CHAPTER 1

Bonding in Solids

1.1 Introduction

Solids are formed when the atoms (molecules) in a liquid state or gaseous state are brought closer into a condensed state and each atom is in close proximity of its neighbours. The condensation into a particular structure of atomic arrangement in solids is determined by the nature and magnitude of the interaction forces between atoms, temperature and pressure. In the process of solidification, the interaction between atoms is such that it reduces the free energy of the system. A system, like a solid, possesses lower energy because of the fact that the electrons occupy lower energy levels than the electrons of typical isolated atom. The state of atoms at an equilibrium separation, thus, corresponds to the condition of stable equilibrium. The interaction forces will be such that the atoms will be at an equilibrium separation to form a crystal of an ordered internal structure.

In general, the chemical bonds that occur in crystals are classified as 1. primary bonds, and 2. secondary bonds. The primary atomic bonds are formed when the interaction forces are relatively strong. The primary bonds are classified as 1. Ionic bonds, 2. Covalent bonds, and 3. Metallic bonds.

The ionic bond is formed between two atoms when one atom transfers an electron to another acceptor atom to give ions of opposite charge. The bonds are formed as a result of strong Coulomb forces. The covalent bond is formed between atoms which share electrons present in the outer most shells. The metallic bond is formed between two metallic atoms which share electron in a delocalized manner. The bond is strong and non-directional.

The secondary bonds are classified into two groups. 1. Permanent dipole bonds: These bonds are formed between molecules that possess permanent dipoles. 2. Fluctuating dipole bonds : These bonds take place among atoms as a result of an asymmetrical distribution of electron densities around their nuclei. The bonding is very weak and is termed fluctuating since the electron density continuously changes with time.

Interatomic Forces

In a gaseous state of matter, the distance of separation between molecules is large. The interatomic force between the atoms or molecules is very weak. The molecules or atoms exist in a continuous motion colliding with each other and the walls of the container in which they are present. When they are brought closer and closer, they first condense into liquid in which the translational motion of the molecules is totally restricted. The energy is then lowered compared to that of free atoms. If the liquid is then condensed to form a solid, the atomic motion is restricted. The atoms will have only vibrational motion, and the rotatory motion, and translational motion are totally absent. The atoms will be held by the bonding forces. The energy of the solid is much lower than that of the liquid state or gaseous state. The atoms in a solid are held by an energy called the bond energy.

The liquid, like the melt of a solid, consists of a short range order that is not stable. There is a continuous agitation of molecules or atoms. The short range order is broken and restored again. This process takes place continuously with a relaxation time. When a solid is formed out of such a state, there is a heat of crystallization that is evolved. The atoms are brought closer to an equilibrium distance at a temperature that is the freezing temperature. In solids, the forces that operate between the atoms are the attractive forces and repulsive forces, and these forces determine the potential energy associated with the atoms in the solid.

Let us examine how does the resultant force between the atoms changes when the atoms are brought closer to each other. At relatively large distances, the attractive force between the atoms dominates. It grows as the interatomic distance diminishes. This variation is shown in Fig. 1.1 as curve 1. When the atoms come sufficiently closer, the repulsive forces come into play ($F_{repul} \propto 1/r^n$) and they grow faster than attractive forces. When the atoms are brought closer, their charge distributions overlap. This overlapping causes electrostatic energy to change. The overlap energy is repulsive at close distances. The repulsion occurs because Pauli exclusion principle prevents multiple occupancy. When atoms reach a distance of separation $r = r_0$ the attractive forces just balance the repulsive forces and the resultant force becomes zero (curve 3). The distance of separation, r_0 is called 'the equilibrium distance'.

The interaction energy U also changes as $F = -\partial U / \partial r$. The interaction energy at $r = r_0$ is called binding energy of pair of atoms. The state defined by $(U)_{r = r_0}$ is a stable equilibrium state. What is said above is valid for all types of primary bonds and the general character of the forces is the same for all types of solids.

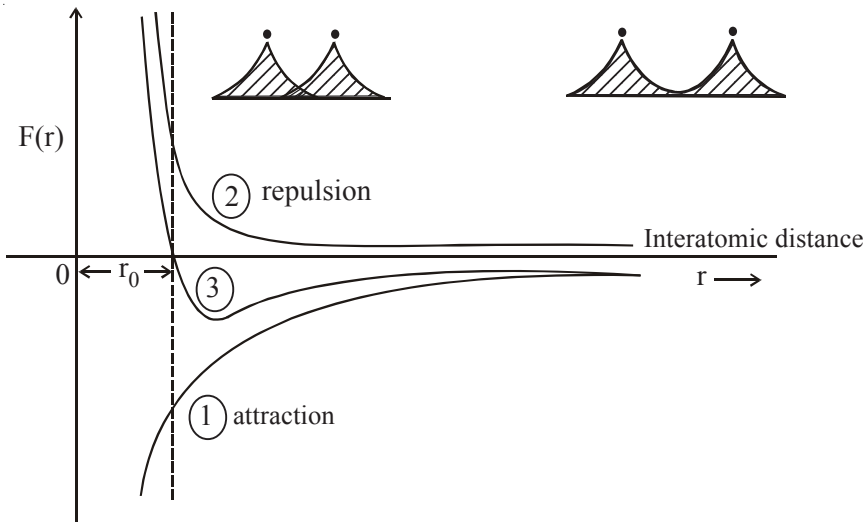


Fig. 1.1 The variation of force between atoms as they are brought closer to each other curve ① attractive force ② repulsive force ③ the resultant force between the atoms. The solid circles and the shaded peaks represent charge distribution overlap.

1.2 Types of Bonding

We shall now see the different types of bonding in crystals in the following sections.

1.2.1 Ionic Bond

Ionic bond is formed when the atoms with small number of electrons on the outer shells, have a tendency to give up electrons to the atoms with an almost filled outer shell. Ionic bond is the simplest type of interatomic bond. By loosing electrons, metallic atoms like alkali-metals, alkaline-earth metals etc., go into the nearest noble gas configuration, while the atoms like halogens take electrons to gain the inert gas configuration. Alkali halides are the simplest type of ionic bonded crystals. The formation of Na C*l* by ionic bonding is shown in Fig. 1.2.

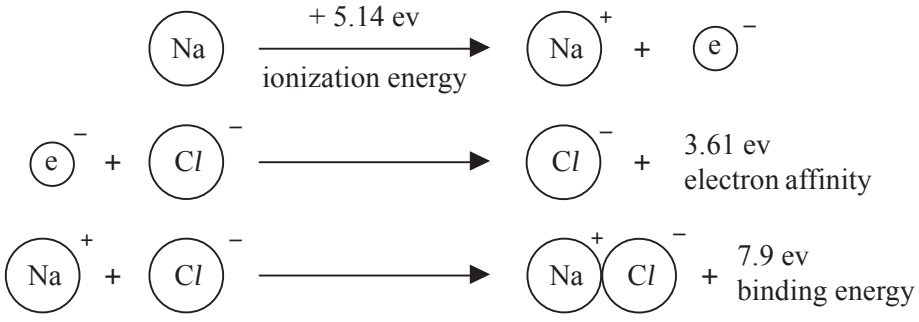


Fig. 1.2 Ionic bonding in Na C*l*.

The ionic crystals consist of positive ions and negative ions. Sodium chloride is the best example for ionic bonding and it has the highest degree of ionic bonding, the sodium atom has one $3S^1$ electron and upon ionization process gives up electron to become sodium ion. The chlorine atom which has half filled p-orbital, takes the electron from sodium, forming chloride ion. The two ions exist as a single unit. The sodium atom with 0.19 nm size is reduced in size to sodium ion with size of 0.095 nm.

