium giving hydroxyl ions (OH^-). According to Arrhenius concept they are strong acids and bases as they are able to completely dissociate and produce H^+ and OH^-ions respectively in the medium. Alternatively, the strength of an acid or basemay also be gauged in terms of Bronsted-Lowiy concept of acids and bases, wherein a strong acid means a good proton donor and a strong base implies a good proton acceptor. Consider the acid-base dissociation equilibrium of a weak acid HA.

$$HA\ \ aq\ + H_2O(l) \rightleftarrows H_3O^+\ \ aq\ + A^-\ \ aq$$

acid	base	conjugate acid	conjugate base

We saw that acid (or base) dissociation equilibrium is dynamic involving a transfer of proton in forward and reverse directions. Now, the question arises that if the equilibrium is dynamic then with passage of time which direction is favoured? What is the driving force behind it? In order to answer these questions we shall deal into the issue of comparing the strengths of the two acids (or bases) involved in the dissociation equilibrium. Consider the two acids HA and H_3O^+ present in the above mentioned acid-dissociation equilibrium. We have to see which amongst them a stronger proton donor is.Whichever exceeds in its tendency of donating a proton over the other shall be termed as the stronger acid and the equilibrium will shift in thedirection of weaker acid. Say. if HA is a stronger acid than H_3O^+, then HA will donate protons and not H_3O^+ and the solution will mainly contain A^- and H_3O^+ ions. The equilibrium moves in the direction of formation of weaker acid and weaker base because the stronger acid donates a proton to the stronger base.

It follows that as a strong acid dissociates completely in water, the resulting base formed would be very weak i.e., strong acids have very weak conjugate bases. Strong acids like perchloric acid ($HClO_4$), hydrochloric acid (HCl), hydrobromic acid (HBr), hydroiodic acid (HI), nitric acid (HNO_3) and sulphuric acid (H_2SO_4) will give conjugate base ions ClO_4^-, Cl^-, Br^-, I^-, NO_3^- and HSO_4^-, which are much weaker bases than H_2O. Similarly a very strong base would give a very weak conjugate acid. On theother hand, a weak acid say HA is only partially dissociated in aqueous medium and thus, the solution mainly contains undissociated HA molecules. Typical weak acids are nitrous acid (HNO_2), hydrofluoric acid (HF) and acetic acid (CH_3COOH). It should be noted that the weak acids have very strong conjugate bases. For exa1nple, NH_2^-, O^{2-} and H^- are very good proton acceptors and thus, much stronger bases than H_2O.

Certain water soluble organic compounds like phenolphthalein and bromothymol blue behave as weak acids and exhibit different colours in their acid (HIn) and conjugate base (In^-) forms.

$$HIn\ \ aq\ + H_2O(l) \rightleftarrows H_3O^+\ \ aq\ + In^-\ \ aq$$

acid indicator colour A	conjugate acid	conjugate base colour B

Such compounds are useful as indicators in acid-base titrations, and finding out H^+ ion concentration.

7.8.1 The Ionization Constant of Water and its Ionic Product

Some substances like water are unique in their ability of acting both as an acid and a base. In presence of an acid, HA it accepts a proton and acts as the base while in the presence of a base, B it acts as an acid by donating a proton. In pure water, one H_2O molecule donates proton and acts as an acid and another water molecules accepts a proton and acts as a base at the same time. The following equilibrium exists:

$$\underset{\text{acid}}{H_2O(l)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons \underset{\text{conjugate acid}}{H_3O^+\ aq} + \underset{\text{conjugate base}}{OH^-\ aq}$$

The dissociation constant is represented by,

$$K=[H_3O^+][OH^-]/[H_2O] \qquad (7.19)$$

The concentration of water is omitted from the denominator as water is a pure liquid and its concentration remains constant. $[H_2O]$ is incorporated within the equilibrium constant to give a new constant, K_w which is called the ionic product of water.

$$K_w=[H^+][OH^-] \qquad (7.20)$$

The concentration of H^+ has been found out experimentally as 1.0 x 10^{-7} M at 298 K. And, as dissociation of water produces equal number of H^+ and OH ions, the concentration of hydroxyl ions, $[OH^-] = [H^+] = 1.0 \text{ x } 10^{-7}$M.

Thus, the value of K_w at 298K,

$$K_w=[H_3O^+][OH^-] = (1.0 \text{ x } 10^{-7}M)^2=1.0 \text{ x } 10^{-14}M^2 \qquad (7.21)$$

The value of K_w is temperature dependent as it is an equilibrium constant.

The density of pure water is 1000 g / L and its molar mass is 18.0 g /mol. From this the molarity of pure water can be given as, H_2O = (1000 g /L)(l mol/ 18.0 g) = 55.55 M.

Therefore, the ratio of dissociated water to that of un-dissociated water can be given as:

10^{-7} / (55.55) = 1.8 x 10^{-9}

We can distinguish acidic, neutral and basic aqueous solutions by the relative values of the and OH^- concentrations:

Acidic: $[H_3O^+] > [OH^-]$, Neutral: $[H_3O^+] = [OH^-]$, Basic: $[H_3O^+] < [OH^-]$

7.8.2 The p^H Scale

Hydronium ion concentration in molarity is more conveniently expressed on a logarithmic scale known as the p^H scale. The p^H of a solution is defined as the negative logarithm to base 10 of the activity (a_{H^+}) of hydrogen ion. In dilute solutions (< 0.01 M), activity of hydrogen ion (H^+) is equal in magnitude to molarity represented by $[H^+]$. It should be noted that activity has no units and is defined as:

$$a_{H^+} = [H^+] / \text{mol } L^{-1}$$

From the definition of p^H, the following can be written,

$$p^H = -\log\ a_{H^+} = -\log\ [H^+] / \text{mol L}^{-1}$$

Thus, an acidic solution of HCl (10^{-2} M) will have a p^H = 2. Similarly, a basic solution of NaOH having $[OH^-]$ = 10^{-4} M and $[H_3O^+]$ = 10^{-10} M will have a p^H = 10. At 25 ^{0}C, purewater has a concentration of hydrogen ions. $[H^+] = 10^{-7}$ M. Hence, the pH of pure water is given as:

$p^H = -\log(10^{-7}) = 7$

Acidic solutions possess a concentration of hydrogen ions, $[H^+] > 10^{-7}$ M, while basic solutions possess a concentration of hydrogen ions, $[H^+] < 10^{-7}$ M. thus, we can summarise that

Acidic solution has $p^H < 7$

Basic solution has $p^H > 7$

Neutral solution has $p^H = 7$

Now again, consider the equation (7.21) at298 K

$K_w = [H_3O^+][OH^-] = 10^{-14}$

Taking negative logarithm on both sides of equation, we obtain

$$\begin{aligned} -\log K_w &= -\log\ [H_3O^+][OH^-] \\ &= -\log[H_3O^+] - \log[OH^-] \\ &= -\log 10^{-14} \end{aligned}$$

$$p^{K_w} = p^H + p^{OH} = 14 \qquad (7.22)$$

Note that although K_w may change with temperature the variations in p^H with temperature are so small that we often ignore it.

p^{K_w} is a very important quantity for aqueous solutions and controls the relative concentrations of hydrogen and hydroxyl ions as their product is a constant. It should be noted that as the p^H scale is logarithmic, a change in p^H by just one unit also means change in $[H^+]$ by a factor of 10. Similarly, when the hydrogen ion concentration, $[H^+]$ changes by a factor of 100, the value of pH changes by 2 units. Now you can realise why the change in p^H with temperature is often ignored.

Measurement of p^H of a solution is very essential as its value should be known when dealing with biological and cosmetic applications. The p^H of a solution can be found roughly with the help of p^H paper that has different colour in solutions of different p^H. Now-a-days p^H paper is available with four strips on it. The different strips have different colours at the same p^H. The pH in the range of 1- 14 can be determined with an accuracy of 0.5 using pH paper.

For greater accuracy p^H meters are used. p^H meter is a device that measures the p^H-dependent electrical potential of the test solution within 0.001 precision. p^H meters of the size of a writing pen are now available in the market. The p^H values of some very common substances are given in Table 7.5.

7.8.3 Factors Affecting Acid Strength

Having discussed quantitatively the strengthsof acids and bases, we come to a stage where we can calculate the p^H of a given acid solution. But, the curiosity rises about why should some acids be stronger than others? What factors are responsible for making them stronger? The answer lies in its being a complex phenomenon. But, broadly speaking we can say that the extent of dissociation of an acid depends on the strength and polarity of the H-A bond.

In general, when strength of H-A bond decreases, that is, the energy required to break the bond decreases, HA becomes a stronger acid. Also, when the H-A bond becomes more polar i.e., the electronegativity difference between the atoms H and A increases and there is marked charge separation, cleavage of the bond becomes easier thereby increasing the acidic nature.

But it should be noted that while comparing elements in the same group of the periodic table, H-A bond strength is a more important factor in determining acidity than its polar nature. As the size of A increases down the group, H-A bond strength decreases and so the acid strength increases. Forexample;

Similarly, H_2S is stronger acid than H_2O.

But, when we discuss elements in the same row of the periodic table, H-A bond polarity becomes the deciding factor for determining the acid strength. As the electronegativity of A increases, the strength of the acid also increases. For example;

7.8.4 Common Ion Effect in theIonization of Acids and Bases

Consider an example of acetic acid dissociation equilibrium represented as:

$$CH_3COOH\ \ aq \rightleftharpoons H^+\ \ aq + CH_3COO^-\ \ aq$$

Or

$$HAc\ \ aq \rightleftharpoons H^+\ \ aq + Ac^-\ \ aq$$

$$K_a = \left[H^+\right]\left[Ac^-\right] /\ \ HAc$$

Addition of acetate ions to an acetic acid solution results in decreasing the concentration of hydrogen ions. [H^+]. Also, if H^+ ions are added from an external source then the equilibrium moves in the direction of un-dissociated acetic acid i.e., in a direction of reducing the concentration of hydrogen ions, [H+]. This phenomenon is an example of common ion effect. It can be defined as a shift in equilibrium on adding a substance that provides more of an ionic species already present in the dissociation equilibrium. Thus, we can say that common ion effect is a phenomenon based on the Le Chatelier's principle discussed in section 7.8.

In order to evaluate the p^H of the solution resulting on addition of 0.05M acetate ion to 0.05M acetic acid solution, we shall consider the acetic acid dissociation equilibrium once again,

Let x be the extent of ionization of acetic acid.

	$HAc\ aq$	$\rightleftharpoons H^+\ aq$	$+\ Ac^-\ aq$
Initial concentration (M) :	0.05	0	0.05
Change in concentration (M) :	$-x$	$+x$	$+x$
Equilibrium concentration (M):	$0.05-x$	x	$0.05+x$

Therefore,

$$K_a = \left[H^+\right]\left[Ac^-\right] / \ HAc \ = \ x \ \ 0.05 + x \ / \ 0.05 - x$$

As K_a is small for a very weak acid,$x << 0.05$. Hence, $0.05 + x \ \approx \ 0.05 - x \ \approx \ 0.05$ Thus,

$1.8 \times 10^{-5} = (x)\ (0.05 + x) / (0.05 - x)$

$= x\ (0.05) / (0.05) = x = [H^+] = 1.8 \times 10^{-5} M$

7.8.5 Hydrolysis of Salts and the pH of their Solutions

Salts formed by the reactions between acids and bases in definite proportions, undergo ionization in water. The cations/anions formed on ionization of salts either exist as hydrated ions in aqueous solutions or interact with water to reform corresponding acids/bases depending upon the nature of salts. The later process of interaction between water and cations/anions or both of salts is calledhydrolysis. The p^H of the solution gets affected by this interaction. The cations (e.g., Na^+ , K^+, $Ca^{2+,}$ Ba^{2+}, etc.) of strong bases and anions (e.g., Cl^- , Br^- , $N0_3^-$, ClO_4^- etc.) of strong acids simply get hydrated but do not hydrolyse, and therefore the solutions of salts formed from strong acids and bases are neutral i.e., their p^H is 7. However, the other categories of salts do undergo hydrolysis.

We now consider the hydrolysis of the salts of the following type:

i. Salts of weak acid and strong base e.g., CH_3COONa.
ii. Salts of strong acid and weak base e.g., NH_4Cl and
iii. Salts of weak acid and weak base, e.g., CH_3COONH_4.

In the first case, CH_3COONa being a salt of weak acid, CH_3COOH and strong base, NaOH gets completely ionised in aqueous solution.

$$CH_3COONa\ \ aq \ \rightarrow\ CH_3COO^-\ \ aq\ +\ Na^+\ \ aq$$

Acetate ion thus formed undergoes hydrolysis in water to give acetic acid and OH- ions

$$CH_3COO^-\ \ aq\ \ +H_2O\ 1\ \ \rightarrow\ CH_3COOH\ \ aq\ \ +OH^-(aq$$

Acetic acid being a weak acid (Ka = 1.8 x10^{-5}) increased of H^+ ion concentration in solution making the solution acidic. Thus, the p^H of NH_4Cl solution in water is less than 7.

Similarly, NH_4Cl formed from weak base, NH_4OH and strong acid, HCl, in water dissociates completely.

$$NH_4Cl \ aq \ \rightarrow NH_4^+ \ aq \ + Cl^- \ aq$$

Ammonium ions undergo hydrolysis with water to form NH_4OH and H^+ ions

$$NH_4^+ \ aq \ + H_2O \ 1 \rightleftarrows NH_4OH \ aq \ + H^+ \ aq$$

Ammonium hydroxide is a weak base (K_a = 1.77x 10^{-5}) and therefore remains almost unionised in solution. This results in increased of H^+ ion concentration in solution making the solution acidic. Thus, the p^H of NH_4Cl solution in water is less than 7.

Consider the hydrolysis of CH_3COONH_4 salt fanned from weak acid and weak base. The ions formed und ergo hydrolysis as follow:

Consider the hydrolysis of CH_3COONH_4 salt fanned from weak acid and weak base. The ions formed undergo hydrolysis as follow:

$$CH_3COO^- + NH_4^+ + H_2O \rightleftarrows CH_3COOH + NH_4OH$$

CH_3COOH and NH_4OH also remain into partially dissociated form:

$$CH_3COOH \rightleftarrows CH_3COO^- + H^+$$

$$NH_4OH \rightleftarrows NH_4^+ + OH^-$$

$$H_2O \rightleftarrows H^+ + OH^-$$

Without going into detailed calculation, it can be said that degree of hydrolysis is independent of concentration of solution, and p^H of such solutions is determined by their p^K values:

$$p^H = 7+1/2\ (p^{K_a} - p^{K_b}) \qquad (7.23)$$

The pH of solution can be greater than 7, if the difference is positive and it will be less than 7, if the difference is negative.

7.9 Buffer Solutions

Many body fluids e.g., blood or urine have definite p^H and any deviation in their p^Hindicates malfunctioning of the body. The control of p^H is also very important in many chemical and biochemical processes. Many medical and cosmetic formulations require that these be kept and administered at a particular pH. The solutions which resist change in p^H on dilution or with the addition of small amounts of acid or alkali are called Buffer Solutions. Buffer solutions of known p^H can be prepared from the knowledge of p_{Ka} of the acid or p_{Kb} of base and by controlling the ratio of the salt and acid or salt and base. A mixture of acetic acid and sodium acetate acts as buffer solution around pH 4.75 and a mixture of ammonium chloride and a1nmonium hydroxide acts as a buffer around pH 9.25.

Designing Buffer Solution

Knowledge of p_{Ka} and p_{Kb} equilibrium constant help us to prepare the buffer solution of known p^H . Let us see how we can do this.

Preparation of Acidic Buffer

To prepare a buffer of acidic p^H we use weak acid and its salt formed with strong base. We develop the equation relating the p^H , the equilibrium constant, K_a of weak acid and ration of concentration of weak acid and its conjugate base. For the general case where the weak acid HA ionizes in water;

$$HA + H_2O \rightleftarrows H_3O^+ + A^-$$

For which we can write the expression

$$K_a = \frac{\left[H_3O^+\right]\left[A^-\right]}{HA}$$

Rearrange the expression we have

$$\left[H_3O^+\right] = K_a \frac{HA}{\left[A^-\right]}$$

Taking logarithms on both sides and rearranging the terms we get

$$p^{K_a} = p^H - \log\frac{\left[A^-\right]}{HA}$$

$$\text{Or } p^H = p^{K_a} + \log\frac{\left[A^-\right]}{HA} \tag{7.24}$$

$$p^H = p^{K_a} + \log\frac{\left[\text{Conjugate base, } A^-\right]}{\text{Acid, HA}} \tag{7.25}$$

The expression (7.25) is known Henderson-Hasselbalch equation

The quantity $\frac{\left[A^-\right]}{HA}$ is the ratio of conjugate base (anion) of the acid and the acid present in the mixture. Since acid is a weak acid, it ionizes to a very little extent and concentration of HA is negligibly different from concentration of acid taken to from buffer. Also, most of the conjugate base,

$\left[A^{-}\right]$ comes from the ionisation of salt of the acid. Therefore, the concentration of conjugate base will be negligibly different from the concentration of the salt. Thus, equation (7.25) takes the form;

$$p^{H} = p^{K_a} + \log \frac{\text{Salt}}{\text{Acid}}$$

In the equation (7.24), if the concentration of $\left[A^{-}\right]$ is equal to concentration of HA, then $p^{H} = p^{K_a}$ because value of log 1 is zero. Thus, we take molar concentration of acid and salt (conjugate base) same, the p^{H} of buffer solution is equal to the p^{K_a} of the acid. So for preparing the buffer solution of the required p^{H} we select the acid whose p^{K_a} is close to the required p^{H}. For acetic acid p^{K_a} value is 4.76, therefore p^{H} of the buffer solution formed by acetic acid and sodium acetate taken in equal molar concentration will be around 4.76.

Similar analysis of buffer made with a weak base and its conjugate acid leads to the result.

$$p^{OH} = p^{K_b} + \log \frac{\left[\text{Conjugate acid, } BH^{+}\right]}{\text{Base, B}} \qquad (7.26)$$

$$p^{OH} = p^{K_b} + \log \frac{\text{Salt}}{\text{Base}}$$

SUMMARY

When the number of molecules leaving the liquid to vapour equals the number of molecules returning to the liquid from vapour, equilibrium is said to be attained and is dynamic in nature. Equilibrium can be established for both physical and chemical processes and at this stage rate of forward and reverse reactions are equal. Equilibrium constant, K_c is expressed as the concentration of products divided by reactants, each term raised to the stoichiometric coefficient.

For reaction, $$a\,A + b\,B \rightleftharpoons c\,C + d\,D$$

$$K_c = \frac{C^c\ D^d}{A^a\ B^b}$$

Equilibrium constant has constant value at a fixed temperature and at this stageall the macroscopic properties such as concentration, pressure, etc. become constant. For a gaseous reaction equilibrium constant is expressed as K_P and is written by replacing concentration terms by partial pressures in K_c expression. The direction of reaction can be predicted by reaction quotient Q_c which is equal to K_c at equilibrium. Le Chatelier's principle states that the change in any factor such as temperature, pressure, concentration, etc. will cause the equilibrium to shift in such a direction so as to reduce or counteract the effect of the change. It can be used to study the effect of various factors such as temperature, concentration, pressure, catalyst and inert gases on the direction of equilibrium and to control the yield of products by controlling these factors. Catalyst does not effect the equilibrium composition of a reaction mixture but increases the rate of chemical reaction by making available a new lower energy pathway for conversion of reactants to products and vice-versa.

All substances that conduct electricity in aqueous solutions are called electrolytes.Acids, bases and salts are electrolytes and the conduction of electricity by their aqueous solutions is due to anions and cations produced by the dissociation or ionization of electrolytes in aqueous solution. The strong electrolytes are completely dissociated. In weak electrolytes there is equilibrium between the ions and the unionized electrolyte molecules. According to Arrhenius, acids give hydrogen ions while bases produce hydroxyl ions in their aqueous solutions. Bronsted-Lowry on the other hand, defined an acid as a proton donor and a base as a proton acceptor. When a Bronsted -Lowry acid reacts with a base, it produces its conjugate base and a conjugate acid corresponding to the base with which it reacts. Thus a conjugate pair of acid-base differs only by one proton. Lewis further generalised the definition of an acid as an electron pair acceptor and a base as an electron pair donor. The p^H scale ($p^H = -\log\,[H^+]$) for the hydrogen ion concentration (activity) has been introduced and extended to other quantities ($p^{OH} = -\log\,[OH^-]$); $p^{K_a} = -\log\,[K_a]$; $p^{K_b} = -\log\,[K_b]$; and $p^{K_w} = -\log\,[K_w]$ etc.). The ionization of water has been considered andwe note that the equation: $p^{K_w} = p^H + p^{OH}$ is always satisfied. The salts of strong acid and weak base, weak acid and strong base, and weak acid and weak base undergo hydrolysis in aqueous solution.The definition of buffer solutions and their basic concepts are discussed briefly.

EXERCISES

7.1 The equilibrium constant for the reaction: $N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)$,

is $K_c = 3.6 \times 10^8$ at 298 K. What is the equilibrium constant for the following reaction,

i. $NH_3(g) \rightleftarrows \frac{1}{2} N_2(g) + {}^3/_2 H_2(g)$

7.2 For the reaction: $2 SO_{2(g)} + O_{2(g)} \rightleftarrows 2 SO_{3(g)}$, $K_c = 280$ at 1000 K.

What is the equilibrium constant for the following decomposition of SO_3 at 1000 K?

$$SO_3(g) \rightleftarrows SO_2(g) + \frac{1}{2} O_2(g).$$

7.3 The reaction: $PCl_5(g) \rightleftarrows PCl_3(g) + Cl_2(g)$ has $K_c = 0.0896$ at a certain temperature. If 0.0860 mol of PCl_5 is placed in an empty 1.00-L flask, what would be the concentrations of PCl_5, PCl_3, and Cl_2 at equilibrium?

7.4 Determine whether the following reactions favor high or low pressures?

(a) $2SO_2(g) + O_2(g) \rightleftarrows 2 SO_3(g)$;

(b) $PCl_5(g) \rightleftarrows PCl_3(g) + Cl_2(g)$;

(c) $CO(g) + 2H_2(g) \rightleftarrows CH_3OH(g)$;

(d) $N_2O_4(g) \rightleftarrows 2 NO_2(g)$;

(e) $H_2(g) + F_2(g) \rightleftarrows 2 HF(g)$;

7.5 Determine whether the following reactions favors high or low temperature?

(a) $2SO_2(g) + O_2(g) \rightleftarrows 2 SO_3(g)$; $\Delta H^o = -180$ kJ

(b) $CO(g) + H_2O(g) \rightleftarrows CO_2(g) + H_2(g)$; $\Delta H^o = -46$ kJ

(c) $CO(g) + Cl_2(g) \rightleftarrows COCl_2(g)$; $\Delta H^o = -108.3$ kJ

(d) $N_2O_4(g) \rightleftarrows 2 NO_2(g)$; $\Delta H^o = +57.3$ kJ

(e) $CO(g) + 2H_2(g) \rightleftarrows CH_3OH(g)$; $\Delta H^o = -270$ kJ

7.6 If the hydrogen ion concentration of a solution is 1.30×10^{-4} M

7.7 What is the concentration $[H^+]$ in a solution with pH = 4.75.

7.8 Which would have a higher pH, a solution whose p^{OH} is 5.42 or a solution whose hydrogen ion concentration is 9.44×10^{-8} M?

7.9 Which would have a more basic pH, a solution whose hydrogen ion concentration is 3.4×10^{-8} M or a solution whose hydroxide ion concentration is 2.6×10^{-5} M?

7.10 Predict whether each of the following salt solutions is expected to be neutral, acid, or basic:

(a) NH_4ClO_4, (b) NaF (c) KI (d) NH_4NO_3 (e) Na_2CO_3

QUESTION BANK

***Very Short Answer Questions* (4Marks)**

1. What is homogenous equilibrium? Write two homogenous reactions?
2. What is heterogeneous equilibrium? Write two heterogeneous reactions.
3. Write the relation between K_P and K_C.
4. Define law of mass action.
5. Discuss the application of Le-Chatelier's Principle for the industrial synthesis of Ammonia?
6. Discuss the application of Le-Chatelier's Principle for the industrial synthesis of sulpur trioxide.
7. Explain the Arrhenius concept of acids and bases?
8. What is a conjugate acid-base pair? Give Example.
9. Define Lewis Acids and Lewis bases?
10. Define P^H?
11. Define ionic product of water? What is its value at room temperature?
12. Give two examples of salts whose aqueous solutions are basic?
13. Give two examples of slats whose aqueous solutions are acidic?
14. Define Buffer solution. Give example for acidic buffer and basic buffer solution.

CHAPTER-8

HYDROGEN AND ITS COMPOUNDS

Hydrogen has the simplest atomic structure among all the elements around us in Nature. In atomic form it consists of only one proton and one electron. However, in elemental form it exists as a diatomic (H_2) molecule and is called dihydrogen. It forms more compounds than any other element. Do you know that the global concern related to energy can be overcome to a great extent by the use of hydrogen as a source of energy? In fact, hydrogen is of great industrial importance as you will learn in this unit.

8.1 Position of Hydrogen in the Periodic Table

Hydrogen is the first element in the periodic table. However, its placement in the periodic table has been a subject of discussion in the past. As you know by now that the elements in the periodic table are arranged according to their electronic configurations.

Hydrogen has electronic configuration $1s^1$. On one hand, its electronic configuration is similar to the outer electronic configuration (ns^1) of alkali metals, which belong to the first group of the periodic table. On the other hand, like halogens (with ns^2np^5 configuration belonging to the seventeenth group of the periodic table) , it is short by one electron to the corresponding noble gas configuration , helium ($1s^2$). Hydrogen, therefore, has resemblance to alkali metals, which lose one electron to form unipositive ions, as well as with halogens, which gain one electron to form uni-negative ion. Like alkali metals, hydrogen forms oxides, halides and sulphides. However, unlike alkali metals, it has a very high ionization enthalpy and does not possess metallic characteristics under normal conditions. In fact, in terms of ionization enthalpy, hydrogen resembles more with halogens, ΔH of Li is 520 kJ mol^{-1}, F is 1680 kJ $mo1^{-1}$ and that of H is 1312 kJ mol^{-1}. Like halogens, it forms a diatomic molecule, combines with elements to form hydrides and a large number of covalent compounds. However, in terms of reactivity, it is very low as compared to halogens.

In spite of the fact that hydrogen, to a certain extent resembles both with alkali metals and halogens, it differs from them as well. Now the pertinent question arises as where should it be placed in the periodic table? Loss of the electron from hydrogen atom results in nucleus (H^+) of ~ l.5x 10^{-3} pm size. This is extremely small as compared to normal atomic and ionic sizes of 50 to 200pm. As a consequence, H^+ does not exist freely and is always associated with other atoms or molecules. Thus, it is unique in behaviour and is, therefore, best placed separately in the periodic table.

8.2 Dihydrogen, H_2

8.2.1 Occurrence

Dihydrogen is the most abundant element in the universe (70% of the total mass of the universe) and is the principal element in the solar atmosphere. The giant planets Jupiter and Saturn consist mostly of hydrogen. However, due to its light nature, it is much less abundant (0. 15% by mass) in the earth's atmosphere. Of course, in the combined form it constitutes 15.4% of the earth's crust and the oceans. In the combined form besides in water, it occurs in plant and animal tissues, carbohydrates, proteins, hydrides including hydrocarbons and many other compounds.

8.2.2 Isotopes of Hydrogen

Hydrogen has three isotopes: protium, ${}^{1}_{1}H$, deuterium, ${}^{2}_{1}H$ or D and tritium, ${}^{3}_{1}H$ or T. Can you guess how these isotopes differ from each other? These isotopes differ from one another in respect of the presence of neutrons. Ordinary hydrogen, protium, has no neutrons, deuterium (also known as heavy hydrogen) has one and tritium has two neutrons in the nucleus. In the year 1934, an American scientist, Harold C. Urey, got Nobel Prize for separating hydrogen isotope of mass number 2 by physical methods.

The predominant form is protium. Terrestrial hydrogen contains 0.0156% of deuterium mostly in the form of HD. The tritium concentration is about one atom per 10^{18} atoms of protium. Of these isotopes, only tritium is radioactive and emits low energy β - particles ($t_{1/2}$, 12.33years).

Since the isotopes have the same electronic configuration, they have almost the same chemical properties. The only difference is in their rates of reactions, mainly due to their different enthalpy of bond dissociation (Table 8.1). However, in physical properties these isotopes differ considerably due to their large mass differences.

Table 8.1 Atomic and physical properties of Hydrogen

Property	Hydrogen	Deuterium	Tritium
Relative abundance (%)	99.985	0.0156	10^{-15}
Relative atomic mass (g mol^{-1})	1.008	2.014	3.016
Melting point / K	13.96	18.73	20.62
Boiling point/ K	20.39	23.67	25.0
Density / gL^{-1}	0.09	0.18	0.27
Enthalpy of fusion/kJ mol^{-1}	0.117	0.197	-
Enthalpy of vaporization/kJ mol^{-1}	0.904	1.226	-
Enthalpy of bond dissociation/kJ mol^{-1} at 298.2K	435.88	443.35	-
Internuclear distance/pm	74.14	74.14	-
Ionization enthalpy/kJ mol^{-1}	1312	-	-
Electron gain enthalpy/kJ mol^{-1}	–73	-	-
Covalent radius/pm	37	-	-
Ionic radius(H^{-})/pm	208		

8.3 Preparation of Dihydrogen, H_2

There are a number of methods for preparing dihydrogen from metals and metal hydrides.

8.3.1 Laboratory Preparation of Dihydrogen

(i) It is usually prepared by the reaction of granulated zinc with dilute hydrochloric acid.

$$Zn + 2H^{+} \rightarrow Zn + H_2$$

(ii) It can also be prepared by the reaction of zinc with aqueous alkali.

$$Zn + 2\,NaOH \rightarrow \underset{\text{Sodium zincate}}{Na_2ZnO_2} + H_2$$

8.3.2 Commercial Production of Dihydrogen

The commonly used processes are outlined below:

(i) Electrolysis of acidified water using platinum electrodes gives hydrogen.

(ii) High purity (> 99.95%) dihydrogen is obtained by electrolysing warm aqueous barium hydroxide solution between nickel electrodes.

(iii) It is obtained as a byproduct in the manufacture of sodium hydroxide and chlorine by the electrolysis of brine solution. During electrolysis, the reactions that take place are:

at anode: $2\,Cl^-(aq) \rightarrow Cl_2(g) + 2\,e^-$

at cathode: $2\,H_2O\,(1) + 2\,e^- \rightarrow H_2(g) + 2\,OH^-(aq)$

The overall reaction is

$$2\,Na_{aq}^{+} + 2\,Cl_{aq}^{-} + 2\,H_2O\,(1) \rightarrow 2\,Na_{aq}^{+} + Cl_2(g) + H_2(g) + 2\,OH_{aq}^{-}$$

(iv) Reaction of steam on hydrocarbons or coke at high temperatures in the presence of catalyst yields hydrogen.

$$C_nH_{2n+2} + n\,H_2O \xrightarrow[Ni]{1270\text{ K}} n\,CO + (2n+1)\,H_2$$

$$\text{e.g.,}\quad CH_4(g) + H_2O(g) \xrightarrow[Ni]{1270\text{ K}} CO(g) + 3\,H_2(g)$$

The mixture of CO and H_2 is called water gas. As this mixture of CO and H_2 is used for the synthesis of methanol and a number of hydrocarbons, it is also called synthesis gas or 'syngas'. Nowadays 'syngas' is produced from sewage, saw-dust, scrap wood, newspapers etc. The process of producing 'syngas' from coal is called 'coal gasification'.

$$C\,(s) + H_2O(g) \xrightarrow{1270\text{ K}} CO\,(g) + H_2\,(g)$$

The production of dihydrogen can be increased by reacting carbon monoxide of syngas mixtures with steam in the presence of iron chromate as catalyst.

$$CO\,(g) + H_2O(g) \xrightarrow[\text{catalyst}]{1270\text{ K}} CO_2\,(g) + H_2\,(g)$$

This is called water-gas shift reaction. Carbon dioxide is removed by scrubbing with sodium arsenite solution. Presently,~ 77% of the industrial dihydrogen is produced from petro-chemicals, 18% from coal, 4% from electrolysis of aqueous solutions and 1% from other sources.

8.4 Properties of Dihydrogen

8.4.1 Physical Properties

Dihydrogen is a colourless, odourless, tasteless, combustible gas. It is lighter than air and insoluble in water. Its other physical properties along with those of deuterium are given in Table 8.1.

8.4.2 Chemical Properties

The chemical behaviour of dihydrogen (and for that matter any molecule) is determined, to a large extent, by bond dissociation enthalpy. The H-H bond dissociation enthalpy is the highest for a single bond between two atoms of any element. What inferences would you draw from this fact? It is because of this factor that the dissociation of dihydrogen into its atoms is only ~ 0.081% around 2000 K which increases to 95.5% at 5000 K. Also, it is relatively inert at room temperature due to the high H-H bond enthalpy. Thus, the atomic hydrogen is produced at a high temperature in an electric arc or under ultraviolet radiations. Since its orbital is incomplete with Is^1 electronic configuration, it does combine with almost all the elements. It accomplishes reactions by (i) loss of the only electron to give H^+, (ii) gain of an electron to form H^-, and (iii) sharing electrons to form a single covalent bond.

The chemistry of dihydrogen can be illustrated by the following reactions:

Reaction with halogens: It reacts with halogens, X_2 give hydrogen halides, HX,

$$H_2(g) + X_2(g) \rightarrow 2\,HX\,(g) \qquad (X = F, Cl, Br, I)$$

While the reaction with fluorine occurs even in the dark, with iodine it requires a catalyst.

Reaction with dioxygen: It reacts with dioxygen to form water. The reaction is highly exothermic.

$$2H_2(g) + O_2(g) \xrightarrow{\text{catalyst or heating}} 2\,H_2O\,(l) \qquad \Delta H^0 = -285.9\text{ kJ mol}^{-1}$$

Reaction with dinitrogen: With dinitrogen it forms ammonia.

$$3H_2(g) + N_2(g) \xrightarrow[\text{Fe}]{\text{673K, 200 atm}} 2\,NH_3\,(g) \qquad \Delta H^0 = -92.6\text{ kJ mol}^{-1}$$

This is the reaction underlined in the manufacture of ammonia by the Haber process.

Reactions with metals: With many metals it combines at high a temperature to yield the corresponding hydrides.

$$H_2(g) + 2\,M(g) \rightarrow 2\,MH(s) \text{ where M is alkali metal}$$

React ions with metal ions and metal oxides: It reduces some metal ions in aqueous solution and oxides of metals (less active than iron) into corresponding metals.

$$H_2(g) + Pd^{2+}_{aq} \rightarrow Pd(s) + 2\,H^+_{aq}$$

$$H_2\,(g) + CuO\,(s) \rightarrow Cu\,(s) + H_2O\,(l)$$

Reactions with organic compounds: It reacts with many organic compounds in the presence of catalysts to give useful hydrogenated products of commercial importance. For example:

i. Hydrogenation of vegetable oils using nickel as catalyst gives edible fats (margarine and vanaspati ghee)

ii. Hydroformylation of olefins yields aldehydes which further undergo reduction to give alcohols.

$$H_2 + CO + RCH{=}CH_2 \rightarrow RCH_2CH_2CHO$$

$$H_2 + RCH_2CH_2CHO \rightarrow RCH_2CH_2CH_2OH$$

8.4.3 Uses of Dihydrogen

- The largest single use of dihydrogen is in the synthesis of ammonia which is used in the manufacture of nitric acid and nitrogenous fertilizers.
- Dihydrogen is used in the manufacture of vanaspati fat by the hydrogenation of polyunsaturated vegetable oils like soyabean, cotton seeds etc.
- It is used in the manufacture of bulk organic chemicals, particularly methanol.

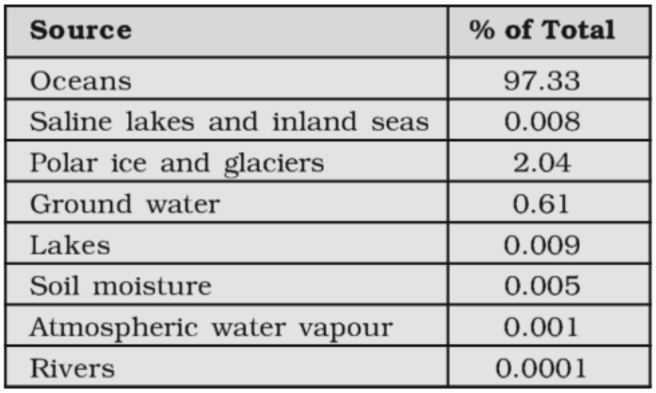
$$CO\,(g) + 2H_2\,(g) \xrightarrow{\text{Cobalt catalyst}} CH_3OH(l)$$

- It is widely used for the manufacture of metal hydrides.
- It is used for the preparation of hydrogen chloride, a highly useful chemical.
- In metallurgical processes, it is used to reduce heavy metal oxides to metals.
- Atomic hydrogen and oxy-hydrogen torches find use for cutting and welding purposes. Atomic hydrogen atoms (produced by dissociation of dihydrogen with the help of an electric arc) are allowed to recombine on the surface to be welded to generate the temperature of 4000 K.
- It is used as a rocket fuel in space research.
- Dihydrogen is used in fuel cells for generating electrical energy. It has many advantages over the conventional fossil fuels and electric power. It does not produce any pollution and releases greater energy per unit mass of fuel in comparison to gasoline and other fuels.

8.5 Water

A major part of all living organisms is made up of water. Human body has about 65% and some plants have as much as 95% water. It is a crucial compound for the survival of all life forms. It is a solvent of great importance. The distribution of water over the earth's surface is not uniform. The estimated world water supply is given in Table 8.2

Table 8.2 Estimated World Water Supply



Source	% of Total
Oceans	97.33
Saline lakes and inland seas	0.008
Polar ice and glaciers	2.04
Ground water	0.61
Lakes	0.009
Soil moisture	0.005
Atmospheric water vapour	0.001
Rivers	0.0001

8.5.1 Hard and Soft Water

Rain water is almost pure (may contain some dissolved gases from the atmosphere). Being a good solvent, when it flows on the surface of the earth, it dissolves many salts. Presence of calcium and magnesium salts in the form of hydrogencarbonate, chloride and sulphate in water makes water 'hard'. Hard water does not give lather with soap. Water free from soluble salts of calcium and magnesium is called Soft water. It gives lather with soap easily.

