Lattice energy of ionic crystals. *Lattice energy is the energy evolved when a crystal is formed from individual ions* (not atoms).

The calculation of lattice energy and cohesive energy of ionic crystals was made by Born and Madelung. According to this theory, let U_{ij} be the interaction energy between ions i and j, and U_i the interaction energy on the ion i due to all other ions, then

$$U_i = \sum_j U_{ij}$$

where the summation extends over all ions except $j = i$. The energy U_i consists of two parts.

(*i*) A central field *repulsive* potential supposed to be of the form $\lambda e^{-r/\rho}$ where λ and ρ are empirical parameters. ρ is a measure of the range of the repulsive interaction. When $r = \rho$ the repulsive interaction is reduced to $\frac{1}{e}$ of the value at $r = 0$.

(*ii*) A coulomb potential $\pm \frac{q^2}{r}$ (in C.G.S. units) depending upon the sign of the charges on the two ions under consideration.

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$$U_{ij} = \lambda e^{-(r_{ij}/\rho)} \pm q^2 / r_{ij}$$

The total lattice energy U_{tot} of a crystal composed of N molecules (or $2N$ ions)

$$U_{tot} = NU_i$$

We do not use $2N$ because interaction of *each pair* is to be considered only *once*.

For the sake of convenience we put

$$r_{ij} = p_{ij} R$$

where p_{ij} is a dimensionless quantity and R the nearest neighbour separation in the crystal. Considering the repulsive interaction only among nearest neighbours, we have $r_{ij} = R$ and

$$U_{ij} = \lambda e^{(-R/\rho)} - \frac{q^2}{R}$$

$$\therefore \quad U_{tot} = NU_i = N \sum U_{ij}$$

$$= N\left(z\lambda e^{(-R/\rho)} - \sum \frac{\pm}{p_{ij}} \frac{q^2}{R}\right)$$

$$= N\left(z\lambda e^{-R/\rho} - \alpha \frac{q^2}{R}\right) \quad \text{...(i)}$$

where z = the number of nearest neighbours for any ion and $\alpha = \sum \frac{\pm}{p_{ij}}$ = *Madelung constant* also known as coulomb energy constant. If we take the reference ion as a negative charge the plus sign will be used for positive ions and minus sign for negative ions.

At the equilibrium separation $R = r_0$ the crystal energy U_{tot} is a minimum.

$$\therefore \quad \frac{dU_{tot}}{dR} = 0$$

or

$$N\frac{dU_i}{dR} = -\frac{Nz\lambda}{\rho} e^{\left(-\frac{R}{\rho}\right)} + \frac{N\alpha q^2}{R^2} = 0$$

Putting $R = r_0$, we have

$$r_0^2 e^{(-r_0/\rho)} = \frac{\rho\alpha q^2}{z\lambda} \quad \text{...(ii)}$$

If the values of ρ and λ are known, the equilibrium separation r_0 can be calculated. Thus U_{tot} the total lattice energy of the crystal of $2N$ ions at their equilibrium separation r_0 is given by putting $R = r_0$ in (*i*) and, we get

$$U_{tot} = N\left(z\lambda e^{-r_0/\rho} - \alpha \frac{q^2}{r_0}\right)$$

Now from (*ii*), $e^{(-r_0/\rho)} = \dfrac{\rho\alpha q^2}{r_0^2 z\lambda}$

$$\therefore \quad U_{tot} = N\left(\frac{\rho\alpha q^2}{r_0^2} - \frac{\alpha q^2}{r_0}\right)$$

$$= -\frac{N\alpha q^2}{r_0}\left(1 - \frac{\rho}{r_0}\right)$$

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The term $\frac{-N\alpha q^2}{r_0}$ is the *Madelung energy*.

Hence Potential energy per ion pair $U_{tot} = \frac{-\alpha q^2}{r_0}\left(1 - \frac{\rho}{r_0}\right)$.

In S.I. units U_{tot} per ion pair $= \frac{-\alpha q^2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{\rho}{r_0}\right)$ and Madelung energy $= \frac{-N\alpha q^2}{4\pi\varepsilon_0 r_0}$

The value of $\frac{\rho}{r_0}$ for *NaCl* is of the order of 1/9, $q = e$ the electronic charge, $\alpha = 1.748$ and $r_0 = 2.81$ Å. Thus the calculated value of lattice energy per ion pair comes out to be $-7.97\ eV$. This is in close agreement with experimental value of $-7.96\ eV$/ion pair.

Q. 38. (a) What is Madelung ... the value of

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