Let us now see how the interaction forces between the ions operate. Consider that the two ions, sodium ion and chloride ion are initially far apart. They approach each other as they are attracted to each other by Coulomb forces. The Coulomb force is given as

$$F_{Coul} = \frac{-(Z_1 q)(+Z_2 q)}{4\pi \in_0 r^{m_1}} = \frac{-Z_1 Z_2 q^2}{4\pi \in_0 r^{m_1}} = \frac{+a}{\gamma^{m_1}} \quad .....(1.1)$$

where m_1 is an exponent that determines the nature of the force. Z_1 and Z_2 are the charges of the ions, q is the charge, r is the intertonic distance and $\in_0$ is the permittivity of free space ($\in_0 = 8.85 \times 10^{-12}$ C/N–m^2).

The repulsive force becomes significant when the ions are brought very close to each other, this repulsive force is expressed as

$$F_{rep} = \frac{b}{r^{\eta}} \quad .....(1.2)$$

where η and b are constants.

The change of energy as the ions come closer to each other can be computed easily.

The potential energy associated with attraction (U_{attr}) and the repulsion (U_{rep}) are given as

$$U_{attr} = -\int \frac{a}{r^{m_1}} dr = \frac{a}{m_1 - 1} \frac{1}{r^{\eta_1 - 1}} + C_1 \quad .....(1.3)$$

$$U_{rep} = -\int \frac{b}{r^{\eta}} dr = \frac{b}{\eta - 1}\left(\frac{1}{r^{\eta - 1}}\right) + C_2 \quad .....(1.4)$$

$\therefore$ The binding energy of the ions is

$$U_b = \frac{-A}{r^m} + \frac{B}{r^{\eta}} + C \quad .....(1.5)$$

where $A = \frac{-a}{m}$; $m = m_1 - 1$; $B = \frac{b}{\eta - 1}$; $\eta - 1 = \eta$;

$C = C_1 + C_2$ (the constants of integration)

when r = infinity, $U_b(\infty) = 0$ i.e., $C = 0$

$\therefore$ $$U_b(r) = \frac{-A}{r^m} + \frac{B}{r^n} \quad .....(1.6)$$

At equilibrium distance, the first derivative of the total-energy should vanish i.e., the forces of attraction and repulsion should balance each other i.e., at $r = r_o$, the equilibrium distance

$$\left(\frac{dU_b}{dr}\right)_{r=r_0} = 0.$$

$$\left[+\frac{A_m}{r_0^{m+1}} - \frac{B_n}{r_0^{n+1}}\right] = 0$$

$$\therefore \quad \frac{r_0^{m+1}}{r_0^{n+1}} = +\left(\frac{A}{B}\right)\frac{m}{n}$$

i.e., $$r_0^{m-n} = +\left(\frac{A}{B}\right)\left(\frac{m}{n}\right) \qquad .....(1.7)$$

Then $$U_{b(r=r_0)} = -\frac{A}{r_0^m} + A\left(\frac{m}{n}\right)\frac{1}{r_0^m}$$

i.e., $$[U_b]_{r=r_0} = -\frac{A}{r_0^m}\left(1-\frac{m}{n}\right) \qquad .....(1.8)$$

In the case of ionic crystals, $m_1 = 2$; $m = 1$

$$\therefore \quad [U_b]_{r=r_0} = \frac{-A}{r_0}\left(1-\frac{1}{n}\right) = -\frac{Z_1 Z_2 q^2}{4\pi \in_0 r_0}\left(1-\frac{1}{n}\right) \qquad .....(1.9)$$

1.2.2 Lattice Energy in Ionic Solids

The above condition that $(du_b/dr)_{r=r_0} = 0$ is the criterion for thermal equilibrium. The stable configuration is possible only when the energy is minimum (curve 3 of Fig. 1.3). Let us see the variation of forces with the distance of separation. This is shown in Fig. 1.1. The net force is zero at the equilbrium position.

When like charges approach each other, they require energy and when unlike charges approach each other they release energy. When the ions are brought closer and closer, there exists a repulsion due to electrons of the adjacent atoms. The Pauli exclusion principle also comes into operation and the electron-repulsion energy becomes significant as the atoms approach closer and closer. The energy (curve 3 in Fig. 1.3), possesses a sharp minimum as the inter atomic distance becomes r_0. This is a stable inter atomic distance. Energy is required to reduce or increase this distance.

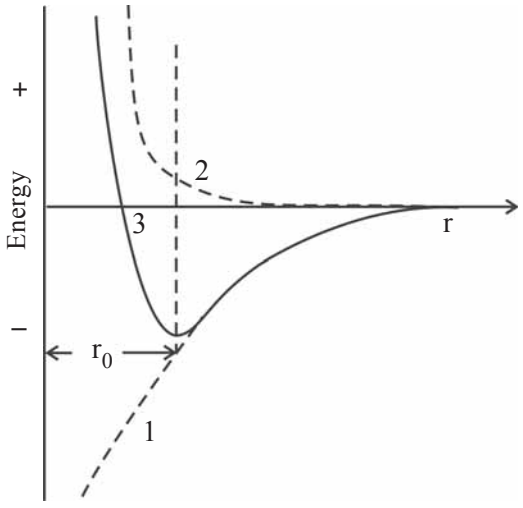


Fig. 1.3 Potential energy variation. The solid line (3) gives the energy of the solid, the resultant of the two energies. The dotted lines (2 and 1) correspond to the repulsive and attractive energies.

Suppose the lattice is built of N_p ion pairs, then the energy of the lattice is obtained as follows.

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

i.e., $$B = \frac{Z_1 Z_2 q^2 r_0^{n-1}}{4\pi \in_0 n}$$

for the U_b eq. (1.9) gives

$$U_b = -\left(\frac{q^2 Z_1 Z_2}{4\pi \in_0 r_0}\right)\left(1-\frac{1}{n}\right)$$

As the lattice is built up of 'N_p' ion pairs, the energy of the lattice is

$$U_{Lat} = -\frac{N_p Z_1 Z_2 q^2}{4\pi \in_0 r_0}\left(1-\frac{1}{n}\right) = \frac{-AN_p}{V_0^{1/3}}\left(1-\frac{1}{n}\right) \quad .....(1.10)$$

where V_0 represents the volume.

The energy trough will be very narrow for strongly bonded atoms. As a result, the slope, dF/dr, of the force curve at $r = r_0$ in Fig. 1.3 becomes very steep. This produces an interatomic distance which is constant within 0.001 Å at a given temperature. In such a case, we can take the ions as hard balls with definite radii.

We can determine the value of B in the expression in eq. (1.2) for a crystal like Na C*l*. The interionic distance is 2.76×10^{-10}m.

The attractive force is

$$F_{att} = \frac{-Z_1 Z_1 e^2}{4\pi \in_0 r^2} = -\frac{\left(1.6 \times 10^{-19}\,C\right)^2}{4\pi\left(8.55 \times 10^{-12}\,C^2/N.m^2\right)\left(2.76 \times 10^{-10}\,m\right)^2}$$

$$= -3.02 \times 10^{-9}\,N.$$

Near $r = r_0$, this is equal to the repulsive force. Then, from eq. (1.6), we get

$$B = \frac{r_0^{n+1}}{n} \times F_{rep}$$

i.e., $$B = \frac{3.01 \times 10^{-9} \times \left(2.76 \times 10^{-10}\right)^{n+1}}{n}$$

n = 9 for Na C*l*.

$$\therefore \qquad B = \frac{3.02\times10^{-9}\times\left(2.76\times10^{-10}\right)^{10}}{9} = 8.6\times10^{-106}\ \text{N . m}^{10}$$

Then, the binding energy for Na^{+}-Cl^{-} pair is

$$U_b = \frac{-q^2}{4p\in_0 r_0} + \frac{8.6\times10^{-106}\ \text{N.m}^{10}}{\left(2.76\times10^{-10}\ \text{m}\right)^9}$$

$$= \frac{-\left(1.6\times10^{-19}C\right)^2}{4\pi\left(8.85\times10^{-12}\right)\left(2.76\times10^{-10}\right)} + \frac{8.6\times10^{-106}}{\left(2.76\times10^{-10}\right)^9}$$

$$\sim -8.34\times10^{-19}\ \text{J} + 0.92\times10^{-19}\ \text{J}$$

$$= -7.42\times10^{-19}\ \text{J}.$$

The bond energy due to attraction is – 5.23 eV and the contribution of the repulsive force to the energy is 0.575 eV.