Hard water forms scum/precipitate with soap. Soap containing sodium stearate ($C_{17}H_{35}COONa$) reacts with hard water to precipitate out Ca/Mg stearate.

$$2\ C_{17}H_{35}COONa_{aq} + M^{2+}_{aq} \rightarrow (C_{17}H_{35}COO)_2M\downarrow\ + 2\ Na^{+}_{aq}$$

M is Ca or Mg

It is, therefore, unsuitable for laundry. It is harmful for boilers as well, because of deposition of salts in the form of scale. This reduces the efficiency of the boiler. The hardness of water is of two types: (i) temporarily hardness, and (ii) permanent hardness.

8.5.2 Temporary Hardness

Temporary hardness is due to the presence of magnesium and calcium hydrogen - carbonates. It can be removed by:

(i) Boiling: During boiling, the soluble $Mg(HCO_3)_2$ is converted into insoluble $Mg(OH)_2$ and $Ca(HCO_3)_2$ is changed to insoluble $CaCO_3$. It is because of low solubility product of $Mg(OH)_2$ is precipitated. These precipitates can be removed by filtration. Filtrate thus obtained will be soft water.

$$Mg\left(HCO_3\right)_2 \xrightarrow{\text{heating}} Mg\left(OH\right)_2\downarrow + 2CO_2\uparrow$$

$$Ca\left(HCO_3\right)_2 \xrightarrow{\text{heating}} CaCO_3\downarrow + H_2O + CO_2\uparrow$$

(ii) Clark's method: In this method calculated amount of lime is added to hard water. It precipitates out calcium carbonate and magnesium hydroxide which can be filtered off.

$$Ca\left(HCO_3\right)_2 + Ca\left(OH\right)_2 \longrightarrow 2\ CaCO_3\downarrow + 2\ H_2O$$

$$Mg\left(HCO_3\right)_2 + 2Ca\left(OH\right)_2 \longrightarrow 2\ CaCO_3\downarrow + Mg\left(OH\right)_2\downarrow + 2\ H_2O$$

8.5.3 Permanent Hardness

It is due to the presence of soluble salts of magnesium and calcium in the form of chlorides and sulphates in water. Permanent hardness is not removed by boiling. It can be removed by the following methods:

(i) Treatment with washing soda (sodium carbonate): Washing soda reacts with soluble calcium and magnesium chlorides and sulphates in hard water to form insoluble carbonates.

$$MCl_2 + Na_2CO_3 \longrightarrow MCO_3\downarrow + 2\ NaCl \qquad (M{=}Mg,\ Ca)$$

$$MSO_4 + Na_2CO_3 \longrightarrow MCO_3\downarrow + Na_2SO_4 \qquad (M{=}Mg,\ Ca)$$

(ii) Calgon 's method : Sodium hexameta - phosphate ($Na_6P_6O_{18}$), commercially called 'calgon', when added to hard water, the following reactions take place.

$$Na_6P_6O_{18} \longrightarrow 2\ Na^{+} + Na_4P_6O_{18}^{\ 2-}$$

$$M^{2+} + Na_4P_6O_{18}{}^{2-} \longrightarrow \left[Na_2MP_6O_{18}\right]^{2-} + 2Na^+ \qquad (M = Mg, Ca)$$

The complex keeps the Mg^{2+} and Ca^{2+} ions in solution.

(iii) Ion-exchange method: This method is also called zeolite/permutit process. Hydrated sodium aluminium silicate is zeolite/permutit. For the sake of simplicity, sodium aluminium silicate ($NaAlSiO_4$) can be written as NaZ. When this is added in hard water, exchange reactions take place.

$$2\ NaZ(s) + M^{2+}(aq) \longrightarrow MZ_2(s) + 2\ Na^+(aq) \qquad (M = Mg, Ca)$$

Permutit/ zeolite is said to be exhausted when all the sodium in it is used up. It is regenerated for further use by treating with an aqueous sodium chloride solution.

$$MZ_2(s) + 2NaCl(aq) \longrightarrow 2\ NaZ(s) + MC1_2(aq)$$

(iv) Synthetic resins method:

Nowadays hard water is softened by using synthetic cation exchangers. This method is more efficient than zeolite process. Cation exchange resins contain large organic molecule with - SO_3H group and are water insoluble. Ion exchange resin (RSO_3H) is changed to RNa by treating it with NaCl. The resin exchanges Na^+ ions with Ca^{2+} and Mg^{2+} ions present in hard water to make the water soft. Here R is resin anion.

$$2\ RNa(s) + M^{2+}(aq) \longrightarrow R_2M(s) + 2Na^+(aq)$$

The resin can be regenerated by adding aqueous NaCl solution.

Pure de-mineralised (de-ionized) water free from all soluble mineral salts is obtained by passing water successively through a cation exchange (in the H^+ form) and an anion exchange (in the OH^- form) resins:

$$2\ RH(s) + M^{2+}(aq) \rightleftarrows MR_2(s) + 2H^+(aq)$$

In this cation exchange process, H^+ exchanges Na^+, Ca^{2+}, Mg^{2+} and other cati.ons present in water. This process results in proton release and thus makes the water acidic. In the anion exchange process:

$$RNH_2(s) + H_2O(l) \rightleftarrows RNH_3{}^+OH^-(s)$$

$$RNH_3{}^+OH^-(s) + X^-_{aq} \rightleftarrows RNH_3{}^+X^-(s) + OH^-$$

OH^- exchanges for anions like Cl^-, $HCO_3{}^-$, $SO_4{}^{2-}$ etc. present in water. OH^- ions, thus, liberated neutralise the H^+ ions set free in the cation exchange.

$$H^+_{aq} + OH^-_{aq} \longrightarrow H_2O(l)$$

The exhausted cation and anion exchange resin beds are regenerated by treatment with dilute acid and alkali solutions respectively.

8.6 Hydrogen Peroxide (H_2O_2)

Hydrogen peroxide is an important chemical used in pollution control treatment of domestic and industrial effluents.

8.6. 1 Preparation

It can be prepared by the following methods.

(i) Acidifying barium peroxide and removing excess water by evaporation under reduced pressure gives hydrogen peroxide.

$$BaO_2.8H_2O(s) + H_2SO_4(aq) \rightarrow BaSO_4(s) + H_2O_2(aq) + 8\,H_2O(I)$$

(ii) Peroxodisulphate, obtained by electrolytic oxidation of acidified sulphate solutions at high current density, on hydrolysis yields hydrogen peroxide.

$$2\,HSO_4^-(aq) \xrightarrow{\text{Electrolysis}} HO_3SOOSO_3H\ (aq) \xrightarrow{\text{Hydrolysis}} 2HSO_4^-(aq) + 2H^+(aq) + H_2O_2(aq)$$

This method is now used for the laboratory preparation of D_2O_2.

$$K_2S_2O_8(s) + 2\,D_2O(l) \rightarrow 2\,KDSO_4(aq) + D_2O_2(1)$$

(iii) Industrially it is prepared by the auto- oxidation of 2-alklylanthraquinols.

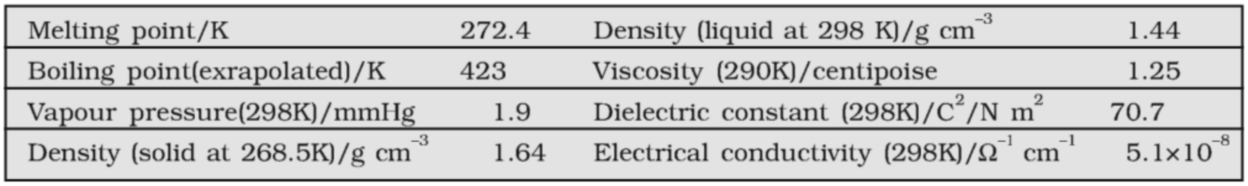
$$2\text{ - ethylanthraquinol } \underset{H_2/Pd}{\overset{O_2\ (air)}{\rightleftarrows}} H_2O_2 + (\text{oxidised product})$$

In this case 1% H_2O_2 is formed. It is extracted with water and concentrated to ~ 30% (by mass) by distillation under reduced pressure. It can be further concentrated to ~ 85% by careful distillation under low pressure. The remaining water can be frozen out to obtain pure H_2O_2.

8.6.2 Physical Properties:

In the pure state H_2O_2 is an almost colourless (very pale blue). Its important physical properties are given in Table 8.3.

Table 8.3 Physical properties of Hydrogen Peroxide

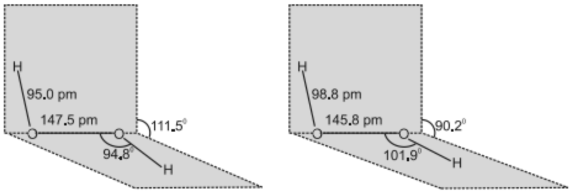


Melting point/K	272.4	Density (liquid at 298 K)/g cm^{-3}	1.44
Boiling point(exrapolated)/K	423	Viscosity (290K)/centipoise	1.25
Vapour pressure(298K)/mmHg	1.9	Dielectric constant (298K)/C^2/N m^2	70.7
Density (solid at 268.5K)/g cm^{-3}	1.64	Electrical conductivity (298K)/Ω^{-1} cm^{-1}	5.1×10^{-8}

H_2O_2 is miscible with water in all proportions and forms a hydrate $H_2O_2.H_2O$ (mp 221K). A 30% solution of H_2O_2 is marketed as ‘100 volume' hydrogen peroxide. It means that one millilitre of 30% H_2O_2 solution will give 100 V of oxygen at STP. Commercially, it is marketed as 10V, which means it contains 3% H_2O_2.

8.6.3 Structure

Hydrogen peroxide has a non-planar structure. The molecular dimensions in the gas phase and solid phase are shown in Fig 8.1



(a) Gas phase (b) Solid phase

Fig. 8.1 (a) H_2O_2 structure in gas phase, dihedral angle is 111.5°. (b) H_2O_2 structure in solid phase at 110K, dihedral angle is 90.2°

8.6.4 Chemical Properties

It acts as an oxidising as well as reducing agent in both acidic and alkaline media. Simple reactions are described below.

(i) Oxidising action in acidic medium

$$2\ Fe^{2+}(aq) + 2\ H^{+}(aq) + H_2O_2(aq) \rightarrow 2\ Fe^{3+}(aq) + 2H_2O(l)$$

$$PbS(s) + 4\ H_2O_2(aq) \rightarrow PbSO_4(s) + 4\ H_2O\ (l)$$

(ii) Reducing action in acidic medium

$$2\ MnO_4^{-} + 6\ H^{+}(aq) + 5\ H_2O_2(aq) \rightarrow 2\ Mn^{2+} + 8\ H_2O + 5O_2$$

$$HOCl + H_2O_2 \rightarrow H_3O^{+} + Cl^{-} + O_2$$

(iii) Oxidising action in basic medium

$$2\ Fe^{2+} + H_2O_2 \rightarrow 2\ Fe^{3+} + 2OH^{-}$$

$$Mn^{2+} + H_2O_2 \rightarrow Mn^{4+} + 2OH^{-}$$

(iv) Reducing action in basic medium

$$I_2 + H_2O_2 + 2\ OH^{-} \rightarrow 2\ I^{-} + 2H_2O + O_2$$

$$2\ MnO_4^{-} + 3\ H_2O_2 \rightarrow 2\ MnO_2 + 3\ O_2 + 2H_2O + 2\ OH^{-}$$

8.6.5 Storage

H_2O_2 decomposes slowly on exposure to light.

$$2\ H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$$

In the presence of metal surfaces or traces of alkali (present in glass containers), the above reaction is catalysed. It is, therefore, stored in wax-lined glass or plastic vessels in dark. Urea can be added as a stabiliser. It is kept away from dust because dust can induce explosive decomposition of the compound.

8.6.6 Uses

Its wide scale use has led to tremendous increase in the industrial production of H_2O_2

Some of the uses are listed below:

(i) In daily life it is used as hair bleach and as a mild disinfectant. As an antiseptic it is sold in the market as perhydrol.

(ii) It is used to manufacture chemicals like sodium perborate and per-carbonate, which are used in high quality detergents

(iii) It is used in the synthesis of hydroquinone, tartaric acid and certain food products and pharmaceuticals (cephalosporin) etc.

(iv) It is employed in the industries as a bleaching agent for textiles, paper pulp, leather, oils, fats, etc.

(v) Nowadays it is also used in Environmental (Green) Chemistry. For example, in pollution control treatment of domestic and industrial effluents, oxidation of cyanides, restoration of aerobic conditions to sewage wastes, etc.

8.7 Heavy Water, D_2O

It is extensively used as a moderator in nuclear reactors and in exchange reactions for the study of reaction mechanisms. It can be prepared by exhaustive electrolysis of water or as a by-product in some fertilizer industries. Its physical properties are given in Table 8.3. It is used for the preparation of other deuterium compounds, for example:

$$CaC_2 + 2D_2O \rightarrow C_2D_2 + Ca\left(OD\right)_2$$

$$SO_3 + D_2O \rightarrow D_2SO_4$$

$$Al_4C_3 + 12\,D_2O \rightarrow 3\,CD_4 + 4\,Al\left(OD\right)_3$$

SUMMARY

Hydrogen is the lightest atom with only one electron. Loss of this electron results in an elemen tary particle, the proton. Thus, it is unique in character. It has three isotopes, namely: protium, deuterium and tritium. Amongst these three, only tritium is radioactive. In spite of its resemblance both with alkali metals and halogens, it occupies a separate position in the periodic table because of its unique properties.

Hydrogen is the most abundant element in the universe. In the free state it is almost not found in the earth's atmosphere. However, in the combined state, it is the third most abundant element on the earth's surface.

Dihydrogen on the industrial scale is prepared by the water-gas shift reaction from petrochemicals. It is obtained as a byproduct by the electrolysis of brine.

The H-H bond dissociation enthalpy of dihydrogen (435.88 kJ mol^{-1} is the highest for a single bond between two atoms of any elements. This property is made use of in the atomic hydrogen torch which generates a temperature of 4000K and is ideal for welding of high melting metals.

Though dihydrogen is rather inactive at room temperature because of very high negative dissociation enthalpy, it combines with almost all the elements under appropriate conditions to form hydrides. All the type of hydrides can be classified into three categories: ionic or saline hydrides, covalent or molecular hydrides and metallic or non-stoichiometric hydrides. Alkali metal hydrides are good reagents for preparing other hydride compounds.

Among the other chemical reactions of dihydrogen, reducing reactions leading to the formation hydrogen halides, water, ammonia, methanol, vanaspati ghee etc. are of great importance. In metallurgical process, it is used to reduce metal oxides. In space programmes, it is used as a rocket fuel. In fact, it has promising potential for use as a non-polluting fuel of the near future (Hydrogen Economy).

Water is the most common and abundantly available substance. It is of a great chemical and biological significance. The ease with which water is transformed from liquid to solid and to gaseous state allows it to play a vital role in the biosphere. Heavy water, D_2O is another important compound which is in manufactured by the electrolytic enrichment of normal water. It is essentially used as a moderator in nuclear reactors. Hydrogen peroxide, H_2O_2 has an interesting non-polar structure and is widely used as industrial bleach and in pharmaceutical and pollution control treatment of industrial and domestic effluents.

EXERCISES

8.1 Justify the position of hydrogen in the periodic table on the basis of its electronic configuration.

8.2 Write the names of isotopes of hydrogen. What is the mass ratio of these isotopes?

8.3 How can the production of dihydrogen, obtained from 'coal gasification', be increased?

8.4 Describe the bulk preparation of dihydrogen by electrolytic method. What is the role of an electrolyte in this process?

8.5 How does the atomic hydrogen or oxy-hydrogen torch function for cutting and welding purposes? Explain.

8.6 What causes the temporary and permanent hardness of water?

8.7 Discuss the principle and method of softening of hard water by synthetic ion- exchange resins.

8.8 Write chemical reactions to justify that hydrogen peroxide can function as an oxidising as well as reducing agent.

QUESTION BANK

***Very Short Answer Questions* (2 Marks)**

1. Describe one method of producing high quality hydrogen?
2. Why is dihydrogen used in welding of high melting metals?
3. Explain the terms hard water and soft water?
4. What is the chemical substance used in calgen method?
5. Mention three uses of H_2O_2 in modern times?
6. Write any two methods of preparation of H_2O_2

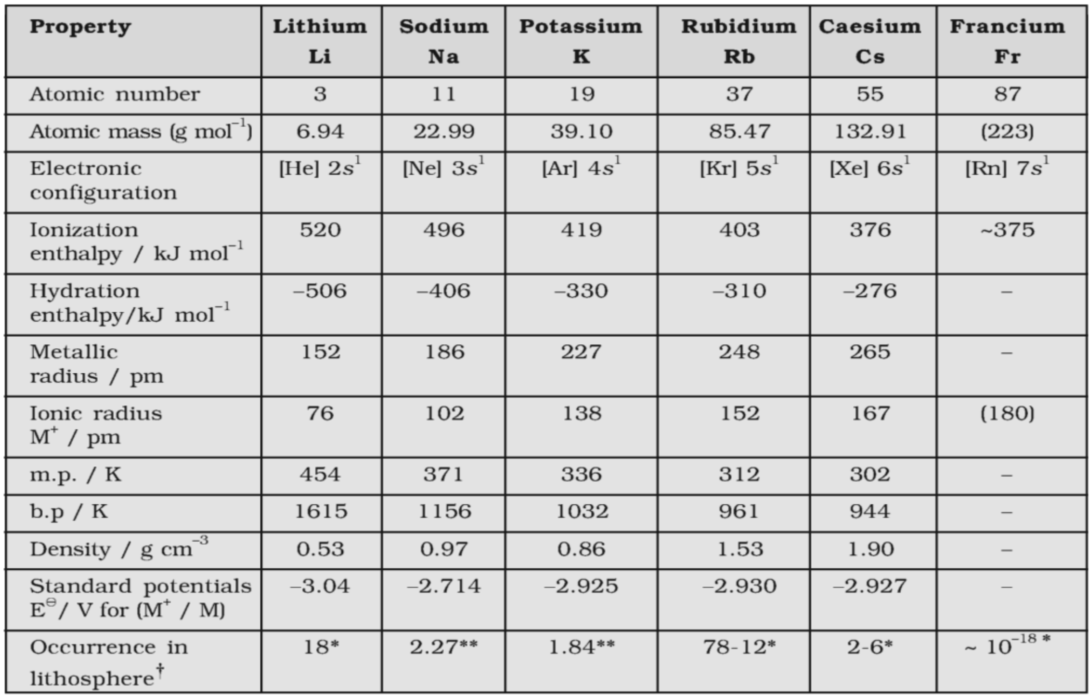
CHAPTER-9

THE S-BLOCK ELEMENTS

The s-block elements of the Periodic Table are those in which the last electron enters the outermost s-orbital. As the s-orbital can accommodate only two electrons, two groups (1 & 2) belong to the s-block of the Periodic Table. Group 1 of the Periodic Table consists of the elements: lithium, sodium, potassium, rubidium, caesium and francium. They are collectively known as the alkali metals. These are so called because they form hydroxides on reaction with water which are strongly alkaline in nature. The elements of Group 2 include beryllium, magnesium, calcium, strontium, barium and radium. These elements with the exception of beryllium are commonly known as the alkaline earth metals. These are so called because their oxides and hydroxides are alkaline in nature and these metal oxides are found in the earth's crust.

Among the alkali metals sodium and potassium are abundant and lithium, rubidium and caesium have much lower abundances (Table 9.1). Francium is highly radioactive; its longest-lived isotope ^{223}Fr has a half-life of only 21 minutes. Of the alkaline earth metals calcium and magnesium rank fifth and sixth in abundance respectively in the earth’s crust. Strontium and barium have much lower abundances. Beryllium is rare and radium is the rarest of all comprising only 10^{-10} per cent of igneous rocks (Table 9.2)

Table 9.1 Atomic and Physical Properties of Alkali Metals



Property	Lithium Li	Sodium Na	Potassium K	Rubidium Rb	Caesium Cs	Francium Fr
Atomic number	3	11	19	37	55	87
Atomic mass (g mol^{-1})	6.94	22.99	39.10	85.47	132.91	(223)
Electronic configuration	[He] $2s^1$	[Ne] $3s^1$	[Ar] $4s^1$	[Kr] $5s^1$	[Xe] $6s^1$	[Rn] $7s^1$
Ionization enthalpy / kJ mol^{-1}	520	496	419	403	376	~375
Hydration enthalpy/kJ mol^{-1}	–506	–406	–330	–310	–276	–
Metallic radius / pm	152	186	227	248	265	–
Ionic radius M^+ / pm	76	102	138	152	167	(180)
m.p. / K	454	371	336	312	302	–
b.p / K	1615	1156	1032	961	944	–
Density / g cm^{-3}	0.53	0.97	0.86	1.53	1.90	–
Standard potentials $E^{\ominus}$/ V for (M^+ / M)	–3.04	–2.714	–2.925	–2.930	–2.927	–
Occurrence in lithosphere†	18*	2.27**	1.84**	78-12*	2-6*	~ 10^{-18} *

**ppm (part per million), ** percentage by weight; † Lithosphere: The Earth’s outer layer: its crust and part of the upper mantle*

The general electronic configuration of s-block elements is [noble gas] ns^1 for alkali metals and [noble gas] ns^2 for alkaline earth metals.

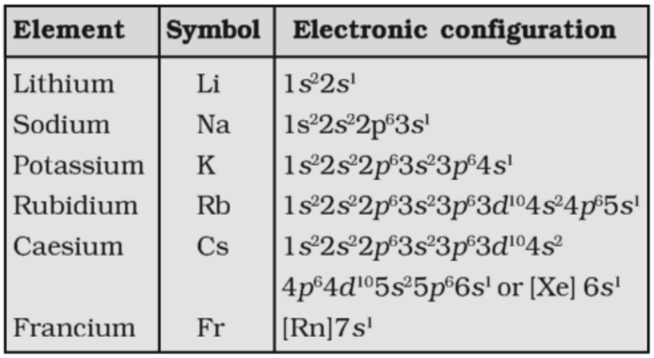
Lithium and beryllium, the first elements of Group I and Group II respectively exhibit some properties which are different from those of the other members of the respective group. In these anomalous properties they resemble the second element of the following group. Thus, lithium shows similarities to magnesium and beryllium to aluminium in many of their properties. This type of diagonal similarity is commonly referred to as diagonal relationship in the periodic table. The diagonal relationship is due to the similarity in ionic sizes and / or charge/ radius ratio of the elements. Monovalent sodium and potassium ions and divalent magnesium and calcium ions are found in large proportions in biological fluids. These ions perform important biological functions such as maintenance of ion balance and nerve impulse conduction.

9. 1 GROUP 1 Elements: Alkali Metals

The alkali metals show regular trends in their physical and chemical properties with the increase in atomic number. The atomic, physical and chemical properties of alkali metals are discussed below.

9. 1.1 Electronic Configuration

All the alkali metals have one valence electron, ns^1 (Table 9.1) outside the noble gas core. The loosely held s-electron in the outermost valence shell of these elements makes them the most electropositive metals. They readily lose electron to give monovalent M^+ ions. Hence they are never found in free state in nature



Element	Symbol	Electronic configuration
Lithium	Li	$1s^2 2s^1$
Sodium	Na	$1s^2 2s^2 2p^6 3s^1$
Potassium	K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
Rubidium	Rb	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$
Caesium	Cs	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$ $4p^6 4d^{10} 5s^2 5p^6 6s^1$ or $[Xe]\ 6s^1$
Francium	Fr	$[Rn] 7s^1$

9. 1.2 Atomic and Ionic Radii

The alkali metal atoms have the largest sizes in a particular period of the periodic table. With increase in atomic number, the atom becomes larger. The monovalent ions (M^+) are smaller than the parent atom. The atomic and ionic radii of alkali metals increase on moving down the group i.e., they increase in size while going from Li to Cs.

9.1.3 Ionization Enthalpy

The ionization enthalpies of the alkali metals are considerably low and decrease down the group from Li to Cs. This is because the effect of increasing size outweighs the increasing nuclear charge, and the outermost electron is very well screened from the nuclear charge.

9.1.4 Hydration Enthalpy

The hydration enthalpies of alkali metal ions decrease with increase in ionic sizes.

$$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$$

Li^+ has maximum degree of hydration and for this reason lithium salts are mostly hydrated, e.g., $LiCl.2H_2O$

9.2 General Characteristics of the Compounds of the Alkali Metals

All the common compounds of the alkali metals are generally ionic in nature. General characteristics of some of their compounds are discussed here.

9.2.1 Oxides and Hydroxides

On combustion in excess of air, lithium forms mainly theoxide, Li_2O (plus some peroxide Li_2O_2), sodium forms the peroxide, Na_2O_2 (and some superoxide NaO_2) whilst potassium, rubidium and caesium form the superoxides, MO_2. Under appropriate conditions pure compounds M_2O, M_2O_2 and MO_2 may be prepared. The increasing stability of the peroxide or superoxide, as the size of the metal ion increases, is due to the stabilisation of large anions by larger cations through lattice energy effects. These oxides are easily hydrolysed by water to form the hydroxides according to the following reactions:

$$M_2O + H_2O \rightarrow 2M^+ + 2\ OH^-$$

$$M_2O_2 + 2\ H_2O \rightarrow 2M^+ + 2\ OH^- + H_2O_2$$

The oxides and the peroxides are colourless when pure, but the superoxides are yellow or orange in colour. The superoxides are also paramagnetic. Sodium peroxide is widely used as an oxidising agent in inorganic chemistry.

The hydroxides which are obtained by the reaction of the oxides with water are all white crystalline solids. The alkali metal hydroxides are the strongest of all bases and dissolve freely in water with evolution of much heat on account of intense hydration.

9.2.2 Halides

The alkali metal halides, MX, (X= F, Cl, Br, I) are all high melting, colourless crystalline solids. They can be prepared by the reaction of the appropriate oxide, hydroxide or carbonate with aqueous hydrohalic acid (HX). All of these halides have high negative enthalpies of formation; the $\Delta_f H^-$ values for fluorides become less negative as we go down the group, whilst the reverse is true for $\Delta_f H^-$ for chlorides, bromides and iodides. F a given metal $\Delta_f H^-$ always becomes less negative from fluoride to iodide.

The melting and boiling points always follow the trend: fluoride > chloride > bromide > iodide. All these halides are soluble in water. The low solubility of LiF in water is due to its high lattice enthalpy whereas the low solubility of CsI is due to smaller hydration enthalpy of its two ions. Other halides of lithium are soluble in ethanol, acetone and ethylacetate; LiCl is soluble in pyridine also.

9.3 Anomalous Properties of Lithium

The anomalous behaviour of lithium is due to the: (i) exceptionally small size of its atom and ion, and (ii) high polarising power (i.e., charge/ radius ratio). As a result, there is increased covalent character of lithium compounds which is responsible for their solubility in organic solvents. Further, lithium shows diagonal relationship to magnesium which has been discussed subsequently.

9.3.1 Points of Difference between Lithium and other Alkali Metals

i. Lithium is much harder. Its m.p. and b.p. are higher than the other alkali metals.

ii. Lithium is least reactive but the strongest reducing agent among all the alkali metals. On combustion in air it farms mainly monoxide, Li_2O and the nitride, Li_3N unlike other alkali metals.

iii. LiCl is deliquescent and crystallises as a hydrate, $LiCl.2H_2O$ whereas other alkali metal chlorides do not form hydrates.

iv. Lithium hydrogen carbonate is not obtained in the solid form while all other elements form solid hydrogen carbonates.

v. Lithium unlike other alkali metals forms no ethynide on reaction with ethyne.

vi. Lithium nitrate when heated gives lithium oxide, Li_2O, whereas other alkali metal nitrates decompose to give the corresponding nitrite.

$$4\,LiNO_3 \rightarrow 2\,Li_2O + 4\,NO_2 + O_2$$

$$2\,NaNO_3 \rightarrow 2\,NaNO_2 + O_2$$

vii. LiF and Li_2O are comparatively much less soluble in water than the corresponding compounds of other alkali metals.

9.3.2 Points of Similarities between Lithium and Magnesium

The similarity between lithium and magnesium is particularly striking and arises because of their similar sizes: atomic radii, Li = 152 pm, Mg = 160 pm; ionic radii: Li^+ = 76 pm, Mg^{2+}= 72 pm. The main points of similarity are:

(i) Both lithium and magnesium are harder and lighter than other elements in the respective groups.

(ii) Lithium and magnesium react slowly with water. Their oxides and hydroxides are much less soluble and their hydroxides decompose on heating. Both form a nitride, Li_3N and Mg_3N_2, by direct combination with nitrogen.

(iii) The oxides, Li_2O and MgO do not combine with excess oxygen to give any superoxide.

(iv) The carbonates of lithium and magnesium decompose easily on heating to form the oxides and CO_2. Solid hydrogen carbonates are not formed by lithium and magnesium.

(v) Both LiCl and $MgC1_2$ are soluble in ethanol.

(vi) Both LiCl and $MgC1_2$ are deliquescent and crystallise from aqueous solution as hydrates, $LiC1.2H_2O$ and $MgC1_2.8H_2O$.

9.4 Biological Importance of Sodium and Potassium

A typical 70 kg man contains about 90 g of Na and 170 g of K compared with only 5 g of iron and 0.06 g of copper.

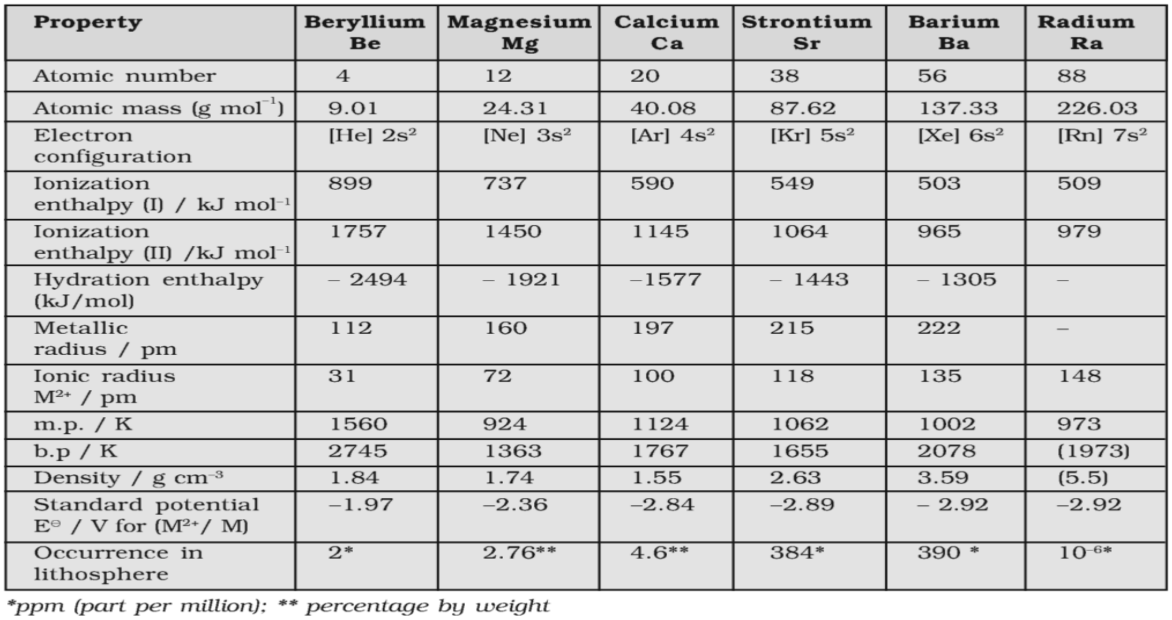
Sodium ions are found primarily on the outside of cells, being located in blood plasma and in the interstitial fluid which surrounds the cells. These ions participate in the transmission of nerve signals, in regulating the flow of water across cell membranes and in the transport of sugars and amino acids into cells. Sodium and potassium, although so similar chemically, differ quantitatively in their ability to penetrate cell membranes, in their transport mechanisms and in their efficiency to activate enzymes. Thus, potassium ions are the most abundant cations within cell fluids, where they activate many enzymes, participate in the oxidation of glucose to produce ATP and, with sodium, are responsible for the transmission of nerve signals.

There is a very considerable variation in the concentration of sodium and potassium ions found on the opposite sides of cell membranes. As a typical example, in blood plasma, sodium is present to the extent of 143 m.mol L^{-1} , whereas the potassium level is only 5 m.mol L^{-1} within the red blood cells. These concentrations change to 10 m. mol L^{-1} (Na^+) and 105 m. mol L^{-1} (K^+). These ionic gradients demonstrate that a discriminatory mechanism, called the sodium-potassium pump, operates across the cell membranes which consumes more than one-third of the ATP used by a resting animal and about 15 kg per 24 h in a resting human.

9.5 Group 2 Elements: Alkaline Earth Metals

The group 2 elements comprise beryllium, magnesium, calcium, strontium, barium and radium. They follow alkali metals in the periodic table. These (except beryllium) are known as alkaline earth metals. The first element beryllium differs from the rest of the members and shows diagonal relationship to aluminium . The atomic and physical properties of the alkaline earth metals are shown in Table 9.2.

Table 9.2 Atomic and Physical Properties of Alkaline Earth Metals

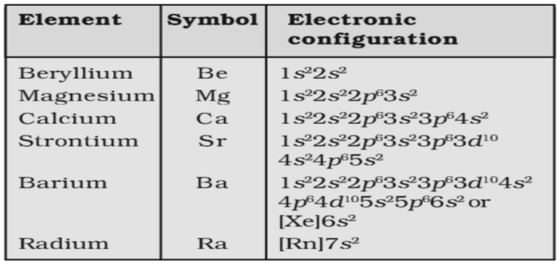


Property	Beryllium Be	Magnesium Mg	Calcium Ca	Strontium Sr	Barium Ba	Radium Ra
Atomic number	4	12	20	38	56	88
Atomic mass (g mol^{-1})	9.01	24.31	40.08	87.62	137.33	226.03
Electron configuration	[He] $2s^2$	[Ne] $3s^2$	[Ar] $4s^2$	[Kr] $5s^2$	[Xe] $6s^2$	[Rn] $7s^2$
Ionization enthalpy (I) / kJ mol^{-1}	899	737	590	549	503	509
Ionization enthalpy (II) /kJ mol^{-1}	1757	1450	1145	1064	965	979
Hydration enthalpy (kJ/mol)	– 2494	– 1921	–1577	– 1443	– 1305	–
Metallic radius / pm	112	160	197	215	222	–
Ionic radius M^{2+} / pm	31	72	100	118	135	148
m.p. / K	1560	924	1124	1062	1002	973
b.p / K	2745	1363	1767	1655	2078	(1973)
Density / g cm^{-3}	1.84	1.74	1.55	2.63	3.59	(5.5)
Standard potential $E^\ominus$ / V for (M^{2+}/ M)	–1.97	–2.36	–2.84	–2.89	– 2.92	–2.92
Occurrence in lithosphere	2*	2.76**	4.6**	384*	390 *	10^{-6}*

**ppm (part per million): ** percentage by weight*

9.5.1 Electronic Configuration

These elements have two electrons in the s-orbital of the valence shell (Table 9.2). Their general electronic configuration may be represented as [noble gas] ns^2. Like alkali metals, the compounds of these elements are also predominantly ionic.



Element	Symbol	Electronic configuration
Beryllium	Be	$1s^2 2s^2$
Magnesium	Mg	$1s^2 2s^2 2p^6 3s^2$
Calcium	Ca	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
Strontium	Sr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ $4s^2 4p^6 5s^2$
Barium	Ba	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$ $4p^6 4d^{10} 5s^2 5p^6 6s^2$ or $[Xe]6s^2$
Radium	Ra	$[Rn]7s^2$

9.5.2 Atomic and Ionic Radii

The atomic and ionic radii of the alkaline earth metals are smaller than those of the corresponding alkali metals in the same periods. This is due to the increased nuclear charge in these elements. Within the group, the atomic and ionic radii increase with increase in atomic number.

9.5.3 Ionization Enthalpies

The alkaline earth metals have low ionization enthalpies due to fairly large size of the atoms. Since the atomic size increases down the group, their ionization enthalpy decreases (Table 9.2). The first ionisation enthalpies of the alkaline earth metals are higher than those of the corresponding Group 1 metals. This is due to their small size as compared to the corresponding alkali metals. It is interesting to note that the second ionisation enthalpies of the alkaline earth metals are smaller than those of the corresponding alkali metals.

9.5.4 Hydration Enthalpies

Like alkali metal ions, the hydration enthalpies of alkaline earth metal ions decrease with increase in ionic size down the group.

$$Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$$

The hydration enthalpies of alkaline earth metal ions are larger than those of alkali metal ions. Thus, compounds of alkaline earth metals are more extensively hydrated than those of alkali metals, e.g., $MgC1_2$ and $CaC1_2$ exist as $MgC1_2.6H_2O$ and $CaC1_2$. $6H_2O$ while NaCl and KCl do not form such hydrates.

9.6 General Characteristics of Compounds of the Alkaline Earth Metals

The dipositive oxidation state (M^{2+}) is the predominant valence of Group 2 elements. The alkaline earth metals form compounds which are predominantly ionic but less ionic than the corresponding compounds of alkali metals. This is due to increased nuclear charge and smaller size. The oxides and other compounds of beryllium and magnesium are more covalent than those formed by the heavier and large sized members (Ca, Sr, Ba). The general characteristics of some of the compounds of alkali earth metals are described below.

(i) Oxides and Hydroxides: The alkaline earth metals burn in oxygen to form the monoxide, MO which, except for BeO, have rock-salt structure. The BeO is essentially covalent in nature. The enthalpies of formation of these oxides are quite high and consequently they are very stable to heat. BeO is amphoteric while oxides of other elements are ionic in nature. All these oxides except BeO are basic in nature and react with water to form sparingly soluble hydroxides.

$$MO + H_2O \rightarrow M\ OH_{\ 2}$$

The solubility, thermal stability and the basic character of these hydroxides increase with increasing atomic number from $Mg(OH)_2$ to Ba $(OH)_2$. The alkaline earth metal hydroxides are, however, less basic and less stable than alkali metal hydroxides. Beryllium hydroxide is amphoteric in nature as it reacts with both acid and alkali.

$$\mathrm{Be\ \ OH}_{\ 2} + 2OH^{-} \rightarrow \left[\mathrm{Be\ \ OH}_{\ 4}\right]^{2-}$$

Beryllate ion

$$\mathrm{Be\ \ OH}_{\ 2} + 2HC1 + 2H_2O \rightarrow \left[\mathrm{Be\ \ OH}_{\ 4}\right]Cl_2$$

(ii) Halides: Except for beryllium halides, all other halides of alkaline earth metals are ionic in nature. Beryllium halides are essentially covalent and soluble in organic solvents. Beryllium chloride has a chain structure in the solid state as shown below:

In the vapour phase $BeC1_2$ tends to form a chloro-bridged dimer which dissociates into the linear monomer at high temperatures of the order of 1200 K. The tendency to form halide hydrates gradually decreases (for example, $MgC1_2$. $8H_2O$, $CaC1_2$. $6H_2O$, $SrC1_2$. $6H_2O$ and $BaC1_2$. $2H_2O$) down the group. The dehydration of hydrated chlorides, bromides and iodides of Ca, Sr and Ba can be achieved on heating; however, the corresponding hydrated halides of Be and Mg on heating suffer hydrolysis. The fluorides are relatively less soluble than the chlorides owing to their high lattice energies.

