Interatomic Forces and Types of Bonding

The interatomic forces exist amongst the atoms of a crystal and are responsible for holding the atoms together to form solid structures. The atoms exert the following two types of forces on one another:

1. The attractive forces arising from the interaction of the negative electron cloud of one atom with the positive nuclear charge on the other. Its magnitude is proportional to some power of the interatomic distances r.
2. The repulsive forces which come into existence when the distance between the atoms is derceased to such an extent that their electronic clouds start overlapping, thus violating the Pauli's exclusion principle. The repulsion between the positively charged nucleu also contributes to the repulsive forces. The magnitude of the total repulsive force is also proportional to some power of r.

Since the attractive forces decrease the potential energy of the system and the repusive forces increase it, the net energy of the system is equal to the algebraic sum of these two energies and is written as

$$U = U_{att} + U_{rep} = -A/r^m + B/r^n \qquad (1)$$

where A, B, m and n are constants which depend upon the nature of the participating atoms; A and B are known as attraction and repulsion constants respectively. Generally $n > m$ which indicates that the increase in repulsive energy is faster than the increase in attractive energy particulary for very small values of interatomic distance. The repulsive forces are, therefore, known as *short range forces*. This means that the repulsive interaction between the nuclei becomes appreciable only for very small distances.

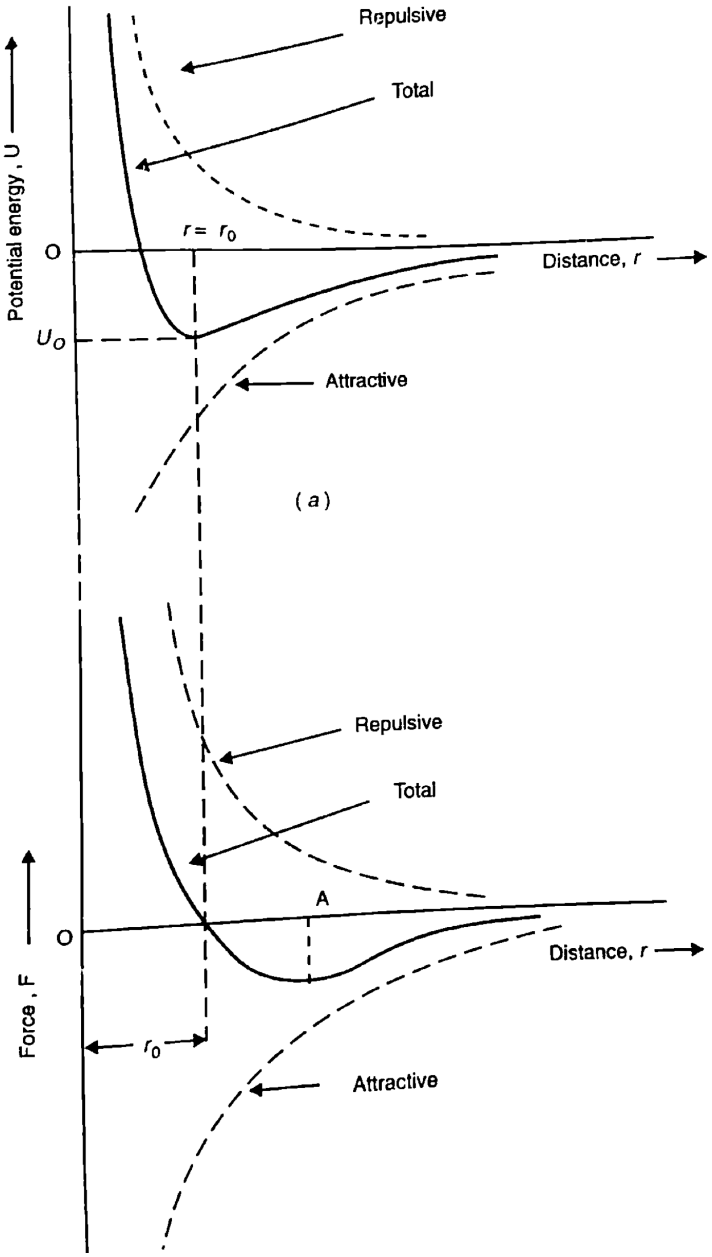

Figure 1:

The variations of attractive energy, repulsice energy and total energy versus interatomic distance are shown in figure. The interatomic distance $r_\circ$ at which the energy of the system becomes minimus is known as the *equilibrium distance* and signifies the formation of a stable chemical bond. At this distance, the system is in the most stable state and energy is required to displace the atoms in either direction.

We also get,

$$F = -dU/dr = -mA/r^{m+1} + nB/r^{n+1} \qquad (2)$$

This gives the total force between the two atoms placed at a distance r from each other. The first term on the right hand side represents the attractive force and the second one represents the repulsive force. At equillibrium distance ($r_\circ$), the attractive force must be equal and opposite to the repulsive force and hence the total force F is zero.

From equation (2), for $r = r_\circ$, we get

$$\begin{aligned} mA/r_\circ^{m+1} &= nB/r_\circ^{n+1} \\ B &= A(m/n)r_\circ^{n+1}/r_\circ^{m+1} = A(m/n)r_\circ^{n-m} \\ r_\circ^{n-m} &= (B/A)(n/m) \end{aligned} \tag{3}$$

From equation (1), the energy at the equilibrium distance $r_\circ$ becomes

$$U_\circ = -A/r_\circ^m + B/r_\circ^n = (-A/r_\circ^m)\,(1 - m/n) \tag{4}$$

Since $m \neq n$, $U_\circ \neq 0$, it follows that, although the attractive force is equal to the repulsive force at equilibrium distance, the attractive energy is not equal to repulsive energy.

$$\text{For } n >> m, \quad U_\circ \approx -A/r_\circ^m,$$

i.e., the total energy is essentially the energy of attraction. Also, if the total energy U has to be minimum at $r = r_\circ$, then

$$\left.\frac{d^2U}{dr^2}\right|_{r=r_\circ} > 0$$

$$-\frac{m(m+1)A}{r_\circ^{m+2}} + \frac{n(n+1)B}{r_\circ^{n+2}} > 0$$

Using equation (3) we find that this condition is satisfied only form $n > m$. It indicates that the repulsive forces should be of shorter range than the attractive forces. This information can also be obtained from figure which show that the minimum in the energy curve is possible obly for $n > m$.

The energy $U_\circ$ at the equilibrium distance $r_\circ$ 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. This is generally of the order of a few electron volts. The cohesive energy may also be defined as the energy released when two atoms are brought close to each other at an equilibrium distance r. In a crystal, an atom is surrounded by more than one atoms which may arrange themselves to form different structures. The most stable structure is that for which the maximum amount of energy is released. Thys an acceptable theory of cohesion can predict themost probable structral arrangement the atoms may assume.

The nature of crystals formed depends upon the nature of interaction between lattices of crystal. These interactions or bonds may be broadly classified into following five categories:

1. Ionic bond
2. Covalent bond
3. Metallic bond
4. Van der Waals forces
5. Hydrogen bond

The first three types of bonds are called primary bonds and the last two types of bonds are called secondary bonds. Many of the crystals exhibit mixed bonding.