

ATOMIC COHESION AND CRYSTAL BINDING

INTRODUCTION

Many solids are *aggregates* of atoms. The arrangement of atoms in any solid material is determined by the character, strength and directionality of the binding forces, cohesive forces or chemical bonds. The bonds are made of attractive and repulsive forces that tend to hold the adjacent atoms or atomic units at a particular spacing such that the opposite forces just balance; and the process of holding them together is known as ***bonding***. Since the particular type of bonding within a material plays a major role in determining the physical, chemical and electrical properties of material, knowledge of the types of *bonding* in materials is required to study materials engineering.

FORCE BETWEEN ATOMS

Electrical forces are responsible in binding the atoms and molecules giving different solid structures. **Magnetic forces have only a weak effect in cohesion, and gravitational forces are negligible.** A crystal of *NaCl* is more stable than a collection of free *Na* and *Cl* atoms. Similarly, a germanium crystal is more stable than a collection of germanium atoms. This implies that germanium atoms attract each other when they get close to each other; i.e., an attractive interatomic force exists which holds the atoms together. This is the force responsible for crystal formation. This also means that the energy of the crystal is lower than that of the free atoms by an amount equal to the energy required to pull the crystal apart into a set of free atoms. This is called the ***binding energy*** (also the ***cohesive energy*** of the crystal).

The forces between atoms can be of two kinds: **attractive forces** which keep the atoms together, and **repulsive forces** which come into play when the solid is compressed. The potential or stored internal energy of a material is the sum of the individual energies of the atoms plus their interaction energy. When the atoms are all in the ground state and infinitely far apart so that they do not interact with each other to form a solid, the potential energy is zero, since this is inversely proportional to some power of the distance of separation. Assuming that the atoms consist of moving electric charges, one of the following two things can happen as the atoms approach each other. Either they attract or repel each other. The potential energy due to the attraction is negative, since the atoms do the work of attraction. The repulsive energy is positive since external work must

be done to bring the atoms together and it is inversely proportional to some power of the interatomic separation r . The net potential energy is the sum of both terms.

potential energy = individual energy of the atoms + interaction energy

Suppose two atoms A and B exert attractive and repulsive forces on each other such that the *bonding force* F , between the atoms may be represented as

$$F(r) = \frac{A}{r^M} - \frac{B}{r^N} \text{ with } N > M \quad 1$$

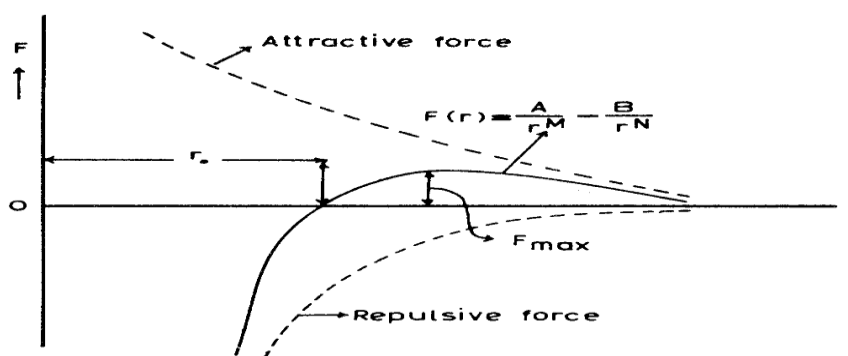


Figure 1 Variation of interatomic forces with interatomic spacing.

where r is the centre to centre, spacing between the atoms A , and B , M and N are constants characteristic of the molecule. 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 values of r than does the first, and N is necessarily greater than M . Since the attractive forces in interatomic bonds are largely electrostatic, M is usually 2 as per Coulomb's law and the value of N is usually 7 to 10.

The equilibrium spacing, r_0 , of the given system is obtained as follows:

$$F(r) = \frac{A}{r^M} - \frac{B}{r^N} \quad 2$$

At the equilibrium spacing $r = r_0$, we have $F(r) = 0$. Thus,

$$0 = \frac{A}{r_0^M} - \frac{B}{r_0^N} \Rightarrow \frac{A}{r_0^M} = \frac{B}{r_0^N} \Rightarrow r_0^{N-M} = \frac{B}{A} \Rightarrow r_0 = \left(\frac{B}{A} \right)^{\frac{1}{N-M}} \quad 3$$

COHESION OF ATOMS AND COHESIVE ENERGY

The potential energy representing the interaction between the two atoms varies greatly with the inter atomic spacing and is obtained by integrating equation

$$F(r) = \frac{A}{r^M} - \frac{B}{r^N} \text{ with, } N > M \text{ gives}$$

$$U(r) = \int F(r) dr = \int \left[\frac{A}{r^M} - \frac{B}{r^N} \right] dr = \int [A r^{-M} - B r^{-N}] dr \quad 1$$

$$U(r) = \frac{A r^{1-M}}{1-M} - \frac{B r^{1-N}}{1-N} + C = - \left[\frac{A}{M-1} \right] \left[\frac{1}{r^{M-1}} \right] + \left[\frac{B}{N-1} \right] \left[\frac{1}{r^{N-1}} \right] + C \quad 2$$

$$U(r) = -\frac{a}{r^m} + \frac{b}{r^n} + C \quad 3$$

Where $a = \frac{A}{M-1}$, $b = \frac{B}{N-1}$, $m = M-1$, $n = N-1$

Setting $U(r) = 0$ when $r = \infty$ we have $C = 0$

Here r is the distance between the centers of the atoms; n and m are positive numbers, a is a positive constant which determines the strength of the attractive force and b is a positive constant which determines the strength of the repulsive force.

The condition under which the particles form a stable lattice is that the function $U(r)$ exhibits a minimum for a finite value of r as shown in Fig. 2. If this minimum exists, then the two atoms form a stable lattice, say a molecule.

Let r_0 be the distance between the atoms for this minimum $U(r)$ to occur. This spacing r_0 is known as **equilibrium spacing** of the system. This minimum energy U_{\min} at $r = r_0$ is negative and hence the energy needed to dissociate the molecule then equals the positive quantity of $(-U_{\min})$. The minimum for $U(r)$ occurs only if m and n satisfy the condition, $n > m$.

Condition 3 implies that the attractive force should vary more slowly with r than the repulsive force. This is obvious from the curves, attractive and repulsive forces shown in Fig. 1. The above said condition may be established mathematically as follows:

$$U(r) = -\frac{a}{r^m} + \frac{b}{r^n} \quad 4$$

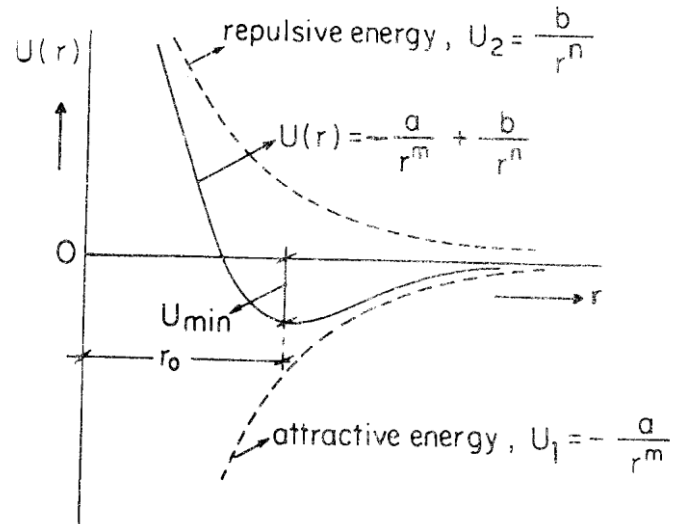


Figure 2 Variation of potential energy with spacing

The potential energy $U(r)$ is minimum for $r = r_0$, thus,

$$\left[\frac{dU}{dr} \right]_{r=r_0} = 0 \quad 5$$

Hence from above equation 5 we have,

$$\left[\frac{dU}{dr} \right]_{r=r_0} = 0 = -\frac{a m}{r_0^{m+1}} - \frac{b n}{r_0^{n+1}} \quad 6$$

$$\frac{a m}{r_0^{m+1}} = \frac{b n}{r_0^{n+1}} \Rightarrow r_0^{n-m} = \left(\frac{b}{a} \right) \left(\frac{n}{m} \right) \Rightarrow r_0 = \left[\left(\frac{b}{a} \right) \left(\frac{n}{m} \right) \right]^{\frac{1}{n-m}} \quad 7$$

At the same time

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

$$\frac{b n(n+1)}{r_0^{n+2}} - \frac{a m(m+1)}{r_0^{m+2}} > 0 \Rightarrow r_0^{m+2} b n(n+1) - r_0^{n+2} a m(m+1) >$$

$$r_0^m b n(n+1) > r_0^n a m(m+1) \Rightarrow b n(n+1) > a m(m+1) r_0^{n-m}$$

$$b n(n+1) > a m(m+1) \left(\frac{b}{a} \right) \left(\frac{n}{m} \right) \Rightarrow n > m \quad 13$$

The forces acting between the atoms are mostly electrostatic in nature and are determined essentially by the extent to which the wave functions of the outer electrons are perturbed by the presence of other atoms at close proximity.

