Core Course XIV
Elective in PHYSICS

Materials Science
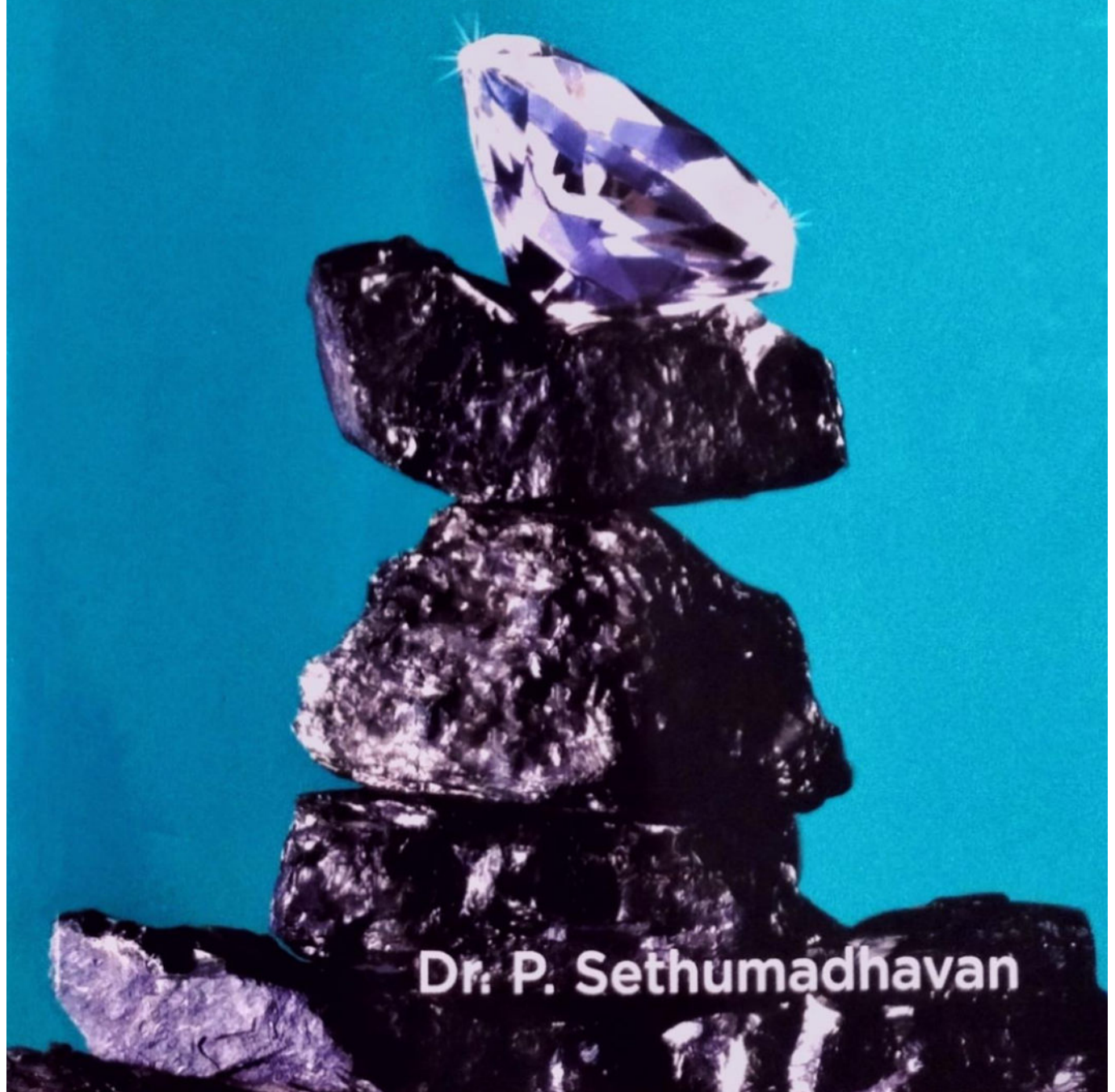
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CHAPTER 1

INTRODUCTION

1.1 Historical perspective

Materials play an important role in our life. This is because every segment of our everyday lives – such as transportation, housing, clothing, medicine, communication, recreation and food production – is influenced by materials in one way or other. Materials are probably more deep rooted in our culture. Historically, the development and advancement of societies have been intimately connected to the means ability to produce materials to fill their needs. This is why early civilizations have been named by the level of their materials development (Stone age, Bronze age, Iron age etc.).

In the very early ages humans have had only a very limited number of materials such as stone, wood, clay, skins etc. As time passes they discovered techniques for producing materials that had properties superior to the earlier ones. Pottery and various metals are examples of this. Later they discovered that the properties of material could be altered by adding other substances and also by heating. At this point onwards material utilization was totally a selection procedure that involved choosing the best material for the application by studying its characteristics. After that scientists came to understand the relationship between structural materials and their properties. This acquired knowledge over the past 100 years led scientists to discover tens of thousands of different materials, which have specialised characteristics that meet the needs of our modern society. These includes metals, plastics, glasses, fibres etc.

The accessibility of suitable materials made significant advancement in the development of many technologies which make human society more comfortable. For example, automobiles would not have been possible without the availability of inexpensive steel. Another example is that electronic devices rely much upon materials known as semiconductors.

1.2 What is materials science

Materials science is the study of properties of solid materials and how those properties are determined by a materials composition and structure.

Or

Materials science involves investigating the relationships that exist between the structures and properties of materials.

This branch grew out of an amalgam of solid state physics, metallurgy and chemistry, since the rich variety of properties of materials cannot be understood within the context of any single discipline. With a basic understanding of the origins of properties, materials can be selected or designed for an enormous variety of applications, ranging from structural steels to microchips. Materials science is therefore important to engineering activities such as electronics, aerospace, telecommunications, information processing, nuclear power and energy conversion. These disciplines come under materials engineering. Materials engineering deals with designing or engineering the structure of a materials to produce a predetermined set of properties on the basics of structure-property correlations. The role of materials scientists is to develop new materials where as a materials engineer is called upon to create new materials or to develop techniques for processing materials.

In the above discussion two terms "structure" and properties deserve some explanation.

Structure of a material refers to the arrangement of its internal components. Subatomic structure involves electrons within the

individual atoms and interactions with the nuclei. On the atomic level, structure encompasses the organisation of atoms or molecules relative to one another. The next larger structural realm is termed microscopic meaning that which is subject to direct observation using microscopes. This is actually the totality of large group of atoms forming the structure. The structure that may be viewed with naked eye are termed macroscope.

Property of materials implies the behaviour exhibited by the materials when subjected to external stimulus. Important properties of materials may be grouped into six different categories: mechanical, electrical, magnetic and deteriorate. For each category there is a characteristic type of stimulus capable of producing responses. Mechanical properties relate deformation to an applied force which include elasticmodulus and strength. When the stimulus is electricfield deformation occurs which gives properties such as electrical conductivity and dielectric strength. The thermal properties of materials can be represented in terms of heat capacity and thermal conductivity. Here the stimulus is heat. Magnetic properties demonstrate the response of a materials to the application of magnetic field. For optical properties, the stimulate is electromagnetic radiation; refractive index and reflectivity are representative optical properties. The deteriorative characteristics relate to the chemical reactivity of materials. It may be remembered that the structure of materials will depend upon how it is processed and materials performance will be a function of its properties. The interrelationship between processing, structure, properties and performance is depicted in the schematic illustration. (Figure 1.1)

Processing → Structure → Properties → Performance
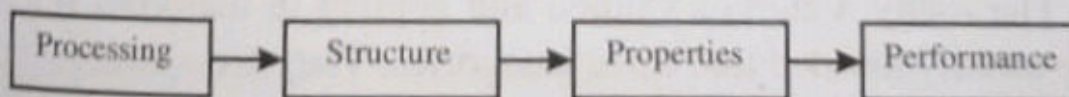
Figure 1.1:   The four components of the discipline of materials science and their interrelationships.

1.3 Why do we study materials science

Human society using tens of thousands of devices for their lives. For making such devices different types of materials are required. For example the main materials used for constructing a train is not suitable to construct a plane or an integrated chip. So first and fore most requirement is selecting the right material from the many thousands that are available. There are several criteria on which the final selection is based. First of all, the in-service conditions of the device must be characterised. This will specify the properties required by the material. We select a material which obeys maximum number of properties or ideal combination of properties. Sometimes it may be necessary to compromise. For example strength and ductility. Normally, a material having high strength will have only limited ductility. In such cases a reasonable compromise between the two.

The second selection consideration is due to deterioration of material properties that may occur during service operation. For example significant reductions in mechanical strength may result from exposure to elevated temperatures or corrosive environments.

Finally the consideration is that of economics: what will be the finished product cost. A material found suitable obeying almost all properties required may be expensive. Again some compromise has to be made.

To meet all these requirements materials must be studied in depth. This will be done by materials scientists and engineers.

1.4 Classification of materials

The many materials studied and applied in materials science are usually divided into three categories. They are

(1) metals (2) ceramics and (3) polymers.

This classification is based primarily on chemical make up and atomic structure. Most materials fall into one group or another.

although there are some intermediates. In addition, there are combinations of two of more of the above three basic material classes. They are called composites materials. Above all there is another classification called advanced materials such as semiconductors, biomaterials, smart materials and nano engineered materials.

1. Metals

Materials in this group are composed of one or more metallic elements such as iron, aluminium, copper, titanium, gold and nickel and often also non metallic elements (carbon, nitrogen and oxygen) in relatively small amounts.

Atoms in metals and their alloys are arranged in a very orderly manner in comparison to the ceramics and polymers and are relatively dense.

Properties

1. These materials are relatively stiff and strong hence are ductile and are resistant to fracture.

   Ductile means capable of large amounts of deformation without fracture.

2. Metals are good conductors of electricity and heat and are not transparent to visible light. This property is due to large number of non-localised electrons in these materials, that is these electrons are not bound to particular atoms.

3. When polished metal surface exhibits lustrous appearance.

4. Some of the metals (Fe, CO, and Ni) have desirable magnetic properties.

2. Ceramics

A ceramic is an inorganic non-metallic solid made up of either metal or non-metal compounds that have been shaped and hardened by heating to high temperatures. i.e., ceramics are componds between metallic and non-metallic elements. Most

of them are okides, nitrides and carbides. Some common ceramic materials are aluminium oxide (Al_2O_3) aluminium silicon dioxide (SiO_2 – silça) Silicon carbide (SiC), Silicon nitride (Si_3N_4) and clay materials and cement.

Properties

1. Ceramic materials are relatively stiff and strong comparable to those of metals.

2. Ceramic are typically very hard, but extremely brittle and highly susceptible to fracture.

3. These materials are insulators. i.e., they do not conduct heat or electricity. In other words they have low thermal and electrical conductivities.

4. These are more resistant to high temperatures and harsh environments than metals and polymers.

5. Cermics may be transparent, translucent or opaque.

6. Some of the oxide ceramics (Fe_3O_4) exhibit magnetic behaviour.

3. Polymers

Polymer, any of a class of natural or synthetic substances composed of very large molecules called molecules that are multiples of simpler chemical units called monomers. The familiar plastic and rubber materials are examples. Most of them are organic compounds that are chemically based on carbon, hydrogen and other non-metallic elements (O, N and Si). Carbon atoms are the back bone of the large molecular structure of polymers. Some of the common and familiar polymers are polyethylene (PE), nylon, polyvinyl chloride (PVC), Polycarbonate (PC), Polystyrene (PS) and silicone rubber.

Properties

1. Polymers are not as stiff nor as strong as other materials.

2. They are extremely ductile and pliable (plastic). This means that polymers can be easily formed into complex shapes.

3. They are relatively inert chemically and unreactive in a large number of environments.

4. These materials have low densities.

5. They have low electrical conductivities and are non-magnetic. One major drawback of polymers is their tendency to soften and or decompose at moderate temperatures which limits their use in some instances.

4. Composites

Composites are materials made up of two or more basic materials (metals, ceramics and polymers). The aim of constructing composites is to achieve a combination of properties that is not displayed by a single material. By doing so we can incorporate the best characteristics of each of basic materials. There are large number of synthetic (manmade) composites are available in the market produced by different combinations metals, ceramics and polymers.

One of the most common and familiar composites is fibre glass, in which small glass fibres are embed within a polymeric material (normally an epoxy or polyester). The glass fibres are relatively strong, stiff and also brittle, where as the polymer is ductile, weak and flexible. Thus the resulting fibre glass is relatively stiff, strong, flexible and ductile. In addition it has a low density.

Another important composites is the carbon fibre reinforced polymer (CFRP). In this carbon fibres are embedded within a polymer. This composites is stiffer and stronger than the glass fibre-reinforced materials. Hence they are more expensive. The CFRP composites are used in some aircrafts and aerospace applications, as well as high-tech sporting equipment like bicycles, golf clubs, tennis rackets and snow-boards. In this book we discuss only synthetic composites. Two naturally occurring composites materials are wood and bone.

1.5 Advanced materials

Materials that are utilised in high technology applications are termed as advanced materials. By high technology we mean a device or product that operates or functions using relatively intricate and sophisticated principles. Examples are electronic equipments such as camcorders, CD, computers fibre optic systems, space craft, aircraft and military rocketry. These advanced materials are typically traditional materials whose properties have been enhanced also newly developed high performance materials. All are making out from our three basic materials and normally are expensive. Advanced materials include semiconductors, biomaterials, smart materials and nano engineered materials. **Smart materials and nano engineered materials are termed as "materials of the future".**

Semiconductors

Semiconductors have electrical properties that are intermediate between the conductors (metals and alloys) and insulators (ceramics and polymers). Further the electrical characteristics of these materials are extremely sensitive to the presence of minute concentrations of imparity atoms, for which the concentrations may be controlled over very small spatial regions. Semiconductors paved the way to advent integrated circuits that revolutionized the electronic and computer industry over past several decades.

Biomaterials

A biomaterial is a substance that has been engineered to interact with biological systems for medical purpose. As a science biomaterials is about fifty years old. Examples of biomaterials include metals, ceramics and polymers. These biomaterials can be found in contact lenses, pacemakers, heart valves, orthopaedic devices and much more. Biomaterials that are employed in components implanted into the human body for replacement of diseased or damaged body parts. These materials must not produce toxic substances and must be compatible with body tissues.

Materials of the future

I. Smart materials

Smart materials also called intelligent or responsive materials that have one or more properties that can be significantly changed in a controlled fashion by external stimuli such as stress, moister, electric or magnetic fields, light, temperature, pH or chemical compounds.

Smart material system consists of a sensor and an actuator. The function of the sensor is to detect an input signal. The actuator performs a responsive and adaptive function. The actuator may be called upon to change shape, position, natural frequency or mechanical characteristics in response to changes in temperature, electric fields and magnetic fields.

Materials used as sensors include optical fibres, piezoelectric materials and micro electromechanical devices (MEMS).

Four types of materials are used for actuators. They are

1. Shape memory alloys: these are metals that after having been deformed, revert back to their original shapes when temperature is changed.

2. Piezo electric ceramics: These materials expand and contract in response to an electric field conversely they also generate and electric field when their dimensions are altered.

3. Magnetostriction materials. These materials also expand and contrast in response to magnetic fields.

4. Electro rheological and magneto rheological fluids. These are fluids that experience dramatic changes in viscosity upon the application of electric and magnetic fields respectively.

One type of smart system is used in helicopters to reduce aerodynamic cockpit noise that is created by the rotating rotor blades. Piezoelectric sensors inserted into the blades monitor blade stresses and deformations, feedback signals from these sensors are

feed into a computer controlled adaptive devices which generates noise cancelling antinoise.

II. Nano engineered materials

To understand the structure of the material scientists usually adopt two approaches. One is called "top down" approach and the other is called "bottom up" approach. In the former approach what they do is studying large and complex structures and then to investigate the fundamental building blocks of structures. But after the advent of scanning tunnelling microscope (STM), the observation of atoms and molecules are possible. By using this possibility scientists started forming new structures of materials by carefully arranging atoms and molecules to get required properties. We call this as "bottom-up" approach. The study of the properties of these materials is termed "nano technology". Nano denotes the dimensions of these structural entities are of the order of nanometres (10^{-6}m). The size less than 100 nm are considered as nano materials. Carbon nanotube is an example for nano material. In the future undoubtedly we can say that nano engineered materials play a crucial role.

UNIVERSITY MODEL QUESTIONS

Section A
(Answer in two or three sentences)

Short answer questions

1. What is materials science?
2. What are the different branches of science involved in materials science?
3. What is the aim of study of materials science?
4. How does the study of materials science important?
5. Define the terms a) structure and b) properties of materials.

6. Draw a schematic diagram of the interrelationship between the four components of the discipline of materials science.

7. Which are the four components of the discipline of materials science?

8. Mention the three classifications of materials science.

9. What are composites materials?

10. What are metals?

11. What are ceramics?

12. What are polymers?

13. Give three examples for metals.

14. Give three examples for ceramic materials.

15. Give the names of any three polymeric materials.

16. What is a carbon fibre reinforced polymer (CFRP)?

17. What is the advantage of CFRP over glass fibre reinforced materials?

18. What are advanced materials?

19. What are biomaterials?

20. What are smart materials?

21. Define

    (a) sensor (b) actuators in smart materials.

22. Mention the two approaches scientists usually adopt to understand the structure of materials.

Section B
(Answer questions in a paragraph of about half a page to one page)

Paragraph / Problem type

1. Materials play an important role in our everyday lives. Justify.

2. Distinguish between the three forms of structures of materials.

3. Why do we study materials science?

4. Write down the properties of metals.

5. What are the properties of ceramics?

6. What are the properties of polymers?

7. Distinguish between metals, ceramics and polymers.

8. Write a brief note on advanced materials.

9. Give brief account of biomaterials.

10. Discuss briefly the components of smart materials.

11. Which are the four types of materials that are used for actuators?

12. Give a brief account of nanoengineered materials.

13. Explain the "bottom up" and bottom up approaches scientists usually adopt to understand the structure of the materials.

Section C
(Answer in about two pages)

Long answer type questions (Essays)

1. Classify materials and discuss their properties.

2. Discuss in detail about the materials of the future.

3. Give an account of nano engineered materials.

CHAPTER 2

BONDS IN MATERIALS

Atomic bonding in solids

2.1 Bonding forces and energies

On the basis of the knowledge of the inter atomic forces that bind the atoms together, many of the physical properties of materials can be predicted. The principles of atomic bonding can be well understood by considering the interaction between two isolated atoms as they are brought into close proximity from an infinite separation. At large distances the interactions are negligible. But as the atoms approach, each exert forces on the other. These forces are of two types, attractive and repulsive and the magnitude of these forces is a function of interatomic distance. The attractive force $\vec{F}_A$ depends on the type of bonding that exists between the atoms. The magnitude of the attractive force varies with distance as shown in figure 2.1(a) when the outer electron shells of the two atoms begin to overlap, a strong repulsive force. $\vec{F}_R$ comes into play. The net force $\vec{F}_N$ between the atoms is thus becomes the sum of both attractive and repulsive forces; that is

$$\vec{F}_N = \vec{F}_A + \vec{F}_R \qquad \qquad \text{..... (1)}$$

When $\vec{F}_A$ and $\vec{F}_R$ are equal and opposite the net force is zero;

that is
$$\vec{F}_A + \vec{F}_R = 0 \qquad \qquad \text{..... (2)}$$

In this context the atoms are said to be in equilibrium state. In this situation the atoms are separated by an equilibrium distance r_0 shown in figure 2.1(b).
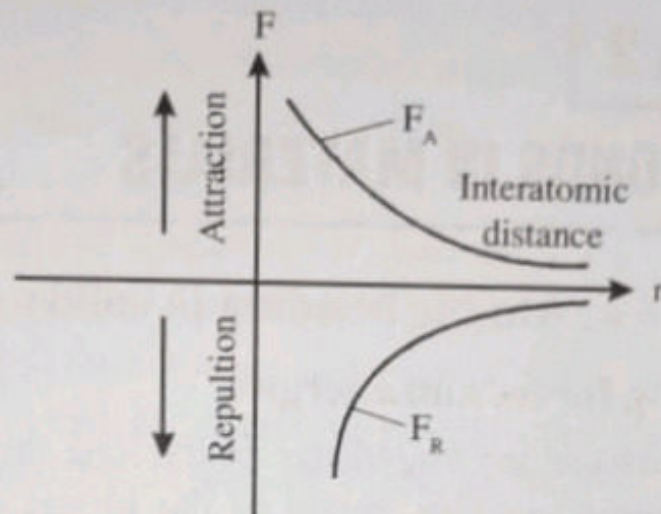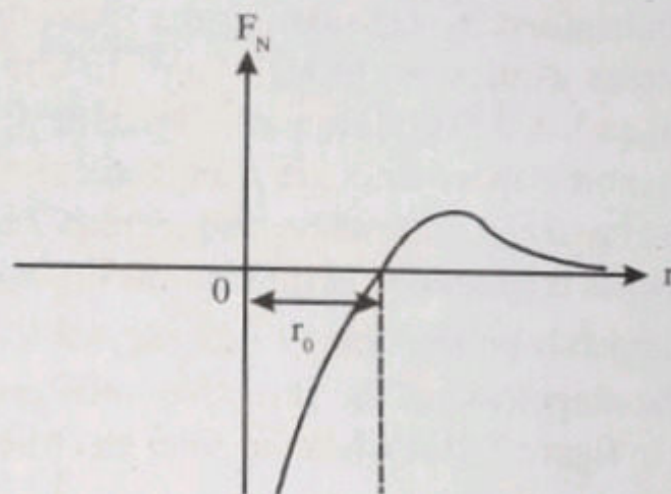
Figure 2.1(a)

Figure 2.1(b)

For many atoms r_0 is approximately 0.3nm. Sometimes it is more convenient to work with potential energies (U) between two atoms rather than forces. Mathematically U(r) and F(r) are related by

$$U(r) = \int F(r)\,dr \qquad \ldots\ldots (3)$$

For atomic systems

$$U_N(r) = \int_\infty^r F_N(r)\,dr \qquad \ldots\ldots (4)$$

Substituting for F_N from equation 1.1, we get

$$U_N(r) = \int_\infty^r F_A \, dr + \int_\infty^r F_R \, dr$$

$$U_N(r) = U_A(r) + U_R(r) \qquad \qquad \dots (5)$$

Where $U_N(r), U_A(r)$ and $U_R(r)$ the net potential energy, attractive potential energy and repulsive potential energy respectively.

The variation of all U(r) with interatomic distance is shown in figure 2.1(c) and 2.1(d).
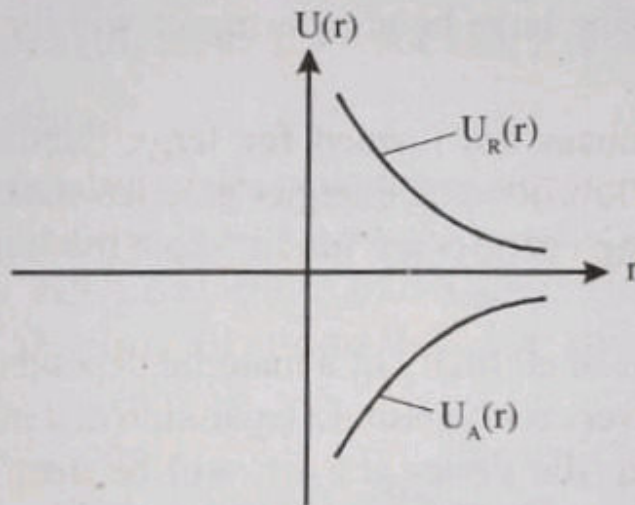
Figure 2.1(c)
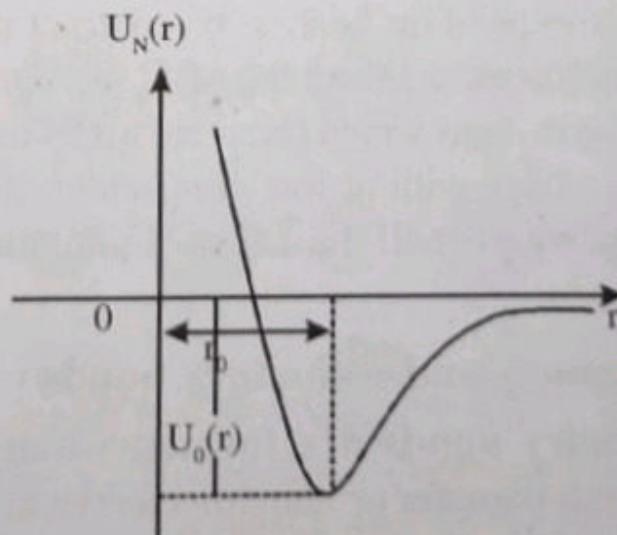
Figure 2.1(d)

Here again r_0 is the equilibrium separation where potential energy is minimum. The potential energy corresponding to this equilibrium position $U_0(r)$ is called bonding energy. **This is the energy needed to separate atoms to an infinite separation.**

Although we discussed an ideal situation involving only two atoms, we get almost the same shape of curve (both) if we repeat it for real materials formed by large number of atoms and so many interactions present. The bonding energy E_0 varies from material to materials. Some of the materials (properties gathered from the shape of the curve and bonding energy is given below.

1. Material having large bonding energies will have high melting points.

2. Solid substances are formed for large bonding energies, whereas for low bonding energies gaseous states are formed. If the bonding energies are intermediate the liquid states are formed.

3. The modulus of elasticity of a material depends on the shape of the force versus interatomic separation distance graph. For stiff materials the slopes at $r = r_0$ will be steep. For flexible materials the slopes at $r = r_0$ are shallower.

4. The coefficient of linear expansions (how much the material will expand on heating or contract on cooling) of materials are related to the shape of U_0 verses r_0 curve. A narrow and deep troughs which occur for high bonding energies, normally correlates with at low coefficient of thermal expansion and relatively small dimensional alterations for changes in temperature.

2.2 Primary and secondary bonds

Primary bonds are formed when the bonding process involves a transfer or sharing electrons between atoms to form a more stable electron configuration.

There are three different types of primary bonds found in solids. They are (i) ionic bonding (ii) covalent bonding and (iii) metallic bonding.

Secondary bonds are from the subtle attraction forces between positive and negative charges. There is no transfer or sharing of electrons involved in secondary bonds. They are usually formed when an uneven charge distribution occurs, creating what is known as a dipole. The total charge is zero, but there is slightly more positive or negative on one end of the atom than on the other. There are three types of secondary bonding arising from different interactions. They are (i) dipole interactions (ii) hydrogen bonding interactions and (iii) molecule - molecule interactions.

Ioning bonding

Ionic bonding is found in compounds composed of both metallic and non-metallic elements. Atoms of a metallic element can easily give up their valence electrons to the non-metallic atoms. In the process of sharing all atoms acquire stable or inert gas configurations, in addition each one becomes ions. Sodium chloride is an example of ionic material. A sodium atom gives out its one valence electron to chlorine atom. As a result sodium acquires a positive charge and chlorine acquires a negative charge. In sodium chloride, sodium and
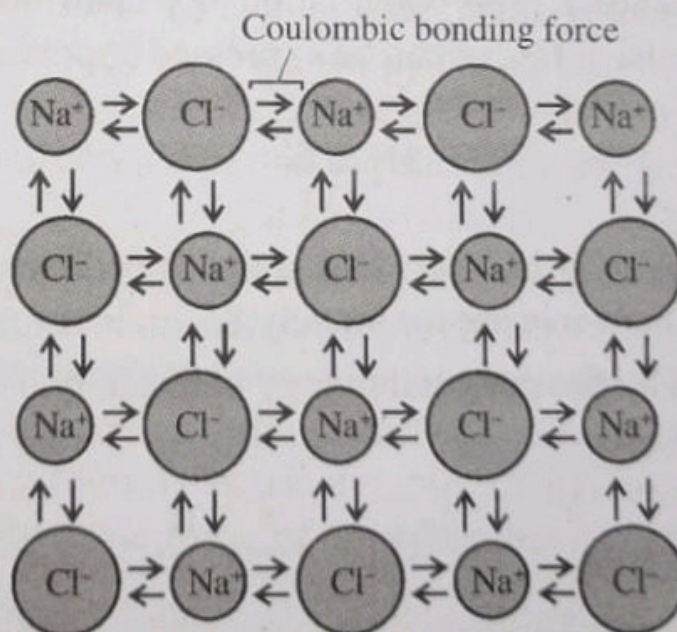

Coulombic bonding force

Figure 2.2: Schematic representation of ionic bonding in sodium chloride (NaCl)

chlorine exist as ions. This bonding (ionic) illustrate schematic
in figure 2.2.

The attractive forces between different ions are Columbic
nature. For two isolated ions the attractive energy U_A is a functi
of the interatomic distance given by

$$U_A = \frac{(Ze)(-Ze)}{4\pi\varepsilon_0 r} = -\frac{Z^2 e^2}{4\pi\varepsilon_0 r}$$

or
$$U_A = -\frac{A}{r}$$
..... (

where
$$A = \frac{Z^2 e^2}{4\pi\varepsilon_0}$$

Two ions cannot continuously approach each other unde
Coulomb attraction on account of exclusion principle. When the
are at a certain small distance apart, they begin to repel each othe
with a force which increases rapidly with decreasing interatomi
distance r. The potential energy contribution of the short range
repulsive forces can be expressed approximately by

$$U_R = \frac{B}{r^n}$$
..... (7

Here B is a constant and n is called repulsive exponent. The
value of n is approximately 8.

The net potential energy between two adjacent atoms is given
by

$$U_N = -\frac{A}{r} + \frac{B}{r^n}$$
..... (8)

From this we can evaluate the bonding energy U_0 using the
following procedure.

1. Differentiate U_N with respect to r and then set the resulting expression equal to zero. Which gives the equilibrium position $r = r_0$.

2. Put this value $r = r_0$ in equation 1.8 to get U_0.

Bonding energies which generally range between 600 and 1500kJ/mol or 3 and 8eV/atom.

Other examples of ionic crystals are $MgCl_2$, MgO, $CsCl_2$, KI and KO.

Properties of ionic solids

1. All ionic solids have high melting points and boiling points. This is because more energy is needed to make the ions mobile, there being a necessity to overcome the strong electrostatic force of attraction created due to the ionic bond. This explains why ionic materials have high melting and boiling points.

2. Pure and dry ionic materials are insulators, because of the non-availability of free electrons. However in solution they conduct electricity because of the movement of charged ions. In a solution the ionic bond is weakened by the solvent molecules. Thus the ions become free to move about and there by become conductors of electricity and the solutions are good electrolytes.

3. Ionic solids are easily soluble in polar solvent like water. This is because the molecules of the polar solvent interact strongly with the ions so as to reduce the attraction between the ions. Also the polar solvents possess high dielectric constants, for example, water has a high dielectric constant of 81. i.e., it will reduce the electrostatic force of attraction between the ions to $\dfrac{1}{81}$ of the original value.

Ionic materials are insoluble in non-polar solvents benzene (C_6H_6), carbon tetrachloride (CCl_4), because their dielectric constants are very low.

4. High hardness and low conductivity are typical properties of these solids.

5. When subjected to stresses, ionic crystals tend to break along certain planes of atoms rather than to deform in a ductile fashion as metals do.

6. The magnitude of the ionic bonding is equal in all directions around an ion, hence it is termed non-directional.

Covalent bonding

The covalent bond is formed by sharing of pairs of valence electrons between like atoms rather than by electron transfer.

A simple example of covalent bonding is found in the chlorine molecule. Here the outer shell of each chlorine atom possesses seven electrons. Each chlorine atom would like to receive and electron and thus form a stable octet. This can be done by sharing of two electrons between pairs of chlorine atoms, there by producing stable diatomic molecules. In other words, each atom contributes one electron for the sharing process. See figure 2.3.

(a)   Two isolated atoms

(b)   Overlap

(c)   The molecular orbital
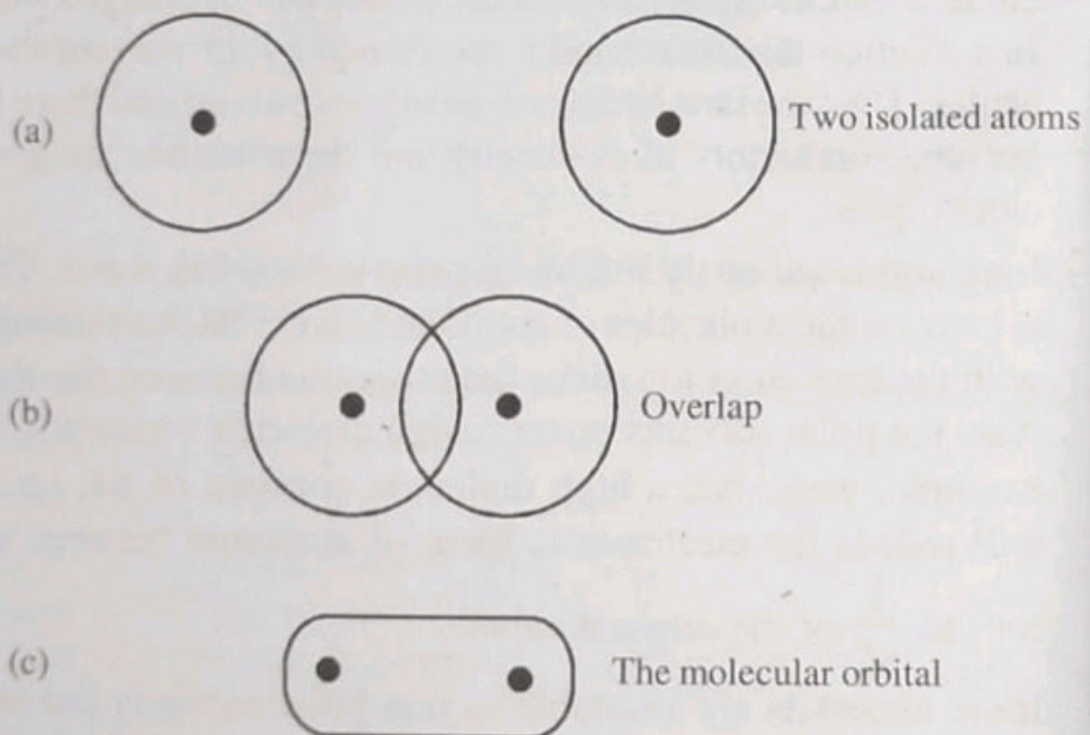
Figure 2.3: Molecular orbital from orbitals

Covalent bonding is schematically illustrated in figure 2.4. The carbon atom has four valence electrons, whereas each of four hydrogen atom has single valence electron. Each hydrogen atom can acquire a helium electron configuration (two is valence electrons) when the carbon atom shares with it one electron. The carbon atom now has four additional shared electrons one from each hydrogen, for a total of eight valence electrons, which is the electron structure of neon. The covalent bond is directional; that is it is between specific atoms and may exist only in the direction between one atom and another that participates in the electron sharing.

Shared electron from hydrogen — Shared electron from carbon
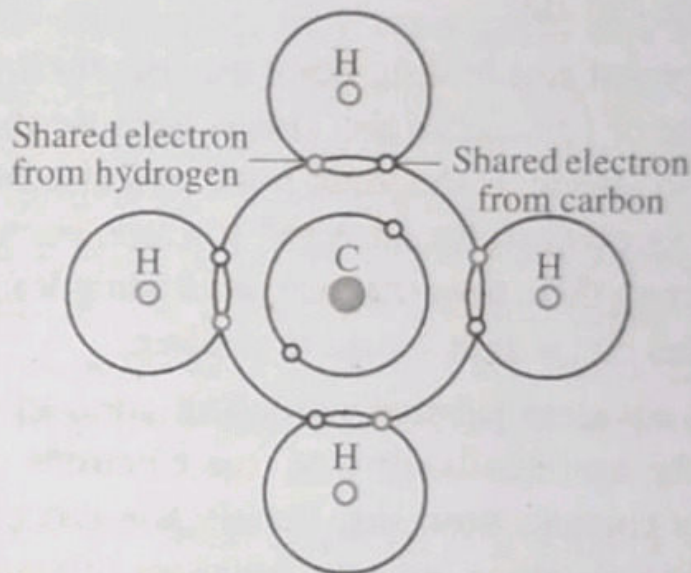
Figure 2.4:   Schematic representation of covalent
bonding in a molecule of methane (CH_4)

Many non metallic element molecules (H_2, Cl_2, F_2 etc.) as well as molecules containing dissimilar atoms such as CH_4, H_2O, HNO_3 and HF are covalently bonded. Further more, this type of bonding is found in solids such as diamond (carbon), silicon and germanium and other solid compounds such as gallium arsenide (GaAs), indium antimonite (InSb) and silicon carbide (SiC).