9.7 Anomalous Behaviour of Beryllium

Beryllium, the first member of the Group 2 metals, shows anomalous behaviour as compared to magnesium and rest of the members. Further, it shows diagonal relationship to aluminium which is discussed subsequently.

I. Beryllium has exceptionally small atomic and ionic sizes and thus does not compare well with other members of the group. Because of high ionisation enthalpy and small size it forms compounds which are largely covalent and get easily hydrolysed.

II. Beryllium does not exhibit coordination number more than four as in its valence shell there are only four orbitals. The remaining members of the group can have a coordination number of six by making use of d-orbitals.

III. The oxide and hydroxide of beryllium , unlike the hydroxides of other elements in the group, are amphoteric in nature.

Diagonal Relationship between Beryllium and Aluminium

The ionic radiusof Be^{2+} is estimated to be 31 pm; the charge/radius ratio is nearly the same as that of the Al^{3+} ion. Hence beryllium resembles aluminium in some ways. Some of the similarities are:

I. Like aluminium, beryllium is not readily attacked by acids because of the presence of an oxide film on the surface of the metal.

II. Beryllium hydroxide dissolves in excess of alkali to give a beryllate ion, $[Be(OH)_4]^{2-}$ just as aluminium hydroxide gives $[Al(OH)_4]^-$

III. The chlorides of both beryllium and aluminiu have Cl^- bridged chloride structure in vapour phase. Both the chlorides are soluble in organic solvents and are strong Lewis acids. They are used as Friedel Craft catalysts.

IV. Beryllium and aluminium ions have strong tendency to form complexes, BeF_4^{2-}, AIF_6^{3-}

9.8 Biological Importance of Magnesium and Calcium

An adult body contains about 25 g of Mg and 1200 g of Ca compared with only 5 g of iron and 0.06 g of copper. The daily requirement in the human body has been estimated to be 200 - 300 mg of Ca.

All enzymes that utilise ATP in phosphate transfer require magnesium as the cofactor. The main pigment for the absorption of light in plants is chlorophyll which contains magnesium. About 99% of body calcium is present in bones and teeth. It also plays important roles in neuromuscular function, interneuronal transmission, cell membrane integrity and blood coagulation. The calcium concentration in plasma is regulated at about 100 mgL^{-1}. It is maintained by two hormones: calcitonin and parathyroid hormone. Do you know that bone is not an inert and unchanging substance but is continuously being solubilised and redeposited to the extent of 400 mg per day in man? All this calcium passes through the plasma.

SUMMARY

The s-Block of the periodic table constitutes Group l (alkali metals) and Group 2 (alkaline earth metals). They are so called because their oxides and hydroxides are alkaline in nature. The alkali metals are characterised by one s-electron and the alkaline earth metals by two s-electrons in the valence shell of their atoms. These are highly reactive metals forming monopositive (M^+) and dipositve (M^{2+}) ions respectively.

There is a regular trend in the properties of the alkali metal with increasing atomic numbers. The atomic and ionic sizes increase and the ionization enthalpies decrease systematically down the group. Somewhat similar trends are observed among the properties of the alkaline earth metals.

The first element in each of these groups, lithium in Group 1 and beryllium in Group 2 shows similarities in properties to the second member of the next group. Such similarities are termed as the 'diagonal relationship' in the period ic table. As such these elements are anomalous as far as their group characteristics are concerned.

The alkali metals are silvery white, soft and low melting. They are highly reactive. The compounds of alkali metals are predominantly ionic. Their oxides and hydroxides are soluble in water forming strong alkalies. The chemistry of alkaline earth metals is very much like that of the alkali metals. However, some differences arise because of reduced atomic and ionic sizes and increased cationic charges in case of alkaline earth metals. Their oxides and hydroxides are less basic than the alkali metal oxides and hydroxides. Monovalent sodium and potassium ions and divalent magnesium and calcium ions are found in large proportions in biological fluids. These ions perform important biological functions such as maintenance of ion balance and nerve impulse conduction.

EXERCISES

8.1 Discuss the general characteristics and gradation in properties of alkaline earth metals.

8.2 Why are alkali metals not found in nature ?

8.3 Compare the alkali metals and alkaline earth metals with respect to ionisation enthalpy

8.4 In what ways lithium shows similarities to magnesium in its chemical behaviour?

QUESTION BANK

Short Answer Questions **(4 Marks)**

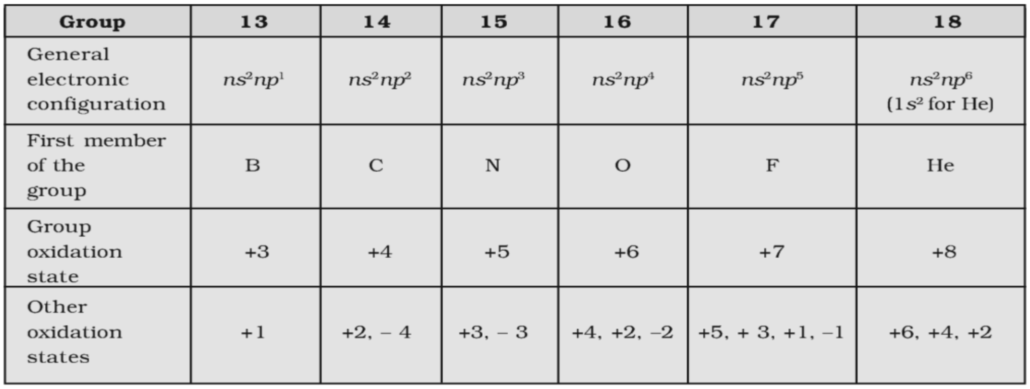
1. Write completely the electronic configuration of K and Rb?
2. Lithium salts are mostly hydrated. Why?
3. In what respects lithium hydrogen carbonate differs from other alkali metal hydrogen carbonates?
4. Give an account of the biological importance of Na^+ and K^+ ions.
5. Write the complete electronic configurations of any two alkaline earth metals?
6. What happens when magnesium metal is burnt in air?
7. Why are alkali metals not found in the Free State in nature?
8. Give an account of the biological importance of Ca^{2+}, Mg^{2+} ions.

CHAPTER -10

THE P-BLOCK ELEMENTS - GROUP 13

In p-block elements the last electron enters the outermost p orbital. As we know that the number of p orbitals is three and, therefore, the maximum number of electrons that can be accommodated in a set of p orbitals is six. Consequently there are six groups of p-block elements in the periodic table numbering from 13 to 18. Boron, carbon, nitrogen, oxygen, fluorine and helium head the groups. Their valence shell electronic configuration is ns^2np^{1-6} (except for He). The inner core of the electronic configuration may, however, differ. The difference in inner core of elements greatly influences their physical properties (such as atomic and ionic radii, ionisation enthalpy, etc.) as well as chemical properties. Consequently, a lot of variation in properties of elements in a group of p-block is observed. The maximum oxidation state shown by a p-block element is equal to the total number of valence electrons (i.e., the sum of the s- and p-electrons). Clearly, the number of possible oxidation states increases towards the right of the periodic table. In addition to this so called group oxidation state, p-block elements may show other oxidation states which normally, but not necessarily, differ from the total number of valence electrons by unit of two. The important oxidation states exhibited by p-block elements are shown in Table 10.1. In boron, carbon and nitrogen families the group oxidation state is the most stable state for the lighter elements in the group. However, the oxidation state two units less than the group oxidation state become progressively more stable for the heavier elements in each group. The occurrences of oxidation states two unit less than the group oxidation states are sometime attributed to the ‘inert pair effect'. The relative stabilities of these two oxidation states-group oxidation state and two units less than the group oxidation state -may vary from group to group and will be discussed at appropriate places.

Table 10.1 General electronic configurations and oxidation states of p-block elements



Group	13	14	15	16	17	18
General electronic configuration	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6 ($1s^2$ for He)
First member of the group	B	C	N	O	F	He
Group oxidation state	+3	+4	+5	+6	+7	+8
Other oxidation states	+1	+2, – 4	+3, – 3	+4, +2, –2	+5, + 3, +1, –1	+6, +4, +2

It is interesting to note that the non-metals and metalloids exist only in the p-block of the periodic table. The non-metallic character of elements decreases down the group. In fact the heaviest element in each p-block group is the most metallic in nature. This change from non- metallic to metallic character brings diversity in the chemistry of these elements depending on the group to which they belong.

In general, non-metals have higher ionisation enthalpies and higher electronegativities than the metals. Hence, in contrast to metals which readily form cations, non-metals readily form anions. The compounds formed by highly reactive non-metals with highly reactive metals are generally ionic because of large differences in their electronegativities. On the other hand compounds formed between non-metals themselves are largely covalent in character because of small differences in their electronegativities. The change of non-metallic to metallic character can be best illustrated by the nature of oxides they form. The non-metal oxides are acidic or neutral whereas metal oxides are basic in nature.

The first member of p -block differs from the remaining members of their corresponding group in two major respects. First is the size and all other properties which depend on size. Thus, the lightest p-block elements show the same kind of differences as the lightest s-block elements, lithium and beryllium. The second important difference, which applies only to the p-block elements, arises from the effect of d-orbitals in the valence shell of heavier elements (starting from the third period onwards) and their lack in second period elements. The second period elements of p-groups starting from boron are restricted to a maximum covalence of four (using 2s and three 2p orbitals). In contrast, the third period elements of p-groups with the electronic configuration $3s^2 3p^n$ have the vacant 3d orbitals lying between the 3p and the 4s levels of energy. Using these d-orbitals the third period elements can expand their covalence above four. For example, while boron forms only [BF], aluminium gives $[AlF_6]^{3-}$ ion. The presence of these d-orbitals influences the chemistry of the heavier elements in a number of other ways. The combined effect of size and availability of d orbitals considerably influences the ability of these elements to form π bonds. The first member of a group differs from the heavier members in its ability to form $p\pi - p\pi$ multiple bonds to itself (e.g., C=C, $C \equiv C$, $N \equiv N$) and to other second row elements (e.g., C=O, C=N, $C \equiv N$, N=O). This type of π - bonding is not particularly strong for the heavier p-block elements. The heavier elements do fonn π bonds but this involves d orbitals ($d\pi - p\pi$ or $d\pi - d\pi$). As the d orbitals are of higher energy than the p orbitals, they contribute less to the overall stability of molecules than does $p\pi - p\pi$ bonding of the second row elements. However, the coordination number in species of heavier elements may be higher than for the first element in the same oxidation state. For example, in +5 oxidation state both N and P form oxoanions : NO_3^- (three-coordination with π -bond involving one nitrogen p-orbital) and PO_4^{3-} (four -coordination involving s, p and d orbitals contributing to the π -bond). In this unit we will study the chemistry of group 13 and 14 elements of the periodic table.

10.1 Group 13 Elements: The Boron Family

This group elements show a wide variation in properties. Boron is a typical non-metal, aluminium is a metal but shows many chemical similarities to boron, and gallium, indium and thallium are almost exclusively metallic in character.

Boron is a fairly rare element, mainly occurs as orthoboric acid, (H_3BO_3), borax, $Na_2B_4O_7 . 10H_2O$, and kernite, $Na_2B_4O_7 . 4H_2O$. In India borax occurs in Puga Valley (Ladakh) and Sambhar Lake (Rajasthan). The abundance of boron in earth crust is less than 0.0001% by mass. There are two isotopic forms of boron ^{10}B (19%) and ^{11}B (81%) . Aluminium is the most abundant metal and the third most abundant element in the earth's crust (8.3% by mass) after oxygen (45.5%) and Si (27.7%). Bauxite, $Al_2O_3 . 2H_2O$ and cryolite, Na_3AlF_6 are the important minerals of aluminium. In India it is found as mica in Madhya Pradesh, Karnataka, Orissa and Jammu. Gallium, indium and thallium are less abundant elements in nature.

The atomic, physical and chemical properties of these elements are discussed below.

10.1.1 Electronic Configuration:

The outer electronic configuration of these elements is ns^2 np^1. A close look at the electronic configuration suggests that while boron and aluminium have noble gas core, gallium and indium have noble gas plus 10 d-electrons, and thallium has noble gas plus 14 f- electrons plus 10 d-electrons cores. This difference in electronic structures affects the other properties and consequently the chemistry of all the elements of this group.

10.1.2 Atomic Radii

On moving down the group, for each successive member one extra shell of electrons is added and, therefore, atomic radius is expected to increase. However, a deviation can be seen. Atomic radius of Ga is less than that of Al. This can be understood from the variation in the inner core of the electronic configuration. The presence of additional 10 d-electrons offer only poor screening effect for the outer electrons from the increased nuclear charge in gallium. Consequently, the atomic radius of gallium (135 pm) is less than that of aluminium (143 pm) .

10.1.3 Ionization Enthalpy

The ionisation enthalpy values as expected from the general trends do not decrease smoothly down the group. The decrease from B to Al is associated with increase in size. The observed discontinuity in the ionisation enthalpy values between Al and Ga, and between In and Tl are due to inability of d- and f-electrons, which have low screening effect, to compensate the increase in nuclear charge.

The order of ionisation enthalpies, as expected, is $\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3$. The sum of the first three ionisation enthalpies for each of the elements is very high. Effect of this will be apparent when you study their chemical properties.

10.1.4 Electronegativity

Down the group, electronegativity first decreases from B to Al and then increases marginally. This is because of the discrepancies in atomic size of the elements.

10.2. Physical Properties

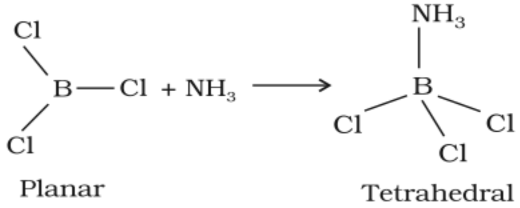
Boron is non-metallic in nature. It is extremely hard and black coloured solid. It exists in many allotropic forms. Due to very strong crystalline lattice, boron has unusually high melting point. Rests of the members are soft metals with low melting point and high electrical conductivity. It is worthwhile to note that gallium with unusually low melting point (303K), could exist in liquid state during summer. Its high boiling point (2676 K) makes it a useful material for measuring high temperatures. Density of the elements increases down the group from boron to thallium.

10.3 Chemical Properties

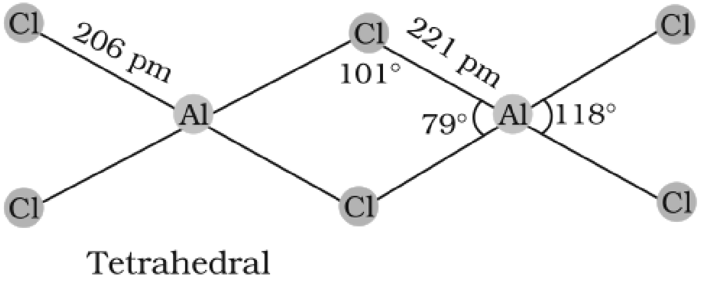
10.3.1 Oxidation state and trends in chemical reactivity

Due to small size of boron, the sum of its first three ionization enthalpies is very high. This prevents it to form +3 ions and forces it to form only covalent compounds. But as we move from B to Al, the sum of the first three ionisation enthalpies of Al considerably decreases, and is therefore able to form Al^{3+} ions. In fact, aluminium is a highly electropositive metal. However, down the group, due to poor shielding effect of intervening d and f orbitals, the increased effective nuclear charge holds ns electrons tightly (responsible for inter pair effect) and thereby, restricting their participation in bonding. As a result of this, only p-orbital electron may be involved in bonding. In fact in Ga, In and Tl, both +1 and +3 oxidation states are observed. The relative stability of +1 oxidation state progressively increases for heavier elements: Al < Ga < ln < Tl. In thallium +1 oxidation state is predominant whereas the +3 oxidation state is highly oxidising in character. The compounds in +1 oxidation state, as expected from energy considerations, are more ionic than those in +3 oxidation state.

In trivalent state, the number of electrons around the central atom in a molecule of the compounds of these elements (e.g., boron in BF_3) will be only six. Such electron deficient molecules have tendency to accept a pair of electrons to achieve stable electronic configuration and thus, behave as Lewis acids. The tendency to behave as Lewis acid decreases with the increase in the size down the group. $BC1_3$ easily accepts a lone pair of electrons from ammonia to form $BC1_3$. NH_3.



$AIC1_3$ achieves stability by forming a dimer



In trivalent state most of the compounds being covalent are hydrolysed in water. For example, the trichlorides on hyrolysis in water form tetrahedral $[M\ (OH)_4]^-$ species; the hybridization state of element M is sp^3. Aluminium chloride in acidified aqueous solution forms octahedral $[Al\ (H_2O)_6]^{3+}$ ion In this complex ion, the 3d orbitals of Al are involved and the hybridisation state of Al is sp^3d^2.

(i) Reactivity towards air:

Boron is unreactive in crystalline form. Aluminium forms a very thin oxide layer on the surface which protects the metal from further attack. Amorphous boron and aluminium metal on heating in air form B_2O_3 and Al_2O_3 respectively. With dinitrogen at high temperature they form nitrides.

$$4\ E(s) + 3\ O_2(g) \xrightarrow{\Delta} 2\ E_2O_3\ (s)$$

$$2\ E(s) + N_2(g) \xrightarrow{\Delta} 2\ EN\ (s) \qquad (E = \text{element})$$

The nature of these oxides varies down the group. Boron trioxide is acidic and reacts with basic (metallic) oxides forming metal borates. Aluminium and gallium oxides are amphoteric and those of indium and thallium are basic in their properties.

(ii) Reactivity towards acids and alkalies:

Boron does not react with acids and alkalies even at moderate temperature; but aluminium dissolves in mineral acids and aqueous alkalies and thus shows amphoteric character.

Aluminium dissolves in dilute HCl and liberates dihydrogen.

$$2\,\text{Al}(\text{s}) + 6\,\text{HC1}(\text{aq}) \rightarrow 2\,\text{A1}^{3+}(\text{aq}) + 6\,\text{Cl}^{-}(\text{aq}) + 3\,\text{H}_2(\text{g})$$

However, concentrated nitric acid renders aluminium passive by forming a protective oxide layer on the surface. Aluminium also reacts with aqueous alkali and liberates dihydrogen.

$$2\,\text{Al}(\text{s}) + 2\,\text{NaOH}(\text{aq}) + 6\,\text{H}_2\text{O}(\text{l}) \rightarrow \underset{\text{Sodium tetrahydroxoaluminate (III)}}{2\text{Na}^{+}[\text{Al}(\text{OH})_4]^{-}(\text{aq})} + 3\,\text{H}_2(\text{g})$$

(iii) Reactivity towards halogens:

These elements react with halogens to form trihalides (except Tl I_3) .

$$2\,\text{E}(\text{s}) + 3\,\text{X}_2(\text{g}) \rightarrow 2\,\text{EX}_3(\text{s}) \qquad (\text{X} = \text{F, Cl, Br, I})$$

10.4 Important Trends and Anomalous Properties of Boron

Certain important trends can be observed in the chemical behavior of group 13 elements. The tri-chlorides, bromides and iodides of all these elements being covalent in nature are hydrolysed in water. Species like tetrahedral $[\text{M(OH)}_4]^-$ and $[\text{M(H}_2\text{O)}_6]^{3+}$, except in boron, exist in aqueous medium.

The monomeric trihalides, being electron deficient, are strong Lewis acids. Boron trifluoride easily reacts with Lewis bases such as NH_3 to complete octet around boron.

$$\text{F}_3\text{B} + :\text{NH}_3 \longrightarrow \text{F}_3\text{B} \leftarrow \text{NH}_3$$

It is due to the absence of d orbitals that the maximum covalence of B is 4. Since the d orbitals are available with Al and other elements, the maximum covalence can be expected beyond 4. Most of the other metal halides (e.g., AlCl_3) are dimerised through halogen bridging (e.g., $\text{A1}_2\text{Cl}_6$). The metal species completes its octet by accepting electrons from halogen in these halogen bridged molecules.

10.5 Some Important Compounds of Boron

Some useful compounds of boron are borax, orthoboric acid and diborane. We will briefly stu dy their chemistry.

10.5. 1 Borax:

It is the most important compound of boron. It is a white crystalline solid of formula $\text{Na}_2\text{B}_4\text{O}_7.10\text{H}_2\text{O}$. In fact it contains the tetranuclear units $[\text{B}_4\text{O}_5\,(\text{OH})_4]^{2-}$ and correct formula; therefore, is $\text{Na}_2[\text{B}_4\text{O}_5\,(\text{OH})_4]$.8 H2O. Borax dissolves in water to give an alkaline solution.

$$\text{Na}_2\text{B}_4\text{O}_7 + 7\,\text{H}_2\text{O} \rightarrow 2\,\text{NaOH} + \underset{\text{Ortho boric acid}}{4\,\text{H}_3\text{BO}_3}$$

On heating, borax first loses water molecules and swells up. On further heating it turns into a transparent liquid, which solidifies into glass like material known as borax bead.

$$Na_2B_4O_7.10\,H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} \underset{\text{sod. meta borate}}{2\,NaBO_2} + \underset{\text{boric anhydride}}{B_2O_3}$$

The metaborates of many transition metals have characteristic colours and, therefore, borax bead test can be used to identify them in the laboratory. For example, when borax is heated in a Bunsen burner flame with CoO on a loop of platinum wire, a blue coloured $Co(BO_2)_2$ bead is formed.

10.5.2 Diborane, B_2H_6

The simplest boron hydride known, is diborane. It is prepared by treating boron trifluoride with $LiAIH_4$ in diethyl ether.

$$4\,BF_3 + 3\,LiAIH_4 \rightarrow 2\,B_2H_6 + 3\,LiF + 3\,AIF_3$$

A convenient laboratory method for the preparation of diborane involves the oxidation of sodium borohydride with iodine.

$$2\,NaBH_4 + I_2 \rightarrow B_2H_6 + 2\,NaI + H_2$$

Diborane is produced on an industrial scale by the reaction of BF_3 with sodium hydride.

$$2\,BF_3 + 6\,NaH \xrightarrow{450K} B_2H_6 + 6\,NaF$$

Diborane is a colourless, highly toxic gas with a b.p. of 180K. Diborane catches fire spontaneously upon exposure to air. It burns in oxygen releasing an enormous amount of energy.

$$B_2H_6 + 3\,O_2 \rightarrow B_2O_3 + 3\,H_2O \qquad \Delta_C H^- = -1976\ kJ\ mol^{-1}$$

Most of the higher boranes are also spontaneously flammable in air. Boranes are readily hydrolysed by water to give boric acid.

$$B_2H_6(g) + 6\,H_2O(l) \rightarrow 2\,B(OH)_3(aq) + 6\,H_2(g)$$

Diborane undergoes cleavage reactions with Lewis bases (L) to give borane adducts, $BH_3.L$

$$B_2H_6 + 2\,NMe_3 \rightarrow 2\,BH_3.NMe_3$$
$$B_2H_6 + 2\,CO \rightarrow 2\,BH_3.CO$$

Reaction of ammonia with diborane gives initially $B_2H_6.2NH_3$ which is formulated as $[BH_2(NH_3)_2]^+[BH_4]^-$; further heating gives borazine, $B_3N_3H_6$ known as "inorganic benzene" in view of its ring structure with alternate BH and NH groups.

$$3\,B_2H_6 + 6\,NH_3 \rightarrow 3\left[BH_2(NH_3)_2\right]^+\left[BH_4\right]^- \xrightarrow{heat} 2\,B_3N_3H_6 + 12\,H_2$$

The structure of diborane is shown in Fig. 10.1(a). The four terminal hydrogen atoms and the two boron atoms lie in one plane. Above and below this plane, there are two bridging hydrogen atoms. The four terminal B-H bonds are regular two centre-two electron bonds while the two bridge (B-H-B) bonds are different and can be described in terms of three centre-two electron bon ds shown in Fig.10.1 (b).

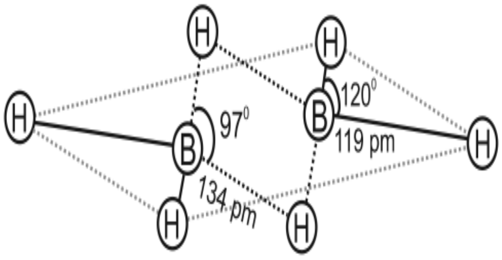


Fig.10.1(a) The structure of diborane, B_2H_6

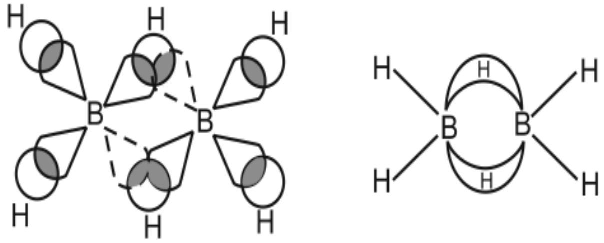


Fig.10.1 (b) Bonding in diborane. Each B atom uses sp3 hy brids for bonding. Out of the four sp3 hy brids on each B atom, one is without an electron shown in broken lines. The terminal B-H bonds are normal 2-centre-2-electron bonds but the two bridge bonds are 3-centre-2-electron bonds. The 3-centre-2-electron bridge bonds are also ref erred to as banana bonds.

Boron also forms a series of hydridoborates; the most important one isthe tetrahedral $[BH_4]^-$ ion. Tetrahydridoborates of several metals are known. Lithium and sodium tetra- hydrtdoborates, also known as borohydrides, are prepared by the reaction of metal hydrides with B_2H_6 in diethyl ether.

$$2\ MH + B_2H_6 \rightarrow 2\ M^+\left[BH_4\right]^- \qquad (M= Li\ or\ Na)$$

Both $LiBH_4$ and $NaBH_4$ are used as reducing agents in organic synthesis. They are useful starting materials for preparing other metal borohydrides.

10.6 Uses of Boron and Aluminium and Their Compounds

Boron being extremely hard refractory solid of high melting point, low density and very low electrical conductivity, finds many applications. Boron fibres are used in making bullet-proof vest and light composite material for aircraft. The boron-10 (^{10}B) isotope has high ability to absorb neutrons and, therefore, metal borides are used in nuclear industry as protective shields and control rods. The main industrial application of borax and boric acid is in the manufacture of heat resistant glasses (e.g., Pyrex) , glass-wool and fibre glass. Borax is also used as a flux for soldering metals, for heat, scratch and stain resistant glazed coating to earthen wares and as constituent of medicinal soaps. An aqueous solution of orthoboric acid is generally used as a mild antiseptic.

Aluminium is a bright silveiy-white metal, with high tensile strength. It has a high electrical and thermal conductivity. On a weight-to-weight basis, the electrical conductivity of aluminium is twice that of copper. Aluminium is used extensively in industry and everyday life. It forms alloys with Cu, Mn, Mg, Si and Zn. Aluminium and its alloys can be given shapes of pipe, tubes, rods, wires, plates or foils and, therefore, find uses in packing, utensil making, construction, aeroplane and transportation industry. The use of aluminium and its compounds for domestic purposes is now reduced considerably because of their toxic nature.

SUMMARY

P-block of the periodic table is unique in terms of having all types of elements - metals, nonmetals and metalloids. There are six groups of p-block elements in the periodic table numbering from 13 to 18. There valence shell electronic configuration is ns^2np^{1-6}(except for He). Differences in the inner core of their electronic configuration greatly influence their physical and chemical properties as a consequence of this, a lot of variation in properties among these elements is observed. In addition to the group oxidation state these elements show other oxidation states different from the total number of valence electrons by unit of two. While the group oxidation state is the most stable for the lighter elements of the group, lower oxidation states become progressively more stable for the heavier elements. The combined effect to size and availability of the orbitals considerably influence the ability of these elements to form π bonds. Absence of d orbital in second period elements limits their maximum covalence to 4 while heavier ones can exceed this.

Boron is a typical non-metal and the other members are metals. The availability of 3 valence electrons ($2s^22p^1$) for covalent bond formation using four orbitals (2s, $2p_x$. $2p_y$ and $2p_z$) leads to the so called electron deficiency in boron compounds. This deficiency makes them good electron acceptor and thus boron compounds behave as Lewis acids. Boron forms covalent molecular compounds with dihydrogen as boranes, the simplest of which is diborane, B_2H_6. Diborane contains two bridging hydrogn atoms between two boron atoms; these bridge bonds are considered to be three-center two-electron bonds. The important compounds of boron with dioxygen are boric acid andd borax. Boric acid, $B(OH)_3$ is a weak monobasic acid; it acts as a Lewis acid by accepting electrons from hydroxy ion. Borax is a white crystalline solid of formula $Na_2\ [B_4O_5(OH)_4\ ].8H_2O$. The borax bead test gives characteristic colours of transition metals. Aluminium exhibits +3 oxidation state. With heavier elements +1 oxidation state gets progressively stabilised on going down the group. This is a consequence of the so called inert pair effect.

EXERCISE

10.1 Discuss the pattern of variation in the oxidation states of B to Tl

10.2 How can you explain higher stability of $BC1_3$ as compared to $TIC1_3$?

10.3 Why does boron triflouride behave as a Lewis acid ?

10.4 Describe the shapes of BF_3 and BH_4^-. Assign the hybridisation of boron in these species.

10.5 Write reactions to justify amphoteric nature of aluminium.

10.6 Suggest reasons why the B-F bond lengths in BF_3(130 pm) and BF_4^- (143 pm) differ.

10.7 Explain structures of diborane

QUESTION BANK

Very Short Answer Questions (2 Marks)

1. Why does BF_3 behave as a Lewis acid?
2. Explain inert pair effect?
3. Give the formula of borazine, What is its common name?
4. Give the formula of a) Borax b) colemanite
5. Give two uses of aluminum?
6. Explain the structure of diborane?
7. Give two uses of Aluminum.
8. What are electron deficient compounds?

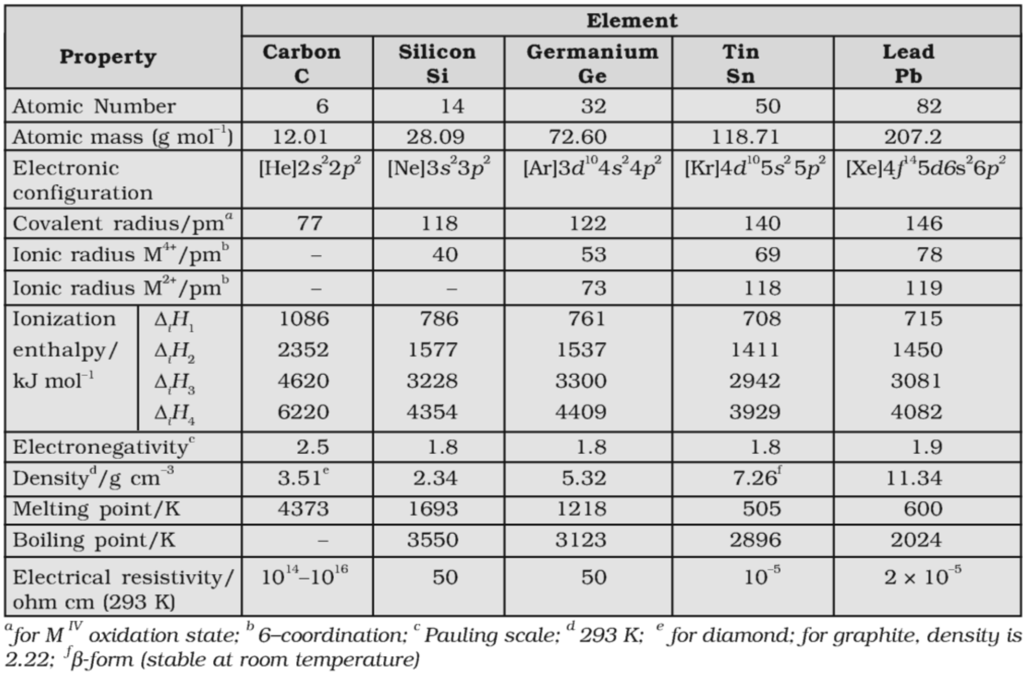
CHAPTER-11

P-BLOCK ELEMENTS - GROUP 14

11.1 Group 14 Elements: The Carbon Family

Carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb) are the members of group 14. Carbon is the seventeenth most abundant element by mass in the earth's crust. It is widely distributed in nature in free as well as in the combined state. In elemental state it is available as coal, graphite and diamond; however, in combined state it is present as metal carbonates, hydrocarbons and carbon dioxide gas (0 .03%) in air. One can emphatically say that carbon is the most versatile element in the world. Its combination with other elements such as hydrogen, oxygen, chlorine and sulphur provides an astonishing array of materials ranging from living tissues to drugs and plastics. Organic chemistry is devoted to carbon containing compounds. It is an essential constituent of all living organisms. Naturally occurring carbon contains two stable isotopes: ^{12}C and ^{13}C. In addition to these, third isotope, ^{14}C is also present. It is a radioactive isotope with half- life 5770 years and used for radiocarbon dating. Silicon is the second (27.7 % by mass) most abundant element on the earth's crust and is present in nature in the form of silica and silicates. Silicon is a very important component of ceramics, glass and cement. Germanium exists only in traces. Tin occurs mainly as cassiterite, SnO_2 and lead as galena, PbS. Ultrapure form of germanium and silicon are used to make transistors and semiconductor devices.

Table 11.1 Atomic and Physical Properties of Group 14 Elements



Property		Element				
		Carbon C	**Silicon Si**	**Germanium Ge**	**Tin Sn**	**Lead Pb**
Atomic Number		6	14	32	50	82
Atomic mass (g mol^{-1})		12.01	28.09	72.60	118.71	207.2
Electronic configuration		$[He]2s^2 2p^2$	$[Ne]3s^2 3p^2$	$[Ar]3d^{10}4s^2 4p^2$	$[Kr]4d^{10}5s^2 5p^2$	$[Xe]4f^{14}5d^6 6s^2 6p^2$
Covalent radius/pm^a		77	118	122	140	146
Ionic radius M^{4+}/pm^b		–	40	53	69	78
Ionic radius M^{2+}/pm^b		–	–	73	118	119
Ionization enthalpy/kJ mol^{-1}	$\Delta_i H_1$	1086	786	761	708	715
	$\Delta_i H_2$	2352	1577	1537	1411	1450
	$\Delta_i H_3$	4620	3228	3300	2942	3081
	$\Delta_i H_4$	6220	4354	4409	3929	4082
Electronegativity^c		2.5	1.8	1.8	1.8	1.9
Density^d/g cm^{-3}		3.51^e	2.34	5.32	7.26^f	11.34
Melting point/K		4373	1693	1218	505	600
Boiling point/K		–	3550	3123	2896	2024
Electrical resistivity/ ohm cm (293 K)		10^{14}–10^{16}	50	50	10^{-5}	2×10^{-5}

^{a}for M^{IV} oxidation state; ^{b}6–coordination; ^{c}Pauling scale; ^{d}293 K; ^{e}for diamond; for graphite, density is 2.22; ^{f}β-form (stable at room temperature)

The important atomic and physical properties of the group 14 elements along with their electronic configuration are given in Table 11.1 Some of the atomic, physical and chemical properties are discussed below:

11.1.1 Electronic Configuration

The valence shell electronic configuration of these elements is ns^2np^2. The inner core of the electronic configuration of elements in this group also differs.

11.1.2 Covalent Radius

There is a considerable increase in covalent radius from C to Si, thereafter from Si to Pb a small increase in radius is observed. This is due to the presence of completely filled d and f orbitals in heavier members.

11.1.3 Ionization Enthalpy

The first ionization enthalpy of group 14 members is higher than the corresponding members of group 13. The influence of inner core electrons is visible here also. In general, the ionisation enthalpy decreases down the group. Small decrease in $\Delta_i H$ from Si to Ge to Sn and slight increase in $\Delta_i H$ from Sn to Pb is the consequence of poor shielding effect of intervening d and f orbitals and increase in size of the atom.

11.1.3 Electronegativity

Due to small size, the elements of this group are slightly more electronegative than group 13 elements. The electronegativity values for elements from Si to Pb are almost the same.

11.1.5 Physical Properties

All group 14 members are solids. Carbon and silicon are non-metals; germanium is a metalloid, whereas tin and lead are soft metals with low melting points. Melting points and boiling points of group 14 elements are much higher than those of corresponding elements of group 13.

11.1.6 Chemical Properties

Oxidation states and trends in chemical reactivity

The group 14 elements have four electrons in outermost shell. The common oxidation states exhibited by these elements are +4 and +2. Carbon also exhibits negative oxidation states. Since the sum of the first four ionization enthalpies is very high, compounds in +4 oxidation state are generally covalent in nature. In heavier members the tendency to show +2 oxidation state increases in the sequence Ge < Sn < Pb. It is due to the inability of ns^2 electrons of valence shell to participate in bonding. The relative stabilities of these two oxidation states vary down the group. Carbon and silicon mostly show +4 oxidation state. Germanium forms stable compounds in +4 because of the presence of d orbital in them. Due to this, their halides undergo hydrolysis and have tendency to form complexes by accepting electron pairs from donor species. For example, the species like, SiF_6^{2-}, $[GeCl_6]^{2-}$, $[Sn(OH)_6]^{2-}$ exist where the hybridisation of the central atom is sp^3d^2.

(i) Reactivity towards oxygen

All members when heated in oxygen form oxides. There are mainly two types of oxides, i.e., monoxide and dioxide of formula MO and MO2 respectively. SiO only exists at high temperature. Oxides in higher oxidation states of elements are generally more acidic than those in lower oxidation states. The dioxides - CO_2, SiO_2 and GeO_2 are acidic, whereas SnO_2 and PbO_2 are amphoteric in nature. Among monoxides, CO is neutral; GeO is distinctly acidic whereas SnO and PbO are amphoteric.

(ii) Reactivity towards water

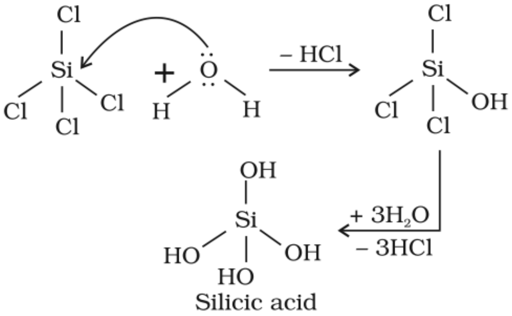
Carbon, silicon and germanium are not affected by water. Tin decomposes steam to form dioxide and hydrogen gas.

$$Sn + 2H_2O \xrightarrow{\Delta} SnO_2 + 2H_2$$

Lead is unaffected by water, probably because of a protective oxide film formation.

