Ans. Potential energy of ionic crystal. To find the value of total binding energy and contribution to the potential of an ionic crystal we shall take up the typical case of sodium chloride. The force of attraction between the Na^+ and Cl^- ions is given by

$$F = \frac{Z_1 Z_2 e^2}{4\pi\varepsilon_0 r^2}$$

This force gives rise to an attractive potential energy term V_a the value of which in S.I units is given by

$$V_a = -\frac{Z_1 Z_2 e^2}{4\pi\varepsilon_0 r^2} = -\alpha \frac{e^2}{4\pi\varepsilon_0 r}$$

where α is a constant known as *Madelung constant*. The force of attraction between the Na^+ and Cl^- ions increases as the distance r between the two ions decreases. When they come *very* close to each other, their electron shells interact, as their cores begin to overlap and Pauli's exclusion principle leads to a repulsive force which increases rapidly with decreasing inter-nuclear distance r. The repulsive energy term arising due to this force of repulsion is given by

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$$V_r = \frac{B}{r^n}$$

The sign of the repulsive energy term is positive.

$\therefore$ Resultant potential energy $V = V_a + V_r = -\frac{\alpha e^2}{4\pi\varepsilon_0 r} + \frac{B}{r^n}$ ...(i)

At the equilibrium separation r_0, V has a minimum value

$$\therefore \quad \left(\frac{dV}{dr}\right)_{r=r_0} = \frac{\alpha e^2}{4\pi\varepsilon_0 r_0^2} - \frac{nB}{r_0^{n+1}} = 0$$

or
$$\frac{\alpha e^2}{4\pi\varepsilon_0 r_0^2} = \frac{nB}{r_0^{n+1}}$$

$$\therefore \quad B = \frac{\alpha e^2 r_0^{n-1}}{4\pi\varepsilon_0 n}$$

Hence
$$V = -\frac{\alpha e^2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{n}\right) \quad ...(ii)$$

The total binding energy of a crystal having N positive and N negative ions is given by

$$V = \frac{N\alpha e^2}{4\pi\varepsilon_0 r_0}\left[1 - \frac{1}{n}\right] \quad ...(iii)$$

In addition to the total potential energy V, as calculated above we must take into account the energy needed to transfer an electron from Na atom to a Cl atom to yield Na^+ and Cl^- ion. If we denote this energy by V_i, then the total potential energy, known as cohesive energy, is given by

$$V_c = V_a + V_r + V_i$$

in which V_a is negative and V_r and V_i are both positive.

From a knowledge of the compressibility of ionic crystals the value of n in relation (i) has been found to be $\simeq 9$.

(b) Total binding energy of the ionic crystal

$$U = -\frac{Ae^2}{r} + \frac{B}{r^n}$$

This relation is the same as given by Eq. (i), where $A = \frac{\alpha}{4\pi\varepsilon_0}$ and $V = U$. Hence, the equilibrium energy at $r = r_0$ will be the same as given by Eq. (ii) by replacing $\frac{\alpha}{4\pi\varepsilon_0} = A$ and $V = U_0$.

$$\therefore \quad U_0 = -\frac{Ae^2}{r_0}\left[1 - \frac{1}{n}\right]$$

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