1.2.3 Ionic Radii and Coordination Number

In discussing the ionic bond, we have just considered two ions. A crystal has a certain number of ions per unit volume that are distributed in three dimensions. They can be considered as having spherical shape with a characteristic value for radius in crystals. There are a large number of ionic crystals, namely, alkali halides, alkaline earth halides, oxides, transition metal oxides etc. The ionic radius of ions in these crystals depends on the coordination number.

Since ions can be treated as hard spheres, carrying a charge of normal parent atom of the crystal. They interact through central electrostatic forces. The crystal structures of ionic compounds to a large extent, are determined by packing of ions together as closely as possible under the strong electrostatic forces. The ratio of the ionic radii in the crystal structure is very important aspect of ionic solids.

A crystal of sodium chloride consists of positive ions (cation, Na^{+}) and negative ions (anion, Cl^{-}). The energy of attraction between the two ions spaced at a distance r_0 apart

$$U_0 = -\frac{Z_1Z_2q^2}{4\pi\in_0 r_0} = \frac{-A}{V_0^{1/3}}$$

where q is the charge of the ion. The reduction of energy on attachment of an electron to an anion, is higher than the increase of energy on detachment of an electron from a cation. The energy of an aggregate composed of positive and negative ions is reduced further due to the fact that each ion of one sign has ions of opposite sign as its nearest neighbours. This does occur as a result of coulomb attraction of the oppositely charged ions. The number of neighbours surrounding an ion and the type of crystal lattice are determined by the ratio of atomic radii of cation and anion. If this is R, then

$$R = r_c / r_a \qquad \text{.....(1.11)}$$

where r_c and r_a are the radii of the cation and anion respectively. The lattice of a crystal is stable only when the cores of the ions of one sign are in direct contact with the cores of opposite sign.

The coordination number z for the ionic lattices depends on the value of R. The following table gives the R values and the corresponding Z values.

R	0.73 – 1.00	0.41 – 0.73	0.22 – 0.41	0.15 – 0.22
Z	8	6	4	3

The example for Z = 8 is cesium chloride (CsC*l*) Fig. 1.4(c), for Z = 6, it is NaC*l* Fig. 1.4(b), and Z = 4, it is CaF_2 or LiF.

The Fig. 1.4(a) gives the coordination polyhedron of an ionic bond that has Z = 6. When this polyhedron is repeated to fill space, the arrangement of atoms in a crystal is shown in Fig. 1.4(b). The alkali metal halides and hydrides, the alkaline earth oxides and silver halides (except AgI) belong to this type of ionic bonding.

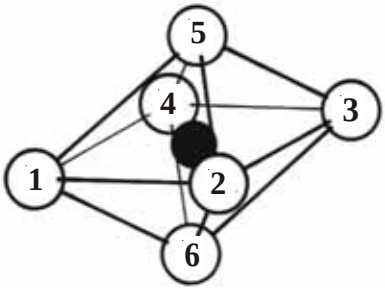


Fig. 1.4(a) Coordination polyhedron for coordination number 6. ● cation ○ anion. The anions 1, 2, 3, 4 are at the apices of the polyhedron.

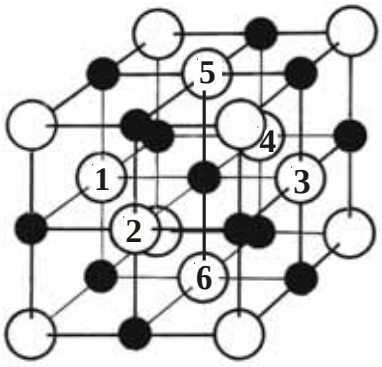


Fig. 1.4(b) The unit cell of a crystal in which Z = 6. The structure is known as rocksalt structure.

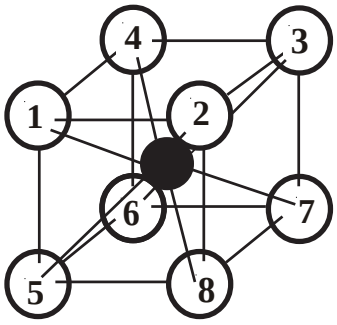


Fig. 1.4 (c) CsC*l*, with coordination number 8.

The structure called the rocksalt structure becomes unstable when the anions come into contact along the coordination polyhedron edges. Then , if a further decrease in r_c/r_a is caused,

the coordination number falls to 4. In a fourfold structure, tetrahedral structure, the anions are at the apices of a tetrahedron. Decreasing r_c/r_a produces an instability on the hard sphere model of f.c.c when the anions touch along the edges of the tetrahedron. From geometrical considerations, the tetrahedron coordination is possible only for $0.414 > r_c / r_a > 0.225$.

Tetrahedral coordination polyhedra may be arranged or stacked to fill space in two ways. They are 1) the structure showing cubic structure and known as zinc blende 2) wurtzite. ZnS is the example and it exists in both the forms with a coordination number '4'.

1.2.4 Properties of Ionic Crystals

A large class crystals like alkali halides, alkaline earth halides, metal oxides, sulphides, selenides etc., belong to the group of ionic crystals. Alkali halides are the most basic crystals for study. We shall briefly give the general properties of the ionic crystals.

The ionic bond is a strong bond. The properties of crystals depend on the lattice energy. Some basic properties like heat of sublimation, melting point, boiling point, solubility etc., show a regular dependence on the inter ionic distance. For example if we take MF, MC*l*, MBr, MI, the halogenides, of alkali metals (Li, Na, K, Rb, Cs), the boiling points and melting points decrease as one goes from fluorides to iodies. In general, the ionic solids possess high melting points.

The ionic compounds exhibit large band gaps and therefore come under the class of insulators. The resistivities of alkali halides will be of the order of $10^{12}\ \Omega$ –cm or more at room temperature. The oxides exhibit much higher resistivities. For example, the resistivity of Al_2O_3 is of the order of $10^{16}\ \Omega$ –cm at room temperature.

The resistivity of all ionic solids decreases with the rise of temperature. That is, they show negative temperature coefficient of resistivity. The resistivity is a strong function of temperature in ionic crystals.

The conduction is basically electrolytic in nature. The ions move through the lattice via the point defects, when electric field is applied to a crystal. The study of electrical conductivity helps to determine the characteristics of defects in ionic crystals.

The defects like point defects and line defects are charged defects. The addition of impurities strongly affects the conductivity of ionic crystals. This is made use of, in making the electrolytic solid state battery cells. Super ionic conductors are useful materials for solid state batteries.

Many ionic crystals are transparent to radiation over a wide wavelength range. Normally the alkalihalides have absorption bands in the infrared region. Therefore, they are useful as infrared filters and windows. When crystals like alkali halides are subjected to high energy radiation like X - rays or γ rays, they get colored i.e., they absorb light in visible radiation at certain wave lengths. The absorption is due to 'Colour centres'**.** The formation of color centers is very important in energy storage utility. Many oxides, sulphides and alkali halides exhibit luminescence properties if they are subjected to external stimuli like high energy radiation or electric field.

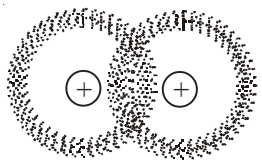
Ionic crystals exhibit high strength. They are also brittle. The fracture takes place along the cleavage planes. The ionic solids are hard. Ionic compounds dissolve in polar solvents.