(iii) Reactivity towards halogen

These elements can form halides of formula MX_2 and MX_4 (where X = F, Cl, Br, I) . Except carbon, all other members react directly with halogen under suitable condition to make halides. Most of the MX_4 are covalent in nature. The central metal atom in these halides undergoes sp^3 hybridisation and the molecule is tetrahedral in shape. Exceptions are SnF_4 and PbF_4, which are ionic in nature. PbI_4 does not exist because Pb-I bond initially formed during the reaction does not release enough energy to unpair 6s electrons and excite one of them to higher orbital to have four unpaired electrons around lead atom. Heavier members Ge to Pb are able to make halides of formula MX_2. Stability of dihalides increases down the group. Considering the thermal and chemical stability, GeX_4 is more stable than Ge whereas Pb is more than PbX_4. Except $CC1_4$, other tetrachlorides are easily hydrolysed by water because the central atom can accommodate the lone pair of electrons from oxygen atom of water molecule in d orbital. Hydrolysis can be understood by taking the example of $SiC1_4$. It undergoes hydrolysis by initially accepting lone pair of electrons from water molecule in d orbitals of Si, finally leading to the formation of $Si(OH)_4$ as shown below :



11.2 Important Trends and Anomalous behaviour of Carbon

Like first member of other groups, carbon also differs from rest of the members of its group. It is due to its smaller size, higher electronegativity, higher ionisation enthalpy and unavailability of d orbitals.

In carbon, only s and p orbitals are available for bonding and, therefore, it can accommodate only four pairs of electrons around it. This would limit the maximum covalence to four whereas other members can expand their covalence due to the presence of d orbitals.

Carbon also has unique ability to form $p\pi - p\pi$ multiple bonds with itself and with other atoms of small size and high electronegativity. Few examples of multiple bonding are: C=C, $C \equiv C$, C = O, C = S, and $C \equiv N$. Heavier elements do not form $p\pi - p\pi$ bonds because their atomic orbitals are too large and diffuse to have effective overlapping.

Carbon atoms have the tendency to link with one another through covalent bonds to form chains and rings. This property is called catenation. This is because C- C bonds are very strong. Down the group the size increases and electronegativity decreases, and, thereby, tendency to show catenation decreases. This can be clearly seen from bond enthalpies values. The order of catenation is C> >Si >Ge = Sn. Lead does not show catenation.

Bond	Bond enthalpy / kJ mol $^{-1}$
C—C	348
Si —Si	297
Ge—Ge	260
Sn—Sn	240

Due to property of catenation and $p\pi - p\pi$ bond formation, carbon is able to show allotropic forms.

11.3 Allotropes of Carbon

Carbon exhibits many allotropic forms; both crystalline as well as amorphous. Diamond and graphite are two well-known crystalline forms of carbon. In 1985, third form of carbon known as fullerenes was discovered by H.W.Kroto, E.Smalley and R.F.Curl. For this discovery they were awarded the Nobel Prize in 1996.

11.3.1 Diamond

It has a crystalline lattice. In diamond each carbon atom undergoes sp^3 hybridisation and linked to four other carbon atoms by using hybridised orbitals in tetrahedral fashion. The C-C bond length is 154 pm. The structure extends in space and produces a rigid three- dimensional network of carbon atoms. In this structure (Fig. 11.1) directional covalent bonds are present throughout the lattice.

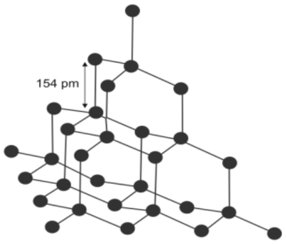


Fig. 11.1 The structure of diamond

It is very difficult to break extended covalent bonding and, therefore, diamond is a hardest substance on the earth. It is used as an abrasive for sharpening hard tools, in making dies and in the manufacture of tungsten filaments for electric light bulbs.

11.3.2 Graphite

Graphite has layered structure (Fig.11.2). Layers are held by vander Waals forces and distance between two layers is 340 pm. Each layer is composed of planar hexagonal rings of carbon atoms. C-C bond length within the layer is 141.5pm. Each carbon atom in hexagonal ring undergoes sp^2 hybridisation and makes three sigma bonds with three neighbouring carbon atoms. Fourth electron forms a π-bond. The electrons are delocalised over the whole sheet. Electrons are mobile and, therefore, graphite conducts electricity along the sheet. Graphite cleaves easily between the layers and, therefore, it is very soft and lippery. For this reason, graphite is used as a dry lubricant in machines running at high temperature, where oil cannot be used as a lubricant.

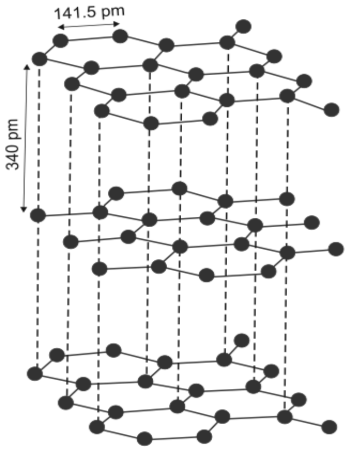


Fig. 11.2 The structure of graphite

11.3.3 Fullerenes

Fullerenes are made by the heating of graphite in an electric arc in the presence of inert gases such as helium or argon. The sooty material formed by condensation of vapourised C^n small molecules consists of mainly C_{60} with smaller quantity of C_{70} and traces of fullerenes consisting of even number of carbon atoms up to 350 or above. Fullerenes are the only pure form of carbon because they have smooth structure without having 'dangling' bonds. Fullerenes are cage like molecules. C_{60} molecule has a shape like soccer ball and called Buckminster fullerene (Fig. 11.3).

It contains twenty six- membered rings and twelve five membered rings. A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings. All the carbon atoms are equal and they undergo sp^2 hybridization. Each carbon atom forms three sigma bonds with other three carbon atoms. The remaining electron at each carbon is delocalised in molecular orbitals, which in turn give aromatic character to molecule. This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C-C distances of 143.5 pm and 138.3 pm respectively. Spherical fullerenes are also called bucky balls in short.

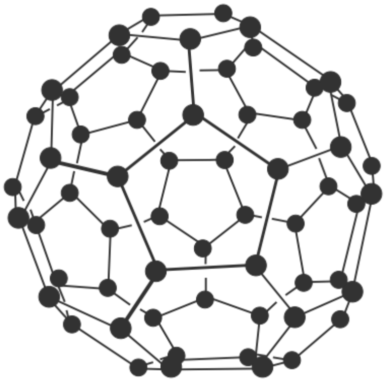


Fig. 11.3 The structure of C_{60} Buckminster fullerene (foot ball shape)

It is very important to know that graphite is thermodynamically most stable allotrope of carbon and, therefore, $\Delta_f H^-$ of graphite is taken as zero. $\Delta_f H^-$ values of diamond and fullerene, C_{60} are 1.90 and 38.1 kJ mol^{-1}, respectively.

Other forms of elemental carbon like carbon black, coke, and charcoal are all impure forms of graphite or fullerenes. Carbon black is obtained by burning hydrocarbons in a limited supply of air. Charcoal and coke are obtained by heating wood or coal respectively at high temperatures in the absence of air.

11.4 Uses of Carbon

Graphite fibers embedded in plastic material form high strength, lightweight composites. The composites are used in products such as tennis rackets, fishing rods, aircrafts and canoes. Being good conductor, graphite is used for electrodes in batteries and industrial electrolysis. Crucibles made from graphite are inert to dilute acids and alkalies. Being highly porous, activated charcoal is used in adsorbing poisonous gases; also used in water filters to remove organic contaminators and in air conditioning system to control odour. Carbon black is used as black pigment in black ink and as filler in automobile tyres. Coke is used as a fuel and largely as a reducing agent in metallurgy. Diamond is a precious stone and used in jewellery. It is measured in carats (1 carat = 200 mg).

SUMMARY

Carbon id a typical non-metal forming covalent bonds employing all its four valence electrons ($2s^2\ 2p^2$). It shows the property of catenation, the ability to form chains or rings not only with C-C single bonds but also with multiple bonds (C=C or $C \equiv C$). The tendency to catenation decreases as C >> Si > Ge~Sn > Pb. Carbon provides one of the best examples of allotropy. Three important allotropes of carbon are diamond, graphite and fullerenes. The members of the carbon family mainly exhibit +4 and +2 oxidation states; compounds in +4 oxidation states are generally covalent in nature. The tendency to show +2 oxidation state increases among heavier elements. Lead in +2 state is stable whereas in +4 oxidation state, it s a strong oxidizing agent.

EXERCISES

11.1 Discuss the pattern of variation in the oxidation states of C to Pb.
11.2 Explain the difference in properties of diamond and graphite on the basis of their structures.
11.3 Explain why is there a pheno1nenal decrease in ionization enthalpy fro1n carbon to silicon?
11.4 What are allotropes? Sketch the structure of two allotropes of carbon namely diamond and graphite. What is the impact of structure on physical properties of two allotropes?
11.5 What do you understand by (a) inert pair effect (b) allotropy and (c) catenation?

QUESTION BANK

Very Short Answer Questions **(2 Marks)**

1. Give the hybridization of carbon in

   a) CO_3^{2-} b) diamond c) graphite d) fullerene

2. What is allotropy? Give the crystalline allotropes of carbon?
3. Why does graphite function as a lubricant?
4. Graphite is a good conductor – explain?

CHAPTER-12

ENVIRONMENTAL CHEMISTRY

You have already studied about environment in your earlier classes. Environmental studies deal with the sum of all social, economical, biological, physical and chemical inter relations with our surroundings. In this unit the focus will be on environmental chemistry. Environmental chemistry deals with the study of the origin, transport, reactions, effects and fates of chemical species in the environment. Let us discuss some important aspects of environmental chemistry.

12.1 Definition of Terms of Air, Water, Soil Pollutions:

Environmental chemistry is the science of chemical phenomenon in the environment. Environment consists of four segments namely Atmosphere, Hydrosphere, Lithosphere and Biosphere. Atmosphere is the protective blanket of gases surrounding the earth. This saves life from the hostile environment of outer space. This segment is commonly referred to as air in environmental study. It consists of four spheres extending upto 500 km from the surface of the Earth. These are Troposphere, Stratosphere, Mesosphere and Thermosphere. Hydrosphere includes all types of water sources – Oceans, Seas, Rivers, Lakes, Streams, Reservoirs, Glaciers and Ground water. This segment is commonly referred to as **water** in environmental pollution study. Lithosphere is the outer mantle of the solid earth consisting of minerals and the soil. This segment in pollution study is referred to as **soil** generally**.** All living species including human beings and animals constitute Biosphere.

All the segments namely Air, Water and Soil are getting polluted due to human activity as well as due to natural calamities. Certain technical terms are used in describing the Air, Water and Soil pollutions. They are:

Pollutant: A substance in nature in greater amounts than natural abundance due to human activity, which has harmful effect on living organisms and mankind, is called a Pollutant.

Contaminant: A material which does not occur in nature but is introduced by human activity into the environment effecting its composition is called Contaminant. If this exerts harmful effect, it is called Pollutant.

Receptor: The medium which is affected by a Pollutant (generally man) is called the Receptor.

Sink: The medium which retains and interacts with a long lived Pollutant is called a Sink.(Oceans are Sinks for atmospheric Carbon dioxide.)

Speciation: The detection of different chemical forms of inorganic, organic or organo-metallic compounds present in the environment causing pollution is called Speciation.

Threshold Limit Value (TLV): The permissible level of a toxic pollutant in the atmosphere to which a healthy industrial worker is exposed during an eight hour day without any harmful effect is called Threshold Limit Value.

Chemical Oxygen Demand (COD): The amount of Oxygen required to oxidize organic substances present in polluted water is called as chemical oxygen demand. It is an important index for the amount of organic substances present in polluted water. COD is determined by oxidizing the organic matter with acidified (50% H_2SO_4) potassium dichromate solution. It is an important parameter for determining the quality of water.

Biochemical Oxygen Demand (BOD): The amount of Oxygen used by suitable microorganisms present in water during 5 days at 20 ^{0}C is called Biochemical Oxygen Demand. It is empirical in nature. For pure water, BOD is about 1 ppm. The municipal sewage has BOD values from 100-4000 ppm. BOD greater than 17 ppm indicates high pollution and is harmful.

12.2 Environmental Pollution

Environmental pollution is the effect of undesirable changes in our surroundings that have harmful effects on plants, animals and human beings. A substance which causes pollution is known as pollutant. Pollutants can be solid, liquid or gaseous substances present in greater concentration than in natural abundance and are produced due to human activities or due to natural happenings. Do you know, an average human being requires nearly 12- 15 times more air than the food. So, even small amounts of pollutants in the air become significant compared to similar levels present in the food. Pollutants can be degradable like discarded vegetables which rapidly break down by natural processes. On the other hand, pollutants which are slowly degradable remain in the environment in an unchanged form for many decades. For example, substances such as dichlorodi-phenyltrichloroethane (DDT), plastic materials, heavy metals, many chemicals, nuclear wastes etc., once released into the environment are difficult to remove. These pollutants cannot be degraded by natural processes and are harmful to living organisms. In the process of environmental pollution, pollutants originate from a source and get transported by air or water or are dumped into the soil by human beings.

12.3 Atmospheric Pollution

The atmosphere that surrounds the earth is not of the same thickness at all heights. There are concentric layers of air or regions and each layer has different density. The lowest region of atmosphere in which the human beings along with other organisms live is called troposphere. It extends up to the height of ~10 km from sea level. Above the troposphere, between 10 and 50 km above sea level lies stratosphere. Troposphere is a turbulent dusty zone containing air, much water vapour and clouds. This is the region of strong air movement and cloud formation. The stratosphere, on the other hand, contains nitrogen, oxygen, ozone and little water vapour. Atmospheric pollution is generally studied as tropospheric and stratospheric pollution. The presence of ozone in the stratosphere prevents about 99.5 per cent of the sun's harmful ultraviolet (UV) radiations from reaching the earth's surface and thereby protecting humans and other animals from its effect.

12.3.1 Tropospheric Pollution

Tropospheric pollution occurs due to the presence of undesirable solid or gaseous particles in the air. The following are the major gaseous and particulate pollutants present in the troposphere:

1. Gaseous air pollutants: These are oxides of sulphur, nitrogen and carbon, hydrogen sulphide, hydrocarbons, ozone and other oxidants.

2. Particulate pollutants: These are dust, mist, fumes, smoke, smog etc.

1. Gaseous air pollutants

(a) Oxides of Sulphur: Oxides of sulphur are produced when sulphur containing fossil fuel is burnt. The most common species, sulphur dioxide, is a gas that is poisonous to both animals and plants. It has been reported that even a low concentration of sulphur dioxide causes respiratory diseases e.g., asthma, bronchitis, emphysema in human beings. Sulphur dioxide causes irritation to the eyes, resulting in tears and redness. High concentration of SO_2 leads to stiffness of flower buds which eventually fall off from plants. Uncatalysed oxidation of sulphur dioxide is slow. However, the presence of particulate matter in polluted air catalyses the oxidation of sulphur dioxide to sulphur trioxide.

$$2SO_2\ g\ + O_2\ g \ \rightarrow\ 2SO_3\ g$$

The reaction can also be promoted by ozone and hydrogen peroxide.

$$SO_2\ g\ + O_3\ g \ \rightarrow\ SO_3\ g\ + O_2\ g$$

$$SO_2\ g\ + H_2O_2\ l \ \rightarrow\ H_2SO_4\ aq$$

(b) Oxides of Nitrogen: Nitrogen and oxygen are the main constituents of air. These gases do not react with each other at a normal temperature. At high altitudes when lightning strikes, they combine to form oxides of nitrogen. NO_2 is oxidised to nitrate ion, NO_3^- which is washed into soil, where it serves as a fertilizer. In an automobile engine, (at high temperature) when fossil fuel is burnt, nitrogen and oxygen combine to yield significant quantities of nitric oxide (NO) and nitrogen dioxide (NO_2) as given below:

$$N_2\ g\ + O_2\ g \xrightarrow{1483K} 2NO\ g$$

NO reacts instantly with oxygen to give NO_2

$$2NO\ g\ + O_2\ g \rightarrow 2NO_2\ g$$

Rate of production of NO_2 is faster when nitric oxide reacts with ozone in the stratosphere.

$$NO\ g\ + O_3\ g \rightarrow NO_2\ g\ + O_2\ g$$

The irritant red haze in the traffic and congested places is due to oxides of nitrogen. Higher concentrations of NO_2 damage the leaves of plants and retard the rate of photosynthesis. Nitrogen dioxide is a lung irritant that can lead to an acute respiratory disease in children. It is toxic to living tissues also. Nitrogen dioxide is also harmful to various textile fibers and metals.

(c) Hydrocarbons: Hydrocarbons are composed of hydrogen and carbon only and are formed by incomplete combustion of fuel used in automobiles. Hydrocarbons are carcinogenic, i.e., they cause cancer. They harm plants by causing ageing, breakdown of tissues and shedding of leaves, flowers and twigs.

(d) Oxides of Carbon

(i) Carbon monoxide: Carbon monoxide (CO) is one of the most serious air pollutants. It is a colour less and odourless gas, highly poisonous to living beings because of its ability to block the delivery of oxygen to the organs and tissues. It is produced as a result of incomplete combustion of carbon. Carbon monoxide is mainly released into the air by automobile exhaust. Other sources, which produce CO, involve incomplete combustion of coal, firewood, petrol, etc. The number of vehicles has been increasing over the years all over the world. Many vehicles are poorly maintained and several have inadequate pollution control equipments resulting in the release of greater amount of carbon monoxide and other polluting gases. Do you know why carbon monoxide is poisonous? It binds to haemoglobin to form carboxy - haemoglobin, which is about 300 times more stable than the oxygen-haemoglobin complex. In blood, when the concentration of carboxy-haemoglobin reaches about 3-4 per cent, the oxygen carrying capacity of blood is greatly reduced. This oxygen deficiency results into headache, weak eyesight, nervousness and cardiovascular disorder. This is the reason why people are advised not to smoke. In pregnant women who have the habit of smoking the increased CO level in blood may induce premature birth, spontaneous abortions and deformed babies.

(ii) Carbon dioxide: Carbon dioxide (CO_2) is released into the atmosphere by respiration, burning of fossil fuels for energy, and by decomposition of limestone during the manufacture of cement. It is also emitted during volcanic eruptions. Carbon dioxide gas is confined to troposphere only. Normally it forms about 0.03 per cent by volume of the atmosphere. With the increased use of fossil fuels, a large amount of carbon dioxide gets released into the atmosphere. Excess of CO_2 in the air is removed by green plants and this maintains an appropriate level of CO_2 in the atmosphere. Green plants require CO_2 for photosynthesis and they, in turn, emit oxygen, thus maintaining the delicate balance. As you know, deforestation and burning of fossil fuel increases the CO_2 level and disturb the balance in the atmosphere. The increased amount of CO_2 in the air is mainly responsible for global warming.

(iii) Global Warming and Greenhouse Effect

About 75 % of the solar energy reaching the earth is absorbed by the earth's surface, which increases its temperature .The rest of the heat radiates back to the atmosphere. Some of the heat is trapped by gases such as carbon dioxide, methane, ozone, chlorofluorocarbon compounds (CFCs) and water vapour in the atmosphere. Thus, they add to the heating of the atmosphere. This causes global warming.

We all know that in cold places flowers, vegetables and fruits are grown in glass covered areas called greenhouse. Do you know that we humans also live in a greenhouse? Of course, we are not surrounded by glass but a blanket of air called the atmosphere, which has kept the temperature on earth constant for centuries. But it is now undergoing change, though slowly. Just as the glass in a greenhouse holds the sun's warmth inside, atmosphere traps the sun's heat near the earth's surface and keeps it warm. This is called natural greenhouse effect because it maintains the temperature and makes the earth perfect for life. In a greenhouse, visible light passes through the transparent glass and heats up the soil and the plants. The warm soil and plants emit infrared radiations. Since glass is opaque to infrared (heat) radiations, it partly reflects and partly absorbs these radiations. This mechanism keeps the energy of the sun trapped in the greenhouse. Similarly, carbon dioxide molecules also trap heat as they are transparent to sunlight but not to the heat radiation. If the amount of carbon dioxide crosses the delicate proportion of 0.03 per cent, the natural greenhouse balance may get disturbed. Carbon dioxide is the major contributor to global warming.

Besides carbon dioxide, other greenhouse gases are methane, water vapour, nitrous oxide, CFCs and ozone. Methane is produced naturally when vegetation is burnt, digested or rotted in the absence of oxygen. Large amounts of methane are released in paddy fields, coal mines, from rotting garbage dumps and by fossil fuels. Chlorofluorocarbons (CFCs) are man-made industrial chemicals used in air conditioning etc. CFCs are also damaging the ozone layer. Nitrous oxide occurs naturally in the environment. In recent years, their quantities have increased significantly due to the use of chemical fertilizers and the burning of fossil fuels. If these trends continue, the average global temperature will increase to a level which may lead to melting of polar ice caps and flooding of low lying areas all over the earth. Increase in the global temperature increases the incidence of infectious diseases like dengue, malaria, yellow fever, sleeping sickness etc.

2. Particulate Pollutants

Particulates pollutants are the minute solid particles or liquid droplets in air. These are present in vehicle emissions, smoke particles from fires, dust particles and ash from industries. Particulates in the atmosphere may be viable or non -viable. The viable particulates e.g., bacteria, fungi, moulds, algae etc., are minute living organisms that are dispersed in the atmosphere. Human beings are allergic to some of the fungi found in air. They can also cause plant diseases.

Non-viable particulates may be classified according to their nature and size as follows:

a) Smoke particulates consist of solid or mixture of solid and liquid particles formed during combustion of organic matter. Examples are cigarette smoke, smoke from burning of fossil fuel, garbage and dry leaves, oil smoke etc.
b) Dust is composed of fine solid particles (over l µm in diameter), produced during crushing, grinding and attribution of solid materials. Sand from sand blasting saw dust from wood works. pulverized coal, cement and fly ash from factories, dust storms etc., are some typical examples of this type of particulate emission.
c) Mists are produced by particles of spray liquids and by condensation of vapours in air. Examples are sulphuric acid mist and herbicides and insecticides that miss their targets and travel through air and form mists.
d) Fumes are generally obtained by the condensation of vapours during sublimation, distillation, boiling and several other chemical reactions. Generally, organic solvents, metals and metallic oxides form fume particles.

The effect of particulate pollutants is largely dependent on the particle size. Air- borne particles such as dust, fumes, mist etc., are dangerous for human health. Particulate pollutants bigger than 5 microns are likely to lodge in the nasal passage, whereas particles of about 1.0 micron enter into lungs easily.

Lead used to be a major air pollutant emitted by vehicles. Leaded petrol used to be the primary source of air -borne lead emission in Indian cities. This problem has now been overcome by using unleaded petrol in most of the cities in India. Lead interferes with the development and maturation of red blood cells.

12.4 Acid rain

We are aware that normally rain water has a pH of 5.6 due to the presence of H^+ ions formed by the reaction of rain water with carbon dioxide present in the atmosphere.

When the pH of the rain water drops below 5.6, it is called acid rain.

Acid rain refers to the ways in which acid from the atmosphere is deposited on the earth's surface. Oxides of nitrogen and sulphur which are acidic in nature can be blown by wind along with solid particles

$$H_2O\ \ l\ + CO_2\ \ g\ \rightleftarrows\ H_2CO_3\ \ aq$$

$$H_2CO_3\ \ aq\ \rightleftarrows H^+\ \ aq\ + HCO_3^-\ \ aq$$

in the atmosphere and finally settle down either on the ground as dry deposition or in water, fog and snow as wet deposition (Fig. 12.1).

Acid rain is a byproduct of a variety of human activities that emit the oxides of sulphur and nitrogen in the atmosphere. As mentioned earlier, burning of fossil fuels (which contain sulphur and nitrogenous matter) such as coal and oil in power stations and furnaces or petrol and diesel in motor engines produce sulphur dioxide and nitrogen oxides. SO_2 and NO_2 after oxidation and reaction with water are major contributors to acid rain, because polluted air usually contains particulate matter that catalyse the oxidation.

$$2SO_2\ \ g\ \ + O_2\ \ g\ \ + 2H_2O\ 1\ \ \rightarrow\ \ 2H_2SO_4\ \ aq$$
$$4NO_2\ \ g\ \ + O_2\ \ g\ + 2H_2O\ 1\ \ \rightarrow\ \ 4HNO_3\ \ aq$$

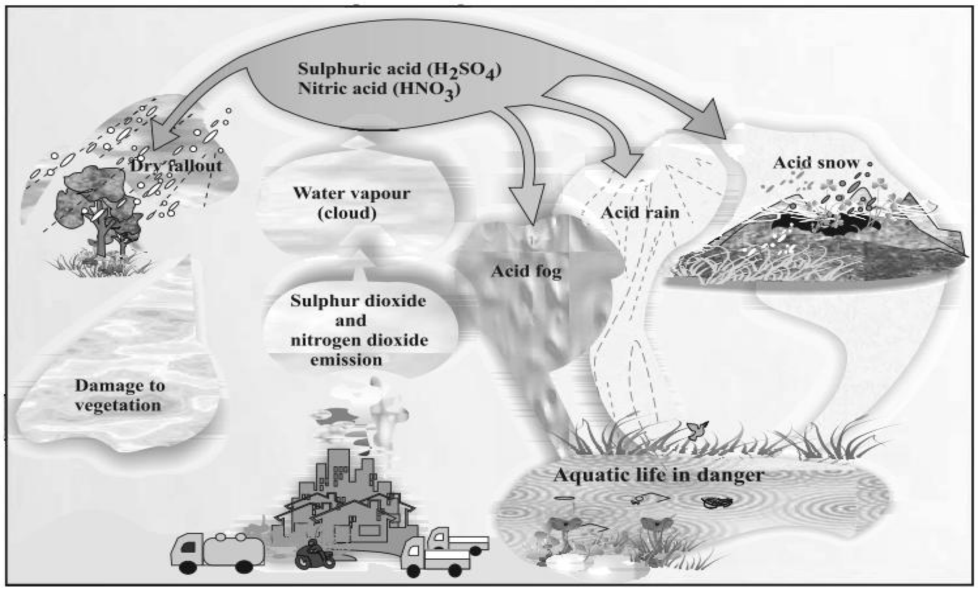


Fig. 12.1 Acid deposition

Ammonium salts are also formed and can be seen as an atmospheric haze (aerosol of fine particles). Aerosol particles of oxides or ammonium salts in rain drops result in wet-deposition. SO_2 is also absorbed directly on both solid and liquid ground surfaces and is thus deposited as dry-deposition.

Acid rain is harmful for agriculture, trees and plants as it dissolves and washes away nutrients needed for their growth. It causes respiratory ailments in human beings and animals. When acid rain falls and flows as ground water to reach rivers, lakes etc. it affects plants and animal life in aquatic ecosystem. It corrodes water pipes resulting in the leaching of heavy metals such as iron, lead and copper into the drinking water. Acid rain damages buildings and other structures made of stone or metal. The Taj Mahal in India has been affected by acid rain.

12.5 Stratospheric Pollution Formation and Breakdown of Ozone

The upper stratosphere consists considerable amount of ozone (O_3), which protects us from the harmful ultraviolet (UV) radiations (λ=255 nm) coming from the sun. These radiations cause skin cancer (melanoma) in humans. Therefore, it is important to maintain the ozone shield.

Ozone in the stratosphere is a product of UV radiations acting on oxygen (O_2) molecules. The UV radiations split apart molecular oxygen into free oxygen (O) atoms. These oxygen atoms combine with the molecular oxygen to form ozone.

$$O_2\; g \xrightarrow{uv} O\; g + O\; g$$

$$O\; g + O_2\; g \overset{\text{UV}}{\rightleftarrows} O_3\; g \qquad (M=N_2+O_2)$$

Ozone is thermodynamically unstable and decomposes to molecular oxygen. Thus, a dynamic equilibrium exists between the production and decomposition of ozone molecules. In recent years, there have been reports of the depletion of this protective ozone layer because of the presence of certain chemicals in the stratosphere. The main reason of ozone layer depletion is believed to be the release of chlorofluorocarbon compounds (CFCs), also known as freons. These compounds are nonreactive, non flammable, non toxic organic molecules and therefore used in refrigerators, air conditioners, in the production of plastic foam and by the electronic industry for cleaning computer parts etc. Once CFCs are released in the atmosphere, they mix with the normal atmospheric gases and eventually reach the stratosphere. In stratosphere, they get broken down by powerful UV radiations, releasing chlorine free radical.

$$CF_2Cl_2\; g \xrightarrow{uv} \dot{Cl}\; g + \dot{C}F_2Cl\; g \qquad \text{(i)}$$

The chlorine radical then react with stratospheric ozone to form chlorine monoxide radicals and molecular oxygen.

$$\dot{Cl}\; g + O_3\; g \rightarrow \dot{Cl}O\; g + O_2\; g \qquad \text{(ii)}$$

Reaction of chlorine monoxide radical with atomic oxygen produces more chlorine radicals.

$$\dot{Cl}O\; g + O\; g \rightarrow \dot{Cl}\; g + O_2\; g \qquad \text{(iii)}$$

The chlorine radicals are continuously regenerated and cause the breakdown of ozone. Thus, CFCs are transporting agents for continuously generating chlorine radicals into the stratosphere and damaging the ozone layer.

12.5.1 The Ozone Hole

In 1980s atmospheric scientists working in Antarctica reported about depletion of ozone layer commonly known as ozone hole over the South Pole. It was found that a unique set of conditions was responsible for the ozone hole. In summer season, nitrogen dioxide and methane react with chlorine monoxide (reaction iv) and chlorine atoms (reaction v) forming chlorine sinks, preventing much ozone depletion, whereas in winter, special type of clouds called polar stratospheric clouds are formed over Antarctica. These polar stratospheric clouds provide surface on which chlorine nitrate formed (reaction

iv) gets hydrolysed to form hypochlorous acid (reaction (vi)). It also reacts with hydrogen chloride produced as per reaction (v) to give molecular chlorine.

$$\overset{\bullet}{\mathrm{Cl}}\mathrm{O}\ \mathrm{g} + \mathrm{NO_2}\ \mathrm{g} \rightarrow \mathrm{ClONO_2}\ \mathrm{g} \qquad \text{(iv)}$$

$$\overset{\bullet}{\mathrm{Cl}}\ \mathrm{g} + \mathrm{CH_4} \rightarrow \overset{\bullet}{\mathrm{C}}\mathrm{H_3}\ \mathrm{g} + \mathrm{HCl}\ \mathrm{g} \qquad \text{(v)}$$

$$\mathrm{ClONO_2}\ \mathrm{g} + \mathrm{H_2O}\ \mathrm{g} \rightarrow \mathrm{HOCl}\ \mathrm{g} + \mathrm{HNO_3}\ \mathrm{g} \qquad \text{(vi)}$$

$$\mathrm{ClONO_2}\ \mathrm{g} + \mathrm{HCl}\ \mathrm{g} \rightarrow \mathrm{Cl_2}\ \mathrm{g} + \mathrm{HNO_3}\ \mathrm{g} \qquad \text{(vii)}$$

When sunlight returns to the Antarctica in the spring, the sun's warmth breaks up the clouds and HOCl and Cl_2 are photolysed by sunlight, as given in reactions (viii) and (ix).

$$\mathrm{HOCl}\ \mathrm{g} \xrightarrow{hv} \overset{\bullet}{\mathrm{O}}\mathrm{H}\ \mathrm{g} + \overset{\bullet}{\mathrm{Cl}}\ \mathrm{g} \qquad \text{(viii)}$$

$$\mathrm{Cl_2}\ \mathrm{g} \xrightarrow{uv} 2\overset{\bullet}{\mathrm{Cl}}\ \mathrm{g} \qquad \text{(ix)}$$

The chlorine radicals thus formed, initiate the chain reaction for ozone depletion as described earlier.

12.5.2 Effects of Depletion of the Ozone Layer

With the depletion of ozone layer, more UV radiation filters into troposphere. UV radiations lead to ageing of skin cataract, sunburn, skin cancer, killing of many phytoplanktons, damage to fish productivity etc. It has also been reported that plant proteins get easily affected by UV radiations which leads to the harmful mutation of cells. It also increases evaporation of surface water through the stomata of the leaves and decreases the moisture content of the soil. Increase in UV radiations damage paints and fibers, causing them to fade faster.

12.6 Water Pollution

Water is essential for life. Without water there would be no life. We usually take water as granted for its purity, but we must ensure the quality of water. Pollution of water originates from human activities. Through different paths, pollution reaches surface or ground water. Easily identified source or place of pollution is called as point source. e.g., municipal and industrial discharge pipes where pollutants enter the water -source. Non point sources of pollution are those where a source of pollution cannot be easily identified, e.g.: agricultural runoff (from farm, animals and crop-lands), acid rain, storm-water drainage (from streets, parking lots and lawns), etc. Table 12.1 lists the major water pollutants and their sources.

Table 12.1 Major water pollutants

Pollutant	Source
Micro-organisms	Domestic sewage
Organic wastes	Domestic sewage, animal excreta and waste, decaying animals and plants, discharge from food processing factories.
Plant nutrients	Chemcial fertilizers
Toxic heavy metals	Industries and chemical factories
Sediments	Erosion of soil by agriculture and strip mining
Pesticides	Chemicals used for killing insects, fungi and weeds
Radioactive substances	Mining of uranium containing minerals
Heat	Water used for cooling in industries

12.6.1 Causes of Water Pollution

(i)Pathogens: The most serious water pollutants are the disease causing agents called pathogens. Pathogens include bacteria and other organisms that enter water from domestic sewage and animal excreta. Human excreta contain bacteria such as Escherichia coli and Streptococcus faecalis which cause gastrointestinal diseases.

(ii) Organic wastes: The other major water pollutant is organic matter such as leaves, grass, trash etc. They pollute water as a consequence of runoff. Excessive phytoplankton growth within water is also a cause of water pollution. These wastes are biodegradable.

The large population of bacteria decomposes organic matter present in water. They consume oxygen dissolved in water. The amount of oxygen that water can hold in the solution is limited. In cold water, dissolved oxygen (DO) can reach a concentration up to 10 ppm (parts per million), whereas oxygen in air is about 200,000 ppm. That is why even a moderate amount of organic matter when decomposes in water can deplete the water of its dissolved oxygen. The concentration of dissolved oxygen in water is very important for aquatic life. If the concentration of dissolved oxygen of water is below 6 ppm, the growth of fish gets inhibited. Oxygen reaches water either through atmosphere or from the process of photosynthesis carried out by many aquatic green plants during day light. However, during night, photosynthesis stops but the plants continue to respire, resulting in reduction of dissolved oxygen. The dissolved oxygen is also used by microorganisms to oxidise organic matter.

If too much of organic matter is added to water, all the available oxygen is used up. This causes oxygen dependent aquatic life to die. Thus, anaerobic bacteria (which do not require oxygen) begin to break down the organic waste and produce chemicals that have a foul smell and are harmful to human health. Aerobic (oxygen requiring) bacteria degrade these organic wastes and keep the water depleted in dissolved oxygen.

Thus, the amount of oxygen required by bacteria to break down the organic matter present in a certain volume of a sample of water is called Biochemical Oxygen Demand (BOD). The amount of BOD in the water is a measure of the amount of organic material in the water, in terms of how much oxygen will be required to break it down biologically. Clean water would have BOD value of less than 5 ppm whereas highly polluted water could have a BOD value of 17 ppm or more.

(iii) Chemical Pollutants: As we know that water is an excellent solvent, water soluble inorganic chemicals that include heavy metals such as cadmium, mercury, nickel etc constitute an important class of pollutants. All these metals are dangerous to humans because our body cannot excrete them. Over the time, it crosses the tolerance limit. These metals then can damage kidneys, central nervous system, liver etc. Acids (like sulphuric acid) from mine drainage and salts from many different sources including raw salt used to melt snow and ice in the colder climates (sodium and calcium chloride) are water soluble chemical pollutants.

The organic chemicals are another group of substances that are found in polluted water. Petroleum products pollute many sources of water e.g., major oil spills in oceans. Other organic substances with serious impacts are the pesticides that drift down from sprays or run off from lands. Various industrial chemicals like polychlorinated biphenyls, (PCBs) which are used as cleansing solvent, detergents and fertilizers add to the list of water pollutants. PCBs are suspected to be carcinogenic. Nowadays most of the detergents available are biodegradable. However, their use can create other problems. The bacteria responsible for degrading biodegradable detergent feed on it and grow rapidly. While growing, they may use up all the oxygen dissolved in water. The lack of oxygen kills all other forms of aquatic life such as fish and plants. Fertilizers contain phosphates as additives. The addition of phosphates in water enhances algae growth. Such profuse growth of algae covers the water surface and reduces the oxygen concentration in water. This leads to anaerobic conditions, commonly with accumulation of abnoxious decay and animal death. Thus, bloom-infested water inhibits the growth of other living organism s in the water body. This process in which nutrient enriched water bodies support a dense plant population, which kills animal life by depriving it of oxygen and results in subsequent loss of biodiversity is known as Eutrophication.

12.6.2 International Standards for Drinking Water

The International Standards for drinking water are given below and they must be followed.

Fluoride: For drinking purposes, water should be tested for fluoride ion concentration. Its deficiency in drinking water is harmful to man and causes diseases such as tooth decay etc. Soluble fluoride is often added to drinking water to bring its concentration upto 1 ppm or 1mg dm^{-3}. The F^- ions make the enamel on teeth much harder by converting hydroxyapatite, $[3(Ca_3(PO_4)_2.Ca(OH)_2]$, the enamel on the surface of the teeth, into much harder fluorapatite, $[3(Ca_3(PO_4)_2.CaF_2]$. However, F^- ion concentration above 2 ppm causes brown mottling of teeth. At the same time, excess fluoride (over 10 ppm) causes harmful effect to bones and teeth, as reported from some parts of Rajasthan.

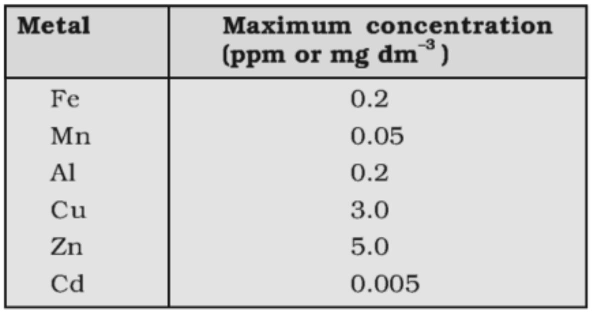
Lead: Drinking water gets contaminated with lead when lead pipes are used for transportation of water. The prescribed upper limit concentration of lead in drinking water is about 50 ppb. Lead can damage kidney, liver, reproductive system etc.

Sulphate: Excessive sulphate (>500 ppm) in drinking water causes laxative effect, otherwise at moderate levels it is harmless.

