

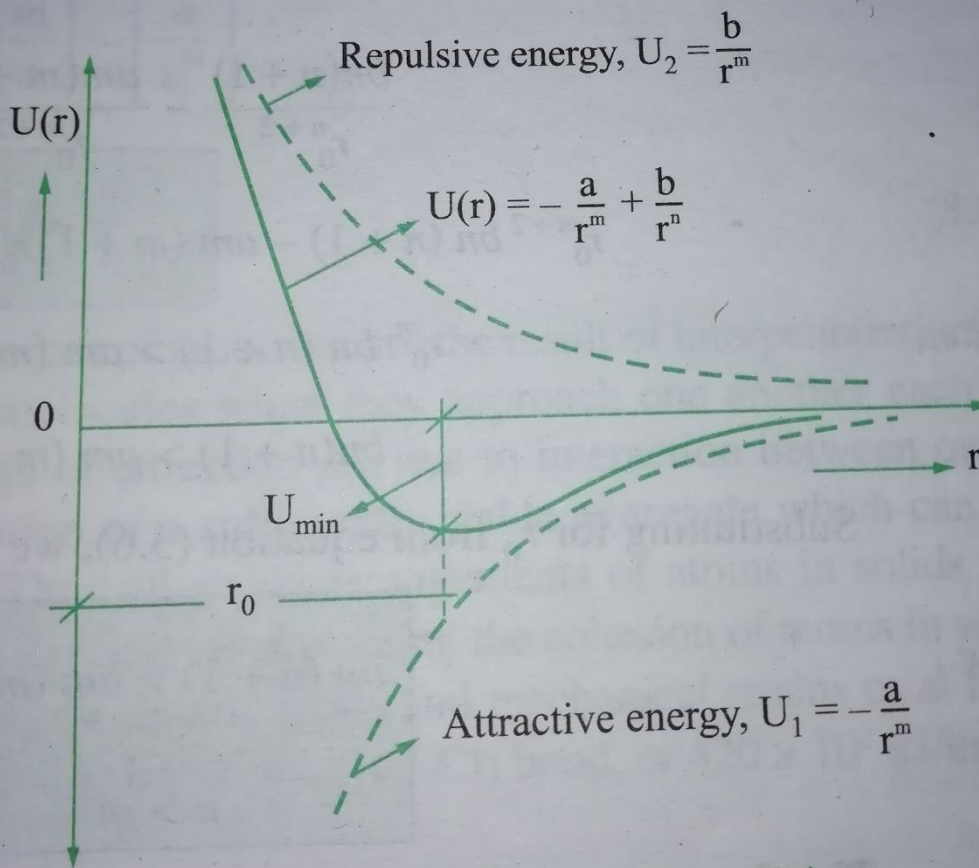
+ C

(3.3)

= N - 1.

and

(3.4)



