



Bonding in Solids

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KEY WORDS

silicon revolution, electronic structure, electrical conductivity, light emitting diodes (LEDs), solid state lasers, solar cells, bonds, mutual forces of attraction, minimum potential energy, valence electrons, ionic or electrovalent bond, sodium chloride, equilibrium spacing, ionization energy, minimum potential energy, dissociation energy, electrostatic attraction, equilibrium spacing, minimum potential energy, attractive and repulsive forces, cohesion and cohesive energy, interatomic spacing, repulsive exponent, calculation of cohesive energy, bonding energy, energy of dissociation, alkali halides, equilibrium energy, lattice energy, Madelung constant, x-ray diffraction, crystal lattice of NaCl, permittivity, electrolysis, dielectric constant, fundamental absorption frequency, cleave, Born-Haber cycle, sublimation energy, lattice energy, heat of dissociation, covalent or non-polar bond, configuration, non-polar substances, molar orbital, homopolar or electron-pair bonding, the coordination number, brittle, semiconductors, electron cloud or electron gas, lubricant, molecular bonds, van der Waals forces, fracture, condensation, molecular solids, hydrogen bonding.

1.1 INTRODUCTION

We in the beginning turn to a description of the bonding in solids considering the electronic structure in atoms. Some solids consist of molecules bound together by very weak forces. We shall not be concerned with these because their properties are essentially those of the molecules. Nor shall we be much concerned with purely ionic solids alone bound by electrostatic forces between ions. The solids considered here are those in which all the atoms can be regarded as bound together. To illustrate how the bonding is reflected in the properties of the solids, we explore the electronic properties of various types of solids. Solids display a wide variety of interesting and useful electronic properties. Good electronic conductivity is one of the characteristic properties of metals; semiconductors are the foundation of the ‘*Silicon revolution*’. But why is tin a metal, silicon a semiconductor and diamond an insulator? Many solid state devices (transistors, photocells, light emitting diodes (LEDs), solid state lasers, solar cells) are based on semiconductors containing carefully controlled amounts of impurity. How do these impurity affect the conductivity? These are some of the basic questions to be addressed; but a basic knowledge of bonding theory and the different mechanisms involved is absolutely essential to extend the study.

Q 1.1 What you understand by bonds in solids? What are the main causes and conditions for bond formation?

Answer: The forces which keep or hold together the atoms or molecules of a substance in the form of groups are called *bonds*. The atoms or molecules in the gaseous and liquid states are loosely-packed and a very little binding force exists among them. Therefore, gases and liquids do not possess any definite shape. If a gas (or liquid) is heated, it expands out indefinitely, showing that little binding force exists among its various atoms. However, atoms and molecules in a solid are closely-packed and are held together by strong mutual *forces of attraction*. Therefore, solids have definite shape and occupy well defined space. If a solid is heated, it does not change its shape easily, showing that a very big force exists that binds the various atoms and molecules. In other words the bonds in solids are very strong compared with that in gases and liquids. The law of nature is to make every system to attain a stable state by acquiring *minimum potential energy*. When two atoms come closer and unite to form molecules, their electrons rearrange themselves in such a way so as to form a stable state.

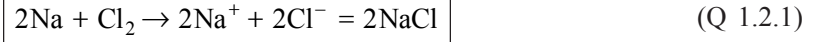
Inference

The formation of bonds between atoms is mainly due to their tendency to attain minimum potential energy. When two atoms tend to form a bond, their *valence electrons* rearrange themselves so as to reach a stable state by acquiring minimum potential energy. In the process, the two atoms lose some energy. The strength of the bond between two atoms would obviously depend upon the energy lost in the process.

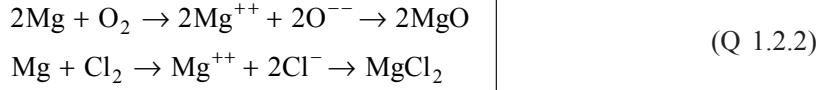
Q 1.2 Describe ionic or electrovalent bonds in solids with suitable examples.

Answer: The bond formed between two atoms by the total transfer of valence electrons from one atom to the other is called an *ionic or electrovalent bond*. Here one or more electrons from an atom may get a transfer to the other atom and the resulting positive and negative ions attract each other. A typical example of an ionic bond is sodium chloride (NaCl) where the bond exists between Na^+ and Cl^- ions.