CALCULATION OF COHESIVE ENERGY

The energy corresponding to the equilibrium position ($r = r_0$) denoted 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 molecule (AB) into an infinite separation. This energy is also called the **energy of dissociation**. It is obtained as follows;

$$U(r) = -\frac{a}{r^m} + \frac{b}{r^n} \quad 14$$

$U(r)$ is minimum for $r = r_0$, thus,

$$U_{\min} = -\frac{a}{r_0^m} + \frac{b}{r_0^n} \quad 15$$

Hence,

$$\left[\frac{dU}{dr} \right]_{r=r_0} = -\frac{a m}{r_0^{m+1}} - \frac{b n}{r_0^{n+1}} = 0 \quad 16$$

Thus,

$$r_0^{n-m} = \left(\frac{b}{a} \right) \left(\frac{n}{m} \right) \quad 17$$

Thus, substituting this in equation 15, we get

$$U_{\min} = -\frac{a}{r_0^m} + \frac{b}{r_0^m} \left(\frac{a}{b} \right) \left(\frac{m}{n} \right) = -\frac{a}{r_0^m} + \frac{a}{r_0^m} \left(\frac{m}{n} \right) = \frac{a}{r_0^m} \left(\frac{m}{n} \right) - \frac{a}{r_0^m}$$

$$U_{\min} = -\frac{a}{r_0^m} \left[1 - \frac{m}{n} \right] \quad 18$$

In conclusion, it may thus be said that the forces of repulsion are the result of interpenetration of outer electronic cell between atoms, ions and molecules when they approach one another each in interatomic or intermolecular distances. The forces of attraction are due to interaction between outer electrons of the two atoms, resulting in the formation of a sufficiently stable aggregate which can be considered as an independent molecular species. Thus, all stable arrangements of atoms in solids are such that the potential energy is a minimum. This is one way of explaining the cohesion of atoms in solid aggregates. Dissociation may occur as a result of strong electric fields and mechanical strains or at high temperature.

BONDING IN SOLIDS

From experience one knows that solids are usually moderately strong and slightly elastic structures. Thus, the individual atoms must be held together in solids by interatomic forces or bonds. However, in addition to these attractive forces there must be a repulsive force because solids are not easily compressed. The attractive forces between the constituent particles in solids are basically electrostatic in origin and the classification of the different types of bonding is strongly dependent on the electronic structure of the atoms concerned, and hence directly related to the periodic table.

A solid is composed of billions of atoms packed closely together and the characteristic properties of this state of matter can be accounted for by their proximity and the forces of attractions that hold the atoms together. The importance of these attractions is evident when we consider a piece of copper wire of which each gram contains $(6.025 \times 10^{23})/63.54$ atoms under normal conditions; the forces of attraction that bind these atoms are very strong. If this is not true, the atoms will easily disintegrate or crumble or the metal will deform under small loads.

According to the strength and directionality, chemical bonds are grouped into **primary** and **secondary**. **Primary bonds** by virtue of their nature are inter atomic bonds, whereas secondary bonds are intermolecular bonds. The attractive forces in primary bonds are directly associated with the valence electrons. The outer cell, which contains the valence electrons, is in a high energy state and hence relatively unstable. If it can acquire more electrons to bring the total up to eight, or lose all its electrons to another, it can become stable. This is how atomic or primary bonds are formed. In fact, each bond is a direct consequence of the exchange or sharing of valence electrons.

The study of the solid structure reveals that there are three strong principle types of primary bonds: **ionic**, **covalent** and **metallic**. These bonds are distinguished on the basis of the positions assumed by the bond electrons during the formation of the bond, **van der Waals** and **hydrogen bonds** are typical examples of secondary bonds and they result from intermolecular attraction. The bonding energy or cohesive energy is the energy of formation of one Kmol of a substance from its atoms or ions. it is equal but opposite in sign to the energy of dissociation of the substance. the bond energy can be calculated s the energy of the atoms or ions at the equilibrium spacing in the crystal structure. Using the state of infinite separation of the atoms or ions as the zero potential. the strength of the bond is measured by the energy required to break it, i.e., the amount of heat which must be supplied to vaporize the solid and hence separate the constituent atoms. the melting points

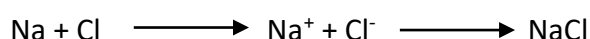
and the boiling points of the elements are dependent on the strength of bond. the stronger the bond, the higher are the melting and boiling points.

THE IONIC BOND

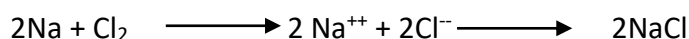
Ionic or heteropolar bonding is the simplest type of chemical bonding to visualize as it is totally electrostatic in nature. The formation of an ionic bond is based on an electrostatic attraction between the positive and negative ions that are derived from the free atoms by the loss or gain of electrons. NaCl and MgO are the example of the ionic bonding.

The creation in ionic bonding is the difference in electro negativity. an ionic bond is the attractive force existing between the positive and negative ion when they are brought into close proximity. These ions are formed when the atoms involved lose or gain electrons in order to stabilize their outer shell electron configuration.

Example of an ionic bond is the bond between the positive sodium ion and negative chlorine ion in sodium chloride. The sodium has a low ionization energy and hence easily loses an electron. The chlorine has a high electron affinity and strongly tends to acquire an electron. when chlorine and sodium atom approach each other, the sodium burns in an atmosphere of chlorine. The sodium gives up its valence electrons, 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 reaction is

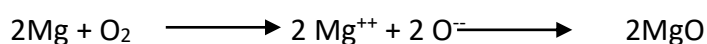
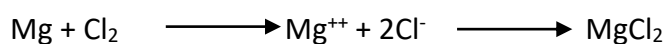


Since chlorine exists as molecules, the chemical reaction must be written as



To release the valence electrons, a kmol of free sodium atoms require an expenditure of energy, $I = 496 \times 10^3 \text{ kJ}$. Acquisition of the electron by kmol of free chlorine atoms results in a release of energy $E_a = 349 \times 10^3 \text{ kJ}$. Thus, to atoms requires a net expenditure of $(I - E_a) = (496 - 349) \times 10^3 \text{ kJ} = 147 \times 10^3 \text{ kJ}$. Once started, the reaction proceeds vigorously with the evolution of light and heat because of the sizable energy decrease resulting from ionic bonding. the final product usually is a large number of salt crystallites.

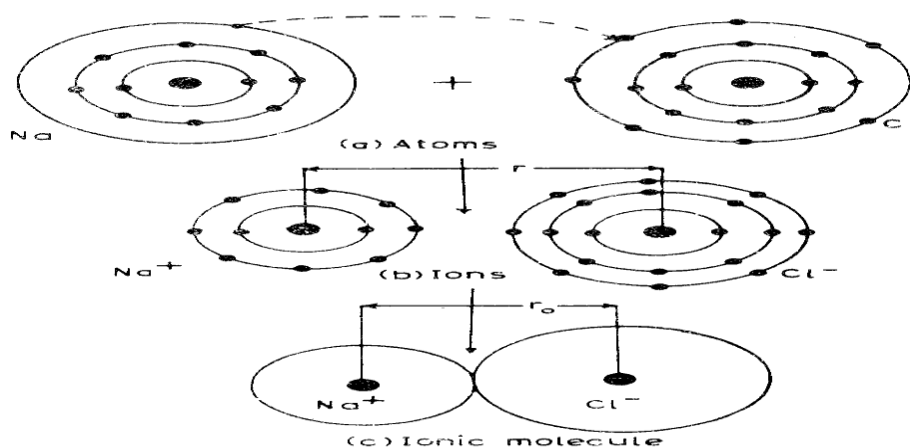
Other examples of ionic crystals are



Following shows the energy absorption and liberation in the formation of NaCl.

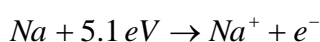
Step No.	Energy absorbed in the formation of NaCl	Energy released in the formation of NaCl
1	Separation of chlorine atoms of the diatomic Cl_2 molecule	Completion of M - Shell of Chlorine
2	Separation of sodium atoms of solid sodium	Lattice energy of Sodium Chloride
3	Separation of electron from sodium atom	

Table 1. energy absorption and energy released in the formation of NaCl



BOND ENERGY OF NaCl MOLECULE

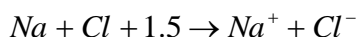
NaCl is one of the best examples of ionic compound and let the sodium and chlorine atoms be free at infinite distance of separation. The energy required to remove the outer electron from the Na atom (ionization energy of sodium atom), leaving it a Na^+ ion is 5.1 eV. That is



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. Hence



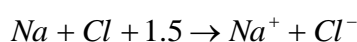
Thus, a net energy of $(5.1 - 3.6) = 1.5$ eV is spent in creating a positive sodium ion and a negative chlorine ion at infinity. Thus



What happens when the electrostatic attraction between Na^+ and Cl^- ions bring 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:

$$\begin{aligned} V &= -\frac{e^2}{4\pi\epsilon_0 r_0} \\ &= -\left[\frac{(1.602 \times 10^{-19})^2}{(4\pi)(8.85 \times 10^{-12})(2.4 \times 10^{-10})(1.602 \times 10^{-19})} \right] eV \\ &= -6 eV \end{aligned}$$

Thus, the energy released in the formation of $NaCl$ molecule starting from neutral Na and Cl atoms having zero potential energies is $(5.1 - 3.6 - 6) = -4.5$ eV. Schematically



This is the energy released. Thus, the entire process evolves an energy of $6 - 1.5 = 4.5$ e V. This means that to dissociate a $NaCl$ molecule into Na and Cl ions, it requires energy of 4.5 e V.

Molecule	Bond length(nm)	Bond energy 9ev)
KCl	0.267	4.4
LiH	0.160	2.5
NaF	0.185	4.7
NaCl	0.236	4.3
NaI	0.271	3.1
NaBr	0.250	3.8

Table 2 Bond lengths and Bond energies of diatomic molecules

CALCULATION OF LATTICE ENERGY OF IONIC CRYSTALS

The lattice energy of an ionic solid will differ from the bond energy of diatomic ionic molecules since, in the former case there will be interactions between more than two ions. The cohesive energy of an ionic crystal is the energy that would be liberated by the formation of the crystal from individual neutral atoms. Cohesive energy is usually expressed in eV/atom, or

eV/molecule or in kJ/kmol, the bond energy of a molecule held together by an ionic bond is not the same as the cohesive energy of the crystal, because in the crystal each ion interacts with all the other ions present and not just with one, two or three of the opposite signs. Sometimes the lattice energy, rather than the cohesive energy, is presented; the lattice energy is that energy evolved when a crystal is formed from individual ions, rather than from individual atoms.