1.3 Covalent Bond and Covalent Crystals

1.3.1 Covalent Bonds in Crystals

It is known that the word 'covalent' describes the sharing of valence electrons by adjacent atoms. Hydrogen molecule is a good example of covalent bonding. The two protons share two electrons of opposite spins. The electrons lie between the hydrogen atoms for major part of the time. To a first approximation, the covalent bond in a hydrogen molecule can be considered to arise from the attraction of positive ions to the intervening pair of electrons with opposite spins as shown in Fig. 1.5.

$H_{\bullet} + H^{\bullet} \rightarrow H : H$ (Hydrogen molecule)



electron pair covalent bond and interaction

Fig. 1.5 Covalent bonding.

In the bonding process of forming the hydrogen molecule, the potential energy of the hydrogen atom is lowered as shown in Fig 1.3, curve 3.

The molecules of fluorine, chlorine, oxygen, nitrogen etc., (the diatomic molecules) are formed on the basis of electron-pair covalent bonds. In these cases, two p-electrons are shared between the atoms. The above examples have single bonds i.e., their coordination number is one. But many elements form multiple bonds, Carbon is the best example. Carbon can form four covalent bonds even though it should form only two-covalent bonds. Sulphur, selenium, tellurium etc., form two bonds; Phosphorous, nitrogen, arsenic, antimony can form three bonds.

The covalent bond is pictured as an overlap of the electron orbitals of the two participating atoms. Pauli's exclusion principle explains why only two electrons can take part in the bond formation. According to it, only two electrons that have the same quantum numbers but opposite spins can pair up. If a third electron has to take part in the bonding, it would have its spin vector in the same sense as either of the earlier electrons. Therefore, it will be repelled. Hund's rule states that, for equivalent orbitals, electrons tend not to share the same orbitals and the electrons occupying different but equivalent orbitals tend to have their spins parallel.

Nitrogen (outer valence electrons $2S^2\ 2p^3$) has three unpaired p-electrons. It can attain the neon noble gas electron configuration ($2S^2\ 2p^6$) by sharing three 2p-electrons with another nitrogen atom to form the diatomic molecule.

The most important covalent bonded material is carbon. The carbon is the basic element for many organic materials like polymeric materials. The carbon atom has the ground state electron configuration $1s^2\ 2s^2\ 2p^2$. Therefore, it should form two covalent bonds with its two half filled 2p-orbitals as per Hund's rule.

However, carbon shows a covalency of four and form four covalent bonds of equal strength. To explain this, let us consider the electron configuration of carbon. There are 2s states and 2p states. The 2s states and 2p states are closely spaced and the energy difference between them is small. Therefore electrons can redistribute themselves as follows (Fig. 1.6).

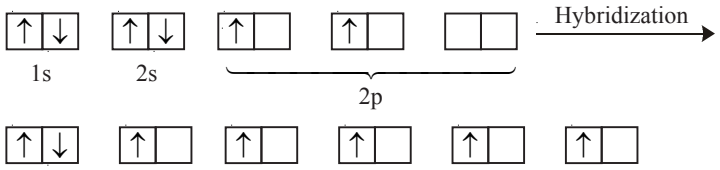


Fig. 1.6 Hybridization of carbon.

The carbon promotes one of its 2s electrons to a 2p orbital, the 2s and three 2p orbitals merge to form sp^3 hybrid orbitals. These are elliptical orbitals which are disposed toward the four corners of a tetra hadron. Each orbital contains one electron. This type of arrangement is known as hybridization. The process of hybridization enables carbon to form four equivalent covalent bonds instead of only two. This process leads to the formation of very stable compounds, or elemental compounds like diamond.

The carbon in the form of diamond exhibits the covalent bonding. The four sp^3 hybrid orbitals are directed symmetrically toward the corners of a regular tetrahedron. This is shown in Fig. 1.7. Each carbon is covalently bonded to four adjacent atoms. Diamond is extremely hard. It has high bond strength and melting point (3550 ^{0}C). Its bond energy is about 711 kJ/mol.

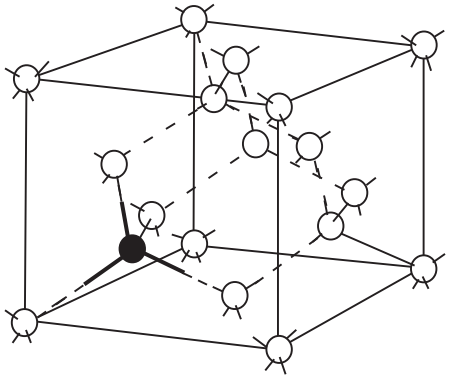


Fig. 1.7 In a Diamond structure, each carbon atom is covalently bonded to four adjacent atoms. The bond angle is 109.5 ^{0}C.

The covalent bonds are highly directional i.e., stereospecific. The coordination numbers for covalently bonded atoms are mostly controlled by radii ratios.

The covalent bonds follow the following characteristics:

1. Multiple bonds have shorter bond lengths.
2. Double bonds are stronger than single bonds. This aspect is very important in polymers.

1.3.2 Properties of Covalent Crystals

The covalent crystals because of their directionality in bonding have different properties compared to ionic crystals. The co-ordination numbers for covalentely bonded crystals are not controlled by radii ratios. There is always a strong covalent attraction only between first neighbours. As with ionic bonds, the lattice energy is associated with covalent crystals. Shortest bond lengths exist only in covalent crystals.

The melting and boiling points of covalent crystals are usually low as compared to those of ionic crystals.

These compound solids exhibit smaller energy band gaps. Pure covalent solids are good insulators at lower temperatures. However, as temperature increases, the conductivity increases. The conduction in most of the covalent solids is electronic in nature. Covalent solids are very hard, for example, diamond is hardest substances known. These solids have high yield strength and are not brittle.

Covalent substances are soluble in non-polar solvents. Hydrogen peroxide, propylene etc., are other examples for a covalent bonding. Silicon and Germanium are excellent examples for covalent bonding. Silicon and Germanium are semiconductors. Silicon and Germanium have the same structure and have a finite number of electrons which are able to leave the covalent bond locations.

1.4 Metallic Bonding

1.4.1 Nature of Metallic Bonding

This is the third type of chemical bonding that is important in materials. It is somewhat intermediate between covalent and ionic bonding. Metals are the major class of materials that are used in engineering. From the scientific point of view also, they place themselves as the most interesting species among different materials.

The atoms are packed relatively close together in a systematic pattern in metallic solids. Metallic atoms i.e., those which possess loosely held valence electrons may be bonded together into a stable solid.

We shall consider the case of a simple metal like sodium. When two sodium atoms are brought closer, the unpaired 3s electrons of the atoms form an electron-pair bond with the spins of the 3s electrons opposed. As a third sodium atom approaches this pair, its 3s electron will be repelled by the 3s electrons of the other two atoms. This is because of Pauli's exclusion principle. However, the energy of the unoccupied 3p states is very nearly the same as the energy of a 3s state. Consequently, the third electron can go over into this state without violating the Pauli exclusion principle. In a similar fashion, a large number of sodium atoms can thus surround any sodium atom. The first sodium atom or the central atom that has only one unpaired electron takes turns forming electron-pair bonds with each of the surrounding atoms. Therefore, the sodium forms less than a whole electron-pair bond with each neighbour. Solid sodium solidifies into a body-centered cubic structure in which each sodium atom is surrounded by eight other atoms. Therefore, each sodium atom can form one-eighth of an electron-pair bond, or one-quarter of an electron bond, with each of its nearest neighbour.

Similarly, copper atoms in crystalline copper are so close together that their outer valence electrons are attracted to the nuclei of their numerous neighbours. Each atom is surrounded by twelve neighbours (closest). The valence electrons are associated with all nuclei and are spread out among all atoms. Now, electrons exist as 'electron gas' in which ion cores are present.

The metallic bond is essentially a covalent bond without saturation. The metal atoms are held together by a mutual sharing of valence electrons. The density of electrons between the atoms is much lower than that is allowed by Pauli exclusion principle. Therefore, the electrons

move freely as gas molecules without expending energy. The metallic bond is nondirectional. The coordination number is very high. The metallic lattice is shown in Fig. 1.8.