The number of covalent bonds that is possible for a particular atom is determined by the number of valence electrons. For N' valence electrons, an atom can covalently bond with at most $8 - N'$

other atoms. For example, $N' = 7$ for chlorine and $8 - 7 = 1$, which means that one Cl atom can bond to only one other atom as in Cl similarly for carbon, $N = 4$ and each carbon atom has $8 - 4 = 4$ electrons to share.

Properties of covalent

1. Covalent crystals tend to be hard and brittle and incapable of appreciable bending. These facts are understandable in terms of the underlying atomic forces. Since the bonds have well defined directions in space, attempts to alter them are strongly resisted by the crystal.

2. The melting point and boiling point are usually low as compared to those of ionic crystals. This is because the covalent bond is not so strong as the ionic bond and also because the atoms are less powerfully attracted towards each other the forces that attract them towards each other being Vander Waals forces, dipoles etc. which are quite weaker.

3. Most of the covalent substances do not conduct electricity because of the non-availability of free electrons or charged ions to carry current. however, certain substances like HCl which exhibit polarity in aqueous solutions behave like ionic substances and allow the passage of electricity.

4. Covalent substances are insoluble in polar solvents like water. However they are soluble in non polar solvents like benzene, carbon disulphide etc. This is because of the covalent nature of the solvent. However, the giant molecules are not soluble in any solvent because of the large size of the molecules.

5. A very interesting property of covalent crystals is the apparent lack of sensitivity of their physical properties to their bonding type. For example, carbon in the diamond structure is the hardest substance and has a very high melting point of

>3350°C. The hardness and melting point then decrease as we proceed to other elements from silicon to lead. Bismuth, for example, melts at about 270°C. The variation in the electrical properties is also pronounced. Diamond is a very good insulator. Silicon and germanium are semiconductors while tin is a good conductor and having low melting point and is very soft. Depending on the number of electrons shared, the bond length and bond energy vary. When the number of electrons shared is more, the bond length between the atoms is decreased and bond energy is increased.

6.   Covent compounds are mostly gases and liquids.

It is possible to have interatomic bonds that are partially ionic and partially covalent. In fact there are only very few compounds exhibit pure ionic of covalent bonding. For a compound, the degree of either bond type depends on the difference in their electro negativities. i.e., the greater the electron negativity, the more the ionic bond. Conversely, the closer the atoms are together it has smaller difference in electronegativity. The greater the degree of covalency.

The percentage ionic character of a bond between elements A and B (A being the most electronegative) may be approximated by the expression.

Percentage ionic character $= [1 - e^{-0.25(X_A - X_B)^2}] \times 100$ where X_A and X_B are the electronegativities for the elements A and B respectively.
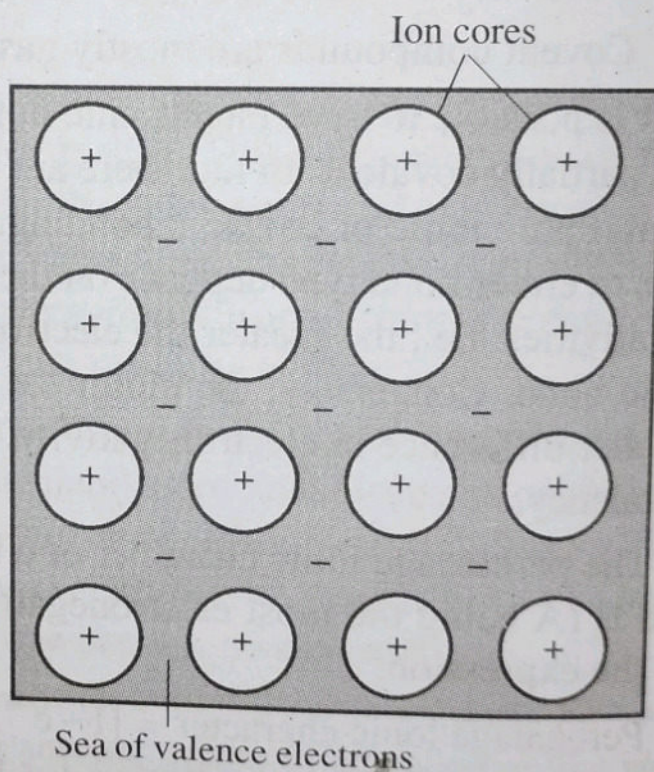
Note

Electron negativity is the ability for an atom of a given chemical element to attract shared electrons in a covalent bond. An atoms electronegativity is affected by both its atomic number and the distance at which valence electrons reside from the charged nucleus. The higher the value of electronegativity, the more strongly that elements attracts the shared electrons.

Metallic bonding

Metallic bonding is found in metals and their alloys. In some respect, the metallic bond is similar to the covalent bond. A relatively simple model has been proposed that very nearly approximates the bonding scheme. Metallic materials that have one, two or at most three valence electrons. With this model, these valence electrons are not bound to any particular atom in the solid and are more or less free to drift throughout entire metal. They may be thought of as belonging to the metal as a whole or forming a "sea of electrons" or an electron cloud. The remaining non valence electrons and atomic nuclei form what are called ion cores, which possess a net positive charge equal in magnitude to the total valence electron charge per atom. A schematic illustration of metallic bonding is depicted in figure 2.5. The free electrons shield the positively charged ion cores from mutually repulsive electrostatic forces, which they would otherwise exert upon one another, consequently the metallic bond is unidirectional in character. In addition the free electrons act as a "glue" to hold their on cores together.

Figure 2.5: Schematic illustration of metallic bonding

Properties of metallic bonding

(i)   The bonding may be weak or strong. Bonding energies range from 68kJ/mol (0.7eV/atom) for mercury to 850kJ/mol (8.8eV/atom) for tungsten.

(ii) Owing to the symmetrical arrangements of the positive ions in space lattice, metals are crystalline.

(iii) The melting temperatures are −39°C to 3410°C for mercury and tungsten respectively.

(iv) Since a large number of free electrons are available, metallic crystals have high electrical conductivity.

(v)   Metallic crystals have higher thermal conductivity because of large number of free electrons.

(vi) Metals are opaque to light since the light energy is absorbed by free electrons. Copper, sodium, silver and aluminium are some examples of metallic crystals.

2.3 Secondary bonding or Vander Waals bonding

Secondary bonds are weak in comparison to the primary bonds. The bonding energies are typically on the order of only 10kJ/mol (0.1eV/atom). Secondary bonding exists between virtually all atoms or molecules, but its presence may be obscurred if any of the three primary bonding types is present. Secondary bonds do not generally involve the valence electrons. Secondary bonding is evidenced for the inert gases, which have stable electron structures and in addition between molecules in molecular structures that are covalently bonded.

Secondary bonding forces arise from atomic or molecular dipoles. In essence an electric dipole exists whenever there is some separation of positive or negative portions of an atom or molecule. The bonding results from the Columbic attraction between the positive end of one dipole and the negative region of an adjacent ones as indicated in figure 2.6.
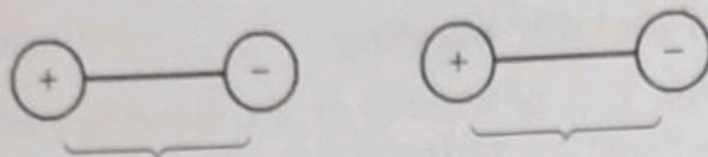
Figure 2.6: Schematic illustration of Vander Waals
bonding between two dipoles

Dipole interactions occur in three ways:

(i)   Interactions between induced dipoles.

(ii) Interactions between induced dipoles and polar molecules.

(iii) Interactions between some molecules that have hydrogen as one of the constituents. It is a special type of secondary bonding called hydrogen bonding. We discuss these one by one.

2.4 Fluctuating induced dipole bonds

A dipole may be created or induced in an atom or molecule that is normally electrically symmetric; that is, the overall special distribution of the electrons in symmetric with respect to the positively charged nucleus as shown in figure 2.7(a). All atoms are experiencing constant vibrational motion that can cause instantaneous and short lived distortions of this electrical symmetry for some of the atoms or molecules and the creation of small electric dipoles as shown figure 2.7(b). One of the dipoles can in turn produce a displacement of the electron distribution of an adjacent molecule or atoms which induces the second one also to become a dipole that is then weakly attracted or bonded to the first; this is one type of Vander Waals bonding. These attractive forces may exist between large numbers of atoms or molecules, which force are temporary and fluctuate with time.

The liquitation and in some cases the solidification of the inert gases and other electrically neutral and symmetrical molecules such as H_2 and Cl_2 are realised because of this type of bonding. Melting and boiling temperatures are extreme low in materials for which

induced dipole bonding predominates; of all possible intermolecu-
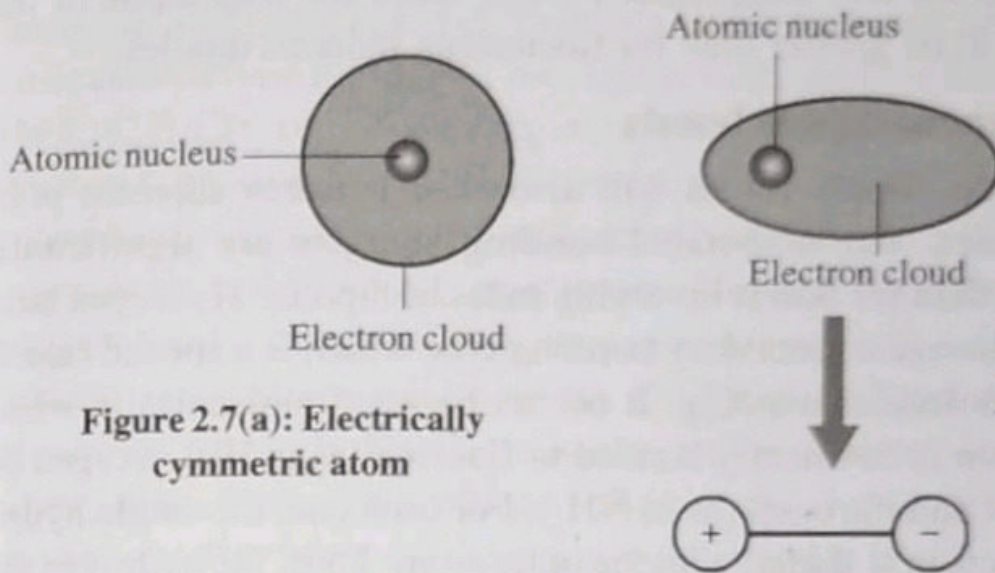lar bonds, these are the weakest.

**Figure 2.7(a): Electrically
cymmetric atom**

Figure 2.7(b): An induced atomic dipole

Polar molecule - Induced dipole bonds

Permanent dipole moments exist in some molecules by virtue
of its unsymmetrical ar-
rangement of positively
and negatively regions.
Such molecules are
termed polar molecules.
Figure 2.8 is a schematic
representation of a hydro-
gen chloride. It possesses
a permanent dipole due to
the separation of net posi-
tive and negative charges
of hydrogen and chlorine
atoms forming HCl.
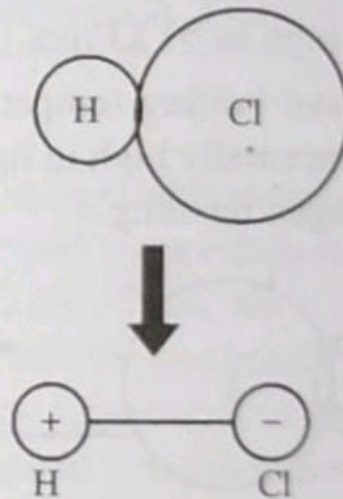
**Figure 2.8 : Schematic representation
of a polar hydrochloride (HCl)**

Polar molecules can also induce dipoles in adjacent non pola molecules and a bond will form as a result of attractive force between the two molecules. Further more the magnitude of the bond will be greater than for fluctuating induced dipoles.

Permanent dipole bonds

Vander Waals forces will also exist between adjacent pola molecules. The associated bonding energies are significantl greater than for bonds involving induced dipoles. Hydrogen bon is the strongest secondary bonding type which is a special case o polar molecular bonding. It occurs between molecules in whic hydrogen is covalently bonded to fluorine (as in HF), oxygen (a in H_2O) and nitrogen (as in NH_3). For each one, the single hydro gen electron is shared with the other atom. Thus, the hydrogen en of the bond is essentially a positively charged bare proton that i unscreened by any electrons. This highly positively charged en of the molecule is capable of a strong attractive force with th negative end of an adjacent molecule as demonstrated in figur 2.9 for HF. In essence, this single proton forms a bridge betwee two negatively charged atoms. The magnitude of hydrogen bon is generally greater than that of other types of secondary bond and may be high as 51 kJ/mol (0.52 eV/molecule).

Melting and boiling temperatures for hydrogen fluoride an water are abnormally high in light of their low molecular weight due to hydrogen bonding.
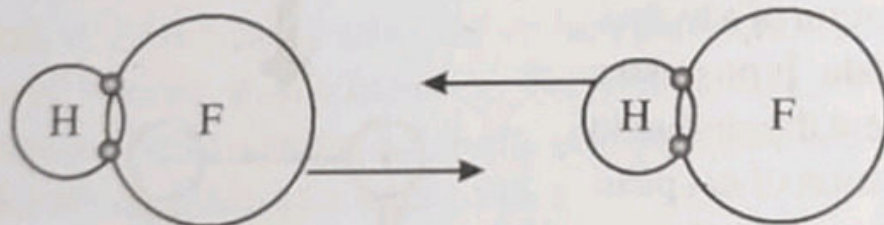

Figure 2.9: Schematic representation of hydrogen bonding in hydrogen fluoride (HF)

Molecules

Many of the common nmolecules are composed of group of atoms that are bound together by strong covalent bonds. Diatomic molecules such as F_2, O_2, H_2, etc. compounds such as H_2O, CO_2, HNO_3, $C_6H_6CH_4$ etc. have strong covalent bonds. In the condensed liquid and solid states, bonds between molecules are weak secondary bonds. Consequently, molecular materials have relatively low melting and boiling temperatures. Most of those that have small molecules composed of a few atoms are gases at ordinary or ambient temperatures and pressures. On the other hand, many of the modern polymers, being molecular materials composed of extremely large molecules, exist as solids; some of their properties are strongly dependent on the presence of Vander Waals and hydrogen secondary bonds.

Anomalous volume expansion of water

Most of the liquids freeze to solids, the solid substances experience an increase in density, correspondingly there is a decrease in volume. One exception is water. Water upon freezing shows an anomalous behaviour of expansion. This expansion is approximately 9%. This behaviour may be explained on the basis of hydrogen bonding.

Explanation

Each H_2O molecule has two hydrogen atoms that can bond to oxygen atoms; further more its oxygen atom can bond to two hydrogen atoms of other H_2O molecules. Thus, for solid ice, each water molecule participates in four hydrogen bonds as shown in the three dimensional schematic of figure 2.10. Here hydrogen bonds are bonds are denoted by dashed lines and each water molecule has 4 nearest neighbour molecules. This structure is relatively open. i.e., the molecules are not closely packed together and as a result density is comparatively low. Upon melting this structure is partially destroyed, such that water molecules become more

closely packed together at room temperature the average number of nearest neighbour water has increased from 4 to 4.5. This leads to an increase in density or decrease in volume.
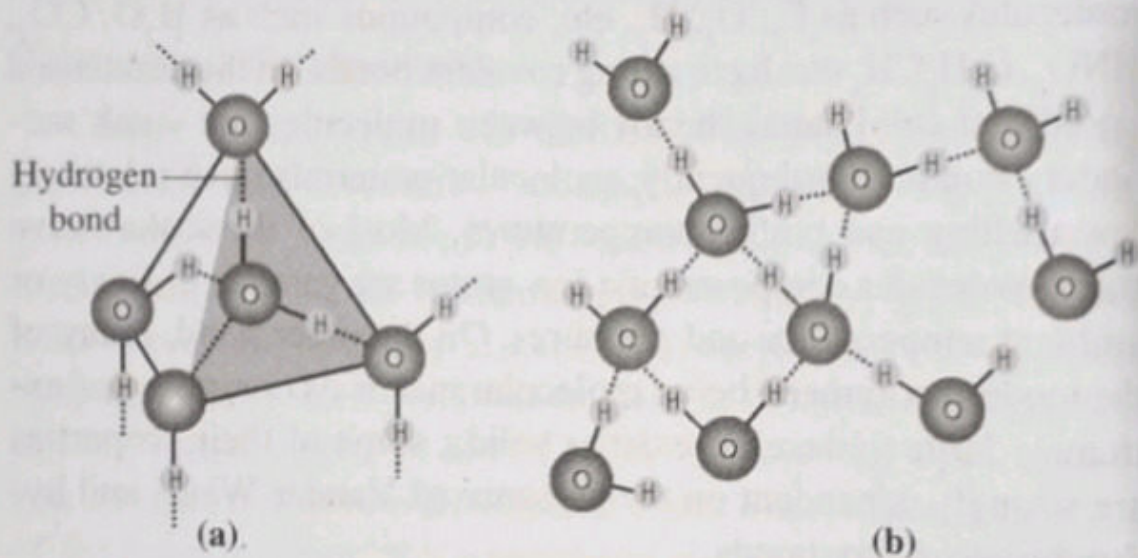
Figure 2.10: The arrangement of water (H_2O) molecules in (a) solid ice and (b) liquid water

Anomalous expansion of water on freezing explains several natural occurring such as

(i) Why ice bergs float; because of density decrease.

(ii) Why in cold countries it is necessary to add antifreeze to an automobiles cooling system. It is due to the expansion, cracking may occur.

(iii) Why freeze thaw cycles break up the pavement streets and cause potholes to form.

Example 1

The net potential energy between two adjacent ions U_N is given by

$$U_N = -\frac{A}{r} + \frac{B}{r^n}$$

Calculate the bonding energy U_0.

Solution

$$U_0 = (U_N)_{r=r_0}$$

$r = r_0$ is the equilibrium spacing.

We have

$$U_N = -\frac{A}{r} + \frac{B}{r^n} \qquad \cdots\cdots (1)$$

Differentiate U_N with respect to r, we get

$$\frac{dU_N}{dr} = \frac{A}{r^2} - \frac{nB}{r^{n+1}}$$

At equilibrium, $\dfrac{dU_N}{dr} = 0$ at $r = r_0$

$$0 = \frac{A}{r_0^2} - \frac{nB}{r_0^{n+1}}$$

$$\frac{A}{r_0^2} = \frac{nB}{r_0^{n+1}}$$

$$A = \frac{nB}{r_0^{n-1}}$$

$$r_0^{n-1} = \frac{nB}{A}$$

$$\therefore \qquad r_0 = \left(\frac{nB}{A}\right)^{\frac{1}{n-1}}$$

Put this in eq (1), we get

$$U_0 = -\frac{A}{\left(\dfrac{n\,B}{A}\right)^{\frac{1}{n-1}}} + \frac{B}{\left(\dfrac{n\,B}{A}\right)^{\frac{n}{n-1}}}$$

or

$$U_0 = -\frac{A}{\left(\dfrac{A}{n\,B}\right)^{\frac{1}{1-n}}} + \frac{B}{\left(\dfrac{A}{n\,B}\right)^{\frac{n}{1-n}}}$$

Example 2

The interaction energy of two particles in the field of each other is given by $U(r) = -\dfrac{a}{r} + \dfrac{b}{r^9}$, where a and be are constants.

a) Show that the particles form a stable compound for

$$r = r_0 = \left(\frac{9b}{a}\right)^{1/8}$$

b) Show that in the stable configuration the energy of attraction is 9 times the energy of repulsion.

c) Show that the potential energy of the two particles in stable configuration is $\dfrac{8}{9}\dfrac{a}{r_0}$.

Solution

$$U(r) = -\frac{a}{r} + \frac{b}{r^9} \qquad\qquad \dots (1)$$

Differentiate with respect to r, we get

$$\frac{dU(r)}{dr} = \frac{a}{r^2} - \frac{9b}{r^{10}} \qquad\qquad \dots (2)$$

a) At equilibrium $r = r_0$

$$\frac{dU(r)}{dr} = 0$$

$$0 = \frac{a}{r_0^2} - \frac{9b}{r_0^{10}}$$

$$\frac{a}{r_0^2} = \frac{9b}{r_0^{10}}$$

$$r_0^8 = 9\frac{b}{a}$$

$$r_0 = \left(\frac{9b}{a}\right)^{\frac{1}{8}}$$

b) At stable equilibrium $r = r_0$, $\dfrac{d^2U(r)}{dr^2}$ must be greater than zero.

Differentiate eq (2) with respect to r again, we get

$$\frac{d^2U(r)}{dr^2} = -\frac{2a}{r^3} + \frac{90b}{r^{11}}$$

at $r = r_0$

$$\frac{d^2U(r)}{dr^2}\bigg|_{r=r_0} = -\frac{2a}{r_0^3} + \frac{90b}{r_0^{11}}$$

Substituting for r_0, we obtain

$$\left.\frac{d^2U(r)}{dr^2}\right|_{r=r_0} = -\frac{2a}{\left(\dfrac{9b}{a}\right)^{3/8}} + \frac{90b}{\left(\dfrac{9b}{a}\right)^{\frac{11}{8}}}$$

$$= -\frac{2}{9^{3/8}}\frac{a^{11/8}}{b^{3/8}} + \frac{90}{(90)^{11/8}}\frac{a^{11/8}}{b^{3/8}}$$

$$= \frac{a^{11/8}}{b^{3/8}}\left(\frac{90}{(a)^{11/8}} - \frac{2}{9^{3/8}}\right)$$

$$= \frac{a^{11/8}}{b^{3/8}}\left(\frac{90}{3^{11/4}} - \frac{2}{3^{3/4}}\right)$$

$$= \frac{a^{11/8}}{b^{3/8}}\left(\frac{90}{20.5} - \frac{2}{2.27}\right)$$

$$> 0.$$

Energy of attraction at $r = r_0$ is

$$\left.U_a\right|_{r=r_0} = \frac{a}{r_0} = \frac{a}{\left(\dfrac{9b}{a}\right)^{1/8}}$$

$$\left.U_a\right|_{r=r_0} = \frac{a^{9/8}}{(9b)^{1/8}} \qquad\qquad \dots\dots (3)$$

Energy of repulsion at $r = r_0$

$$U_b \Big|_{r=r_0} = \frac{b}{r_0^9} = \frac{b}{\left[\left(\dfrac{9b}{a}\right)^{\frac{9}{8}}\right]}$$

$$U_b \Big|_{r=r_0} = \frac{a^{9/8}}{9^{9/8} b^{1/8}} \qquad\qquad ..... (4)$$

$\dfrac{Eq\,3}{Eq\,4}$ gives

$$\frac{U_a \Big|_{r=r_0}}{U_b \Big|_{r=r_0}} = \frac{9^{9/8}}{9^{1/8}} = 9$$

i.e., $\quad U_a \Big|_{r=r_0} = 9 U_b \Big|_{r=r_0}$.

c) $\quad U_0(r) = U(r)\Big|_{r=r_0} = -\dfrac{a}{r_0} + \dfrac{b}{r_0^9}$

$$U_0(r) = -\frac{a}{r_0}\left(1 - \frac{b}{a\,r_0^8}\right)$$

Substituting for r_0

$$U_0(r) = -\frac{a}{r_0}\left[1 - \frac{b}{a\left(\dfrac{9b}{a}\right)}\right]$$

$$U_0(r) = -\frac{8}{9}\frac{a}{r_0}$$

Example 3

The net potential energy U_N between two adjacent ions is sometimes represented by the equation

$$U_N = -\frac{C}{r} + De^{\frac{-r}{\rho}}$$

Where r is the interionic separation and C, D and ρ are constants whose values depend on the specific material.

Derive an expression for the bonding energy U_0 in terms of the interionic separation r_0 and the constants D and ρ.

Solution

We have

$$U_N = -\frac{C}{r} + De^{\frac{-r}{\rho}} \qquad \qquad ..... (1)$$

To find the equilibrium separation differentiate eq (1) and set equal to zero at $r = r_0$.

$$\frac{dU}{dr} = \frac{C}{r^2} - \frac{D}{\rho}e^{\frac{-r}{\rho}}$$

At $r = r_0$, $\frac{dU}{dr} = 0$ we get

$$0 = \frac{C}{r_0} - \frac{D}{\rho}e^{\frac{-r_0}{\rho}}$$

$$\frac{C}{r_0} = \frac{D}{\rho} e^{\frac{-r_0}{\rho}}$$

$$\therefore \quad C = \frac{D}{\rho} r_0 \, e^{\frac{-r_0}{\rho}}$$

The bonding energy

$$U_0 = U_N \Big|_{r=r_0}$$

$$U_0 = -\frac{C}{r_0} + De^{\frac{-r_0}{\rho}}$$

Substituting for C, we get

$$U_0 = -\frac{D}{\rho} \frac{r_0 e^{\frac{-r_0}{\rho}}}{r_0} + De^{\frac{-r_0}{\rho}}$$

$$U_0 = De^{\frac{-r_0}{\rho}} \left(1 - \frac{1}{\rho} \right)$$

Example 4

Compute the percentage ionic character of the interatomic bond for the compound MgO. The electronegatives of Mg and O are 1.2 and 3.5 respectively.

Solution

The percentage ionic character is given by

$$\% \text{ ionic charactor} = \left[1 - e^{-0.25(X_A - X_B)^2} \right] \times 100$$

Here $X_{Mg} = 1.2$ and $X_O = 3.5$

∴ % ionic character

$$= \left[1 - e^{-0.25(1.2 - 3.5)^2} \right] \times 100$$

$$= [1 - e^{-0.25 \times 5.29}] \times 100$$

$$= (1 - e^{-1.3225}) \times 100$$

$$= (1 - 0.266) \times 100$$

$$= 73.4\%.$$

It shows that MgO has 73.4% of ionic character and 26.6% of covalent character.

Example 5

Calculate the percentage covalent character of GaP. The electronegativities of Ga and P are 1.6 and 2.1 respectively.

Solution

We have

$$\% \text{ ionic character} = \left[1 - e^{-0.25 \times (X_A - X_B)^2} \right] \times 100$$

Here $X_{Ga} = 1.6$ and $X_P = 2.1$

$$(X_{Ga} - X_P)^2 = (1.6 - 2.1)^2 = (-0.5)^2 = 0.25$$

∴ % ionic character
$$= [1 - e^{-0.25 \times 0.25}] \times 100$$

$$= [1 - e^{-0.0625}] \times 100$$

$$= (1 - 0.9394) \times 100$$

$$= 0.0606) \times 100$$

$$= 6.06\%.$$

It means that GaP has 6.1% of ionic character hence the remaining $100 - 6.6 = 93.94\%$ of covalent character.

UNIVERSITY MODEL QUESTIONS

Section A
(Answer in two or three sentences)

Short answer questions

1. How do we study the physical properties of materials?
2. What are the two types of interatomic forces?
3. Draw the graphical variation of interatomic forces with interatomic separation.
4. Give a schematic representation of the variation of net potential energy with interatomic distance.
5. What is meant by bonding energy?
6. Define (a) primary bonds and (b) secondary bonds.
7. Which are the three different types of primary bonding?
8. Which are the three different types of secondary bonding?
9. Write down an expression for the net potential energy between two adjacent atoms.
10. Give a schematic representation of ionic bonding in sodium chloride crystal.
11. What is covalent bonding?
12. Give a schematic representation of covalent bonding in a molecule of methane.
13. Most of the covalent substances do not conduct electricity. Why?
14. What is the relation between ionic bonding and the electronegativities of the elements forming the compound?
15. What happens to the degree of covalency when the difference in electronegativity increases?
16. Define the term "electronegativity".
17. What is metallic bonding?
18. Give a schematic illustration of metallic bonding.
19. What is the origin of Vander Waals bonding?
20. Give the three types of dipole interactions in secondary bonding.

21. What is hydrogen bonding?

22. Give a schematic representation of hydrogen bonding in hydro fluoride.

23. What is meant by anomalous volume expansion of water?

24. Give three natural happenings that occur due to anomalous expansion of water.

Section B
(Answer questions in a paragraph of about half a page to one page)

Paragraph / Problem type

1. What are the informations that we can gather from the potent energy curve?

2. Distinguish between primary and secondary bonds.

3. What is an ioning bonding?

4. How do we calculate the bonding energy from the net potent energy between two adjacent atoms?

5. What are the properties of ionic solids?

6. Explain the covalent bonding of CH_4.

7. How do we calculate the number of covalent bonds that is possib for a particular atom?

8. What are the properties exhibited by covalent compounds?

9. Distinguish between ionic and covalent bondings.

10. What are the properties exhibited by metallic compounds?

11. Discuss briefly about polar molecule - induced dipole bonds.

12. Briefly explain about the permanent dipole bonds.

13. Explain the anomalous expansion of water on the basis of hydrog bonding.

14. For an $Na^+ - Cl^-$ ion pair attractive and repulsive energies are giv by

$$U_A = -\frac{1.436}{r}$$

$$U_R = \frac{7.32 \times 10^{-6}}{r^8}$$

Calculate the bonding energy between the two ions.   [−5.324]

15. Show that the potential energy of two particles in the stable configuration is equal to $\frac{-4a}{5r_0^2}$ for the net potential energy

$$U_N = \frac{-a}{r^2} + \frac{b}{r^{10}} .$$

16. The potential energy of a diatomic molecule is given in terms of the interatomic distance r by the expression

$$U(r) = \frac{-a}{r^2} + \frac{b}{r^{10}}$$

Calculate the dissociation energy. $a = 1.44 \times 10^{-39}$ Jm^2 and $b = 2.19 \times 10^{-115}$ Jm^{10}.

17. Assume that the energy of two particles in the field of each other is given by the expression

$$U(r) = -\frac{a}{r} + \frac{b}{r^8} .$$

a) Show that the two particles form a stable compound for

$$r = r_0 = \left(\frac{8b}{a} \right)^{1/7}$$

b) Calculate the bonding energy $\left(\dfrac{-7}{8} \dfrac{a}{r_0} \right)$

18. Calculate the percentage ionic character of CsF. $X_{Cs} = 0.7$ and $X_F = 40$.

19. Calculate the percentage covalent character of FeO. $X_{Fe} = 1.8$ and $X_O = 3.5$.

20. The net potential energy between two atoms is given by

$$U_{(r)} = -\frac{a}{r^m} + \frac{b}{r^n}$$

Show that the minimum for U(r) occurs only for $n > m$.

Section C

(Answer in about two pages)

Long answer type questions (Essays)

1. Discuss the fluctuating induced dipole bonds in secondary bond

2. Discuss the primary and secondary bonding in detail.

Hints to problems

14. $U_N = -\dfrac{1.436}{r} + \dfrac{7.32 \times 10^{-6}}{r^8}$ ..... (1)

Find r_0, for this find $\dfrac{dU}{dr}$ set equal to zero for $r = r_0$ we

$r_0 = 0.236$

Put this in eq (1) to get U_0

$$U_0 = (U_N)\Big|_{r=r_0} = -\frac{1.436}{r_0} + \frac{7.32 \times 10^{-6}}{r_0^8}$$

$$= -5.324.$$

15. $U_N = -\dfrac{a}{r^2} + \dfrac{b}{r^{10}}$

$$\frac{dU_N}{dr} = \frac{2a}{r^3} - \frac{10b}{r^{11}}$$

At equilibrium $\dfrac{dU_N}{dr} = 0$

$$0 = \frac{2a}{r_0^3} - \frac{10b}{r_0^{11}}$$

Put this in eq (1) for $r = r_0$

$$U_0 = -\frac{a}{r_0^2} + \frac{b}{r_0^{10}}$$

$$U_0 = -\frac{a}{r_0^2}\left(1 - \frac{b}{ar_0^8}\right)$$

$$U_0 = -\frac{a}{r_0^2}\left(1 - \frac{b}{a\dfrac{5b}{a}}\right)$$

$$= -\frac{4}{5}\frac{a}{r_0^2}$$

16. Dissociation energy $= -$ Bonding energy

$U_0 = 4.33 \times 10^{-12} V$

where $r_0 = 0.408nm$.

17. $\dfrac{dU}{dr}\bigg|_{r=r_0} = 0$ gives r_0

$U_0 = U(r)\bigg|_{r=r_0}$

18. % of ionic bonding $= 93.4$

see example 4 or 5

$\therefore$ % covalent bonding

$= 100 - 93.4 = 6.6\%$.

19. See example 5

% ionic bonding 51.47

$\therefore$ % covalent bonding

$$= 48.53$$

20. $U(r) = -\dfrac{a}{r^m} + \dfrac{b}{r^n}$

$$\dfrac{dU}{dr} = \dfrac{ma}{r^{m+1}} - \dfrac{nb}{r^{n+1}} \qquad \cdots\cdots (1)$$

At equilibrium $\dfrac{dU}{dr}\bigg|_{r=r_0} = 0$

$$\dfrac{ma}{r_0^{m+1}} - \dfrac{nb}{r_0^{n+1}}$$

$$r_0 = \left[\dfrac{b}{a}\dfrac{n}{m}\right]^{\frac{1}{n-m}}$$

The minimum of $U(r)$ occurs for

$\dfrac{d^2U}{dr^2}\bigg|_{r=r_0} > 0$ Differentiate eq (1) with respect to r, we get

$$\dfrac{-am(m+1)}{r_0^{m+2}} + \dfrac{-bn(n+1)}{r_0^{n+2}} > 0$$

$$\dfrac{bn(n+1)}{r_0^{n+2}} > \dfrac{am(m+1)}{r_0^{m+2}}$$

$$r_0^m\, bn(n+1) > am(m+1)r_0^n$$

$$bn(n+1) > am(m+1)r_0^{n-m}$$

Substituting for r_0, we get $bn(n+1) > am(m+1)\dfrac{b}{a}\dfrac{n}{m}$ give

$n > m$.

CHAPTER 3
CRYSTALS

Crystalline and noncrystalline materials

Matter exists in three states namely solids, liquids and gases. As the atoms or molecules in solids are attached to one another with strong forces of attraction, the solids have definite volume and shape. In this chapter we shall deal with physical properties of crystals.

Single crystals and polycrystals

Single crystals

The crystalline state of a solid is characterised by regular or periodic arrangement of atoms or molecules. The crystalline solids may be subdivided into single crystals and polycrystals. In single crystals the periodicity of atoms extends throughout the material. Diamond, quartz, mica, silicon etc. are examples of single crystals. Single crystals exist in nature, but they also be produced artificially. They are ordinary difficult to grow, because the environment must be carefully controlled.

If the extremities of a single crystal are permitted to grow without any external constraint, the crystal will assume a regular geometric shape having flat faces as with some of the gemstones; the shape is indicative of the crystal structure. Within the past few years, single crystals have become extremely important in many of our modern technologies, in particular electronic microcircuits which employ single crystals of silicon and other semiconductors.

Polycrystals

A polycrystalline is an aggregate of a number of small crystallites with random orientations separated by well defined boundaries. Metals and ceramics are polycrystals. There are various

stages in the solidification of a polycrystalline specimen. Initially small crystals or nuclei form at various positions. These have random crystallographic orientations as indicated by the square grid in figure 3.1. The small grains grow by the successive addition from the surrounding liquid of atoms to the structure of each. The extremities of adjacent grains impinge on one another as the solidification process approaches completion. The crystallographic orientation varies from grain to grain. Also there exists some atomic mismatch. Within the region where two grains meet; this area is called a grain boundary.
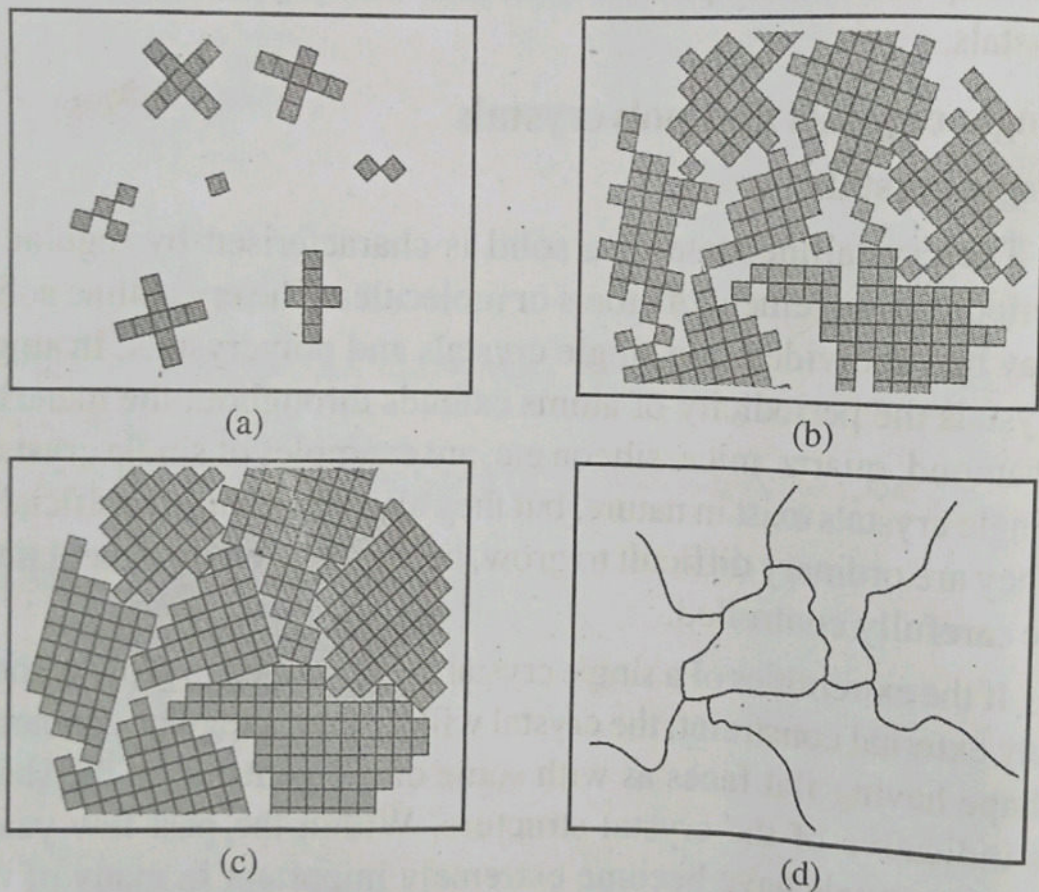
Figure 3.1: Schematic diagrams of the various stages in the solidification of a polycrystalline material; the square grids depict unit cells

(a) Small crystallite nuclei (b) Growth of the crystallites; the obstruction of some grains that are adjacent to one another is also shown. (c) Upon completion of solidification, grains having irregular shapes have formed (d) The grain structure as it would appear under the microscope; dark lines are the grain boundaries.