Let us now consider the case *NaCl* which is one of the best examples of an ionic compound. Ionic crystals are strongly bound with binding energies (cohesive energies) of about 5-10 eV per molecule. This is the energy required to dissociate the lattice into positive and negative ions at infinite separation. Two common types of structures found in ionic crystals are *NaCl* structure which is face-centered cubic and *CsCl* which is body-centered cubic. The calculation of binding energy of ionic crystals generally requires knowledge of forces acting between the constituent particles.

In the classical Born- Madelung theory of ionic crystals, it is assumed that the electrons are transferred from electropositive atoms (Na, Ca, K, Mg) to electronegative atoms (O, F, Cl). The stability of an ionic crystal depends on the balancing of at least three forces: the **electrostatic**, or **Coulomb forces** between the ions which give a resultant attraction falling off with the square of the distance; **Vander Waals forces** of attraction diminishing according to the seventh power of the distance (usually neglected); and the **interionic repulsive forces** falling off still more rapidly with distance. The resultant of the attractive and repulsive forces is to lead to an equilibrium position of minimum potential energy; i.e.; of greatest stability as shown in Fig. 3.

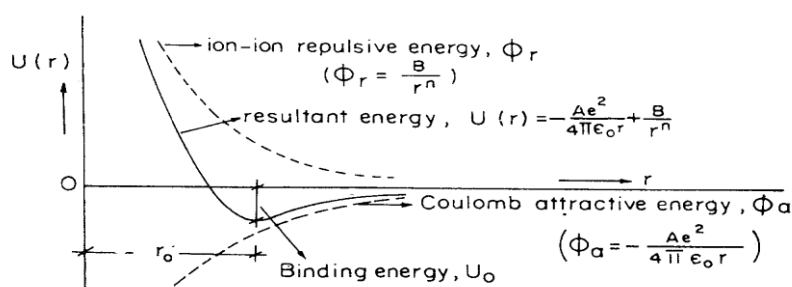


Figure 3 Schematic representation of lattice energy of NaCl as a function of interatomic spacing

For two ions of charges $Z_1 e$ and $Z_2 e$ separated by a distance r , the attractive energy is

$$-\frac{Z_1 Z_2 e^2}{4 \pi \epsilon_0 r} \text{ and therefore this energy is } -\frac{e^2}{4 \pi \epsilon_0 r}, -\frac{4 e^2}{4 \pi \epsilon_0 r}, -\frac{9 e^2}{4 \pi \epsilon_0 r} \text{ if both the atoms are}$$

respectively monovalent, divalent and trivalent. For the whole crystal the Coulomb potential energy may be written as $-\frac{A Z_1 Z_2 e^2}{4 \pi \epsilon_0 r}$. This term represents the net Coulomb potential energy of anyone ion due to the presence of all other similar and dissimilar ions present in the crystal. The minus sign shows that the net Coulomb energy is attractive. The constant A is known as **Madelung constant**.

To prevent the lattice from collapsing, there must also be repulsive forces between the ions. These repulsive forces become more noticeable when the electron shells of neighbouring ions begin to overlap and they increase strongly in this region with decreasing values of r . That is, this repulsive force arises from the interaction of the electron clouds surrounding an atom. Born, in his early work made the simple assumption that the repulsive energy due to the overlap of the outer electron shells between two ions is inversely proportional to some power of the distance r or equal to $\frac{B}{r^n}$. Focusing our attention again on one particular ion, we may thus write for the repulsive energy of this ion due to the presence of all other ions in the crystal as $\frac{B}{r^n}$, n -is called **repulsive exponent**.

Now, the total energy of one ion due to the presence of all others is given by

$$U(r) = -\frac{A Z_1 Z_2 e^2}{4 \pi \epsilon_0 r} + \frac{B}{r^n} \quad 1$$

For the univalent alkali halides

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

The total energy per kmol of the crystal is

$$U(r) = N_A \left[\frac{B}{r^n} - \frac{A e^2}{4 \pi \epsilon_0 r} \right] \quad 3$$

The **P.E.** will be minimum at the equilibrium spacing r_0 .

Thus,

$$\left[\frac{dU}{dr} \right]_{r=r_0} = N_A \left[\frac{A e^2}{4 \pi \epsilon_0 r_0^2} - \frac{B n}{r_0^{n+1}} \right] = 0 \quad 4$$

Or

$$\frac{A e^2}{4 \pi \epsilon_0 r_0^2} = \frac{B n}{r_0^{n+1}} \Rightarrow \frac{r_0^{n+1}}{r_0^2} = \frac{4 \pi \epsilon_0 B n}{A e^2} \Rightarrow B = \frac{A e^2 r_0^{n-1}}{4 \pi \epsilon_0 n} \quad 5$$

Substituting this value of B in equation 3 and putting $r = r_0$ we get the total **equilibrium energy** per kmol of the crystal.

Thus,

$$U(r)_{r=r_0} = U_0 = N_A \left[\frac{A e^2 r_0^{n-1}}{4 \pi \epsilon_0 n r_0^n} - \frac{A e^2}{4 \pi \epsilon_0 r_0} \right] = U_2 - U_1 \quad 6$$

Where U_1 and U_2 represent net Coulomb attraction energy and repulsive potential

Thus,

$$\begin{aligned} U_0 &= -\frac{A e^2 N_A}{4 \pi \epsilon_0} \left[\frac{1}{r_0} - \frac{r_0^{n-1}}{n r_0 r_0^{n-1}} \right] \\ &= -\frac{A e^2 N_A}{4 \pi \epsilon_0 r_0} \left[1 - \frac{1}{n} \right] \quad 7 \\ &= -\frac{A e^2 N_A}{4 \pi \epsilon_0 r_0} \left[\frac{n-1}{n} \right] \end{aligned}$$

This equilibrium energy U_0 is called the lattice energy. This is defined as the energy released in the process when the constituent ions are placed in their respective positions in the crystal lattice or this is the amount of energy which is spent to separate the solid ionic crystal into its constituent ions. It is experimentally measured from the **Born-Haber cycle data**. The comparison of the two values will enable us to assess the merits of the above theory of ionic lattices.

The **binding energy** or **cohesive energy** per molecule of the ionic crystal $NaCl$ is 7.95 eV, similarly in $NaCl$ the energy U_1 due to Coulomb attraction is 8.94 eV with $r_0 = 0.282$ nm and the Madelung constant = 1.75. Substituting $U_0 = -766 \times 10^6$ joule/kmol in equation (25), we get $n = 9$.

CALCULATION OF MADELUNG CONSTANT OF IONIC CRYSTALS

Madelung constant represents the effect of a specific geometrical array of ions on the electrostatic potential energy. It is a property of the crystal structure and depends on the lattice parameters, anion-cation distances, or molecular volume of the crystal. Before considering a three-dimensional crystal lattice, we shall discuss the calculation of Madelung constant in a linear chain of ions of alternate signs as in Fig. 4.

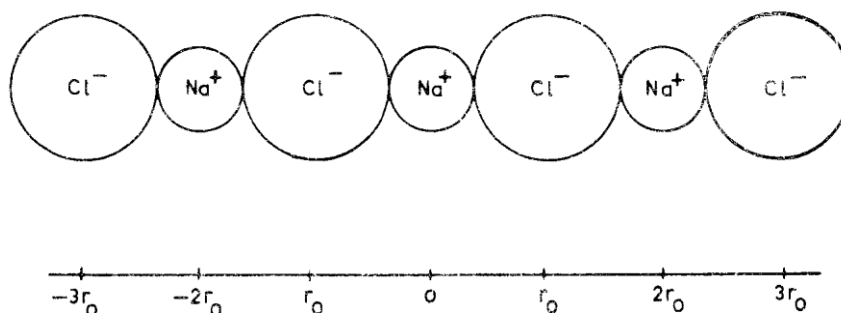


Figure 4 A hypothetical one-dimensional $NaCl$ lattice.

Let us pick up a positive ion for reference, and let r_0 be the shortest distance between adjacent ions. This ion has two negative ions as its neighbours on either side at a distance r_0 . Now the **attractive Coulomb energy** due to the nearest neighbours is

$$-\frac{e^2}{4\pi\epsilon_0 r_0} + \left[-\frac{e^2}{4\pi\epsilon_0 r_0} \right] = -\frac{2e^2}{4\pi\epsilon_0 r_0} \quad 8$$

Similarly, the **repulsive energy** due to the two positive ions at a distance of $2r_0$ is

$\frac{2e^2}{4\pi\epsilon_0 (2r_0)}$ and the attractive Coulomb energy due to the two next neighbours at a distance $3r_0$ is

$-\frac{2e^2}{4\pi\epsilon_0 (3r_0)}$ and so on. Thus, the total energy due to all the ions in the linear array is

$$\begin{aligned} &= -\frac{2e^2}{4\pi\epsilon_0 (r_0)} + \frac{2e^2}{4\pi\epsilon_0 (2r_0)} - \frac{2e^2}{4\pi\epsilon_0 (3r_0)} + \frac{2e^2}{4\pi\epsilon_0 (4r_0)} \\ &= -\frac{e^2}{4\pi\epsilon_0 r_0} \left[2 \left(1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \dots \right) \right] = -\frac{e^2}{4\pi\epsilon_0 r_0} [2 \log(1+1)] = -\frac{e^2}{4\pi\epsilon_0 r_0} [2 \log 2] \quad 9 \end{aligned}$$

Thus $(2 \log 2)$ is the **Madelung constant** per molecule of the ionic solid. Hence $(2 N_A \log 2)$ is the **Madelung constant** per Kmol of the ionic solid.