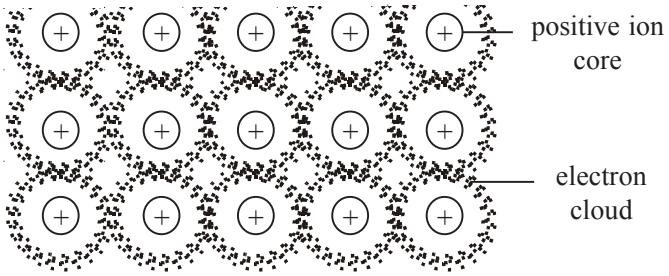


Fig. 1.8 Metallic lattice.

A large number of metals like Al, Cl Mg, Ti, Ni, Zn, etc., have 12 neighbors for each atom. Other metals like Li, Na, K, V, Mn, W and Fe (at room temperature) have eight neighbours for each atom. The binding energy for potassium is about 89.6 KJ/mol, for Nickel it is 423 KJ/mol, Zinc, it is 131 KJ/mol.

1.4.2 Properties of Metallic Bonding

Metallic bonding is weaker than ionic and covalent bonding, but stronger than Vanderwaals' bonding.

Metals possess high thermal and electrical conductivities. This is because of the free electron movement in the lattice. Metals exhibit ductility. They are brittle below a certain temperature. Metals exhibit brittle to ductile fracture transition at a certain temperature. Many metals like tungsten are tough. But some metal like pure silver, aluminium, gold are soft and malleable. Their melting points vary from 64 ^{0}C (Potassium) to 2000 ^{0}C [Titanium (1812 ^{0}C), Molydenum, Tungsten]. Metallic alloys are extremely useful for all engineering applications. Their high conducting values (gold, platinum, silver, copper etc.,) make them useful as electrodes in scientific and technical devices. Metals are opaque to light and they reflect light energy very efficiently.

1.5 Hydrogen Bonding

A chemical bond, in which a hydrogen atom of one molecule is attracted to an electronegative atom, of the same or another molecule is called 'Hydrogen bond'. Hydrogen forms bonding with electronegative nitrogen, oxygen, or fluorine atom, usually of another molecule. The interaction which occurs when a hydrogen atom, covalently bonded to an electronegative atom (as in AH), interacts with another atom Y to form the aggregate AH ··· Y.

The shortest and strongest bond is indicated as AH, while the secondary and weaker interaction is written as H ··· Y. Thus, AH is a proton donor, while (Y) is a proton acceptor which often contains lone pair electrons and can act as a base.

Hydrogen atom acts as a bridge between two atoms, holding one atom by a covalent bond and the other atom by a hydrogen bond. The hydrogen bond is represented by dotted line (…..), while covalent bond is represented by the solid line(____).

..... $H^{\delta+} - A^{\delta-}$ ..... $H^{\delta+} - A^{\delta-}$ ..... $H^{\delta+} - A^{\delta-}$

Examples:

1. Hydrogen fluoride (HF)—The hydrogen atom while remaining bonded with fluorine atom, forms another weak bond with fluorine atom of adjacent bonding molecule. Hence, the formation of a hydrogen bonding results in the formation of a cluster of hydrogen fluoride (HF) molecules as $(HF)_n$, as shown below.

   …...HF……HF…..HF….HF…..HF…

   Hydrogen fluoride can be solidified at low temperatures. In solid form ,it contains long zig-zag chains of molecules as shown in Fig. 1.9.

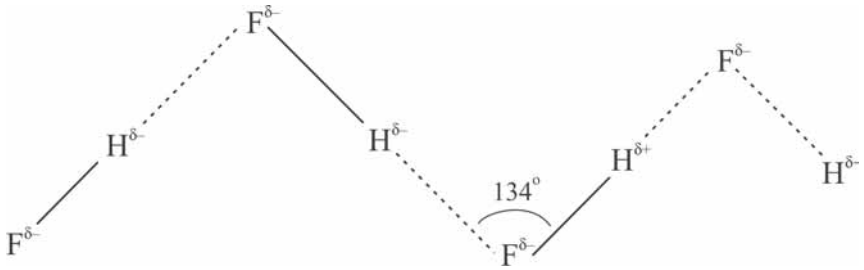


Fig. 1.9 Hydrogen bonding $(HF)_n$ in HF solid state.

Covelent bonding is a strong bond. Compared to it, hydrogen bond is much weaker. The strength of a hydrogen bond is of the order of 10^{-40} KJ-mol^{-1} as compared to the normal covalent bond that would have 40 KJ mol^{-1}. The bond length is longer in hydrogen bonding than that in covalent bonding. In the case of HF molecule, the covalent bond length is 109 pm while the bond length between F and H is 155 pm.

It should be noted that strong electronegativity of the other atom or molecule is a must for the formation of hydrogen bonding. Two good examples we can cite here are: ammonia (NH_3) and water (H_2O).

In the case of ammonia, (NH_3), the electronegative nitrogen atom forms a bond with three hydrogen atoms. As nitrogen is more electronegative and hydrogen acquires a positive charge, the bond takes place with good strength. Because of the above reason, ie the existence of positive and negative sites, the molecules of ammonia is associated through hydrogen bonding in long chains. The bonding is shown in the Fig. 1.10.

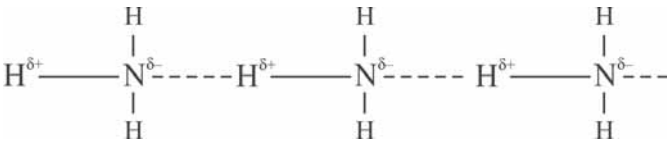


Fig. 1.10 Ammonia bonding, NH_3.

One of the conditions for hydrogen bonding is the size of electronegative atoms or molecule should be small. For example, in the case of NH_3 and HCl, only NH_3 shows hydrogen bonding and not HCl. This is because of the fact that N is smaller than Cl.

Water is a good example of polar molecule that exhibits hydrogen bonding. Apart from two (O-H) bonds, water molecule has oxygen atoms forming two hydrogen bonds as shown in the Fig. 1.11.

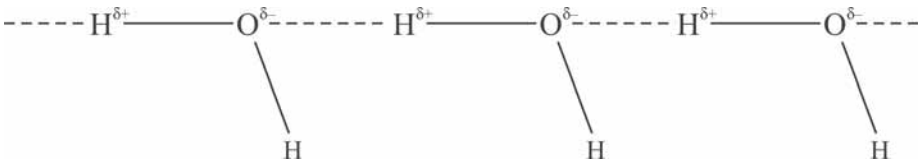


Fig. 1.11 Hydrogen bonding in H_2O.

In H_2O, four hydrogen atoms, two by covalent bonding and two hydrogen bonds tetrahedrally surround each oxygen atom. The molecular formula is $(H_2O)_n$. In the solid form, ice is a very interesting crystal. The crystal lattice consists of linked hexagonal rings of water molecules with considerable open space in the center of the ring. All naturally occurring ice crystals are hexagonal in shape and all snowflakes reflect this basic six-sided **crystal** habit.

Good examples of crystals in which hydrogen bonding plays very important role in determining their properties are Potassium dihydrogen phosphate (KH_2PO_4, KDP) and Ammonium di hydrogen phosphate ($NH_4H_2PO_4$, ADP). KDP is a ferroelectric below 120K and piezoelectric even at room temperature. KDP exhibits electro-optic effect. ADP is anti-ferroelectric and piezoelectric.

The strongest hydrogen bonds are formed between the most electronegative (A) atoms such as fluorine, nitrogen, and oxygen which interact with (Y) atoms having electronegativity greater than that of hydrogen (C, N, O, S, Se, F, Cl, Br, I).

