(P.U. 2007; Pbi., Univ. 2003, 2002, 2001, ...

Ans. (*a*) Bonding. There are three states of matter solid, liquid and gas. The atoms in a ... are closely packed but are in a state of vibration about their fixed position. The nucleus of an a... can be considered at rest due to its large mass. It is, therefore, the orbital electrons which ... responsible for most of the characteristics of the solid. *The ability to hold the atoms or ions toge... is called bonding.* The basic requirements of all types of bonding is that all bound systems sh... have minimum energy in their stable form. When some atoms combine to form a stable molecule ... is implied that in so doing they have decreased the energy of the system to a minimum.

The forces acting between the atoms are electrostatic in nature. These forces are determin... essentially by the way in which the outer electrons of the composing atoms are distributed in spa... The physical properties of the solids are determined, to a large extent by the electron distribu... and it is thus possible on an empirical basis to divide solids into different groups correspondin... different types of electron distribution.

Types of bonding: The individual atoms of a crystalline solid are held together as one sys... with different types of bonds existing between them. These bonds are classified into *five* ideali... types.

(*i*) Ionic bonding. Examples:- *NaCl*, *LiF* (Due to transfer of valence electrons).

(*ii*) Co-valent bonding. Examples:- diamond, *Si C* (Sharing of valence electrons).

(*iii*) Van der Waal bonding. Example:- solid Argon (electrons remain associated with origi... molecules).

(*iv*) Hydrogen bonding. Example:- ice

(*v*) Metallic bonding. *Cu*, *Ag*, *Fe* are examples. (valence electrons are essentially free)

These bonds are fundamentally electric in origin, but except for ionic bonds which ar... through essentially quantum mechanical considerations.

It may be added that the above classification is arbitrary. Many solids fall into intermedia... categories.

(*b*) **Cohesion energy.** From the very existence of solids, two general conclusions can b... drawn.

(*i*) There must be an *attractive force* between atoms or molecules in a solid which keeps the... together.

(*ii*) There must also be a *repulsive force* acting between the atoms. This is why large extern... pressure is required to compress a solid to any appreciable extent.

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When two identical or non-identical atoms, which form a molecule, are brought from infinity to a close proximity, they first attract each other and then, if they are brought closer than a certain distance, repel each other. In other words, a kind of spring effect takes place. As the potential V is related to the force by the relation $F = \frac{-dV}{dr}$, the resulting potential is a function of distance of separation r. The variation of corresponding potential energy V in eV with distance r in Å is shown in Fig. 3.1.

The attractive force gives rise to a negative potential and the repulsive force gives rise to a positive potential shown by dotted curves. The resultant potential energy is shown by full line curve. It has a minimum at a distance r_0 and represents the equilibrium position, where the attractive and the repulsive forces balance each other and potential energy has a maximum negative value. The potential energy $V(r_0)$ at a distance r_0 is thus responsible for keeping the atoms bound in a solid and gives the *cohesive* or *binding energy* of the solid.

The potential energy $V(r_0)$ is a negative quantity. The positive quantity $-V(r_0) = D$ is called the *dissociation energy* of the molecule.

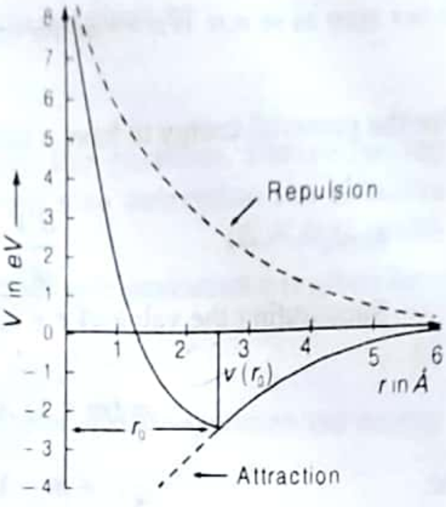

Fig. 3.1

The cohesive energy of a solid is defined as the energy which will be given out in the process of the formation of a crystal by bringing neutral atoms from infinity to the position of equilibrium separation.

If the potential energy due to attraction V_a is supposed to vary as the mth power of the distance and that due to repulsion V_r as nth power of r, then

$$V_a \propto \frac{1}{r^m} = -\frac{A}{r^m} \text{ and } V_r \propto \frac{1}{r^n} = \frac{B}{r^n}$$

$\therefore$ Resultant potential or cohesive energy

$$V = V_a + V_r = -\frac{A}{r^m} + \frac{B}{r^n}$$

where A and B are constants of proportionality. The cohesive energy is generally expressed in eV per atom.

The force between the two atoms is given by

$$F = \frac{-dV}{dr} = \frac{mA}{r^{m+1}} - \frac{nB}{r^{n+1}}$$

At $r = r_0$ the attractive and repulsive forces balance each other and $F(r_0) = 0$. In other words at $r = r_0$

$$\frac{mA}{r_0^{m+1}} - \frac{nB}{r_0^{n+1}} = 0$$

or

$$\frac{m}{n} = \frac{B}{A} r_0^{m-n}$$

or

$$r_0^{m-n} = \frac{A}{B}\frac{m}{n} \quad \text{... } (i)$$

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Hence, the potential energy in the equilibrium state

$$V(r_0) = \frac{-A}{r_0^m} + \frac{B}{r_0^n} = \frac{-A}{r_0^m}\left[1 - \frac{B}{A} r_0^{m-n}\right] = \frac{-A}{r_0^m}\left[1 - \frac{m}{n}\right]$$

Although the attractive and repulsive forces are in equilibrium at $r = r_0$, the potential energy is not zero as $m \neq n$. If $n >> m$ the total energy is essentially the energy of attraction given by $\frac{-A}{r_0^m}$.

For the potential energy to have a minimum at $r = r_0$ we have $\left|\frac{d^2V}{dr^2}\right|_{r=r_0}^{0} > 0$ *i.e.*, it must be positive.

Now,
$$\frac{d^2V}{dr^2} = \frac{-m(m+1)A}{r^{m+2}} + \frac{n(n+1)B}{r^{n+2}} > 0$$

Substituting the value of $r = r_0$ from (*i*), we have

$$-m(m+1)A \times \frac{B}{A}\frac{n}{m}\left(\frac{1}{r_0^{n+2}}\right) + \frac{n(n+1)B}{r_0^{n+2}} > 0$$

or
$$-m - 1 + n + 1 > 0$$

or
$$n - m > 0 \quad \text{or} \quad n > m$$

In other words, a minimum in the energy curve is possible only if $n > m$. *Thus the formation of a chemical bond requires that the repulsive forces be of shorter range than the attractive forces.*

The energy $V(r_0)$ at the equilibrium distance r_0 is called the *binding energy*, the *energy of cohesion* or *dissociation energy* of the molecule. This much energy is required to separate the atoms of a diatomic molecule to an infinite distance apart.

The cohesive energy may also be defined as the energy released when two atoms are brought close to each other at the equilibrium distance r_0.

Larger the energy released, more stable the bond formed and hence more stable is the crystal structure.

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