CHAPTER 3

Fig. 3.2 Variation of potential energy with spacing

le then equals the positive quantity of $(-U_{\min})$. The
he condition

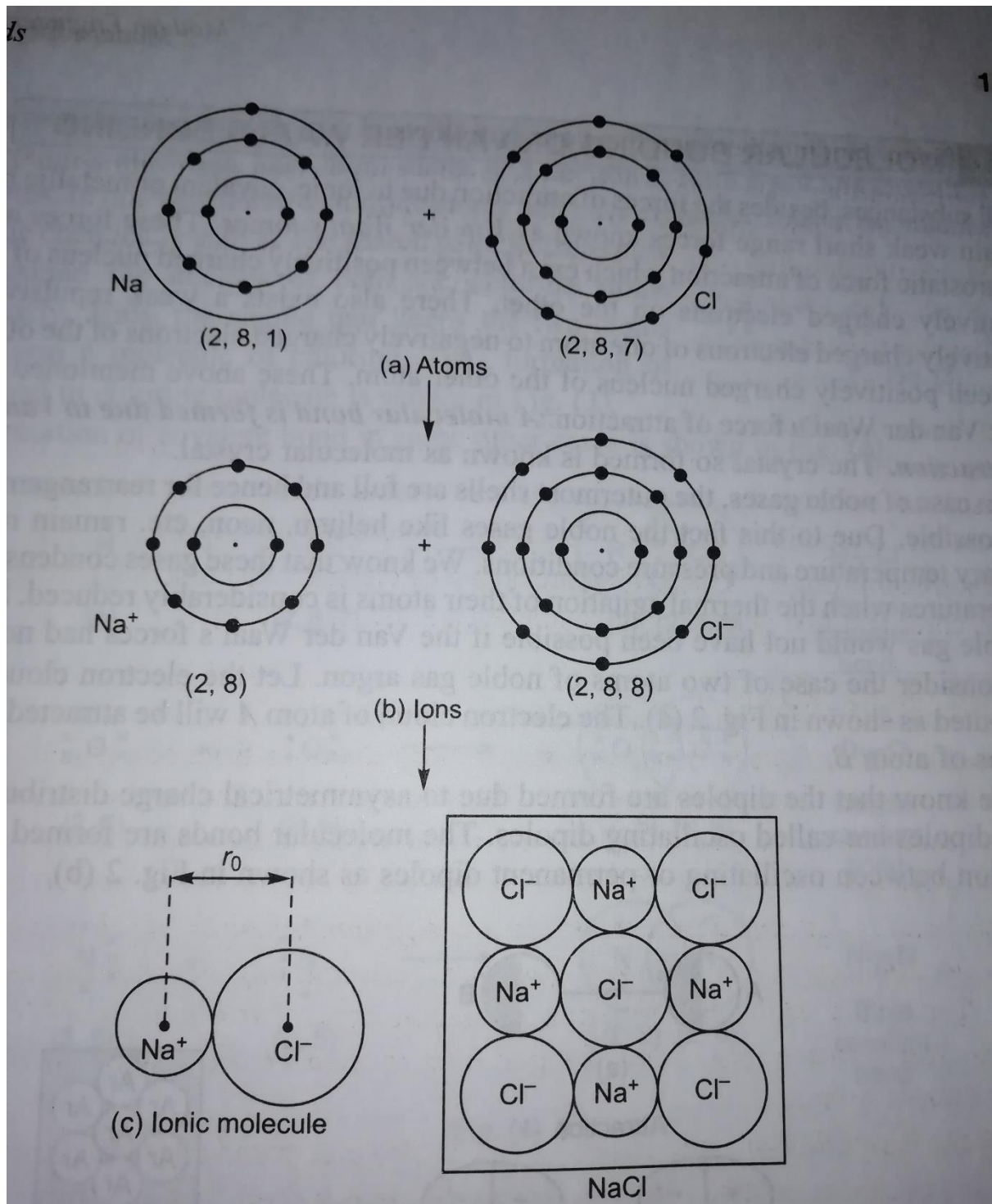
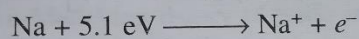


Fig. (1) Showing ionic bonding

NaCl Molecule

VII. BOND ENERGY OF NaCl MOLECULE

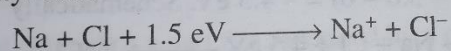
NaCl is one of the best examples of ionic compound and let the sodium and chlorine atoms be free at infinite distance of separation. The energy required to remove the outer electron from the Na atom (ionisation energy of sodium atom), leaving it as an Na^+ ion is 5.1 eV. That is



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 $(5.1 - 3.6) = 1.5 \text{ eV}$ 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 brings them together to the equilibrium spacing $r_0 = 0.24 \text{ nm}$? 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:

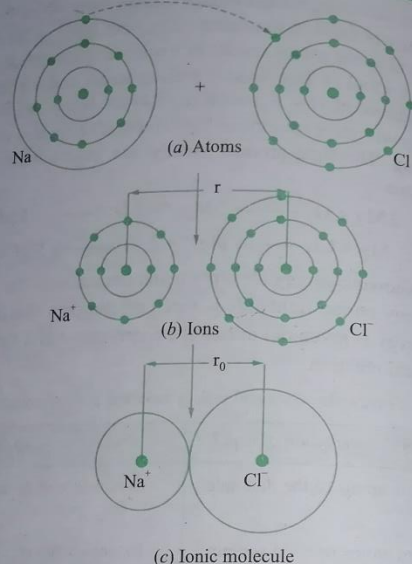
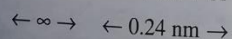
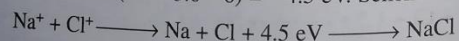