The weaker the hydrogen bond, the shorter the lifetime of the complex it forms. An important aspect of weak hydrogen bond formation is that the different molecular aggregates which do form can be easily and reversibly transformed. Thus the small energy changes resulting in the rapid making and breaking of hydrogen bonds in biological systems are of great importance; for example, hydrogen bonding determines the configuration of the famous α-helix of DNA, and the structures of most proteins, thereby serving an important function in determining the nature of all living things.

1.6 Secondary (Van der Waals) Bonding

Primary bonding (ionic, covalent and metallic) is strong and the energies involved range from about 100 to 1000 kJ/mole. In contrast, secondary bonding is weak, involving energies ranging from about 0.1 to 10 kJ/mole. While this type of bonding, also referred to as “residual”, is weak, it is essential in the functioning of our environment.

The energy difference between the liquid and vapor states of a given system is given by the heat of vaporization, i.e. the heat required to convert a given liquid into a vapor (normally) at the boiling point temperature at 1 atm pressure. The energy difference is due to intermolecular attraction between molecules at close distance of separation. This phenomenon of attraction through secondary bonding can best be considered between a single pair of molecules, but recognizing that the forces are of longer range.

The following intermolecular forces are identified.

1. ***Dipole-Dipole Interaction:*** Molecules with permanent dipoles (such as water, alcohol and other organic compounds with functional groups) exert a net attractive force on each other as a result of varying degrees of alignment of oppositely charged portions of the molecules . For two polar molecules with a dipole moment of (μ) separated by a distance of (r), the energy of attraction can be quantified as:

$$\mu = L.\partial q \qquad .....(1.12)$$

where L is the distance of separation of the charges. In molecules, the dipole moment is given by the vector sum of electronic charges of the polar bonds. Thus, because of molecular geometry (symmetry), molecules such as CCl_4 exhibit no dipole-moment.

The Dipole-Dipole interaction is given by

$$E_{Dipole-Dipole} = -\frac{2}{3}\frac{\mu^4}{Dr^6} \times \frac{1}{kT} \qquad .....(1.13)$$

where μ is the dipole moment, r is the distance of approach of the oppositely charged molecular portions, k is the Boltzmann constant and T is the absolute temperature in K.

The molar energies of attraction associated with dipole-dipole interaction range from 0 to about 10 kJ/mole. These forces are primarily responsible for the liquid state (at room temperature) of most polar organic molecules; they are a contributing factor for H_2O to be liquid at room temperature, and are responsible for alcohol being a liquid.

2. ***Dipole-Induced Dipole Interaction:*** A dipole in one molecule can interact with and polarize the electrons of a neighboring non-polar molecule, thus generating an induced dipole which will experience an attractive force with the polarizing, polar dipole. Debye showed that in a molecule with a "polarizability" of (α) the attractive potential arising from dipole-induced dipole interaction is given as:

$$E_{Dipole-Induced\ dipole} = -\frac{2\alpha\mu^2}{Dr^6} \qquad .....(1.14)$$

Induced dipole interaction is important in aqueous solutions and very effective during adsorption of inert molecules on active solid substrates.

3. ***London Dispersion Forces:*** It is a well-known fact that all substances, including rare gases and hydrogen, assume liquid state at finite temperature, an indication of the existence of attractive interatomic and intermolecular forces, even in the absence of permanent dipole systems. The origin of this force has been proposed by F. London in 1930. Accordingly, orbiting electrons will at any instant generate a "temporary dipole", the

configuration of which changes as the electrons move. Since all atoms of a given system similarly experience temporary instantaneous dipole moments, their effect is expected to be cancelled because of the statistically random orientation of dipoles. It is evident that, should the dipoles be synchronized in a given assembly of atoms, then, a net attractive force would result. But, such an attractive force constitutes a lowering of the energy of a given system, synchronization can and will take place because all systems will attempt to assume minimum energy configuration. The London dispersion force can be formulated as:

$$E_{London} = -K\frac{\alpha^2}{r^6} \qquad .....(1.15)$$

where k and α are constants, r is the distance between molecules.

The attractive London forces are small, as manifested by the very low boiling points of some of the rare gases, hydrogen and nitrogen. The dispersion forces are much weaker then covalent bonds within molecules. Dispersion forces occur in addition to dipole-dipole interactions. The molecules is liquids, which have temporary fluctuating dipoles, have low boiling points.

1.7 Cohesive Energy

The energy required to bind the atoms or ions in a molecule is called cohesive energy. It is also the energy necessary to dissociate a molecule into atoms.

While discussing about ionic bond, we have considered two ions in the eq. (1.9). We just have extended it to 'N' ion pairs in eq. (1.10). Let us take up now the same in a general case.

Madelung constant 'A' represents the effect of the interaction of all the ions on any ion in the ionic crystal. All the ions in the lattice will be contributing to the energy of cohesion. We shall discuss a simple way of evaluating the Madelung constant for a crystal like NaCl. In ionic crystal, individual atoms do not exist. Every anion is surrounded by a certain number of cations and every cation is surrounded by as many anions. The coordination number is determined by the ratio of cation and anion radii.

Consider a crystal as arrays of ions (NaCl) as shown in Fig. 1.12., where a two dimensional array is shown. Let u_{ij} be the interaction energy between any two ions i and j. The interactions are pair-wise additive, the total interaction energy between i^{th}

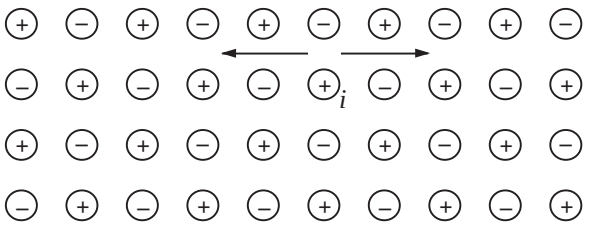


Fig. 1.12 Array of ion pairs in an ionic crystal.

ion taken as a reference ion, and all the other ions in the crystals is given as a summation over all pairs of ions as given below.

$$u_i = \sum_j{}' u_{ij}(r_{ij}) \qquad \text{.....(1.16)}$$

where $\sum_j{}'$ indicates that the summation is taken to include all ions except j = i (i.e., the same ion). This interaction energy does not depend whether the reference ion 'i' is positive or negative or the position of the ion in the array or crystal.

The term u_{ij} consists of first the long-range coulombic interaction. It is a central force as has already been stated, the second force is the short range interaction. We have defined the coulomb energy as

$$u_{ij} = -\frac{Z_i Z_j e^2}{4\pi \in_0 r_{ij}} \qquad \text{.....(1.17)}$$

Suppose $r_{ij} = p_{ij}\, r_0$ and r_0 is the shortest distance between unlike ions in the crystal. Then the total electrostatic energy between the i^{th} ion and other ions in the crystal is given as

$$\sum_j{}' + \frac{Z_i Z_j e^2}{p_{ij} 4\pi \in_0 r_{ij}} \qquad \text{.....(1.18)}$$

$$= -\frac{Z_i Z_j A}{4\pi \in_0 r_0} \qquad \text{.....(1.19)}$$

where $A = \sum_j{}' \mp \frac{1}{p_{ij}}$ .....(1.20)

The constant A called Madelung constant is introduced in the eqn. (1.6) already.

Madelung constant is the property of a particular crystal structure. It can be calculated.

We consider one row of ions in Fig. 1.4 for NaCl. Consider the ions on either side of the reference ion 'i'.

$$u_{i+1} = \frac{e^2}{4\pi \in_0 r_0}$$

$$u_{i,\, i-1} = \frac{e^2}{4\pi \in_0 r_0}$$

$\therefore$ The net energy is $\frac{-2e^2}{4\pi \in_0 r_0}$.

The next two ions on either side contribute

$$\frac{2e^2}{4\pi \in_0 2r_0}$$

The next-two ions on the either side contribute

$$\frac{-2e^2}{4\pi \in_0 .3r_0}$$

This can be done upto the end of the chain on either side which can be taken as $-\propto$ to $+\propto$.

