Binding Energy of Ionic Crystals

The binding energy of ionic crystals was first calculated by Born and Madelung in 1910 and was later modified by Born and Mayer.

The theory developed by Born and Madelung is based on the assumption that the ionic crystals are built up of positive and negative ions each having a spherically symmetric charge distribution as in rare gas atoms. Thus the force between any two ions depends only on the distance between the ions and is independent of the direction of approach. The force between the ions is assumed to be mainly electrostatic. Thus the main contribution to the binding energy arises from electrostatic interaction and is called the Madelung energy. The ions tend to acuire such an arrangement in a crystal structure which results in the maximum attractive interaction amongst themselves.

These exist two types of interactions in ionic crystals, one is long range Coulomb's eloectrostatic interaction which may be attractive or repulsive in nature, and the other is short range repulsive interaction which comes into play when the interionic distance becomes so small that the electronic clouds of ions start overlapping. The Coulomb's electrostatic interaction energy between tow ions with charges $\pm q$ is given by $\pm q^2/r$, where the positive sign stands for electrostatic repulsive energy, i.e., the energy of ions with like charges, and the negative sign stands for attractive energy. The short range repulsive energy is given by β/r^n, where β and n are constants. The earlier calculations of Born and Madelung were based onthis expression for replusive energy. Later, Born and Mayer, based on the quantum mencahincal calculations of force between the ions, replaced this expression by another one of the form $\lambda e^{-r/\rho}$, where λ represents the strength and ρ the range of repulsive interaction. This repulsive energy is also known as the *central field repulsive potential*.

SInce each ion in an ionic crystal is surrounded by a large number of ions of similar or opposite type, the total interaction energy or the *cohesive energy* of an *ith* ion is given by

$$U_i = \sum_{i \neq j} U_{ij} \tag{1}$$

where U_{ij} is the interaction energy between the *ith* and *jth* ions and may be written as

$$U_{ij} = \lambda \exp\left(-r_{ij}/\rho\right) \pm q^2/r_{ij} \tag{2}$$

The constants ρ and λ can be empirically determined from the observed values of lattice constant and compressibility. The positive sign in equation (2) is used for interaction between opposite charges.

If the crystal contains N molecules, i.e., N positive ions and N negative ions, the total lattice energy of the total binding energy of the lattice becomes

$$U_{tot} = NU_i \tag{3}$$

Here we have used N rather than $2N$ because each pair of $i - j$ interactions must be considered only once while determing the total binding energy. For convenience, we introduce a dimensionless quantity p_{ij} such that

$$r_{ij} = p_{ij}R \tag{4}$$

where R is the nearest neighbour separatio in the crystal. The factor p_{ij} thus defines the distance between any two ions in terms of the nearest neighbour distance. If ions i and j are the nearest neighbours, then

$$r_{ij} = R$$

$$\Rightarrow p_{ij} = 1$$

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From equations (2) and (4), we get

$$U_{ij} = \lambda \exp\left(-p_{ij}R/\rho\right) \pm q^2/\left(p_{ij}R\right)$$

The equation (1) becomes

$$U_i = \sum_{j \neq i} \left[\lambda \exp\left(-p_{ij}R/\rho\right) \pm q^2/\left(p_{ij}R\right)\right] \tag{5}$$

Assuming that the repulsive interaction (first term) is effective for the nearest neighbours only and there are z neighbours of the *ith* ion, the expression (5) for the cohesive energy of the *ith* ion takes the form

$$U_i = z\lambda \exp(-R/\rho) \pm \sum_j q^2/(p_{ij}R)$$
$$= z\lambda \exp(-R/\rho) - \alpha q^2/R \tag{6}$$

From equation (3), the lattice energy becomes

$$U_{tot} = NU_i = N\left(z\lambda e^{-R/\rho} - \alpha q^2/R\right) \tag{7}$$

Here α is a constant called the *Madelung constant* and is given by

$$\alpha = \sum_{j \neq i} \mp 1/p_{ij} \tag{8}$$

The choice of sign depends upon the type of reference ion. If the reference ion is negative, the positive sign is used for a positive ion and the negative sign for negative ion. Thus the value of Madelung constant depends on the lattice structure. It is basically a correction factor that determines the magnitude of the error introduced by considering only the nearest neighbour interaction.

At the nearest neighbour equilibrium distance, R_0, we have
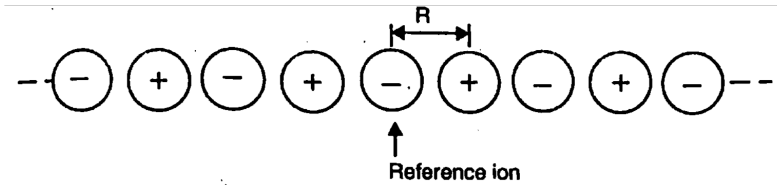
$$\frac{dU_{tot}}{dR} = 0$$

Therefore, from equation (7), we get

$$N\frac{dU_i}{dR}\bigg|_{R=R_0} = -\frac{Nz\lambda}{\rho}e^{-R_0/\rho} + \frac{N\alpha q^2}{R_0^2} = 0$$

$$\Rightarrow e^{R_0/\rho} = \frac{\rho \alpha q^2}{z\lambda R_0^2}$$

The equation (7) can now be written as

$$U_{tot} = N\left(z\lambda \frac{\rho\alpha q^2}{z\lambda R_0^2} - \frac{\alpha q^2}{R_0}\right)$$
$$= -\left(\frac{N\alpha q^2}{R_0}\right)\left[1 - \frac{\rho}{R_0}\right] \tag{9}$$

The first term resembles the second term of equation (7). It, therefore, represents the electrostatic interaction energy or the Madelung energy. The second term represents the contribution of the short

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Reference ion

range repulsive interaction.

The similar expression for cohesive energy of the *ith* ion is

$$U_i = \frac{U_{tot}}{N} = -\left(\frac{\alpha q^2}{R_0}\right)\left[1 - \frac{\rho}{R_0}\right] \tag{10}$$

For the range $\rho \sim 0.1R_0$, U_i is dominated by the Madelung contribution. It increases rapidly for low value of ρ/R_0 which indicates that the repulsive interaction has a very short range.

From equations (9) and (10), it follows that the lattice energy of a crystal and the cohesive energy of an ion in the crystal can be determined if the values of R_0, α and ρ are known. The equilibrium distance R_0 is, in general, determined empirically , the range ρ is determined from the knowledge of the bulk modulus of the crystal, and the Madelung constant is determined theoretically from the geometry of the crystal structure.

Evaluation of the Madelung Constant

Considering the simplest case of a one-dimensional crystal consisting of alternate positive and negative ions with interionic distance R as shown in Figure. The Madelung constant, α, can be expressed as

$$\alpha = \sum_{j\neq i} \mp \frac{1}{p_{ij}} = 2\left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \cdots\right] \tag{11}$$

This expression is written taking a negative ion as the reference ion. The factor of 2 appears because similar ions are present on both side of the reference ion. Using the series expansion

$$\ln(1 + x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \cdots$$

and putting $x = 1$ in it, we get

$$\ln 2 = 1 = 1/2 + 1/3 - 1/4 + \cdots$$

Therefore, equation (11) gives

$$\alpha = 2\ln 2 = 1.38 \tag{12}$$

For the actual three-dimensional crystals, the evaluation of the Madelung constant is not so simple. The values of Madelung constant for NaCl, CsCl, ZnS structures are 1.75, 1.76, and 1.64 respectively. In general, the higher values of the Madelung constat indicate the stronger Madelung contribution to the cohesive energy and hence greater stability of the structure.

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