Nitrate: The maximum limit of nitrate in drinking water is 50 ppm. Excess nitrate in drinking water can cause disease such as methemoglobinemia ('blue baby' syndrome) .

Other metals: The maximum concentration of some common metals recommended in drinking water is given in Table 12.2.

Table 12.2 Maximum prescribed concentration of some metals in drinking water



Metal	Maximum concentration (ppm or mg dm^{-3})
Fe	0.2
Mn	0.05
Al	0.2
Cu	3.0
Zn	5.0
Cd	0.005

12.7 Soil Pollution

India being agriculture based economy gives high priority to agriculture, fisheries and livestock development. The surplus production is stored by governmental and non-governmental organizations for the lean season. The food loss during the storage also needs special attention. Have you ever seen the damages caused to the crops, food items by insects, rodents, weeds and crop diseases etc? How can we protect them? You are acquainted with some insecticides and pesticides for protection of our crops. However, these insecticides, pesticides and herbicides cause soil pollution. Hence, there is a need for their judicious use.

12.7.1 Pesticides

Prior to World War II, many naturally occurring chemicals such as nicotine (by planting tobacco plants in the crop field), were used as pest controlling substance for major crops in agricultural practices.

During World War II, DDT was found to be of great use in the control of malaria and other insect-borne diseases. Therefore, after the war, DDT was put to use in agriculture to control the damages caused by insects, rodents, weeds and various crop diseases. However, due to adverse effects, its use has been banned in India.

Pesticides are basically synthetic toxic chemicals with ecological repercussions. The repeated use of the same or similar pesticides give rise to pests that are resistant to that group of pesticides thus making the pesticides in effective. Therefore, as insect resistance of DDT increased, other organic toxins such as Aldrin and Dieldrin were introduced in the market by pesticide industry. Most of the organic toxins are water insoluble and non-biodegradable. These high persistent toxins are, therefore, transferred from lower trophic level to higher trophic level through food chain (Fig.12.2). Over the time, the concentration of toxins in higher animals reaches a level which causes serious metabolic and physiological disorders.

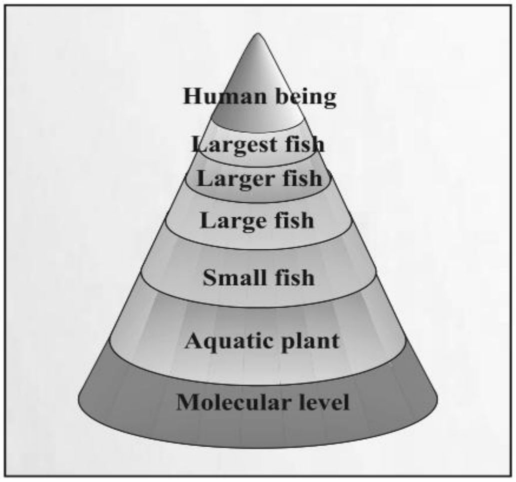


Fig. 12.2 At each tropic level the pollutant get 10% concentrated

In response to high persistence of chlorinated organic toxins, a new series of less persistent or more bio-degradable products called organo-phosphates and carbamates have been introduced in the market. But these chemicals are severe nerve toxins and hence more harmful to humans. As a result, there are reports of some pesticides related deaths of agricultural field workers. Insects have become resistant to these insecticides also. The insecticide industry is engaged in developing new groups of insecticides. But one has to think, is this only solution to pest menace?

These days, the pesticide industry has shifted its attention to herbicides such as sodium chlorate ($NaC1O_3$), sodium arsinite ($NaAsO_3$) and many others. During the first half of the last century, the shift from mechanical to chemical weed control had provided the industry with flourishing economic market. But one must remember that these are also not environment friendly.

Most herbicides are toxic to mammals but are not as persistent as organo-chlorides. These chemicals decompose in a few months. Like organo-chlorides, these too become concentrated in the food web. Some herbicides cause birth defects. Studies show that corn- fields sprayed with herbicides are more prone to insect attack and plant disease than fields that are weeded manually.

Pesticides and herbicides represent only a very small portion of widespread chemical pollution. A large number of other compounds that are used regularly in chemical and industrial processes for manufacturing activities are finally released in the atmosphere in one or other form.

12.8 Industrial Waste

Industrial solid wastes are also sorted out as biodegradable and non-degradable wastes. Biodegradable wastes are generated by cotton mills, food processing units, paper mills, and textile factories.

Non-biodegradable wastes are generated by thermal power plants which produce fly ash; integrated iron and steel plants which produce blast furnace slag and steel melting slag. Industries manufacturing aluminium, zinc and copper produce mud and tailings. Fertilizer industries produce gypsum. Hazardous wastes such as inflammables, composite explosives or highly reactive substances are produced by industries dealing in metals, chemicals, drugs, pharmaceuticals, dyes, pesticides, rubber goods etc.

The disposal of non-degradable industrial solid wastes, if not done by a proper and suitable method, may cause serious threat to the environment. New innovations have led to different uses of waste material. Nowadays, fly ash and slag from the steel industry are utilised by the cement industry. Large quantities of toxic wastes are usually destroyed by controlled incineration, whereas small quantities are burnt along with factory garbage in open bins. Moreover, solid wastes if not managed effectively, affect the components of the environment.

12.9 Strategies to Control Environmental Pollution

After studying air, water, soil and industrial waste pollution in this unit, by now you must have started feeling the need of controlling environmental pollution: How can you save your immediate environment? Think of the steps/ activities, which you would like to undertake for controlling air, water, soil and industrial waste pollution in your neighbourhood. Here, an idea about the strategies for the management of waste is given.

12.9.1 Waste Management

Solid waste is not the only waste, which you see in your household garbage box. Besides household discards, there are medical, agricultural, industrial and mining wastes. The improper disposal of wastes is one of the major causes of environmental degradation. Therefore, the management of wastes is of utmost importance.

12.9.2 Collection and Disposal

Domestic wastes are collected in small bins, which are then transferred to community bins by private or municipal workers. From these community bins, these are collected and carried to the disposable site. At the site, garbage is sorted out and separated into biodegradable and non-biodegradable materials. Non-biodegradable materials such as plastic, glass, metal scraps etc. are sent for recycling. Biodegradable wastes are deposited in landfills and are converted into compost.

The waste if not collected in garbage bins, finds its way into the sewers. Some of it is eaten by cattle. Non-biodegradable wastes like polythene bag, metal scraps, etc. choke the sewers and cause inconvenience. Polythene bags, if swallowed by cattle can cost their lives also.

As a normal practice, therefore, all domestic wastes should be properly collected and disposed. The poor management causes health problems leading to epidemics due to contamination of ground water. It is specially hazardous for those who are in direct contact with the waste such as rag pickers and workers involved in waste disposal, as they are the ones who handle waste materials mostly without protective device such as gloves or water proof boots and gas masks. What can you do for them?

12.10 Green Chemistry

12.10.1 Introduction

It is well known fact that self-sufficiency in food has been achieved in India since late 20th century by using fertilizers and pesticides and exploring improved methods of farming, good quality seeds, irrigation etc. But over - exploitation of soil and excessive use of fertilizers and pesticides have resulted in the deterioration of soil, water and air.

The solution of this problem does not lie in stopping the process of development that has been set in; but to discover methods, which would help in the reduction of deterioration of the environment. Green chemistry is a way of thinking and is about utilising the existing knowledge and principles of chemistry and other sciences to reduce the adverse impact on environment. Green chemistry is a production process that would bring about minimum pollution or deterioration to the environment. The byproducts generated during a process, if not used gainfully, add to the environmental pollution. Such processes are not only environmental unfriendly but also cost-ineffective. The waste generation and its disposal both are economically unsound. Utilisation of existing knowledge base for reducing the chemical hazards along with the developmental activities is the foundation of green chemistry. Have you perceived the idea of green chemistry? It is well known that organic solvents such as benzene, toluene, carbon tetrachloride etc., are highly toxic. One should be careful while using them.

As you know, a chemical reaction involves reactants, attacking reagents and the medium in which the reaction takes place. Extent of any reaction depends upon physical parameters like temperature, pressure and use of catalyst. In a chemical reaction, if reactants are fully converted into useful environmental friendly products by using an environment friendly medium then there would be no chemical pollutants introduced in the environment.

During a synthesis, care must be taken to choose starting materials that can be converted into end products with yield approximately upto 100 percent. This can be achieved by arriving at optimum conditions of synthesis. It may be worthwhile to carry out synthetic reactions in aqueous medium since water has high specific heat and low volatility. Water is cost effective, noninflammable and devoid of any carcinogenic effects.

12.10.2 Green Chemistry in day-to-day Life

(i) Dry Cleaning of Clothes

Tetra chlroroethene ($Cl_2C{=}CC1_2$) was earlier used as solvent for dry cleaning. The compound contaminates the ground water and is also a suspected carcinogen. The process using this compound is now being replaced by a process, where liquefied carbondioxide, with a suitable detergent is used. Replacement of halogenated solvent by liquid CO_2 will result in less harm to ground water. These days hydrogen peroxide (H_2O_2) is used for the purpose of bleaching clothes in the process of laundary, which gives better results and makes use of lesser amount of water.

(ii) Bleaching of Paper

Chlorine gas was used earlier for bleaching paper. These days, hydrogen peroxide (H_2O_2) with suitable catalyst, which promotes the bleaching action of hydrogen peroxide, is used.

(iii) Synthesis of Chemicals

Ethanal (CH_3CHO) is now commercially prepared by one step oxidation of ethene in the presence of ionic catalyst in aqueous medium with an yield of 90%.

$$H_2C{=}CH_2 + O_2 \xrightarrow[\text{Pd(III)/Cu(II) in water}]{\text{Catalyst}} CH_3CHO \quad (90\%)$$

Green chemistry, in a nutshell, is a cost effective approach which involves reduction in material, energy consumption and waste generation.

SUMMARY

Environrnental chemistry plays a major role in environment. Chemical species present in the environment are either naturally occurring or generated by human activities. Environmental pollution is the effect of undesirable changes in the surrounding that have harmful effects on plants, animals and human beings. Pollutants exist in all the three states of matter. We have discussed only those pollutants, which are due to human activities, and can be controlled. Atmospheric pollution is generally studied as tropospheric and stratospheric pollution. Troposphere is the lowest region of the atmosphere ($\approx$10 km) in which man along with other organisms including plants exist, whereas stratosphere extends above troposphere up to 50 km above sea level. Ozone layer is one of the important constituents of stratosphere. Tropospheric pollution is basically due to various oxides of sulphur, nitrogen, carbon, halogens and also due to particulate pollutants. The gaseous pollutants come down to the earth in the form of acid rain. 75% of the solar energy reaching earth is absorbed by the earth surface and rest is radiated back to the atmosphere. These gases mentioned above trap the heat which results into global warming. It is important to realise that these very gases are also responsible for the life on the earth as they trap the requisite amount of solar energy for the sustenance of life. The increase in the greenhouse gases is raising the temperature of the earth's atmosphere which, if not checked , may eventually result in melting of polar ice caps and consequently may submerge the costal land mass. Many human activities are producing chemicals, which are responsible for the depletion of ozone layer in the stratosphere, leading to the formation of ozone hole. Through the ozone hole, ultraviolet radiations can penetrate into the earth's atmosphere causing mutation of genes. Water is the elixir of life but the same water, if polluted by pathogens, organic wastes, toxic heavy metals, pesticides etc., will turn into poison. Therefore, one should take care to follow international standards to maintain purity levels of drinking water. Industrial wastes and excessive use of pesticides, result into pollution of land mass and water bodies. Judicious use of chemicals required for agricultural practices can lead to sustainable development. Strategies for controlling environmental pollution can be: (i) waste management i.e., reduction of the waste and proper disposal, also recycling of materials and energy, (ii) adopting methods in day-to-d ay life, which results in the reduction of environmental pollution. The second method is a new branch of chemistry, which is in its infancy known as green chemistry. It utilizes the existing knowledge and practices so as to bring about reduction in the production of pollutants.

EXERCISES

1 Define environmental chemistry.

2 Explain tropospheric pollution in 100 words.

3 Carbon monoxide gas is more dangerous than carbon dioxide gas. Why? List gases which are responsible for greenhouse effect.

4 Statues and monuments in India are affected by acid rain. How?

5 What are the reactions involved for ozone layer depletion in the stratosphere? What do you mean by ozone hole? What are its consequences?

6 What are the major causes of water pollution? Explain.

7 Have you ever observed any water pollution in your area? What measures would you suggest to control it?

8 What do you mean by Biochemical Oxygen Demand (BOD)?

9 Do you observe any soil pollution in your neighbourhood? What eflorts will you make for controlling the soil pollution'?

10 What are pesticides and herbicides? Explain giving examples.

11 What do you mean by green chemistry? How will it help decrease environmental pollution?

12 What would have happened if the greenhouse gases were totally missing in the earth's atmosphere? Discuss.

13 A large number of fish are suddenly found floating dead on a lake. There is no evidence of toxic dumping but you find an abundance of phytoplankton. Suggest a reason for the fish kill.

14 How can domestic waste be used as manure?

15 For your agricultural field or garden you have developed a compost producing pit. Discuss the process in the light of bad odour, flies and recycling of wastes for a good produce.

QUESTION BANK

***Very Short Answer Questions* (2marks)**

1. List out four Gaseous pollutants present in the polluted air?
2. What are green house gases?
3. Which acids cause acid rain? And what is its pHvalue.
4. Name two adverse effects caused by acid rains?
5. What is ozone hole? Where it was first observed?
6. What is green house effect? And how is it caused?
7. What are the harmful effects caused by ozone layer depletion?
8. Define Eutrophication of lake?
9. What is the importance of Green Chemistry?

CHAPTER-13

ORGANIC CHEMISTRY – SOME BASIC PRINCIPLES AND TECHNIQUES AND HYDRO CORBONS

In the previous unit you have learnt that the element carbon has the unique property called catenation due to which it forms covalent bonds with other carbon atoms. It also forms covalent bonds with atoms of other elements like hydrogen, oxygen, nitrogen, sulphur, phosphorus and halogens. The resulting compounds are studied under a separate branch of chemistry called organic chemistry. This unit incorporates some basic principles and techniques of analysis required for understanding the formation and properties of organic compounds.

13.1 General Introduction

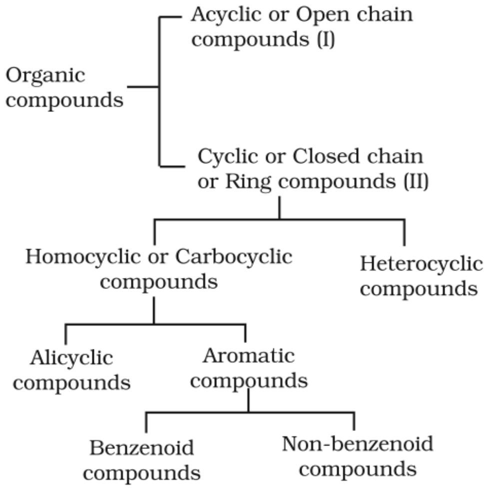
Organic compounds are vital for sustaining life on earth and include complex molecules like genetic information bearing deoxyribonucleic acid (DNA) and proteins that constitute essential compounds of our blood, muscles and skin. Organic chemicals appear in materials like clothing, fuels, polymers, dyes and medicines. These are some of the important areas of application of these compounds.

Science of organic chemistry is about two hundred years old. Around the year 1780, chemists began to distinguish between organic compounds obtained from plants and animals and inorganic compounds prepared from mineral sources. Berzilius, a Swedish chemist proposed that a 'vital force' was responsible for the formation of organic compounds. However, this notion was rejected in 1828 when F. Wohler synthesised an organic compound, urea from an inorganic compound, ammonium cyanate.

The pioneering synthesis of acetic acid by Kolbe (1845) and that of methane by Berthelot (1856) showed conclusively that organic compounds could be synthesised from inorganic sources in a laboratory.

13.2 Classification of Organic Compounds

The existing large number of organic compounds and their ever -increasing numbers has made it necessary to classify them on the basis of their structures. Organic compounds are broadly classified as follows:

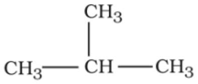


I. Acyclic or open chain compounds

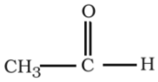
These compounds are also called as aliphatic compounds and consist of straight or branched chain compounds, for example:

CH_3CH_3

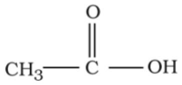
Ethane


$CH_3-CH(CH_3)-CH_3$

Isobutane


$CH_3-C(=O)-H$

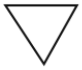
Acetaldehyde

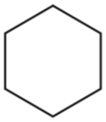

$CH_3-C(=O)-OH$

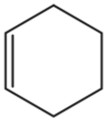
Acetic acid

II. Alicyclic or closed chain or ring compounds

Alicyclic (aliphatic cyclic) compounds contain carbon atoms joined in the form of a ring (homocyclic). Sometimes atoms other than carbon are also present in the ring (heterocylic). Some examples of this type of compounds are:


Cyclopropane


Cyclohexane


Cyclohexene

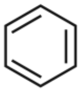

Tetrahydrofuran

These exhibit some of the properties similar to those of aliphatic compounds

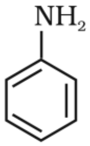
Aromatic compounds

Aromatic compounds are special types of compounds. These include benzene and other related ring compounds (benzenoid). Like alicyclic compounds, aromatic comounds may also have hetero atom in the ring. Such compounds are called hetrocyclic aromatic compounds. Some of the examples of various types of aromatic compounds are:

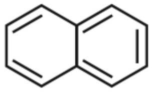
Benzenoid aromatic compounds



Benzene

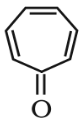


Aniline



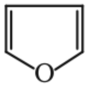
Naphthalene

Non-benzenoid compound

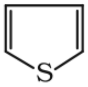


Tropolone

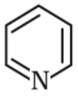
Heterocyclic aromatic compounds



Furan



Thiophene



Pyridine

Organic compounds can also be classified on the basis of functional groups, into families or homologous series.

Functional Group

The functional group may be defined as an atom or group of atoms joined in a specific manner which is responsible for the characteristic chemical properties of the organic compounds. The examples are hydroxyl group (-OH), aldehyde group (-CHO) and carboxylic acid group (-COOH) etc.

Homologous Series

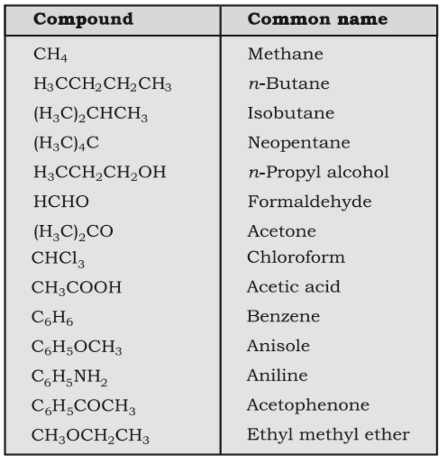
A group or a series of organic compounds each containing a characteristic functional group forms a homologous series and the members of the series are called homologues. The members of a homologous series can be represented by general molecular formula and the successive members differ from each other in molecular formula by a $-CH_2$ unit. There are a number of homologous series of organic compounds. Some of these are alkanes, alkenes, alkynes, haloalkanes, alkanols, alkanals, alkanones, alkanoic acids, amines etc.

13.3 Nomenclature of Organic Compounds

Organic chemistry deals with millions of compounds. In order to clearly identify them, a systematic method of naming has been developed and is known as the IUPAC (International Union of Pure and Applied Chemistry) system of nomenclature. In this systematic nomenclature, the names are correlated with the structure such that the reader or listener can deduce the structure from the name.

Before the IUPAC system of nomenclature, however, organic compounds were assigned names based on their origin or certain properties. For instance, citric acid is named so because it is found in citrus fruits and the acid found in red ant is named formic acid since the Latin word for ant is formica. These names are traditional and are considered as trivial or common names. Some common names are followed even today. For example, Buckminster fullerene is a common name given to the newly discovered C_{60} cluster (a form of carbon) noting its structural similarity to the geodesic domes popularised by the famous architect R. Buckminster Fuller. Common names are useful and in many cases indispensable, particularly when the alternative systematic names are lengthy and complicated. Common names of some organic compounds are given in Table 13. 1.

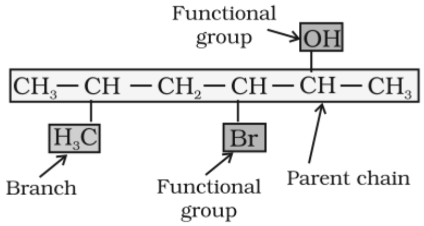
Table 13.1 Common or Trivial names of some organic compounds



Compound	Common name
CH_4	Methane
$H_3CCH_2CH_2CH_3$	*n*-Butane
$(H_3C)_2CHCH_3$	Isobutane
$(H_3C)_4C$	Neopentane
$H_3CCH_2CH_2OH$	*n*-Propyl alcohol
HCHO	Formaldehyde
$(H_3C)_2CO$	Acetone
$CHCl_3$	Chloroform
CH_3COOH	Acetic acid
C_6H_6	Benzene
$C_6H_5OCH_3$	Anisole
$C_6H_5NH_2$	Aniline
$C_6H_5COCH_3$	Acetophenone
$CH_3OCH_2CH_3$	Ethyl methyl ether

13.3.1 The IUPAC System of Nomenclature

A systematic name of an organic compound is generally derived by identifying the parent hydrocarbon and the functional group(s) attached to it. See the example given below.

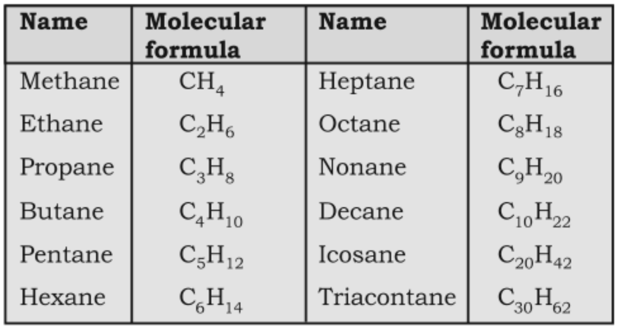


By further using prefixes and suffixes, the parent name can be modified to obtain the actual name. Compounds containing carbon and hydrogen only are called hydrocarbons. A hydrocarbon is termed saturated, if it contains only carbon-carbon single bonds. The IUPAC name for a homologous series of such compounds is alkane. Paraffin (Latin: little affinity) was the earlier name given to these compounds. Unsaturated hydrocarbons are those, which contain at least one carbon- carbon double or triple bond.

13.3.2 IUPAC Nomenclature of Alkanes

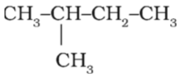
Straight chain hydrocarbons: The names of such compounds are based on their chain structure, and end with suffix '-ane' and carry a prefix indicating the number of carbon atoms present in the chain (except from CH_4 to C_4H_{10} where the prefixes are derived from trivial names). The IUPAC names of some straight chain saturated hydrocarbons are given in Table 13.2. The alkanes in Table 13.2 differ from each other by merely the number of $-CH_2$ groups in the chain. They are homologues of alkane series.

Table 13.2 IUPAC names of some unbranched saturated hydrocarbons



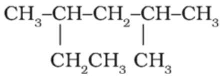
Name	Molecular formula	Name	Molecular formula
Methane	CH_4	Heptane	C_7H_{16}
Ethane	C_2H_6	Octane	C_8H_{18}
Propane	C_3H_8	Nonane	C_9H_{20}
Butane	C_4H_{10}	Decane	$C_{10}H_{22}$
Pentane	C_5H_{12}	Icosane	$C_{20}H_{42}$
Hexane	C_6H_{14}	Triacontane	$C_{30}H_{62}$

Branched chain hydrocarbons: In a branched chain compound small chains of carbon atoms are attached at one or more carbon atoms of the parent chain. The small carbon chains (branches) are called alkyl groups. For example:



$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3$

(a)

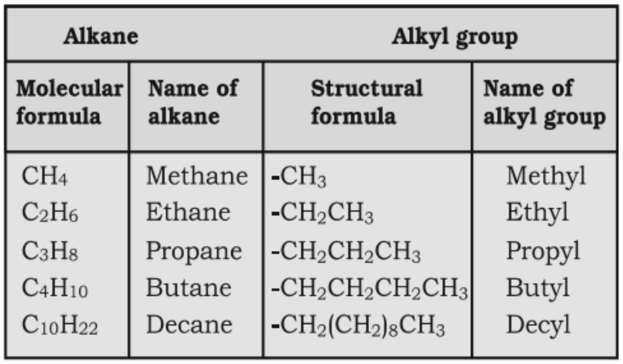


$CH_3-\underset{\underset{CH_2CH_3}{|}}{CH}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$

(b)

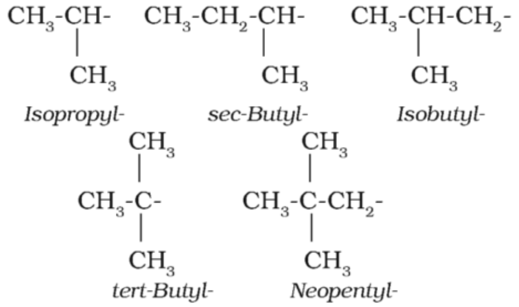
In order to name such compounds, the names of alkyl groups are prefixed to the name of parent alkane. An alkyl group is derived from a saturated hydrocarbon by removing a hydrogen atom from carbon. Thus, CH_4 becomes $-CH_3$ and is called methyl group. An alkyl group is named by substituting 'yl ' for 'ane' in the corresponding alkane. Some alkyl groups are listed in Table 13.3.

Table 13.3 Some alkyl groups



Alkane		Alkyl group	
Molecular formula	Name of alkane	Structural formula	Name of alkyl group
CH_4	Methane	$-CH_3$	Methyl
C_2H_6	Ethane	$-CH_2CH_3$	Ethyl
C_3H_8	Propane	$-CH_2CH_2CH_3$	Propyl
C_4H_{10}	Butane	$-CH_2CH_2CH_2CH_3$	Butyl
$C_{10}H_{22}$	Decane	$-CH_2(CH_2)_8CH_3$	Decyl

Abbreviations are used for some alkyl groups. For example, methyl is abbreviated as Me, ethyl as Et, propyl as Pr and butyl as Bu. The alkyl groups can be branched also. Thus, propyl and butyl groups can have branched structures as shown below.



$$\underset{\underset{CH_3}{|}}{CH_3\text{-}CH\text{-}} \qquad \underset{\underset{CH_3}{|}}{CH_3\text{-}CH_2\text{-}CH\text{-}} \qquad \underset{\underset{CH_3}{|}}{CH_3\text{-}CH\text{-}CH_2\text{-}}$$

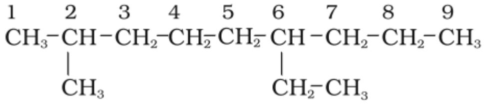
$$\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{CH_3\text{-}C\text{-}}} \qquad \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{CH_3\text{-}C\text{-}CH_2\text{-}}}$$

Common branched groups have specific trivial names. For example, the propyl groups can either be n-propyl group or isopropyl group. The branched butyl groups are called sec-butyl, isobutyl and tert-butyl group. We also encounter the structural unit, $-CH_2C(CH_3)_3$, which is called neopentyl group.

Nomenclature of branched chain alkanes:

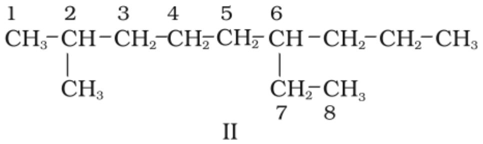
We encounter a number of branched chain alkanes. The rules for naming them are given below.

1. First of all, the longest carbon chain in the molecule is identified. In the example (I) given below, the longest chain has nine carbons and it is considered as the parent or root chain. Selection of parent chain as shown in (II) is not correct because it has only eight carbons.



$$\overset{1}{CH_3}-\underset{\underset{CH_3}{|}}{\overset{2}{CH}}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{CH_2}-\underset{\underset{CH_2-CH_3}{|}}{\overset{6}{CH}}-\overset{7}{CH_2}-\overset{8}{CH_2}-\overset{9}{CH_3}$$

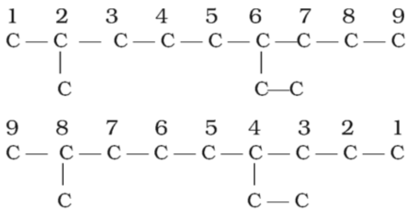
I



$$\overset{1}{CH_3}-\underset{\underset{CH_3}{|}}{\overset{2}{CH}}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{CH_2}-\underset{\underset{\underset{7\quad 8}{CH_2-CH_3}}{|}}{\overset{6}{CH}}-CH_2-CH_2-CH_3$$

II

2. The carbon atoms of the parent chain are numbered to identify the parent alkane and to locate the positions of the carbon atoms at which branching takes place due to the substitution of alkyl group in place of hydrogen atoms. The numbering is done in such a way that the branched carbon atoms get the lowest possible numbers. Thus, the numbering in the above example should be from left to right (branching at carbon atoms 2 and 6) and not from right to left (giving numbers 4 and 8 to the carbon atoms at which branches are attached).

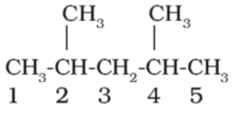


$$\overset{1}{C}-\underset{\underset{C}{|}}{\overset{2}{C}}-\overset{3}{C}-\overset{4}{C}-\overset{5}{C}-\underset{\underset{C-C}{|}}{\overset{6}{C}}-\overset{7}{C}-\overset{8}{C}-\overset{9}{C}$$

$$\overset{9}{C}-\underset{\underset{C}{|}}{\overset{8}{C}}-\overset{7}{C}-\overset{6}{C}-\overset{5}{C}-\underset{\underset{C-C}{|}}{\overset{4}{C}}-\overset{3}{C}-\overset{2}{C}-\overset{1}{C}$$

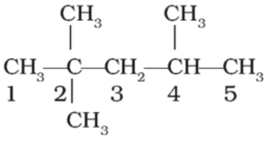
3. The names of alkyl groups attached as a branch are then prefixed to the name of the parent alkane and position of the substituents is indicated by the appropriate numbers. If different alkyl groups are present, they are listed in alphabetical order. Thus, name for the compound shown above is: 6-ethyl-2-methylnonane. [Note: the numbers are separated from the groups by hyphens and there is no break between methyl and nonane.]

4. If two or more identical substituent groups are present then the numbers are separated by commas. The names of identical substituents are not repeated, instead prefixes such as di (for 2), tri (for 3), tetra (for 4), penta (for 5), hexa (for 6) etc. are used. While writing the name of the substituents in alphabetical order, these prefixes, however, are not considered. Thus, the following compounds are named as:



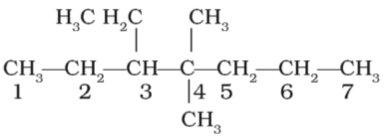
$CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2-\overset{\overset{CH_3}{|}}{C}H-CH_3$

2,4-Dimethylpentane



$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\overset{\overset{CH_3}{|}}{C}H-CH_3$

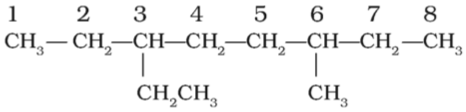
2,2,4-Trimethylpentane



$CH_3-CH_2-\overset{\overset{H_3C\,H_2C}{|}}{C}H-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_2-CH_3$

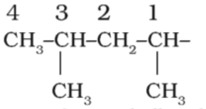
3-Ethyl-4,4-dimethylheptane

5. If the two substituents are found in equivalent positions, the lower number is given to the one coming first in the alphabetical listing. Thus, the following compound is 3-ethyl-6-methyloctane and not 6-ethyl-3-methyloctane.



$CH_3-CH_2-\underset{\underset{CH_2CH_3}{|}}{C}H-CH_2-CH_2-\underset{\underset{CH_3}{|}}{C}H-CH_2-CH_3$

6. The branched alkyl groups can be named by following the above mentioned procedures. However, the carbon atom of the branch that attaches to the root alkane is numbered 1 as exemplified below.

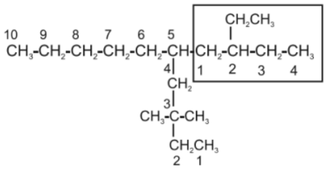


$CH_3-\underset{\underset{CH_3}{|}}{C}H-CH_2-\underset{\underset{CH_3}{|}}{C}H-$

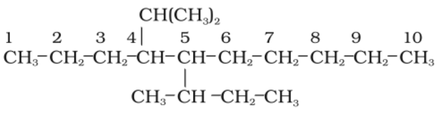
1,3-Dimethylbutyl-

The name of such branched chain alkyl group is placed in parenthesis while naming the compound. While writing the trivial names of substituents' in alphabetical order, the prefixes iso- and neo- are considered to be the part of the fundamental name of alkyl group. The prefixes sec- and tert- are not considered to be the part of the fundamental name. The use of iso and related common prefixes for naming alkyl groups is also allowed by the IUPAC nomenclature as long as these are not further substituted. In multi- substituted compounds, the following rules may also be remembered:

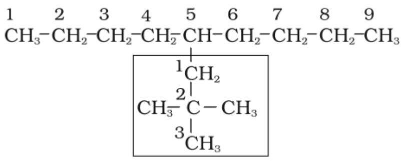
- If there happens to be two chains of equal size, then that chain is to be selected which contains more number of side chains.
- After selection of the chain, numbering is to be done from the end closer to the substituent.



5-(2-Ethylbutyl)-3,3-dimethyldecane
[and not 5-(2,2-Dimethylbutyl)-3-ethyldecane]



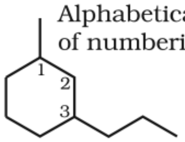
5-sec-Butyl-4-isopropyldecane



5-(2,2-Dimethylpropyl)nonane

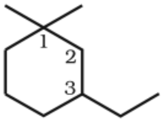
Cyclic Compounds: A saturated monocyclic compound is named by prefixing 'cyclo' to the corresponding straight chain alkane. If side chains are present, then the rules given above are applied. Names of some cyclic compounds are given below.

Cyclopentane



Alphabetical order of numbering

1-Methyl-3-propylcyclohexane



More branched carbon gets lower number

3-Ethyl-1,1-dimethylcyclohexane (not 1-ethyl-3,3-dimethylcyclohexane)

13.3.3 Nomenclature of Organic Compounds having Functional Group(s)

A functional group, as defined earlier, is an atom or a group of atoms bonded together in a unique manner which is usually the site of chemical reactivity in an organic molecule. Compounds having the same functional group undergo similar reactions. For example, CH_3OH, CH_3CH_2OH and $(CH_3)_2CHOH$ having -OH functional group liberate hydrogen on reaction with sodium metal. The presence of functional groups enables systematisation of organic compounds into different classes. Examples of some functional groups with their prefixes and suffixes along with some examples of organic compounds possessing these are given in Table 13.4.

First of all, the functional group present in the molecule is identified which determines the choice of appropriate suffix. The longest chain of carbon atoms containing the functional group is numbered in such a way that the functional group is attached at the carbon atom possessing lowest possible number in the chain. By using the suffix as given in Table 13.4, the name of the compound is arrived at.

In the case of polyfunctional compounds, one of the functional groups is chosen as the principal functional group and the compound is then named on that basis. The remaining functional groups, which are subordinate functional groups, are named as substituents using the appropriate prefixes. The choice of principal functional group is made on the basis of order of preference. The order of decreasing priority for some functional groups is: -COOH, $-SO_3H$, -COOR (R=alkyl group), -COCl, $-CONH_2$, -CN, -HC=O, > C= O, -OH, $-NH_2$, C=C, $C\equiv C$.

The -R, C_6H_5-, halogens (F, Cl, Br, I), $-NO_2$, alkoxy (-OR) etc. are always prefix substituents. Thus, a compound containing both an alcohol and a keto group is named as hydroxyl alkanone since the keto group is preferred to the hydroxyl group.

For example, $HOCH_2(CH_2)_3CH_2COCH_3$ will be named as 7-hydroxyheptan -2-one and not as 2-oxoheptan -7-ol. Similarly, $BrCH_2CH=CH_2$ is named as 3-bromoprop- 1-ene and not l-bromoprop-2-ene.

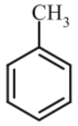
If more than one functional group of the same type is present, their number is indicated by adding di, tri, etc. before the class suffix. In such cases the full name of the parent alkane is written before the class suffix. For example $CH_2(OH)$ $CH_2(OH)$ is named as ethane-1,2-diol. However, the ending - ne of the parent alkane is dropped in the case of compounds having more than one double or triple bond; for example, CH_2=CH- CH=CH_2 named as buta-1,3-diene.

13.3.4 Nomenclature of Substituted Benzene Compounds

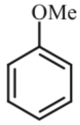
For IUPAC nomenclature of substituted benzene compounds, the substituent is placed as prefix to the word benzene as shown in the following examples. However, common names (written in bracket below) of many substituted benzene compounds are also universally used.

Table 13.4 Some functional groups and classes of organic compounds

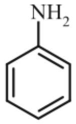
Class of compounds	**Functional group structure**	**IUPAC group prefix**	**IUPAC group suffix**	**Example**
Alkanes	-	-	-ane	Butane, $CH_3(CH_2)_2CH_3$
Alkenes	>C=C<	-	-ene	But-1-ene, $CH_2=CHCH_2CH_3$
Alkynes	-C≡C-	-	-yne	But-1-yne, $CH\equiv CCH_2CH_3$
Arenes	-	-	-	Benzene, 
Halides	-X (X=F,Cl,Br,I)	halo-	-	1-Bromobutane, $CH_3(CH_2)_2CH_2Br$
Alcohols	-OH	hydroxy-	-ol	Butan-2-ol, $CH_3CH_2CHOHCH_3$
Aldehydes	-CHO	formyl, or oxo	-al	Butanal, $CH_3(CH_2)_2CHO$
Ketones	>C=O	oxo-	-one	Butan-2-one, $CH_3CH_2COCH_3$
Nitriles	-C≡N	cyano	nitrile	Pentanenitrile, $CH_3CH_2CH_2CH_2CN$
Ethers	-R-O-R-	alkoxy-	-	Ethoxyethane, $CH_3CH_2OCH_2CH_3$
Carboxylic acids	-COOH	carboxy	-oic acid	Butanoic acid, $CH_3(CH_2)_2CO_2H$
Carboxylate ions	$-COO^-$	-	-oate	Sodium butanoate, $CH_3(CH_2)_2CO_2^-\ Na^+$
Esters	-COOR	alkoxycarbonyl	-oate	Methyl propanoate, $CH_3CH_2COOCH_3$
Acyl halides	-COX (X=F,Cl,Br,I)	halocarbonyl	-oyl halide	Butanoyl chloride, $CH_3(CH_2)_2COCl$
Amines	$-NH_2$, >NH,>N-	amino-	-amine	Butan-2-amine, $CH_3CHNH_2CH_2CH_3$
Amides	$-CONH_2$, -CONHR, $-CONR_2$	-carbamoyl	-amide	Butanamide, $CH_3(CH_2)_2CONH_2$
Nitros	$-NO_2$	nitro	-	1-Nitrobutane, $CH_3(CH_2)_3NO_2$



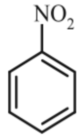
Methylbenzene (Toluene)



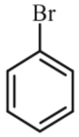
Methoxybenzene (Anisole)



Aminobenzene (Aniline)

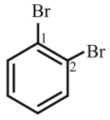


Nitrobenzene



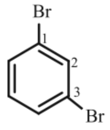
Bromobenzene

If benzene ring is disubstituted , the position of substituents is defined by numbering the carbon atoms of the ring such that the substituents are located at the lowest numbers possible. For example, the compound (b) is named as 1,3-dibromobenzene and not as 1,5-dibromobenzene.