Then

$$\frac{A}{r_0} = 2\left[\frac{1}{r_0} - \frac{1}{2r_0} + \frac{1}{3r_0} - \frac{1}{4r_0} + ...\right] \quad .....(1.21)$$

Thus, the factor two comes in, because there are two ions, one left side and the other on the right side at equal distance.

or $$A = 2\left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + ...\right] \quad .....(1.22)$$

i.e., $$A = 2\,l\text{n}\,2 \quad .....(1.23)$$

Thus, the Madelung constant for one dimensional chain is A = 2 *l*n 2.

The cohesive energy decreases monotonously in alkali halides with the generic formula, M^+X^-, where M^+ can be Li^+, Na^+, K^+ or Rb^+ and X^- can be F^-, Cl^-, Br^-, and I^- for same M^+ ion. Thus, the following Table 1.2 gives the cohesive energies for a series of compounds. 'A' depends only on the type of the lattice and is independent of the lattice dimensions and the kind of ions.

The attractive potential energy U of the lattice energy is proportional to $\frac{1}{r_0}$.

The calculated Madelung constants for a few crystals are given below.

NaCl	1.74756
CsCl	1.76267
$M^{++}X_2^-$	5.03878
Rutile	4.816

For isolated Na^+Cl^- molecule, the Madelung constant has a value equal to one. But in a crystal of NaCl, it is 1.74756 i.e., about 75% more.

If there are 'N' ion pairs, 'Z' is the ion valence, e the elementary charge, 'r_0' is the distance of separation.

Then $$U_{coul} = -A\frac{NZ^2e^2}{4\pi\epsilon_0} \times \frac{1}{r_0} \quad \text{.....(1.24)}$$

If $Z_{cation} \neq$ Z anion, and Z is taken as the largest common factor.

1.8 Born Repulsive Exponent

The repulsive energy is given as $\frac{B}{r^n}$. B is evaluated in the eq. (1.6). 'n' is called the Born exponent. It is evaluated on the basis of compressibility studies in ionic crystals. During the compression of a crystal, the ions are pushed to closer distances and hence their electron outer shells interact vigorously. Therefore, the study of compressibility gives the information about repulsive forces. The study of compressibility helps is in the estimation of born exponent. If N_p is the number of ion pairs per unit volume, x is the compressibility of the crystal, then,

$$\frac{1}{\chi} = \frac{n-1}{9}A\frac{Z^2e^2}{4\pi\epsilon_0} \cdot \frac{N_p}{r_0^4} \quad \text{.....(1.25)}$$

The value of n is nearly 10 for many ionic crystals. The value of n and the lattice energies for a number of alkali halides is given in the Table 1.2.

Table 1.2 The values of Born's exponent and lattice energies calculated and measured. The energies mentioned are in KCal/mole.

	LiF	LiCl	LiBr	LiI	NaF	NaCl	NaBr	NaICsF	CsF	CsCl	CsBr	CsI
n	6.2	7.3	7.7	7.0	6.4	8.4	8.3	8.0	10.2	10.6	10.5	11.1
U(calculated) KCal/mole	240	194	183	165.7	210	180.9	170	157	176	152	146	138.6
measured in KCal/mole	242	199	188.8	177.7	214	182	173.6	163	172	155.4	149	142.4

The compressibility and repulsion exponent are inversely proportional to one another. Many cases, the value of n is high confirming the fact that the ions can be regarded as hard spheres ($n \rightarrow \infty$) which are arranged in the lattice in such a way that the nearest neighbours touch each other. The repulsion force is principally due to Pauli exclusion principle Knowing the exponent value allows us to calculate the lattice energy, the main part of which is due to coulomb energy. The values of Madelung constants for various crystals are

NaCl – 1.748 ; CsCl - 1.763 ; CaF_2 – 5.039 ; ZnS – 1.641.

Questions

1. Explain the types of interatomic forces.
2. Mention various types of bondings that can exist between atoms.
3. Explain how the force of attraction between two atoms or ions vary as they are brought closer.
4. Explain what is 'ionic bonding'.
5. When two ions are brought closer, what is the nature of energy components between them?
6. What is Coulomb energy? How does it vary with the distance between ions.
7. What do you mean by 'repulsive force' between ions? How does it arise?
8. Derive the expression for the lattice energy of an ionic crystal like NaCl.
9. What is Madelung constant?
10. What is a coordination number? Give examples.
11. Explain covalent bonding? What is Hybridization?
12. Explain the bonding in diamond. Give some examples for covalent bonding. In what way covalent bonding is different from ionic bonding?
13. What is a metal? Explain the meaning of electron gas. How is it formed?
14. Give the general properties of ionic solids.
15. Show the minimum cation/anion radius ratio for a coordination number of 6 is 0.414.
16. Explain the formation of Hydrogen bonding. Compare it with covalent bond.
17. Explain how vander Waals bonds are formed.
18. What is cohesive energy. Obtain an expression for cohesive energy of ionic solids.
19. What are ionic solids ? Give examples. Explain formation of an ionic solid.
20. Explain what is cohesive energy ? How do you get the cohesive energy of a molecule like NaCl ?
21. Write short notes on

    1. Binding energy of NaCl molecule 2. Metallic bonding
22. Explain the formation of Van der Waals bonding. Give suitable examples.
23. Write a short notes on

    (a) Dispersive forces (b) Formation of NH_3
24. Discuss the formation of hydrogen bonding with suitable examples.
25. What is the meaning of equilibrium distance between two atoms when they are brought closer. Does it change with temperature ?

26. Discuss with suitable examples, the formation of covalent, metallic and Van der Waals bonding.
27. The ionisation of energy of K is 4.1 ev and the electron affinity of Cl is 3.6 ev. What is the energy required to form a K^+ and Cl^- ion pair ?

Objective Questions

I. Choose the correct choice in the following objective questions.

1. Choose the correct statement
   (a) Primary and secondary bonds are formed by interatomic forces.
   (b) An ionic bond is highly directional.
   (c) Secondary bonds are formed by the electrostatic attraction of electric dipoles or molecules.
   (d) Secondary bonds are formed as a result of coulomb forces between two ions.
2. Ionic solids
   (a) are soluble in polar solvents and they are insulators
   (b) are good conductors and possess low melting points
   (c) are soluble in non polar solvents
3. An ionic bond is
   (a) a homo polar bond
   (b) a heteropolar bond
   (c) an unidirectional bond
   (d) formed by sharing of electrons by two atoms.
4. The repulsive forces occur when two atoms are brought closer because
   (a) the cohesive forces become zero
   (b) the nuclei come too close
   (c) Pauli exclusion principle prevents multiple occupancy of the orbits by electrons
   (d) the electrons are scattered away
5. Secondary bonds are formed
   (a) as a result of an asymmetrical distribution of electron densities around the atoms' nuclei
   (b) as a result of strong coulomb interaction
   (c) as a result of repulsive forces only
   (d) as a result of sharing of electrons in the outer most shells.
6. The attractive force between a pair of K^+ and F^- ions is (the ionic radius of K^+ ion is 1.33 angstroms and the ionic radius of F^- ions is 1.36 angstroms)
   (a) 3.18×10^{-9} N
   (b) 3180×10^{-9} N
   (c) 3.18×10^{-12} N
   (d) 3.18×10^{-9} N.
7. The force of repulsion between a pair of K^+ and F^- ions is 3.18×10^{-9} N. Then the value of 'b' in the repulsive force $nb / r_0 n + 1$ is (the radius of K^+ ion is 1.33 angstrom and the radius of F^- ions is 1.36 Å, the value of n = 8)
   (a) 1.09×10^{-86} N m^8
   (b) 2.93×10^{-96} N m^9
   (c) 3.18×10^{-9} N m
   (d) 3.18×10^{-1} N m.

