Bonding

Bonding :- The atoms and molecules in a crystal are held together by the interatomic forces. In all the cases these forces are electrostatic in nature and there is a difference in the distribution of outer electrons of different atoms of various crystals. Due to these differences the mechanical, electrical and magnetic properties of the crystals are different. There are three states of matter, solid, liquid and gases. The atoms in solid are closely packed but are in a state of vibration about their fixed position. The orbital electrons are responsible for most of the characteristics of the solid. The ability to hold the atoms or ions together is called bonding. The basic requirements of all types of bonding is that all bound systems should have minimum energy in their stable form.

Types of bonding :- The bonding in a crystal are classified in to five types. (1) Ionic bonding (ii) Co-valent bonding (iii) Vander Waal's bonding (iv) Hydrogen bonding (v) metallic bonding.
Ex- NaCl, LiF

(i) Ionic bonding :- NaCl, LiF (Due to transfer of valance electron).

(ii) Covalent bonding :- Diamond, SiC (Sharing of valence electron)

(iii) Vander Waal's bonding :- Solid Argon (electron remain associated with original molecule)

(iv) Hydrogen bonding :- ice.

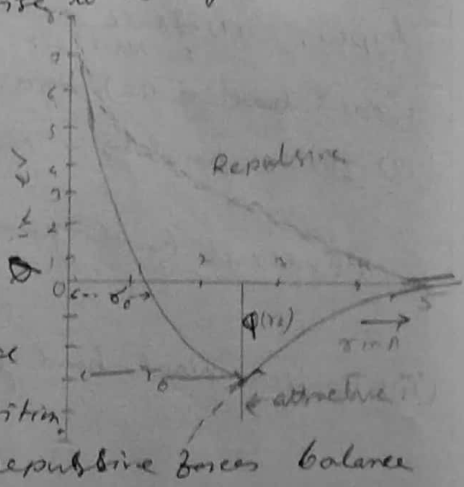
(v) Metallic bonding :- Cu, Ag Fe etc. vallence electrons are essentially free).

Force between atoms :-

For the existance of the solids there are two types forces acting between the atoms or molecules in a solid
(i) one is attractive forces which keep the atoms or molecules together.
(ii) Another is repulsive forces between them. Hence a large external pressure is required to compress a solid to any appreciable extent.

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 ie a kind of spring effect takes place. As the potential ϕ is related to the force by the relation $F = -\frac{d\phi}{dr}$, the resulting potential is a function of distance of separation r. The variation of corresponding potential energy ϕ in ev with distance r in $\mathring{A}$ is shown in the fig below.

The attractive force give rise to a negative potential and the repulsive force gives rise to a positive potential shown by dotted line. The resultant P.E. is shown by full line curve. It has a minimum at a distance r_0 and represent the equilibrium position where the attractive and the repulsive forces balance



each other and P.E has a maximum negative value i.e. the P.E $\phi(r_0)$ at a distance r_0 is then necessary for keeping the atoms bound in a solid and gives the cohesive or binding energy of the solid.

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 ϕ_a is supposed to vary as the nth power of the distance~~

If ϕ_a is the P.E due to attraction which is supposed to vary as the nth power of distance and due to repulsion ϕ_r as mth power of distance,

$$\phi_a \propto \frac{1}{r^n} \quad \text{and} \quad \phi_r \propto \frac{1}{r^m}$$

$$\therefore \phi_a = \frac{-\mu}{r^n} \quad \text{and} \quad \phi_r = \frac{\lambda}{r^m}$$

where μ and λ are constants.