When sodium is burnt in an atmosphere of chlorine, the sodium gives up its valence electron to the chlorine, each of the resulting ions then has a stable filled shell of outer electrons, and a strong *electrostatic attraction* is set up that bonds the Na^+ cation and the Cl^- anion into a very stable molecule NaCl at the *equilibrium spacing*. The relevant equation is:



Magnesium oxide and magnesium chloride are two more examples of ionic crystals and the relevant equations are



NaCl is one of the best examples of ionic crystal and let the sodium and chlorine atoms be free at infinite distance of separation. The energy required to remove the outer electron from the Na atom (*ionization energy of sodium atom*), leaving it a Na^+ ion is 5.1 eV. i.e.,



The electron affinity of chlorine is 3.6 eV; thus, when the removed electron from sodium atom is added to chlorine atom, 3.6 eV of energy is released and the chlorine atom becomes negatively charged ion. Hence

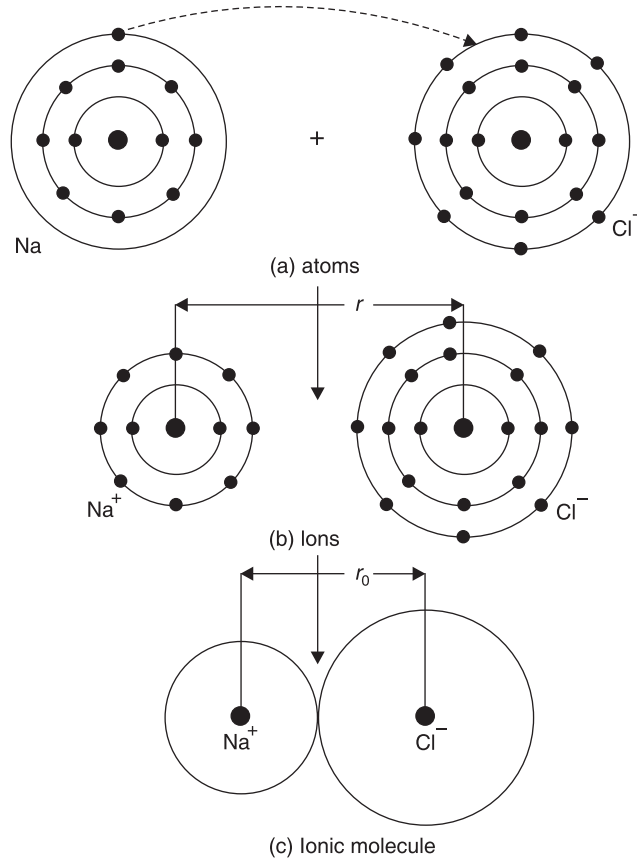
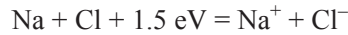


Fig. Q 1.2.1 Schematic representation of the formation of sodium chloride

Table Q 1.2.1 Energy absorbed and energy released in the formation of NaCl

S. No.	Energy absorbed in the formation of NaCl	S. No.	Energy released in the formation of NaCl
1	Separation of chlorine atoms of the diatomic Cl ₂ molecule	1	Completion of M-shell of chlorine atom
2	Separation of sodium atoms from sodium solid	2	Lattice energy of sodium chloride
3	Separation of electron from sodium atom		

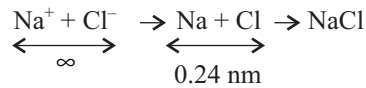
Thus a net energy of $(5.1 - 3.6) = 1.5$ eV is spent for creating a positive sodium ion and a negative chlorine ion at infinity. Now



What happens when the electrostatic attraction between Na⁺ and Cl⁻ ions brings them together to the *equilibrium spacing* $r_0 = 0.24$ nm? At the equilibrium position, the *potential energy* will be minimum and the energy released in the formation of NaCl molecule is called the *bond energy* of the molecule and it is obtained as follows:

$$\begin{aligned}
 V &= -\frac{e^2}{4\pi \epsilon_0 r_0} \text{ joule} = -\frac{e}{4\pi \epsilon_0 r_0} \text{ electron volt} \\
 V &= -\frac{1.6 \times 10^{-19}}{4\pi \times 8.85 \times 10^{-12} \times 2.4 \times 10^{-10}} = -6 \text{ eV}
 \end{aligned}
 \tag{Q 1.2.3}$$