Anisotropy

Substances which exhibit same physical properties in all directions are said to be isotropic. In other words the physical properties are independent of the crystallographic direction along which physical properties are measured. Glass, NaCl, metals etc are isotropic. However the physical properties of single crystals of some substances depend on the crystallographic direction in which measurements are taken. This directionality of properties is called anisotropy. For example the elasticmodulus, the electrical conductivity and the refractive index may have different values in different directions of crystals. Single crystalline diamond, quartz, wood, composite materials are examples of anisotropic materials.

The directionality of properties is associated with the symmetry of the crystal structure. The degree of anisotropy increases with deareasing structural symmetry.

It may be noted that a crystal can be isotropic or anisotropic for a certain property and the same crystal can be isotropic for one property but anisotropic for another property. Cubic crystals are good examples. Any cubic crystal is necessarily isotropic for electrical conductivity but not for young's modulus.

In the case of polycrystalline materials the crystallographic orientations of the individual grains are totally random. Eventhough each grain may be anisotropic, a substance composed of the grain aggregate behaves isotropically. Also the magnitude of a measured property represents some average of the directional values. Sometimes the grains in polycrystalline materials have a preferential crystallographic orientation then the material is said to have a texture.

Noncrystalline solids (Amorphous)

These are solids characterised by the random arrangement of atoms or molecules. The periodicity, if at all present, extends upto a distance of a few atomic diameters only. In other words; these

solids exhibit short range order. Glass, plastics, rubbers, cement, paraffin wax etc. are non crystalline solids (amorphous).

The ceramic compound silicon dioxide may exist in crystalline and non crystalline states. See figure 3.2. Whether a crystalline or amorphous solid forms depends on the ease with which a random atomic structure in the liquid can transform to an ordered state during solidification. For example rapidly cooling liquid through the freezing temperatures favours the formation of a non crystalline solid, since only little time is allowed for the ordering process.

• Silicon atom
O Oxygen atom

(a)

(b)
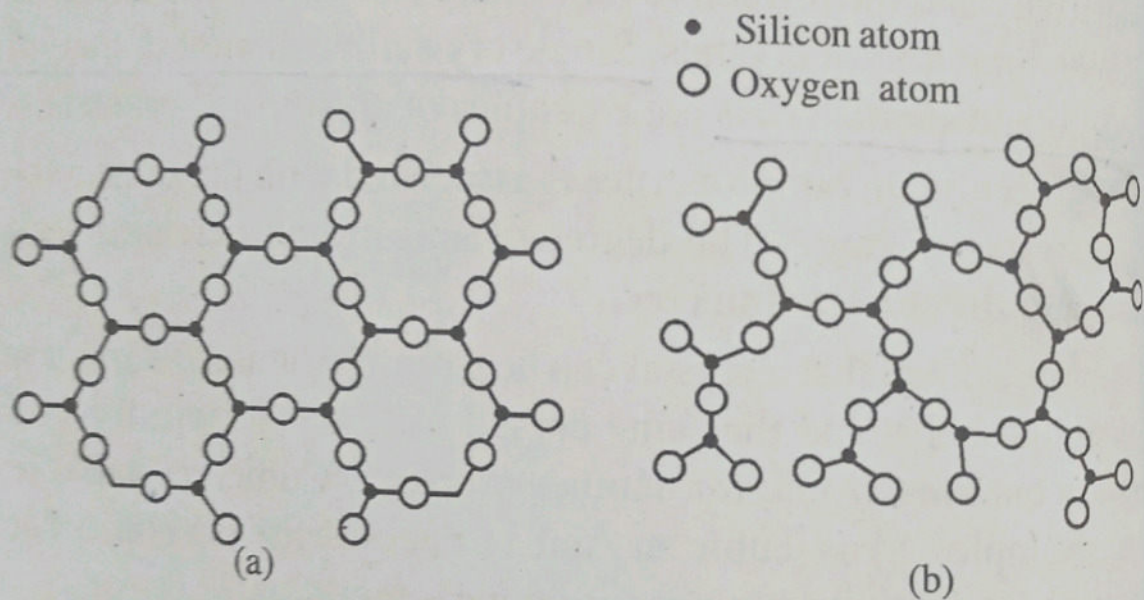
Figure 3.2: Two dimensional schemes of the structure of (a) crystalline silicon dioxide and (b) noncrystalline silicon dioxide

Metallic crystal structures

The atomic bounding in this group of materials is metallic and thus non directional in nature, this leads to relatively large number of nearest neighbours and dense atomic packings for most metallic crystal structures.

Most of the common metals exhibit simple crystal structure such as cubic, face centred cubic and hexagonal close packed. Here our aim is to see how atoms are packed in these crystal structures. For this we have to familiar with certain crystal structure terms such as coordination number, number of second nearest neighbour

nearest neighbour distance, atomic radius number of atoms per unit cell and atomic packing factor.

Coordination number or number of nearest neighbours (N)

It is defined as the number of equidistant neighbour that an atom has in the given structure. It is denoted by N.

Greater the coordination number, the more closely packed up will be the structure.

For SC structure, N = 6
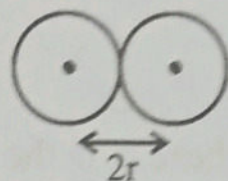
For BCC structure, N = 8

For FCC structure, N = 12

Figure 3.3

Nearest neighbour distance

The distance between the centres of two nearest neighbouring atoms is called nearest neighbour distance. If r is the radius of the atom, the nearest neighbour distance is 2r.

For SC structure, $2r = a$

For BCC structure, $2r = \dfrac{\sqrt{3}}{2}a$

For FCC structure, $2r = \dfrac{a}{\sqrt{2}}$

Number of second nearest neighbours

It is the number of equidistant atoms nearest to first nearest number.

There are 12 second nearest neighbours at distance $\sqrt{2}a$ for SC. There are 6 second nearest neighbours at distance a in BCC. There are 6 second nearest neighbours at distance a in FCC structures.

Atomic radius (r)

It is defined as half the distance between nearest neighbours in a crystal without impurity.

For SC, $r = \dfrac{a}{2}$, for BCC, $r = \dfrac{\sqrt{3}}{4} a$ and for FCC, $r = \dfrac{a}{2\sqrt{2}}$

Number of atoms per unit cell

The number of effective lattice points (atoms) per unit cell given by

$$n_{eff} = n_i + \frac{n_f}{2} + \frac{n_c}{8}$$

where n_i is the number of lattice points (atoms) completely inside the cell and n_f and n_c represent the lattice points occupying face centre and corner positions of the cell respectively.

For SC structure:

$$n_i = 0, \; n_f = 0 \; \text{and} \; n_c = 8$$

$\therefore \qquad n_{eff} = 1 \times 0 + \dfrac{1}{2} \times 0 + \dfrac{1}{8} \times 8 = 1$

For BCC structure:

$$n_i = 1, \; n_f = 0 \; \text{and} \; n_c = 8$$

$\therefore \qquad n_{eff} = 1 \times 1 + \dfrac{1}{2} \times 0 + \dfrac{1}{8} \times 8 = 2$

For FCC structure:

$$n_i = 0, \; n_f = 6 \; \text{and} \; n_c = 8$$

$\therefore \qquad n_{eff} = 1 \times 0 + \dfrac{1}{2} \times 6 + \dfrac{1}{8} \times 8 = 4$

Atomic packing fraction (APF)

The packing of atoms in a unit cell of the crystal structure of material is represented by atomic packing fraction (APF).

It is defined as the ratio of volume occupied by the atoms in a unit cell to that of the unit cell.

i.e., $$APF = \frac{\text{Volume of the atoms per unit cell}}{\text{Volume of the unit cell}}$$

$$= \frac{n_{eff} \times \text{Volume of each atom}}{\text{Volume of the unit cell}}$$

$$APF = \frac{v}{V}$$

Packing factor of simple cubic crystal structure

The simple cubic crystal structure of unit cell consists of atoms located at the corners only (each atom at each corner) and these atoms touch each other along the cube edges. Thus in sc structures we have

lattice constant, $a = 2r$

In sc each atom is surrounded by six equidistant nearest neighbours and hence the coordination number is 6.

Moreover each corner atom is shared by eight unit cells. Hence the share of each corner atom to a unit cell is one-eighth of an atom.

∴ The total number of atoms in effect in one unit cell $= \frac{1}{8} \times 8 = 1$

In other words the effective number of lattice points in a simple cubic cell is one. Thus sc is a primitive cell.

∴ Volume of all the atoms in a unit cell $v = 1 \times \frac{4}{3}\pi r^3$

Volume of the unit cell, $V = a^3 = (2r)^3$

∴ The packing factor, $P \cdot F = \frac{v}{V} = \frac{4\pi r^3}{3(2r)^3}$

i.e., $P \cdot F = \dfrac{\pi}{6} = 0.52$ or 52%.

Since only half the space of unit cell is filled with atoms can say that sc structure is loosely packed structure.

Only one element polonium at a certain temperature exh this structure.
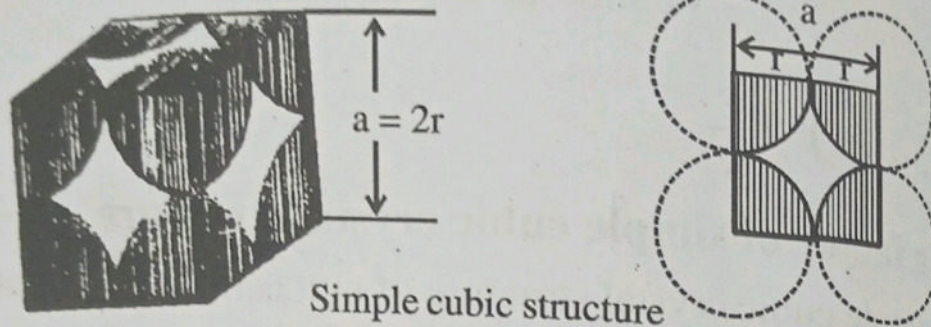
Simple cubic structure

Figure 3.4

Packing factor of body centred cubic structure

In this structure of unit cell there are 8 atoms at the corners another atom at the body centre. The atoms at the corners do touch each other but the corner atom touches the body centre al the body diagonal. Hence the coordination number is 8.
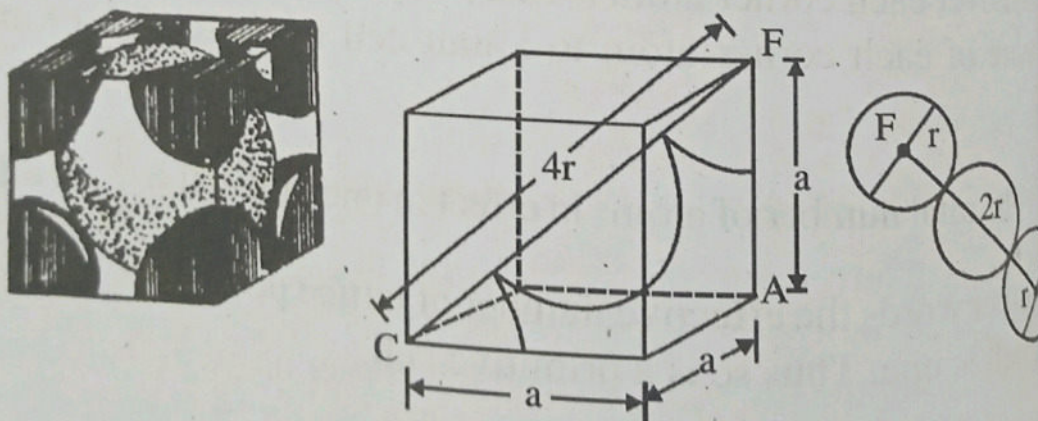
Figure 3.5 : Body centred cubic structure

The number of atoms in the unit cell $= 8 \times \dfrac{1}{8} + 1 = 2$

$\therefore$ Volume of the atoms in the unit cell $v = 2 \times \dfrac{4}{3} \pi r^3$

Volume of the unit cell, $V = a^3$

∴   Packing factor, $P \cdot F = \dfrac{v}{V} = \dfrac{8\pi r^3}{3a^3}$ ..... (1)

From the figure, we have

$$(AC)^2 = a^2 + a^2 = 2a^2$$

$$(FC)^2 = (AC)^2 + (AF)^2$$

$$(FC)^2 = 2a^2 + a^2 = 3a^2$$

$$(4r)^2 = 3a^2$$

$$r = \dfrac{\sqrt{3}}{4}a$$

Put this in eqn (1), we get

$$P \cdot F = \dfrac{8\pi}{3} \dfrac{\left(\dfrac{\sqrt{3}}{4}a\right)^3}{a^3} = \dfrac{\sqrt{3}\,\pi}{8} = 0.68 = 68\%.$$

Li, Na, K and Cr exhibit this structure.

Packing factor of face centred cubic structure

In this structure there are eight atoms at eight corners of the unit cell and six atoms at the centres of six faces. The atoms touch each other along the face diagonal. Each corner atom is shared by 8 surrounding unit cells and each of face centred atom is shared by 2 surrounding unit cells.

∴   The total number of atoms in the unit cell

$$= 8 \times \dfrac{1}{8} + 6 \times \dfrac{1}{2} = 4$$

(a)   (b)
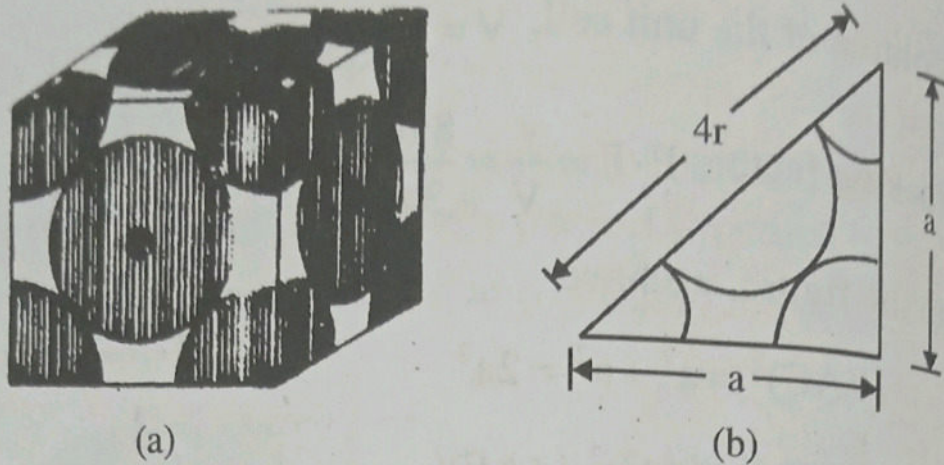
Figure 3.6: Face centred cubic structure

Volume of all atoms in the unit cell, $v = 4 \times \dfrac{4}{3} \pi r^3$

Volume of the unit cell, $V = a^3$

$\therefore$ The packing factor, $P \cdot F = \dfrac{v}{V}$

i.e., $P \cdot F = \dfrac{16 \pi r^3}{3 \times a^3}$ .....

From the figure we have

$$(4r)^2 = a^2 + a^2 = 2a^2$$

or $r = \dfrac{a}{2\sqrt{2}}$

Put this in eqn (1), we get

$$P \cdot F = \dfrac{16\pi \times a^3}{3a^3 (2\sqrt{2})^3} = \dfrac{\pi}{3\sqrt{2}} = 0.74$$

Copper, aluminium, lead and silver exhibit this structure. T
is a close packed structure.

Note: The coordination number of each atom in fcc is 12. W
the coordination number of an atom is less than 12, we
it as a loose packed structure.

Packing factor of hexagonal close packed structures (hcp)

The very name hexagonal indi-
cates that hcp structure has the
shape of hexagon. The unit cell of
this contains one atom at each cor-
ner, one atom each at the centre of
the hexagonal faces and three more
atoms within the body of the cell.
The atoms touch each other along
the edge of the hexagon. Thus

$a = 2r.$

The top layer of the hexagon
contains seven atoms. Each corner
atom is shared by 6 surrounding
hexagonal cells and the centre
atom is shared by 2 surrounding
cells. The three atoms within the
body of the cell are fully contrib-
uting to the cell.
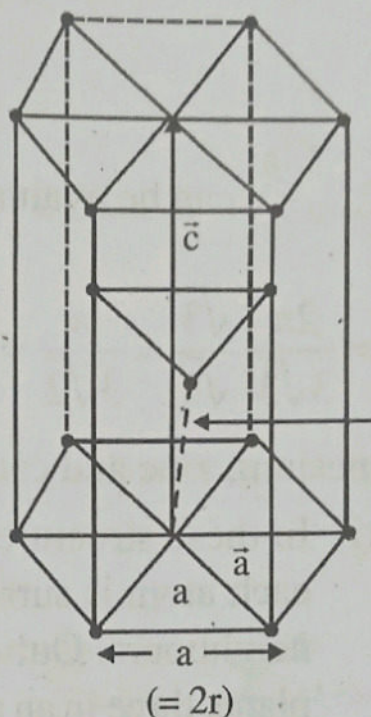
Figure 3.7: Hexogonal close
packed structure

Thus the total number of atoms in the unit cell

$$= 6 \times \frac{1}{6} + 6 \times \frac{1}{6} + 1 \times \frac{1}{2} + 1 + \frac{1}{2} + 3 = 6$$

∴ Volume of atoms in the unit cell, $v = 6 \times \frac{4}{3}\pi r^3$

$$v = \frac{24}{3}\pi \left(\frac{a}{2}\right)^3 = \pi a^3$$

Volume of the unit cell (hexagon), $V = \frac{3\sqrt{3}}{2}a^2 c$

(where c be the height of the unit cell and a be its edge).

∴ Packing factor, $PF = \dfrac{v}{V} = \dfrac{\pi a^3}{\dfrac{3\sqrt{3}}{2}a^2 c} = \dfrac{2\pi}{3\sqrt{3}}\left(\dfrac{a}{c}\right)$

$\dfrac{a}{c}$ can be evaluated to be $\sqrt{\dfrac{3}{8}}$

∴ $P \cdot F = \dfrac{2\pi}{3\sqrt{3}}\dfrac{\sqrt{3}}{\sqrt{8}} = \dfrac{\pi}{3\sqrt{2}} = 0.74$ or 74%.

Magnesium, zinc and cadmium exhibit this structure.

Note : (i) In these structures the coordination number is 12. i.e, each atom is surrounded by 12 similar and equal sized neighbours. Out of these 12 neighbours, six lie in one plane, three in an adjacent parallel plane above this plane and three in a similar plane below it.

(ii) Volume of the hexagon = base area × height = base area × c
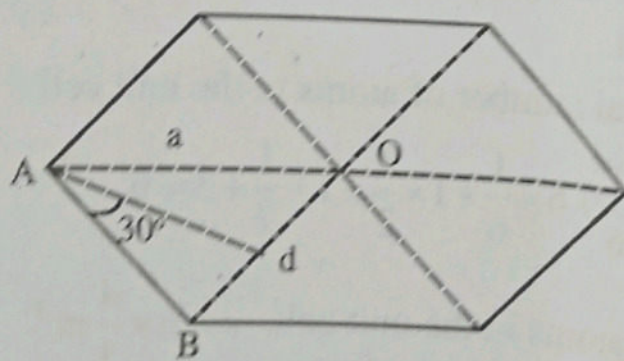
Figure 3.8

Base area = 6 × Area of $\triangle A\,OB$.

$= 6 \times \dfrac{1}{2} AO \times Bd$

But $\dfrac{Ad}{AB} = \cos 30°$ ∴ $Ad = AB\cos 30 = a\dfrac{\sqrt{3}}{2}$

$$\text{Base area} = 6 \times \frac{1}{2} \times a \times a \frac{\sqrt{3}}{2} = \frac{3\sqrt{3}}{2} a^2$$

$$\therefore \text{Volume of the hexagon} = \frac{3\sqrt{3}}{2} a^2 c.$$

To evaluate $\dfrac{a}{c}$

The three body atoms lie in a horizontal plane at $\dfrac{c}{2}$ from the orthocentres of alternate equilateral traingles.

From the figure

Figure 3.9

$$AZ^2 = AX^2 + ZX^2$$

$$a^2 = \left(\frac{2}{3} \times \text{median}\right)^2 + \frac{c^2}{4}$$

$$a^2 = \frac{a^2}{3} + \frac{c^2}{4}, \qquad a^2 - \frac{a^2}{3} = \frac{c^2}{4}$$

$$\frac{2}{3}a^2 = \frac{c^2}{4}, \qquad \frac{a^2}{c^2} = \frac{3}{8}$$

$$\therefore \qquad \frac{a}{c} = \sqrt{\frac{3}{8}}$$
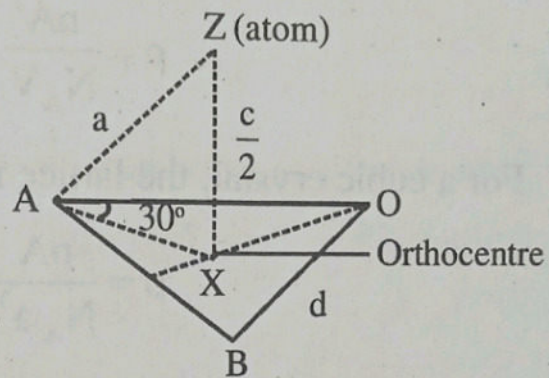
Density computations

Consider a crystal of lattice constant a having unit cell volume V. Let ρ be the density of the crystal.

If A is the atomic weight of the material and N_A the avagradro number. Thus $\dfrac{A}{\rho}$ of the material will contain N_A atoms. Hence

atoms in the unit cell occupy a volume $\dfrac{A_n}{\rho N_A}$. This is equal to V.

i.e.,
$$V = \dfrac{A_n}{\rho N_A}$$

or
$$\rho = \dfrac{nA}{N_A V} \qquad \qquad \ldots\ldots (2)$$

For a cubic crystal, the lattice is a, thus $V = a^3$

∴
$$\rho = \dfrac{nA}{N_A a^3}$$

or
$$a = \left(\dfrac{nA}{N_A \rho} \right)^{1/3} \qquad \qquad \ldots\ldots (3)$$

Example 1

Copper has fcc structure and its atomic radius is 0.128nm. Calculate its density. Take the atomic weight of copper as 63.5 g/mol.

Solution

The number of atoms per unit cell for fcc structure,

$$n = 4.$$

Volume of the unit cell,

$$V = a^3$$

where $a = 2\sqrt{2}\, r$

$$V = (2\sqrt{2}\, r)^3 = 16\sqrt{2}\, r^3.$$

∴

We have

$$\rho = \frac{nA}{VN_A} = \frac{4 \times 63.5}{16\sqrt{2}\,r^3 \times 6.023 \times 10^{23}}$$

$r = 0.128 \times 10^{-9}\,m$ given

$r = 1.28 \times 10^{-8}\,cm$

$$\rho = \frac{4 \times 63.5}{16\sqrt{2}\,(1.28 \times 10^{-8})^3 \times 6.023 \times 10^{23}}$$

$\rho = 8.89\,gcm^{-3}$.

Example 2

Calculate the lattice constant for α- iron belonging to bcc struc-ture. Take the density of α- iron as $7.86 \times 10^3\,kgm^{-3}$ and the atomic weight of iron as 55.85.

Solution

For bcc structure, the volume of the unit cell,

and $\qquad V = a^3$

$\qquad n = 2$

$\qquad \rho = 7.86 \times 10^3\,kgm^{-3}$

$\qquad A = 55.85 \times 10^{-3}\,kg/mol$

Using

$$a = \left(\frac{nA}{N_A \rho} \right)^{1/3}$$

$$a = \left(\frac{2 \times 55.85 \times 10^{-3}}{6.02 \times 10^{23} \times 7.86 \times 10^3} \right)^{1/3}$$

$a = 0.124\,nm.$

Example 3

Zinc has hcp structure. The height of the unit cell is 0.494n The nearest neighbour distance is 0.21. The atomic weight of z is 65.37. Calculate the volume of the unit cell and density of zi

Solution

$$a = 0.27 \times 10^{-9} \, m$$

$$c = 0.494 \times 10^{-9} \, m$$

Volume of the unit cell

$$V = \frac{3 \times \sqrt{3} \times (0.27 \times 10^{-9})^2 \times (0.494 \times 10^{-9})}{2}$$

$$V = 9.356 \times 10^{-29} \, m^3.$$

The number of atoms belonging to a unit cell of

hcp, $n = 6$.

Using

$$\rho = \frac{nA}{N_A V}$$

$$\rho = \frac{6 \times 65.37 \times 10^{-3}}{6.02 \times 10^{23} \times (9.356 \times 10^{-29})}$$

$$\rho = 6964 \, kgm^{-3}.$$

Linear and planar densities

The linear density of a crystal is related to directional equivalency. This means that equivalent directions have identical linear densities. The corresponding parameter for crystallographic planes is planar density.

Linear density (LD)

It is defined as the number of atoms per unit length whose centres lie on the direction vector for a specific crystallographic direction.

$$LD = \frac{\text{Number of atoms centred on the direction vector}}{\text{length of direction vector}}$$

The unit of LD is m^{-1}. For example the linear density of [110] direction for the fcc crystal,

$$LD_{110} = \frac{2\,\text{atoms}}{4R} = \frac{1}{2R}$$

Planar density

It is defined as **the number of atoms per unit area that are centred on a particular crystallographic plane.**

$$PD = \frac{\text{Number of atoms centred on a plane}}{\text{Area of plane}}.$$

The unit of PD is m^{-2}. For example planar density (110) plane within an fcc unit cell

$$PD_{110} = \frac{2\,\text{atoms}}{8r^2\sqrt{2}}$$

$$= \frac{1}{4\sqrt{2}\,r^2}$$

$\because$ Area of planar region

$$= (4r)\,2r\sqrt{2}$$

$$= 8\sqrt{2}\,r^2$$

Polymorphism and allotropy

Polymorphism

Polymorphism is a common phenomenon of crystalline materials.

It describes the ability of a substance to exist as two or more crystalline phases that have different arrangements of the molecules in the solid state but are otherwise identical in terms of chemical content.

Some common examples of polymorphs are calcite and aragonite. The composition of these two minerals is $CaCO_3$, but calcite is rhombohedral while aragonite is orthorhombic. Diamond and graphite, both of which are pure carbon are also polymorphs. Diamond, however is cubic, while graphite is hexagonal.

Iron is also polymorphic. This is one of the secrets to the success of iron to combine with other elements to form alloys to dramatically extend its range as an engineering material.

Allotropy

The property of some metals and alloys that exhibit different crystalline structure at different temperatures and pressures is called allotropy.

Allotropy is a very important property of materials; these allotropic changes are the basis for heat treatment of many engineering materials.

For example, below 912°C, iron has bcc crystal structure and is called α-iron. But above 912°C iron is called γ-iron with fcc crystal structure.

There are two crystalline forms of sulphur in solid states like rhombic sulphur and monoclinic sulphur. These two forms are called allotropes of sulphur. Rhombic sulphur is stable at a temperature lower than 96°C.

UNIVERSITY MODEL QUESTIONS
Section A
(Answer questions in one or two sentences)

Short answer questions

1. What are crystalline solids? Give an example.
2. Distinguish between single and polycrystals.
3. What are amorphous solids? Give an example.
4. What is meant by isotropy of a materials?
5. What is meant by anisotropy of materials.
6. What are non crystalline solids? Give two examples.
7. Define
   a) Coordination number
   b) Nearest neighbour distance.
8. How do we calculate the number of atoms per unit cell?
9. What is meant by atomic packing factor?
10. Write down an expression for the density of a crystal structure and explain the symbols.
11. Define
    a) linear density and
    b) planar density of crystals.
12. What is meant by polymorphism of crystalline materials?
13. What is meant by allotropy of materials?
14. $CaCO_3$ is a polymorphic material. Explain.
15. Iron is an allotropic material. Explain.

Section B
(Answer questions in a paragraph of about half a page to one page)

Paragraph / Problem type

1. How does a polycrystal is formed?
2. Distinguish between isotropy and an isotropy of materials.

3. A crystal may be isotropic or anisotropic for a certain property. Justify.

4. Distinguish between crystalline and non crystalline solids.

5. Calculate the number of atoms per unit cell for

   a) SC structure

   b) BCC structure

   c) FCC structure.

6. Calculate the atomic packing factor of simple cubic crystal.

7. Show that the atomic packing factor of BCC structure is 68%.

8. Find the packing factor of FCC structure.

9. Find the volume of the hexagonal close packed unit cell.

10. Show that the $\dfrac{a}{c}$ ratio for an ideal hcp lattice is $\sqrt{\dfrac{3}{8}}$.

11. Show that the packing factor of hcp structure is 74%.

12. How do we compute the density of crystal structures?

13. Distinguish between linear and planar densities of crystals.

14. Molybdenum has a bcc crystal structure, an atomic radius of 0.1363nm and an atomic weight of 95.94 g/mole. Compute its density.   [10.22 gcm^{-3}]

15. Calculate the radius of a palladium atom, given that Pd has an fcc crystal structure, a density of 12.0 gcm^{-3} and an atomic weight of 106.4g/mol.   [0.138nm]

16. Titanium has an hcp crystal structure and a density of 4.51gcm^{-3}. What is the volume of its unit cell?   [1.06×10^{-28}m^3]

17. Magnesium has an hcp crystal structure, a $\dfrac{c}{a}$ ratio of 1.624 and a density of 1.74gcm^{-3}. Compute the atomic radius for Mg.

                    [0.160 nm]

18. Cobalt has an hcp crystal structure, an atomic radius of 0.1253nm and a c/a ratio of 1.623. Calculate the volume of the unit cell.

                    [6.64×10^{-2}(nm)^3]

Hints to problems

14. $\rho = \dfrac{nA}{N_A V} = \dfrac{2 \times 95.94}{6.02 \times 10^{23} \, V}$

$r = 0.1363 \times 10^{-7} \, cm$

$a = \dfrac{4r}{\sqrt{3}}$

$V = a^3 = \left(\dfrac{4r}{\sqrt{3}} \right)^3$

15. $a = \left(\dfrac{nA}{N_A \rho} \right)^{1/3} = \left(\dfrac{4 \times 106.4}{6.02 \times 10^{23} \times 12} \right)^{1/3}$

$r = \dfrac{a}{2\sqrt{2}}$ for fcc.

16. $\rho = \dfrac{nA}{N_A V}$

$V = \dfrac{nA}{N_A \rho}$, $n = 6$, $A = 47.87$.

17. $a = \left(\dfrac{nA}{N_A \rho} \right)^{1/3}$ $n = 6$, $\rho = 1.74$

$r = \dfrac{a}{2}$

$V = \dfrac{3\sqrt{3}}{2} a^2 c$

$\dfrac{V}{r} = 3\sqrt{3} \, \dfrac{c}{a} = 3\sqrt{3} \times 1.624.$

18. $\dfrac{V}{r} = 3\sqrt{3} \, \dfrac{c}{a}.$

CHAPTER 4

IMPERFECTIONS IN SOLIDS

Introduction

In the first three chapters we dealt with the properties of crystals under the assumption that, the atomic arrangements in crystals are perfectly regular and continuous throughout. In other words we dealt with ideal crystals. However, in actual crystals imperfections or defects are always present. **The term imperfection or defect is used to describe any deviation from the perfect periodic array of atoms in crystals.** No crystal is ideal. Imperfections or defects are always present in crystals. The study of these imperfections are important in the sense that many of the properties of crystals such as mechanical strength, ductility, crystal growth, dielectric strength, electrical and magnetic properties etc. are greatly affected by the imperfections in crystals.

The structural imperfections can be classified on the basis of their geometry as

(i) point defects (zero dimensional defects)

(ii) line defects (one dimensional defects)

(iii) surface defects (two dimensional defects) and

(iv) volume defects (three dimensional defects). We shall discuss these one by one.

Point defects

Point defects are also called zero dimensional defects since point is a zero dimensional object. Here we discuss only two defects: (i) vacancies and (ii) self interstitials.

Vacancies

Vacancy is the simplest type of point defect in a crystal. This refers to a missing atom or vacant atomic site. Such defects may arise either from imperfect packing during the original crystallisation or from thermal vibrations of the atoms at high temperatures. In the latter case, when the thermal energy due to vibration is increased there is an increased probability that individual atom will jump out of their positions of lowest energy. For most crystals, this thermal energy is of the order of 1eV per vacancy. Vacancies may be single or two or more of them.

All crystalline solids contain vacancies and it is not possible to create a crystal without vacancy. The existence of vacancies is explained using principles of thermodynamics. The presence of vacancies increases the entropy of the crystal.

The equilibrium number of vacancies N_v for a given quantity of material is given by

$$N_v = N e^{\frac{-E_v}{kT}} \qquad \qquad \text{..... (1)}$$

where N is the total number of atomic sites, E_v is the energy required for the formation of a vacancy, T is the absolute temperature in kelvin and k is the Boltzmann's constant. The value of k is 1.38×10^{-23} J/atom or 8.62×10^{-5} eV/atom K. For most of the metals $\dfrac{N_v}{N}$ is of the order of 10^{-4}, when the temperature is below the melting point of the crystal.

$$\frac{N_v}{N} = 10^{-4}$$

or

$$N_v = 10^{-4} N$$

It implies that in 10,000 lattice sites there is only one vacancy.

In the vacancy there is no bonding, hence the value of Φ mechanical strength of the crystal at that point is reduced.

Example 1

The fraction of vacancy sites in a metal is 1×10^{-10} at 500°C. What will be the fraction of vacancy sites at 1000°C.

Solution

We have

$$N_v = Ne^{\frac{-E_v}{kT}}$$

$$\therefore \quad \frac{N_v}{N} = e^{\frac{-E_v}{kT}}$$

$$10^{-10} = e^{\frac{-E_v}{kT}}$$

$$10^{10} = e^{\frac{E_v}{kT}}$$

Take natural log on both sides, we get

$$23.03 = \frac{E_v}{kT}$$

$$E_v = 23.03 \times kT$$

$$= 23.03 \times 8.62 \times 10^{-5} \times 773 \qquad (\because T = 773K)$$

$$= 1.53eV.$$

Again

$$\frac{N_v}{N} = e^{\frac{-1.53}{8.62 \times 10^{-5} \times 1273}} \qquad (\because T = 1273K)$$

$$= e^{-13.94}$$

$$= 8.83 \times 10^{-7}$$

Example 2

Calculate the fraction of atom sites that are vacant for copper at its melting temperature 1357K. Assume $E_v = 0.90 \, eV/atom$.

Solution

We have

$$N_v = Ne^{\frac{-E_v}{kT}}$$

$$\frac{N_v}{N} = e^{\frac{-E_v}{kT}}$$

$$= e^{\frac{-0.9}{8.62 \times 10^{-5} \times 1357}}$$

$$= e^{-7.69} = 4.5 \times 10^{-4}$$

Example 3

Calculate the energy for vacancy formation in silver, given that the equilibrium number of vacancies at 800°C is $3.6 \times 10^{13} cm^{-3}$. The atomic weight and density at 800°C for silver are 107.9g/mol and 9.5 gcm^{-3}.