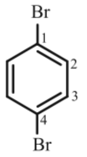
(a)

1,2-Dibromobenzene



(b)

1,3-Dibromobenzene



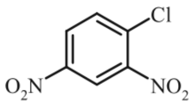
(c)

1,4-Dibromobenzene

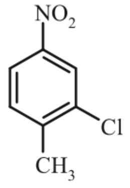
In the trivial system of nomenclature the terms ortho (o), meta (m) and para (p) are used as prefixes to indicate the relative positions 1,2- ; 1,3- and 1,4 - respectively. Thus, 1,3-dibromobenzene (b) is named as m-dibromobenzene (meta is abbreviated as m-) and the other isomers of dibromobenzene 1,2-(a) and 1,4-(c) , are named as ortho (or just o-) and para (or just p-) -dibromobenzene, respectively.

For tri- or higher substituted benzene derivatives, these prefixes cannot be used and the compounds are named by identifying substituent positions on the ring by following the lowest locant rule. In some cases, common name of benzene derivatives is taken as the base compound.

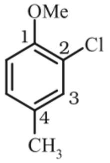
Substituent of the base compound is assigned number 1 and then the direction of numbering is chosen such that the next substituent gets the lowest number. The substituents appear in the name in alphabetical order. Some examples are given below.



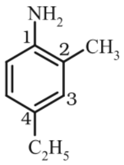
1-Chloro-2,4-dinitrobenzene (not 4-chloro,1,3-dinitrobenzene)



2-Chloro-1-methyl-4-nitrobenzene (not 4-methyl-5-chloro-nitrobenzene)



2-Chloro-4-methylanisole

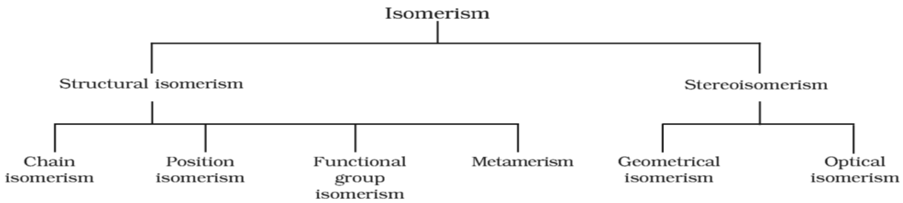


4-Ethyl-2-methylaniline

When a benzene ring is attached to an alkane with a functional group, it is considered as substituent, instead of a parent. The name for benzene as substituent is phenyl (C_6H_5 -, also abbreviated as Ph).

13.4 Isomerism

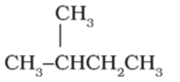
The phenomenon of existence of two or more compounds possessing the same molecular formula but different properties is known as isomerism. Such compounds are called as isomers. The following flow chart shows different types of isomerism.

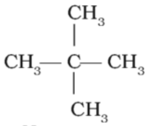


13.4.1 Structural isomerism:

(i) Chain isomerism: Compounds having the same molecular formula but different carbon skeletons, these are referred to as chain isomers and the phenomenon is termed as chain isomerism. For example, C_5H_{12} represents three compounds:

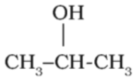
$CH_3CH_2CH_2CH_2CH_3$
Pentane


$CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}}}HCH_2CH_3$
Isopentane
(2-Methylbutane)

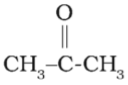

$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3$
Neopentane
(2,2-Dimethylpropane)

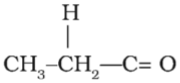
(ii) Position isomerism: When two or more compounds differ in the position of substituent atom or functional group on the carbon skeleton, they are called position isomers and this phenomenon is termed as position isomerism. For example, the molecular formula C_3H_8O represents two alcohols:

$CH_3CH_2CH_2OH$
Propan-1-ol


$CH_3-\overset{OH}{\overset{|}{C}}H-CH_3$
Propan-2-ol

(iii) Functional group isomerism: Two or more compounds having the same molecular formula but different functional groups are called functional isomers and this phenomenon is termed as functional group isomerism. For example, the molecular formula C_3H_6O represents an aldehyde and a ketone:


$CH_3-\overset{O}{\overset{||}{C}}-CH_3$
Propanone


$CH_3-CH_2-\overset{H}{\overset{|}{C}}=O$
Propanal

(iv) Metamerism: It arises due to different alkyl chains on either side of the functional group in the molecule. For example, $C_4H_{10}O$ represents methoxypropane ($CH_3OC_3H_7$) and ethoxyethane ($C_2H_5OC_2H_5$).

13.4.2 Stereoisomerism

The compounds that have the same constitution and sequence of covalent bonds but differ in relative positions of their atoms or groups in space are called stereoisomers. This special type of isomerism is called as stereoisomerism and can be classified as geometrical and optical isomerism.

13.5 Fundamental Concepts in Organic Reaction Mechanism

13.5.1 Fission of a Covalent Bond

A covalent bond is formed when electrons are shared between two atoms in the conventional sense. A single bond (sigma bond) is thus made up of two electrons. Now a chemical reaction takes place when old bonds are broken and new ones are formed. A covalent bond can get cleaved either by: 1. Homolytic cleavage, or by 2. Heterolytic cleavage.

1. Homolytic fission:

Homolytic fission is where each atom of the bond keeps an electron each resulting in species called free radicals. Radicals are important intermediates in organic chemistry and we will talk about them later. As the bond breaks to give two similar species each keeping an electron this form of bond breaking is called Homolytic Fission. A radical is an atom, molecule, or ion that has an unpaired valence electron. These unpaired electrons make free radicals highly chemically reactive.

2. Heterolytic fission

In this case we can see that one of the atoms bear a negative charge after bond cleavage indicating that it has both the electrons of the bond and the other has no electrons at all. Hence it is electron deficient and becomes positively charged. This is called Heterolytic Fission. In a case the C atom carries a positive charge it is called a carbocation (carbonium) and in the case it carries both the electrons of the broken bond and is negatively charged, it is quite instinctively called a Carbanion. Carbocation and Carbanions are the most important carbon intermediates in organic chemistry and hence warrant further discussion.

13.5.2 Electrophiles and Nucleophiles:

An electrophile is an atom or molecule that can accept an electron pair from an electron rich species and form a covalent bond. Electrophiles are positively or neutral charged atoms or molecules having free orbitals for incoming electrons.

Electrophiles are called Lewis acids due to their ability to accept electrons. An electrophile is created when an atom or a molecule lacks electrons to obey the octet rule or have a positive charge that needed to be neutralized in order to become stable.

In organic chemistry, electrophiles undergo addition and substitution reaction. For example, the addition of halogens to alkenes occurs via electrophilic addition reactions.

Ionic electrophiles:H^+ (proton), Cl^+ (chloronium) , Br^+ (bromonium), $^+NO_2$ (Nitronium), $> C^+$ carbonium

Neutral electrophiles (Lewis acids): $AlCl_3$, BF_3, $ZnCl_2$, $FeCl_3$, SO_3

A nucleophile is an atom or molecule which can donate electron pairs, and due to their ability, it is also called Lewis base. Nucleophiles can donate electrons to electrophiles. Molecules having π bonds or atoms or molecules having free electron pairs act as nucleophiles.

Nucleophiles are normally negatively charged. Even neutrally charged molecules with electron rich atoms can behave as nucleophiles. Nucleophiles also give you an idea about specific reactions such as Nucleophilic addition and Nucleophilic substitution reaction.

Neutral nucleophiles(Lewis bases): NH_3, H_2O, R-OH, R-NH_2, R_3-N

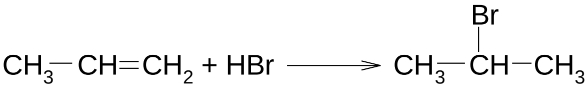
Ionic nucleophiles: X^- (halide ions), OH^- (hydroxide), R^- (alkoxide), CN^- (cyanide), $< C^-$ (carbanion)

13.6 Types of Reactions

The chemical reactions involved in the carbon compounds are of four types.

i) Addition reactions ii) Elimination reactions iii) Substitution reactions iv) Rearrangement reactions.

i) Addition reactions:- Addition of atoms or groups to unsaturated system, without removing any atoms or groups from the molecule is called addition reaction.



$$CH_3-CH=CH_2 + HBr \longrightarrow CH_3-\overset{\displaystyle Br}{\overset{|}{C}}H-CH_3$$

ii) Elimination reactions:- In these reactions, atoms or groups are removed from the adjacent carbon atoms of a organic compound. In this process multiple bonds are formed between the adjacent carbon atoms.

Ex:- Alkene is formed by the action of alcoholic KOH on alkyl halide.

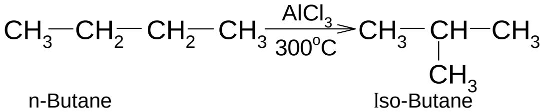
$$CH_3-CH_2Br + KOH \longrightarrow CH_2=CH_2 + KBr + H_2O$$

iii) Substitution reactions:- These are the reactions in which an atom or a group attached to a carbon atom in a organic compound is replaced by another atom or group.

$$CH_4 + Cl_2 \xrightarrow{\text{uv light}} CH_3Cl + HCl$$

iv) Rearrangement reactions:- These are the reactions in which the products get formed by the rearrangement of atoms or groups in the reactant molecules.

$$\underset{\text{Ammonium cyanate}}{NH_4CNO} \xrightarrow{\triangle} \underset{\text{Urea}}{H_2NCONH_2}$$



$$CH_3-CH_2-CH_2-CH_3 \xrightarrow[300^oC]{AlCl_3} CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}H-CH_3$$

n-Butane Iso-Butane

Hydrocarbons

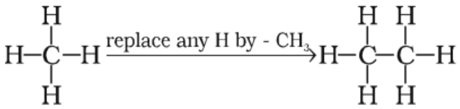
The term 'hydrocarbon' is self-explanatory which means compounds of carbon and hydrogen only. Hydrocarbons play a key role in our daily life. You must be familiar with the terms 'LPG' and 'CNG' used as fuels. LPG is the abbreviated form of liquified petroleum gas whereas CNG stands for compressed natural gas. Another term 'LNG' (liquified natural gas) is also in news these days. This is also a fuel and is obtained by liquifaction of natural gas. Petrol, diesel and kerosene oil are obtained by the fractional distillation of petroleum found under the earth's crust. Coal gas is obtained by the destructive distillation of coal. Natural gas is found in upper strata during drilling of oil wells. The gas after compression is known as compressed natural gas. LPG is used as a domestic fuel with the least pollution. Kerosene oil is also used as a domestic fuel but it causes some pollution. Automobiles need fuels like petrol, diesel and CNG. Petrol and CNG operated automobiles cause less pollution. All these fuels contain mixture of hydrocarbons, which are sources of energy. Hydrocarbons are also used for the manufacture of polymers like polythene, polypropene, polystyrene etc. Higher hydrocarbons are used as solvents for paints. They are also used as the starting materials for manufacture of many dyes and drugs. Thus, you can well understand the importance of hydrocarbons in your daily life. In this unit, you will learn more about hydrocarbons.

13.7 Classification

Hydrocarbons are of different types. Depending upon the types of carbon-carbon bonds present, they can be classified into three main categories - (i) saturated (ii) unsaturated and (iii) aromatic hydrocarbons. Saturated hydrocarbons contain carbon-carbon and carbon-hydrogen single bonds. If different carbon atoms are joined together to form open chain of carbon atoms with single bonds, they are termed as alkanes. On the other hand, if carbon atoms form a closed chain or a ring, they are termed as cycloalkanes. Unsaturated hydrocarbons contain carbon-carbon multiple bonds - double bonds, triple bonds or both. Aromatic hydrocarbons are a special type of cyclic compounds. You can construct a large number of models of such molecules of both types (open chain and close chain) keeping in mind that carbon is tetravalent and hydrogen is monovalent. For making models of alkanes, you can use toothpicks for bonds and plasticine balls for atoms. For alkenes, alkynes and aromatic hydrocarbons, spring models can be constructed.

13. 8 Alkanes

As already mentioned, alkanes are saturated open chain hydrocarbons containing carbon - carbon single bonds. Methane (CH_4) is the first member of this family. Methane is a gas found in coal mines and marshy places. If you replace one hydrogen atom of methane by carbon and join the required number of hydrogens to satisfy the tetravalence of the other carbon atom, what do you gets? You get C_2H_6 .This hydrocarbon with molecular formula C_2H_6 is known as ethane. Thus you can consider C_2H_6 as derived from CH_4 by replacing one hydrogen atom by -CH_3 group. Go on constructing alkanes by doing this theoretical exercise i.e., replacing hydrogen atom by - CH_3 group. The next molecules will be C_3H_8, C_4H_{10}…



These hydrocarbons are inert under normal conditions as they do not react with acids, bases and other reagents. Hence, they were earlier known as paraffins (latin: parum, little; affinis, affinity). Can you think of the general formula for alkane family or homologous series? The general formula for alkanes is C_nH_{2n+2}, where n stands for number of carbon atoms and 2n+2 for number of hydrogen atoms in the molecule. Can you recall the structure of methane? According to VSEPR theory, methane has a tetrahedral structure (Fig. 13. 1) which is multiplanar, in which carbon atom lies at the centre and the four hydrogen atoms lie at the four corners of a regular tetrahedron. All H-C-H bond angles are of 109.5°.

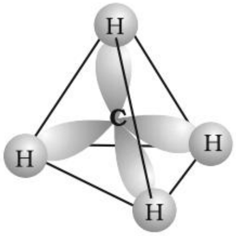


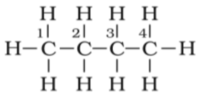
Fig. 13.1 Structure of methane

In alkanes, tetrahedra are joined together in which C-C and C-H bond lengths are 154 pm and 112 pm respectively (Unit 12). You have already read that C-C and C-H sigma (σ) bonds are formed by head-on overlapping of sp^3 hybrid orbitals of carbon and 1s orbitals of hydrogen atoms.

Nomenclature and Isomerism

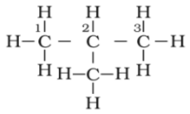
You have already read about nomenclature of different classes of organic compounds. Nomenclature and isomerism in alkanes can further be understood with the help of a few more examples. Common names are given in parenthesis. First three alkanes - methane, ethane and propane have only one structure but higher alkanes can have more than one structure. Let us write structures for C_4H_{10}. Four carbon atoms of C_4H_{10} can be joined either in a continuous chain or with a branched chain in the following two ways:

I



Butane (*n*- butane), (b.p. 273 K)

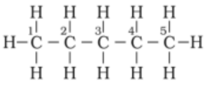
II



2-Methylpropane (isobutane)
(b.p.261 K)

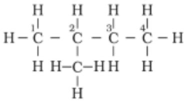
In how many ways, you can join five carbon atoms and twelve hydrogen atoms of C_5H_{12}? They can be arranged in three ways as shown in structures III –V.

III



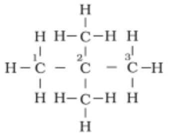
Pentane (*n*-pentane)
(b.p. 309 K)

IV



2-Methylbutane (isopentane)
(b.p. 301 K)

V



2,2-Dimethylpropane (neopentane)
(b.p. 282.5 K)

Structures I and II possess same molecular formula but differ in their boiling points and other properties. Similarly structures III, IV and V possess the same molecular formula but have different properties. Structures I and II are isomers of butane, whereas structures III, IV and V are isomers of pentane. Since difference in properties is due to difference in their structures, they are known as structural isomers. It is also clear that structures I and III have continuous chain of carbon atoms but structures II, IV and V have a branched chain. Such structural isomers which differ in chain of carbon atoms are known as chain isomers. Thus, you have seen that C_4H_{10} and C_5H_{12} have two and three chain isomers respectively.

Based upon the number of carbon atoms attached to a carbon atom, the carbon atom is termed as primary (1°), secondary (2°), tertiary (3°) or quaternary (4°). Carbon atom attached to no other carbon atom as in methane or to only one carbon atom as in ethane is called primary carbon atom. Terminal carbon atoms are always primary. Carbon atom attached to two carbon atoms is known as secondary. Tertiary carbon is attached to three carbon atoms and neo or quaternary carbon is attached to four carbon atoms. Can you identify 1°, 2°, 3° and 4° carbon atoms in structures I to V? If you go on constructing structures for higher alkanes, you will be getting still larger number of isomers. C_6H_{14} has got five isomers and C_7H_{16} has nine. As many as 75 isomers are possible for $C_{10}H_{22}$.

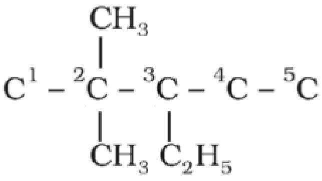
In structures II , IV and V, you observed that -CH_3 group is attached to carbon atom numbered as 2. You will come across groups like -CH_3, -C_2H_5 , -C_3H_7 etc. attached to carbon atoms in alkanes or other classes of compounds .These groups or substituents are known as alkyl groups as they are derived from alkanes by removal of one hydrogen atom General formula for alkyl groups is C_nH_{2n+1}. Let us recall the general rules for nomenclature already discussed.

If it is important to write the correct IUPAC name for a given structure, it is equally important to write the correct structure from the given IUPAC name. To do this, first of all, the longest chain of carbon atoms corresponding to the parent alkane is written. Then after numbering it, the substituents are attached to the correct carbon atoms and finally valence of each carbon atom is satisfied by putting the correct number of hydrogen atoms. This can be clarified by writing the structure of 3-ethyl-2,2-dimethylpentane in the following steps :

i) Draw the chain of five carbon atoms: C - C - C - C - C

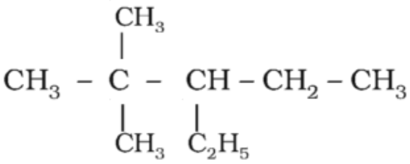
ii) Give number to carbon atoms: C^1- C^2- C^3- C^4- C^5

iii) Attach ethyl group at carbon 3 and two methyl groups at carbon 2



$$C^1-{}^2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-{}^3\underset{\displaystyle C_2H_5}{C}-{}^4C-{}^5C$$

iv) Satisfy the valence of each carbon atom by putting requisite number of hydrogen atoms :



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-\underset{\displaystyle C_2H_5}{CH}-CH_2-CH_3$$

Thus we arrive at the correct structure.

Preparation

Petroleum and natural gas are the main sources of alkanes. However, alkanes can be prepared by following methods:

1) From unsaturated hydrocarbons

Hydrogen gas adds to alkenes and alkynes in the presence of finely divided catalysts like platinum, palladium or nickel to form alkanes. This process is called hydrogenation. These metals adsorb dihydrogen gas on their surfaces and activate the hydrogen - hydrogen bond. Platinum and palladium catalyse the reaction at room temperature but relatively higher temperature and pressure are required with nickel catalysts.

$$\underset{\text{Ethene}}{CH_2 = CH_2} + H_2 \xrightarrow{Pt/Pd/Ni} \underset{\text{Ethane}}{CH_3 - CH_3}$$

2) From Alkyl halides

i) Alkyl halides (except fluorides) on reduction with zinc and dilute hydrochloric acid give alkanes

$$\underset{\text{Chloromethane}}{CH_3 - Cl} + H_2 \xrightarrow{Zn,\ H^+} \underset{\text{Methane}}{CH_4} + HCl$$

ii) Alkyl halides on treatment with sodium metal in dry ethereal (free from moisture) solution give higher alkanes. This reaction is known as Wurtz reaction and is used for the preparation of higher alkanes containing even number of carbon atoms.

$$\underset{\text{Bromomethane}}{CH_3Br} + 2Na + BrCH_3 \xrightarrow{\text{dry ether}} \underset{\text{Ethane}}{CH_3 - CH_3} + 2NaBr$$

3) From Carboxylic acids

Sodium salts of carboxylic acids on heating with soda lime (mixture of sodium hydroxide and calcium oxide) give alkanes containing one carbon atom less than the carboxylic acid. This process of elimination of carbon dioxide from a carboxylic acid is known as decarboxylation.

$$\underset{\text{Sodium ethanoate}}{CH_3COO^-Na^+} + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$$

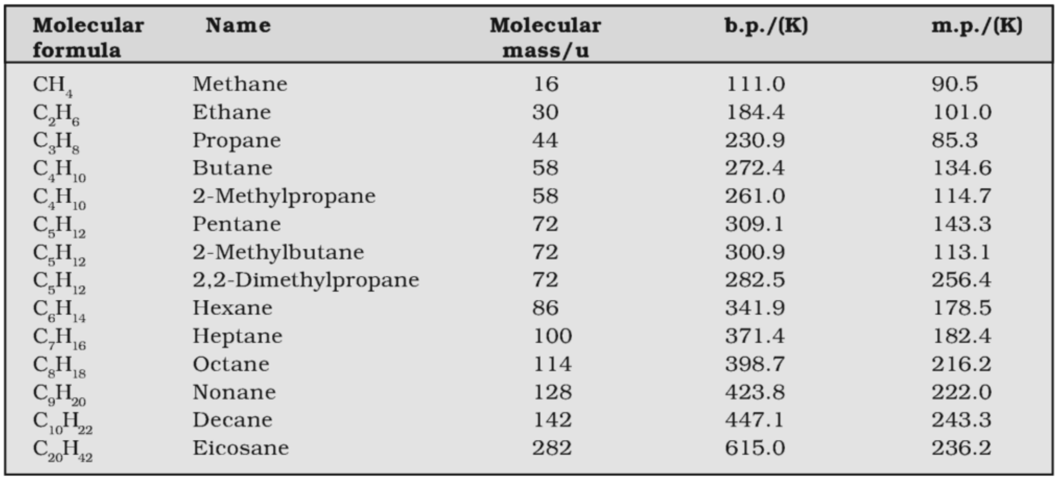
Properties

Physical properties

Alkanes are almost non-polar molecules because of the covalent nature of C-C and C-H bonds and due to very little difference of electronegativity between carbon and hydrogen atoms. They possess weak Van der Waals forces. Due to the weak forces, the first four members, $C_1$to C_4 are gases, C_5 to C_{17} are liquids and those containing 18 carbon atoms or more are solids at 298 K. They are colourless and odourless. What do you think about solubility of alkanes in water based upon non- polar nature of alkanes? Petrol is a mixture of hydrocarbons and is used as a fuel for automobiles. Petrol and lower fractions of petroleum are also used for dry cleaning of clothes to remove grease stains. One of this observation, what do you think about the nature of the greasy substance? You are correct if you say that grease (mixture of higher the basis alkanes) is non -polar and, hence, hydrophobic in nature. It is generally observed that in relation to solubility of substances in solvents, polar substances are soluble in polar solvents, whereas the non-polar ones in non-polar solvents i.e., like dissolves like.

Boiling point (b.p.) of different alkanes are given in Table 13.2 from which it is clear that there is a steady increase in boiling point with increase in molecular mass. This is due to the fact that the intermolecular van der Waals forces increase with increase of the molecular size or the surface area of the molecule.

Table 13.1 Variation of melting points and boiling points oa Alakanes



Molecular formula	Name	Molecular mass/u	b.p./(K)	m.p./(K)
CH_4	Methane	16	111.0	90.5
C_2H_6	Ethane	30	184.4	101.0
C_3H_8	Propane	44	230.9	85.3
C_4H_{10}	Butane	58	272.4	134.6
C_4H_{10}	2-Methylpropane	58	261.0	114.7
C_5H_{12}	Pentane	72	309.1	143.3
C_5H_{12}	2-Methylbutane	72	300.9	113.1
C_5H_{12}	2,2-Dimethylpropane	72	282.5	256.4
C_6H_{14}	Hexane	86	341.9	178.5
C_7H_{16}	Heptane	100	371.4	182.4
C_8H_{18}	Octane	114	398.7	216.2
C_9H_{20}	Nonane	128	423.8	222.0
$C_{10}H_{22}$	Decane	142	447.1	243.3
$C_{20}H_{42}$	Eicosane	282	615.0	236.2

You can make an interesting observation by having a look on the boiling points of three isomeric pentanes viz., (pentane, 2-methylbutane and 2, 2-dimethylpropane). It is observed (Table 13.1) that pentane having a continuous chain of five carbon atoms has the highest boiling point (309.l K) whereas 2, 2 - dimethylpropane boils at 282.5K. With increase in number of branched chains, the molecule attains the shape of a sphere. This results in smaller area of contact and therefore weak intermolecular forces between spherical molecules, which are overcome at relatively lower temperatures.

Chemical properties

As already mentioned, alkanes are generally inert towards acids, bases, oxidizing and reducing agents. However, they undergo the following reaction s under certain conditions.

Substitution reactions

One or more hydrogen atoms of alkanes can be replaced by halogens, nitro group and sulphonic acid group. Halogenation takes place either at higher temperature (573-773 K) or in the presence of diffused sunlight or ultraviolet light. Lower alkanes do not undergo nitration and sulphonation reactions. These reactions in which hydrogen atoms of alkanes are substituted are known as substitution reactions. As an example, chlorination of methane is given below:

Halogenation (free radical mechanism)

$$CH_4 + Cl_2 \xrightarrow{h\nu} \underset{\text{Chloromethane}}{CH_3Cl} + HCl$$

$$CH_3Cl + Cl_2 \xrightarrow{h\nu} \underset{\text{Dichloromethane}}{CH_2Cl_2} + HCl$$

$$CH_2Cl_2 + Cl_2 \xrightarrow{h\nu} \underset{\text{Trichloromethane}}{CHCl_3} + HCl$$

$$CHCl_3 + Cl_2 \xrightarrow{h\nu} \underset{\text{Tetrachloromethane}}{CCl_4} + HCl$$

Mechanism

(i) Initiation : The reaction is initiated by homolysis of chlorine molecule in the presence of light or heat. The Cl-Cl bond is weaker than the C-C and C-H bond and hence, is easiest to break.

$$Cl-Cl \xrightarrow[\text{homolysis}]{h\nu} \underbrace{\dot{Cl} + \dot{Cl}}_{\text{Chlorine free radicals}}$$

(ii) Propagation: Chlorine free radical attacks the methane molecule and takes the reaction in the forward direction by breaking the C-H bond to generate methyl free radical with the formation of H-Cl.

$$CH_4 + \dot{Cl} \xrightarrow{h\nu} \dot{C}H_3 + H-Cl$$

The methyl radical thus obtained attacks the second molecule of chlorine to form CH3- Cl with the liberation of another chlorine free radical by homolysis of chlorine molecule.

$$\dot{C}H_3 + Cl-Cl \xrightarrow{h\nu} CH_3-Cl + \underset{\substack{\text{Chlorine}\\ \text{free radical}}}{\dot{C}l}$$

$$CH_3Cl + \dot{Cl} \rightarrow \dot{C}H_2Cl + HCl$$

$$\dot{C}H_2Cl + Cl-Cl \rightarrow CH_2Cl_2 + \dot{Cl}$$

(iii) Termination: The reaction stops after some time due to consumption of reactants and / or due to the following side reactions:

The possible chain terminating steps are:

$$\dot{Cl} + \dot{Cl} \rightarrow Cl-Cl$$

$$H_3\dot{C} + \dot{C}H_3 \rightarrow H_3C-CH_3$$

$$H_3\dot{C} + \dot{Cl} \rightarrow H_3C-Cl$$

Combustion

Alkanes on heating in the presence of air or dioxygen are completely oxidized to carbon dioxide and water with the evolution of large amount of heat.

$$CH_4(g)+2O_2(g) \rightarrow CO_2(g)+2H_2O(l); \quad \Delta_c H^\ominus = -890\,kJ\,mol^{-1}$$

Controlled oxidation

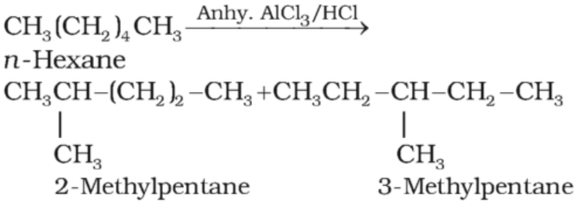
Alkanes on heating with a regulated supply of dioxygen or air at high pressure and in the presence of suitable catalysts give a variety of oxidation products.

$$2CH_4 + O_2 \xrightarrow{Cu/523K/100atm} \underset{\text{Methanol}}{2CH_3OH}$$

$$CH_4 + O_2 \xrightarrow[\Delta]{Mo_2O_3} \underset{\text{Methanal}}{HCHO} + H_2O$$

Isomerism

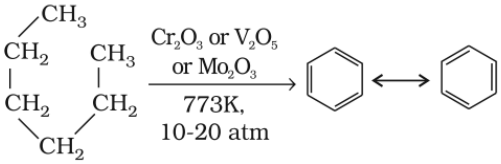
n-Alkanes on heating in the presence of anhydrous aluminium chloride and hydrogen chloride gas isomerise to branched chain alkanes. Major products are given below. Some minor products are also possible which you can think over. Minor products are generally not reported in organic reactions.



$$\underset{n\text{-Hexane}}{CH_3(CH_2)_4CH_3} \xrightarrow{\text{Anhy. }AlCl_3/HCl} \underset{\text{2-Methylpentane}}{CH_3\underset{CH_3}{\underset{|}{C}}H-(CH_2)_2-CH_3} + \underset{\text{3-Methylpentane}}{CH_3CH_2-\underset{CH_3}{\underset{|}{C}}H-CH_2-CH_3}$$

Aromatization

n-Alkanes having six or more carbon atoms on heating to 773K at 10-20 atmospheric pressure in the presence of oxides of vanadium , molybenum or chromium supported over alumina get dehydrogenated and cyclised to benzene and its homologues. This reaction is known as aromatization or reforming.



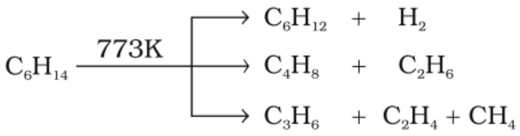
Reaction with steam

Methane reacts with steam at 1273 K in the presence of nickel catalyst to form carbon monoxide and dihydrogen. This method is used for industrial preparation of dhydrogen gas

$$CH_4 + H_2O \xrightarrow[\Delta]{Ni} CO + 3H_2$$

Pyrolysis

Higher alkanes on heating to higher temperature decompose into lower alkanes, alkenes etc. Such a decomposition reaction into smaller fragments by the application of heat is called pyrolysis or cracking.



$$C_6H_{14} \xrightarrow{773K} C_6H_{12} + H_2$$
$$C_6H_{14} \xrightarrow{773K} C_4H_8 + C_2H_6$$
$$C_6H_{14} \xrightarrow{773K} C_3H_6 + C_2H_4 + CH_4$$

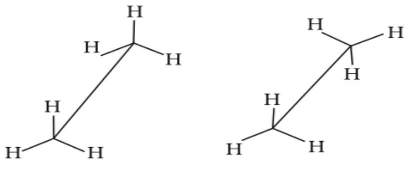
Conformations

Alkanes contain carbon-carbon sigma (σ) bonds. Electron distribution of the sigma molecular orbital is symmetrical around the internuclear axis of the C-C bond which is not disturbed due to rotation about its axis. This permits free rotation about C-C single bond. This rotation results into different spatial arrangements of atoms in space which can change into one another. Such spatial arrangements of atoms which can be converted into one another by rotation around a C-C single bond are called conformations or conformers or rotamers. Alkanes can thus have infinite number of conformations by rotation around C-C single bonds. However, it may be remembered that rotation around a C-C single bond is not completely free. It is hindered by a small energy barrier of 1-20 kJ mol-1 due to weak repulsive interaction between the adjacent bonds. Such a type of repulsive interaction is called torsional strain.

Conformations of ethane: Ethane molecule (C_2H_6) contains a carbon - carbon single bond with each carbon atom attached to three hydrogen atoms. Considering the ball and stick model of ethane, keep one carbon atom stationary and rotate the other carbon atom around the C-C axis. This rotation results into infinite number of spatial arrangements of hydrogen atoms attached to one carbon atom with respect to the hydrogen atoms attached to the other carbon atom. These are called conformational isomers (conformers). Thus, there are infinite numbers of conformations of ethane. However, there are two extreme cases. One such conformation in which hydrogen atoms attached to two carbons are as closed together as possible is called eclipsed conformation and the other in which hydrogens are as far apart as possible is known as the staggered conformation. Any other intermediate conformation is called a skew conformation. It may be remembered that in all the conformations, the bond angles and the bond lengths remain the same. Eclipsed and the staggered conformations can be represented by Sawhorse and Newman projections.

1. Sawhorse projections

In this projection, the molecule is viewed along the molecular axis. It is then projected on paper by drawing the central C-C bond as a somewhat longer straight line. Upper end of the line is slightly tilted towards right or left hand side. The front carbon is shown at the lower end of the line, whereas the rear carbon is shown at the upper end. Each carbon has three lines attached to it corresponding to three hydrogen atoms. The lines are inclined at an angle of 120° to each other. Sawhorse projections of eclipsed and staggered conformations of ethane are depicted in Fig. 13.2.

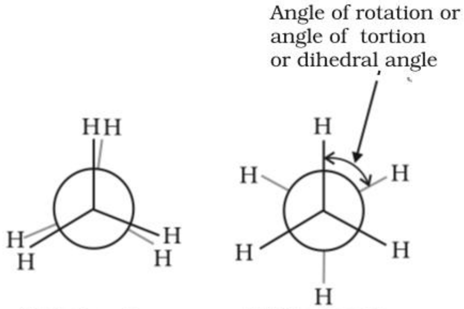


(i) Eclipsed (ii) Staggered

Fig. 13.2 Sawhorse projection of ethane

2. Newman projections

In this projection, the molecule is viewed at the C-C bond head on. The carbon atom nearer to the eye is represented by a point. Three hydrogen atoms attached to the front carbon atom are shown by three lines drawn at an angle of 120° to each other. The rear carbon atom (the carbon atom away from the eye) is represented by a circle and the three hydrogen atoms are shown attached to it by the shorter lines drawn at an angle of 120° to each other. The Newman's projections are depicted in Fig.13.3.



(i) Eclipsed (ii) Staggered

Fig. 13.3 Newman's projection of ethane

Relative stability of conformations:

As mentioned earlier, in staggered form of ethane, the electron clouds of carbon-hydrogen bonds are as far apart as possible. Thus, there are minimum repulsive forces, minimum energy and maximum stability of the molecule. On the other hand, when the staggered form changes into the eclipsed form, the electron clouds of the carbon - hydrogen bonds come closer to each other resulting in increase in electron cloud repulsions. To check the increased repulsive forces, molecule will have to possess more energy and thus has lesser stability. As already mentioned, the repulsive interaction between the electron clouds, which affects stability of a conformation, is called torsional strain. Magnitude of torsional strain depends upon the angle of rotation about C-C bond. This angle is also called dihedral angle or torsional angle. Of all the conformations of ethane, the staggered form has the least torsional strain and the eclipsed forrm, the maximum torsional strain. Thus it may be inferred that rotation around C-C bond in ethane is not completely free. The energy difference between the two extreme forms is of the order of 12.5 kJ mol^{-1}which is very small. Even at ordinary temperatures, the ethane molecule gains thermal or kinetic energy sufficient enough to overcome this energy barrier of 12.5kJ mol^{-1} through intermolecular collisions. Thus, it can be said that rotation about carbon-carbon single bond in ethane is almost free for all practical purposes. It has not been possible to separate and isolate different conformational isomers of ethane.

13.9 Alkenes

Alkenes are unsaturated hydrocarbons containing at least one double bond. What should be the general formula of alkenes? If there is one double bond between two carbon atoms in alkenes, they must possess two hydrogen atoms less than alkanes. Hence, general formula for alkenes is C_nH_{2n}. Alkenes are also known as olefins (oil forming) since the first member, ethylene or ethene (C_2H_4) was found to form an oily liquid on reaction with chlorine.

Structure of double bond

Carbon -carbon double bond in alkenes consists of one strong sigma (σ) bond (bond enthalpy about 397 kJ mol^{-1} due to head-on overlapping of sp^2 hybridised orbitals and one weak pi (π) bond (bond enthalpy about 284 kJ mol^{-1} obtained by lateral or sideways overlapping of the two 2p orbitals of the two carbon atoms. The double bond is shorter in bond length (134 pm) than the C--C single bond (154 pm). You have already read that the pi (π) bond is a weaker bond due to poor sideways overlapping between the two 2p orbitals. Thus, the presence of the pi (π) bond makes alkenes behave as sources of loosely held mobile electrons. Therefore, alkenes are easily attacked by reagents or compounds which are in search of electrons.

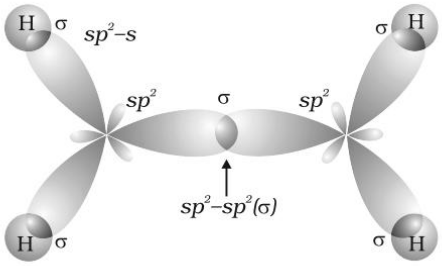


Fig. 13.4 Orbital picture of ethane depicting σ bonds

Such reagents are called electrophilic reagents. The presence of weaker π -bond makes alkenes unstable molecules in comparison to alkanes and thus, alkenes can be changed into single bond compounds by combining with the electrophilic reagents. Strength of the double bond (bond enthalpy, 681kJ mol-1) is greater than that of a carbon-carbon single bond in ethane (bond enthalpy, 348 kJ mol-1 .Orbital diagrams of ethene molecule are shown in Figs. 13.4 and 13.5.