This is the energy released. Thus the entire process evolves an energy of $6 - 1.5 = 4.5$ eV. This means that to dissociate a NaCl molecule into Na and Cl ions, an amount of 4.5 eV of energy will be required. Schematically



Q 1.3 Discuss the variation of interatomic force between atoms with spacing between them with a suitable graph. Compute the cohesive energy of this system by drawing a similar curve between potential energy and spacing.

Answer: We assume here that in a solid material the following two types of forces act between the atoms:

- (i) *attractive forces* which keep the atoms together forcing them to form a solid.
- (ii) *repulsive forces* which come into play when a solid is compressed.

Such forces, however, act in the case of liquids also and even in single molecule. But mere existence of these forces between atoms does not guarantee the formation of a stable chemical bond. This may be established by considering two atoms say A and B exerting attractive and repulsive forces on each other such that the bonding force F , between the atoms may be represented as:

$$F(r) = \frac{A}{r^M} - \frac{B}{r^N} \quad (\text{Q 1.3.1})$$

The first term represents the *attractive force* and the second term the *repulsive force*. Near the equilibrium position the second term must increase more rapidly for diminishing value of r than does the first, and N is necessarily greater than M .

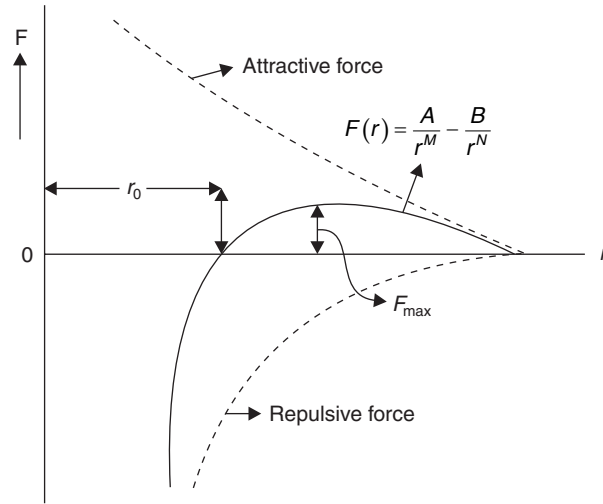


Fig. Q 1.3.1 Variation of interatomic force with interatomic spacing

At the equilibrium spacing,

$$F(r) = 0 \text{ when } r = r_0$$

$$\begin{aligned} \frac{A}{r_0^M} &= \frac{B}{r_0^N} \\ r_0 &= \left[\frac{B}{A} \right]^{\frac{1}{N-M}} \end{aligned} \quad (\text{Q 1.3.2})$$

Cohesion and Cohesive Energy

The potential energy representing the interaction between the atoms varies greatly with the *interatomic spacing* and the same is obtained as follows:

$$\begin{aligned} U(r) &= \int F(r) dr = \int \left[\frac{A}{r^M} - \frac{B}{r^N} \right] dr \\ &= - \left[\frac{A}{M-1} \right] \left[\frac{1}{r^{M-1}} \right] + \left[\frac{B}{N-1} \right] \left[\frac{1}{r^{N-1}} \right] + C \end{aligned}$$

