

CHAPTER I

INTRODUCTION



1.1 Definition of the Cohesive Energy

Solids may be divided into crystalline and amorphous substances. We will only be treating the former here. The term 'crystalline solids' refers to aggregates of atoms, molecules or their ions arrange in a regular repetition¹. One of the major goals of the theory of solids is to show why solids are what they are. In particular, one can attempt to calculate the cohesive energy of the solid. To discuss cohesion we compare the total energy of the solid, kinetic plus potential, with the energy of same number of free neutral atoms at infinite separation. A crystal can only be stable if its total energy is lower than the total energy of the atoms or molecules when free. The difference between the free atom energy and solid energy is defined as 'the cohesive energy'².

1.2 The Cohesive Energy of the Five Types of Crystals

The crystals can be classified in terms of the type of bonding between atoms into five categories : crystals of inert gases or molecular crystals, ionic crystals, covalent crystals, hydrogen-bonded crystals and metal crystals¹⁻⁴.

1.2.1 Crystals of Inert Gases or Molecular Crystals²

The inert gas crystals are composed of atoms which have very high ionization energies. The outermost electronic shells of the atoms are completely filled, and the distribution of electronic charge in the free atom is not really rigid. At any instant of time, there is likely to be a nonvanishing electric dipole moment from the motion of the electrons. An instantaneous dipole moment of magnitude P_1 on one atom produces an electric field E of magnitude $2P_1/R^3$ at the center of the second atom distant R from the first atom. The field will induce an instantaneous dipole moment $P_2 = \alpha E = 2\alpha P_1/R^3$ on the second atom where α is the electronic polarizability. Therefore the attractive interaction is due to the dipole - dipole interaction which is known as the van der Waals interaction. The potential energy of the dipole moment is

$$U(R) \approx -\frac{2P_1 P_2}{R^3} = -\frac{4\alpha P_1^2}{R^6}, \quad (1.1)$$

or can be rewritten as $-\frac{C}{R^6}$, C is a constant.

As two atoms are brought together, their electron clouds overlap. Then according to the Pauli principle, the electron distribution of atoms with closed shells can overlap only if accompanied by the partial promotion of electrons to unoccupied higher energy states of the atoms. Thus the

electron overlapping increases the total energy of the system and gives a repulsive contribution to the interaction.

Experimental data on the inert gases can be fitted well by an empirical repulsive potential of the form $\frac{B}{R^{12}}$, where B is a positive constant. The total potential energy of two atoms at separation R is

$$U(R) = \frac{B}{R^{12}} - \frac{C}{R^6} \quad (1.2)$$

The constants B and C are empirical parameters determined from measurements made in the gas phase. The quantity of the cohesive energy depends on the types of binding. Inert gas crystals require energy of the order of 0.1 eV./molecule to vaporize. The following table gives some examples of the inert gas crystals and the values of the cohesive energies extrapolated to 0°K and zero atmospheric pressure

Inert Gas Crystals	Cohesive Energy ²	
	kcal/mole	eV.
Ne	0.45 ± 0.01	0.02
Ar	1.85	0.08
Kr	2.67	0.116
Xe	3.83 ± 0.05	0.17

Table 1.1 The cohesive energy of the inert gas crystals

1.2.2 Ionic Crystals^{1,2,5}

An ionic crystal is formed by alternating arrangement of positive and negative ions side by side. Each ion may be regarded as a hard sphere which cannot approach another closer than a certain distance. The ions arrange themselves in whatever crystal structure gives the strongest attractive interaction compatible with the repulsive interaction which sets in at short distance between ion cores. The repulsive interaction between ions with inert gas configuration are similar to those between inert gas atoms. The van der Waals part of attractive interaction in ionic crystals makes a relatively small contribution to the cohesive energy, of the order of 1 or 2 percent. The main contribution to the cohesive energy of the ionic crystals is electrostatic, especially the attractive interaction between ions of opposite signs, and is called the 'Madelung energy'.

If U_{ij} is the interaction energy between ions i and j , the total energy of any ion i is

$$U_i = \sum'_j U_{ij} \quad , \quad (1.3)$$

where the summation includes all ions except $j = i$.

The term U_{ij} can be written as the sum of the central field repulsive potential of the form $\lambda \exp(-r/\rho)$, where

λ and ρ are empirical parameters, and a Coulomb potential $\pm \frac{q^2}{r}$. Thus

$$U_{ij} = \lambda \exp(-r_{ij}/\rho) \pm \frac{q^2}{r_{ij}}, \quad (1.4)$$

where the plus sign is taken for the like charge and the minus sign for unlike charges. The final expression for the total lattice energy of ionic crystal of $2N$ ions at their equilibrium separation R_0 may be written in the form²

$$U_{\text{total}} = -\frac{Nc q^2}{R_0} \left(1 - \frac{\rho}{R_0}\right), \quad (1.5)$$

and its value is about 10 eV./atom as in the table 1.2.

The cohesive energies of ionic crystal with NaCl structure obtained at room temperature and atmospheric pressure, with no correction for changes in R_0 and U from absolute zero.