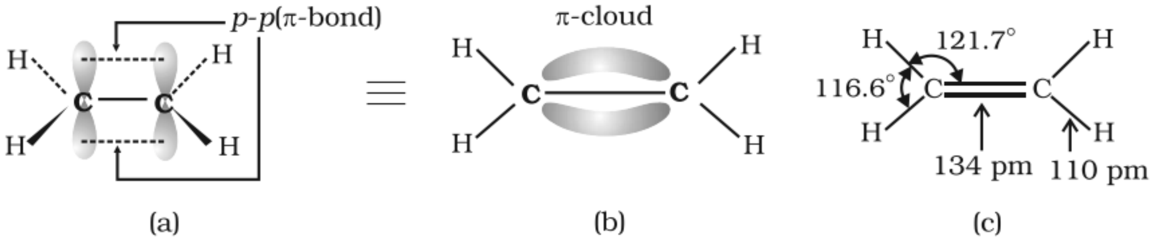
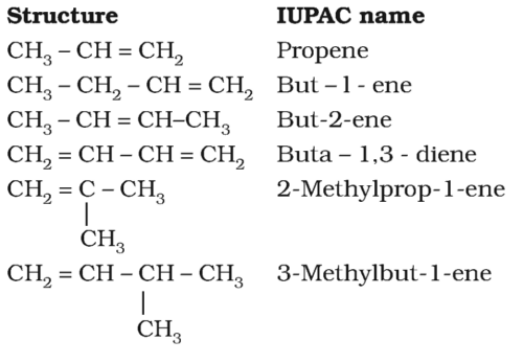


Fig. 13.5 Orbital picture of ethane showing formation of a) π -bond b) π -clouds c) bond angle and lengths

Nomenclature

For nomenclature of alkenes in IUPAC system , the longest chain of carbon atoms containing the double bond is selected. Numbering of the chain is done from the end which is nearer to the double bond. The suffix 'ene' replaces 'ane' of alkanes. It may be remembered that first member of alkene series is: CH_2 (replacing n by 1 in C_nH_{2n} known as methene but has a very short life. As already mentioned, first stable member of alkene series is C_2H_4 known as ethylene (common) or ethene (IUPAC).

IUPAC names of a few members of alkenes are given below:

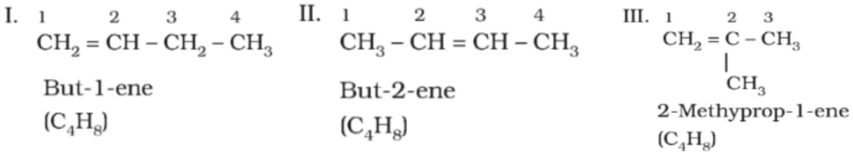


Structure	IUPAC name
$CH_3 - CH = CH_2$	Propene
$CH_3 - CH_2 - CH = CH_2$	But – 1 - ene
$CH_3 - CH = CH–CH_3$	But-2-ene
$CH_2 = CH - CH = CH_2$	Buta – 1,3 - diene
$CH_2 = \underset{\underset{CH_3}{\mid}}{C} - CH_3$	2-Methylprop-1-ene
$CH_2 = CH - \underset{\underset{CH_3}{\mid}}{CH} - CH_3$	3-Methylbut-1-ene

Isomerism

Alkenes show both structural and geometrical isomerism.

Structural isomerism: As in alkanes , ethane (C_2H_4) and propene (C_3H_6) can have only one structure with respect to the position of double bond but alkenes higher than propene have different structures. Alkanes possessing C_4H_8 as molecular formula can be written in the following three ways:



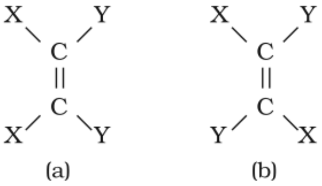
I. $\overset{1}{C}H_2 = \overset{2}{C}H - \overset{3}{C}H_2 - \overset{4}{C}H_3$ But-1-ene (C_4H_8)

II. $\overset{1}{C}H_3 - \overset{2}{C}H = \overset{3}{C}H - \overset{4}{C}H_3$ But-2-ene (C_4H_8)

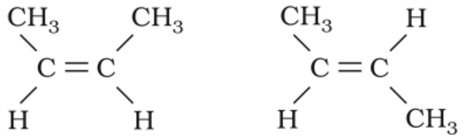
III. $\overset{1}{C}H_2 = \underset{\underset{CH_3}{\mid}}{\overset{2}{C}} - \overset{3}{C}H_3$ 2-Methyprop-1-ene (C_4H_8)

Structures I and III, and II and III are the examples of chain isomerism whereas structures I and II are position isomers.

Geometrical isomerism: Doubly bonded carbon atoms have to satisfy the remaining two valences by joining two atoms or groups. If the two atoms or groups attached to each carbon atom are different , they can be represented by YX C = C XY like structure. YX C = C XY can be represented in space in the following two ways:

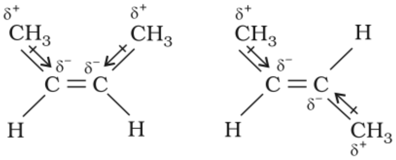


In (a), the two identical atoms i.e., both the X or both the Y lie on the same side of the double bond but in (b) the two X or two Y lie across the double bond or on the opposite sides of the double bond. This results in different geometry of (a) and (b) i.e. disposition of atoms or groups in space in the two arrangements is different. Therefore, they are stereoisomers. They would have the same geometry if atoms or groups around C=C bond can be rotated but rotation around C=C bond is not free. It is restricted. For understanding this concept, take two pieces of strong cardboards and join them with the help of two nails. Hold one cardboard in your one hand and try to rotate the other. Can you really rotate the other cardboard? The answer is no. The rotation is restricted. This illustrates that the restricted rotation of atoms or groups around the doubly bonded carbon atoms gives rise to different geometries of such compounds. The stereoisomers of this type are called geometrical isomers. The isomer of the type (a) , in which two identical atoms or groups lie on the same side of the double bond is called cis isomer and the other isomer of the type (b) , in which identical atoms or groups lie on the opposite sides of the double bond is called trans isomer . Thus cis and trans isomers have the same structure but have different configuration (arrangement of atoms or groups in space) . Due to different arrangement of atoms or groups in space, these isomers differ in their properties like melting point, boiling point, dipole moment, solubility etc. Geometrical or cis-trans isomers of but-2-ene are represented below:



cis-But-2-ene (b.p. 277 K) *trans*-But-2-ene (b.p. 274 K)

Cis form of alkene is found to be more polar than the trans form. For example , dipole moment of cis-but-2-ene is 0.33 Debye, whereas, dipole moment of the trans form is almost zero or it can be said that trans-but-2-ene is non-polar. This can be understood by drawing geometries of the two forms as given below from which it is clear that in the trans-but-2-ene, the two methyl groups are in opposite directions, Therefore, dipole moments of C-CH_3 bonds cancel, thus making the trans form non-polar.

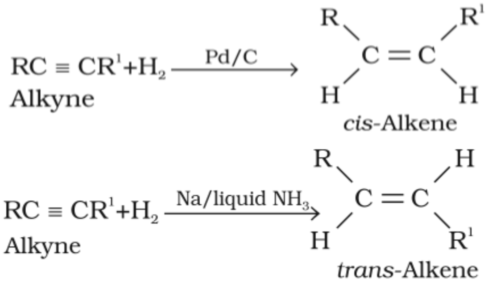


cis-But-2-ene ($\mu = 0.33D$) *trans*-But-2-ene ($\mu = 0$)

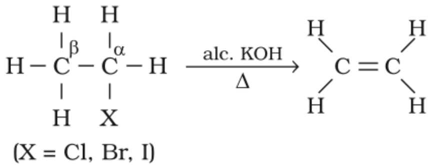
In the case of solids, it is observed that the trans isomer has higher melting point than the cis form. Geometrical or cis- trans isomerism is also shown by alkenes of the types XYC = CXZ and XYC = CZW

Preparation

From Alkynes: Alkynes on partial reduction with calculated amount of dihydrogen in the presence of pailadised charcoal partially deactivated with poisons like sulphur compounds or quinoline give alkenes. Partially deactivated palladised charcoal is known as Lindlar 's catalyst. Alkenes thus obtained are having cis geometry. However, alkynes on reduction with sodium in liquid ammonia form trans alkenes.



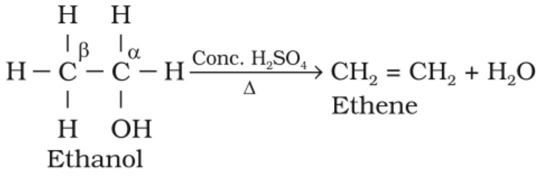
From alkyl halides: Alkyl halides (R-X) on heating with alcoholic potash (potassium hydroxide dissolved in alcohol, say, ethanol) eliminate one molecule of halogen acid to form alkenes. This reaction is known as dehydrohalogenation i.e., removal of halogen acid. This is example of atom is eliminated from the J3 carbon atom (carbon atom next to the carbon to which halogen is attached).



$$H_3C-CH_2X \xrightarrow[\Delta]{\text{alc. KOH}} H_2C=CH_2$$

Nature of halogen atom and the alkyl group determine rate of the reaction. It is observed that for halogens, the rate is: iodine > bromine > chlorine, while for alkyl groups it is: tert > secondary > primary.

From alcohols by acidic dehydration: You have read during nomenclature of different homologous series in Unit 12 that alcohols are the hydroxy derivatives of alkanes. They are represented by R-OH. Where, R is C_nH_{2n+1}. Alcohols on heating with concentrated sulphuric acid form alkenes with the elimination of one water molecule. Since a water molecule is eliminated from the alcohol molecule in the presence of an acid, this reaction is known as acidic dehydration of alcohols. This reaction is also the example of β -elimination reaction since -OH group takes out one hydrogen atom from the β -carbon atom.



$$H_3C-CH_2OH \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} CH_2=CH_2 + H_2O$$

Properties

Physical properties

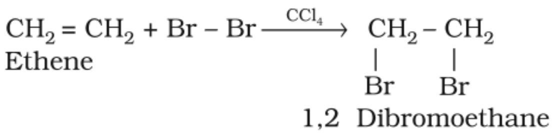
Alkenes as a class resemble alkanes in physical properties, except in types of isomerism and difference in polar nature. The first three members are gases, the next fourteen are liquids and the higher ones are solids. Ethene is a colourless gas with a faint sweet smell. All other alkenes are colourless and odourless, insoluble in water but fairly soluble in non- polar solvents like benzene, petroleum ether. They show a regular increase in boiling point with increase in size i.e., every - CH_2 group added increases boiling point by 20-30 K. Like alkanes, straight chain alkenes have higher boiling point than isomeric branched chain compounds.

Chemical properties

Alkenes are the rich source of loosely held pi (π) electrons, due to which they show addition reactions in which the electrophiles add on to the carbon-carbon double bond to form the addition products. Some reagents also add by free radical mechanism. There are cases when under special conditions, alkenes also undergo free radical substitution reactions. Oxidation and ozonolysis reactions are also quite prominent in alkenes. A brief description of different reactions of alkenes is given below:

1 Addition of dihydrogen: Alkenes add up one molecule of dihydrogen gas in the presence of finely divided nickel, palladium or platinum to form alkanes.

2 Addition of halogens: Halogens like bromine or chlorine add up to alkene to form vicinal dihalides. However, iodine does not show addition reaction under normal conditions. The reddish orange colour of bromine solution in carbon tetrachloride is discharged when bromine adds up to an unsaturation site. This reaction is used as a test for unsaturation. Addition of halogens to alkenes is an example of electrophilic addition reaction involving cyclic halonium ion formation which you will study in higher classes.

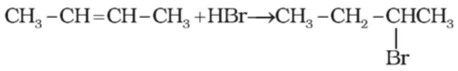


$$\underset{\text{Ethene}}{CH_2=CH_2} + Br-Br \xrightarrow{CCl_4} \underset{\text{1,2 Dibromoethane}}{\underset{Br}{\underset{|}{CH_2}}-\underset{Br}{\underset{|}{CH_2}}}$$

3 Addition of hydrogen halides: Hydrogen halides (HCl, HBr,HI) add up to alkenes to form alkyl halides. The order of reactivity of the hydrogen halides is HI > HBr > HCl. Like addition of halogens to alkenes, addition of hydrogen halides is also an example of electrophilic addition reaction. Let us illustrate this by taking addition of HBr to symmetrical and unsymmetrical alkenes

Addition reaction of HBr to symmetrical alkenes

$$CH_2=CH_2+H-Br\longrightarrow CH_3-CH_2-Br$$

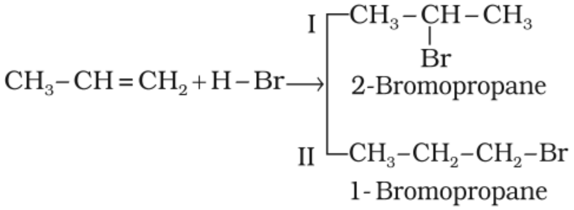


$$CH_3-CH=CH-CH_3+HBr\rightarrow CH_3-CH_2-\underset{Br}{\underset{|}{C}}HCH_3$$

Addition reactions of HBr to symmetrical alkenes (similar groups attached to double bond) take place by electrophilic addition mechanism.

Addition reaction of HBr to unsymmetrical alkenes (Markovnikov Rule)

How will H- Br add to propene ? The two possible products are I and II.

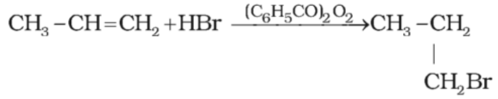


$$CH_3-CH=CH_2+H-Br\longrightarrow \begin{cases} \text{I} \quad \underset{\text{2-Bromopropane}}{CH_3-\underset{Br}{\underset{|}{C}}H-CH_3} \\ \text{II} \quad \underset{\text{1-Bromopropane}}{CH_3-CH_2-CH_2-Br} \end{cases}$$

Markovnikov, a Russian chemist made a generalization in 1869 after studying such reactions in detail. These generalisations led Markovnikov to frame a rule called Markovnikov rule. The rule states that negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses lesser number of hydrogen atoms. Thus according to this rule, product I i.e., 2-bromopropane is expected. In actual practice, this is the principal product of the reaction.

Anti Markovnikov addition or peroxide effect or Kharash effect

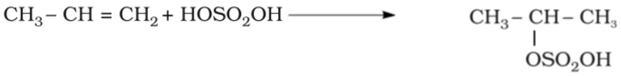
In the presence of peroxide, addition of HBr to unsymmetrical alkenes like propene takes place contrary to the Markovnikov rule. This happens only with HBr but not with HCI and HI. This addition reaction was observed by M.S. Kharash and F.R. Mayo in 1933 at the University of Chicago. This reaction is known as peroxide or Kharash effect or addition reaction anti to Markovnikov rule.



$$CH_3-CH=CH_2+HBr \xrightarrow{(C_6H_5CO)_2O_2} CH_3-\underset{CH_2Br}{CH_2}$$

1-Bromopropane

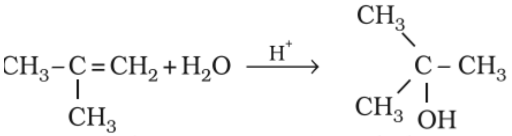
Addition of sulphuric acid: Cold concentrated sulphuric acid adds to alkenes in accordance with Markovnikov rule to form alkyl hydrogen sulphate by the electrophilic addition reaction.



$$CH_3-CH=CH_2+HOSO_2OH \longrightarrow CH_3-\underset{OSO_2OH}{CH}-CH_3$$

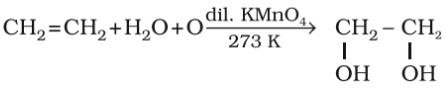
Propyl hydrogen sulphate

Addition of water: In the presence of a few drops of concentrated sulphuric acid alkenes react with water to form alcohols, in accordance with the Markovnikov rule.



2-Methylpropene 2-Methylpropan-2-ol

Oxidation: Alkenes on reaction with cold, dilute, aqueous solution of potassium permanganate (Baeyer's reagent) produce vicinal glycols. Decolorisation of $KMnO_4$ solution is used as a test for unsaturation.



$$CH_2=CH_2+H_2O+O \xrightarrow[273\ K]{dil.\ KMnO_4} \underset{OH}{CH_2}-\underset{OH}{CH_2}$$

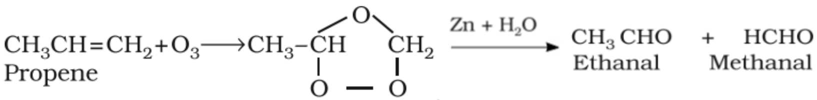
Ethane-1, 2-diol
(Glycol)

b) Acidic potassium permanganate or acidic potassium dichromate oxidises alkenes toketones and/ or acids depending upon the nature of the alkene and the experiment al conditions.

$$(CH_3)_2C=CH_2 \xrightarrow{KMnO_4/H^+} (CH_3)_2C=O + CO_2+H_2O$$

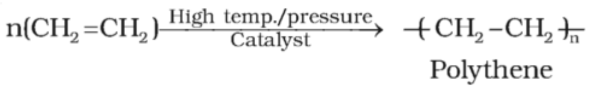
2-Methlypropene Propan-2-one

Ozonolysis : Ozonolysis of alkenes involves the addition of ozone molecule to alkene to form ozonide, and then cleavage of the ozonide by Zn-H_2O to smaller molecules. This reaction is highly useful in detecting the position of the double bond in alkenes or other unsaturated compounds.



Propene ozonide

Polymerisation: You are familiar with polythene bags and polythene sheets. Polythene is obtained by the combination of large number of ethene molecules at high temperature, high pressure and in the presence of a catalyst. The large molecules thus obtained are called polymers. This reaction is known as polymerisation. The simple compounds from which polymers are made are called monomers. Other alkenes also undergo polymerisation.



$$n(CH_2=CH_2) \xrightarrow[\text{Catalyst}]{\text{High temp./pressure}} \underset{\text{Polythene}}{-\!\!\left(CH_2-CH_2\right)\!\!-_n}$$

Polymers are used for the manufacture of plastic bags, squeeze bottles, refrigerator dishes, toys, pipes, radio and T.V. cabinets etc. Polypropene is used for the manufacture of milk crates, plastic buckets and other moulded articles. Though these materials have now become common, excessive use of polythene and polypropylene is a matter of great concern.

13.10 Alkynes

Like alkenes, alkynes are also unsaturated hydrocarbons. They contain at least one triple bond between two carbon atoms. The number of hydrogen atoms is still less in alkynes as compared to alkenes or alkanes. Their general formula is C_nH_{2n-2}.

The first stable member of alkyne series is ethyne which is popularly known as acetylene. Acetylene is used for arc welding purposes in the form of oxyacetylene flame obtained by mixing acetylene with oxygen gas. Alkynes are starting materials for a large number of organic compounds. Hence, it is interesting to study this class of organic compounds.

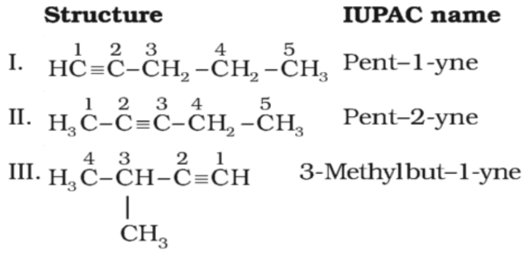
13.10.1 Nomenclature and Isomerism

In common system, alkynes are named as derivatives of acetylene. In IUPAC system, they are named as derivatives of the corresponding alkanes replacing 'ane' by the suffix 'yne'. The position of the triple bond is indicated by the first triply bonded carbon. Common and IUPAC names of a few members of alkyne series are given in Table 13.3.

Table 13.2 Common and IUPAC names Alkynes (C_nH_{2n-2})

Value of n	Formula	Structure	Common name	IUPAC name
2	C_2H_2	$H\text{-}C\equiv CH$	Acetylene	Ethyne
3	C_3H_4	$CH_3\text{-}C\equiv CH$	Methylacetylene	Propyne
4	C_4H_6	$CH_3CH_2\text{-}C\equiv CH$	Ethylacetylene	But-1-yne
4	C_4H_6	$CH_3\text{-}C\equiv C\text{-}CH_3$	Dimethylacetylene	But-2-yne

You have already learnt that ethyne and propyne have got only one structure but there are two possible structures for butyne - (i) but-1-yne and (ii) but-2-yne. Since these two compounds differ in their structures due to the position of the triple bond, they are known as position isomers. In how many ways, you can construct the structure for the next homologue i.e., the next alkyne with molecular formula C_5H_8 ? Let us try to arrange five carbon atoms with a continuous chain and with a side chain. Following are the possible structures:



Structure **IUPAC name**

I. $H\overset{1}{C}\equiv\overset{2}{C}-\overset{3}{C}H_2-\overset{4}{C}H_2-\overset{5}{C}H_3$ Pent–1-yne

II. $H_3\overset{1}{C}-\overset{2}{C}\equiv\overset{3}{C}-\overset{4}{C}H_2-\overset{5}{C}H_3$ Pent–2-yne

III. $H_3\overset{4}{C}-\underset{\displaystyle CH_3}{\overset{3}{C}H}-\overset{2}{C}\equiv\overset{1}{C}H$ 3-Methylbut–1-yne

Structures I and II are position isomers and structures I and III or II and III are chain isomers.

13.10.2 Structure of Triple Bond

Ethyne is the simplest molecule of alkyne series. Structure of ethyne is shown in Fig. 13.6. Each carbon atom of ethyne has two sp hybridised orbitals. Carbon-carbon sigma (σ) bond is obtained by the head-on overlapping of the two sp hybridised orbitals of the two carbon atoms. The remaining sp hybridised orbital of each carbon atom undergoes overlapping along the internuclear axis with the 1s orbital of each of the two hydrogen atoms forming two C-H sigma bonds. H-C-C bond angle is of 180°. Each carbon has two unhybridised p orbitals which are perpendicular to each other as well as to the plane of the C-C sigma bond. The 2p orbitals of one carbon atom are parallel to the 2p orbitals of the other carbon atom, which undergo lateral or sideways overlapping to form two pi (π) bonds between two carbon atoms. Thus ethyne molecule consists of one C-C σ bond, two C-H σ bonds and two C-C π bonds. The strength of $C \equiv C$ bond (bond enthalpy 823 kJ mol^{-1}) is more than those of C=C bond (bond enthalpy 681 kJ mol^{-1} and C-C bond (bond enthalpy 348 kJ mol^{-1}). The $C \equiv C$ bond length is shorter (120 pm) than those of C=C (133 pm) and C-C (154 pm). Electron cloud between two carbon atoms is cylindrically symmetrical about the internuclear axis. Thus, ethyne is a linear molecule.

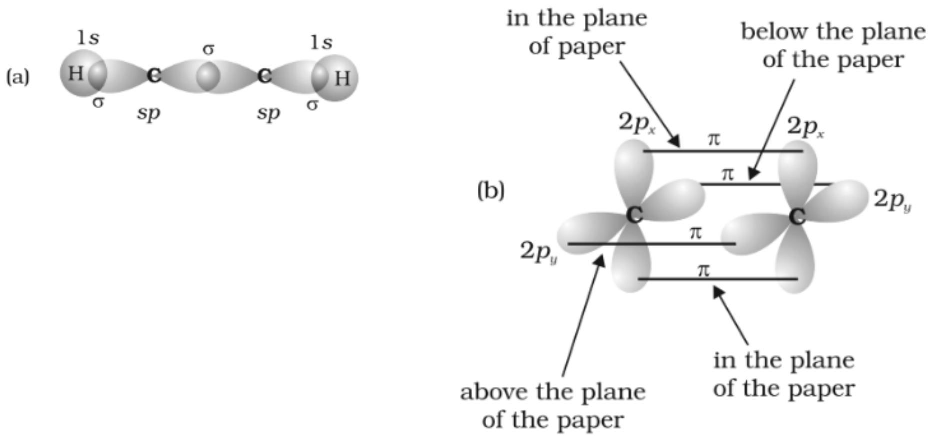


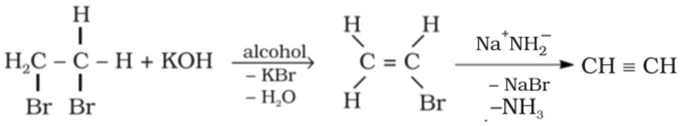
Fig. 13.6 Orbital picture of ethyne showing a) sigma overlaps b) pi overlaps

13.10.3 Preparation

1. From calcium carbide: On industrial scale, ethyne is prepared by treating calcium carbide with water.

$$CaC_2 + H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

2. From vicinal dihalides: Vicinal dihalides on treatment with alcoholic potassium hydroxide undergo dehydrohalogenation. One molecule of hydrogen halide is eliminated to form alkenyl halide which on treatment with sodamide gives alkyne.



$$H_2\underset{Br}{C}-\overset{H}{\underset{Br}{C}}-H + KOH \xrightarrow[-KBr,\ -H_2O]{alcohol} \overset{H}{\underset{H}{C}}=\overset{H}{\underset{Br}{C}} \xrightarrow[-NaBr,\ -NH_3]{Na^+NH_2^-} CH \equiv CH$$

13.10.4 Properties

Physical properties

Physical properties of alkynes follow the same trend of alkenes and alkanes. First three members are gases, the next eight are liquids and the higher ones are solids. All alkynes are colourless. Ethyene has characteristic odour. Other members are odourless. Alkynes are weakly polar in nature. They are lighter than water and immiscible with water but soluble in organic solvents like ethers, carbon tetrachloride and benzene. Their melting point, boiling point and density increase with increase in molar mass.

Chemical properties

Alkynes show acidic nature, addition reactions and polymerisation reactions as follows :

A. Acidic character of alkyne: Sodium metal and sodamide ($NaNH_2$) are strong bases. They react with ethyne to form sodium acetylide with the liberation of hydrogen gas. These reactions have not been observed in case of ethene and ethane thus indicating that ethyne is acidic in nature in comparison to ethene and ethane. Why is it so? Has it something to do with their structures and the hybridisation? You have read that hydrogen atoms in ethyne are attached to the sp hybridized carbon atoms whereas they are attached to sp^2 hybridized carbon atoms in ethene and sp^3 hybridised carbons in ethane. Due to the maximum percentage of s character (50%), the sp hybridised orbitals of carbon atoms in ethyne molecules have highest electronegativity; hence, these attract the shared electron pair of the C-H bond of ethyne to a greater extent than that of the sp^2 hybridised orbitals of carbon in ethene and the sp^3 hybridised orbital of carbon in ethane. Thus, in ethyne, hydrogen atoms can be liberated as protons more easily as compared to ethene and ethane. Hence, hydrogen atoms of ethyne attached to triply bonded carbon atom are acidic in nature. You may note that the hydrogen atoms attached to the triply bonded carbons are acidic but not all the hydrogen atoms of alkynes.

$$HC \equiv CH + Na \rightarrow \underset{\text{Monosodium ethynide}}{HC \equiv C^{-}Na^{+}} + \tfrac{1}{2}H_2$$

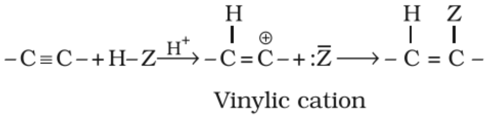
$$HC \equiv C^{-}Na^{+} + Na \rightarrow \underset{\text{Disodium ethynide}}{Na^{+}C^{-} \equiv C^{-}Na^{+}} + \tfrac{1}{2}H_2$$

$$CH_3 - C \equiv C - H \quad + \quad Na^{+}NH_2^{-} \rightarrow \underset{\text{Sodium propynide}}{CH_3 - C \equiv C^{-}Na^{+}} \quad + \quad NH_3$$

These reactions are not shown by alkenes and alkanes, hence used for distinction between alkynes, alkenes and alkanes.

B. Addition reactions: Alkynes contain a triple bond, so they add up, two molecules of hydrogen, halogen, hydrogen halides etc.

Formation of the addition product takes place according to the following steps.



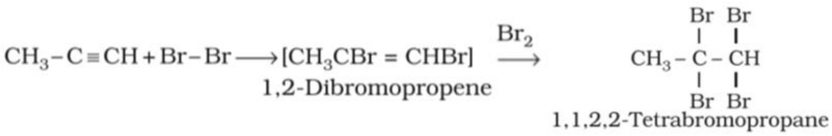
$$-C \equiv C- + H-Z \xrightarrow{H^{+}} \underset{\text{Vinylic cation}}{-\overset{H}{\overset{|}{C}} = \overset{\oplus}{C}-} + :\overline{Z} \longrightarrow -\overset{H}{\overset{|}{C}} = \overset{Z}{\overset{|}{C}}-$$

The addition product formed depends upon stability of vinylic cation. Addition in unsymmetrical alkynes takes place according to Markovnikov rule. Majority of the reactions of alkynes are the examples of electrophilic addition reactions. A few addition reactions are given below:

(i) Addition of hydrogen:

$$HC\equiv CH+H_2 \xrightarrow{Pt/Pd/Ni} [H_2C=CH_2] \xrightarrow{H_2} CH_3-CH_3$$

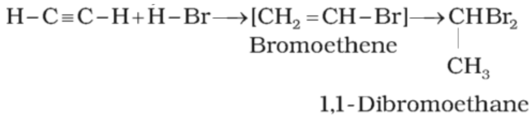
(ii) Addition of halogens:



$$CH_3-C\equiv CH+Br-Br \longrightarrow \underset{\text{1,2-Dibromopropene}}{[CH_3CBr=CHBr]} \xrightarrow{Br_2} \underset{\text{1,1,2,2-Tetrabromopropane}}{CH_3-CBr_2-CHBr_2}$$

(ii) Addition of hydrogen halides:

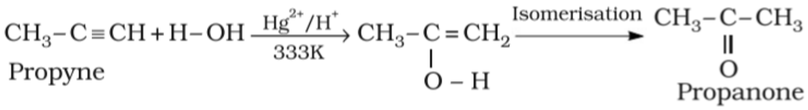
Two molecules of hydrogen halides (HCl, HBr, HI) add to alkynes to form gem dihalides(In which two halogen atoms are attached to same carbon atoms).



$$H-C\equiv C-H+H-Br \longrightarrow \underset{\text{Bromoethene}}{[CH_2=CH-Br]} \longrightarrow \underset{\text{1,1-Dibromoethane}}{CHBr_2-CH_3}$$

(iv) Addition of water:

Like alkanes and alkenes, alkynes are also immiscible and do not react with water. However, one molecule of water adds to alkynes on warming with mercuric sulphate and dilute sulphuric acid at 333 K to form carbonyl compounds.

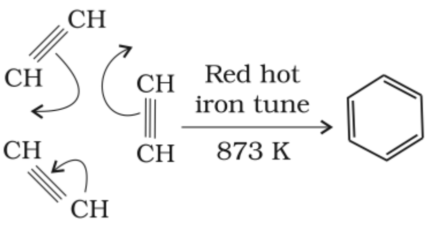


$$\underset{\text{Propyne}}{CH_3-C\equiv CH}+H-OH \xrightarrow[333K]{Hg^{2+}/H^+} CH_3-\underset{\underset{O-H}{|}}{C}=CH_2 \xrightarrow{\text{Isomerisation}} \underset{\text{Propanone}}{CH_3-\underset{\underset{O}{\|}}{C}-CH_3}$$

(v) Polymerisation:

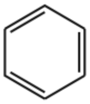
(a) Linear polymerisation: Under suitable conditions, linear polymerisation of ethyne takes place to produce polyacetylene or polyethyne which is a high molecular weight polyene containing repeating units of (CH = CH - CH =CH) and can be represented as -CH =CH - CH=CH)$_n$-. Under special conditions, this polymer conducts electricity. Thin film of polyacetylene can be used as electrodes in batteries. These films are good conductors, lighter and cheaper than the metal conductors.

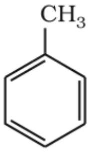
(b) Cyclic polymerisation: Ethyne on passing through red hot iron tube at 873K undergoes cyclic polymerization. Three molecules polymerise to form benzene, which is the starting molecule for the preparation of derivatives of benzene, dyes, drugs and large number of other organic compounds. This is the best route for entering from aliphatic to aromatic compounds as discussed below:



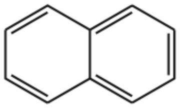
13.11 Aromatic Hydrocarbon

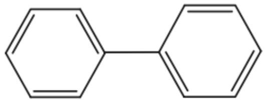
These hydrocarbons are also known as 'arenes'. Since most of them possess pleasant odour (Greek; aroma meaning pleas ant smelling), the class of compounds was named as ' aromatic compounds '. Most of such compounds were found to contain benzene ring. Benzene ring is highly unsaturated but in a majority of reactions of aromatic compounds, the unsaturation of benzene ring is retained. However, there are examples of aromatic hydrocarbons which do not contain a benzene ring but instead contain other highly un saturated ring. Aromatic compounds containing benzene ring are known as benzenoids and those not containing a benzene ring are known as non-benzenoids. Some examples of arenes are given below:


Benzene



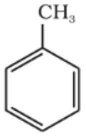
Toluene


Naphthalene

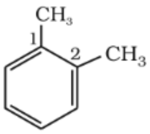

Biphenyl

13.11.1Nomenclature and Isomerism

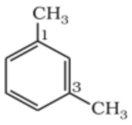
The nomenclature and isomerism of aromatic hydrocarbons has already been discussed. All six hydrogen atoms in benzene are equivalent; so it forms one and only one type of monosubstituted product. When two hydrogen atoms in benzene are replaced by two similar or different monovalent atoms or groups, three different position isomers are possible. The 1, 2 or 1, 6 is known as the ortho (o-) , the 1, 3 or 1, 5 as meta (m-) and the 1, 4 as para (p-) disubstituted compounds. A few examples of derivatives of benzene are given below:



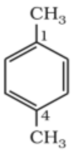
Methylbenzene
(Toluene)



1,2-Dimethylbenzene
(*o*-Xylene)



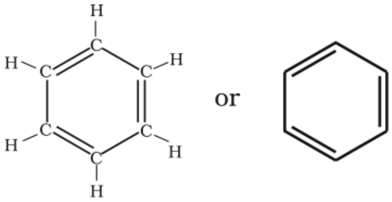
1,3 Dimethylbenzene
(*m*-Xylene)



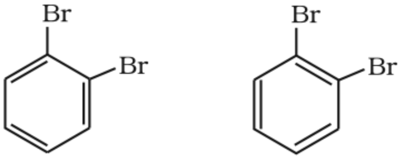
1,4-Dimethylbenzene
(*p*-Xylene)

13.11.2 Structure of Benzene

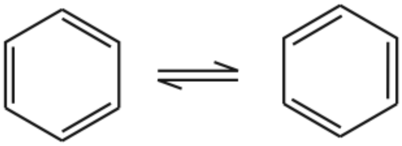
Benzene was isolated by Michael Faraday in 1825. The molecular formula of benzene, C6H6, indicates a high degree of unsaturation. This molecular formula did not account for its relationship to corresponding alkanes, alkenes and alkynes which you have studied in earlier sections of this unit. What do you think about its possible structure? Due to its unique properties and unusual stability, it took several years to assign its structure. Benzene was found to be a stable molecule and found to form a trtozonide which indicates the presence of three double bonds. Benzene was further found to produce one and only one monosubstituted derivative which indicated that all the six carbon and six hydrogen atoms of benzene are identical. On the basis of this observation August Kekule in 1865 proposed the following structure for benzene having cyclic arrangement of six carbon atoms with alternate single and double bonds and one hydrogen atom attached to each carbon atom.



The Kekule structure indicates the possibility of two isomeric 1,2-dibromobenzenes. In one of the isomers, the bromine atoms are attached to the doubly bonded carbon atoms whereas in the other, they are attached to the singly bonded carbons.



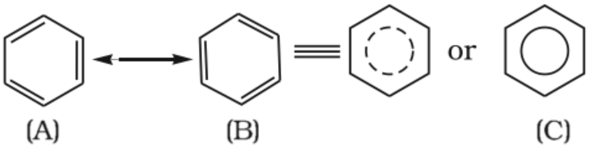
However, benzene was found to form only one ortho disubstituted product. This problem was overcome by Kekule by suggesting the concept of oscillating nature of double bonds in benzene as given below.



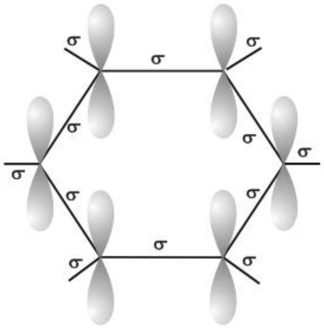
Even with this modification, Kekule structure of benzene fails to explain unusual stability and preference to substitution reactions than addition reactions, which could later on be explained by resonance.

Resonance and stability of benzene

According to Valence Bond Theory, the concept of oscillating double bonds in benzene is now explained by resonance. Benzene is a hybrid of various resonating structures. The two structures, A and B given by Kekule are the main contributing structures. The hybrid structure is represented by inserting a circle or a dotted circle in the hexagon as shown in (C). The circle represents the six electrons which are delocalised between the six carbon atoms of the benzene ring.



The orbital overlapping gives us better picture about the structure of benzene. All the six carbon atoms in benzene are sp^2 hybridized. Two sp^2 hybrid orbitals of each carbon atom overlap with sp^2 hybrid orbitals of adjacent carbon atoms to form six C-C sigma bonds which are in the hexagonal plane. The remaining sp^2 hybrid orbital of each carbon atom overlaps with s orbital of a hydrogen atom to form six C-H sigma bonds. Each carbon atom is now left with one unhybridised p orbital perpendicular to the plane of the ring as shown below:



The unhybridised p orbital of carbon atoms are close enough to form a π bond by lateral overlap. There are two equal possibilities of forming three π bonds by overlap of p orbitals of C_1- C_2, C_3 - C_4, C_5 - C_6 or C_2 - C_3, C_4 - C_5, C_6 - C_1 respectively as shown in the following figures.

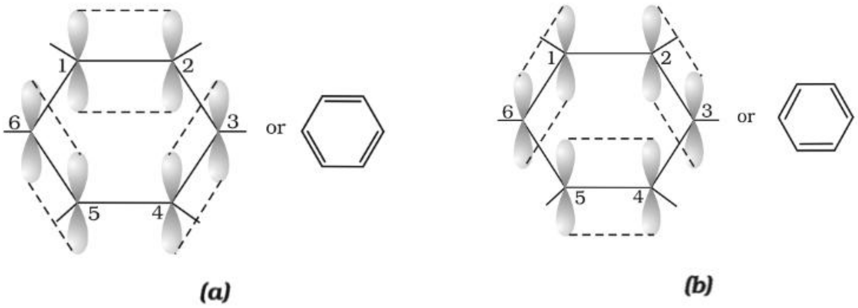


Fig. 13.7 Kekule structures of benzene

Structures shown in Fig. 13.7(a) and (b) correspond to two Kekule's structure with localised π bonds. The internuclear distance between all the carbon atoms in the ring has been determined by the X-ray diffraction to be the same; there is equal probability for the p orbital of each carbon atom to overlap with the p orbitals of adjacent carbon atoms [Fig. 13.7 (c)]. This can be represented in the form of two doughtnuts (rings) of electron clouds [Fig. 13.7 (d)], one above and one below the plane of the hexagonal ring as shown below:

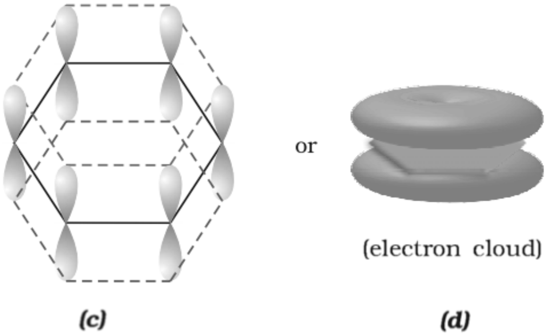


Fig. 13.7 π electron cloud on benzene

The six π electrons are thus delocalised and can move freely about the six carbon nuclei, instead of any two as shown in Fig. 13.7 (a) or (b). The delocalised π electron cloud is attracted more strongly by the nuclei of the carbon atoms than the electron cloud localised between two carbon atoms. Therefore, presence of delocalized π electrons in benzene makes it more stable than the hypothetical cyclohexatriene.