In three dimensions the series does present greater difficulty and it is not possible to sum the series conveniently as in the case of one-dimensional lattice. For definiteness let us consider the

lattice of the $NaCl$ structure represented in Fig. 5.

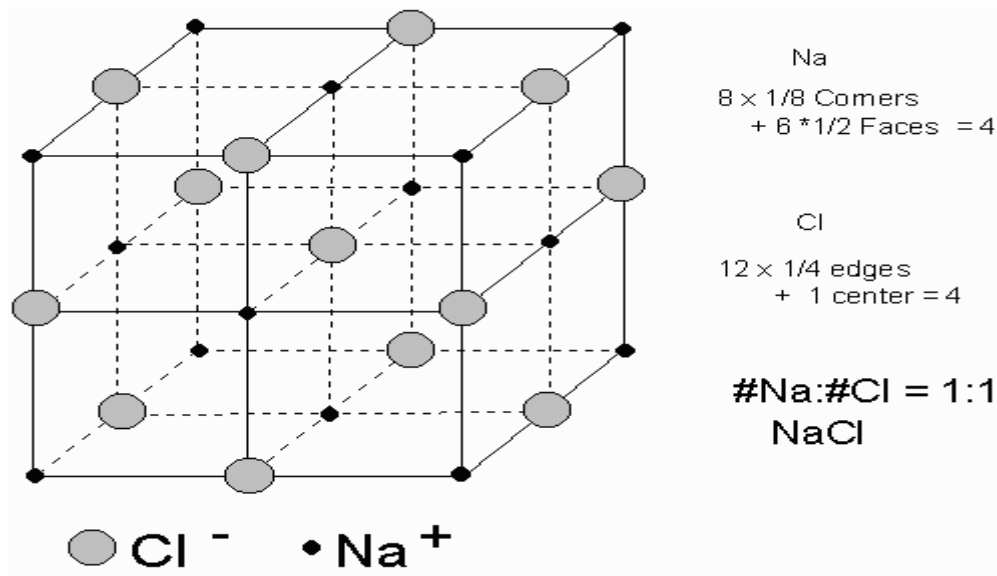


Figure 5 $NaCl$ structure.

The total potential energy is obtained by adding all the attractive and repulsive energies between all the ions. The sodium ion Na^+ at point A is coordinated by 6 Cl^- ions at a distance r_0 .

Therefore, the attractive potential energy of the sodium ion at A due to these 6 Cl^- ions is

$$\frac{6e^2}{4\pi\epsilon_0 r_0}, \text{ Similarly } 12 Na^+ \text{ ions at } \sqrt{2} r_0 \text{ and } 6 Na^+ \text{ ions at } 2 r_0 \text{ respectively contribute } \frac{12e^2}{4\pi\epsilon_0 \sqrt{2} r_0}$$

and $\frac{6e^2}{4\pi\epsilon_0 (2r_0)}$ respectively. Thus, the Coulomb energy of this Na^+ ion at A in the field of all other

ions is

$$U = -\frac{6e^2}{4\pi\epsilon_0 r_0} + \frac{12e^2}{4\pi\epsilon_0 \sqrt{2} r_0} - \frac{8e^2}{4\pi\epsilon_0 \sqrt{3} r_0} + \frac{6e^2}{4\pi\epsilon_0 (2r_0)} + \dots$$

$$U = -\frac{e^2}{4\pi\epsilon_0 r_0} \left[6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \dots \right] \quad 10$$

For a kmol of the crystal, the total Coulomb energy is

$$U = -\frac{N_A e^2}{4\pi\epsilon_0 r_0} \left[6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \dots \right] = -\frac{N_A A e^2}{4\pi\epsilon_0 r_0} \quad 11$$

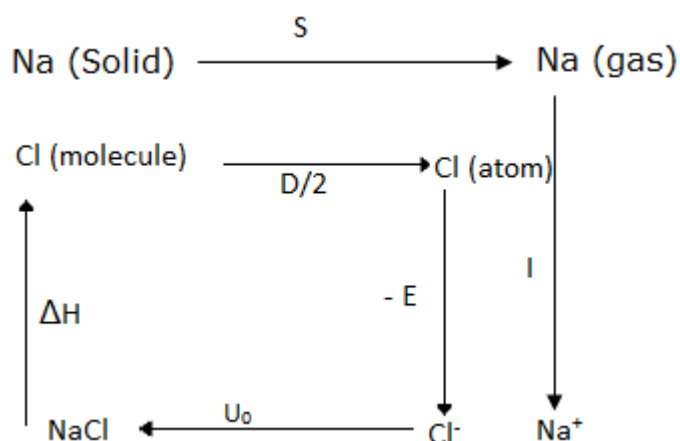
The constant A is called **Madelung constant** and $A = 1.75$ for $NaCl$ structure.

Crystal structure	Madelung constant
Sodium chloride	1.747558
Cesium chloride	1.762670
Zinc blende	1.6381

Table 3. Madelung constant for some structures.

THE BORN - HABER CYCLE

The formation of $NaCl$ molecule may be visualised as occurring in different steps, each of which results in energy absorption or evolution. All experimental check on the calculated values of the lattice energies may be obtained from Born - Haber cycle.



The Born - Haber cycle $NaCl$ crystal can be represented as:

- Initially start with sodium and chlorine molecule. Solid sodium is vapourised by **sublimation energy (s)** while chlorine molecule is dissociated into its constituent atoms by supplying **dissociative energy (d)**. $D/2$ is the dissociation energy per chlorine atom.
- The outer electron of Na gaseous atom is removed by applying the **ionisation energy (I)** and this electron is added to Cl atom. As chlorine atom has the **electron affinity E** , an energy E is given out.
- The two ions ($Na^+ + Cl^-$) are arranged in the lattice and hence the **lattice energy (U_0)** is released.
- And get the starting point by supplying an energy **ΔH Heat of dissociation**.

$$S + \frac{D}{2} + I - E = 0,$$

$$U_0 = + \frac{D}{2} + I - E$$

All quantities excepting U_0 are experimentally determinable. Hence the lattice energy U_0 can be calculated. For NaCl solid, on substitute in above equation the value of $S = 108.8 \times 10^3$ kJ/kmol, $D = 242.8 \times 10^3$ kJ/kmol, $I = 494.0 \times 10^3$ kJ/kmol, $E = 464.2 \times 10^3$ kJ/kmol and $\Delta H = 410.2 \times 10^3$ kJ/kmol, gives the lattice energy $U_0 = 770.4 \times 10^3$ kJ/kmol. The experimental value obtained from Born - Haber cycle data agrees well with the calculated value. This indicates that the electrostatic theory is quite satisfactory for ionic crystals.

PROPERTIES OF IONIC SOLIDS

All ionic or electrovalent compounds are rigid and crystalline in nature. From x-ray diffraction it has been confirmed that the constituents of the crystals are ions and not atoms. The ionic bond is fairly strong.

All ionic solids have high melting and boiling points. This is because more energy is needed to make the ions mobile, there being a necessity to overcome the strong electrostatic force of attraction created due to the ionic bond in addition to the already existing interatomic force of gravitational attraction.

Pure and dry ionic compounds are insulators, because of the non availability of free electrons. However, in solution they conduct electricity because of the movement of the charged ions instead of free electrons. In a solution the ionic bond is weakened by the solvent molecules. Thus, the ions become free to move about and thereby become conductors of electricity and the solution are good electrolytes.

Ionic solids are easily soluble in polar solvent like water. This is because molecules of the polar solvent interact strongly with the ions so as to reduce the attraction between the ions. Also, the polar solvent possesses high dielectric constants. Water has high dielectric constant of 81, it will reduce the electrostatic force of attraction between the ions to $1/81$ of the original value.

Ionic compounds are soluble in non-polar solvents like (C_6H_6) , carbon tetrachloride (CCl_4) , because their dielectric constants are very low.

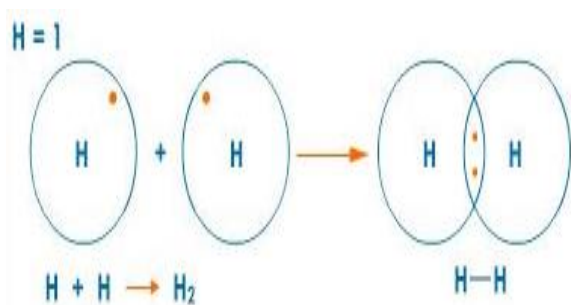
Reaction between ionic compounds in solution state is always fast. This is because in a solution, ionic substances exist as ions and chemical reactions take place between the ions. The ionic crystals are transparent for all frequencies up to the value called the *fundamental absorption frequency*. At 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 along certain planes of atoms rather than to deform in a ductile fashion as metals do.

COVALENT BOND

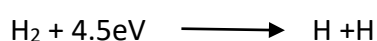
The covalent bond is formed by sharing of pairs of valence electrons between like atoms rather than by electron transfer. The outer shell of the chlorine possesses seven electrons. Each chlorine atom would like to gain an electron to form a stable octet. This can be done by sharing two electrons between pairs of chlorine atoms, thereby producing stable diatomic molecules. Each atom contributes one electron for the sharing process.