Ionic Crystals	Cohesive energy compared to free ions ⁵	
	kcal/mole	eV.
LiF	-242.3	10.51
NaCl	-182.6	7.92
KBr	-158.5	6.88
RbI	-144.9	6.29

Table 1.2 The cohesive energy of the ionic crystals

1.2.3 Covalent Crystals^{6,7}

Stable covalent bonds or homopolar bonds are formed in the solid state primarily between nonmetallic atoms like nitrogen, oxygen, carbon fluorine, and chlorine. Other elements like silicon, germanium, arsenic and selenium form bonds that are partly covalent, partly metallic; the transition metals are also thought to have a certain amount of covalent character to their bonds. A prerequisite for strong covalent bonding is that each atom should have at least one half filled orbital. Only then can the energy be lowered by sharing each bonding electron in the orbitals of two atom simultaneously. The more the bonding orbitals overlap, the more the energy is lowered and the stronger the bond. The amount of overlap is limited either by electrostatic repulsion or by the exclusion principle. The covalent bond formed by overlapping orbitals also tends to lie in the direction in which the orbital is concentrated, the maximum amount of overlap being obtained in this way. An indication of both bond strength and directionality, then can be inferred from the electron probability function. The cohesive energy of covalent crystals lie in the order of 10 eV./atom.

Bond	Bond energy ⁶	
	kcal/mole	eV.
H - H	104.2	4.5
C - C	83.1	3.6
Si - Si	42.2	1.8
Ge - Ge	37.6	1.6
P - P	51.3	2.2

Table 1.3 Bond energy of the Covalent crystals

1.2.4 Hydrogen - bonded Crystals⁷

Most of the bonds which we have so far been concerned have an energy lying in the range 50-100 kcal/mole. But there is one very common bond, whose energy is very much less than this, called the hydrogen bond in which a single hydrogen atom appears to be bonded to two distinct atoms of which at least one is usually, though not always, oxygen. The hydrogen bond is particularly important. While its energy is of the order of 6 kcal/mole, it is stronger than the van der Waals force. Energies of hydrogen bonds are tabulated as

Bond	Bond energy ⁷ kcal/mole - H bond
O - H - - - 0	3 - 7
C - H - - - 0	2 - 6
O - H - - - 0	4 - 7
N - H - - - 0	3 - 4

Table 1.4 Bond energy of the hydrogen - bonded crystals

1.2.5 Metallic Crystals.

There are two types of metallic crystals : one consists of transition group elements and rare earth elements, where the atom has an incomplete inner shell such as 3d, 4f, etc., and the other consists of other elements called simple metals. Valence electrons which are in the outermost shell of an atom, largely contribute to the crystal bonding of a simple metal. It is believed that in a transition metal some inner shell electrons also participate in bonding through the homopolar bond mentioned above¹.

In a general way, by freeing each electron from localization on a particular atom, the uncertainty in its position coordinate is increased; hence by the Heisenberg

principle, the spread of momentum is reduced. This lowers the average kinetic energy of the electrons, and thus binds the system together. The calculation of total cohesive energy are amongst the most difficult to get right and to verify in principle, in the whole theory of metals. In the simplest case, we consider two main contributions, working in opposite direction. First as the atoms approach and overlap, and electron is able to move in a larger region, where it has, on the average, potential energy becomes lower. On the other hand, as we compress the electron gas, the Fermi energy is pushed up thus increasing the average kinetic energy of the electrons. At the metallic density these forces are in equilibrium⁴. The value of cohesive energy of some simple metals are tabulated below.

Simple Metals	Cohesive energy ⁸	
	kcal/mole	eV.
Li	36.5	.1.99
Na	26	1.30
K	22.6	1.15
Rb	18.9	1.08
Cs	18.8	1.04

Table 1.5 The cohesive energy of simple metals

1.3 Methods for Calculating the Cohesive Energy

We will consider the alkali metals in which their outermost electron configurations are alike. The first method that will be referred to is that of Fröhlich's⁹ in which the cellular approximation¹⁰ was utilized for the calculation of the cohesive energy of the alkali metals. The lowest state energy was obtained in terms of r_0 . The value of r_0 can be determined by the requirement that the wave functions and its derivative near $r = r_0$ passed over continuously to the free atom wave functions at $r = r_0$. Details and results of this method are presented in chapter II.

As is known, the WKB method is one of the powerful theoretical tools available. Imai¹¹ therefore developed a further refinement of this procedure which gave a better approximation of the solution in the neighbourhood of the turning points. Kuhn¹² then applied Imai's wave function¹¹ form to the determination of the minimum ground state energy and the atomic sphere radius in the alkali metals. The steps of these calculations are given in chapter III.

In chapter IV, following Wigner and Seitz^{10,13} the ground state energy is obtained by using the numerical calculation with the reconstructed potential by Cowley¹⁴ et.al.. The cohesive energy then can be also obtained.

The results are compared at the end of the chapter with those of Wigner and Seitz^{10,13}, who were the first to use the spherical cell approximation, which required the use of Prokofjew's¹⁵ potential for Na. in the calculation.

Some discussions are presented in the last chapter.