Fig. 3.3 Schematic representation of the formation of an ionic molecule of sodium chloride

$$\begin{aligned}
 V &= -\frac{e^2}{4\pi\epsilon_0 r_0} \\
 &= -\left[\frac{(1.602 \times 10^{-19})^2}{(4\pi)(8.85 \times 10^{-12})(2.4 \times 10^{-10})} \right] \text{joule} \\
 &= -\left[\frac{(1.602 \times 10^{-19})^2}{4\pi(8.85 \times 10^{-22} \times 2.4)(1.602 \times 10^{-19})} \right] \text{eV} \\
 &= -6 \text{ eV}
 \end{aligned}$$

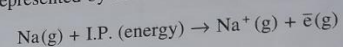
Thus the energy released in the formation of NaCl molecule starting from neutral Na and Cl atoms having zero potential energies is $(5.1 - 3.6 - 6) = -4.5 \text{ eV}$. Schematically



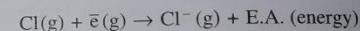
This is the energy released. Thus the entire process evolves an energy of $6 - 1.5 = 4.5 \text{ eV}$. This means that to dissociate a NaCl molecule into Na and Cl ions, it requires an energy of 4.5 eV .

2.3 BOND DISSOCIATION ENERGY OF NaCl MOLECULE

NaCl is considered to be the ideal representative of ionic compound. In order to find the bond dissociation energy corresponding to a single NaCl molecule, let us begin with the consideration that the sodium and chlorine atoms are initially free when they are at infinite distance of separation. The energy required to remove the outer electron from the Na atom is equal to its ionization potential. When this energy is absorbed by the sodium atom, it gets ionized and a positively charged Na^+ ion is formed. The ionization process of a Na atom is represented by the reaction



Similarly, when an electron is taken from infinity and added to a neutral chlorine atom to form a negatively charged chlorine ion, an energy equivalent to its electron affinity is released. The formation of chlorine ion is given by the reaction



The net amount of energy absorbed (spent) in the process of formation of positive sodium ion and a negative chlorine ion at infinity is thus given by

$$\Delta E = \text{I.P.} - \text{E.A.}$$

Combining the above two reactions, we have



In the above reactions, the ions are infinitely separated, but now let, the Coulomb attraction between them bring the two ions closer together so that an ion-pair is formed. When the two ions are at an equilibrium separation, a stable NaCl molecule is formed. In the process, an energy equal to the potential energy is released at equilibrium separation, i.e.

$$U_c = -\frac{e^2}{4\pi\epsilon_0 R_c}$$

where ϵ_0 is the absolute permittivity of free space and air. Its numerical value is given by

$$\epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2 \text{N}^{-1} \text{m}^{-2}, \text{ and } \frac{1}{4\pi\epsilon_0} = 9 \times 10^9 \text{ Nm}^2 \text{C}^{-2}$$

Since, the entire process (starting from neutral Na and Cl atoms till the formation of NaCl molecule) consists of three steps: (i) removal of an electron from Na atom (first ionization energy), (ii) the addition of an electron to the Cl atom (electron affinity of Cl), and (iii) the formation of the ionic molecule (Coulomb attraction), the net energy evolved is

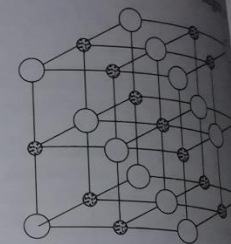


Fig. 2.4 Sodium chloride crystal structure

as $-\frac{AZ_1Z_2e^2}{4\pi\epsilon_0 r}$. This term represents the net Coulomb potential energy of any one ion due to the presence of all other similar and dissimilar ions present in the crystal. The minus sign shows that the Coulomb energy is attractive. The constant A is known as *Madelung constant*.