The simplest case of a single bond is in the hydrogen molecule. In the hydrogen molecule H_2 , when two isolated H atoms each with its electron in the ground state 1s orbital approach each other, the 1s clouds begin to overlap. Each electron is attracted to the other nucleus and the overlap increases. The two atomic orbitals merge into a molecular orbital. Within the molecular orbital, the two electrons are attracted to both nuclei. When the repulsive forces have been balanced by the attractive forces within the molecule, a stable molecule results, having a stability greater than that of the two isolated atoms. The covalent bonding is also known as *homopolar or electron-pair bonding*. It is a common type of bonding in organic molecules and in many inorganic molecules.



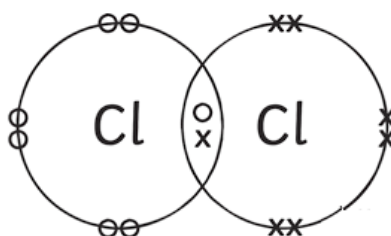
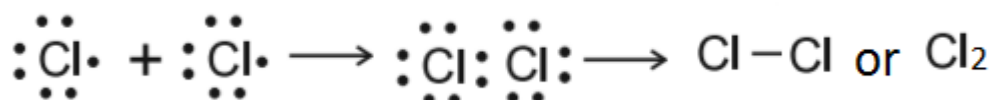
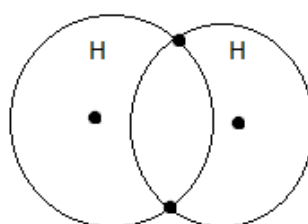
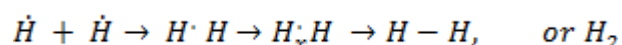
In the molecular orbital of H_2 , two electrons are equally shared between the nuclei and cannot be specifically identified with either nucleus. The two shared electrons are more likely to be found between the two nuclei and thus the electron density is relatively large.

The balance between attractive and repulsive forces in the hydrogen molecule occurs at a separation of 0.074 nm. Hence 4.5 eV energy must be required to break the covalent bond in the hydrogen molecule into hydrogen atoms.

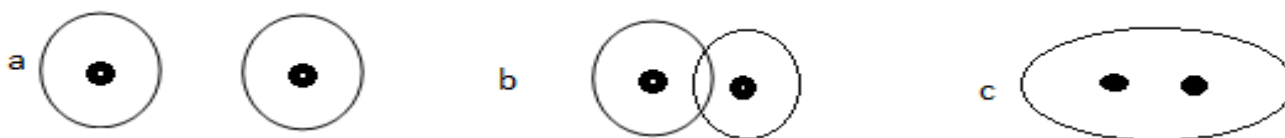


If N represents the number of electrons present in the valence shell of an electrically neutral atom, then $(8 - N)$ is the number of electrons which are required to obtain a stable octet. This is also the maximum number of covalent bonds which an atom can form with the adjacent atoms. Thus $(8 - N)$ is the coordination number in normal covalent bonding.

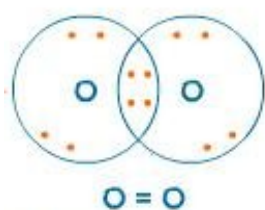
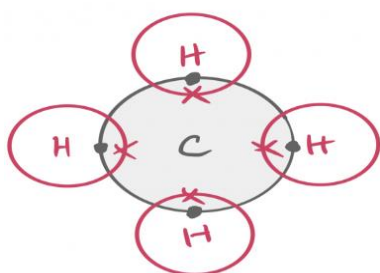
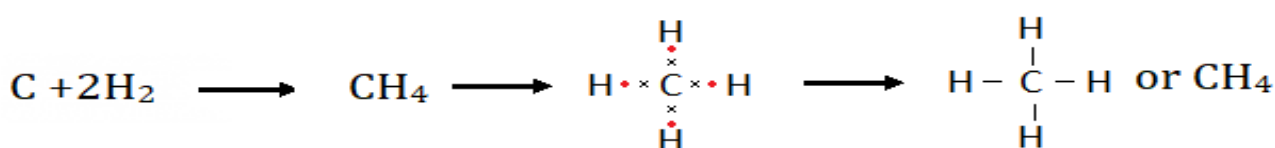
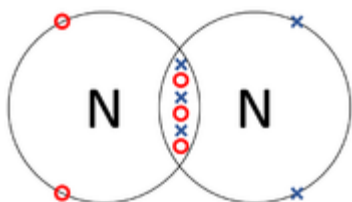
A covalent bond is usually indicated by showing two electrons between the symbol for the atoms $H:H$. It is desired to make clear that one electron has come from each atom, they may be indicated $H\cdot H$. Here the dot electron has come from the atom to the left and \times electron has come from atom on the right. The actual bond is generally represented by $H-H$. Thus,



In the element chlorine, each atom has seven electrons in the outer shell. When two atoms of chlorine tend to form a chlorine molecule, one electron from each atom is shared with the other.



Other examples of covalent bonds are



SATURATION IN COVALENT BONDS

Hydrogen molecule can be stable with only two atoms. If the third hydrogen atom is brought near the hydrogen molecule H_2 , it is repelled. This means that the covalent bond exhibits saturation. It is not possible for molecule H_3 to be formed by covalent forces, it can be H_2 molecule is in the ground state, electron spins are anti aligned ($\uparrow\downarrow$). When a hydrogen atom with a spin ($1/2$) approaches the H_2 molecule and if there is to be chemical bonding by covalent forces, it can be formed by exchange of spins between H and H_2 . There are only two ways in which the single electron

spin (\uparrow) of the hydrogen atom can be interact with the H_2 molecule. One is by exchanging the spin with the one electron having the spin (\uparrow) or with the other electron having the spin (\downarrow). If the hydrogen atom electron having the spin (\uparrow) exchanges with the hydrogen molecules `electron having spin (\uparrow), the two spins are aligned in the same direction and the exchange force between the hydrogen atom and the molecule is repulsive. Suppose the hydrogen atoms electron having spin (\uparrow) exchanges with the hydrogen molecules electron having spin (\downarrow) the electron spins of the hydrogen molecule will be aligned which is disallowed by Pauli's exclusion principle. So, the only possible exchange between the H_2 molecule and the H atom is repulsive and so the molecule H_3 cannot be formed

DIRECTINAL NATURE OF COVALENT BOND

The covalent bond formed as a result of paring of two electrons in atomic orbitals of two atoms. The bond then should lie along the direction of the overlapping atomic orbitals. Hence covalent bonds will have strong directional preferences unlike ionic bonds. Accordingly, to quantum mechanics, the electron is associated with a wave and It can be described in terms of the wave function $\psi (x, y, z)$. the physical significance of ψ is that the square of ψ , ($|\psi|^2$) represents the probability of finding the electron at any instant in unit volume.

The solution of Schrodinger wave equation gives rise to three constants, called quantum numbers. One is called *principal quantum number* ' n ' which can take integral values from 1 to ∞ . The other is called angular momentum quantum number ' l ' which can take values from 0 to $(n - 1)$. The third one is called magnetic quantum number ' m ' which can take only integral values from $m_l = - l$ to $m_l = + l$ including zero in steps of one. The wave functions ψ_{n,l,m_l} are called orbitals. According to different l values, the orbitals are classified as

$l = 0$ is called 's' orbital

$l = 1$ is called 'p' orbital

$l = 2$ is called 'd' orbital

$l = 3$ is called 'f' orbital

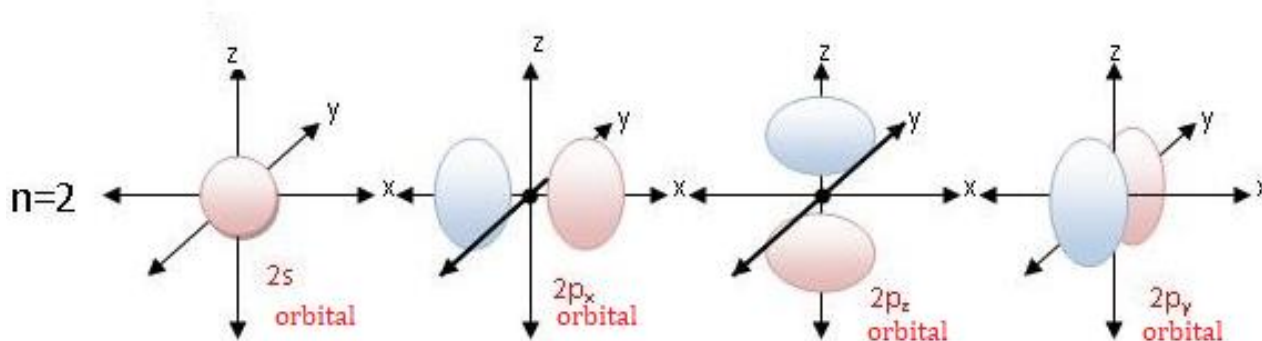
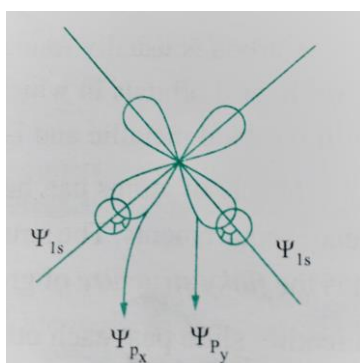


Fig: different orbitals

Covalent bonds are not only formed by pure s orbitals or pure p orbitals but can also be formed by the overlapping of s and p orbitals called **hybrid bonding**.



**Fig. A Overlapping of orbitals
In water molecule**

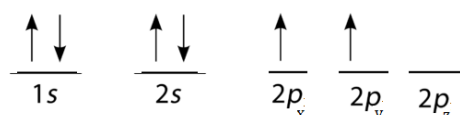
In the bond formation, the two hydrogen atoms use $1s$ orbitals. The water molecule, which shows that p_x and p_y orbitals should be used.