Solution

We have

$$N_v = Ne^{\frac{-E_v}{kT}} \qquad \ldots\ldots (1)$$

The number of sites,

$$N = \frac{N_A \rho}{A_{A_s}}$$

$$N = \frac{6.02 \times 10^{23} \times 9.5}{107.9}$$

$$N = 0.53 \times 10^{23}$$

Put the values of N_v, N in eq (1), we get

$$3.6\times10^{17} = 0.53\times10^{23} \times e^{\frac{-E_v}{kT}}$$

$$\frac{3.6}{0.53}\times10^{-6} = e^{\frac{-E_v}{kT}}$$

$$6.39\times10^{-6} = e^{\frac{-E_v}{kT}}$$

Take natural log on both sides, we get

$$-11.9 = -\frac{E_v}{kT}$$

$$\therefore \quad E_v = 11.9\times kT = 11.9\times8.62\times10^{-5}\times1073$$

$$= 1.10eV/atom.$$

Self interstitial defect

An interstitial defect is a type of point defect where an atom of the same or of a different type occupies an interstitial site in the crystal structure. When the atom is of the same type as those already present they are known as a self-interstitial defect.

Alternatively, small atoms in some crystals may occupy interstitial sites, such as hydrogen in palladium. Interstitials sites may exist in small concentrations in thermodynamic equilibrium. Interstitials can also be produced by bombarding a crystal with elementary particles having energy above the displacement threshold. The presence of interstitial defects can modify the physical and chemical properties of materials.

Two dimensional representations of a vacancy and a self-interstitial defect is depicted in figure 4.1.
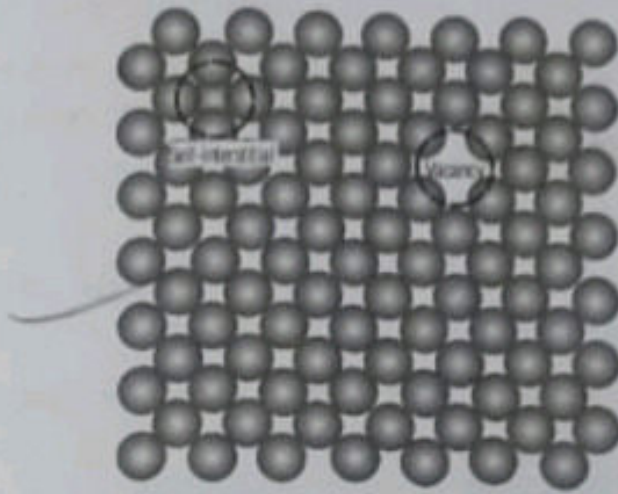
Figure 4.1:   Two-dimensional representations of
a vacancy and a self-interstitial

Impurities in solids

A pure crystal such as iron, silver, NaCl, brass etc., is not made up of one type of atom or atoms. Impurity atoms will always be present. This will result in crystalline impurity point defects such as substitutional and interstitial.

It is impossible to refine crystals in excess of 99.999%. At this level of purity it contains 0.001% of impurity. We can say that there are 10^{22} to 10^{23} impurity atoms will be present in one cubic metre of material. Most familiar metals are not 100% pure. Rather they are alloys, in which impurity atoms have been added intentionally to get specific characteristics to the material. ordinarily alloying is used in metals to improve mechanical strength and corrosion resistance. For example sterling silver is an alloy consists of 92.5% silver and 7.5% copper. Normally pure silver is highly corrosion resistant, but also very soft. Alloying with silver significantly increases the mechanical strength without depreciating the corrosion resistance appreciably.

The addition of impurity atoms will result in the formation of solid solution. With regard to alloys (solid solution) solute and solvent are terms that commonly used in analogy with liquid

solution. Solvent represents the element that is present in the greatest amount and solute represents the element present in a minor concentration.

Solid solution

A solid solution is formed as the solute atoms are added to the solvent atoms.

The solid solutions are of two types. They are substitutional and interstitial.

Substitutional solid solutions

These result from replacing the particle that should occupy a lattice site with a different particle.

For example substituting a K^+ ion for a Na^+ ion in NaCl. If Ca^{2+} ion is substituted for a Na^+ ion, the second Na^+ ion must leave the crystal so that it doesn't pickup an electric charge to maintain the electrical neutrality. There are several features of solute and solvent atoms that determine the degree to which solute dissolves in solvent.

(i) Atomic size factor

When the difference in atomic radii between the two atom types (solvent and solute) is less than about $\pm 15\%$ appreciable amount of solute may be accommodated in this type of solid solution.

(ii) Crystal structure

For appreciable solid solubility the crystal structures for both atom type must be the same.

(iii) Electronegativity

The more electropositive one element and the more electronegative the other element, the greater is the likelihood that they will form an intermetallic compound instead of a substitutional solid solution.

(iv) Valencies

Other factors being equal, a metal will have more of a tendency

to dissolve another metal of higher valency than one of a lower valency.

For example a substitutional solid solution is formed for copper and nickel. This is because all four conditions required are met. The atomic radii for copper and nickel are 0.128 and 0.125nm respectively. Thus first condition is fulfilled. Since both have same crystal structures the second condition is also met.

The third requirement is satisfied since their electronegativities are 1.9 and 1.8. The difference is very small. Finally the valency of copper is +1 and that of nickel is +2 hence tendency to dissolve is higher.

Interstitial solid solutions

These are formed when impurity atoms (solute) fill the voids of the solvent atoms. For metallic materials that have relatively high atomic packing factors, their interstitial positions are relatively small. Consequently the atomic diameter of an interstitial must be smaller than the solvent atom to occupy the voids of solvent atoms. Normally, the maximum allowable concentration of interstitial impurity atoms is low (less than 10%). Even very small impurity atoms are ordinarily larger than the interstitial sites. The consequence is that impurity atoms produce some lattice strains to adjacent solvent atoms.

For example carbon forms an interstitial solid solution when added to iron. The maximum concentration of

Interstitial impurity atom
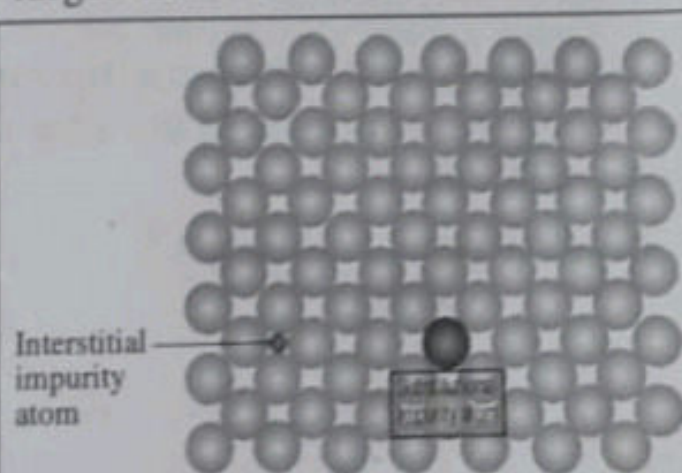
Figure : 4.2: Two-dimensional schematic representations of substitutional and interstitial impurity atoms

carbon is about 2%. The atomic radius of the carbon $(0.071 nm)$ is much less than that for iron $(0.124 nm)$.

A two dimensional schematic representations of substitutional and interstitial impurity atoms are shown in figure 4.2.

Specification of composition

An alloy contains two or more elements. The percentage of the elements that occur in an alloy is usually expressed by the term composition or concentration. It can be done in two ways. One is in terms of mass percent the other one is in terms of atom percentage. **The mass percent is defined as the ratio of the mass of a particular element and the mass of the alloy.**

Suppose an alloy consists of two atoms 1 and 2 with masses m_1 and m_2 respectively mass percentage of m_1,

$$C_1 = \frac{m_1}{m_1 + m_2} \times 100 \qquad \cdots (1)$$

Similary, mass percent of m_2,

$$C_2 = \frac{m_2}{m_1 + m_2} \times 100 \qquad \cdots (2)$$

The atom percent is defined as the ratio between number of moles an element present in the alloy to the total number of moles of the alloy.

The atom percent of element 1,

$$n_{m_1} = \frac{m_1'}{A_1} \qquad \cdots (3)$$

where m_1' denotes the mass of element 1 in grams and A_1 is its atomic mass. Thus concentration in terms of atom percent is

$$C_1' = \frac{n_{m_1}}{n_{m_1} + n_{m_2}} \times 100 \qquad \dots (4)$$

similarly

$$C_2' = \frac{n_{m_2}}{n_{m_1} + n_{m_2}} \times 100 \qquad \dots (5)$$

Composition conversion

Suppose we want to convert from mass % to atom %, sometimes it is necessary.

Conversion from mass percent to atom percent

Consider two atoms 1 and 2 in an alloy. Let C_1 and C_2 be the mass percent of elements 1 and 2 respectively. Similarly C_1' and C_2' be the atom percent of elements 1 and 2 respectively.

Total mass of the alloy

$$M' = m_1' + m_2' \qquad \dots (6)$$

Prime is used to denote that mass is expressed in grams, we have

$$C_1' = \frac{n_{m_1}}{n_{m_1} + n_{m_2}} \times 100$$

But $\quad n_{m_1} = \dfrac{m_1'}{A_1}$ and $n_{m_2} = \dfrac{m_2'}{A_2}$

$$\therefore \quad C_1' = \frac{m_1'/A_1}{\dfrac{m_1'}{A_1} + \dfrac{m_2'}{A_2}} \times 100 \qquad \dots (7)$$

From eq (1), we get

$$C_1 = \frac{m_1'}{m_1' + m_2'} \times 100$$

$$C_1 = \frac{m_1'}{M'} \times 100$$

or

$$m_1' = \frac{C_1 M'}{100} \qquad \qquad \cdots\cdots (8)$$

Similarly $m_2' = \dfrac{C_2 M'}{100}$ $\qquad \qquad \cdots\cdots (9)$

Substituting eq 8 and 9 in eq 7, we get

$$C_1' = \frac{\dfrac{C_1 M'}{100\, A_1}}{\dfrac{C_1 M'}{100\, A_1} + \dfrac{C_2 M'}{100\, A_2}} \times 100$$

$$C_1' = \frac{C_1 M' / A_1}{\dfrac{C_1 M'}{A_1} + \dfrac{C_2 M'}{A_2}} \times 100$$

$$C_1' = \frac{C_1 / A_1}{\dfrac{C_1}{A_1} + \dfrac{C_2}{A_2}} \times 100$$

or

$$C_1' = \frac{C_1 A_2}{C_1 A_2 + C_2 A_1} \times 100 \qquad \cdots\cdots (10)$$

Using $\quad C_1' + C_2' = 100$

$$C_1' = 100 - C_2'$$

Put this in eq (10), we get

$$100 - C_2' = \frac{C_1 A_2}{C_1 A_2 + C_2 A_1} \times 100$$

$$C_2' = 100 - \frac{C_1 A_2}{C_1 A_2 + C_2 A_1} \times 100$$

$$C_2' = 100 \left(1 - \frac{C_1 A_2}{C_1 A_2 + C_2 A_1} \right)$$

$$\therefore \quad C_2' = \frac{C_2 A_1}{C_1 A_2 + C_2 A_1} \times 100 \qquad \qquad \dots (11)$$

Conversion from atom percent to mass percent

From eq 10, we have

$$C_1' = \frac{C_1 A_2}{C_1 A_2 + C_2 A_1} \times 100 \qquad \qquad \dots (12)$$

$$\therefore \quad C_1' A_1 = \frac{C_1 A_1 A_2}{C_1 A_2 + C_1 A_1} \times 100 \qquad \qquad \dots (13)$$

From eq 11, we have

$$C_2' = \frac{C_2 A_1}{C_1 A_2 + C_2 A_1} \times 100 \qquad \qquad \dots (14)$$

$$\therefore \quad C_2' A_2 = \frac{C_2 A_1 A_2}{C_1 A_2 + C_2 A_1} \times 100 \qquad \qquad \dots (15)$$

Adding eq 13 and 15, we get

$$C_1' A_1 + C_2' A_2 = \frac{A_1 A_2 (C_1 + C_2)}{C_1 A_2 + C_2 A_1} \times 100$$

Using $C_1 + C_2 = 100$, we get

$$C_1' A_1 + C_2' A_2 = \frac{A_1 A_2 \times 100^2}{C_1 A_2 + C_2 A_1} \qquad \cdots (16)$$

$\dfrac{\text{Eq 13}}{\text{Eq 16}}$ gives

$$\frac{C_1' A_1}{C_1' A_1 + C_2' A_2} = \frac{C_1}{100}$$

$$\therefore \quad C_1 = \frac{C_1' A_1}{C_1' A_1 + C_2' A_2} \times 100$$

Using this we can convert atom% to mass%.

Similarly, $\dfrac{\text{Eq 15}}{\text{Eq 16}}$ gives

$$C_2 = \frac{C_2' A_2}{C_1' A_1 + C_2' A_2} \times 100 \qquad \cdots (17)$$

Example 4

What is the composition, in atom percent of an alloy that consists of 92.5 mass% Ag and 7.5 mass% Cu. $A_{Ag} = 107.87$ and $A_{Cu} = 63.55$.

Solution

Atom percent,

$$C_1' = \frac{C_1 A_2}{C_1 A_2 + C_2 A_1} \times 100$$

at% of Ag,

$$C_{Ag}' = \frac{C_{Ag} A_{Cu}}{C_{Ag} A_{Cu} + C_{Cu} A_{Ag}}$$

$$\left. \begin{array}{l} C_{Ag} = 92.5 \\ C_{Cu} = 7.5 \end{array} \right\} \text{ given}$$

$$A_{Ag} = 107.87 \text{ g/mol}$$

$$A_{Cu} = 63.55 \text{ g/mol}$$

$$\therefore \quad C_{Ag}' = \frac{92.5 \times 63.55}{92.5 \times 63.55 + 7.5 \times 107.87} \times 100$$

$$C_{Ag}' = \frac{5878.375}{6687.4} \times 100$$

$$C_{Ag}' = 87.9 \text{ at\%}$$

$$C_{Ag}' + C_{Cu}' = 100$$

$$C_{Cu}' = 100 - C_{Ag}' = 100 - 87.9$$

$$C_{Cu}' = 12.1 \text{ at\%.}$$

Example 5

What is the composition, in mass percent of an alloy that consists of 5 at% Cu and 95 at% Pt. $A_{Cu} = 63.55$, $A_{Pt} = 195.08$.

Solution

Mass percent

$$C_1 = \frac{C_1' A_1}{C_1' A_1 + C_2' A_2} \times 100$$

$$C_{Cu} = \frac{C_{Cu}' A_{Cu}}{C_{Cu}' A_{Cu} + C_{Pt}' A_{Pt}} \times 100$$

$$C_{Cu} = \frac{5 \times 63.55 \times 100}{5 \times 63.55 + 95 \times 195.08}$$

$$C_{Cu} = \frac{31775}{317.75 + 18532.6}$$

$$C_{Cu} = \frac{31775}{18850.35}$$

$$= 1.68 \text{ mass}\%.$$

Using

$$C_{Cu} + C_{Pt} = 100$$

$$C_{Pt} = 100 - C_{Cu}$$

$$= 98.32 \text{ mass}\%.$$

Example 6

What is the composition, in atom percentage, of an alloy that contains 33g of copper and 47g zinc.

$$A_{Cu} = 63.55 \text{ and } A_{Zn} = 65.41.$$

Solution

$$\text{at}\%, \ C_1' = \frac{n_{m_1}}{n_{m_1} + n_{m_2}} \times 100$$

where $n_{m_1} = \dfrac{m_1'}{A_1} = \dfrac{33}{63.55}$

$$n_{m_1} = 0.5193$$

$$n_{m_2} = \dfrac{m_2'}{A_2} = \dfrac{47}{65.41}$$

$$= 0.7185$$

$$C_{Cu}' = \dfrac{0.5193 \times 100}{0.5193 + 0.7185}$$

$$= \dfrac{51.93}{1.2378}$$

$$= 41.95 \text{ at\%}.$$

Using $C_{Cu}' + C_{Zn}' = 100$

$$C_{Zn}' = 100 - 41.95$$

$$= 58.05 \text{ at\%}.$$

Atomic pointdefects

Point defects are defects of zero dimensionality, i.e., they do not possess lattice structure in any dimension. In metals we found three point defects: vacancies, self interstitials and impurity atoms. Here we discuss point defects in ceramic compounds. Ceramic materials contain ions at atleast two kinds, defects of each type may occur. For example in NaCl, Na interstitials and vacancies and Cl interstitials and vacancies may occur. As the size of an ion is relatively large, the probability of occurance of anion interstitials are very low. Thus we have only three types: Anion vacancy, cation varancy and cation interstitials. They are schematically represented in figure 4.3(a).

Figure 4.3(a) Schematic representations of cation and anion vacancies and a cation interstitial
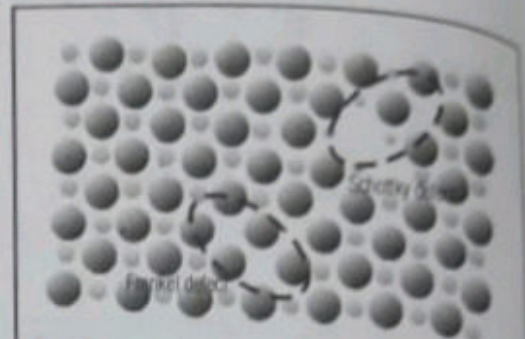
Figure 4.3(b) Schamatic diagram showing Frenkel and Schottky defects in ionic solid

There are three types of point defects found in ceramics. They are Frenkel defect, Schottky defect and nonstoichiometric defect.

Frenkel defect

Frenkel defect is formed when a cation leaving its normal position and moving into an interstitial site.

When this defect occurs there is no change in charge because the cation maintains the same positive charge as an interstial. See figure 4.3(b).

Schottky defect

The defect occurs when a cation and an anion removed from the interior of the crystal and placing them both at an external surface. As a result a pair of cation vacancy – anion vacancy is formed. This is known as Schottky defect.

Here also the neutrality of the charge is maintained, since cations and anions have the same charge and for every anion vacancy there exists a cation vacancy. See figure 4.3(b).

It may be noted that the ratio of cations to anions is not altered by the formation of either a Frenkel defect or a Schottky defect. If no other defects are present the material is said to be stoichiometric.

Stoichiometry

It is defined as a state for ionic compounds where in there is the exact ratio of cations to anions.

For example NaCl is stoichiometric if $\dfrac{Na^+}{Cl^-} = 1$. If there is any deviation from this it is known as nonstoichiometric.

Nonstoichiometric defect

Any deviation from the ratio of cation and anion equal to one results in a defect known as nonstoichiometric defect.

This defect occurs in some of the ceramic materials in which two valence states exist for one of the ion types. Iron oxide (FeO) is one such material. Fe exists in both Fe^{2+} and Fe^{3+} states. The number of each of these depends on temperature and the oxygen pressure. The formation of Fe^{3+} ion disrupts the electroneutrality of the crystal by introducing an excess +1 charge, which must be offset by some type of defect. This may be accomplished by the formation of one Fe^{2+} vacancy for every two Fe^{3+} ions are formed. The crystal is no longer stoichiometric because there is one more O ion than Fe ion. However the crystal remains electrically neutral. The nonstoichiometric defect indicates a deficiency of Fe. Thus chemical formula for iron oxide is written as $Fe_{1-x}O$, where x is some small and variable fraction less than one.

The equilibrium number of both Frenkel and Schottky defects that can occur in a crystal can be calculated by using

$$N_{fr} = Ne^{\frac{-E_{fr}}{2kT}} \qquad\qquad ..... (18)$$

N_{fr} is the number of cation vacancy / cation interstitial defect pairs, N is the total number of lattice sites and E_{fr} is the energy required for the formation of each Frenkel defect. Similarly for Schottky defect.

$$N_s = Ne^{\frac{-E_s}{2kT}}$$ ..... (19)

The number of sites in a metal,

$$N = \frac{N_A \rho}{A_{metal}}.$$

Figure 4.3(c) Schematic representations of an Fe^{2+} vacancy in FeO that results from the formation of two Fe^{3+} ions
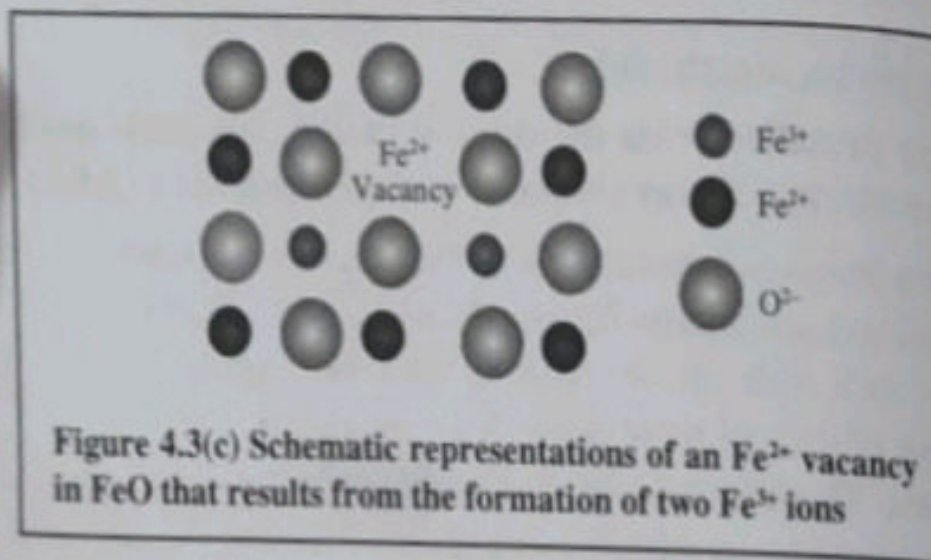
Example 7

Calculate the number of Schottky defects per cubic metre in potassium chloride at 500°C. The energy required to form each Schottky defect is 2.6eV and density of KCl at 500°C is 1.955 gcm⁻³

$$A_K = 39.10 \, g/mol$$

$$A_{Cl} = 35.45 \, g/mol.$$

Solution

The equilibrium number of Schottky defects,

$$N_s = Ne^{\frac{-E_s}{2kT}}$$ ..... (1)

$$E_s = 2.6eV$$

$$k = 8.62 \times 10^{-5} \, eV/K$$

$$T = 500 + 273 = 773K$$

$$\rho = 1.955 \times 10^3 \, kgm^{-3}$$

Number of lattice sites,

$$N = \frac{\rho N_A}{A_K + A_{Cl}}$$

$$N = \frac{1.955 \times 10^3 \times 6.023 \times 10^{23}}{39.10 \times 10^{-3} + 35.45 \times 10^{-3}}$$

$$N = 1.58 \times 10^{28} \text{ lattice sites per } m^3.$$

$$N_s = 1.58 \times 10^{28} \times e^{\frac{-2.6}{2 \times 8.62 \times 10^{-5} \times 773}}$$

$$N_s = 5.31 \times 10^{19} \text{ defects } m^{-3}.$$

Example 8

Calculate the number of Frenkel defects per cubic metre in silver chloride at 350°C. The energy for defect formation is 1.1eV and the density of AgCl is 5.50 gcm⁻³ at 350°C. $A_{Ag} = 107.87 \, g/mol$ and $A_{Cl} = 35.45 \, g/mol.$

Solution

The equilibrium number of Frenkel defects,

$$N_{fr} = Ne^{\frac{-E_{fr}}{2kT}} \qquad\qquad \dots (1)$$

$$E_{fr} = 1.1eV$$

$$k = 8.62 \times 10^{-5} \, eVK^{-1}$$

$$T = 350 + 273 = 623 \, K$$

$$\frac{E_{fr}}{2kT} = \frac{1.1}{2 \times 8.62 \times 10^{-5} \times 623}$$

$$= 10.24 \qquad\qquad \dots (2)$$

$$e^{\frac{E_s}{2kT}} = e^{-10.24} = 3.53 \times 10^{-5}$$

The number of lattice sites,

$$N = \frac{\rho N_A}{A_{Ag} + A_{Cl}}$$

$$\rho = 5.50 \times 10^3 \, kgm^{-3}$$

$$A_{Ag} = 107.87 \times 10^{-3} \, kgmol^{-1}$$

$$A_{Cl} = 35.45 \times 10^{-3} \, kgmol^{-1}$$

$$\therefore \quad N = \frac{5.50 \times 10^3 \times 6.023 \times 10^{23}}{107.87 \times 10^{-3} + 35.45 \times 10^{-3}}$$

$$N = \frac{5.50 \times 6.023 \times 10^{29}}{107.87 + 35.45}$$

$$N = \frac{33.1265 \times 10^{29}}{143.32}$$

$$N = 2.311 \times 10^{28} \text{ lattice sites per } m^3$$

$$N_{fr} = 2.311 \times 10^{28} \times 3.57 \times 10^{-5}$$

$$= 8.25 \times 10^{23} \text{ defects/} m^3$$

Dislocations

We found that point defects are the irregularities or deviations from ideal arrangement around a point or an atom in the crystalline material.

Dislocations are the irregularities or deviations from ideal arrangement in entire row of lattice points.

Dislocations are called line defect since the defects are found

in a line. So it is a one dimensional imperfection. There are two basic types of dislocations: The edge dislocation and screw dislocation. Mixed dislocations, combining aspects of both types, are also common.

Edge dislocation

An edge dislocation is a defect where in extra half-plane of atoms is introduced midway through the crystal, distorting nearby planes of atoms.

Figure 4.4(a) shows a perfect crystal, the top figure showing a three dimensional view and the bottom one showing the atoms on the front face. A perfect crystal is considered to be made up of vertical planes parallel to one another and to the side faces. If one of these vertical planes does not extend from the top to the bottom of the crystal but ends partway within the crystal, as shown in figure 4.4(b), a dislocation is present.

In a perfect crystal, the atoms are in equilibrium positions and all the bond lengths are in equilibrium value. In an imperfect crystal on the right (figure 4.4(b)). The edge of the incomplete plane, the atoms are squeezed and are in a state of compression. The bond lengths have been compressed to smaller than the equilibrium value. Just below the edge, the atoms are pulled apart and are in a state of tension. The bond lengths have been stretched to above the normal values. The distorted configuration extends all along the edge in to the crystal. Thus as the region o

An incomplete plane in a crystal results
in an edge dislocation

Figure 4.4(a)   Figure 4.4(b)

maximum distortion is centred around the edge of the incomplete plane, this distortion represents a line imperfection and is called an edge dislocation.

Screw dislocation

Screw location is the defect of a crystal that results from a displacement of the atoms in one part of a crystal relative to the rest of the crystal, forming a spiral ramp around the dislocation line.

A screw dislocation is depicted in figure 4.5.

The figure shows what happens when one part of the crystal is displaced relative to the rest of the crystal and the displacement terminates within the crystal.
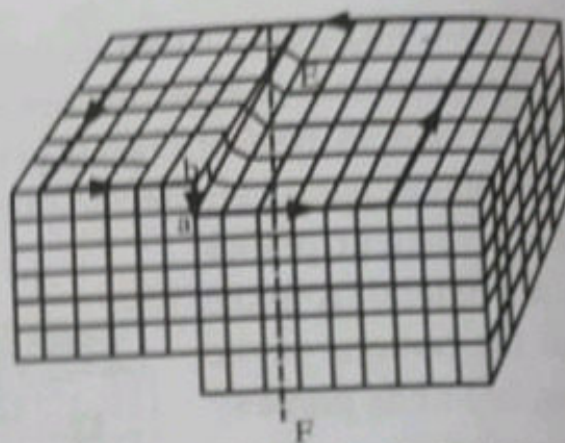
Figure 4.5: Screw dislocation

The row of atoms marking the termination of the displacement is the screw dislocation. EF indicates the dislocation line.

Burger's vector

The Burger's vector is a vector which indicates howmuch and in what direction the lattice above the slip plane has been shifted with respect to the lattice below the slip plane.

The Burgers vector is perpendicular to the edge dislocation. I is ab shown in figure 4.6(b).

In screw dislocation, the Burger's vector lies parallel to th dislocation line along the axis of a line of atoms in the same plan In the figure 4.5, vector ab is the Burger's vector.
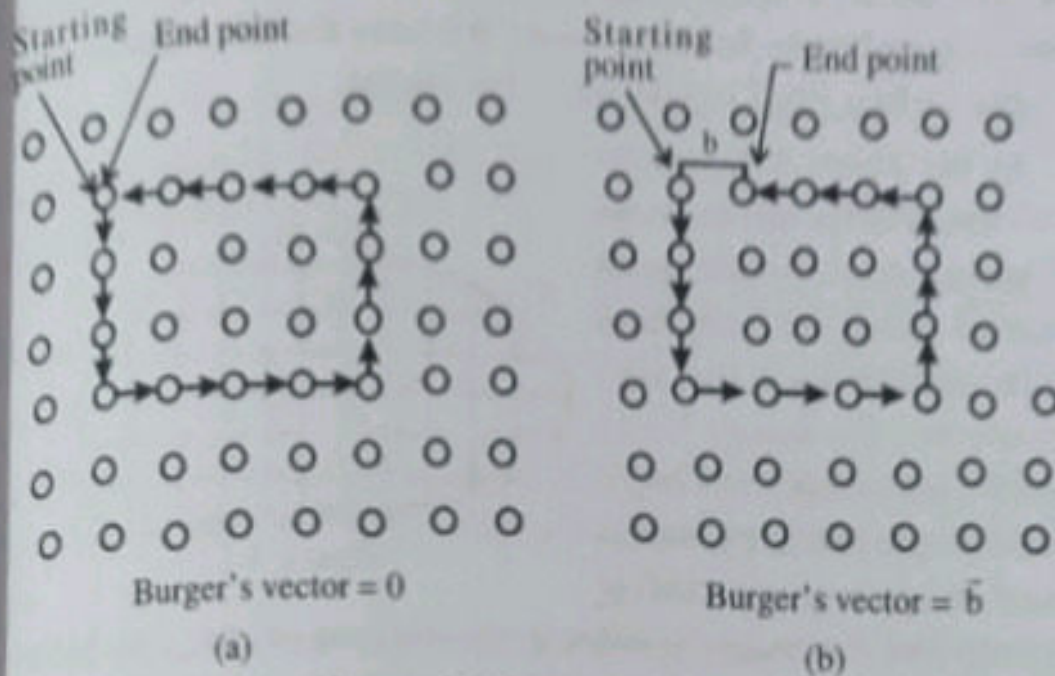
Figure 4.6: Burger's vector

Interfacial defects

In the last section, we dealt with line defects. No we discuss planer defects of crystals.

Planar defect (surface defect) is a discontinuity of a perfect crystal structure across a plane.

Interfacial defects are boundaries that have two dimensions and normally separate regions of the materials that have different crystal structures and / or crystallographic orientations.

Interfacial defects exist at an angle between two faces of a crystal. These imperfections include external surfaces, twin boundaries, grain boundaries, stacking faults and phase boundaries.

External surface defect

One of the most obvious boundaries is the external surface along which crystal structure terminates. Since all the crystals are of finite sizes, so there will be always on external surface of that crystal and this external surface itself a kind of defect. Or at the surfaces

the periodicity of the crystal is disrupted. External surface leads to breaking of bonds. In other words it breaks the lattice periodicity so the surface itself is a defect in the crystal.

In the figure 4.7, we can see that every inside atom forming four bonds with nearest atoms but each atom at the surface has not all four bonds but the bonds break and we know that breaking of bonds requires energy, so that extra energy is provided to the

External boundary of the crystal
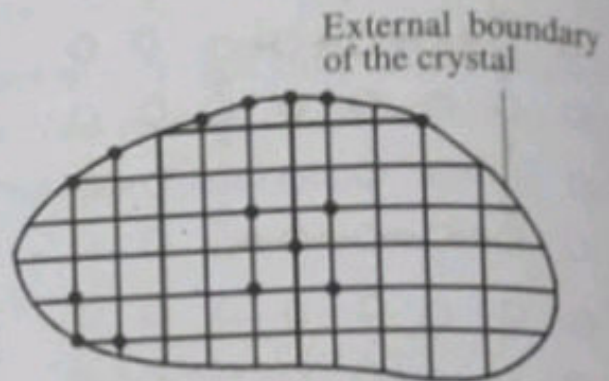
Figure 4.7

crystal and the energy resides in the surface atoms. The higher energy of the surface atoms is called surface energy of the crystal. This is called external surface defect

Grain boundary (defect)

Grain boundaries surface defect which separate crystals or grains of different orientation in a poly crystalline during crystalization or grain boundaries are the region of orientations mismatch. The shape of the grain is usually influence by the presence of surrounding grains. As a result, grain on one side of the boundary is rotated with respects the other side of the boundary grain. So

Grain boundary

Grain II

Grain I

Figure 4.8
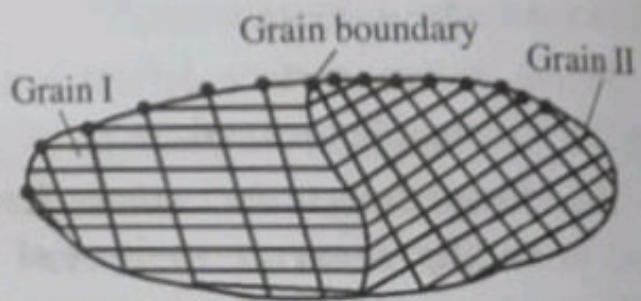
Grain boundary
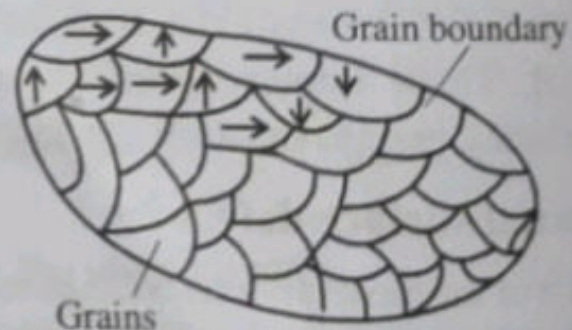
Grains

Figure 4.9: Poly crystal grain boundary

there is a rotation and the rotation is represented by a rotation axis and a rotation angle.

Classification of grain boundary is based on the magnitude of angle of rotation. There are two types. They are:

1. Small angle boundary

If the angle of rotation is small ($< 5°$) called small angle boundary.

2. Large angle boundary

If the angle of rotation is large ($> 5°$) called large angle boundary. There is another classification based on the relationship of rotation axis.

They are (1) Tilt boundary (2) Twist boundary.

If the rotation axis is parallel to the boundary is called tilt boundary. If the rotation axis is perpendicular to the boundary is called twist boundary. See figures below.
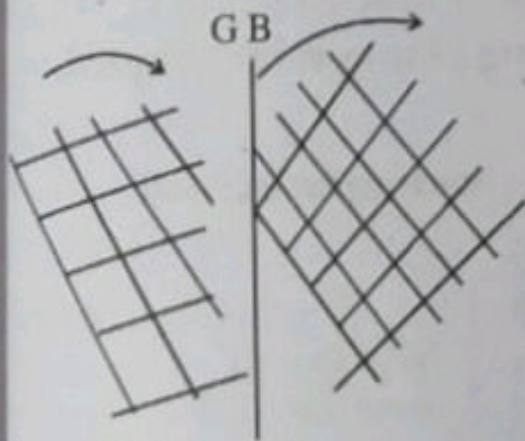
Figure 4.10(a): Tilt boundary   Figure 4.10(b): Twist boundary
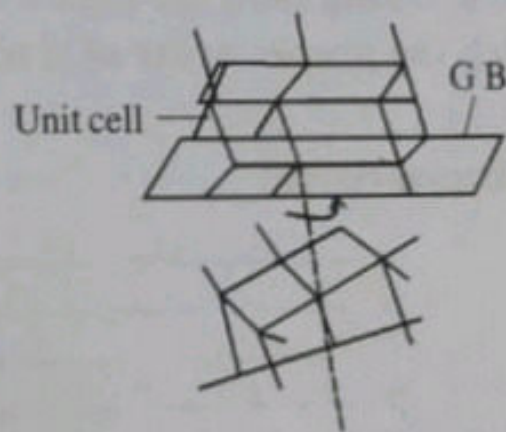
Twin boundaries

It is a boundary in a crystal such that crystals on either side are mirror images of each other.