i.e.,
$$U(r) = -\frac{a}{r^m} + \frac{b}{r^n} + C$$

Setting $U = 0$, when $r = \infty$, we get $C = 0$ and hence

$$\boxed{U(r) = -\frac{a}{r^m} + \frac{b}{r^n}} \quad (\text{Q 1.3.3})$$

where n is the *repulsive exponent*

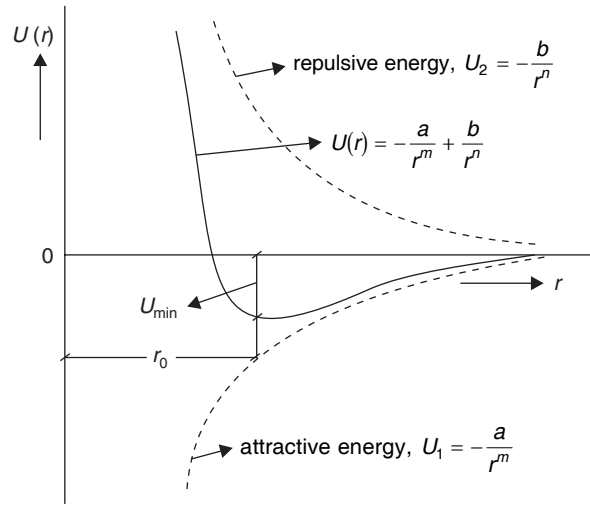


Fig. Q 1.3.2 Variation of potential energy with spacing

When $r = r_0$ (the equilibrium spacing), $U(r)$ exhibits a minimum. Thus

$$\left[\frac{dU}{dr} \right]_{r=r_0} = 0 = \frac{am}{r_0^{m+1}} - \frac{bn}{r_0^{n+1}}$$

or
$$r_0 = \left[\left(\frac{b}{a} \right) \left(\frac{n}{m} \right) \right]^{\frac{1}{n-m}}$$

and
$$\left[\frac{d^2U}{dr^2} \right]_{r=r_0} = -\frac{am(m+1)}{r_0^{m+2}} + \frac{bn(n+1)}{r_0^{n+2}} > 0$$

i.e.,
$$r_0^{m+2} bn(n+1) - am(m+1)r_0^{n+2} > 0$$

$$bn(n+1) > am(m+1)r_0^{n-m}$$

Substituting for r_0 and simplifying, one gets,

$$n > m \quad (\text{Q 1.3.4})$$

Computation of Cohesive Energy

The energy corresponding to the equilibrium position ($r = r_0$), symbolized by $U(r_0)$ is called the *bonding energy* or the *energy of cohesion* of the molecule. This is the energy required to dissociate the two atoms of the molecules (AB) into an infinite separation. The energy is also therefore called *energy of dissociation*.

Thus

$$U_{min} = -\frac{a}{r_0^m} + \frac{b}{r_0^n} \quad (\text{Q 1.3.5})$$

$$\left[\frac{dU}{dr} \right]_{r=r_0} = \frac{ma}{r_0^{m+1}} - \frac{nb}{r_0^{n+1}} = 0$$

Thus

$$r_0^n = r_0^m \left[\frac{b}{a} \right] \left[\frac{n}{m} \right] \quad (\text{Q 1.3.6})$$

Substituting this in Eqn. (1.3.5)

$$U_{min} = -\frac{a}{r_0^m} \left[1 - \frac{m}{n} \right] \quad (\text{Q 1.3.7})$$

As an example, 4.4 eV of energy is required to break one (H — Cl) bond, or 420×10^3 kJ/kmol. The total energy of one ion due to the presence of all others is given by:

$$U(r) = -\left[\frac{Z_1 Z_2 A e^2}{4\pi \epsilon_0 r} \right] + \frac{B}{r^n} \quad (\text{Q 1.3.8})$$

For the univalent *alkali halides*

$$U(r) = -\frac{Ae^2}{4\pi \epsilon_0 r} + \frac{B}{r^n}$$

The total energy per kmol of the crystal is:

$$U(r) = N_A \left[\frac{B}{r^n} - \frac{Ae^2}{4\pi \epsilon_0 r} \right]$$

The potential energy will be zero at $r = r_0$ and

$\frac{dU}{dr} = 0$ and the final equation for the *equilibrium energy* becomes

$$U_0 = - \left[\frac{Ae^2 N_A}{4\pi \epsilon_0 r_0} \right] \left[\frac{n-1}{n} \right] \quad (\text{Q 1.3.9})$$

with N_A the Avogadro's number. The *equilibrium energy* U_0 is also called the *lattice energy*. A is called *Madelung constant*.

Q 1.4 Write a note on the properties of ionic crystals.

Answer: (i) *Crystal structure:* Most of the ionic solids have fine crystalline structure. It has been found by *x-ray diffraction* that the constituents of these crystals are ions and not atoms. For instance, in the case of NaCl, each Na^+ ion is surrounded by six Cl^- ions at equal distances. Similarly, each Cl^- is surrounded by six Na^+ ions. The result is, we get *crystal lattice* of NaCl.