Fig A shows the by plane of water molecule. It is observed that p_x and p_y orbitals lie mutually perpendicular to each other in xy plane. To obtain maximum possible overlap between $1s$ orbitals of hydrogen atoms and, p_x and p_y orbital of oxygen atom, it is necessary for hydrogen atoms to approach along the x and y axes. This leads to the overlap as shown in fig A and H O H bond angle should amount to 90° . It is experimentally observed that the value

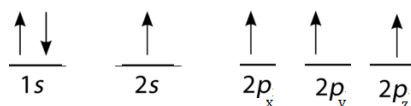
of the bond angle is 104.5° which is due to the repulsion between two hydrogen atoms and also due to some contribution to the bond of $2s$ electrons of oxygen atoms.

HYBRIDIZATION

The occupancy of the orbitals of the carbon atom is



This shows that $1s$, $2s$ spins are paired, while $2p$ electron spins are not paired and they are available for bonding. But when the carbon atoms approach each other, one s electron is excited to the p level and the electronic configuration becomes as



This shows that there are four unpaired electron spins. The bonding directions of these orbitals are disposed toward four corners of a regular tetrahedron with bond angles 109.5° . This

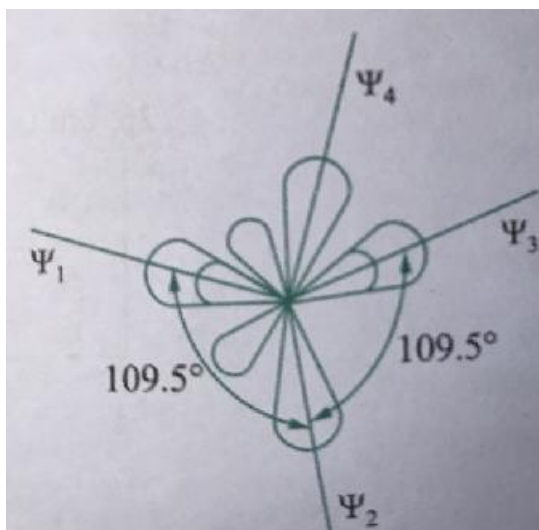


Fig A sp^3 hybrid wave functions

arrangement of orbitals is called **hybridization** and the four orbitals are called sp^3 hybrids as shown in Fig A. the four bonds are of equal strength. Covalent bonds in diamond, CCl_4 , CH_4 exhibits this tetrahedral symmetry.

Hybridization is the mixing of the valence shell of the same atom to form new orbitals with the same energy and similar shape. The resulting orbitals are called **hybrid orbitals**. Hybridization involves the following steps: promotion of one of pure orbitals in the excited atom are hybridized

the paired electrons in an orbital to an orbital of higher energy. The atom is now in the excited state and, pure orbitals in the excited atom are hybridized or mixed to form hybrid orbitals having definite in shape.

The three-dimensional arrangement of carbon atoms is called the diamond structure. The strength of the covalent bond is aptly illustrated by the strength and hardness of the diamond. Carbon is usually found as graphite rather than as diamond. The graphite structure results from the sp^2 hybrid orbitals in which 3 bonds are formed in a plane with interbond angles 120° , with the fourth p orbital metallic and is therefore non – directional.

Sheet of atoms can bond each other by weak secondary bonds. These weak bonds have no valence requirements. The structure which results from bonding the sheets together as shown in Fig B, and is the flaxy structure of graphite. Because the bonds holding the sheets together are weak, the sheets can readily slide past each other. The case of sliding accounts for the lubricating properties of graphite. Both diamond and graphite have the same chemical composition, but the manner in which the atoms are arranged has a vast effect on physical properties. The metallic orbital

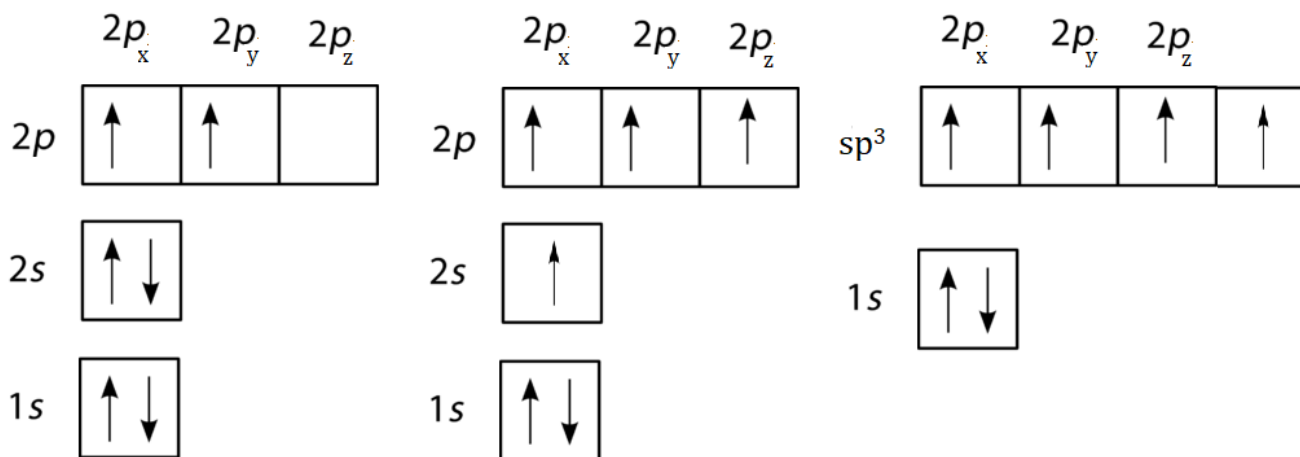


Fig B 1. Carbon in the ground state

2. in the excited state

3. in the hybridized state

accounts from the fact that graphite is an electrical conductor while diamond is not. Graphite is used as 'lead' in pencil for its softness and as lubricant, for the weak van der Waals force between the sheets, in important applications.

The important points are

- i) Attainment of octet configuration or noble gas configuration is not essential in covalent bond formation. (In borontrifluoride, each fluorine atom has a noble gas configuration, but the boron atom has only six electrons in its outermost orbit.)
- ii) The paired electrons shared by atoms should be of opposite spin. This rule is called the **rule of two**. Thus, two electrons forming the pair which shared between the two atoms can occupy the available stable orbital in either atom without violating Pauli's exclusion principle.
- iii) depending on whether the electron pairs are shared equally or unequally between the atoms, covalent bonds can be subdivided into non – polar and polar bonds respectively.

Hydrogen to hydrogen bond during the formation of H₂ molecule is a non – polar covalent bond, as the electron pair is shared equally between the hydrogen atoms. Chlorine to chlorine bond is also non -polar covalent bond.

Hydrogen to chlorine bond is polar covalent bond since the electron pair is more shifted towards chlorine because of its high affinity/ electronegativity for electrons. This results in slightly negative charged - δ chlorine end and an equal positively charged + δ hydrogen end, in HCl molecule.

PROPERTIES OF COVALENT COMPOUNDS

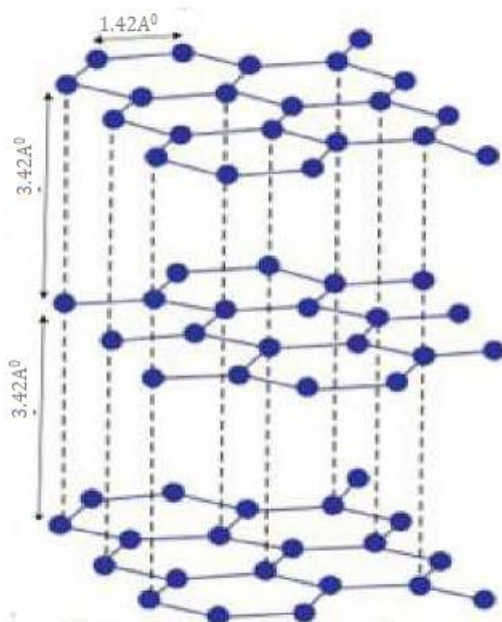
- (i) Covalent compounds are mostly gases and liquids.
- (ii) Covalent crystals tend to be hard and brittle, and incapable of appreciable bending. These facts are understandable in terms of the underlying atomic forces. Since the bonds have well defined directions in space, attempts to alter them are strongly resisted by the crystal.
- (iii) The melting point and boiling points are usually low as compared to those of ionic crystals. This is because the covalent bond is not so strong as the ionic bond and also because the atoms are less powerfully attracted towards each other, the forces that attract them towards each other being Vander Waals forces, dipole, etc. which are quite weak.
- (iv) Most of the covalent substances do not conduct electricity because of the non-availability of free electrons or charged ions to carry the current. However, certain substances like HCl which exhibit polarity in aqueous solutions behave like ionic substances and allow the passage of electricity through them accompanied by their own decomposition thereby acting as electrolytes.
- (v) Covalent substances are insoluble in polar solvents like water. However, they are soluble in non-polar solvents like benzene, carbon disulphide, etc. This is because of the covalent nature of the solvent. However, the giant molecules are not soluble in any solvent because of the large size of the molecules.
- (vi) A very interesting property of covalent crystals is the apparent lack of sensitivity of their physical properties to their bonding type. For example, carbon in the diamond structure is the hardest substance and has a very high melting point of 3280 K. The hardness and melting point then decrease as we proceed to other elements in column IV of the periodic table from silicon to lead. Tin, for example, is very soft and has a low melting point. The variation in the electrical properties is also pronounced. Diamond is very good insulator. Silicon and germanium are well known semiconductors while tin is a good conductor. Depending on the number of electrons shared, the bond length and bond energy vary. When the number of electrons shared is more, the bond length between the atoms is decreased and bond energy is increased. Diamond, silicon, germanium, silicon carbide, tin and rutile are some examples of covalent crystals.