C

B

A

C

B

A ──────── Mirror plane

C.......➤ B
B.......➤ C
A.......➤ A
C.......➤ B
B ➤ C

} Crystal structure

{ C
B
A
C
B }

{ Mirror image of the crystal above the plane }
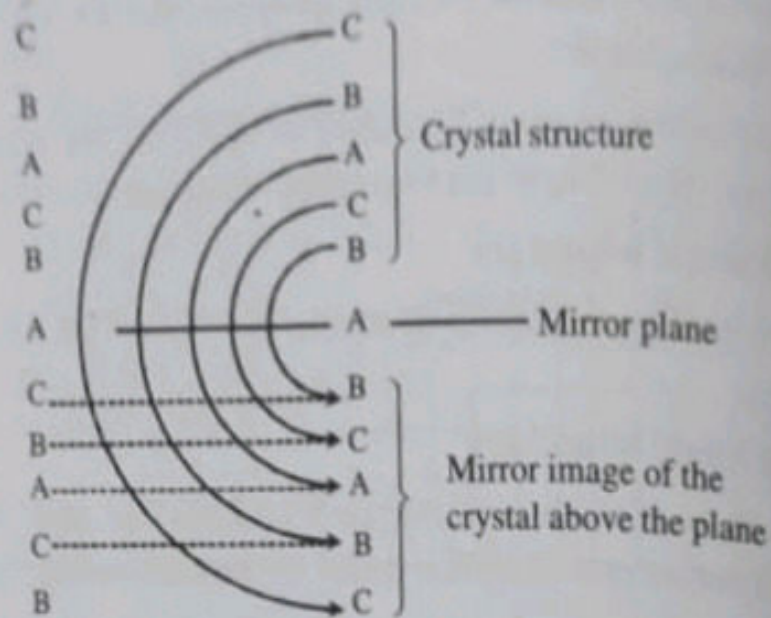
Figure 4.11: Twin boundary

Stacking faults

It is a fault in the stacking sequence of a crystal.

A stacking fault is a planar defect that occurs in crystals in which the proper order of stacking planes is interrupted.

Original crystals   **Stacking fault crystal**

```
        C
        B ...........................➤ C
        A ...........................➤ B
        C ...........................➤ A   } No change in
        B ...........................➤ C   }  orientation CCP
        A ...........................➤ B
           ◄..........................➤ A  ...... C- plane missing
           + fault                      B
        B                               A
        A                               C   } No change
        C                               B
        B                               A
        A                               C
```
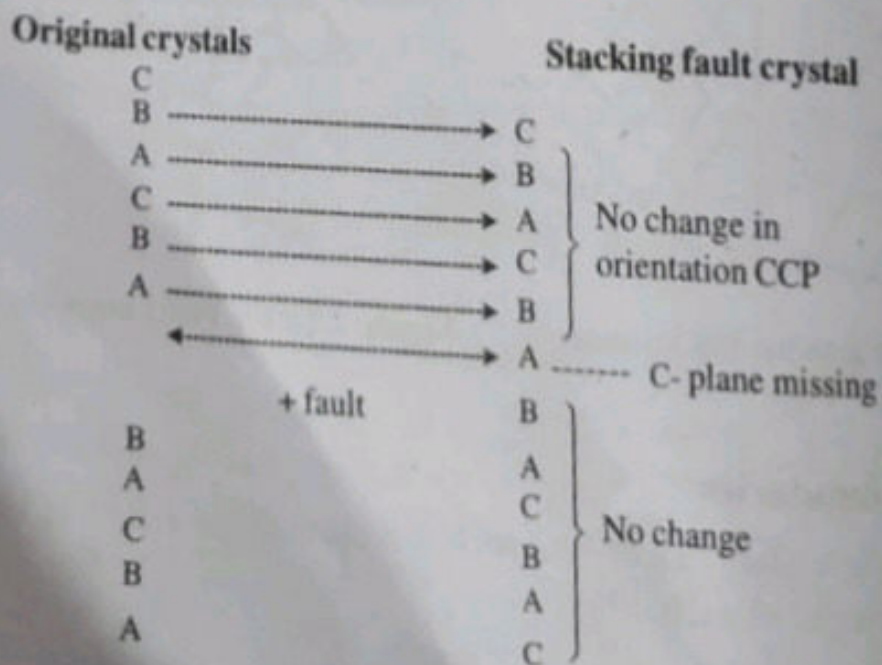
Figure 4.12: Stacking fault

Consider a crystal whose arrangement is CBACBACBA .... suppose one of the C-plane is missing (see figure 4.12). As a result of this missing C- plane the sequence of arrangements above the C-plane is translated down. However the arrangements below the C-plane is unaltered. This defect is called stacking fault.

Bulk or volume defects

Bulk or volume defects are three dimensional imperfections that occur in a crystal.

The volume defects are created by precipitates. Volume defects include voids, pores, crakes and foreign inclusions in crystalline materials. Pores can occur when a cluster of point defects combine together to form a three dimensional imperfection. This type of defect has a tremendous effect on the performance of materials.

Cracking arise when there is only small electrostatic dissimilarity between the stacking sequence of close packed planes in metals.

Foreign particles inclusions create large voids or non-crystalline regions which have the dimensions of at least 1 to 3nm are also called volume imperfections. When clusters of atoms are missing, a large vacancy or void is created which is also a volume imperfection.

Effects crystal imperfection

1. The addition of impurities (making imperfections) in the case of semiconductors increases the electrical conductivity. But in the case of metals it decreases the electrical conductivity.

2. The colour of a crystal is due to the selective absorption of some component of the visible spectrum by certain imperfections are called colour centres which are present in the crystal. These imperfections may be interstitial impurity atoms such as transition metal ions. Alternatively, they may be vacancies in the structure produced by deviations from stoichiometry so that there are present excess positive ions accom-

panied by negative vacancies or excess negative ions accompanied by positive vacancies. Thus when excess Zn is present in ZnO it takes a yellow colour. Excess lithium in LiF turns the crystal red. Excess potassium in KCl makes the crystal appear violet.

3. The imperfections account for

   (i) flow and future characteristics.

   (ii) crystal growth.

   (iii) diffusion mechanisms.

   (iv) creep characteristics of real metals and alloys.

   (v) annhealing and precipitation.

   (vi) oxidation and corrosion.

   (vii) yield strength, fracture strength plasticity, thermal conductivity, dielectric strength etc.

4. The defects influence the properties of the solids in the following different ways.

   (i) The defects may scatter conduction electrons in a metal, increasing its electrical resistance by several percent in many pure metals and much more in alloys.

   (ii) Some defects, even if present sparingly, decrease the strength of the crystal.

   (iii) Pure salts having impurities and imperfections are often coloured.

   (iv) Hysteresis loss of ferromagnets.

5. Imperfections do not always affect the properties of materials adversely. There are many situations in which controlled amount of imperfection can bring about specific characteristics desired in a crystal. For example carbon steel is a material whose properties are improved by imperfections in the cubic crystal structure of iron, increase the mechanical strength of iron.

UNIVERSITY MODEL QUESTIONS
Section A
(Answer in two or three sentences)

Short answer type questions

1. What is meant by the term imperfection in crystals?

2. Why the study of defects in crystals are important?

3. Classify the crystal defects on the basis of geometry.

4. Which are the point defects?

5. What is the effect of presence of vacancies in a crystal?

6. Write down an expression for the equilibrium number of vacancies in a crystal and explain the symbols used.

7. What is the effect of selfinterstitials in crystals?

8. Draw a schematic representation of a vacancy and a selfinterstitials.

9. What is solid solution? Mention two of its types.

10. Mention two features affecting the degree to which solute dissolves in solvent.

11. What is substitutional solid solution?

12. How does valency of metals influence in the formation of substitutional solid solution?

13. How does interstitial solution form?

14. Give an example of interstitial solid solution.

15. Give the schematic representations of substitutional and interstitial impurity atoms.

16. What is meant by the term "composition" of alloys?

17. Define the term "mass percent" in alloys.

18. Define the term "atom present" in alloys.

19. Write down the conversion formula from mass percent to atom percent and explain the symbols used.

20. Mention three point defects in crystals.

CHAPTER 5

DIFFUSION IN SOLIDS

Introduction

The term diffusion refers to the movement of atoms. Diffusion can take place in gases, liquids and solids. In solids, particularly diffusion occurs due to thermally activated random motion of atoms unless the material is at absolute zero temperature (zero kelvin), individual atoms keep vibrating and eventually move within the material. Diffusion in solids is a very slow process because the density of solids is very high as compared to liquids and gases. In materials science it is frequently necessitates the addition of other material to achieve desired properties. **This transfer of mass is accomplished by diffusion. Thus diffusion is defined as the phenomenon of material transport by atomic motion.** This chapter deals with the atomic mechanisms by which diffusion occurs, the mathematics of diffusion and the diffusing species on the rate of diffusion.

The phenomenon of diffusion may be demonstrated by taking two metals say copper and nickel. These two metal bars are joined together to have intimate contact between the two faces as shown in figure 5.1 (a). The combined system is called a diffusion couple. This couple is heated for a long period at a high temperature below the melting point of both and cool to room temperature. chemical analysis shows that pure copper and nickel are found at the extreme ends separated by an alloy region. Concentration of both metals found to vary with position. It is depicted in figure 5.2.
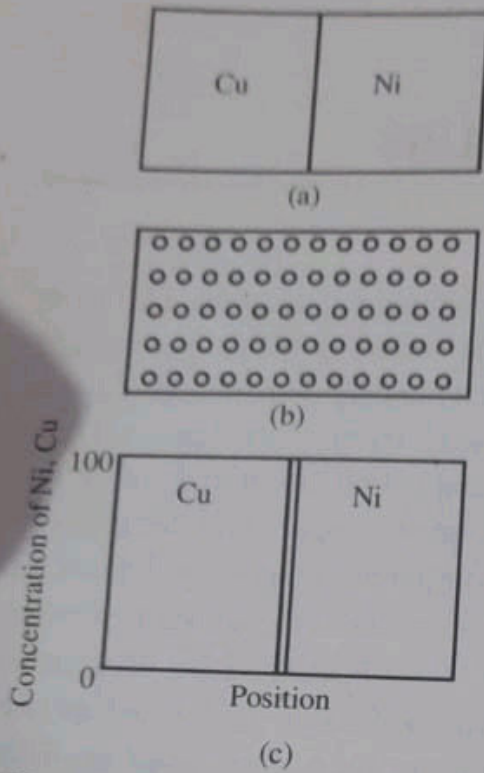
Figure 5.1: (a) A copper-nickel diffusion before a high-temperature heat treatment (b) Schematic representations of Cu (closed circles) and Ni (open circles) atom locations within the diffusion couple (c) Concentrations and nickel as a function of position across couple.
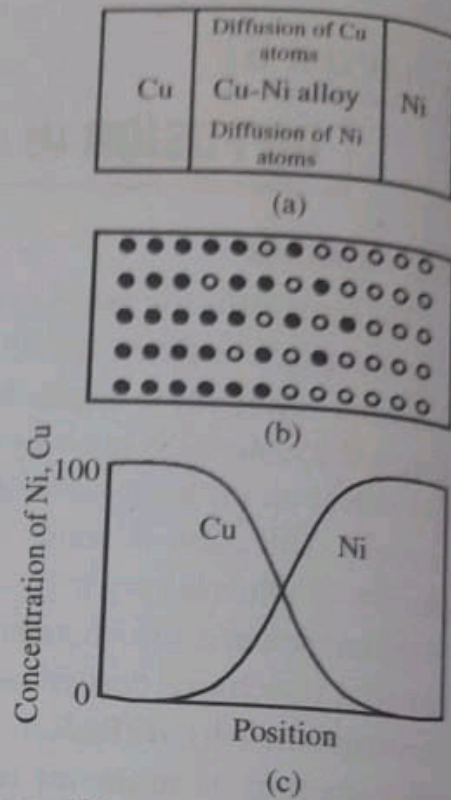
Figure 5.2: (a) A copper-nickel diffusion couple after a high-temperature heat treatment, showing the alloyed diffusion zone, (b) Schematic representations of Cu (closed circles) and Ni (open circles) atom locations within the couple, (c) Concentrations of copper and nickel as a function of position across the couple.

This implies that copper atoms have migrated or diffused into nickel and vice-versa. This process is called interdiffusion or impurity diffusion. Diffusion also occurs for a single crystal where atoms exchange their positions. This is termed as selfdiffusion.

Diffusion mechanisms

From atomic point of view, diffusion is the migration of atoms from lattice site to lattice site. Actually atoms in solid materials

are in constant motion i.e., rapidly changing positions. For an atom to make such a move, two conditions are to be satisfied. **They are 1) there must be an empty adjacent site and 2) the atom must have sufficient energy to break bonds with its neighbour atoms and then cause some lattice distortion during the displacement.** This energy is vibration in nature. At a specific temperature a small fraction of the total number of atoms is capable of diffusion due to its vibrational energy. This fraction increases with increasing temperature.

Several different models for this have been proposed. Here we discuss only two of them. They are :

1) vacancy diffusion and 2) interstitial diffusion.

Vacancy diffusion

Vacancy diffusion is a process by which an atom from a lattice site move to an adjacent vacancy site.

For this process to occur there must exist vacancies. Vacancies are due to defects. Thus vacancy diffusion is a function of number of vacancies available. We know that large number of vacancies are present when the metal is heated when an atom moves from a site to a vacancy, a vacancy is produced at the former position of the atom. In other words we can say that vacancies change their

Motion of a host or
substitutional atom
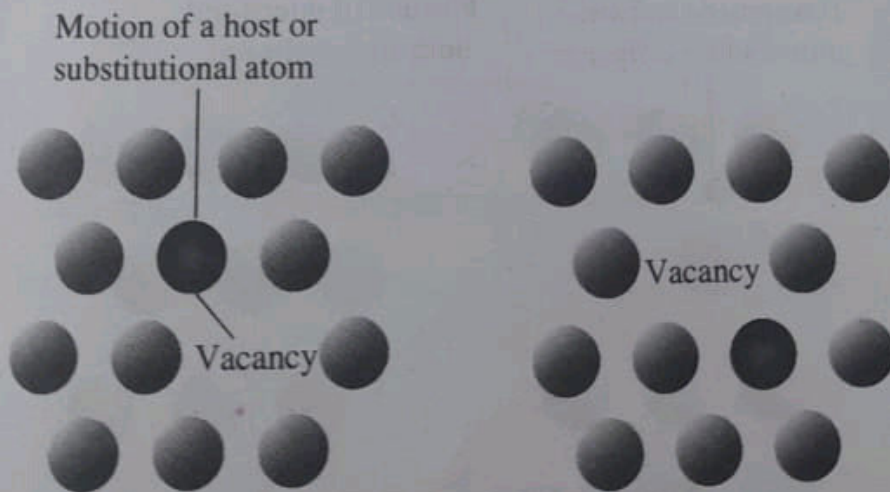
Figure 5.3: Schematic representations of vacancy diffusion

positions. Diffusion of atoms in direction corresponds to the motion of vacancies in the opposite direction. Diffusion may occur in the same metal known as self diffusion, for this impurity atom must be substituted for host atoms. Atoms of one metal can also move to another metal kept in contact. This is known as interdiffusion process. This is depicted in figure 5.3.

Interstitial diffusion

Interstitial diffusion is a process by which an atom migrates from one interstitial position to a neighbouring interstitial position that is vacant.

This type of mechanism is found for interdiffusion of impurities such as hydrogen, carbon, nitrogen, oxygen etc. This is because these atoms are small enough to fit into the interstitial positions. Substitutional impurity atoms, creating self diffusion, rarely go for interstitial diffusion.

In most metal alloys interstitialdiffusion occurs much faster than vacancy diffusion since interstitial atoms are smaller and thus more mobile. i.e., the probability of occurrence of interstitial diffusion is more comparing to vacancy diffusion.

The schematic representation of interstitial diffusion is depicted in figure 5.4.
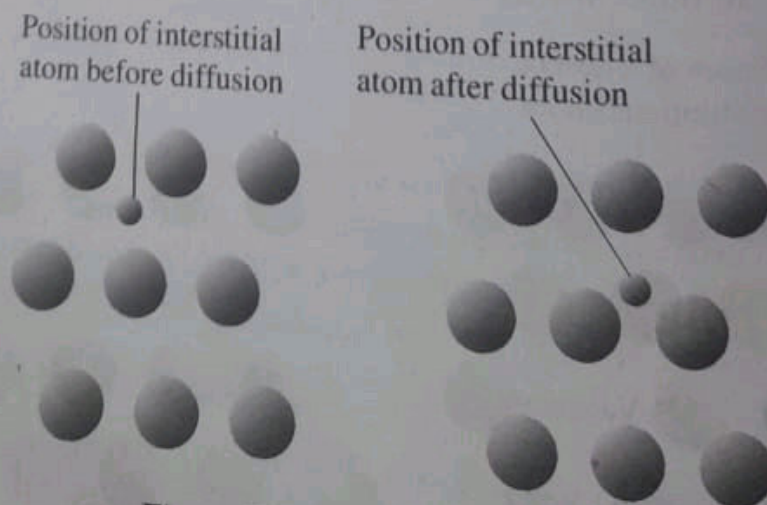
Figure 5.4: Interstitial diffusion

Steady state diffusion

We found that diffusion is a process of transfer of atoms. In a macroscopic sense it is a transfer of mass. Hence diffusion is a time dependent process. So often it needs to know the rate of mass transfer. This is usually expressed as diffusion flux (J). **It is defined as the mass (M) or number of atoms diffusing** through unit area perpendicular to the surface in unit time.

i.e.,
$$J = \frac{M}{At} \qquad ..... (1)$$

Where M is the mass that diffuses in time t through an area A. In differential form equation (1) can be put in the form.

$$J = \frac{1}{A}\frac{dM}{dt} \qquad ..... (2)$$

Its unit is $kgm^{-2}s^{-1}$ or atoms $m^{-2}s^{-1}$.

If the diffusion flux does not change with time it is known as steady state physically the steady state condition is attained when the concentration of the diffusing species on both sides of an alloy are held constant.

If C_1 and C_2 are the concentrations at positions x_1 and x_2 respectively, then the concentration gradient

$$= \frac{C_1 - C_2}{x_1 - x_2}$$

In differential form concentration gradient $= \dfrac{dC}{dx}$

Thus diffusion flux

$$J \propto \frac{dC}{dx}$$

or

$$J = D\frac{dC}{dx}$$

Where D is called diffusion coefficient.

In the above expression there is a mathematical inconsistency. On the L.H.S diffusion takes from higher concentration to lower concentration (decreasing), but on the L.H.S $\frac{dC}{dx}$ is increasing, since the derivative is positive. So to make the equation mathematically consistent we put a negative sign.

Thus $$J = -D\frac{dC}{dx} \qquad \dots (3)$$

The unit of D is m^2s^{-1}. Equation (2) is called Fick's first law.

Nonsteady state diffusion

If the diffusion flux $D\frac{dC}{dx}$ changes with position and the concentration gradient changes with time, diffusion is said to be non-steady state. Thus the governing equation is a partial differential equation as C is a function of x and t.

$$\frac{dC}{dt} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right)$$

or $$\frac{dC}{dt} = D\frac{\partial^2 C}{\partial x^2} \qquad \dots (4)$$

It is known as Fick's second law.

A physically meaningful solution to the partial differential will be obtained by specifying the appropriate conditions (two). The solution to eq (4) is found to be

$$C(x, t) = A - B\, \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \qquad \dots (5)$$

where $\operatorname{erf}\left(\dfrac{x}{2\sqrt{Dt}}\right)$ is called the Gaussian error function. This function is defined as

$$\operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = \frac{2}{\sqrt{\pi}} \int_{0}^{\frac{x}{2\sqrt{Dt}}} e^{-y^2}\,dy$$

At $x = 0,\ \operatorname{erf}(0) = 0$

At $x = \infty$

$$\operatorname{erf}(\infty) = \frac{2}{\sqrt{\pi}} \int_{0}^{\infty} e^{-y^2}\,dy$$

$$= \frac{2}{\sqrt{\pi}} \frac{\sqrt{\pi}}{2} = 1$$

At $x = -\infty$

$$\operatorname{erf}(\infty) = \frac{2}{\sqrt{\pi}} \int_{0}^{-\infty} e^{-y^2}\,dy = -1$$

where $\displaystyle\int_{0}^{\infty} e^{-y^2}\,dy = \frac{\sqrt{\pi}}{2}$ is used (see example 3).

While solving the partial differential equation (4), the following assumptions are made

1. Before diffusion, diffusing solute atoms in the solid atoms are uniformly distributed with concentration C_0.

2. The value of x at the surface is zero and increases with distance into the solid.

3. The time is taken to be zero the instant before the diffusion process begins. These boundary conditions are stated as

For $t = 0$, $C = C_0$ $0 \leq x \leq \infty$

For $t > 0$, $C = C_s$ at $x = 0$

C_s is the constant surface concentration

and $C = C_0$ at $x = \infty$.

Now we can apply these conditions to the solution eq (5).

For $t = 0$, $C = C_0$, eq (5) gives

$$C(x, 0) = C_0 = A - B \, \mathrm{erf}(\infty)$$

$$\therefore \qquad C_0 = A - B \qquad\qquad\qquad \ldots\ldots (6)$$

For $t > 0$, $C = C_s$ at $x = 0$, eq (5) gives

$$C(0, t) = C_s = A - B \, \mathrm{erf}(0)$$

$$C_s = A \qquad\qquad (\because \quad \mathrm{erf}(0) = 0) \qquad \ldots\ldots (7)$$

$$\therefore \qquad C(x, t) - C_0 = A - B \, \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right) - (A - B)$$

$$C(x, t) - C_0 = B - B \, \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$C(x, t) - C_0 = B\left(1 - \mathrm{erf}\frac{x}{2\sqrt{Dt}}\right)$$

or

$$\frac{C(x, t) - C_0}{B} = 1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$\frac{C(x, t) - C_0}{A + B - A} = 1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$\frac{C(x, t) - C_0}{A - (A - B)} = 1 - erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$\frac{C(x, t) - C_0}{C_s - C_0} = 1 - erf\left(\frac{x}{2\sqrt{Dt}}\right) \qquad \text{..... (8)}$$

This gives the solution. Knowing C_0 and C_s, $C(x, t)$ is the concentration at depth x after a time t can be calculated.

Note : Error function values can be taken from error function tables.

If we want to evaluate the specific concentration of a salute say

$$C(x, t) = C_1$$

then $\dfrac{C_1 - C_0}{C_s - C_0}$ the L.H.S of eq (8) becomes a constant so R.H.S

should also be a constant.

i.e., $$\frac{x}{2\sqrt{Dt}} = \text{constant}$$

or $$\frac{x^2}{Dt} = \text{constant} \qquad \text{..... (9)}$$

Usually an alloy say iron-carbon has a uniform carbon concentration. For some applications, it is necessary to harden the surface of alloy. This can be accomplished by increasing the surface concentration. This process is called carburization. For this alloy is exposed at an elevated temperature to an atmosphere rich in a hydrocarbon gas such as methane CH_4. The time of exposition can be calculated by using eq (8). see example 1.

Note : The boundary condition stated above where the surface concentration is held constant is well suited for semi-infinite solid. A bar of solid is considered to be semi-solid

if none of the diffusing atoms reaches the bar end during the time over which diffusion takes place.

Example 1

An alloy (iron-carbon) has a uniform concentration of 0.25 mass% and is to be treated at 950°C. If the concentration of carbon at the surface is suddenly brought to an maintained at 1.20 mass%, how long will it take to achieve a carbon content of 0.80 mass% at a position 0.5mm below the surface. $D = 1.6 \times 10^{-11} m^2 s^{-1}$. The error function z corresponding to 0.4210 is 0.392.

Solution

$$\left.\begin{array}{l} C_0 = 0.25 \text{ mass\% of C} \\ C_S = 1.20 \text{ mass\% of C} \\ C(x, t) = 0.80 \text{ mass\% of C} \\ x = 5 \times 10^{-4} m \\ D = 1.6 \times 10^{-11} m^2 s^{-1} \\ t = ? \end{array}\right\} \text{given}$$

From eq (8), we have

$$\frac{C(x, t) - C_0}{C_S - C_0} = 1 - erf\left(\frac{D}{2\sqrt{Dt}}\right)$$

Substituting all the values, we get

$$\frac{0.8 - 0.25}{1.2 - 0.25} = 1 - erf\left(\frac{5 \times 10^{-4}}{2\sqrt{1.6 \times 10^{-11} t}}\right)$$

$$L.H.S = \frac{0.55}{0.95} = 0.579$$

$$0.579 = 1 - erf\left(\frac{5 \times 10^{-4}}{2\sqrt{1.6 \times 10^{-11} t}}\right)$$

$$\text{erf}\left(\frac{5\times10^{-4}}{2\sqrt{1.6\times10^{-11}t}}\right)=1-0.579=0.421$$

$$\text{erf}\left(\frac{62.5}{t^{\frac{1}{2}}}\right)=0.421$$

$$\text{erf}\left(\frac{62.5}{t^{\frac{1}{2}}}\right)=\text{erf}(0.392)\ \text{gives}$$

$$\frac{62.5}{t^{\frac{1}{2}}}=0.392$$

$$t=\left(\frac{62.5}{0.392}\right)^2=24520.72\ s$$

$$t=\frac{24520.72}{60\times60}\ \text{hours}$$

$$t=7.06\ \text{hours}$$

Note : Usually error function is calculated from error function tables.

Example 2

The diffusion coefficients for copper in aluminium at 500 and 600°C are 4.8×10^{-14} and $5.3\times10^{-13}\ m^2s^{-1}$ respectively. Determine the approximate time at 500°C that will produce the same diffusion result as a 10 hour heat treatment at 600°C.

Solution

We know that while achieving specific concentration of solute,

$\frac{x}{2\sqrt{Dt}}$ is a constant.

i.e., $$\frac{x_1}{2\sqrt{D_1 t_1}} = \frac{x_2}{2\sqrt{D_2 t_2}}$$

But $x_1 = x_2$ given

$$\therefore \qquad D_1 t_1 = D_2 t_2$$

$$D_{500} t_{500} = D_{600} t_{600}$$

or $$t_{500} = \frac{D_{600} t_{600}}{D_{500}}$$

$$t_{500} = \frac{5.3 \times 10^{-13} \times 10}{4.8 \times 10^{-14}} = 110.4 h.$$

Example 3

Show that erf $(\infty) = 1$

Solution

By definition

$$erf(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-y^2} dy$$

$$\therefore \qquad erf(\infty) = \frac{2}{\sqrt{\pi}} \int_0^{\infty} e^{-y^2} dy$$

Let $$I = \frac{2}{\sqrt{\pi}} \int_0^{\infty} e^{-y^2} dy \qquad\qquad ..... (1)$$

or $$I = \frac{2}{\sqrt{\pi}} \int_0^{\infty} e^{-x^2} dx \qquad\qquad ..... (2)$$

Eq (1) × Eq (3) gives

$$I^2 = \frac{4}{\pi} \int_0^\infty \int_0^\infty e^{-(x^2+y^2)} dx\, dy$$

Put $x = r\cos\theta$, $y = r\sin\theta$

$$x^2 + y^2 = r^2$$

∴ and $dx\, dy = r\, dr\, d\theta$.

Here r goes from 0 to ∞ and θ goes from 0 to $\pi/2$. Hence

$$I^2 = \frac{4}{\pi} \int_0^\infty \int_0^{\pi/2} e^{-r^2} r\, dr\, d\theta$$

$$I^2 = \frac{4}{\pi} \int_0^{\pi/2} d\theta \int_0^\infty e^{-r^2} r\, dr$$

$$I^2 = \frac{4}{\pi} \cdot \frac{\pi}{2} \int_0^\infty e^{-r^2} r\, dr$$

$$I^2 = 2 \int_0^\infty e^{-r^2} r\, dr$$

Put $r^2 = t$, then $2r\, dr = dt$

..... (1)

$$I^2 = 2 \int_0^\infty e^{-t} \frac{dt}{2} = \int_0^\infty e^{-t} dt$$

..... (2)

$$I^2 = [-e^{-t}]_0^\infty = [-e^{-\infty} - -e^{-0}]$$

$$I^2 = 0 + 1 = 1$$

$$\therefore \qquad I = 1$$

i.e., $\qquad$ erf $(\infty) = 1$

Example 4

From the given error function table, evaluate z corresponding to erf 0.421.

z	erf(z)
0.35	0.3794
z	0.4210
0.40	0.4284

Solution

From the given table, we have

$$\frac{z - 0.35}{0.40 - 0.35} = \frac{0.4210 - 0.3794}{0.4284 - 0.3794}$$

$$\frac{z - 0.35}{0.05} = \frac{0.0416}{0.049}$$

$$z - 0.35 = 0.8489 \times 0.05$$

$$z - 0.35 = 0.42445$$

$$\therefore \qquad z = 0.392$$

Factors that influence diffusion

In diffusion process (steady state as well as non-steady state) the diffusion coefficient plays a major role because it is an indication of the rate at which diffusion takes place. There are two factors which influence diffusion coefficient. They are 1) species and 2) temperature. The diffusing species as well as host materials influence D. It is found that there is significant difference in magnitude between self diffusion and interstitial diffusion.

Another influencing factor is temperature. When temperature is increased diffusion coefficient is found to increase.

The temperature dependence of the diffusion coefficient is given by

$$D = D_0 e^{\frac{-E_d}{RT}}$$

..... (10)

Where D_0 is the diffusion coefficient at 0K, E_d is the activation energy for diffusion, R is the universal gas constant and T is the temperature in kelvin.

Activation energy is defined as the energy required to produce the diffusion motion of one mole of atoms. It is measured in J/mol or eV/atom.

A table of diffusion data (D_0 and D) at various temperatures for different metals are given below.

Table 5.1 Diffusion Data

Host Metal	D_0(m²/s)	Activation Energy E_d		Calculated Values	
		kJ/mol	eV/atom	T(°C)	D(m²/s)
α-Fe (BCC)	2.8×10^{-4}	251	2.60	500 / 900	3.0×10^{-21} / 1.8×10^{-15}
γ-Fe (FCC)	6.0×10^{-5}	284	2.94	900 / 1100	1.1×10^{-17} / 7.8×10^{-16}
α-Fe	6.2×10^{-7}	80	0.83	500 / 900	2.4×10^{-12} / 1.7×10^{-10}
γ-Fe (FCC)	2.3×10^{-5}	148	1.53	900 / 1100	6.9×10^{-12} / 6.3×10^{-11}
Cu	7.8×10^{-5}	211	2.19	500	4.2×10^{-19}
Cu	2.4×10^{-5}	189	1.96	500	4.0×10^{-18}
Al	2.3×10^{-4}	144	1.49	500	4.2×10^{-14}
Al	6.5×10^{-5}	136	1.41	500	4.1×10^{-14}
Al	1.2×10^{-4}	131	1.35	500	1.9×10^{-13}
Ni	2.7×10^{-5}	256	2.65	500	1.3×10^{-22}

Taking natural log on both sides of equation (10), we get

$$\ln D = \ln D_0 - \frac{E_d}{RT} \qquad \ldots\ldots (11)$$

Since D, D_0, E_d and R are constants, it gives a straight line on the graph $\ln D$ versus $\frac{1}{T}$.

$$Y = mx + C$$

$$m = -\frac{E_d}{R} \text{ slope of the y-x graph}$$

$$C = \ln D_0, \text{ y-intercept of y-x graph.}$$

It shows that from $\ln D$ versus $\frac{1}{T}$ graph, we can calculate D_0 and E_d.

The plot of the logarithm of the various diffusion coefficient versus the reciprocal of absolute temperature is given below in figure 5.5.
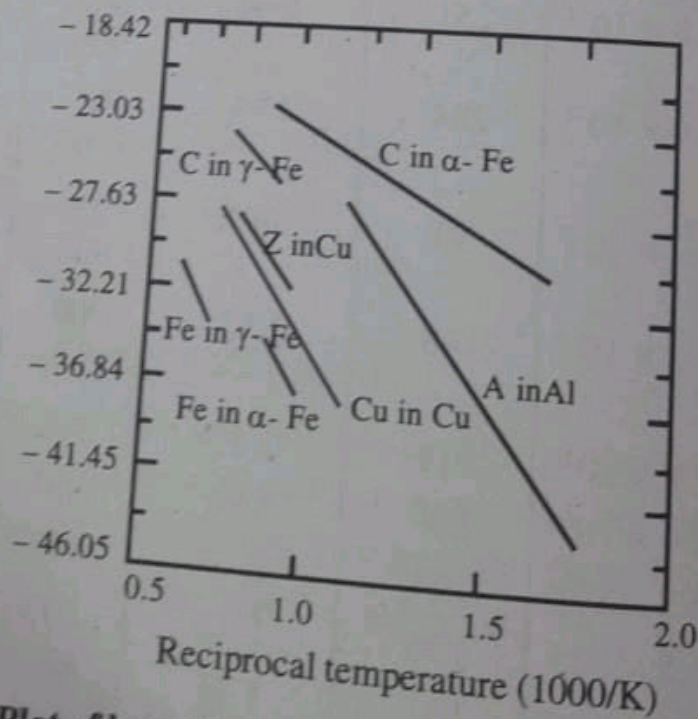
Figure 5.5: Plot of logarithmic diffusion coefficient versus $\frac{1}{T}$

Example 5

Calculate the diffusion coefficient of Zn in Cu at 500°C.

$$D_0 = 2.4 \times 10^{-5} m^2 s^{-1}, E_d = 1.96 \text{ eV/atom}.$$

Solution

We have $D = D_0 e^{\frac{-E_d}{RT}}$

$$R = 8.62 \times 10^{-5} eV / atom - K$$
$$T = 500 + 273 = 773K$$

$$D = 2.4 \times 10^{-5} k e^{\frac{-1.96}{8.62 \times 10^{-5} \times 773}}$$

$$D = 2.4 \times 10^{-5} \times e^{-29.42}$$

$$= 2.4 \times 10^{-5} \times 1.67 \times 10^{-13}$$

$$= 4.0 \times 10^{-18} m^2 s^{-1}.$$

Example 6

Compute the diffusion coefficient of carbon in γ-Fe at 900°C. $D_0 = 2.3 \times 10^{-5} m^2 s^{-1}$ and $E_d = 1.53 eV / atom$.

Solution

Using $D = D_0 e^{\frac{-E_d}{RT}}$

$$D = 2.3 \times 10^{-5} \times e^{\frac{-1.53}{8.62 \times 10^{-5} \times 1173}}$$

$$D = 2.3 \times 10^{-5} \times e^{-15.132}.$$

$$D = 2.3 \times 10^{-5} \times 2.68 \times 10^{-7}$$

$$D = 6.16 \times 10^{-12} m^2 s^{-1}.$$

Example 7

Calculate the activation energy for the diffusion of copper in gold from the following data

$$D_1 = 3.981 \times 10^{-13} \, m^2 s^{-1} \text{ at } 1250K$$

$$D_2 = 3.548 \times 10^{-16} \, m^2 s^{-1} \text{ at } 909K.$$

Solution

We have

$$D = D_0 e^{\frac{-E_d}{RT}}$$

$$D_1 = D_0 e^{\frac{-E_d}{RT_1}} \qquad \qquad \cdots (1)$$

$$D_2 = D_0 e^{\frac{-E_d}{RT_2}} \qquad \qquad \cdots (2)$$

$\dfrac{Eq(1)}{Eq(2)}$ gives

$$\frac{D_1}{D_2} = e^{\frac{E_d}{R}\left(\frac{-1}{T_1} + \frac{1}{T_2}\right)}$$

Substituting the values of D_1 D_2, T_1 and T_2, we get

$$\frac{3.981 \times 10^{-13}}{3.548 \times 10^{-16}} = e^{\frac{E_d}{R}\left(\frac{-1}{1250} + \frac{1}{909}\right)}$$

$$1.122 \times 10^3 = e^{\frac{E_d}{R} \times 3 \times 10^{-4}}$$

Taking natural log on both sides, we get

of copper in

$$\ln(1.122 \times 10^3) = \frac{E_d}{R} \times 3 \times 10^{-4}$$

$$7.023 = \frac{E_d \times 3 \times 10^{-4}}{R}$$

$$E_d = \frac{7.023 \times R}{3 \times 10^{-4}}$$

$$E_d = \frac{7.023 \times 8.62 \times 10^{-5}}{3 \times 10^{-4}}$$

$$E_d = 2.02\,eV/atom.$$

.... (1)

Aluminium for integrated circuit interconnects

.... (2)

Here we discuss how does the study of diffusion process in metals enabled us to construct sophisticated integrated circuits which are essential for computers. Integrated circuit (IC) chip is a thin square wafer having dimensions of 6mm × 6mm × 4mm. In this millions of interconnected electronic components and circuits are embedded. Usually an IC is made of silicon, to which specific and extremely minute and controlled impurities are added. For some ICs the impurities are added using high temperature diffusion process. To connect the various electronic components IC has to be provided with conducting paths to facilitate the passage of current flow. These paths are called interconnects. To have high electrical conductivity for these paths suitable materials must be chosen. Silver, copper, gold and aluminium are highly conductive materials. On the basis of conductivities silver is the best choice and aluminium is the last choice.

