

Binding Energy of Crystals of Inert Gases

The molecular crystals of the inert gases have low melting points. The atoms of these crystals have their outermost shells completely filled and thus have very little tendency to gain, lose or even share the valence electrons with neighbouring atoms. Due to completely filled shells, these atoms have spherically symmetric electronic charge distribution. Hence these gases, except He³ and He⁴, usually form *fcc* crystals in the solid state.

Consider a molecular crystal consisting of N atoms. If U_{ij} represents the interaction energy between the atoms i and j of the crystal, then the cohesive energy of the i th atom is given by

$$U_i = \sum_{j \neq i} U_{ij} \quad (1)$$

and the lattice energy of the crystal is

$$U_{tot} = \frac{1}{2} N U_i = \frac{1}{2} N \sum_{j \neq i} U_{ij} \quad (2)$$

Here the factor $N/2$ is used instead of N to represent the number of distinct $i - j$ atomic pairs which contribute to the interaction energy. As in the case of ionic crystals, the interaction energy, U_{ij} , of molecular crystals is due to the following two types of interactions:

1. Van der Waals or London interactions,
2. Repulsive interaction.

1. Van der Waals Interaction It is a dipole induced interaction which exists in two neighbouring atoms so as to produce weak attractive force between the atoms. These interactions are also known as *dispersion bond*.

Let p_i be the instantaneous dipole moment of the i th atom caused by some fluctuations in the charge distribution on the j th atom. This dipole moment produces an electrostatic dipole field E at the center of the j th atom whose magnitude in CGS units is

$$E = 2 \frac{p_i}{r_{ij}^3} \quad (3)$$

This field further produces an instantaneous dipole moment p_j at the j th atom of magnitude

$$p_j = \alpha_e E = 2\alpha_e p_i / r_{ij}^3 \quad (4)$$

where α_e is the electronic polarizability. These two dipoles interact with each other in such a way as to produce a net attractive force as shown in figure. The potential energy associated with the attraction of two dipoles is given as

$$U_{att} \approx -\frac{2p_i p_j}{r_{ij}^3} = -\frac{4\alpha_e p_i^2}{r_{ij}^6} \quad (5)$$

From equation (4), it follows that α_e has dimensions of [length]³. Therefore, $\alpha_e p_i^2$ has a dimension of [length]⁵ × [charge]². Hence, in equation (5), $\alpha_e p_i^2$ may be written as $e^2 r_0^5$ where r_0 is the atomic radius.

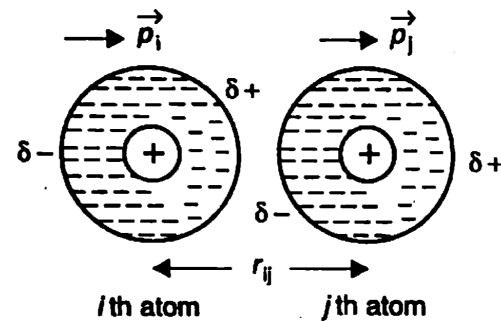


Figure 1: An instantaneous dipole moment p_i of the i th atom induces a dipole moment p_j on the j th atom.

The equation ((5)) then becomes

$$U_{att} \approx -4e^2 r_0^5 / r_{ij}^6 \approx -10^{-58} / r_{ij}^6 \text{ ergs} \quad (6)$$

$$= -B / r_{ij}^6$$

where we have used $r_0 \approx 10^{-8} \text{ cm}$ and $B \approx 10^{-58} \text{ erg cm}^6$.

Since U_{att} varies as r_{ij}^{-6} , it follows that the van der Waals interaction is a short range interaction which increases rapidly with decrease in r_{ij} .

2. Repulsive interaction As described in case of ionic crystals, the repulsive interaction comes into play for very short distances between the atoms when the electron clouds of the atoms begin to overlap and the Pauli's exclusion principle is disobeyed. The energy due to this interaction may be expressed as the power law of the type $U_{rep} = \text{const}/r_{ij}^n$ or by the expression $U_{rep} = \lambda e^{-r_{ij}/\rho}$, where λ and ρ represent the strength and range of repulsive interaction respectively. The present case, we shall express U_{rep} by an empirical relation of the type.

$$U_{rep} = \frac{C}{r_{ij}^{12}} \quad (7)$$

where C is a positive constant.