Hence the total P.E is given by

$$\phi = \phi_r + \phi_a = \frac{\lambda}{r^m} - \frac{\mu}{r^n} \quad \text{------} (1)$$

The force between the atoms can be written as

$$F = -\frac{d\phi}{dr} = \frac{\lambda m}{r^{m+1}} - \frac{\mu n}{r^{n+1}} \quad \text{------} (2)$$

At $r = r_0$, the attractive and repulsive forces balance each other and ϕ has maximum negative value ϕ_0 and so

$$F = -\left(\frac{d\phi}{dr}\right)_{r=r_0} = 0$$

$$\therefore \frac{\lambda m}{r_0^{m+1}} - \frac{\mu n}{r_0^{n+1}} = 0$$

$$\text{or} \quad \frac{\lambda m}{r_0^{m+1}} = \frac{\mu n}{r_0^{n+1}}$$

$$r_0^{n-m} = \frac{\mu}{\lambda}\,\frac{n}{m} \longrightarrow (2)$$

Hence at $r = r_0$, the value of P.E. is given by

$$\phi_0 = \frac{\lambda}{r_0^m} - \frac{\mu}{r_0^n}$$

$$= \frac{-\mu}{r_0^n}\left[1 - \frac{\lambda}{\mu} r_0^{n-m}\right]$$

$$\text{or} \quad \phi_0 = \frac{-\mu}{r_0^n}\left[1 - \frac{n}{m}\right] \longrightarrow (3)$$

~~Hence~~ At $r = r_0$, the attractive and repulsive forces balance each other and potential energy is not zero because $m \neq n$ when $m >> n$, $\phi_0 = -\frac{\mu}{r^n}$.

At $r = r_0$, ϕ should be minimum and in this case $\left(\frac{d^2\phi}{dr^2}\right)_{r=0} > 0$ ie $\left(\frac{d^2\phi}{dr^2}\right)_{r=r_0}$ = +ve quantity.

$$\frac{d^2\phi}{dr^2} = -\frac{\mu n(n+1)}{r^{n+2}} + \frac{\lambda m(m+1)}{r^{m+2}} \longrightarrow (5)$$

putting $r = r_0$, we have

$$\left(\frac{d^2\phi}{dr^2}\right)_{r=r_0} = -\frac{\mu n(n+1)}{r_0^{n+2}} + \frac{\lambda m(m+1)}{r_0^{m+2}} > 0$$

or $$-\frac{n(n+1)}{r_0^{n+2}} r_0^{n-m} \lambda \frac{m}{n} + \frac{\lambda m(m+1)}{r_0^{m+2}} > 0$$ {putting the value of μ from (3).

or $$-\frac{m(n+1)\lambda}{r_0^{m+2}} + \frac{m(m+1)\lambda}{r_0^{m+2}} > 0$$

or $$\frac{m\lambda}{r_0^{m+2}}(m+1-n-1) > 0$$

or $$m - n > 0 \text{ or } m > n \longrightarrow (6)$$

Hence in the formation of chemical compound the repulsive forces should be shorter range than the attractive forces.

The energy $\phi(r_0)$ 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 ~~be~~ also be defined as the energy released when two atoms are brought close to each other at the equilibrium distance r_0.

Example

The energy of two particles in the field of each other at a separation r is given by

$$\phi = -\frac{\alpha}{r} + \frac{\beta}{r^8}$$ where α and β are constants.

At what separation they will form a stable compound?

Sol^n At the separation r the potential energy between the two particles in the field of each other is

$$\phi = -\frac{\alpha}{r} + \frac{\beta}{r^8}$$

At $r = r_0$, the P.E ~~ϕ is~~ will be minimum and both the particles form a stable compound.

$$\therefore \left(\frac{d\phi}{dr}\right)_{r=r_0} = 0$$

$$\therefore \frac{d\phi}{dr} = +\frac{\alpha}{r^2} - \frac{8\beta}{r^9}$$

Hence $$\left(\frac{d\phi}{dr}\right)_{r=r_0} = +\frac{\alpha}{r^2} - \frac{8\beta}{r^9} = 0$$

or $$\frac{\alpha}{r_0^2} - \frac{8\beta}{r_0^9} = 0$$

or $$\alpha = \frac{8\beta}{r_0^7}$$

or $$r_0 = \left(\frac{8\beta}{\alpha}\right)^{1/7}$$

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