After having done the deposition of interconnects, it is necessary to subject the IC chip to other heat treatments where the temperature goes up to 500°C. At this temperature silver has significant diffusion

from the interconnects into the silicon, as a result interconnects will be destroyed. To overcome this difficulty we have to select a material which has low diffusion coefficient material in silicon. Among the conductive materials aluminium has least diffusion coefficient. So aluminium is the best material for interconnects.

Copper interconnects are also used to fabricate ICs.

Diffusion in ionic materials

The diffusion process in ionic materials is more complicated than that for metals. This is because ionic materials contain two types of ions of opposite charge. Both of them will take part in diffusive motion. Usually diffusion in ionic materials occur by vacancy diffusion maintaining charge neutrality. In order to maintain charge neutrality, the following may be said about vacancies. 1) ion vacancies occurring pairs 2) they form in non-stiochiometric compounds and 3) they are created by substitutional impurity ions having different charge states than host ions. The diffusive motion of a single ion is associated wills transference of charge. In order to maintain localised charge neutrality in the vicinity of this ion, it is necessary that another species having an equal and opposite charge accompany the ion's diffusive motion. These charged species include another vacancy. As a result of this the rate of diffusion of these pairs is limited by the diffusion rate of the slowest moving species.

When an external electric field is applied across an ionic solid, the charged ions diffuse to the respective polarity of the electric field. This ionic motion gives rise to an electric current.

Since the electrical conductivity is a function of diffusion coefficient, much of the diffusion data for ionic solids come from electrical conductivity of metals.

Diffusion in polymeric materials

Here our aim is to study the diffusive motion of small foreign molecules such as O_2, H_2O, CO_2, CH_4 methane etc through

polymers. The diffusive motion of chain of atoms within the polymer, ofcourse, take place. A polymers permeability and absorption characteristics relate to the degree to which foreign substances diffuse into the material. This will tend to chemical reactions of polymers and degradation of foreign materials.

The diffusive motion of foreign materials takes place through amorphous as well as crystalline regions. The rate of diffusion is more in the first. This is because amorphous regions are more open. This diffusive motion is considered to be analogous to interstitial diffusions in metals. i.e., in polymers diffusive motion occurs through small voids between polymer chains from one open amorphous region to an adjacent open one.

Two more points to be noted. If the size of the foreign molecule is smaller the diffusion rate is faster. The other is that if the foreign molecules are inert than that react with polymer the diffusion rate is faster.

The diffusion flux (J) of gas through a polymeric material having thickness Δx, is directly proportional to the pressure gradient $\dfrac{\Delta P}{\Delta x}$.

i.e.,
$$J \propto \frac{\Delta P}{\Delta x}$$

or
$$J = -P_M \frac{\Delta P}{\Delta x} \qquad \dots (12)$$

where P_M is called permecibility coefficient and ΔP is the difference in pressure across the polymeric material. This is nothing but the modified form of Fick's first law.

The permeability coefficient P_M can be approximated as the product of diffusion coefficient (D) and the solubility (S) of the diffusing species in the polymer. This is valid only for small molecules in nonglassy polymers.

..... (13)

i.e., $P_M = DS$

The unit of P_M is $cm^3 STP) cm / cm^3 - sPa$

This has several applications in everyday life. Polymeric materials are used to food and beverage packing, an to mobile tyres filled with gas, to separate one chemical species from another. Using Fick's law (eq-12) we can calculate the diffusion thereby gives information how long does the diffusing species intact.

For example plastic bottles are used for soda. Soda contains CO_2 dissolved in water. The CO_2 molecules slowly diffuse through the polymeric bottle. Using Fick's first law we can calculate how long the bottle can hold CO_2. (see example 8).

Example 8

A soda bottle has a surface area of $500 cm^2$ and wall thickness of 0.05cm containing $750 cm^3$ of CO_2. The pressure of CO_2 inside and outside are 400kPa and 0.4kPa respectively.

$$P_M = 0.23 \times 10^{-13} (cm^3 STP)(cm) / cm^2 s\, Pa$$

$$P_1 = 0.4kPa = 400\,Pa$$

$$P_2 = 400kPa = 400,000\,Pa$$

$$\Delta P = P_4 - P_2 = -399600\,Pa$$

$$\Delta x = 0.05cm$$

$$P_M = 0.23 \times 10^{-13}$$

Using $J = -P_M \dfrac{\Delta P}{\Delta x}$

$$J = -0.23 \times 10^{-13} \times \frac{-399600}{0.05}$$

$$= 1.83 \times 10^{-7}.$$

The flow rate of CO_2 through the wall of bottle.

$$V_{CO_2} = JA = 1.83 \times 10^{-7} \times 500$$

$$= 9.15 \times 10^{-5} \, cm^3/s$$

∴ The time taken by 750cm³ CO_2 (V) through the bottle is

$$t = \frac{V}{V_{CO_2}} = \frac{750}{9.15 \times 10^{-5}}$$

$$t = \frac{750 \times 10^5}{9.15} = 81.97 \times 10^5 \, s$$

$$t = 2276.94 \ hours$$

$$t = \frac{2276.94}{24} \ days$$

$$t = 94.9$$

$$t = about\ 3\ months.$$

UNIVERSITY MODEL QUESTIONS
Section A
(Answer questions in two or three sentences)

Short answer type

1. What is meant by diffusion?
2. What is the cause of diffusion in metals?
3. What is self diffusion?
4. What are the two condition to be satisfied for atomic diffusion ?
5. Mention two models of diffusion type.
6. What is meant by vacancy diffusion?
7. What is interstitial diffusion?

CHAPTER 6

CERAMICS AND ITS PROPERTIES

Introduction

Ceramics are nonmetallic inorganic substances, which are brittle and have good thermal and electrical insulating properties. Most ceramics are compounds between metallic elements and nonmetallic elements for which the interatomic bonds are predominantly ionic but having some covalent character. The term ceramic comes from the Greek word keramikos which means "burnt stuff" indicating that desirable properties of these materials are normally achieved through a high temperature heat treatment process called firing.

Human have found applications for ceramics for the past 30,000 years. Every day new and different applications are being discovered. This truly makes ceramics a stone age material with space age qualities. Ceramics can be divided into two classes: traditional and modern. Ceramics the primary raw material is clay is considered to be traditional. Some traditional ceramics are

1. Porcelain

It is developed in China. Heating a clay mineral known as Kaolin in a kiln, a type of oven. It is strong, hard durable and resistant to chemicals, heat and thermal shock. Combines well with glazes and paints. porcelain is a white material that provides an excellent base for decorative pottery and art much like white paper porcelain was an expensive material that was considered as the most prestigious form of pottery. It is still used today for premium table ware and decorative items. Porcelain is also used as an electric

insulating material in equipments such as power transformers and in construction components such as bathroom fixtures.

2. Bone china

It is exclusively produced in U.K. It is a type of porcelain made with bone as a key ingredient. It is considered as premium material due to its history of being manufactured in U.K to produce high quality tableware and ornamental items.

3. Earthenware

It is made with selected clays and other materials and is not heated to the point of vitrification that gives porcelain and other ceramics their glassy, translucent and nonporus properties. Earthenware is opaque, porus and is softer than porcelain.

It has low mechanical strength and can easily chipped and scratched. Requires less energy to produce than most other ceramics and is relatively inexpensive. An opaque colour that is often similar to clay with browns, reds and oranges being common. Earthenware must be glazed to be watertight. It is used to make inexpensive tiles and pottery such as flower pots.

4. Stoneware

Stoneware is fired at a temperature above earthenware but below porcelain. This results in a vitreous or semivitreous ceramic that is watertight but not as translucent and white as porcelain.

Stoneware is often valued for its earthy look and relative strength as compared to earthenware. Its properties are similar to porcelain apart from its appearance. Stoneware is used to make both expensive and inexpensive pottery and tiles.

5. Glass ceramics

A ceramic produced with a process of controlled crystallization that has properties similar to glass with the strength and durability of ceramics. Glass ceramics are created with advanced manufacturing processes that produce materials with desirable traits

such as high mechanical strength, zero porosity, durability, translucency, low thermal expansion, high temperature stability, high chemical durability, biocompatiability and superconductivity.

It is used to make cooktops, cookware, bakeware medicinal devices, scientific and industrial equipment.

6. Fired bricks

Bricks produced by heating minerals such as sand and clay are ceramics.

In general they are durable, heavy, brittle and can withstand high temperatures. It is used to make walls, landscaping, fire places and chimneys.

Note: Silicon is a ceramic material due to its chemical properties. Silicate materials are extremely abundant as they make up about 90% of the Earth's crust. Clays and sand that are used to create common ceramics are silicon based. For example, the kaolinite used to make porcelain and the silica used to make fired bricks are silicate materials.

After significant progress has been made in understanding the fundamental character of these materials and of the phenomena that occur in them that are responsible for their unique properties a new generation of these materials has evolved and termed as modern ceramics or simply ceramics.

On the basis of their applications ceramics materials divided into six. They are (1) glasses (2) clay products (3) refractories (4) abrasives (5) cements and (6) advanced ceramics. Further the glasses are subdivided into two: glasses and glass ceramics. Clay products are subdivided into two: structural clay products, refractories are subdivided into four: fire clay, silica, basic and special. The classification is shown in figure 6.1.
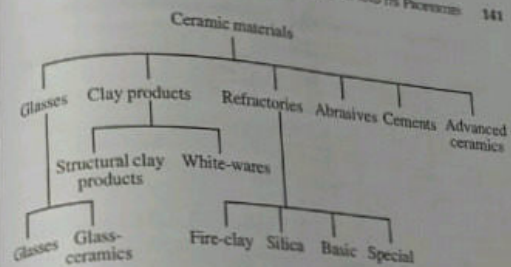
Figure 6.1: Classification of ceramic materials on the basis of application

Now we discuss each ceramic material one by one.

Glasses

Glasses come under the general name ceramics. Glasses are noncrystalline silicates (SiO_2) containing small amount of other oxides such as Na_2O (soda), CaO (Lime), Al_2O_3, B_2O_3, K_2O, MgO, TiO_2 and Al_2O_3. The addition of oxides influences the properties of glass. Some familiar glasses are soda lime glass, Borosil glass, crown glass, flint glass, fibre glass etc. A typical sodalimeglass consists of about 74 mass % of SiO_2, 16 mass % Na_2O, 5 mass % CaO and 1 mass % Al_2O_3. The compositions of several common glass materials and their characteristics and uses are given in table 6.1. Glasses are relatively easy to make and are optically transparent. They are used as containers, lenses, fibreglass etc.

Table 6.1: Compositions and characteristics of some glasses

Glass type	Composition (Mass %)						Characteristics and applications
	SiO_2	Na_2O	CaO	Al_2O_3	B_2O_3	Other	
Fused silica	>99.5						High melting temperature, very low coefficient of expansion (thermally shock resistant)
96% Silica (Vycor)	96				4		Thermally shock and chemically resistant – laboratory ware
Borosilicate (Pyrex)	81	3.5		2.5	13		Termally shock and chemically resistant – ovenware
Container (soda-lime)	74	16	5	1		4MgO	Low melting temperature, easily worked also durable
Fibre glass	55		16	15	10	4MgO	Easily drawn into fibres – glass resin composites
Optical flint	54	1				37PbO, 8K₂O	High density and high index of refraction – optical lenses
Glass-ceramic (Pyroceram)	43.5	14		30	5.5	6.5TiO₂, 0.5As₂O₃	Easily fabricated, strong, resists thermal shock – ovenware

Glass-Ceramics

Glass-ceramics are fine grained polycrystalline material.

Glass-ceramics are made from noncrystalline glasses by subjecting it to proper high temperature heat treatment called crystallization. It is due to crystallization small glass ceramic grains are produced. The transformation from noncrystalline state to crystalline state is a phase transformation. To promote crystallization process usually titanium dioxide is added in the glass during heat treatment.

Characteristics

1. They have high mechanical strengths
2. Low coefficients of thermal expansion which avoids thermal shock.
3. Able to withstand relatively high temperatures.
4. Good dielectric properties.

5. Glass ceramics are made optically transparent or opaque.
6. Easy to fabricate.

Uses

Glass-ceramics are manufactured commercially under the trade names of Pyroceram, Corningware, Cercor and Vision. The most common uses for these materials are as ovenware tableware, ovenwindows and range tops. This is possible because of their strength, high temperature withstand capability and its resistance to thermal shock.

2. They are used for electronic packaging because of their good dielectric property.

3. In printed circuit boards glass-ceramics are used as substrates and as electrical insulators.

4. Used for architectural cladding and for heat exchangers and regenerators.

Clay products

One of the most important ceramic raw materials is clay. When clay is mixed with water in the proper proportions, we get a plastic mass that is very amenable to shaping. The formed piece is dried to remove some of the moisture. After that it is fired at an elevated temperature to improve its mechanical strength. We get clay products. Clay products are broadly classified into two: the structural clay products and the whitewares. Structural clay products include building brick, paving brick, terra-cotta facing tile, roofing tile and drainage pipe.

Whiteware is any of a broad class of ceramic products that are white to off-white in appearance and contains a significant vitreous and glass component.

Clay is the most important of the ingredients of making whitewares. The clay used in whiteware products is kaolin also known as china clay from which a white, translucent vitreous

ceramic can be made. It can be fired at high temperatures without deforming. It imparts whiteness to the finished ware. Kaolin is formed principally from the mineral kaolinite, a hydrous aluminosilicate with a fine, platy structure china clays are composed of mostly of well ordered kaolinite with no impurities. Lower grade whitewares are usually made of ball clalys which contains ordered and disordered kaolinite plus other clay minerals and impurities. These impurities particularly iron oxides render the fired ware off white to gray or tan in colour.

Whitewares include porcelain, pottery, tableware, china and sanitary ware.

Refractories

Refractories is one of the classes of ceramics which is resistant to decomposition by heat, pressure and chemical attack and retains strength and form at high temperatures. Refractories are polycrystalline, polyphase, inorganic, nonmetallic, porus and heterogeneous. They are composed of oxides or carbides, nitrides etc. of the following materials: silicon, aluminium, magnesium, calcium, boron, chromium and zirconium.

Refractory materials are used in furnaces, kilns, incinerators and reactors. They are also used to make crucibles and moulds for casting glass and metals. Depending upon the composition of materials in refractory ceramic their performance vary. Based on this refractory material is classified into four namely fireclay, silica, basic and special refractories.

Fireclay refractories

The primary ingredients for the fireclay refractories are high purity fireclays. It has mainly two components namely Al_2O_3 and SiO_2. 25 to 45 mass % alumina and 75 to 55 mass % of silica. The manufacturing process involves four steps, raw material processing, forming, firing and final processing. The resulting product can

withstand high temperature up to 1587°C. Upgrading the alumina content will increase the maximum withstand temperature.

They are used to make fire clay bricks used in furnace construction to confine hot atmospheres and to thermally insulate structural members from excessive temperatures. For fireclay bricks strength is not important because support of structural loads is not usually required.

Silica refractories

It is also called as acid refractories. The prime ingredient of silica refractories is silica. Silica materials can withstand high temperature. They are used in the arch roofs of steel and glass making furnaces. They are also used as containment vessels because they are resistant to slags that are rich in silica.

Basic refractories

The refractories that are rich in periclase or magnesia (MgO) are termed basic. They may also contain calcium, chromium and iron compounds. The presence of silica adversely affect their high temperature performance. Basic refractories are especially resistant to attack by slags containing high concentrations of MgO and CaO and find extensive use in some steel making hearth furnaces.

Special refractories

High purity oxide materials such as Al_2O_3, SiO_2, MgO, BeO, ZrO_2 which are having little porosity are special refractories. Carbon, graphite and siliconcarbide are also special refractories. Siliconcarbide has been used for electrical resistance heating elements, as a crucible material and in internal furnace components. Though carbon and graphite are very refractory but find limited application because they are susceptible to oxidation in excess of about 800°C.

Abrasives

Abrasives are ceramic materials, often minerals, that is used to

shape or finish a work piece through rubbing, which leads to part of the work piece to worn away by friction. While finishing a material often means polishing it to gain a smooth, reflective surface, the process can also involve roughening as in satin or beaded finishes. In short the ceramics which are used to cut, grind and polish other softer materials are known as abrasives.

Abrasives are hard, tough and are not easily fracture.

Diamonds both natural and synthetic are used as abrasives. However they are relatively expensive. The more common ceramic abrasives are silicon carbide, tungsten carbide, aluminium oxide and silica sand. These are used in a wide variety of industrial, domestic and technological applications.

In grinding wheels abrasives are coated by means of an organic resin. Another example we are familiar with sand paper. Here abrasives (sands) are coated on special type of paper or cloth material. This is used to polish wood, metals and other ceramics.

Cements

Cement, plaster of paris and lime come under a group ceramics and classified as inorganic cements. When these materials is mixed with water, they form a paste that subsequently sets and hardens. It is useful in the construction of solid and rigid structures in any shape. When mixed with water chemical reaction takes place and they become a single cohesive structure. Unlike refractory materials, cements create strong chemical bonding at room temperature.

Of this group of materials portland cement is extensively used. It is produced by grinding and intimately mixing clay and lime bearing minerals in the proper proportions and then heating the mixture to about $1400°C$ in a rotary kiln. This process is called calcination. This produces physical and chemical changes in the raw materials. The resulting product called clinker is then grind into a very fine powder to which a small amount of gypsum

$(CaSO_4 \cdot 2H_2O)$ to retard the setting process. This product is portland cement. The properties of portland cement including setting time and strength depends on its composition.

Several different constituents are found in portland cement. Two of them are tricalcium silicate $(3CaO \cdot SiO_2)$ and the other one is dicalcium silicate $(2CaO \cdot SiO_2)$.

When water is added to portland cement hydration reaction begins, the hydrated products are in the form of gels that form the cementitious bond. These are first manifested as setting which takes places soon after mixing, usually within several hours. Hardening of the mass follows as a result of further hydration, a relatively slow process that may continue for long years. It may be noted that the process by which cement hardens is not one of drying but further hydration process which water actually participates in a chemical bonding reaction.

Portland cement is also called as hydraulic cement because its hardness develops by chemical reaction with water. Other cement materials such as lime are nonhydraulic because compounds other than water such as CO_2 are involved in the hardening process.

Advanced ceramics

The term advanced ceramics refers to all the products made from inorganic, high purity compounds through a series of specialised manufacturing processes.

Alumina, aluminium nitride, zirconia, silicon carbide, silicon nitride and titanium based materials are examples of advanced ceramics.

Advanced ceramics can be used for purposes due to their permeability, electric and magnetic properties, insulation, conduction, etc. Furthermore advanced ceramics are utilised in optical fibre communications systems, in microelectro mechanical systems (MEMS), as ball bearings, and in applications that exploit the piezoelectric behaviour of a number of ceramic metals. We

will discuss optical fibres, ceramic ball bearings and piezoelectric ceramics.

Optical fibres

Optical fibre is a new and advanced ceramic material that is used in our modern communication systems. The optical fibre is made of extremely high purity silica, which must be free of even minute levels of contaminants and other defects that absorb, scatter and attenuate a light beam. Very advanced and sophisticated processing techniques have been developed to produce fibres that meet the rigid restrictions required for this application.

Ceramic ball bearings

Another important application of advanced ceramic material is in ball bearings. A bearing consists of balls and races that are in contact with rub against one another when in use. In the past both ball and race components have been made of bearing steels that are very hard, extremely corrosion resistant and may be polished to a very smooth surface finish over past decade or so silicon nitride (Si_3N_4) balls have begun replacing steel balls in a number of applications, since several properties of Si_3N_4 make it a more desirable material. In most instances races are still made of steel, because its tensile strength is superior to that of silicon nitride. This combination of ceramic balls and steel races is termed hybrid bearing.

Advantages of ceramic ball bearings over traditional ball bearings

1. The hybrid ball bearing weighs less than the conventional ball bearing. This is because the density of Si_3N_4 (3.2 gcm^{-3}) is less than steel (7.8 gcm^{-3}).

2. The centrifugal loading is less in the hybrids because of its small mass; as a result they may operate at higher speeds (about 20% - 40% more).

3. The Si_3N_4 balls are more rigid than steel balls since the modulus of elasticity of Si_3N_4 is higher. Because of this Si_3N_4 undergoes lower deformation.

4. Since Si_3N_4 is harder than steel its lifetime is longer.

5. Silicon nitrides have superior strength than steel, silicon nitride undergoes lower wear rates.

6. Since the coefficient of friction of Si_3N_4 is 30% that of steel, Si_3N_4 produces less heat due to friction. This increases the grease life.

7. Ceramic materials are more corrosion resistant than metal alloys, the silicon nitride balls may be used in more corrosive environments and at higher operating temperatures.

8. Si_3N_4 is an insulator and steel is a conductor. Because of this ceramic bearing are immune to arcing damage.

Uses of ceramic bearings

1. The hybrid bearings are used in line skates, bicycles, electric motors, machine tool spindles, precision medical hand tools.

2. They are used in textile industry.

3. Used for food processing and also for chemical equipments.

However there are some challenges in making the silicon nitride bearing material. They are

1. processing technique to yield a pore-free material.

2. fabrication of spherical pieces that require minimums of machining.

3. polishing technique to produce a smoother surface finish than steel balls.

Piezoelectric ceramics

Some ceramic materials exhibit the phenomenon of piezoelectricity. **When a material is subjected to a mechanical strain an electric field (voltage) is developed in the material.**

This phenomenon is called piezoelectric effect. The inverse piezo electric is also displayed by these materials. When a material is subjected to an electric field (voltage), a mechanical strain is developed in the material called inverse piezoelectric effect.

Piezoelectric materials may be used as transducers between electrical mechanical energies. A transducer is a device converts variations in pressure into an electrical signal or vice versa. One of the uses of piezoelectric ceramics was in SONAR. SONAR stands for sound navigation and ranging. It works on the principle of reflection method. Here ultrasonic waves are sent through ocean from a transmitter. These waves get reflected back from the objects such as rock, submarine in their path, if any. The reflected waves travel back and received by the detector. Note the time difference between the transmitting wave and the receiving wave say t. Using the formula

$$distance = speed \times time$$

$$2s = vt \text{ or } s = \frac{vt}{2}$$
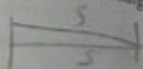
knowing v, the speed of sound wave the distance s can be calculated.

A piezoelectric crystal is caused to oscillate by an electric signal which produces high frequency mechanical vibrations that are transmitted through ocean. Upon encountering an object, these signals are reflected back and another piezoelectric material receives this reflected vibrational energy, which it then converts back into an electrical signal. Distance from the ultrasonic source and reflecting body is determined from the elapsed time between sending and receiving signals.

Other applications of that used piezoelectric devices are found in automotive, computer and medical sectors. Some of these applications are automotive wheel balances, seat belt buzzers, tread-wear indications keyless door entry and airbag sensors in vehicles.

They are also used in computers as microactuators for hand disks and notebook transformers, in ink-jet printing heads, ultrasonic welders and smoke detectors. In medical field they are used in insulin pumps, ultrasonic therapy and in ultrasonic cataract removal devices.

Commonly used piezoelectric ceramics are barium titanate, lead zirconate, lead zirconate-titanate and potassium niobate.

Stress-strain behaviour of materials

Breaking strength of a material

Breaking strength is the ability of a material to withstand load. It is measured in force per unit area. i.e. stress (σ).

$$\sigma = \frac{F}{A} \qquad \qquad —(1)$$

Its unit is pascal (Nm^{-2}). Higher units MPa (10^6 Pa) or GPa (10^9 Pa) are used to measure stress.

There are three ways in which the load may be applied namely
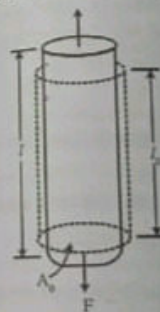
Figure 6.2(a)

Schematic illustration of how a tensile load produces an elongation and positive linear strain. Dashed lines represent the shape before deformation; solid lines, after deformation
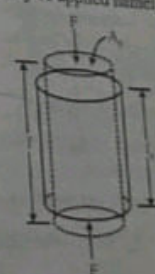
Figure 6.2(b)

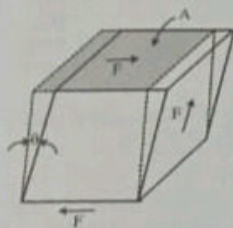Schematic illustration of how a compressive load produces contraction and a negative linear strain

Figure 6.2(c)

Schematic representation of
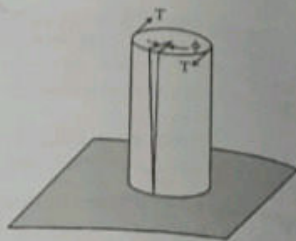shear strain γ, where
$\gamma = \tan \theta$

Figure 6.2(d)

Schematic representation of tor-
sional deformation (i.e., angle of
twist ϕ) produced by an applied
torque T.

tension, compression or shear. See the figure 6.2 (a, b and c). Many loads produce torsion rather than shear. It is depicted in 6.2 (d). Corresponding to each load there exist a breaking stress. If the load is tension the corresponding breaking stress is called tensile strength. If the load produces compression the corresponding breaking stress is called compressive strength and so on.

Tensile strength

Tensile strength indicates the resistance of a material to breaking under tension.

Tensile strength is measured as the maximum stress $\left(\sigma_u = \frac{F}{A}\right)$ **that a material can support without fracture**

To study the mechanical behaviour of a material we perform stress-strain test.

If a load is static or changes slowly with time and is applied uniformly over a cross section, the mechanical behaviour of the material may be ascertained by a simple stress-strain test. One of

the most important common mechanical stress-strain tests is performed in tension called tension test.

Tension test

This test is performed to find the breaking stress of metallic materials. The test is performed as follows. A specimen material is subjected to a gradually increasing tensile load that is applied uniaxially along the long axis of the specimen. A standard tensile specimen is shown in figure 6.3. Normally the cross of the specimen is circular, but rectangular specimens are also used. This specimen configuration was chosen so that, during testing, deformation is confined to the narrow centre region and also to reduce the likelihood of fracture at the ends of the specimen.
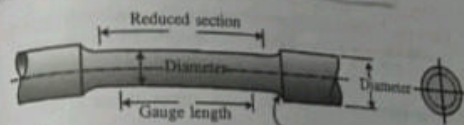
Figure 6.3: A standard tensile specimen with circular cross section

The specimen is mounted by its ends into the holding grips of the testing apparatus (see figure 6.4). The tensile testing machine is designed to elongate the specimen at a constant rate.

Note down the instantaneous applied loads and the corresponding elongations. Continue the process till the specimen is permanently deformed and usually fractured. The output of such a tensile test is recorded as load versus elongation.
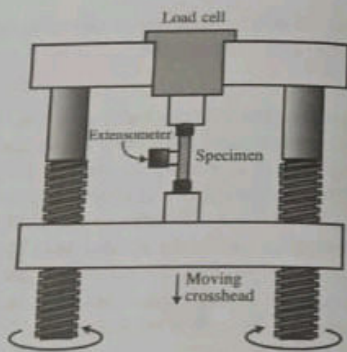
Figure 6.4: Schematic representation of the apparatus used to conduct tensile stress-strain tests. The specimen is elongated by the moving crosshead

From these observations we can draw stress-strain graph

$$\text{stress,} \quad \sigma = \frac{F}{A} \quad\quad \text{..... (2)}$$

$$\text{strain,} \quad \varepsilon = \frac{\Delta l}{l} \quad\quad \text{..... (3)}$$

From the graph we can find out the tensile breaking strength along with other several useful informations.

Stress-strain behaviour of ceramics

Flexural strength

The stress-strain behaviour of brittle ceramics cannot be understood by a tensile test because of three reasons.

1. It is difficult to prepare test specimens having the required property.

2. It is difficult to grip brittle materials without fracturing them.

3. Ceramics fail after only about 0.1% strain, which necessitates that tensile specimens be perfectly aligned to avoid the bending stresses, which are not easily calculated.

To overcome these difficulties we go for measuring its flexural strength. Flexure meaning the action of bending.

Flexural strength also known as modulus of rupture or bend strength or transverse rapture strength is a material property defined as the stress in a material just before it yields in a flexure test.

OR

Flexural strength is the ability of the material to withstand bending forces applied perpendicular to its longitudinal axis.

The transverse bending test is most frequently employed in which a specimen having either a circular or rectangular cross section is bent until fracture using a three point flexural test technique.

For a rectangular sample under load in a three point bending set up is shown in figure 6.5.
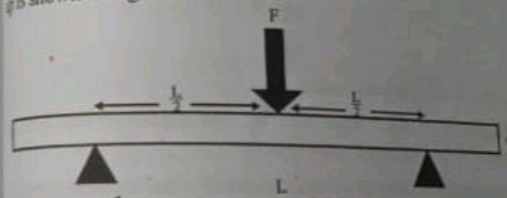
Figure 6.5

By definition

Flexural strength,

$$\sigma_{fs} = \text{stress} = \frac{Mc}{I}$$
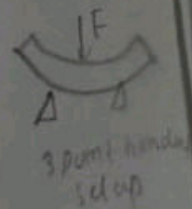
where M is the maximum bending moment, c is the distance from the centre of specimen and I is the geometrical moment of inertia.

For rectangular specimen

$$M = \frac{FL}{4}, \quad c = \frac{d}{2}$$

$$I = \frac{bd^3}{12},$$

where b is the breadth and distance thickness of the specimen.

$$\therefore \quad \sigma_{fs} = \frac{3FL}{2bd^2} \qquad \cdots (4)$$

Similarly for circular cross section

$$M = \frac{FL}{4}, \quad c = R$$

$$I = \frac{\pi R^4}{4}$$

$$\therefore \quad \sigma_{fs} = \frac{FL}{\pi R^3} \qquad \cdots (5)$$

where R is the specimen radius.

Equations 4 and 5 show that we can calculate the flexural strength by conducting flexure test.

Characteristic flexural strength values of some ceramic materials are given in table 6.2.

Table 6.2: Flexural strength and modulus of elasticity

Material	Flexural Strength (MPa)	Modulus of Elasticity (GPa)
Silicon nitride (Si_3N_4)	250-1000	304
Zirconia (ZrO_2)	800-1500	205
Silicon carbide (SiC)	100-820	345
Aluminum oxide (Al_2O_3)	275-700	393
Glass-ceramic (Pyroceram)	247	120
Mullite ($3Al_2O_3$-$2SiO_2$)	185	145
Spinel ($MgAl_2O_4$)	110-245	260
Magnesium oxide (MgO)	105	225
Fused silica (SiO_2)	110	73
Soda-lime glass	69	69

Elastic behaviour

From the data available from the flexure test we obtain several values of strain and stress. Using these draw a graph between strain on the horizontal axis and stress on the vertical axis. This gives us the elastic stress-strain behaviour of ceramic material.

Since $\dfrac{\text{stress}}{\text{strain}}$ gives modulus of elasticity, it is given by the slope of the stress-strain graph.

From the graph is seen that stress and strain relationship is linear which is analogous to tensile test results for metals. A typical stress-strain behaviour to fracture for aluminium oxide and glass are given in figure 6.6 for comparison. The corresponding breaking is marked as (x) in the figure. From the graph it can also be noted that neither material experiences plastic deformation prior to fracture.

(breaking point)
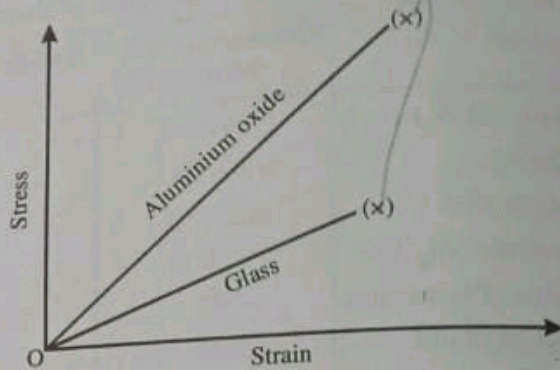
Figure 6.6: Stress-strain behaviour

Modulus of elasticity for several ceramic materials are also given in table 6.2.

UNIVERSITY MODEL QUESTIONS

Section A

(Answer questions in two or three sentences)

Short answer questions

1. What is meant by firing process?
2. Why new ceramics are termed as stone age material with space age qualities?
3. Classify ceramics.
4. What is porcelain?
5. What is bone china?
6. What are the uses of porcelain?
7. What are the uses of earthenware?
8. What is stoneware?
9. What are the uses of stoneware?
10. What is glass ceramics?

11. What are th
12. Give two u
13. What are tl
14. Classify m
15. What are g
16. Give exan
17. What are t
18. What are t
19. Write dov
20. Classify c
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22. Write dov
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35. Give ar
36. What a
37. What a
38. What i
39. What a
40. What i

CHAPTER 7

POLYMERS AND ITS PROPERTIES

Introduction

In chapter 1, we classified materials into metals, ceramics and polymers. Here we discuss the material carbon. Carbon has various polymorphic forms such as graphite, diamond, graphene and fullerenes. This group of materials does not fall within any of the above class. Graphite is sometimes classified as ceramics. The diamond, one of the polymorphs of carbon exhibits the structure of zinc blends which is a crystal. Here we confine our attention to the structure and characteristics of different polymorphs of carbon.

Diamond

Diamond is one of the polymorphic forms of carbon at room temperature and atmospheric pressure. Its crystal structure is similar to that of zinc sulphide in which carbon atoms occupy all positions (both Zn and S). The unit cell of diamond is shown in figure 7.1. In this structure each carbon atom bonds to four other carbon atoms and these bonds are totally covalent. This is called the diamond cubic crystal structure. Germanium, silicon and graytin show the same crystal structure below 13°C.

Figure 7.1: A unit cell for the diamond cubic crystal structure

Physical properties of diamond

1. It is the hardest known material.

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Uses

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Graphite

Graphit
structure is
more stabl

2. It has very low electrical conductivity.

   The above two properties are due to its crystal structure and the strong interatomic covalent bonds.

3. It has an unusually high thermal conductivity and is optically transparent in the visible and infrared regions of electromagnetic spectrum.

4. It has a high refractive index of refraction.

Uses

1. Diamonds are utilised to grind or cut other soft materials. Example is glass cutter.

2. Relatively large diamond single crystals are used as gem stones.

Synthetic diamonds produce techniques have been developed in the industry. Most of the diamonds available in the market are man-made ones.

Recently techniques to produce diamond thin films have been developed. The very interesting thing is that the optical properties of diamond films approach those of the bulk diamond material. These properties enabled us to produce new and better products. For example, the surfaces of drills, dies, bearings, knives and other tools have been coated with diamond films to increase surface hardness. Some lenses have been made stronger while remaining transparent by the application of diamond coatings. Diamond coatings also have been applied to loud speaker tweeters and to high precision micrometers. Another very important application of diamond films is to coat on the surface of machine components such as gears, optical recording heads and disks.

Graphite

Graphite is another polymorphic form of carbon. Its crystal structure is distinctly different from that of diamond and is also more stable than diamond at ambient temperature and pressure.

The graphite structure composed of layers of hexagonally arranged carbon atoms. Within the layers each carbon atom is bonded to three coplanar neighbour atoms by strong covalent bonds. The fourth bonding electron participates in a weak vander Waals types of bond between the layers.

Properties

1. As a consequence of these weak interplanar bonds, interplanar cleavage is facile which gives rise to the excellent lubricative properties of graphite.

2. The electrical conductivity is relatively high in crystallographic directions parallel to the hexagonal sheets.

3. Another important property of graphite is its high strength and chemical stability at elevated temperatures.

4. Graphite has high thermal conductivity, low coefficient of thermal expansion and high resistance to thermal shock.

Uses

1. It is used as heating elements for electric furnaces, as electrodes for arc welding

2. Graphites are used in casting molds for metal alloys and ceramics.

3. They are used in high temperature refractories.

Figure 7.2: The structure of graphite

4. Graphites are also used for electrical contacts, such as electrodes in batteries.

The structure of graphite is given above.