(ii) *Melting and boiling points:* Ionic solids have high melting and boiling points. It is because considerable external energy is required to overcome the electrostatic forces existing between the ions in such a solid.

(iii) *Electrical conductivity:* Pure and dry ionic solids are good insulators because all the electrons are tightly bound with the ions involved in the bond formation. However, such solids show electrical conductivity when;

- (a) the temperature is raised. At high temperature, the electrostatic forces between the ions are greatly reduced so that some of the ions themselves transport the charge in the material.
- (b) dissolve easily in solvents like water. When an ionic solid is dissolved easily in water, the electrostatic forces are considerably weakened (by 80 times) due to high permittivity of water. The result is that the ions become free and wander about in the solution. If now a field is applied, these ions will themselves carry the charge in the solution (*electrolysis*). The permittivity of water is about 80.

(iv) *Solubility:* Ionic compounds easily dissolve in solvents like water (H_2O). It is because molecules of water strongly interact with the crystal ions to destroy the forces of attraction between the ions. Ionic compounds are insoluble in non-polar solvents like benzene (C_6H_6), carbon tetrachloride (CCl_4), because their *dielectric constants* are very low.

(v) *Other properties:* Reaction between ionic compounds in solution state is always fast. This is because in a solution, ionic substances exist as ions and chemical reactions take place between the ions. Ionic crystals are transparent for all frequencies up to the value called the fundamental *absorption frequency*. At frequencies higher than this, they are opaque. High hardness and low conductivity are typical properties of these solids. When subjected to stresses, ionic crystals tend to cleave (break) along certain planes of atoms rather than to deform in a ductile fashion as metals do.

Below are given, some important relations used in the study of other properties of ionic crystals.

(a) The expressions for bulk modulus and compressibility are respectively listed now:

$$K = \frac{Ae^2(n-1)}{72\pi\epsilon_0 r_0^4}$$

and

$$\beta = \frac{1}{K} = \frac{72\pi\epsilon_0 r_0^4}{Ae^2(n-1)} \quad (\text{Q 1.4.1})$$

where A is Madelung constant and N_A is Avogadro's number.

(b) *The Born-Haber cycle for NaCl crystal*

- (i) Initially we start with solid sodium and chlorine molecules. Solid sodium is vaporized by subjecting the *sublimation energy* (S) while chlorine molecule is dissociated into its constituent atoms by supplying *dissociation energy* (D). Hence $\frac{D}{2}$ is the dissociation energy per chlorine atom.
- (ii) The outer electron of Na gaseous atom is removed by applying the ionisation energy (I) and this electron is added to Cl atom. As the chlorine atom has the electron affinity E , an energy E is given out.
- (iii) The two ions ($\text{Na}^+ + \text{Cl}^-$) are arranged in the lattice and hence the *lattice energy* (U_0) is released.
- (iv) We again reach to the starting point by supplying an energy (ΔH) known as *heat of dissociation*.

Thus

$$S + \frac{D}{2} + I - E + \Delta H - U_0 = 0$$

$$U_0 = S + \frac{D}{2} + I - E + \Delta H \quad (\text{Q 1.4.2})$$

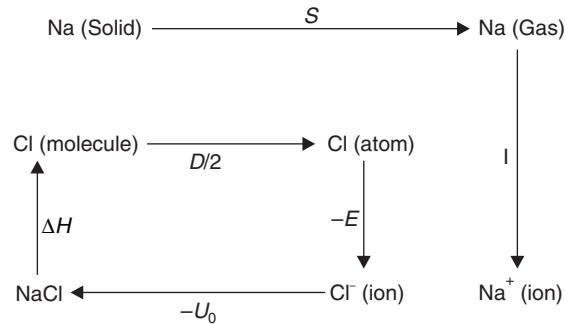


Fig. Q 1.4.1 *Born-Haber cycle for NaCl crystal*

Q 1.5 Discuss briefly the binding mechanism in covalently bonded crystals with suitable sketches.

Answer: The bond formed between two atoms by sharing of valence electrons is called a *covalent* or *non-polar bond*. Such bonds are mainly found in organic molecules and in non-electrolytes, e.g. chlorine,