8. The value of 'b' is 2.93 × 10-96 N.m^9 . The ionic distance between a pair of ions is 2.69 Å , then the repulsive energy is
   (a) $+1.07 \times 10^{-19}$ J
   (b) -1.07×10^{-19} J
   (c) 1.07×10^{19} J
   (d) 1.07 e V.

9. The Coulomb energy and the repulsive energy between a pair of ions are E_1 and E_2. respectively Then, the net potential energy V for the ionic pair is
   (a) $E_1 + E_2$ (b) $E_1 - E_2 = -4$
   (c) $E_1 + E_2 = 4$ (d) $-E_1 + E_2 = -4$

10. For Cs*Cl* crystal, the cation-to-anion radius ratio is 0,934. Then
   (a) Twelve Cl^- ions pack around the Cs^+ ion
   (b) Six Cl^- ions pack around the Cs^+ ion
   (c) Six Cs^+ ions pack around the Cl^- ions
   (d) eight Cl^+ ions pack around the Cs^+ ion

11. For Na*Cl* crystal, the ratio of the cation-to-anion ratio is 0.525. Then,
   (a) only six Cl^- ions pack around one Na^+ ions
   (b) only four Cl^- ions pack around one Na^+ ion
   (c) twelve Cl^- ions pack around one Na^+ ion
   (d) eight Na^+ ions pack around one Cl^- ion

12. (A) As the ratio of cation-to-anion radius decreases, fewer anions can surround a central cation in an ionic crystal.
   (B) The ionic bond is directional in character.
   Then, the validity of the statements (A) and (B) is,
   (a) Both A and B are wrong
   (b) both A and B are correct
   (c) A is correct, B is wrong
   (d) A is wrong , B is correct

13. As the size of the ion in a group in the periodic table (like Li, Na, K, Rb) increases, the lattice energy of the ionic solids (Li*Cl*, Na*Cl*, K*Cl*, Rb*Cl*) formed with the same type of anion
   (a) decreases
   (b) increases
   (c) remains unaltered
   (d) does not follow any rule.

14. The bonding energy between two atoms corresponds to
   (a) the maximum of the repulsive energy
   (b) the minimum point in the energy vs interatomic distance curve
   (c) the maximum of the energy vs interatomic distance curve
   (d) the minimum of repulsive force.

15. Secondary bonds are formed
   (a) as a result of an asymmetrical distribution of electron densities around the atoms' nuclei
   (b) as a result of strong coulomb interaction
   (c) as a result of repulsive forces becoming large
   (d) as a result of sharing of electrons in the outer most shells.

16. One of the following is an ionic crystal
   (a) Silicon (b) gallium arsenide
   (c) zinc oxide (d) iron

17. Choose the correct statement
   (a) Ionic bonds are formed by electrostatic forces and are highly directional
   (b) Covalent bonds can be formed only in diamond
   (c) Covalent bonds are highly directional
   (d) Polymeric material are formed by ionic bonding

18. The amorphous substances possess
   (a) long - range order
   (b) short - range order
   (c) ionic bonds only
   (d) covalent bonds only.

19. An amorphous substance is represented
    (a) by a square lattice
    (b) by a strict periodic lattice
    (c) grains and grain boundaries
    (d) by not a well-defined coordination number of atoms

20. The number of Cl^- ions surrounding each Na^+ ion in NaCl crystal is
    (a) 5 (b) 12
    (c) 8 (d) 6

21. Choose the incorrect statement
    (a) the coordination of each type of ion in CsCl crystal is 8
    (b) a metal that crystallizes in bcc structure becomes a bad conductor
    (c) A unit cell of an ionic crystal shares some of its ions with other unit cells
    (d) The ionic crystals are hard, insulating and possess normally - high melting points

22. Which of the following does not apply to bonding in metals
    (a) mobility of valency electrons
    (b) delocalization of electrons
    (c) overlapping orbitals
    (d) highly directed bonds

23. The crystal structure of CsCl is
    (a) bcc
    (b) simple cube
    (c) hexagonal close packing
    (d) face centered tetragonal

24. Among the three compounds NaCl , KCl, CsCl, LiCl, the one that has the greatest ionicity is
    (a) NaCl (b) CsCl
    (c) KCl (d) LiCl

25. In the compounds LiCl, NaCl, KCl, RbCl, CsCl, the one that has the highest melting point is
    (a) NaCl (b) RbCl
    (c) CsCl (d) KCl

26. In the compounds NaF, NaCl, NaBr, NaI, the one that has the least melting point is
    (a) NaI (b) NaF
    (c) NaBr (d) NaCl

27. The total number of sodium ions per unit cell of NaCl is
    (a) 6 (b) 2
    (c) 8 (d) 4

28. Most of the ionic substances
    (a) are soluble in polar solvents like water
    (b) are good conductors in solid state
    (c) possess too many Voids in the solid state
    (d) contain - highly directional bonds

29. The favorable condition for metallic bond formation is
    (a) there should be orbitals completely filled with electrons
    (b) the nuclear charge of the atom should be low
    (c) the element should have low ionization potential
    (d) the number of valence electrons should be low

II. Fill in the Blanks

1. The primary bonds are (i) _____ (ii) _____ (iii) _____ bonds.
2. A melt of a solid consists of _____ order that is not stable.
3. The repulsive forces between atoms become significant only if atoms are _____ from each other.

4. Born's exponent is evaluated from the _____ studies in ionic crystals.
5. The compressibility of a crystal is _____ proportional to the repulsive exponent.
6. The units of the lattice energy is _____ .
7. The alkali halides show absorption bands in _____ region of the electromagnetic spectrum.
8. The alkali halides can be used as _____ filters and windows.
9. The carbon in the from of diamond exhibits _____ bonding.
10. Multiple bonds in covalent bonding have _____ bond length.
11. Metals basically have _____ structures.
12. The metallic bond is essentially a _____ bond without saturation.
13. The _____ bond is non directional.
14. The metals possess high thermal and electrical conductivities. This is because of _____ movement in the lattice.
15. For hydrogen bonding, the size of electron negative atoms should be _____
16. In the case of NH_3, the nitrogen atom is electro _____ and hydrogen acquires a _____ charge.
17. In H_2O, four hydrogen atoms, two by _____ bonding, and two hydrogen bonds tetrahedrally surround each _____ atom.
18. London-dispers ion forces play the vital role in _____ bonding.
19. Rare gases can condense and exist in liquid form because of _____ bonding.

III. True or False

1. The secondary bonds are formed between the molecules that possess permanent dipole moment

[True/False]

2. The energy of attraction between two ions of opposite charges is given by the expression Z_1

$$Z_2 \frac{q^2}{r^2}$$

[True/False]

3. Madelung constant is dependent on the lattice dimensions and the nature of ions forming ionic crystal

[True/False]

4. For an isolated NaCl molecule the Madelung constant is equal to 1.747

[True/False]

5. The bonding in an oxide Fe_2O_3 is ionic

[True/False]

6. Ionic crystals dissolve in polar solvents

[True/False]

7. The bonding between two nitrogen atoms in N_2 molecule is ionic

[True/False]

8. The carbon in the form of a diamond exhibits Vander waal bonding

[True/False]

9. The covalent bonds are highly directional or stereo specific

[True/False]

10. Covalent crystals are highly soluble in polar solvents

[True/False]

11. Compared to ionic solids, covalent solids have very long bond lengths

[True/False]

12. Pure sodium exists as a liquid only

[True/False]

13. A metallic bond is essentially a covalent bond without saturation

[True/False]

14. Al_2O_3 is an example of covalent bonding

[True/False]

15. Nitrogen molecule (N_2) is formed due to dipole interaction

[True/False]

16. In carbon, hybridisation between S and P orbitals takes place

[True/False]

17. The weakest hydrogen bonds are formed between the most electronegative

[True/False]

18. HC*l* shows hydrogen bonding

[True/False]

19. All ionic crystals are semiconductors

[True/False]

20. Hydrogen molecule is an example of hydrogen bonding

[True/False]