METALLIC BOND

The metallic bond is similar to the covalent bond, but it is quite different in others. In the covalent bond, two atoms are linked together by pairs of electrons shared between them. In metallic bonding, the valence electrons, which hold the atoms together are not bound to individual atoms or pairs of atoms but move freely throughout the whole metal. The similarity to the covalent bond lies in the sharing of electrons. The difference is that electrons belong to the metal as a whole rather than to any particular atom.

Metallic elements have low ionization energies and hence, in this bonding, atoms of the same element or different elements give their valence electrons to form an electron cloud or say “*electron gas*” throughout the space occupied by atoms. Having given up their valence electrons, the atoms are in that they are primarily electrostatic, but are between the ions and the electrons.

Most of the atoms in metals have one or two valence electrons. These electrons are loosely held by their atoms and therefore, can be easily released to the common pool to form an electron cloud. The electrostatic interaction between the positive ions and the electron gas holds the metal together. The high electrical and thermal conductivities of metals follow from the ability of the free electrons to migrate through their crystal structures while all the electrons in ionic and covalent crystals are bound to particular atoms.

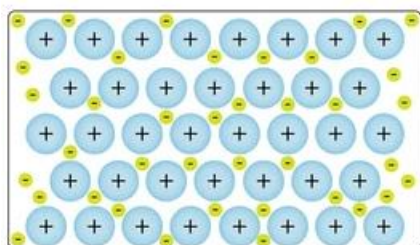


Graphite structure illustrating molecules connected by metallic bond

Unlike other crystals, metals may be deformed without fracture, because the electron gas permits atoms to slide past one another by acting as a lubricant. In Carbon covalent bond exists, so it is an extremely bad conductor. In graphite, bonds are formed in which covalency is not fully achieved and these bonds can break and reform fairly easily as in metallic bond. For this reason, graphite is an electrical conductor. If a potential difference is applied between any two points in metal piece, the electron gas will form the negatively charged part to the positively charged part, constituting an electric current.

PROPERTIES OF METALLIC CRYSTALS

- (i) Bonding energies and melting temperatures are found very wide in these bonding e.g., bonding may be weaker or stronger, energies range from 64×10^3 kJ/kmol (0.7 eV/atom) for mercury to 850×10^3 kJ/kmol (8.8 eV/atom) for tungsten. Their respective melting points are -39 and 3410°C .
- (ii) Due to the symmetrical arrangements of the positive ions in a space lattice, metals are crystalline.
- (iii) Metallic bonds being weak, metals have a melting point moderate to high, i.e., the melting points of metallic crystals are lower than those of the electrovalent crystals.
- (iv) Since a large number of free electrons are available, metallic crystals have high electrical conductivity.
- (v) Metallic crystals have higher thermal conductivity because of the availability of large number of free electrons which act as carriers of heat.
- (vi) Metals are opaque to light since the light energy is absorbed by free electrons. Copper, sodium, silver, aluminum, etc. are examples of metallic crystals.

INTERMOLECULAR BONDS

⊕ positive Metal ion, ⊖ negative electron cloud
Metallic bonding

The forces that hold molecules together to form a solid are considerably weaker than atomic bonds and are often referred to as secondary bonds. They are also known as van der Waals bonds, which primary bonds result either from transfer of electrons or from sharing of electrons, secondary bonds do not generally involve the valence electrons at all. Secondary bonds are those comparatively weak intermolecular of electrons in

asymmetrical molecules. Dipoles may be permanent as in the case of hydrogen fluoride and water molecules, or they may be temporary, as in the case of noble gases. The three types of intermolecular bonds are dispersion bonds, dipole bonds, and hydrogen bonds.

DISPERSION BONDS

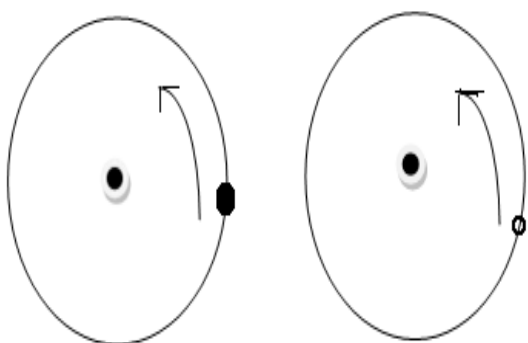


Fig A dispersion effect in hydrogen molecule H_2 , showing momentarily polarization, negative on right and positive on the left

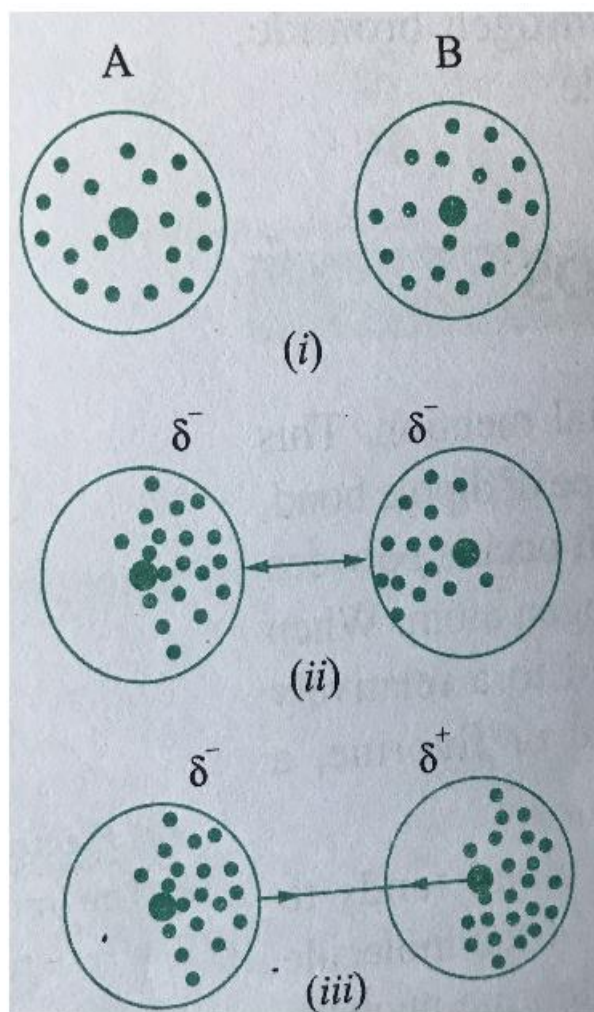


Fig B dispersion forces between two atoms of argon

Bonds of first type are made possible largely because the electrons of adjacent atoms in a molecule tend to repel each other, as the electrons revolve around their nuclei, they tend to keep in phase as illustrated in Fig A, for a hydrogen molecule. The result is that the molecule has a small fluctuating net charge on each end and acts as an oscillating dipole. The hydrogen molecule in fig A, is instantaneously charged negatively on the right end and positively on the left. This fluctuating charge on one molecule tends to interact with fluctuating charge on a neighbouring molecule, resulting in a net attraction. The strength of the bond depends on the ease with which one atom can influence the other. Molecules of the inert gases, which consists of single atoms, are held together by dispersion forces when the gases are solidified.

Atoms of noble gases found, have little attraction for one another and with rare exception they remain monoatomic at ordinary temperatures. Only at extremely low temperatures, when thermal vibrations have been greatly reduced, do these gases condense. It is this condensation which makes it evident that there is weak interatomic attraction which pull the atoms together as van der Waals forces.

Two atoms of noble gases, argon is in close proximity to each other. If the electron clouds are evenly distributed as in Fig B (i), then there will be no resultant displacement in either atom and they will neither attract nor repel each other. If, however, an uneven distribution of the electron clouds is present as in(ii), the atoms will repel each other, but if the electron clouds are distributed as in (iii), the electron cloud of atom A will be attracted by the 'unprotected' nucleus of the atom B

The displacement of the electrical charges necessary to produce a dipole is temporary and random so that a molecule, as a whole, over a period of time has no resultant dipole. However, if it has a displacement at any one instant it will induce another in a nearby neighbour and a force of attraction will be set up between the two. It is thought that such interaction must be largely responsible for van der Waals bonding between non – polar atoms and molecules.

DIPOLE BONDS

A molecule of the hydrogen chloride gas contains one atom of hydrogen and one atom of chloride, covalently bonded H – Cl. In this covalent – bonded hydrogen chloride (HCl) molecule, the

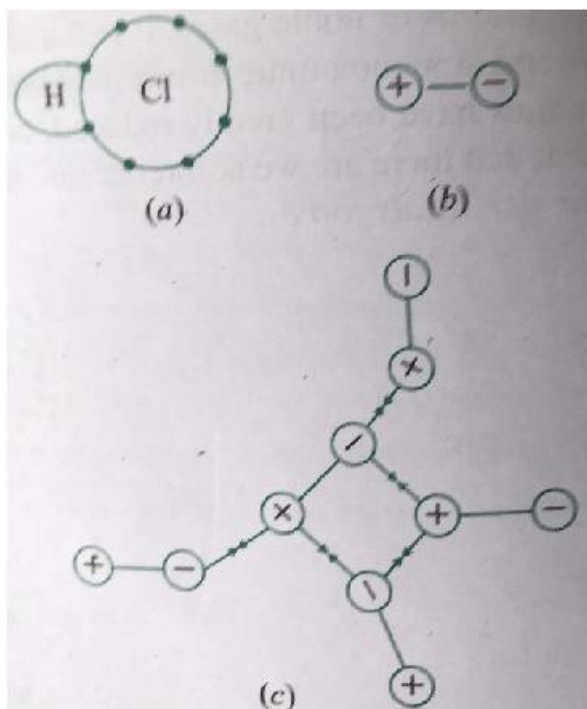


Fig A dipole bonds (a) Electric imbalance in HCl molecule, (b) Imbalance produces electric dipole, (c) Resulting dipole produces mechanism for secondary forces of attraction

Net effect of the electron – sharing process is to give the chlorine atom a slightly negative charge while the hydrogen atom has a corresponding positive charge. The magnitude of the charges while are actually quite small, being 0.272×10^{-19} coulomb with 1.6×10^{-19} coulomb for a single electron. the spacing of the atoms is 0.128nm , resulting in a dipole moment of 3.48×10^{-30} coulomb – meter (1.045 Debye unit). Adjacent HCl molecules therefore attract each other by means of the electrostatic attraction between their oppositely charged ends.