From equations (6) and (7), the total interaction energy, U_{ij} , between the atoms i and j of the crystal can be written as

$$U_{ij} = -\frac{B}{r_{ij}^6} + \frac{C}{r_{ij}^{12}}$$

or in another form, it is expressed as

$$U_{ij} = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \quad (8)$$

Here ϵ and σ are the parameters related to B and C as

$$4\epsilon\sigma^6 = B, \text{ and } 4\epsilon\sigma^{12} = C$$

The values of ϵ and σ are empirically determined. The equation (8) represents a potential known as *Lennard-Jones Potential* and is plotted in figure.

From equation (2), the expression for lattice energy of the total binding energy of the crystal becomes

$$U_{tot} = \frac{1}{2} N (4\epsilon) \sum_{j \neq i} \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \quad (9)$$

It may be noted that equation (9) has been written without considering the kinetic energy of the atoms of the crystal. The we obtain

$$U_{tot} = \frac{1}{2} N (4\epsilon) \sum_{j \neq i} \left[\left(\frac{\sigma}{p_{ij}R} \right)^{12} - \left(\frac{\sigma}{p_{ij}R} \right)^6 \right] \quad (10)$$

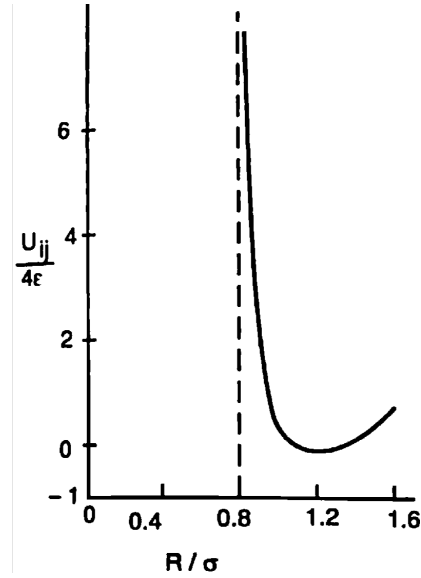


Figure 2: A plot of Lennard-Jones potential versus R/σ . The minimum occurs for $R/\sigma = 1.122$.

For *fcc* structure, we have

$$\sum_j p_{ij}^{-12} = 12.131 \quad \text{and} \quad \sum_j p_{ij}^{-6} = 14.454 \quad (11)$$

Since there are 12 nearest neighbours of an atom in *fcc* structure, the major contribution to the interaction energy arises from the nearest neighbours. The equilibrium distance R_0 is obtained from the condition that at $R = R_0$, $dU_{tot}/dR = 0$. Therefore, from equation (10), we get

$$-2N\epsilon \left[12 \times 12.131 \left(\sigma^{12}/R_0^{13} \right) - 6 \times 14.454 \left(\sigma^6/R_0^7 \right) \right] = 0$$

which gives

$$R_0/\sigma = 1.09 \quad (12)$$

The factors of 12 and 6 correspond to the number of first and second nearest neighbours of an atom in an *fcc* structure respectively. This value of R_0/σ matches closely with the independently determined values for molecular crystals of inert gases. (R_0/σ for Ne, Ar, Kr, and Xe are 1.14, 1.11, 1.10, and 1.09 respectively.)

The slight variation from the theoretical value of 1.09 can be explained from quantum effects. It can, therefore, be concluded that the Lennard-Jones potential given by equation (8) is the correct potential existing between the atoms of the inert gas which binds them together.

The final expression for binding energy of inert gas crystals at absolute zero temperature and zero pressure is obtained by using equations (11) and (12) in equation (10), i.e.,

$$U_{tot}(R_0) = \frac{1}{2}N(4\epsilon) \left[12.131 (\sigma/R_0)^{12} - 14.454 (\sigma/R_0)^6 \right] \quad (13)$$

$$= -2.15(4N\epsilon) \quad (14)$$

It may be noted that this value of binding energy is obtained by neglecting the kinetic energy of atoms. This expression is valid for crystals of all the inert gases. A more correct expression can be obtained by considering the kinetic energy effect and applying the quantum mechanical corrections. Based on these considerations, Bernardes obtained correction factors which reduce the binding energy to 28, 10, 6, and 4 percent of the value given by equation (14) for Ne, Ar, Kr, and Xe respectively.