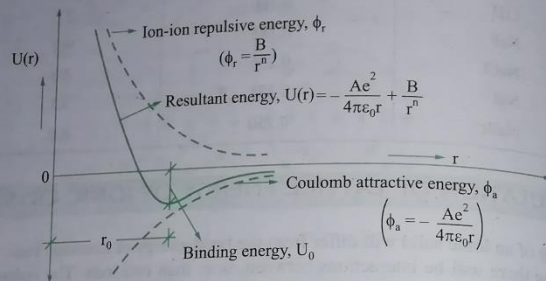


Fig. 3.4 Schematic representation of lattice energy of NaCl as a function of interatomic spacing

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 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, 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

$$U(r) = -\frac{AZ_1Z_2e^2}{4\pi\epsilon_0 r} + \frac{B}{r^n}$$

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

Thus

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

or

$$\frac{Ae^2}{4\pi\epsilon_0 r_0^2} = \frac{Bn}{r_0^{n+1}}$$

$$\begin{aligned} \frac{r_0^{n+1}}{r_0^2} &= \frac{4\pi\epsilon_0 Bn}{Ae^2} \\ B &= \frac{Ae^2 r_0^{n-1}}{4\pi\epsilon_0 n} \end{aligned} \quad (3.14)$$

Substituting this value of B in equation (3.12) and putting $r = r_0$, we get the total equilibrium energy per kmol of the crystal.

Thus

$$[U]_{r=r_0} = U_0 = -\frac{N_A Ae^2}{4\pi\epsilon_0 r_0} + \frac{N_A Ae^2 r_0^{n-1}}{4\pi\epsilon_0 n r_0^n}$$

$$U_0 = -U_1 + U_2 \quad (3.15)$$

i.e., where U_1 and U_2 represent the net Coulomb attractive energy and repulsive potential.

Thus

$$U_0 = -\frac{Ae^2 N_A}{4\pi\epsilon_0} \left[\frac{1}{r_0} - \frac{r_0^{n-1}}{n r_0^n} \right]$$

$$U_0 = -\frac{Ae^2 N_A}{4\pi\epsilon_0 r_0} \left[1 - \frac{1}{n} \right]$$

$$U_0 = -\left[\frac{Ae^2 N_A}{4\pi\epsilon_0 r_0} \right] \left[\frac{n-1}{n} \right] \quad (3.16)$$

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 (3.16), we get $n = 9$.

IX. 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 calculations of Madelung constants in a linear chain of alternating signs as in Fig. 3.5.

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

$$U = - \frac{\alpha e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n}\right)$$

\therefore This is the magnitude of the energy needed to separate an ionic crystal into individual ions (not ... (5)

In an NaCl crystal, the equilibrium distance r_0 between ions is 2.81×10^{-10} m, $\alpha = 1.748$ and $1/4\pi\epsilon_0 = 9 \times 10^9 \text{ Nm}^2 \text{ C}^{-2}$.

The potential energy of an ion of either sign is

$$\begin{aligned} U &= - \frac{\alpha e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n}\right) \\ &= - \frac{(9 \times 10^9 \text{ Nm}^2 \text{ C}^{-2}) (1.748) (1.60 \times 10^{-19} \text{ C})^2}{2.81 \times 10^{-10} \text{ m}} \left(1 - \frac{1}{9}\right) \\ &= -1.27 \times 10^{-18} \text{ J} = -7.96 \text{ eV}. \end{aligned}$$

Because we may not count each ion more than once, only half this potential energy, or -3.98 eV , represents the contribution *per ion* to the cohesive energy of the crystal.

Some energy is needed to transfer an electron from a Na atom to a Cl atom to form a $\text{Na}^+ - \text{Cl}^-$ ion pair. This electron transfer energy is the difference between the $+5.14 \text{ eV}$ ionization energy of Na and the -3.61 eV electron affinity of Cl, or $+1.53 \text{ eV}$. Each atom thus contributes $+0.77 \text{ eV}$ to the cohesive energy.

554

\therefore the total cohesive energy per atom in the NaCl crystal is

$$E_{\text{cohesive}} = (-3.98 + 0.77) \text{ eV/atom} = -3.21 \text{ eV/atom}.$$

Properties : (i) Most ionic solids are hard, brittle and have high
(ii) They are soluble in polar liquids like water.