The attraction is small compared with that between ions because the charge on an ion is at least equal to that of electron. Dipole bonds are consequently much weaker than ionic bonds, but at the same time are considerably stronger than dispersion bonds. HBr, SO_2 , HCN are the example of dipole bonds.

HYDROGEN BONDS

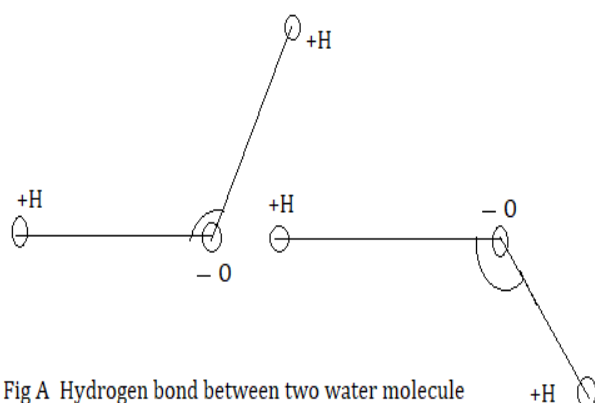


Fig A Hydrogen bond between two water molecule

The hydrogen bond observes a special and must be considered as a special type of bond, but one that is considerably stronger. It occurs between molecules in which one end is a hydrogen atom. When a hydrogen atom is covalently bonded to a relatively large atom such as nitrogen, oxygen or fluorine, a powerful permanent dipole is set up.

This is because the electron cloud tends to become concentrated around that part of the molecule containing the nitrogen, oxygen and fluoride nucleus, thus leaving the positively charged hydrogen nucleus relatively 'unprotected'. Consequently, a strong permanent dipole is created that can bond to other similar dipoles with a force near that involved in the ionic bond. In water, the hydrogen and oxygen atoms are held together by covalent bonds in a configuration shown in Fig A. the four types of chemical bonding in solids are shown in Fig B. the four types of chemical bonding in solids shown in Fig B.

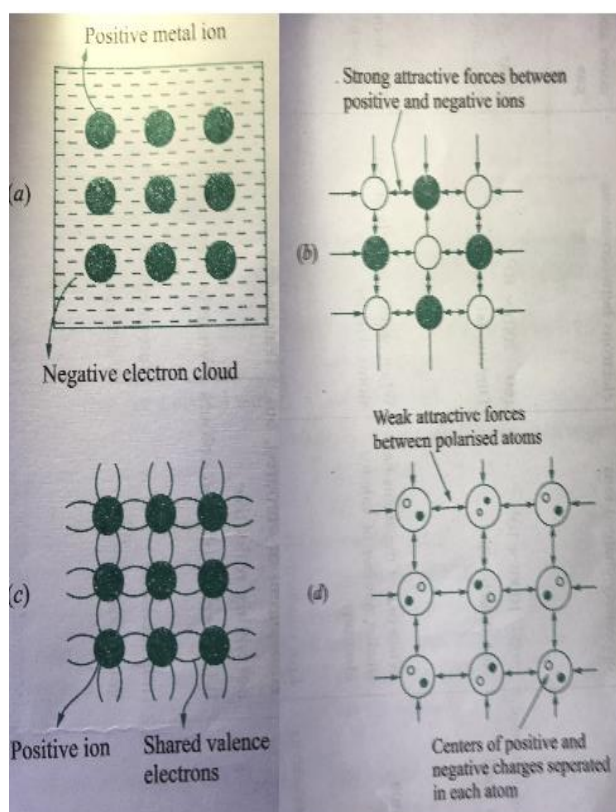


Fig B four types of chemical bonding in solids; (a) Metallic bonding, (b) Ionic bonding, (c) Covalent bonding, (d) Van der Waals bonding

VAN DER WAALS BONDING

Noble gas atoms which have close – shell structure and are represented as spherical rigid charge distributions. Such electron distributions are reluctant to overlap when any two atoms are brought close to each other. But there must be some attractive forces between atoms bringing about

the cohesion and finally the solidification. Of these forces, one is the van der Waals force we are interested in. These are weak forces arising out of the attractive interaction between fluctuating electric dipoles. By chance, for a fraction of the second, there could be more number of electrons on one side of the nucleus than on the other. This destroys the spherical symmetry of the electron charge distribution and momentarily displaces the centre of the negative charge (the electrons) from the centre of the positive charge (the nucleus). Thus, an atom becomes a tiny electric dipole which is capable of inducing an electric dipole moment in the neighbouring atom. The two dipoles attract each other, though weakly, resulting in the van der Waals binding. As the electron charge distribution keeps fluctuating, the electric dipoles in question are called fluctuating dipoles.

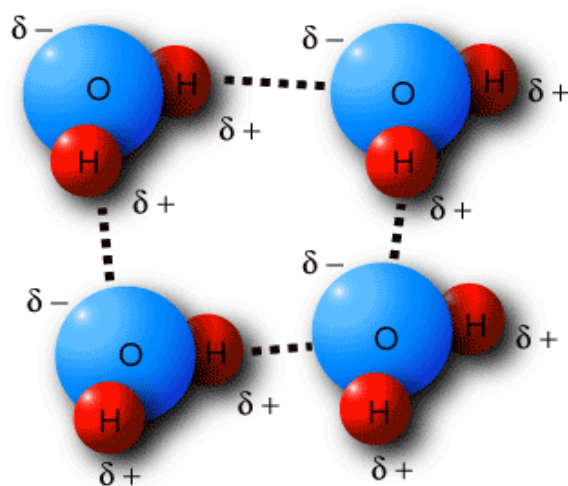


Figure 11 Schematic diagram of van der Waals bonding.

Suppose we have two atoms 1 and 2 of a noble gas separated by distance r . As described above, when atom 1 acquires an instantaneous electric dipole moment \mathbf{p}_1 ; an instantaneous electric dipole moment \mathbf{p}_2 may be induced in atom 2 because of the polarization caused by the electric field \mathbf{E} of the atomic dipole 1 at atom 2. It is now a trivial exercise in electrostatics to show that the interaction energy of two dipoles \mathbf{p}_1 and \mathbf{p}_2 ($= -p_2 \cdot E$) varies with separation as $1/r^6$. This interaction energy is essentially the van der Waals binding energy of the two atoms.

An alternative explanation of van der Waals interaction is the quantum mechanical basis in which the creation of the electric dipole is attributed to the zero-point electronic motion. In fact, the van der Waals interaction more completely identified as the van der Waals-London interaction turns out to be a quantum effect. The quantum mechanical calculation confirms $1/r^6$ dependence of the interaction. The interaction is expressed as A/r^6 , where A is a constant involving the Planck constant.

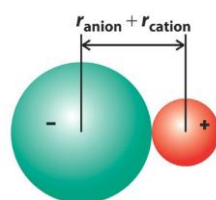
This implies that the interaction vanishes when the Planck constant is taken as zero, proving that the van der Waals interaction has its proper explanation in quantum physics.

It must be noticed that the van der Waals bonds are neither saturable nor directional. Barring Helium, all the noble gases crystallize in the close-packed FCC structure. These weakly-bound crystals are transparent insulators and characterized by low melting points.

ATOMIC SIZE

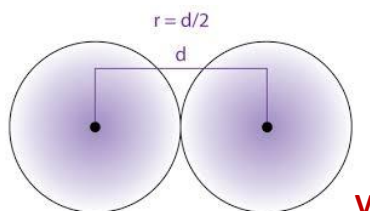
IONIC RADII

Ionic radius is the distance between the nearest neighbouring cation and anion.



EMPERICAL RADII/ ATOMIC REDII

The atomic radius of a chemical element is a measure of the size of its atoms, usually the mean or typical distance from the center of the nucleus to the boundary of the surrounding shells of electrons.

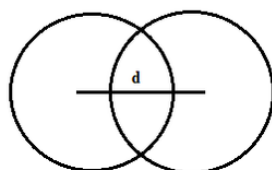


VARIATION OF IONIC RADII

The **ionic radius** is the distance between the nucleus and the electron in the outermost shell of an **ion**. When an electron is added to an atom, forming an anion, the added electron repels other electrons, resulting in an increase in the size of the atom.

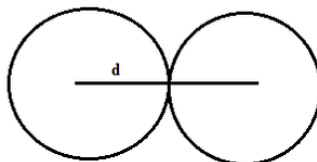
COVALENT RADII

Covalent radius is half of the internuclear separation between the nuclei of two single-bonded atoms of the same species (homonuclear).



METALLIC RADII

Metallic radius is the half of the experimentally determined distance between nuclei of nearest neighbours in solids.

**VAN DER WAALS RADII**

Van der Waals radii are established from contact distances between non-bonding atoms in touching molecules or atoms. It is defined as one half of the distance between the nuclei of the two adjacent atoms belonging to two neighbouring molecules of an elements in the solid state.

Metallic radius is the half of the experimentally determined distance between nuclei of nearest neighbours in solids.