X-Ray diffraction data reveals that benzene is a planar molecule. Had any one of the above structures of benzene (A or B) been correct, two types of C-C bond lengths were expected. However, X-ray data indicates that all the six C-C bond lengths are of the same order (139 pm) which is intermediate between C-C single bond (154 pm) and C-C double bond (133 pm. Thus the absence of pure double bond in benzene accounts for the reluctance of benzene to show addition reactions under normal conditions, thus explaining the unusual behaviour of benzene.

13.11.3 Aromaticity

Benzene was considered as parent 'aromatic' compound. Now, the name is applied to all the ring systems whether or not having benzene ring, possessing following characteristics.

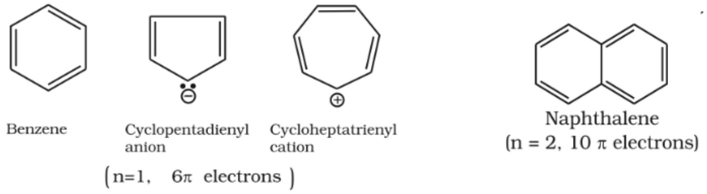
(i) Planarity

(ii) Complete delocalisation of the π electrons in the ring

(iii) Presence of (4n + 2) π electrons in the ring where n is an integer (n = 0, 1, 2, . . .).

This is often referred to as Hiickel Rule.

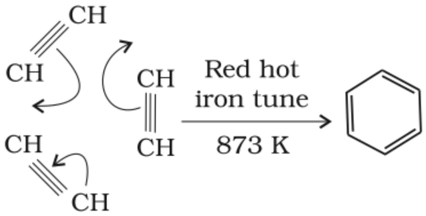
Some examples of aromatic compounds are given below:



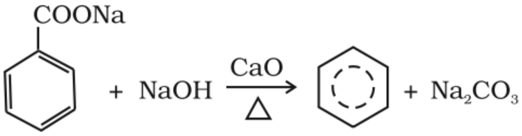
13.11.4 Preparation of Benzene

Benzene is commercially isolated from coal tar. However, it may be prepared in the laboratory by the following methods.

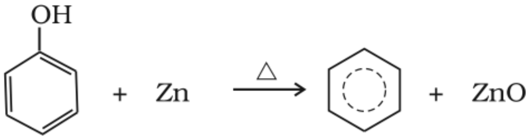
(i) Cyclic polymerisation of ethyne: Ethyne on passing through red hot iron tube at 873K undergoes cyclic polymerization. Three molecules polymerise to form benzene, which is the starting molecule for the preparation of derivatives of benzene, dyes, drugs and large number of other organic compounds. This is the best route for entering from aliphatic to aromatic compounds as discussed below:



(ii) Decarboxylation of aromatic acids: Sodium salt of benzoic acid on heating with sodalime gives benzene.



(iii) Reduction of phenol: Phenol is reduced to benzene by passing its vapours over heated zinc dust



13.11.5 Properties

Physical properties

Aromatic hydrocarbons are non-polar molecules and are usually colourless liquids or solids with a characteristic aroma. You are also familiar with naphthalene balls which are used in toilets and for preservation of clothes because of unique smell of the compound and the moth repellent property. Aromatic hydrocarbons are immiscible with water but are readily miscible with organic solvents. They burn with sooty flame.

Chemical properties

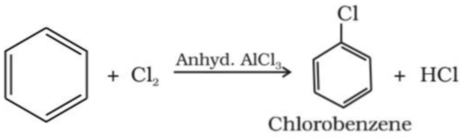
Arenes are characterized by electrophilic substitution reactions. However, under special conditions they can also undergo addition and oxidation reactions.

Electrophilic substitution reactions

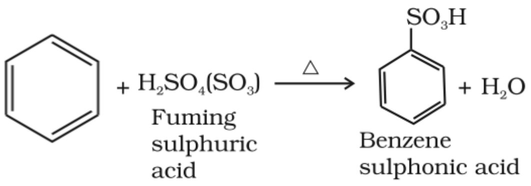
The common electrophilic substitution reactions of arenes are nitration, halogenation, sulphonation, Friedel Craft's alkylation and acylation reactions in which attacking reagent is an electrophile (E^+)

(i) Nitration: A nitro group is introduced into benzene ring when benzene is heated with a mixture of concentrated nitric acid and concentrated sulphuric acid (nitrating mixture).

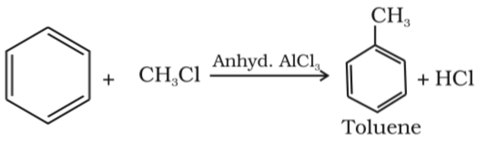
(ii) Halogenation: Arenes react with halogens in the presence of a Lewis acid like anhydrous $FeCl_3$, $FeBr_3$ or $AlCl_3$ to yield haloarenes.



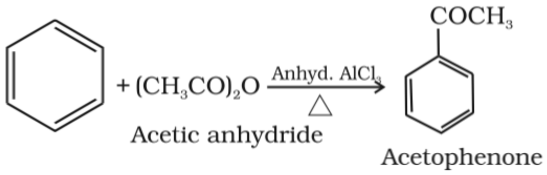
(iii) Sulphonation: The replacement of a hydrogen atom by a sulphonic acid group in a ring is called sulphonation. It is earned out by heating benzene with fuming sulphuric acid (oleum).



(iv) Friedel-Crafts alkylation reaction: When benzene is treated with an alkyl halide in the presence of anhydrous aluminium chloride, alkylbenene is formed.



(v) Friedel-Crafts acylation reaction: The reaction of benzene with an acyl halide or acid anhydride in the presence of Lewis acids ($AlCl_3$) yields acyl benzene.



SUMMARY

In this unit we have learnt some basic concepts in structure and reactivity of organic compounds which are formed due to covalent bonding. The nature of the covalent bonding in organic compounds can be described in terms of orbitals hybridization concept. According to which carbon can have sp3, sp2, and sp hybridized orbitals. Sp3, sp2 and sp hybridized carbons are found in compounds methane ethene and ethyne respectively. The tetrahedral shape of methane, planar shape of ethane and linear shape of ethyne can be understood on the basis of this concept.

Organic compounds can be classified on the basis of their structure or the functional groups they contain. A functional group is an atom or group of atoms bonded together in a unique fashion and which determines the physical and chemical properties of the compounds. The naming of the organic compounds is carried out by following a set of rules laid down by the International Union of pure and applied chemistry. In IUPAC nomenclature, the names are correlated with the structure in such a way that the reader can reduce the structure from the name.

Organic reaction mechanism concepts are based on the structure of the substrate molecule, fission of a covalent bond etc. A covalent bond may be cleaved in heterolytic or hemolytic fission which produce ions and free radicals respectively. The electron pair donar is known as nucleophile and electron pair acceptor known as electro file. Organic reactions can be broadly classified into substitution, addition, elimination and rearrangement reactions.

Hydrocarbons are the compounds of carbon and hydrogen only. Hydrocarbons are mainly obtained from coal and petroleum, which are the major sources of energy. Petrochemicals are the prominent starting materials used for the manufacture of a large nu1nber of com1nercially important products. LPG (liquefied petroleum gas) and CNG (compressed natural gas), the main sources of energy for domestic fuels and the automobile industry are obtained from petroleum. Hydrocarbons are classified as open chain saturated (alkanes) and unsaturated (alkenes and alkynes), cyclic (alicyclic) and aromatic, according to their structure.

The important reactions of alkanes are free radical substitution, combustion, oxidation and aromatization. Alkenes and alkynes undergo addition reactions, which are mainly electrophilic additions. Aromatic hydrocarbons, despite having unsaturation, undergo mainly electrophilic substitution reactions. These undergo addition reactions only under special conditions. Alkanes show conformational isomerism due to free rotation along the C-C sigma bonds. Out of staggered and the eclipsed conformations of ethane, staggered conformation is more stable as hydrogen atoms are farthest apart. Alkenes exhibit geometrical (cis-trans) isomerism due to restricted rotation around the carbon-carbon double bond.

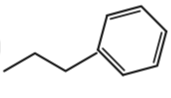
Benzene and benzenoid compounds show aromatic character. Aromaticity, the property of being aromatic is possessed by compounds having specific electronic structure characterised by Huckel (4n+2)pi electron rule. The nature of groups or substituents attached to benzene ring is responsible for activation or deactivation of the benzene ring towards further electrophilic substitution and also for orientation of the inco1ning group. Some of the polynuclear hydrocarbons having fused benzene ring system have carcinogenic property.

EXCERCISE

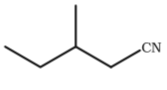
1 Write the conformations of ethane?

2 Write the IUPAC of

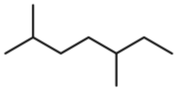
(a)



(b)



(c)



3 How does ethyne react with a) bromine b) hydrogen

4 What is substitution reaction give to examples

5 Give to examples each per position and functional isomerism?

6 Explain the mechanism of halogenation of methane?

7 Explain the classification of hydrocarbons?

8 Describe two methods of ethane?

9 Discuss Markownikov's and Kharash effect?

10 Explain aromatic electrophilic substitution reactions of benzene?

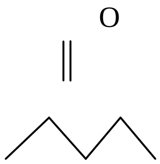
11 Give two methods of preparations of acetalyene?

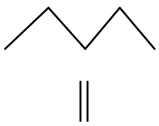
12 Explain how many types organic reactions are possible?

QUESTION BANK

1. Write the regents required for conversion of benzene to methyl benzene.
2. How is nitrobenzene prepared.
3. Write the IUPAC names of

a) $CH_3 - CH_2 - CH_2 - CH - CH_2.$ b)





4. Write the structure of :

(i) Pent-2-ene (ii) 3,4-Dimethyl-hept-3-ene

(iii) 2-Ethylbut-1-ene (iv) 1-Phenylbut-1-ene

Short Answer Questions **(4 Marks)**

5. Complete the following reaction and name the products A, B, and C.

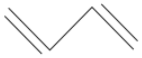
$$CaC_2 \xrightarrow{H_2O} A \xrightarrow{\text{not metal tube}} B \xrightarrow{AlCl_3 + CH_3Cl} C$$

6. What is dehydro 740alogenations? Write the equation for the formation of alkene from alkyl halide.

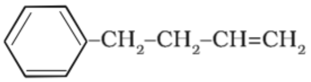
7. Give two examples each for position and functional isomerism.
8. How is ethylene prepared from ethyl alcohol? Write the reaction.
9. What is the product formed when sodium propionate is heated with soda lime.
10. Write IUPAC names of the following compounds.

(a) $CH_3CH=C(CH_3)_2$ (b) $CH_2=CH-C \equiv C-CH_3$

(c)



(d)



11. Describe two methods of preparation as ethane.
12. Describe two methods of preparation as ethylene.
13. Give two methods of preparation of acetylene.
14. Describe any two methods of preparation of benzene write equations.

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VOCATIONAL BRIDGE COURSE

CHEMISTRY – First Year (w.e.f. 2018-2019)

WEIGHTAGE OF MARKS

S.No. Chapter No.	Chapters	Number of Periods	Weightage
1.	Atomic Structure	10	04
2.	Classification of Elements and Periodicity of	10	04
3.	Chemical Bonding and Molecular Structure	10	04
4.	States of Matter: Gases and Liquids	08	04
5.	Stiochiometry	07	02
6.	Thermodynamics	05	02
7.	Chemical Equilibrium and Acids-Bases	08	04
8.	Hydrogen and its Compounds	04	02
9.	The s– block Elements: (Alkali And Alkaline Earth Metals)	04	04
10.	P- Block Elements:Group-13 (Boron family)	04	02
11.	P - Block Elements: Group-14 (Carbon Family)	04	02
12.	Environmental Chemistry	04	02
13.	Organic Chemistry- Some Basic Principles and	12	04
	Total	**90**	**40**

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VOCATIONAL BRIDGE COURSE
CHEMISTRY – First Year (w.e.f. 2018-2019)
MODEL QUESTION PAPER

Time: 1 ½ Hours **Max.Marks: 25**

Section – A 5x1=5

Note:

i) *Answer any **five** of the following questions*

ii) *Each question carries **one** mark.*

1. Assign oxidation number of Cr in $K_2Cr_2O_7$.
2. Why is Hydrogen used in welding as high melting metals?
3. Write about diagonal relationship of Li and Mg..
4. What is green house effect?
5. Define molarity.
6. Write any two uses of H_2O_2.
7. Write about anomalous properties of carbon
8. Write two harmful effects caused by ozone layer depletion.

Section – B 5x4=20

Note:

i) *Answer any **five** of the following questions*

ii) *Each question carries **four** marks.*

9. What are the postulates of Bohr's model of hydrogen atom?
10. Write an essay on s, p, d, and f block elements.
11. What is hybridization? Explain the hybridization in CH_4 molecule.
12. Write the postulates of the Kinetic molecular theory.
13. (i) What are intensive and extensive properties (ii) Explain Inert Pair effect.
14. Define Lewis acids and Lewis bases. Give examples.
15. Give an account of the biological importance of Na^+ and Mg^{+2} ions.
16. Describe two preparation methods of Ethylene

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CHEMISTRY – First Year (w.e.f. 2018-2019)

QUESTION BANK

Chapter 1: ATOMIC STURCTURE

***Short Answer Questions* (4 Marks)**

1. What are the postulates of Bohr's model of hydrogen atom?
2. Explain various series of line spectra in hydrogen atom?
3. What are the evidences in favour of dual behavior of electron?
4. Explain the significance of n, *l*, m_l and m_s quantum numbers?
5. Define atomic orbitals, write the shapes of s, p, and d orbitals?
6. Define Aufbau Principle, Pauli's exclusion Principle and Hund's rule of maximum multiplicity?

Chapter2: CLASSIFICATION OF ELEMENTS AND PERIODICITY OF PROPERTIES

***Short Answer Questions* (4 Marks)**

7. State modern periodic law? How many groups and periods are present in the long form of the periodic table?
8. Write an essay on s, p, d and f block elements?
9. What is periodic property? How the following properties vary in a group and in a period, explain?

   a) Atomic radius b) Electron gain enthalpy?
10. What is periodic property? How the following properties vary in a group and in a period?

    a) Ionisation Enthalpy   b) Electro negativity.
11. Why secondary Ionisation Enthalpy is greater than primary Imisation enthalpy, explain it?

Chapter 3: CHEMICAL BONDING AND MOLECULAR STRUCTURE

Short Answer Questions **(4 Marks)**

12. Explain the formation of Ionic bond?
13. What are the factors favorable for the formation of Ionic bond.
14. How do you predict the shapes of the following molecules making use of VSEPR theory?

    a) $Xe F_2$ b) $Br F_s$ c) $Cl F_3$ d) SF_4
15. Explain the structure of CH_4 molecule.
16. Explain the hybridisation involved in PCl_5 molecule.
17. Explain the hybridization involved in SF_6 molecule.
18. What is Hydrogen bond? What are the different types of hydrogen bonds. Give example.

Chapter 4: STATES OF MATTER: GASES AND LIQUIDS

Very Short Answer Questions **(01 Mark)**

1. What is Ideal gas?
2. Give the values of gas constant in different units?
3. Sate Graham's law of diffusion?
4. How many times methane diffuse faster than sulphar dioxide
5. State Dolton's law of Partial Pressure?
6. Give the relation between the Partial Pressure of a gas and its mole fraction?
7. Give an equation to calculate the kinetic energy of gas molecules?
8. What is Boltzman's constant? Give its value?
9. What is Rms speed?
10. What is Average speed?
11. What most probable speed?
12. What is surface tension.
13. Write the postulates of the kinetic molecular theory. (04 Marks)

Chapter 5: STOICHEMISTRY

***Very Short Answer Questions* (2 Marks)**

14. How many number of moles of glucose present in 540 gms of glucose.
15. The empirical formula of a compound is CH_2O its molecular weight is 90. Calculate the molecular formula of the compound.
16. Define the molar mass.
17. Define normality?
19. Write formulas for the following compounds.

    a) Mercury (II) Chloride b) Nickel (II) Sulphate c) Tin (IV) orise

    d) Thallium (I) Sulpate e) Iron (III) Sulphate f) Chromium (III) Oxide.

20. Assign oxidation number to the underlined elements in each of the following species.

    a) $NaH_2\underline{P}O_4$ b) $NaH\underline{S}O_4$ c) $H_4\underline{P}_2O_7$ d) $K_2\underline{Mn}O_4$

    e) CaO2 f) $Na\underline{B}H_4$ g) $H_2\underline{S}_2O_7$

Chapter 6: THERMODINAMICS

***Very Short Answer Questions* (2 Marks)**

21. State the first law of the thermodynamics. (2 Marks)
22. What are intensive and extensive properties? (2 Marks)
23. Define the Enthalpy of combustion? (2 Mrks)
24. State Hess's law of constant Heat summation? (1 Mark)
25. Define Entropy, Gibbs energy? (1 Mark)
26. State the second law of thermodynamics?
27. State third law of thermo dynamics?

Chapter 7: CHEMICAL EQUILIBRIUM AND ACID - BASES

***Very Short Answer Questions* (4 Marks)**

28. What is homogenous equilibrium? Write two homogenous reactions?
29. What is heterogenous equilibrium? Write two heterogenous reactions.
30. Write the relation between K_P and K_C.

31. Define law of mass action.
32. Discuss the application of Le-Chatelier’s Principle for the industrial synthesis of Ammonia?
33. Discuss the application of Le-Chatelier’s Principle for the industrial synthesis of sulpur trioxide.
34. Explain the Arrhenius concept of acids and bases?
35. What is a conjugate acid-base pair? Give Example.
36. Define Lewis Acids and Lewis bases?
37. Define P^H?
38. Define ionic product of water? What is its value at room temperature?
39. Give two examples of salts whose aqueous solutions are basic?
40. Give two examples of slats whose aqueous solutions are acidic?
41. Define Buffer solution. Give example for acidic buffer and basic buffer solution.

Chapter 8: HYDROGEN AND ITS COMPOUNDS

Very Short Answer Questions **(2 Marks)**

42. Describe one method of producing high quality hydrogen?
43. Why is dihydrogen used in welding of high melting metals?
44. Explain the terms hard water and soft water?
45. What is the chemical substance used in calgen method?
46. What are the uses of hydrogen fule?
47. Mention three uses of H_2O_2 in modern times?
48. Write any two methods of preparation of $H_2O_{2.}$

Chapter 9: THE S-BLOCK ELEMENTS

Short Answer Questions **(4 Marks)**

49. Write completely the electronic configuration of K and Rb?
50. Lithium salts are mostly hydrated. Why?
51. In what respects lithium hydrogen carbonate differs from other alkali metal hydrogen carbonates?
52. Describe important uses of caustic soda?

53. Describe important uses of sodium carbonates?
54. Give an account of the biological importance of Na^+ and K^+ ions.
55. Write the complete electronic configurations of any two alkaline earth metals?
56. What happens when magnesium metal is burnt in air?
57. Lithium carbonate is not so stable to heat & the other alkali metal carbonates. Explain.
58. Why is gypsum added to cement?
59. Why are alkali metals not found in the free state in nature?
60. Describe the importance of plaster of Paris?
61. Give an account of the biological importance of Ca^{2+}, Mg^{2+} ions.

Chapter 10: THE P-BLOCK ELEMENTS – GROUP – 13.

***Very Short Answer Questions* (2 Marks)**

62. Why does BF_3 behave as a Lewis acid?
63. Explain inert pair effect?
64. Give the formula of borazine, What is its common name?
65. Give the formula of a) Borax b) colemanite
66. Give two uses of aluminum?
67. Explain the structure of diborane?
68. Give two uses of Aluminum.
69. What are electron deficient compounds?

Chapter 11: THE P-BLOCK ELEMNETS – GROP – 14.

***Very Short Answer Questions* (2 Marks)**

70. Give the hybridization of carbon in

    a) CO_3^{2-} b) diamond c) graphite d) fullerene
71. Why is CO poisonous?
72. What is allotropy? Give the crystalline allotropes of carbon?
73. Name any two man-made silicates?
74. Why does graphite function as a lubricant/
75. Graphite is a good conductor – explain?
76. What is synthesis gas?

77. What is producer gas?

78. How does CO_2 increases the green house effect?

79. Write the use of ZSM-5.

80. What is the use of dry ice?

81. Why is diamond hard?

82. Explain a) Allotropy b) inert pair effect c) catenation.

Chapter 12: ENVIRONMENTAL CHEMISTRY

***Very Short Answer Questions* (2 Marks)**

83. List out four Gaseous pollutants present in the polluted air?

84. What are green house gases?

85. Which acids cause acid rain? And what is its p^H value.

86. Name two adverse effects caused by acid rains?

87. What is ozone hole? Where was it first observed?

88. What is green house effect? And how is it caused?

89. What are the harmful effects caused by ozone layer depletion?

90. Define Eutrophication of lake?

91. What is the importance of Green Chemistry?

Chapter 13: ORGANIC CHEMISTRY – SOME BASIC PRINCIPLES AND TECHNIQUES AND HYDRO CORBONS

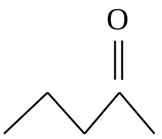
***Very Short Answer Questions* (2 Marks)**

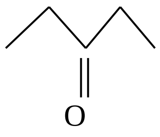
92. Write the regents required for conversion of benzene to methyl benzene.

93. How is nitrobenzene prepared.

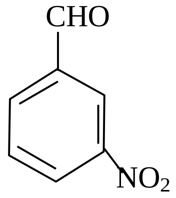
94. Write the IUPAC names of

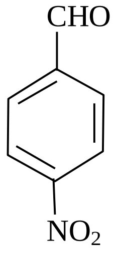
95. a) $CH_3 - CH_2 - CH_2 - CH = CH_{2.}$ b)





c)





96. Write the structure of : a) Tri chloro ethanoic acid.

b) Neo pentane c) P-nitro benzal de hyde.

Short Answer Questions **(4 Marks)**

97. Complete the following reaction and name the products A, B, and C.

$$CaC_2 \xrightarrow{H_2O} A \xrightarrow{\text{n ot metal tube}} B \xrightarrow{AlCl_3 + CH_3Cl} C$$

98. What is dehydro halogenation? Write the equation for the formation of alkene from alkyl halide.

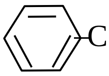
99. Give two examples each for position and functional isomerism.

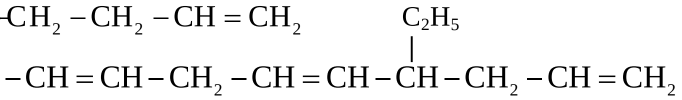
100. How is ethylene prepared from ethyl alcohol? Write the reaction.

101. What is the product formed when sodium propionate is heated with soda lime.

102. Write IUPAC names of the following compounds.

a)  b) $CH_2 = CH - C \equiv C - CH_3$ c) $CH_3CH = C(CH_3)_2$.

b)  $-CH_2 - CH_2 - CH = CH_2$

c) e) 

$$CH_3 - CH = CH - CH_2 - CH = CH - \underset{}{\overset{\overset{C_2H_5}{|}}{C}H} - CH_2 - CH = CH_2$$

103. Describe two methods of preparation as ethane.

104. Describe two methods of preparation as ethylene.

105. Give two methods of preparation of acetylene.

106. Describe any two methods of preparation of benzene write equations.

BOARD OF INTERMEDIATE EDUCATION, A.P, VIJAYAWADA

VOCATIONAL BRIDGE COURSE

CHEMISTRY – Second Year (w.e.f. 2019-2020)

QUESTION BANK

Chapter 1: SOLID STATE

***Very Short Answer Questions* (1 Mark)**

1. Define the term amorphous.
2. What is Shottky defect?
3. What is Frenkel defect?
4. Why X-rays are needed to probe the crystal structure?

***Short Answer Questions* (4 Marks)**

5. Derive Bragg’s equation.

Chapter2: SOLUTIONS

***Very Short Answer Questions* (1 Mark)**

7. Define the term solution.
8. Define molarity.
9. Define molality.
10. Define mole fraction.
11. State Raoult’s law.
12. State Henry’s law.
13. Define osmotic pressure.
14. What are isotonic solutions?
15. Calculate the amount of benzoic acid (C_6H_5COOH) required for preparing 250ml of 0.15M solution in methanol.

Short Answer Questions **(4 Marks)**

16. A solution of glucose in water is labeled as 10% w/w. What would be the molarity of the solution?
17. What is relative lowering of vapour pressure? How is it useful to determine the molar mass of a solute?
18. Determine the osmotic pressure of a solution prepared by dissolving 25mg of K_2SO_4 in two litre of water at 25^oC assuming that it is completely disassociated.
19. Calculate the amount of benzoic acid (C_6H_5COOH) required for preparing 250ml of 0.15M solution in methanol.

Chapter 3: ELECTROCHEMISTRY AND CHEMICAL KINETICS

Very Short Answer Questions **(1 Mark)**

20. What is a galvanic cell or a voltaic cell? Give one example.
21. How is galvanic cell represented on paper as per IUPAC convention? Give one example.
22. State Faraday's first law of electrolysis.
23. State Faraday's second law of electrolysis.
24. What is a primary battery? Give one example.
25. Give one example for a secondary battery. Give the cell reaction.
26. Give the cell reaction of nickel-cadmium secondary battery.
27. What is a fuel cell? How is it different from a conventional galvanic cell?
28. What is metallic corrosion? Give one example.
29. Give the electro-chemical reaction that represents the corrosion or rusting of iron.
30. Define the speed or rate of a reaction.
31. What are the units of rate of reaction?
32. What is rate law? Illustrate with an example.
33. Define Order of a reaction. Illustrate your answer with an example.
34. Define molecularity of a reaction. Illustrate with an example.
35. What is the effect of temperature on the rate constant?

***Short Answer Questions* (4 Mark)**

36. What are galvanic cells. Explain the working of a galvanic cell with a neat sketch taking Daniel cell as example.
37. What is electrolysis? Give Faraday's first law of electrolysis.
38. What are primary and secondary batteries? Give one example for each.
39. What are fuel cells? How are they different from galvanic cells? Give the construction of H_2, O_2 fuel cell.
40. What is metallic corrosion? Explain it with respect to iron corrosion.
41. Define and explain the order of a reaction. How is it obtained experimentally?
42. What is ''molecularity '' of a reaction? How is it different from the 'order' of a reaction? Name one bimolecular and one trimolecular gaseous reactions.

Chapter 4: SURFACE CHEMISTRY

***Very Short Answer Questions* (1 Mark)**

43. What is adsorption ? Give one example.
44. What is absorption ? Give one example.
45. Distinguish between adsorption and absorption. Give one example of each.
46. Amongst adsoprtion, absorption which is a surface phenomena and why ?
47. What is the difference between physisorption and chemisorption?
48. Out of physisorption and chemisorption, which can be reversed ?
49. Define "promoters" and "poisons" in the phenamenon of catalysis.
50. What is homogeneous catalysis ? How is it different from heterogeneous catalysis?
51. Give two examples for homogeneous catalytic reactions.
52. Give two examples for heterogeneous catalysis.
53. Can catalyst increase the yield of reaction ?
54. What are lyophilic and lyophobic sols ? Give one example for each type.
55. Give two examples of lyophobic sols.
56. What is an emulsion ? Give two examples.

Short Answer Questions (4 Marks)

57. What are different types of adsorption ? Give any four differences between characteristics of these different types.
58. What is catalysis ? How is catalysis classified ? Give two examples for each type of catalysis.
59. How are colloids classified on the basis of nature of the dispersion medium?
60. How are colloids classified on the basis of interaction between dispersed phase and dispersion medium ?
61. How do emulsifiers stabilize emulsion ? Name two emulsifiers.

Chapter 5: GENERAL PRINCIPLES OF ETALLURGY

Very Short Answer Questions (1 Mark)

62. What is the role of depressant in froth floatation ?
63. State the role of silica in the metallurgy of copper.
64. Explain "poling".
65. What is the role of cryolite in the metallurgy of aluminium ?
66. Give the composition of the following alloys.

    a) Brass b) Bronze c) German silver
67. Explain the terms gangue and slag.
68. Write any two ores with formulae of the following metals:

    a) Aluminium b) Zinc c) Iron d) Copper
69. What is blister copper? Why is it so called ?
70. Explain magnetic separation of impurities from an ore.
71. Give two uses each of the following metals:

    a) Zinc b) Copper c) Iron d) Aluminium

Short Answer Questions (4 Marks)

72. Giving examples to differentiate roasting and calcination.
73. Explain the purification of sulphide ore by froth floatation method.

Chapter 6: *p*-BLOCK ELEMENTS

GROUP 15 ELEMENTS

***Very Short Answer Questions* (1 Mark)**

75. Why are the compounds of bismuth more stable in +3 oxidation state ?
76. What is inert pair effect ?

***Short Answer Questions* (4 Marks)**

77. Discuss the general characteristics of Group – 15 elements with reference to their electronic configuration, oxidation state, atomic size, ionization enthalpy and electronegativity.
78. Discuss the trends in chemical reactivity of group – 15 elements.

GROUP 16 ELEMENTS

***Very Short Answer Questions* (1 Mark)**

79. How does ozone react with ethylene ?
80. Write any two uses each for O3 and H2SO4.

***Short Answer Questions* (4 Marks)**

81. Describe the manufacture of H_2SO_4 by contact process.
82. How is ozone prepared? How does it react with the following ?
    a) PbS b) KI c) Hg d) Ag
83. Complete the following
    a) $KCl + H_2SO_4$ (conc) $\longrightarrow$ b) $\xrightarrow{\text{Conc.}H_2SO_4}$
    Sucrose
    b) $Cu + H_2SO_4$ (conc) $\longrightarrow$ d) $C + H_2SO_4$ (conc)
    $\longrightarrow$

GROUP 17 ELEMENTS

***Very Short Answer Questions* (1 Mark)**

84. What happens when Cl2 reacts with dry slaked lime ?
85. Chlorine acts as an oxidizing agent – explain with two examples.
86. How is chlorine manufactured by Deacon’s method ?
87. Chlorine acts as a bleaching agent only in the presence of moisture – explain.

Short Answer Questions (4 Marks)

88. How can you prepare Cl_2 from HCl and HCl from Cl_2 ? Write the reactions.

GROUP 18 ELEMENTS

Very Short Answer Questions (1 Mark)

89. Which of the following does not exist ?

    a) $XeOF_4$ b) XeF_2 c) XeF_4 d) XeF_6

90. Explain the structure of XeO_3.

Short Answer Questions (4 Marks)

91. Explain the structures of a) XeF_2 and b) XeF_4
92. Explain the structures of a) XeF_6 and b) $XeOF_4$

Chapter 7: *d*- and *f*- BLOCK ELEMENTS and COORDINATION COMPOUNDS

Very Short Answer Questions (1 Mark)

93. What are transition elements ? Give examples.
94. Why are d-block elements called transition elements?
95. Write the electronic configuration of Co^{2+} and Mn^{2+}.
96. Why Zn^{2+} is diamagnetic whereas Mn^{2+} is paramagnetic?
97. Aqueous Cu^{2+} ions are blue in colour, where as Aqueous Zn^{2+} ions are colourless. Why?
98. What are complex compounds? Give examples
99. What is an alloy? Give example.
100. What is lanthanoid contraction?
101. What are coordination compounds? Give two examples.
102. What is a ligand?

Short Answer Questions (4 Marks)

103. Why do the transition metal ions exhibit characteristic colours in aqueous solution. Explain giving examples.
104. Explain the catalytic action of Iron(III) in the reaction between I^- and $S_2O_8^{2+}$ ions.
105. Explain Werner’s theory of coordination compounds with suitable examples.

106. Using IUPAC norms write the formulas for the following:

    (i) Tetrahydroxozincate(II) (ii) Hexaamminecobalt(III) sulphate

    (iii) Potassium tetrachloropalladate(II) and

    (iv) Potassium tri(oxalato)chromate(III)

107. Using IUPAC norms write the systematic names of the following:

    (i) $[Co(NH_3)_6]Cl_3$(ii) $[Pt(NH_3)2Cl(NH_2CH_3)]Cl$ (iii) $[Ti(H_2O)_6]^{3+}$ and (iv) $[NiCl_4]^{2-}$

Chapter 8: POLYMERS

Very Short Answer Questions (1 Mark)

108. What are polymers ? Give example.
109. What is vulcanization of rubber ?
110. What is biodegradable polymer ? Give one example of a biodegradable polyester?
111. What is PHBV ? How is it useful to man ?

Short Answer Questions (4 Marks)

112. Write the names and structures of the monomers used for getting the following polymers (i) Polyvinyl chloride (ii) Teflon (iii) Bakelite (iv) Polystyrene.
113. Explain the purpose of vulcanization of rubber.

Chapter 9: BIOMOLECULES

Very Short Answer Questions (1 Mark)

114. Define Carbohydrates.
115. Name the different types of carbohydrates on the basis of their hydrolysis. Give one example for each.
116. Name the vitamin responsible for the coagulation of blood.
117. Why are vitamin A and vitamin C essential to us? Give their important sources.

Short Answer Questions (4 Marks)

118. Write the importance of carbohydrates.
119. Explain the denaturation of proteins.
120. Write notes on vitamins.

123. Give the sources of the following vitamins and name the diseases caused by their deficiency (a) A (b) D (c) E and (d) K

Chapter 10: CHEMISTRY IN EVERYDAY LIFE

***Very Short Answer Questions* (1 Mark)**

124. What are drugs ?
125. What are antacids ? Give example.
126. What are antihistamines ? Give example.
127. What are tranquilizers? Give example.
128. What are analgesics? How are they classified?
129. What are narcotic analgesics? Give example .
130. What are non-narcotic analgesics? Give example.
131. What are antimicrobials?
132. What are antibiotics? Give example.
133. What are antiseptics? Give example.
134. What are disinfectants? Give example.
135. What are artificial sweetening agents? Give example.
136. Why do we require artificial sweetening agents?
137. What are food preservatives? Give example.

***Short Answer Questions* (4 Marks)**

139. What are analgesics ?How are they classified ? Give examples.
140. What are different types of microbial drugs? Give one example for each.
141. Write the characteristic properties of antibiotics.
142. What are broad spectrum and narrow spectrum antibiotics? Give one example for each.
143. Write notes on antiseptics and disinfectants.
144. What are the main categories of food additives?

Chapter 11: HALOALKANES AND HALOARENES

***Very Short Answer Questions* (1 Mark)**

145. Write the structures of the following compounds. (i) 2-chloro-3-methylpentane

146. What are ambident nucleophiles?

147. What are Enantiomers?

148. Give the IUPAC names of the following compounds: (i) ClCH2CH=CH CH2Br

149. Write the structures of the following organic halides. (i) 2-Choro-1-phenylbutane

(ii) p-bromochlorobenzene

Short Answer Questions **(4 Marks)**

150. A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochlorocompound C_5H_9Cl in bright sunlight. Identify the hydrocarbon.

151. How will you carry out the following conversions? i). Ethane to bromomethene

Chapter 12: ORGANIC COMPOUNDS CONTAINING C, H AND O

(Alcohols, Phenols, Ethers, Aldehydes, Ketones and Carboxylic Acids)

ALCOHOLS, PHENOLS, ETHERS

Very Short Answer Questions **(1 Mark)**

152. Give the reagents used for the preparation of phenol from chlorobenzene.

153. Name the reagents used in the following reactions. i). Oxidation of primary alcohol to carboxylic acid ii). Oxidation of primary alcohol to aldehyde

154. Write the equations for the following reactions.

i). Bromination of phenol to 2,4,6-tribromophenol ii). Benzyl alcohol to benzoic acid.

155. Write the structures for the following compounds

i). Ethoxyethane ii). Ethoxybutane iii). Phenoxyethane

***Short Answer Questions* (4 Marks)**

156. Give the equations for the preparation of phenol from Cumene.
157. Explain the acidic nature of phenols and compare with that of alcohols.
158. Ethanol with H_2SO_4 at 443K forms ethane while at 413 K it forms ethoxy ethane. Explain the mecnanism.
159. With a suitable example write equations for the following:
    i). Reimer-Tiemann reaction.
    ii). Williamsons ether synthesis.
160. How are the following conversions carried out?
    i). Benzyl chloride to Benzyl alcohol ii). 2-butanone to 2-butanol
161. Write the names of the reagents and equations for the preparation of the following ethers by Williamson's synthesis:
    i). 1-Propoxypropane ii). 1-Methoxyethane

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

***Very Short Answer Questions* (1 Mark)**

162. Write the reaction showing α – halogenations of carboxylic acid and give its name.
163. List the reagents needed to reduce carboxylic acid to alcohol.
164. Compare the acidic strength of acetic acid, Chloroacetic acid, benzoic acid and Phenol.

***Short Answer Questions* (4 Marks)**

165. Write the oxidation products of: Acetaldehyc, Acetone and Acetophenone
166. Describe the following:

    i). Cross aldol condensation ii) Decarboxylation

167. Explain the following terms. Give an example of the reaction in each case.

    i). Cyanohydrin ii). Aldol iii). Oxime

168. Describe the following.

    i). Cannizaro reaction ii). Decarboxylation

Chapter 13: ORGANIC COMPOUNDS CONTAINING NITROGEN

(Amines, Diazonium Salts, Alkyl Cyanides & Alkyl Isocyanides)

***Very Short Answer Questions* (1 Mark)**

169. Write equations for Carbylamine reaction of any one aliphatic amine.

170. Give structures of A,B and C in the following reaction.

$$C_6H_5N_2Cl \xrightarrow{\boxed{CuCN}} \overset{\boxed{H_2O/H^+}}{A} \xrightarrow{\boxed{NH_3\Delta}} B \longrightarrow$$

171. Accomplish the following conversions:

    i). Benzoic acid to benzamide ii). Aniline to p-bromoaniline

***Short Answer Questions* (4 Marks)**

172. Give one chemical test to distinguish between the following pairs of compounds.

    i) Methylamine and dimethylamine

    ii) Aniline and N-methylaniline

    iii) Ethylamine and aniline

173. How do you prepare Ethyl cyanide and Ethyl isocyanide from a common alkylhalide?