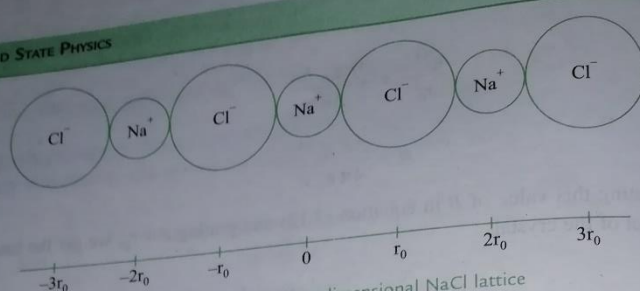


Fig. 3.5 A hypothetical one-dimensional NaCl lattice

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

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

$$\begin{aligned} & -\frac{2e^2}{4\pi\epsilon_0 r_0} + \frac{2e^2}{4\pi\epsilon_0 (2r_0)} - \frac{2e^2}{4\pi\epsilon_0 (3r_0)} + \dots \\ &= -\frac{e^2}{4\pi\epsilon_0 r_0} \left[2 \left(1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \dots \right) \right] \\ &= -\frac{e^2}{4\pi\epsilon_0 r_0} [2 \log(1+1)] \\ &= -\frac{e^2}{4\pi\epsilon_0 r_0} [2 \log 2] \end{aligned} \quad (3.17)$$

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. 3.6.

The total potential energy is obtained by adding all the attractive and repulsive energies between all the ions. The sodium ion Na^+ at the 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 $\frac{6e^2}{4\pi\epsilon_0 r_0}$.

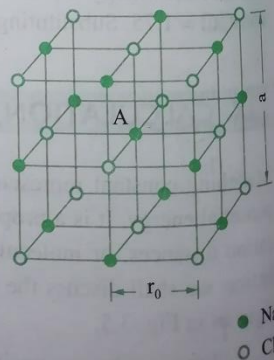


Fig. 3.6 NaCl structure

Similarly 12 Na^+ ions at $\sqrt{2} r_0$ and 6 Na^+ ions at $2r_0$ 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

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

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

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

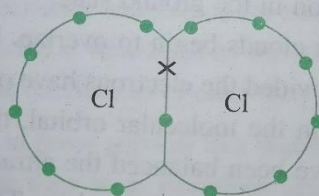
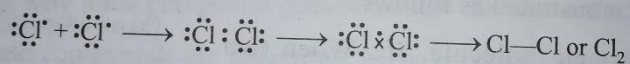
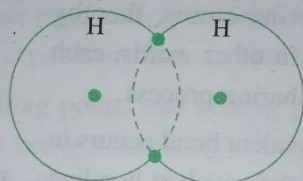
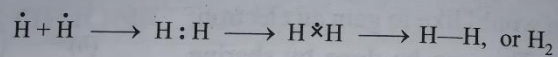
$$U = -\frac{N_A e^2}{4\pi\epsilon_0 r_0} \left[6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \dots \right]$$

$$U = -\frac{N_A e^2 A}{4\pi\epsilon_0 r_0} \quad (3.18)$$

The constant A is called Madelung constant and $A = 1.75$ for NaCl structure. Note that in equation (3.18) $(Z_+)(Z_-)$ must be 1 for monovalent alkali halides such as NaCl, KCl, etc. For divalent alkali earth metal halides such as CaF₂, $(Z_+)(Z_-)$ is 4.

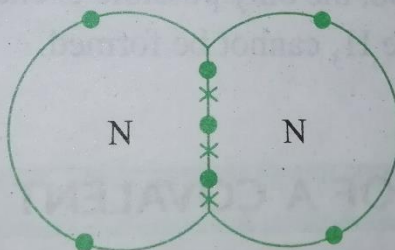
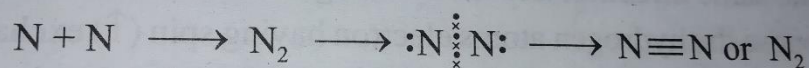