Fullerenes

Hary Kroto and Richard Smalley around 1980 discovered a new class of carbon material called carbon 60 (C_{60}). It is another polymorphic form of carbon. It exists in discrete molecular form and consists of a hollow spherical cluster of sixty carbon atoms; a single molecule is denoted by C_{60}. Each molecule is composed of groups of carbon atoms that are bonded to one another to form both hexagon (six carbon atoms) and pentagon (five carbon atoms) geometrical configurations. One such molecule is shown in figure 7.3.
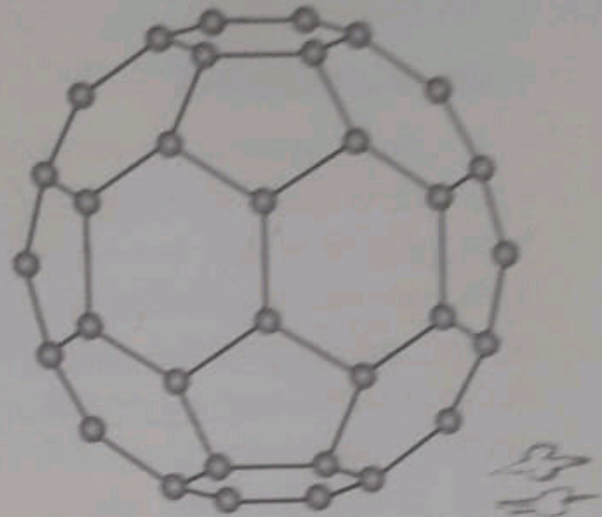
Figure 7.3: The structure of C_{60} molecule

A single C_{60} molecule altogether consists of 20 hexagons and 12 pentagons, which are arrayed such that no two pentagons share a common side. Thus the surface of this molecule exhibits the symmetry of a soccer ball. The material composed of C_{60} molecules is known as buckminsterfullerene, named in honour of R. Buckminster Fuller who invented the geodesic dome; each C_{60} is simply a molecular replication of such a dome which is often referred to as "buckyball" for short. The term fullerene is used to denote the class of materials that are composed of this type of molecule. The C_{60} units form a crystalline structure and pack together in a face-centred cubic array. The fullerene material is electrically insulating. However with proper impurity additions, it can be made highly conductive and semiconductive. Presently, we know that C_{60} doped with alkali metals become superconducting at $T_c = 5K$.

At present many methods are available to prepare C_{60} moles in large quantities, so the study of this molecular form of carbon is

advancing in many areas. Any research work on fullerene has got immense scope and potential in the field of nanotechnology. They find use in catalytic chemistry, biomolecular recognition, as molecular sieves, nanoreactors and also as inhibitors to the activity of HIV virus, etc.

Carbon nanotubes

Carbon nanotube is another molecular form of carbon. Its structure consists of a single sheet of graphite rolled into a tube, both ends of which are cupped with C_{60} fullerene hemispheres. This structure is schematically represented in figure 7.4. Since the tube diameters are of the order of nanometre (i.e. 100 nm or less), this carbon tube is called nanotubes. Each nanotube is a single molecule composed of millions of atoms; the length of the molecule is 1000 times greater than its diameter.

Nanotubes have some unique and technologically promising properties.
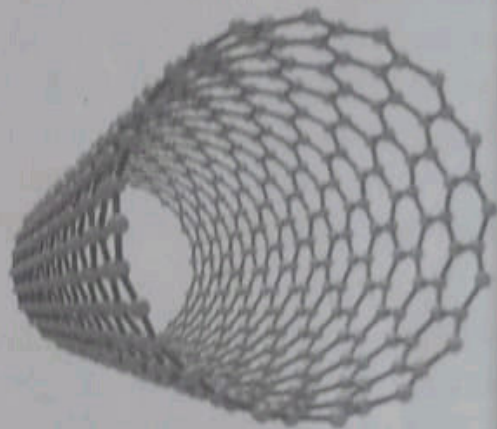
Figure 7.4: The structure of a carbon nanotube

Properties

1. They are extremely strong stiff and relatively ductile.
2. The tensile strengths of single walled nanotubes ranges from 50 to 200 GPa, which is greater than that of carbon fibres.
3. This is the strongest known material.
4. The elastic modulus values are of the order of terapascal (10^{12} Pa) relatively.
5. Nanotubes have low densities.

Uses

1. Carbon nanotubes as reinforcement in composite materials.

2. Since the nanotubes behave electrically as either a metal or a semiconductor depending upon the impurity atoms added, they have been used in flat panel and full colour displays of TVS and monitors of computers. Carbon nanotubes in these are field emitters.

3. They are cheaper to produce and require only lower power than CRT and liquid displays.

4. Carbon nanotubes can find applications in the fabrications of diodes and transistors, will result in nanoelectronic devices.

There is a scope of wide applications in different fields such as electronics in terms of thin films, electronic devices like MOSFET, JFET and in electrical ceramics.

The structure of polymers

Introduction

We are familiar with so many materials such as wood, rubber, cotton, wool, leather and silk; they are all naturally occurring polymers, proteins, enzymes, starches and cellulose are important in biological and physiological processes in plants and animals these are also natural polymers. The molecular structures of this group of material have been studied and researchers developed synthetic polymers from small organic molecules such as plastics, rubbers and fibre materials. The synthetic polymers can be produced inexpensively and their properties are superior to their natural counterparts. The properties of polymers related to their structure of the materials. In this section we deal with the relationship between structure and some of the physical and chemical properties.

Hydrocarbon molecules

Most of the polymers are organic in origin and are hydrocarbons

i.e. they are composed of hydrogen and carbon. In hydrocarbons intramolecular bonds are covalent. Each carbon atom has four electrons that may participate in covalent bonding, whereas every hydrogen atom has only one bonding electron. A single covalent bond exists when each of the two bonding atoms contributes one electron as shown in figure 7.5 for methane. Double and triple bonds between two
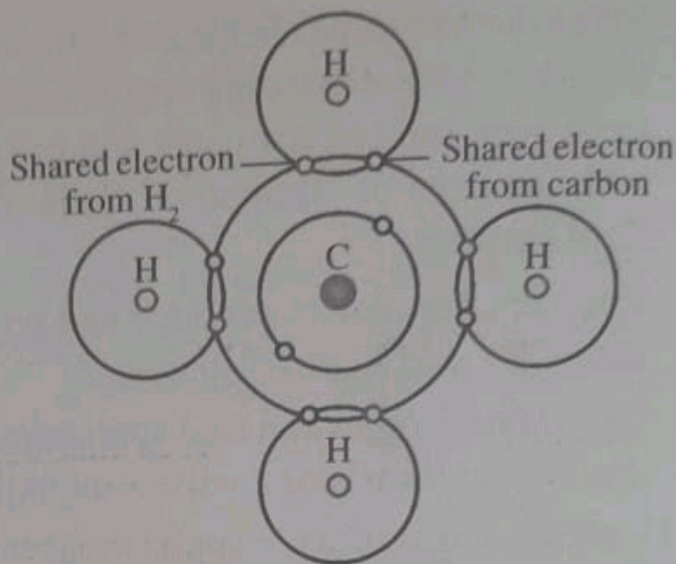
Figure 7.5: Schematic representation of covalent bonding in a molecule of methane (CH_4)

carbon atoms involve the sharing of two or three pairs of electrons, respectively. For example in ethylene (C_2H_4) has two carbon atoms are doubly bonded and each is single bonded to two hydrogen atoms.

Methane (CH_4) ethylene (C_2H_4) and acetylene (C_2H_2) are represented by the structural formula as shown below.

1. Methane CH_4, H–C–H having four single bonds with H above and below the central C.

2. Ethylene C_2H_4, C=C with H H above and H H below, Four single bonds are one double bond.
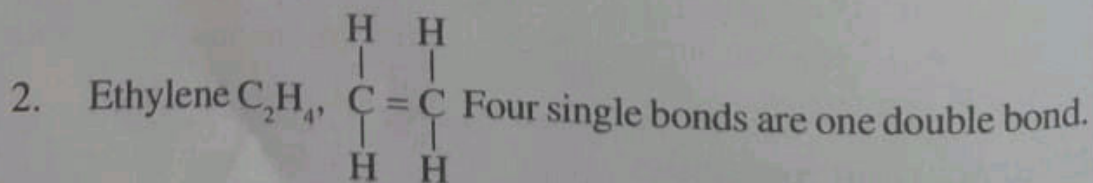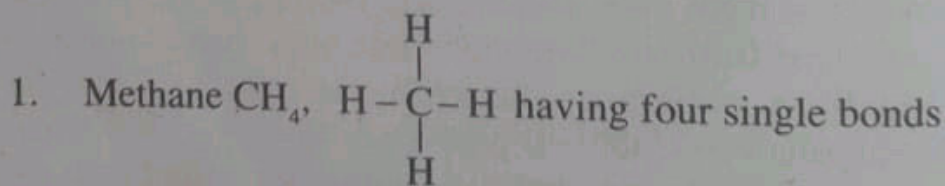
3. Acelyne C_2H_2, $H-C\equiv C-H$ Two single bonds and one triple bond.

Molecules that have double and triple bonds are termed unsaturated and for saturated hydrocarbons have all single bonds.

Some of the hydrocarbons belong to the paraffin family are methane (CH_4), ethane (C_2H_6), propane (C_3H_8) and butane (C_4H_{10}), whose structures are given below. The covalent bonds in each molecule are strong but only weak hydrogen vander waals bonds exist between molecules, thus they have relatively low melting and boiling points. It is also seen that boiling temperatures rise with increasing molecular weight. See table 7.1.

Table 7.1: Molecular structures for some of the paraffin compounds.

Name	Composition	Structure	Boiling Point (°C)
Methane	CH_4	$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$	-164
Ethane	C_2H_6	$\begin{array}{c} H\ \ H \\ |\ \ \ | \\ H-C-C-H \\ |\ \ \ | \\ H\ \ H \end{array}$	-88.6
Propane	C_3H_8	$\begin{array}{c} H\ \ H\ \ H \\ |\ \ \ |\ \ \ | \\ H-C-C-C-H \\ |\ \ \ |\ \ \ | \\ H\ \ H\ \ H \end{array}$	-42.1
Butane	C_4H_{10}		-0.5
Pentane	C_5H_{12}		36.1
Hexane	C_6H_{14}		69.0

Hydrocarbon compounds with the same composition may have different atomic arrangements, a phenomena termed as isomers. For example there are two isomers for butane. They are normal butane and isobutane. Their structures are given below.

Normal butane
$$\begin{array}{cccc} H & H & H & H \\ | & | & | & | \\ H-C-C-C-C-H \\ | & | & | & | \\ H & H & H & H \end{array}$$

Isobutane
$$\begin{array}{c} H \\ | \\ H-C-H \\ H \quad | \quad H \\ | \quad | \quad | \\ H-C-C-C-H \\ | \quad | \quad | \\ H \quad H \quad H \end{array}$$
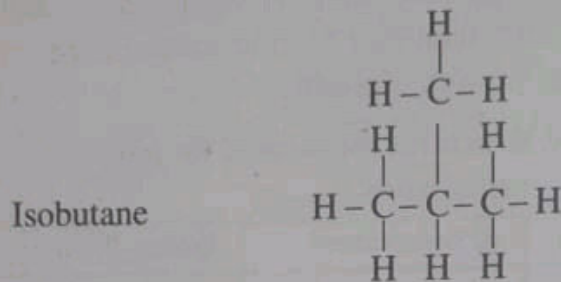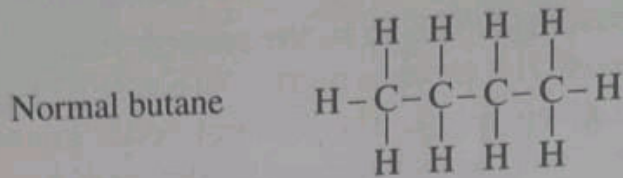
Some of the physical properties of hydrocarbons will depend upon the isomeric state. For example, the boiling temperatures for normal butane and isobutane are –0.5 and –12.3°C respectively.

Polymer molecules

The term polymer means many parts. Poly means many and mer is a Greek word meaning part. The term monomer refers to the small molecule from which a polymer is synthesised.

Polymer molecules are gigantic molecules in comparison to the hydrocarbons. It is because of large size of polymer molecules they are often referred to as macromolecules, within each molecule, the atoms are bound together by covalent bonds.

For carbon chain polymers, the back bone of each chain is a string of carbon atoms. Many times each carbon atom singly bonds to two adjacent carbon atoms on either side, represented schematically as follows (Two dimension):

$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}$$
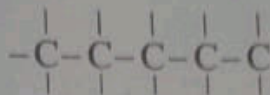
Each of the two remaining valence electrons of every carbon atom may be involved in side bonding with atoms or radicals that are positioned adjacent to the chain. It may also be noted that both chain and side double bonds are also possible.

Formation of polymer molecules

When a monomer is reacted under proper conditions with an initiator or a catalyst, a polymer molecule is formed.

For example ethylene (C_2H_4) is monomer and is a gas at ambient temperature and pressure. Its molecular structure is

$$\overset{H}{\underset{H}{\overset{|}{C}}} = \overset{H}{\underset{H}{\overset{|}{C}}}$$
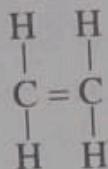
when this ethylene gas is reacted under appropriate conditions with a catalyst R, it will transform to polyethylene (PE), which is a solid polymeric material. The process begins when an active centre is formed by the reaction between catalyst species (R) and ethylene monomer. This is represented as follows:

$$R\cdot + \overset{H}{\underset{H}{\overset{|}{C}}} = \overset{H}{\underset{H}{\overset{|}{C}}} \longrightarrow R - \overset{H}{\underset{H}{\overset{|}{C}}} = \overset{H}{\underset{H}{\overset{|}{C}}} -$$
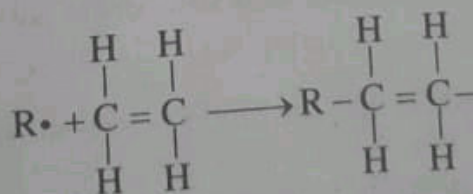
The active centre is denoted by ($R\cdot$).

By the sequential addition of monomer to this active growing chain, a polymer is formed. It is represented as follows:

$$R - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} = \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} \bullet \ + \ \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} = \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} \longrightarrow R' - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} \bullet$$
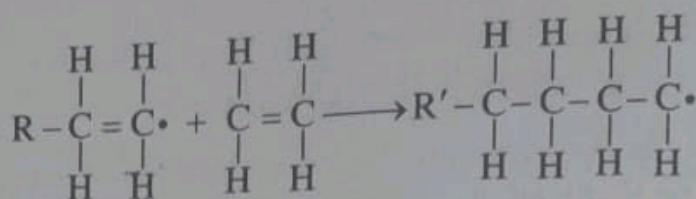
Repeating we get polyethylene molecule.

The polyethylene structure can also be represented as

$$\left(\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} \right)_n$$

or $(CH_2 - CH_2)_n$
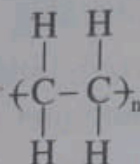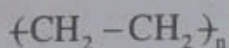
where n indicates the number of times the monomer repeats.

In a three dimensional model representation carbon atoms form zigzag pattern shown in figure 7.6.

● C ○ $\overset{\displaystyle .}{H}$
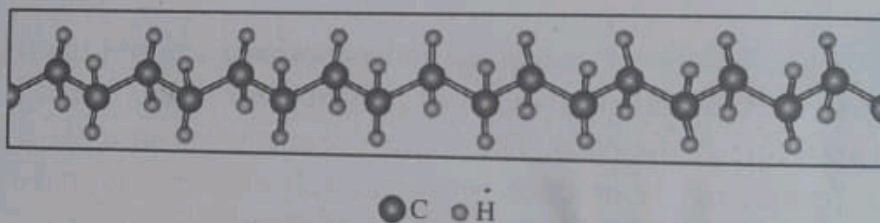
Figure 7.6: Zigzag back bone structure of polyethylene

It may also be noted that the angle between the singly bonded carbon atom is not actually $180°$ as we have shown, $\overset{180°}{C{=}C}$, but rather close to $109°$.

Other examples

1. Tetrafluoroethylene $CF_2 = CF_2$ is a monomer. This can polymerise to give polytetrafluoroethylene (PTFE) called teflon (trade name). Its structure is represented as follows:

$$n \begin{bmatrix} \overset{F}{\underset{F}{\overset{|}{\underset{|}{C}}}} = \overset{F}{\underset{F}{\overset{|}{\underset{|}{C}}}} \end{bmatrix} \longrightarrow \left(\overset{F}{\underset{F}{\overset{|}{\underset{|}{C}}}} - \overset{F}{\underset{F}{\overset{|}{\underset{|}{C}}}} \right)_n$$
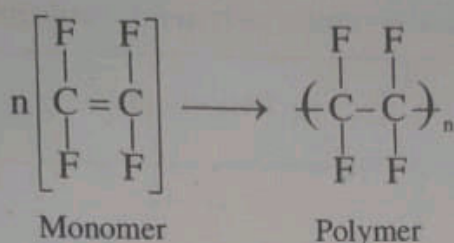
Monomer   Polymer

2. Vinyl chloride $CH_2 = CHCl$ is a monomer. It is a variant of ethylene C_2H_4 in which one of the hydrogen atom is replaced by chlorine atom.

When vinyl chloride is polymerised, we get polyvinyl chloride. It is represented as follows.

$$n \begin{bmatrix} \overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}} = \overset{H}{\underset{Cl}{\overset{|}{\underset{|}{C}}}} \end{bmatrix} \longrightarrow \left(\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}} - \overset{Cl}{\underset{Cl}{\overset{|}{\underset{|}{C}}}} \right)_n$$

Monomer   Polymer
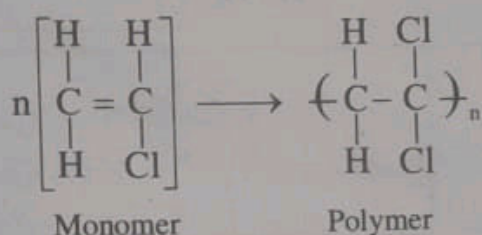
Homopolymers

When all the repeating units along a chain in a polymer are of the same type, is called homopolymer.

Copolymers

When the chains of a polymer are composed of two or different repeat units are termed as copolymers.

Examples are polyethylene vinyl acetate (PEVA), nitrile rubber and acrylonitrile butadiene styrene (ABS).

✻ The number of active bonds present in a monomer is termed as functionality. When an active bond that may react to form two covalent bonds with other monomers is termed as bifunctional when a monomer has three bonds to react with other monomers is termed as trifunctional.

A list of repeat units of some common polymeric material are give in table 7.2 below.

Table 7.2: A list of common polyments and their repeat units

No	Polymer	Repeat unit	Molecular formula of repeat unit
1	Polyethylene	$\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ -\text{C}-\text{C}- \\ | \quad | \\ \text{H} \quad \text{H} \end{array}$	C_2H_4
2	Polyvinyl chloride	$\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ -\text{C}-\text{C}- \\ | \quad | \\ \text{H} \quad \text{Cl} \end{array}$	C_2H_3Cl
3	Polytetrafluoro-ethylene	$\begin{array}{c} \text{F} \quad \text{F} \\ | \quad | \\ -\text{C}-\text{C}- \\ | \quad | \\ \text{F} \quad \text{F} \end{array}$	C_2F_4
4	Polypropylene	$\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ -\text{C}-\text{C}- \\ | \quad | \\ \text{H} \quad \text{CH}_3 \end{array}$	C_3H_6
5	Polysterene	$\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ -\text{C}-\text{C}- \\ | \\ \text{H} \quad \bigodot \end{array}$	C_8H_8
6	Polymethyl methacrylate	$\begin{array}{c} \text{H} \quad \text{CH}_3 \\ | \quad | \\ \text{C}-\text{C} \\ | \quad | \\ \text{H} \quad \text{C}-\text{O}-\text{CH}_3 \\ \quad \quad \| \\ \quad \quad \text{O} \end{array}$	$C_5O_2O_8$

7	Nylon 6,6		$C_{12}H_{20}N_2O_2$
8	Polycarbonate		$C_{15}O_{16}O_2$

Molecular weight calculation

The molecular weight of a compound is calculated as follows:

Count the number of atoms of each element present in the compound and then multiply that number by the element's atomic weight. Adding all we get the molecular weight of the compound.

Example

Molecular weight of NaCl. It contains one atom of Na, whose atomic weight is 23 and one atom of Cl, whose atomic weight is 35.

$\therefore$ Molecular weight of NaCl $= 1 \times 23 + 1 \times 35 = 58$.

Molecular weight of acetic acid CH_3COOH. It contains four hydrogen (Atwt 1) atoms two carbon atoms (Atwt 12) and 3 oxygen atoms (Atwt 16)

$\therefore$ Molecular weight $= 4 \times 1 + 2 \times 12 + 2 \times 16$

$= 4 + 24 + 32 = 60.$

Here we will discuss how to calculate the molecular weight of polymers from its chain length. We found that polymers have very long chains. It is seen that polymers with large chains have large

molecular weights. During the process of polymerisation all chains will not grow to the same length. This means that polymer chains are distributed i.e. molecular weights are distributed so we have to find the average molecular weight. This can be done in two ways. One is called number average molecular weight, the other one is called weight average molecular weight.

Number average molecular weight

To find the number average molecular weight divide the chains into a series of size ranges. Let n_1 be the number of chains in the molecular weight range M_1' and M_2'.

So the molecular weight of that chain,

$$M_1 = n_1 \frac{(M_1' + M_2')}{2} = n_1 \bar{M}_1$$

where $\bar{M}_1$ is the average of the molecular range M_1' and M_2' similarly

Molecular weight of the second chain containing n_2 number in the molecular range M_2' and M_3' is

$$M_2 = n_2(M_2' + M_3') = n_2 \bar{M}_2$$

and so on.

Therefore the total molecular weight of all the chains

$$M = M_1 + M_2 + \cdots \cdots M_n$$

i.e.
$$M = n_1 \bar{M}_1 + n_2 \bar{M}_2 + \cdots \cdots n_n \bar{M}_n$$

∴   The number average molecular weight of the polymer,

$$\bar{M}_N = \frac{M}{N}$$

where N is the total number of chains. i.e. $N = n_1 + n_2 + n_3 + \cdots \cdots$.

i.e. $$\bar{M}_N = \frac{M_1 + M_2 + M_3 + \cdots\cdots}{N}$$

$$\bar{M}_N = \frac{n_1\bar{M}_1 + n_2\bar{M}_2 + n_3\bar{M}_3 + \cdots\cdots}{N}$$

$\dfrac{n_1}{N}$ is the first fractional number of chains denoted by x_1 similarly others.

Thus

i.e. $$\bar{M}_N = x_1\bar{M}_1 + x_2\bar{M}_2 + \cdots\cdots$$

or $$\bar{M}_N = \sum_{i=1}^{n} x_i \bar{M}_i \qquad \text{..... (1)}$$

This is the expression for number average molecular weight.

Weight average molecular weight

We found that the number average molecular weight is defined on the basis of the number fraction of chains within each size range. **The weight average molecular weight is defined on the basis of weight fraction of molecules within various size ranges.**

∴   Weight average molecular weight, $\bar{M}_w$

$$\bar{M}_w = \sum_{i=1}^{n} w_i \bar{M}_i \qquad \text{..... (2)}$$

where w_i is the weight fraction of molecules within the same size interval and $\bar{M}_i$ is the mean molecular weight within a size range.

Degree of polymerisation

The degree of polymerisation (DP) is a term used to express the average chain size of a polymer. **Degree of polymerisation is**

defined as the ratio of the number average molecular weight ($\bar{M}_N$) and the repeat unit molecular weight m. (monomer)

i.e.

$$DP = \frac{\bar{M}_N}{m} \qquad \qquad \dots (3)$$

Repeat unit molecular weight is m

Consider a polyvinylchloride polymer:
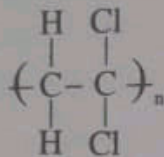
In this repeating unit (monomer) is
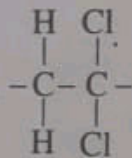
It contains two carbon atoms three hydrogen atoms and one chlorine atom.

The molecular weight of repeating monomer

m = 2 × Atwt of C + 3 Atwt of H + 1 × Atwt of Cl

Example 1

The number average molecular weight of a polysterene is 500,000 g/mol. Compute the degree polymerisation.

Solution

Polysterene : $(C_8H_8)_n$

Molecular weight of repeat unit,

m = 8 × Atwt of C + 8 × Atwt of H

= 8 × 12.01 + 8 × 1.0078

Usir

Example

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(a) polyte

6,6 and (

Solution

a) The

Mol

b) The

Mol

c) The r

$$= 96.08 + 8.0624$$

$$= 104.1424 \text{ g / mol}$$

Using

$$DP = \frac{\bar{M}_N}{m} = \frac{500,000}{104.1424} = 4801.1$$

Example 2

Compute repeat unit molecular weights for the following (a) polytetrafluoroethylene (b) polymethyl methacrylate (c) nylon 6,6 and (d) polyethylene teraphthalate. ($C_{12}H_8O_4$)

Solution

a) The repeat unit of polytetrafluoroethylene is

$$C_2F_4$$

Molecular weight of C_2F_4

$$= 2 \times \text{Atwt of C} + 4 \times \text{Atwt of F}$$

$$= 2 \times 12.01 + 4 \times 18.9936$$

$$= 100 \text{ g / mol}$$

b) The repeat unit of polymethyl methacrylate is
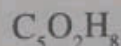
$$C_5O_2H_8$$

Molecular weight of $C_5O_2H_8$

$$= 5 \times \text{Atwt of C} + 2 \times \text{Atwt of O} + 8 \times \text{Atwt of H}$$

$$= 5 \times 12.01 + 2 \times 15.999 + 8 \times 1.0078$$

$$= 60.05 + 31.998 + 8.0624$$

$$= 100 \text{ g / mol}$$

c) The repeat unit of nylon 6,6 is

$$C_{12}H_{20}N_2O_2 \text{ (see table 7.2)}$$
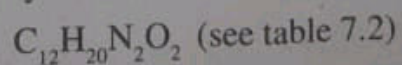
∴   Molecular weight of nylon 6,6
= 12 × Atwt of C + 20 × Atwt of H +
2 × Atwt of N_2 + 2 × Atwt of O
= $12 \times 12.01 + 20 \times 1.0098 + 2 \times 14.0067 + 2 \times 15.499$
= $144.12 + 20.156 + 28.0134 + 31.998$
= 224.2874 g / mol

d)   The repeat unit of polyethylene teraphthalate is
$$C_{10}H_8O_4$$
∴   Molecular weight
= 10 × Atwt of C + 8 × Atwt of H + 4 × Atwt of O
= $10 \times 12.01 + 8 \times 1.0098 + 4 \times 15.999$
= $120.1 + 8.0624 + 63.996$
= 192.1584 g / mol
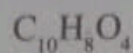
Example 3

Molecular weight data for a polytetrafluoroethylene material are given below. Compute (a) the number average molecular weight (b) the weight average molecular weight and (c) the degree of polymerisation.

Molecular weight range (g/mol)	x_i	w_i
10,000 - 20,000	0.03	0.01
20,000 - 30,000	0.09	0.04
30,000 - 40,000	0.15	0.11
40,000 - 50,000	0.25	0.23
50,000 - 60,000	0.22	0.24
60,000 - 70,000	0.14	0.18
70,000 - 80,000	0.08	0.12
80,000 - 90,000	0.04	0.07

Solution

a) The number average molecular weight

$$\bar{M}_N = \sum_{i=1}^{n=8} x_i \bar{M}_i$$

$$\bar{M}_N = x_1\bar{M}_1 + x_2\bar{M}_2 + x_3\bar{M}_3 + \cdots\cdots x_8\bar{M}_8 \qquad \cdots (1)$$

$$\bar{M}_1 = \frac{10,000 + 20,000}{2} = 15,000$$

$$\bar{M}_2 = \frac{20,000 + 30,000}{2} = 25,000$$

$$\bar{M}_3 = \frac{30,000 + 40,000}{2} = 35,000$$

$$\bar{M}_4 = \frac{40,000 + 50,000}{2} = 45,000$$

$$\bar{M}_5 = \frac{50,000 + 60,000}{2} = 55,000$$

$$\bar{M}_6 = \frac{60,000 + 70,000}{2} = 65,000$$

$$\bar{M}_7 = \frac{70,000 + 80,000}{2} = 75,000$$

$$\bar{M}_8 = \frac{80,000 + 90,000}{2} = 85,000$$

$$\therefore \quad \bar{M}_N = 10^3(0.45 + 2.25 + 5.25 + 11.25 + 12.1 + 9.1 + 6 + 3.4)$$

$$= 10^3 \times 49.8$$

$$= 49800 \text{ g/mol}$$

b) The weight average molecular weight,

$$\bar{M}_w = \sum_{i=1}^{n=8} w_i \bar{M}_i \qquad\qquad ..... (2)$$

$w_1 = 0.01, \quad \bar{M}_1 = 15,000$

$w_2 = 0.04, \quad \bar{M}_2 = 25,000$

$w_3 = 0.11, \quad \bar{M}_3 = 35,000$

$w_4 = 0.23, \quad \bar{M}_4 = 45,000$

$w_5 = 0.24, \quad \bar{M}_5 = 55,000$

$w_6 = 0.18, \quad \bar{M}_6 = 65,000$

$w_7 = 0.12, \quad \bar{M}_7 = 75,000$

$w_8 = 0.07, \quad \bar{M}_8 = 85,000$

Putting these values in eq (2), we get

$$\bar{M}_w = 0.01 \times 15 \times 10^3 + 0.04 \times 25 \times 10^3 + 0.11 \times 35 \times 10^3 +$$

$$0.23 \times 45 \times 10^3 + 0.24 \times 55 \times 10^3 + 0.18 \times 65 \times 10^3 +$$

$$0.12 \times 75 \times 10^3 + 0.07 \times 85 \times 10^3$$

$$\bar{M}_w = 10^3 (0.15 + 1 + 3.85 + 10.35 + 13.2 + 15.6 + 9 + 5.95)$$

$$\bar{M}_w = 59.1 \times 10^3 \text{ g / mol}$$

c) Degree of polymerisation

$$DP = \frac{\bar{M}_N}{m} \qquad\qquad ..... (3)$$

The given polymer is polytetrafluoroethylene is

$$C_2F_4$$

The molecular weight of tetrafluoroethylene,

$$m = 2 \text{ Atwt of C} + 4 \text{ Atwt of F}$$

$$= 2 \times 2.01 + 4 \times 18.9984$$

$$= 24.02 + 75.9936 = 100$$

$$\therefore \quad DP = \frac{49,800}{100} = 498$$

Example 4

From the given data table for polyvinyl chloride compute (a) the number average molecular weight (b) the degree of polymerisation and (c) the weight average molecular weight.

Molecular weight range (g/mol)	x_i	w_i
5,000 - 10,000	0.05	0.02
10,000 - 15,000	0.16	0.10
15,000 - 20,000	0.22	0.18
20,000 - 25,000	0.27	0.29
25,000 - 30,000	0.20	0.26
30,000 - 35,000	0.08	0.13
35,000 - 40,000	0.02	0.02

Solution

a) The number average molecular weight,

$$\bar{M}_N = \sum_{i=1}^{7} x_i \bar{M}_i \qquad \qquad \text{..... (1)}$$

$$x_1 = 0.05, \quad \overline{M}_1 = \frac{5,000 + 10,000}{2} = 7,500$$

$$x_2 = 0.16, \quad \overline{M}_2 = \frac{10,000 + 15,000}{2} = 12,500$$

$$x_3 = 0.22, \quad \overline{M}_3 = \frac{15,000 + 20,000}{2} = 17,500$$

$$x_4 = 0.27, \quad \overline{M}_4 = \frac{20,000 + 25,000}{2} = 22,500$$

$$x_5 = 0.20, \quad \overline{M}_5 = \frac{25,000 + 30,000}{2} = 27,500$$

$$x_6 = 0.08, \quad \overline{M}_6 = \frac{30,000 + 35,000}{2} = 32,500$$

$$x_7 = 0.02, \quad \overline{M}_7 = \frac{35,000 + 40,000}{2} = 37,500$$

$$\overline{M}_N = 0.05 \times 7,500 + 0.16 \times 12,500 + 0.22 \times 17,500$$

$$+ \, 0.27 \times 22,500 + 0.20 \times 27,500 + 0.08 \times 32,500$$

$$+ \, 0.02 \times 37,500$$

$$\overline{M}_N = 375 + 2000 + 3850 + 6075 + 5500 + 2600 + 750$$

$$\overline{M}_N = 21,150 \text{ g / mol}$$

b) The degree of polymerisation, $DP = \dfrac{\overline{M}_N}{m}$ where m is the molecular weight of the repeating unit i.e. vinylchloride C_2H_3Cl.

$\therefore$ Molecular weight of C_2H_3Cl

$= 2 \times$ Atwt of C $+ 3 \times$ Atwt of H $+ 1 \times$ Atwt of Cl

$= 2 \times 12.01 + 3 \times 1.01 + 1 \times 35.45$

$= 24.02 + 3.03 + 35.45 = 62.5$ g / mol

$\therefore \quad DP = \dfrac{21,150}{62.50} = 338.4$

$$\bar{M}_w = w_1\bar{M}_1 + w_2\bar{M}_2 + w_3\bar{M}_3 + w_4\bar{M}_4$$

$$+ w_5\bar{M}_5 + w_6\bar{M}_6 + w_7\bar{M}_7$$

$$\bar{M}_w = 0.02 \times 7,500 + 0.10 \times 12,500 + 0.18 \times 17,500$$

$$+ 0.29 \times 22,500 + 0.26 \times 27,500 + 0.13 \times 32,500$$

$$+ 0.02 \times 37,500$$

$$\bar{M}_w = 150 + 1250 + 3150 + 6525 + 7150 + 4225 + 750$$

$$\bar{M}_w = 23,200 \text{ g / mol}.$$

Molecular shape

So far we considered polymer molecules as lines, neglecting the zigzag arrangements of the backbone atoms (see figure 7.6). The single chain bonds are capable of rotating and bending in three dimensions. We found that the angle between the singly bonded carbon atom is 109°, not 180°. In actual 3D, situation is different. Consider the chain atoms in figure 7.7(a). In this, a third carbon atom may lie at any point on the cone of revolution and still sub-tend an angle of about 109° with the bond between the other two atoms. When successive such atoms are positioned we get a straight

chain as shown in figure 7.7(b). On the other hand, chain bending and twisting are possible when there is a rotation of the chain atoms into other positions as shown in figure 7.7(c).

Figure 7.7(a)

Figure 7.7(a), (b) and (c). Showing how polymer chain shape is influenced by the positioning of backbone carbon atoms. The above discussion shows that a single chain molecule composed of many chain atoms might assume a shape of the form given in figure 7.8. This chain having large number of bends, twists and kinks. The end to end distance of the polymer chain 'r' is also indicated.
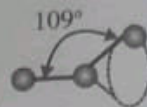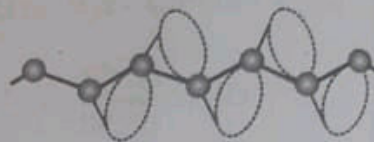
Figure 7.7(b)
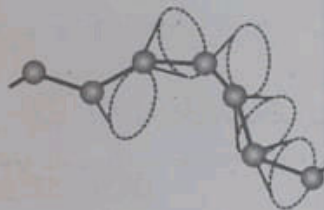
Figure 7.7(c)
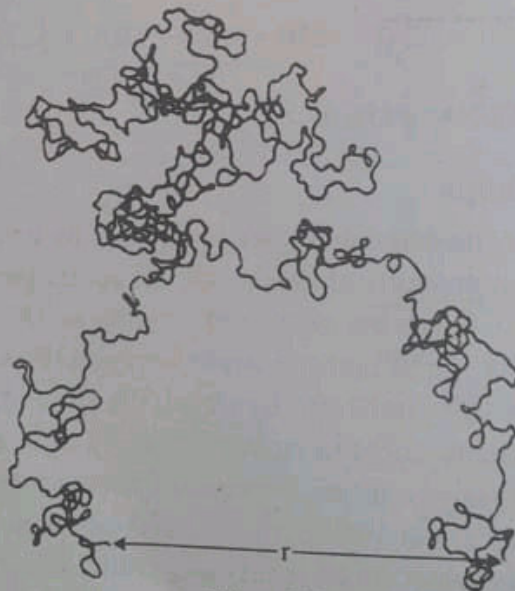
Figure 7.8

The above number of mo link leads to neighbouring line. These ran sible for a nun elastic extensio

Some of the depend on the applied stresse upon the repea carbon double ence of large s For example po see table 7.2, (polyethylene cl

Molecular st

The physica molecular wei Modern polym rol the structur erties. There ar

1. linear poly
2. branched
3. cross linke
4. network p
5. various iso

1. Linear pol

Linear poly

The above discussion shows that polymers consists of large number of molecular chains, each of which may bend, coil and kink leads to extensive intertwining and entanglement of neighbouring chain molecules is analogous to a tangled fishing line. These random coils and molecular entanglements are responsible for a number of important properties of polymers such as elastic extensions shown by the rubber materials.

Some of the mechanical and thermal properties of polymers depend on the ability of chain segments for rotation in response to applied stresses or thermal vibrations. Rotational ability depends upon the repeat unit structure. For example a chain which has a carbon double bond $(C = C)$ is rotationally rigid. Also the presence of large side group of atoms restricts rotational movement. For example polysterene molecules which has a phenyl side group (see table 7.2, (5)) are more resistant to rotational motion than the polyethylene chains which don't have side group.

Molecular structure

The physical properties of polymers depend upon two factors molecular weights and their structure of the molecular chains. Modern polymer synthesis techniques revealed that we can control the structure of molecular chains thereby changing their properties. There are five types of molecular structures. They are

1. linear polymers
2. branched polymers
3. cross linked polymers
4. network polymers and
5. various isomeric configurations.