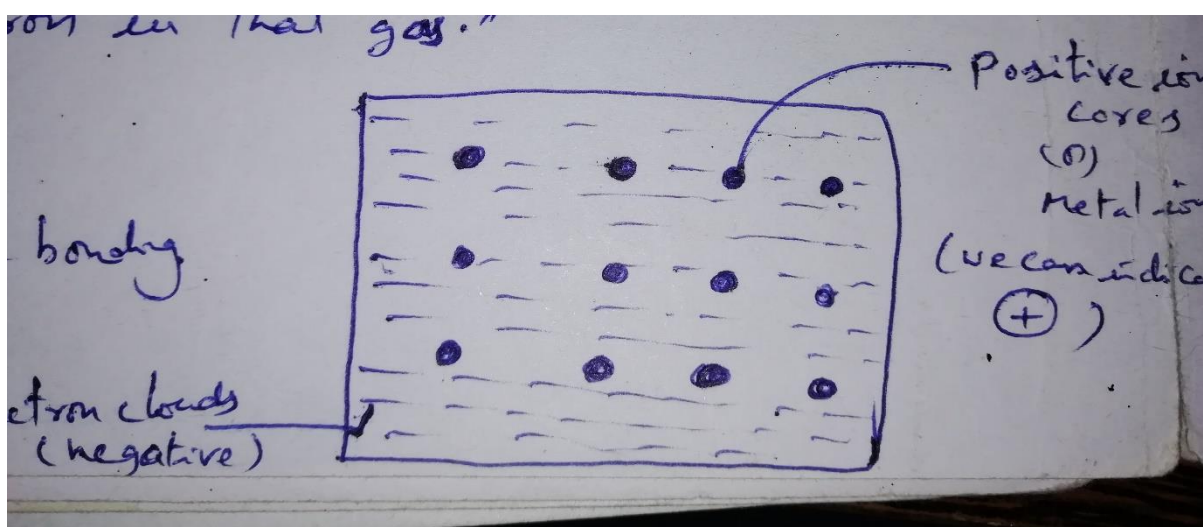
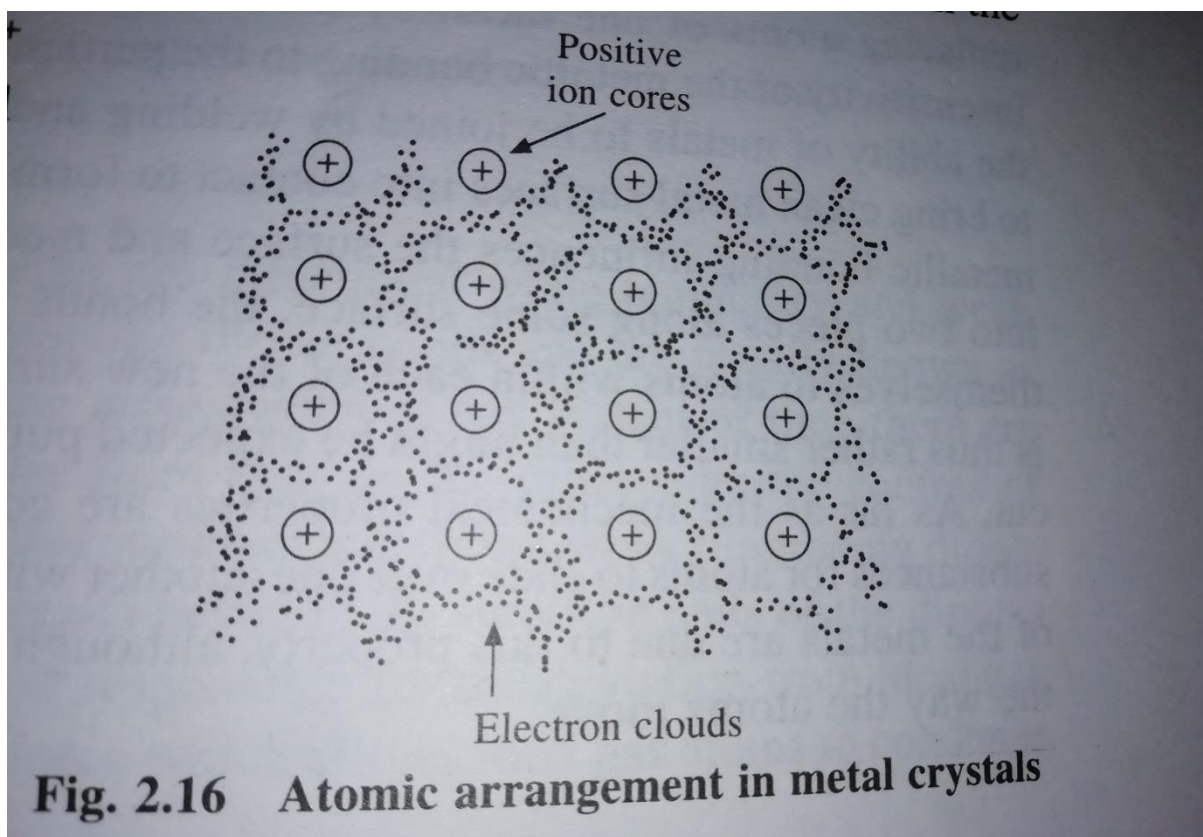
Say the dot electron has come from the atom on to the left and x electron has come from the atom on to the right. The actual bond is generally represented as H—H. Thus