1. Linear polymers

Linear polymers are those in which the repeat units are

joined end to end in single chains.

These long chains are flexible and may be thought of as a mass of spaghetti, as represented schematically in figure 7.9(a).
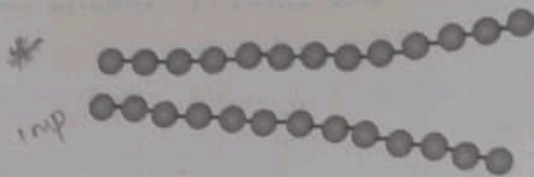
Figure 7.9(a): Linear polymers

In the figure 7.9(a), each circle represents a repeat unit. In linear polymers there may be extensive vander Waals and hydrogen bonding between the chains. Polyethylene, polyvinyl chloride, polysterene, polymethyl methacrylate, nylon and the fluorocarbons are linear chain polymers. See also table 7.2.

2. Branched polymers

Branched polymers are those in which side branch chains are connected to the main linear chains.

This is depicted schematically in figure 7.9(b) given below.
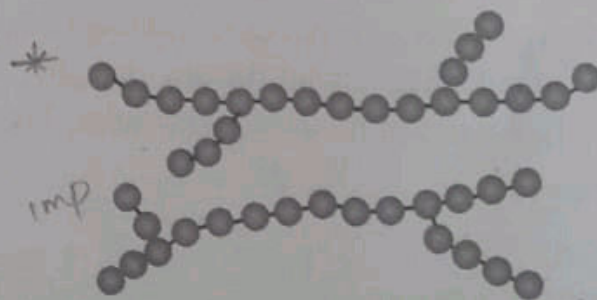
Figure 7.9(b): Branched chain polymers

The branches are considered to be part of the main chain molecule, may result from side reactions that occur during synthesis of the polymer. It is due to these branches, the chain packing effi-

ciency is reduced which results in a lowering of the polymer density. The polymers that form linear structures may also be branched. For example high density polyethylene is basically a linear polymer whereas low density polyethylene contains short chain branches.

3. Cross linked polymers

Cross linked polymers are polymers in which adjacent linear chains are joined one to another at various positions by covalent bonds.

Cross linked polymers are schematically represented in figure 7.9(c) given below.
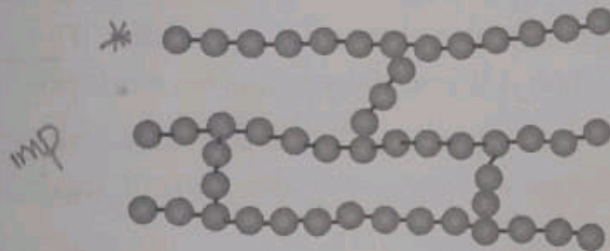
Figure 7.9(c): Cross linked polymers

The cross linking process in a polymer occurs either during synthesis or by a non-reversible chemical reactions. The cross linking is accomplished by additive atoms or molecules that are covalently bonded to the chains. Many of the rubber elastic materials are cross linked in rubbers. This process is called vulcanization.

4. Network polymers

Network polymers are polymers in which the multifunctional monomers (basic repeat unit) forming three or four active covalent bonds results in 3 dimensional networks.

This is shown in figure 7.9(d) below.

imp
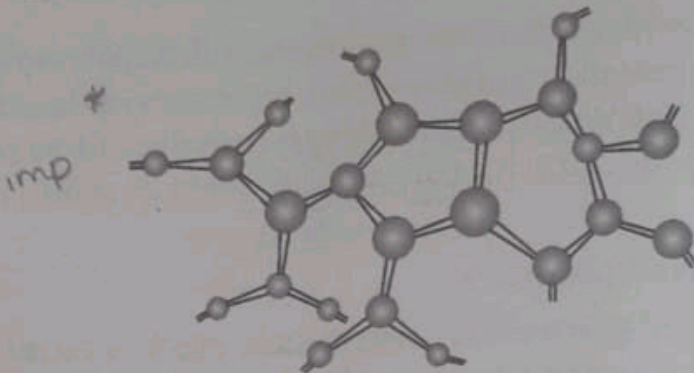
Figure 7.9(d): Network polymers

It may be noted that a polymer actually a highly cross linked may also be considered as a network polymer. These materials have distinctive mechanical and thermal properties. The epoxies polyurethanes and phenol formaldehyde are network polymers.

Polymers are not usually of one distinctive structure type. For example a predominantly linear polymer might have limited branching and cross linking.

Molecular configurations

Configuration refers to arrangements of units along the axis of the chain.

Polymers having more than one side atom or group of atoms bounded to the main chain, the regularity and symmetry of the side group arrangement can significantly influence the properties of the polymers. To understand this consider the repeat unit

$$
\begin{array}{cc}
H & H \\
| & | \\
-C-C- \\
| & | \\
H & \text{Ⓡ}
\end{array}
$$
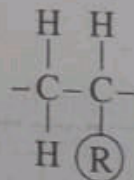
where R represents an atom or side group other than hydrogen (e.g., Cl, CH_3 etc.) There are two possible arrangements of R. In

one arrangement the R side groups of successive repeats are bound to alternate carbon atoms as follows:

$$-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle R}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle R}{C}}-$$
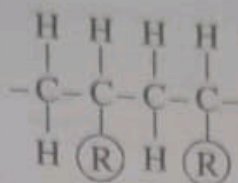
This arrangement is termed as head to tail configuration.

In the second arrangement R groups are bound to adjacent carbon atoms as shown below:

$$-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle R}{C}}-\overset{\displaystyle H}{\underset{\displaystyle R}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-$$
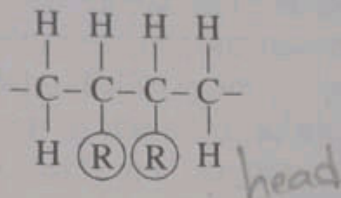
head

This arrangement is termed as head to tail configuration. In this configuration often a polar repulsion occurs between the two adjacent R groups. In most polymers, the head to tail configuration predominates.

Isomerism in polymers

When different atomic configurations are for the same composition of polymers, they are said to be isomers of the polymer.

Isomers are further classified into several subclasses. Two of them are stereoisomerism and geometrical isomerism.

Stereoisomerism

Stereoisomerism also called as spatial isomerism is a form of isomerism in which molecules have the same molecular formula and sequence of bonded atom but differ in the three dimensional orientations of their atoms in space.

Stereoisomers can be subdivided into two: one is called isotac-
tic and the other is called syndiotactic.

Tacticity is a term used to describe the way pendant groups (R)
on a polymer chain arranged on a polymer backbone. The tacticity
of a polymer is determined by what side of the polymer chain the
pendant groups are on. This relative position can have dramatic
effects on the physical properties of the polymer.

When a monomer adds to the end of the polymer chain, the
monomer can either join the pendant group on the same side as all
of the other pendant groups or it can join the pendant group on the
side away from the pendant group. If the monomer adds to the
polymer back bone with the pendant group (R) on the same as the
previous pendant group this is called isotactic configuration. If the
monomer adds to the opposite side of the polymer backbone it is
called syndiotactic configuration. If there is no order to the way
the pendant group adds (random) the polymer is said to be atactic
and the corresponding configuration is called atactic configura-
tion. Isotactic, syndiotactic and atactic configurations are (2 and 3
D) given below in figure 7.10 (a, b and c)
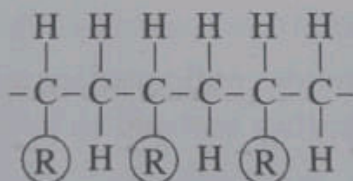
Figure 7.10(a): Two dimensional linear 2D isotactic configuration
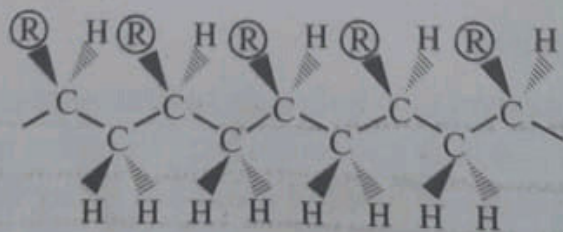
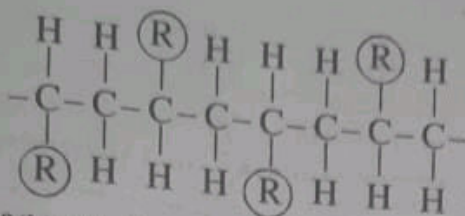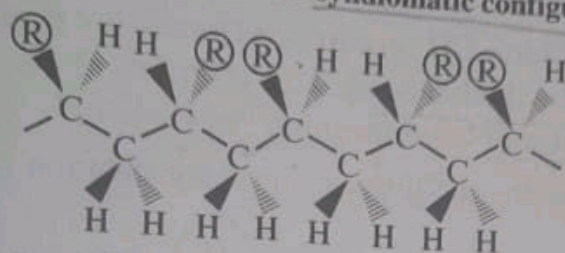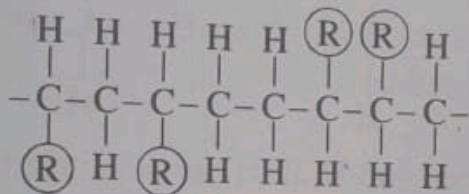The three dimensional isotactic configuration

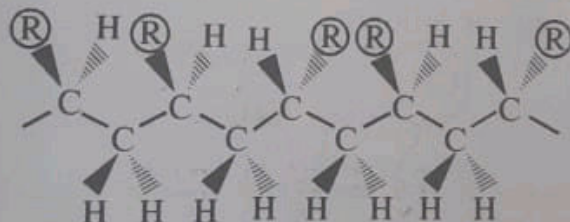**Figure 7.10(b): The linear 2D syndiomatic configuration**

The three dimensional syndiomatic configuration

(No order)

**Figure 7.10(c): The linear 2D atactic configuration**

The three dimensional atactic configuration

Geometrical isomerism

Geometrical isomerism is a form of isomerism describing the orientation of functional groups within a molecule.

In general geometrical isomers contain double bonds which cannot rotate like single bond atoms. The rotation is restricted also by ring structure. For example consider the isoprene repeat unit having the structure.
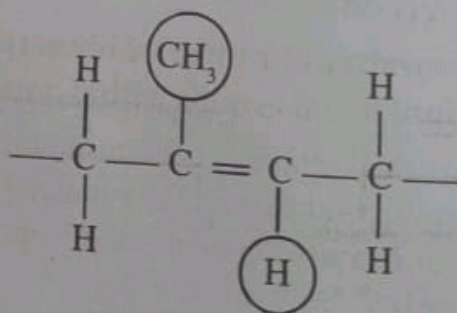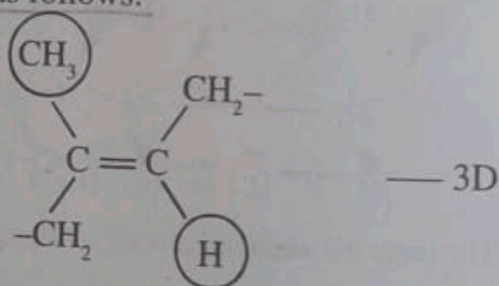
$$CH_3 \quad H$$
$$C=C$$
$$-CH_2 \quad CH_2-$$
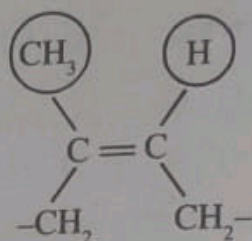
In this structure CH_3 group and H atom are positioned on the same side of the double bond. This is termed as cis structure. The prefix cis is a Latin word meaning "this side of".

For cis-isoprene the linear chain representation is as follows:

$$H \quad CH_3 \quad H \quad H$$
$$-C-C=C-C-$$
$$H \quad\quad\quad H$$
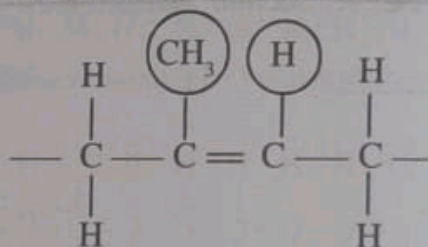
If the CH_3 group and H atom are positioned on the opposite sides of the double bond, it is termed as trans structure. The prefix trans is a Latin word meaning "the other side of". The structure of trans isoprene is as follows:

$$CH_3 \quad CH_2-$$
$$C=C$$
$$-CH_2 \quad H$$

— 3D

$$H \quad CH_3 \quad\quad H$$
$$-C-C=C-C-$$
$$H \quad\quad H \quad H$$

This is the linear trans structure of isoprene.

Trans polyisoprene is sometimes called gutta percha. This has properties distinctly different from natural rubber as a result of its configurational alteration.

It may be noted that conversion of trans to cis or vice versa is not possible by a simple chain bond rotation because the chain double bond is extremely rigid.

Summarising the subheading molecular weight (size), molecular shape, molecular structure and molecular configurations, we can say the following: Molecular characteristics of polymers is given by four factors. They are

1. repeat unit configuration
2. size (molecular weight)
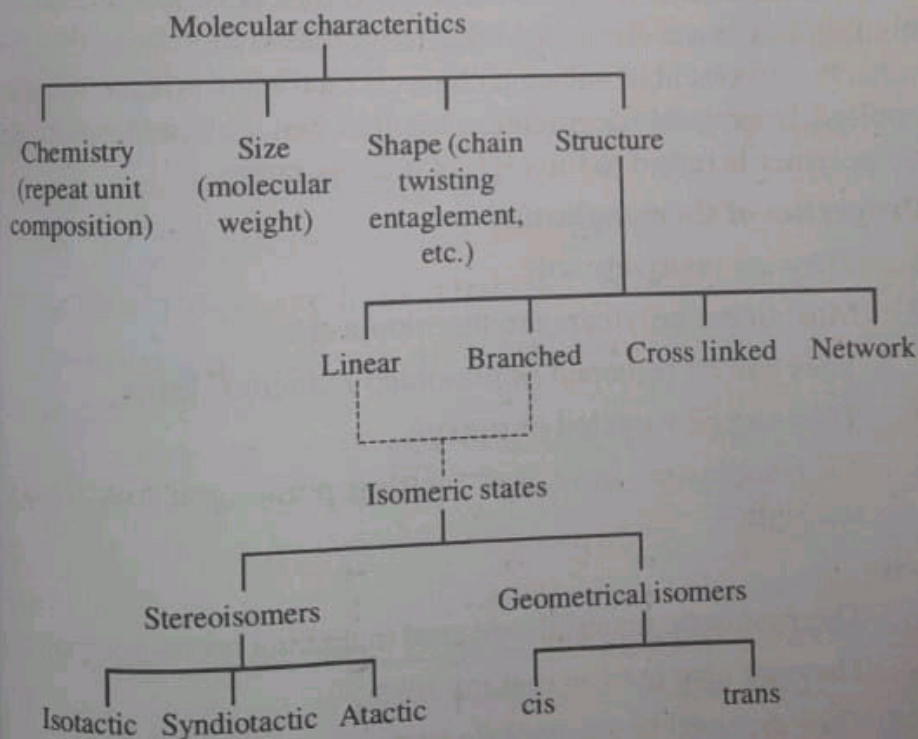3. shape (chain twisting coiling and bending) and

Molecular characteritics

- Chemistry (repeat unit composition)
- Size (molecular weight)
- Shape (chain twisting entaglement, etc.)
- Structure
  - Linear
  - Branched
  - Cross linked
  - Network

Isomeric states
- Stereoisomers
  - Isotactic
  - Syndiotactic
  - Atactic
- Geometrical isomers
  - cis
  - trans

Figure 7.11: Taxonomy chart

4. molecular structure (linear, branched, cross linked and net-work structures are possible in addition to several isomeric configurations such as isotactic, syndiotactic, atactic, cis and trans. The molecular characteristics taxonomy chart is given in figure 7.11.

Thermoplastic and thermosetting polymers

Thermoplastics

Thermoplastics are polymers that can be softened through heating before being processed then left to cool and harden.

Once cooled, they show no changes in chemical properties, meaning they can be remelted and re-used several times.

Polyester, polypropylene, polystrene, teflon, acrylic, polyvinyl chloride etc. are thermoplastic polymers or called thermoplastics.

On a molecular level, as the temperature is raised secondary binding forces are diminished due to increased motion so that the relative movement of adjacent chains is facilitated when a stress is applied. Irreversible degradation results when molten thermoplastic polymer is raised to too high of a temperature.

Properties of thermoplastics

1. They are relatively soft
2. Most linear polymers are thermoplastics.
3. They can be reshaped or remolded numerous times.
4. They can be recycled or reused.
5. Thermoplastics have low melting points and low tensile strength.

Uses

1. Thermoplastic materials are used in making sports equipment.
2. They are also used in making toys.
3. They are used in automobile parts.

4. They are used in making CDs and DVDs.

5. Containers like shampoo bottles, drinking bottles and food storage containers are made up of thermoplastic polymers.

Note: Thermoplastics are fabricated by the simultaneous application of heat and pressure.

Thermosetting polymers

Thermoset is a polymer material that strengthens when heated but cannot be remoulded or heated after initial formation.

Epoxy, silicone, polyurethane, phenolic, vulcanised rubbers, polyester resins are examples of thermosetting polymers or called also thermosets.

Properties

1. They become permanently hard during their formation.

2. They are stronger than thermoplastics and have better dimensional stability.

3. They have high melting point and high tensile strength.

4. Thermosets are network polymers.

5. They cannot be recycled or remoulded. (reshaped)

Why thermosets are hard ?

Thermosets are network polymers. Network polymers have covalent cross links between adjacent molecular chains. During heating these bonds anchor the chains together to resist the vibrational and rotational chain molecules at high temperatures. Thus materials do not soften when heated.

Uses

1. Thermostats are used for producing electrical goods such as circuit breakers as well as components such as panels and insulators.

2. They are used for manufacturing construction equipment panels.

3. Thermosets are used for manufacturing heat shields.

4. They are also used in agricultural feeding troughs, motor components and disc break pistons.

Stress-strain behaviour of polymers

The mechanical properties of polymers such as strength, toughness, hardness, hardenability, brittleness, malleability, ductility, creep and slip, resilience, tactique etc. are specified with the same parameters that are used for metals - i.e. modulus of elasticity, yield strengths, and tensile strengths. These mechanical parameters are ascertained by simple stress-strain test. But the mechanical properties of polymers are highly sensitive to the strain rate, the temperature and the nature of the environment (the presence of water, oxygen, organic solvents etc.). Considering these factors some modifications with regard to stress-strain behaviour of metals are required when it is applied to polymers.

There are three different types of stress-strain behaviour observed for polymers. They are

1. the stress-strain behaviour of brittle polymer

2. the stress-strain behaviour of plastic polymer and

3. the stress-strain behaviour of elastic polymers.

The stress-strain behaviour of brittle polymer

The stress-strain behaviour of a brittle polymer is shown in figure 7.12 below.

The graph shows that a very little strain is produced in the brittle polymer when subjected to stress of the order of mega pascals. The point marked as (x) indicates the brittle point. Moreover the stress-strain relation is linear.
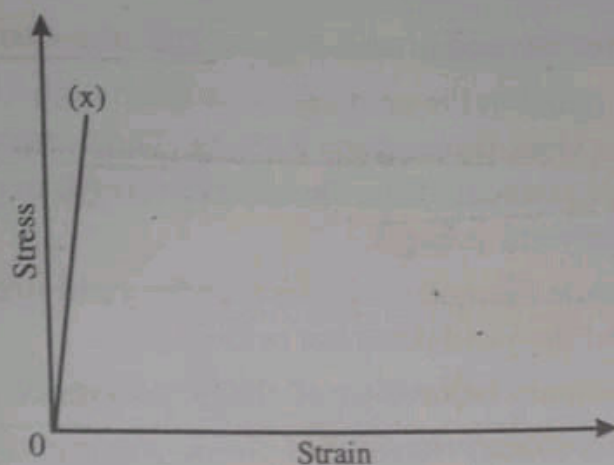
Figure 7.12: The stress-strain behaviour of brittle polymer

The stress-strain behaviour of plastic polymer

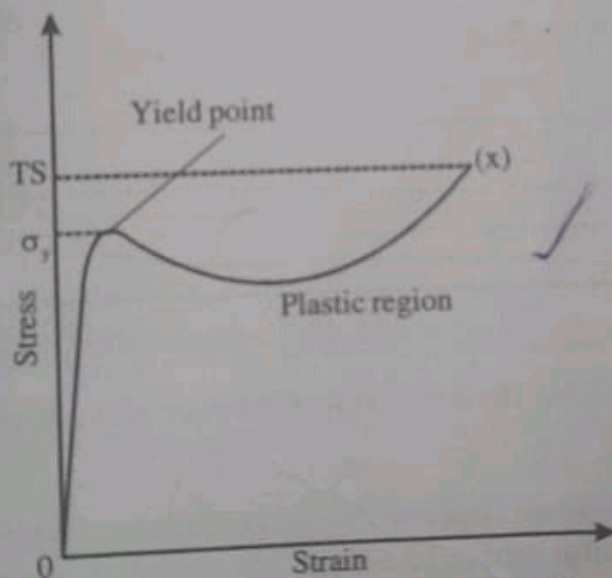The stress-strain behaviour of plastic polymer is given in figure 7.13 below.

Figure 7.13: The stress-strain behaviour of plastic polymer

The behaviour of plastic polymer is similar to that of metals. Initially there is an elastic region where stress is directly proportional to strain. The maximum point on the curve gives yield point

which is just beyond elastic region. The stress corresponding to maximum point on the curve give yield strength (σ_y). The point marked as (x) corresponds to fracture. The corresponding stress gives tensile strength (TS). The tensile strength may be greater or less than the yield strength.

If the tensile strength is smaller than the yield strength the curve ends beyond the yield point but below it.

The stress-strain behaviour of elastic polymers

The stress-strain behaviour of elastic polymers is given in figure 7.14.
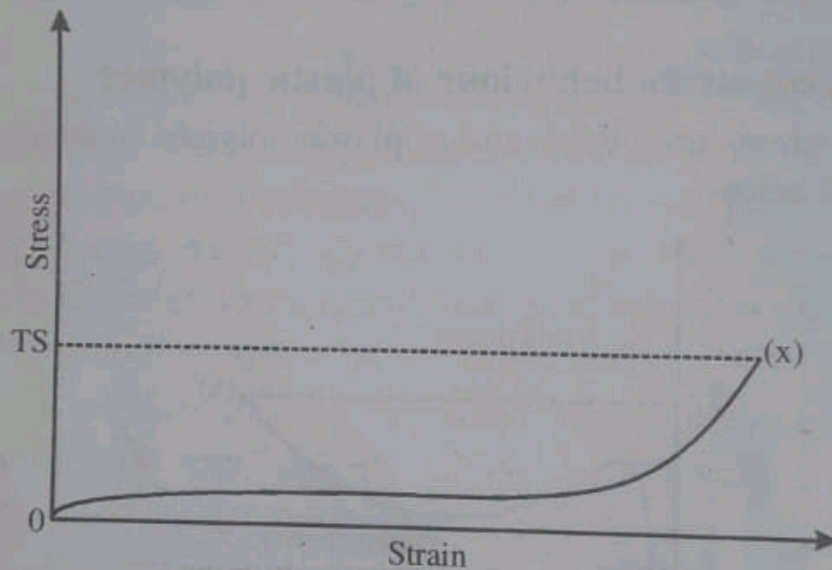

Figure 7.14: The stress-strain behaviour of elastic polymer

The deformation displayed by the curve is totally elastic – Elastic polymers exhibit rubber like elasticity, which means that large recoverable strains produced for low stress levels. These polymers are termed as elastomers. The highest point marked on the curve as (x) gives the breaking point. The corresponding stress gives tensile strength (TS).

The influence of temperature on the stress-strain behaviour

The stress-strain behaviour of polymers are strongly influenced by variation in temperature. The stress-strain behaviour of a particular polymer is shown at different temperatures in figure 7.15.
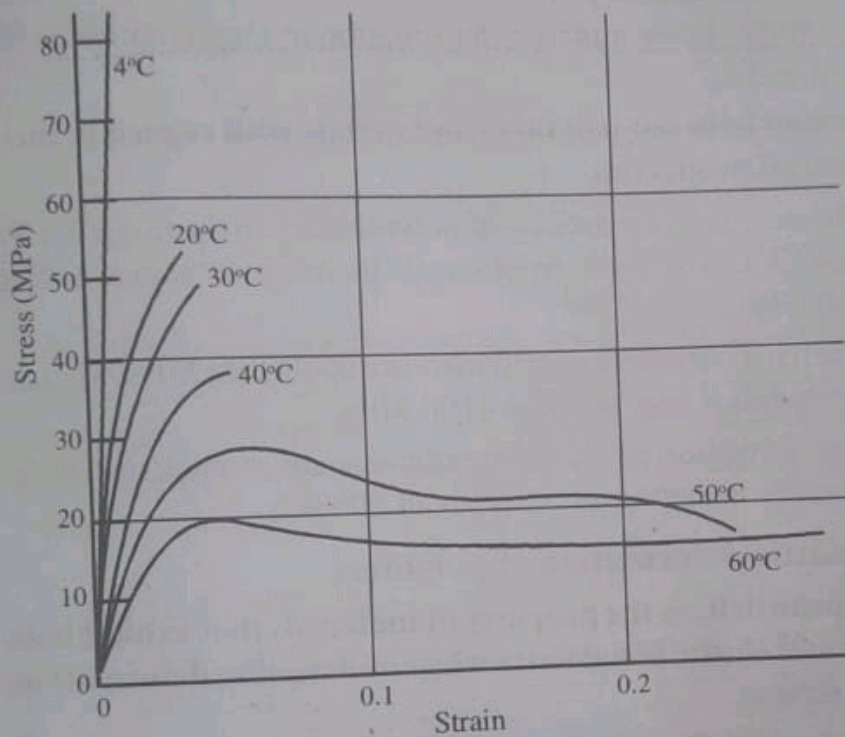

Figure 7.15: Stress-strain graph at different temperatures

From the graph the following things may be observed.

1. When temperatures increases its elastic modulus $\left(\dfrac{\text{stress}}{\text{strain}}\right)$ decreases, since the slope of the graph $\left(\dfrac{\text{stress}}{\text{strain}}\right)$ decreases.

2. The tensile strength (TS) of the polymer also decreases as temperature increases. Tensile strength is the maximum stress corresponding to the end point of the curve.

3. The ductility of the polymer is largest at low temperature. Ductility is the ability of a material to get stretched into wire by pulling. Ductility indicates that how easily a material gets deformed under tensile stress. With rise in temperature the ductility increases.

4. Polymer shows a plastic deformation at temperatures at 50° and 60°C.

Distinction between polymers and metals with regard to their mechanical properties

1. The modulus of elasticity of polymers are in the range 7 MPa to 4 GPa, where as that of metals the range is between 48 to 410 GPa.

2. The tensile strength of polymers are about 100 MPa, whereas for metals it may go up to 4100 MPa.

3. The elongation produced in polymers are more than 1000%, whereas in metals it is only about 100%.

Viscoelastic deformation of polymers

Viscoelasticity is the property of materials that exhibit both viscous and elastic behaviours when undergoing deformation, (under stress).

The elastic deformation is instantaneous and the viscous drag takes time. After the load removal, the elastic deformation is immediately reversible and recoverable, whereas the viscous drag is not reversible.

For elastic deformation the load-time graph and the corresponding strain-time graph is given
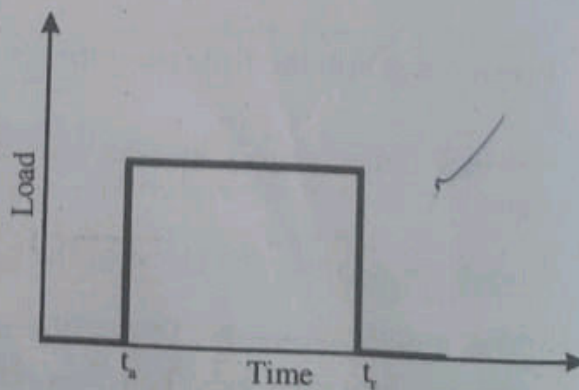

Figure 7.16(a)

in figures 7.16(a) and 7.16(b). Here the load is applied instanta-
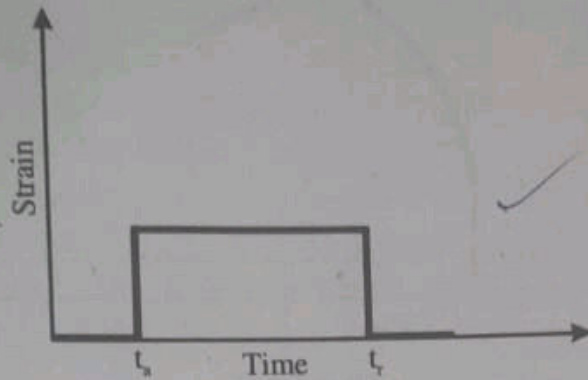neously at time t_a and release at t_r.

Figure 7.16(b)

For totally viscous behaviour the strain is not instantaneous in
response to an applied stress the deformation is delayed or depen-
dant on time. This deformation is not reversible or completely re-
covered after the stress is released. The strain-time behaviour of
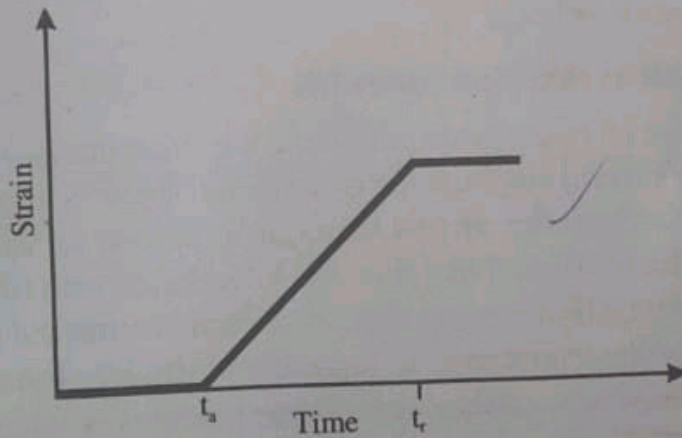totally viscous material is given in figure 7.17.

Figure 7.17

For a viscoelastic material the strain-time behaviour in response
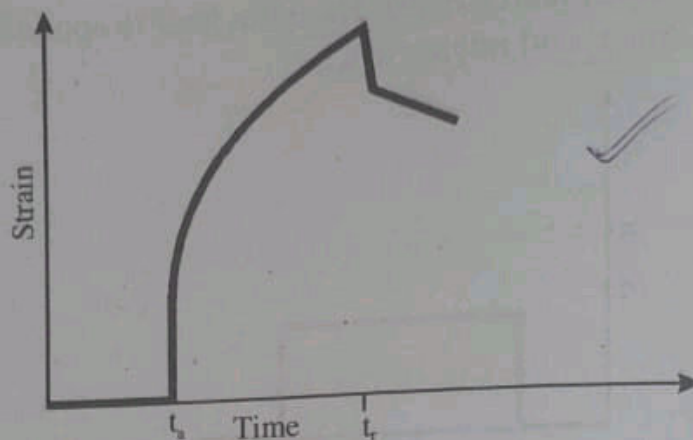to load given in figure 7.16(a) is given in figure 7.18.

Figure 7.18

One familiar polymer that shows viscoelastic nature is silicone. This is known as "silly putty". When it is rolled into a ball and dropped onto a horizontal surface is bounces elasticity, the rate of deformation during the bounce is very rapid. If this ball is pulled under tension with a gradually increasing applied stress the material elongates or flows like highly viscous liquid. For all viscoelastic materials the rate of strain determines whether it is due to elasticity or viscosity or both.

Viscoelastic relaxation modulus

In the case of viscoelastic polymers, the stress necessary to produce a given strain is a function of time. i.e. stress is a function of time. So the elasticity of this material is termed as viscoelastic modulus. But it is found that this stress decreases with time due to molecular relaxation process that takes place within the polymer. So we introduce a new term to represent elasticity of viscoelastic polymer termed as viscoelastic relaxation modulus denoted by $E_r(t)$. **It s is defined as the ratio between time dependent stress $\sigma(t)$ and the strain ε_0.**

i.e.

$$E_r(t) = \frac{\sigma(t)}{\varepsilon_0} \qquad \dots\dots (4)$$

This is measured at constant temperature since change in temperature influences the stress-strain behaviour of the polymer.

Viscoelastic creep

When a viscoelastic material is subjected to a constant stress it experiences time dependent increase in strain. This phenomenon is called viscoelastic creep. The associated modulus is called viscoelastic creep modulus $E_c(t)$. **It is defined as the ratio between constant stress to the time dependent strain keeping temperature constant.**

i.e.
$$E_c(t) = \frac{\sigma_0}{\varepsilon(t)}$$
.....(5)

It may also be noted that $E_c(t)$ is also temperature dependent

Note: Creep is the property of a material which indicates the tendency of material to move slowly and deform permanently under the influence of external mechanical stress.

UNIVERSITY MODEL QUESTIONS

Section A

(Answer questions in two or three sentences)

Short answer questions

1. Write down the four names of polymorphs of carbon.

2. Draw the unit cell for diamond cubic crystal.

3. Write down any two properties of diamond.

4. Write down two applications diamond thin film.

5. Give any two uses of graphite.

6. Draw the structure of graphite.

7. Draw the structure of a C_{60} molecule.

8. Give the properties of fullerenes.

9. What are carbon nanotubes?

10. Explain briefly about fullerene.
11. What are the composites of polymers?
12. Give a schematic representation of covalent bonding in a molecule of methane.
13. Give the structural formula of the following.

   (a) CH_4 (b) C_2H_4 and (c) C_2H_2

14. Distinguish between the saturated and unsaturated hydrocarbons.
15. What types of bonding are present in paraffin family?
16. Why the family members of paraffin have low melting and boiling points?
17. What are isomers?
18. Which are the two isomers of butane?
19. Give the structural formula of normal and isobutane.
20. Why polymers are referred to as macromolecules?
21. How does a polymer molecule form?
22. What are homopolymers?
23. What are copolymers?
24. Give two examples of copolymers.
25. What is meant by functionality with regard to copolymers?
26. Explain the terms bifunctional and trifunctional.
27. What is meant by number average molecular weight?
28. What is meant by weight average molecular weight?
29. What is meant by degree of polarisation?
30. What is the information given by molecular shape?
31. What are the two factors that give physical properties of polymers?
32. What are linear polymers?
33. What are branched polymers?
34. What are cross-linked polymers?
35. What are network polymers?
36. What is meant by isomerism in polymers?

37. Classify stereoisomers.

38. What is meant by isotactic configuration?

39. What is meant by syndiobatic configuration?

40. What is meant by atactic configuration?

41. What is meant by geometrical isomerism?

42. What are thermoplastics?

43. Give three examples of thermoplastic polymers.

44. What are thermosetting polymers?

45. Why thermosets are hard?

46. What is meant by viscoelasticity?

47. Define viscoelastic relaxation modulus.

48. Define viscoelastic creep modulus.

49. Draw the strain-time graph of viscous deformation.

50. Draw the strain-time graph of viscoelastic deformation.

Section B
(Answer questions in a paragraph of about half a page to one page)

Paragraph / Problem type

1. Briefly explain diamond as one of the polymorphic forms of carbon.

2. What are the properties of diamond?

3. What are the uses of diamond?

4. How diamond thin film is fabricated?

5. Give a brief account of the structure of graphite.

6. What are the properties of graphite?

7. What is fullerene?

8. Give any two uses of carbon nanotubes.

9. Give examples of natural polymers.

10. Explain the carbon chain polymers.

11. Explain briefly the formation of polyethylene.

12. How do we calculate the molecular weight of a compound?

13. Distinguish between the number average and weight average molecular weight.

14. How do we calculate the number average molecular weight?

15. How do we calculate the weight average molecular weight?

16. Give a brief account of molecular shape.

17. Distinguish between stereoisomerism and geometrical isomerism.

18. Write a brief note on molecular configuration.

19. Explain geometrical isomerism taking isosprene as example.

20. Distinguish between cis and trans isomers.

21. What are the factors on which molecular characteristics of polymers depend?

22. What are the properties of thermoplastics?

23. What are the uses of thermoplastics?

24. What are the uses of thermostats?

25. What is the importance of stress-strain behaviour of polymers?

26. Write down the three different types of stress-strain behaviour of polymers.

27. Give a brief account of stress-strain behaviour of brittle polymer.

28. Explain briefly the stress-strain behaviour of plastic polymer.

29. Explain the stress-strain behaviour of elastic polymer briefly.

30. Give a brief account of the influence of temperature on the stress-strain behaviour of polymers.

31. Distinguish between metals and polymers with regard to their mechanical properties.

32. Distinguish between elastic and viscous deformations.