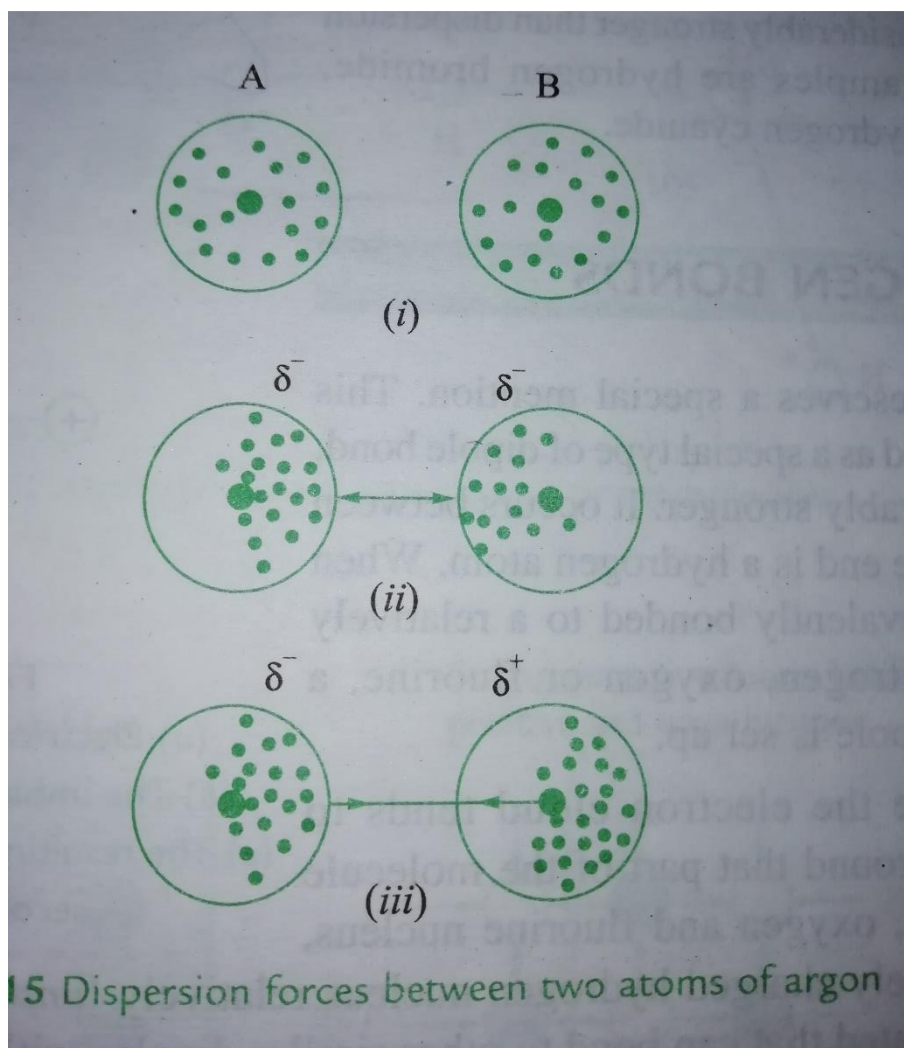


the element chlorine each atom 1

Other examples are:







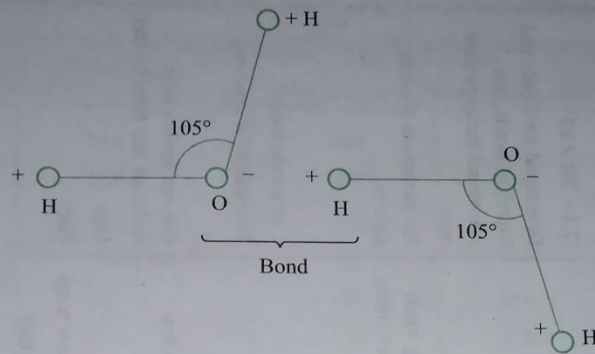


Fig 3.17 Hydrogen bond between two water molecules

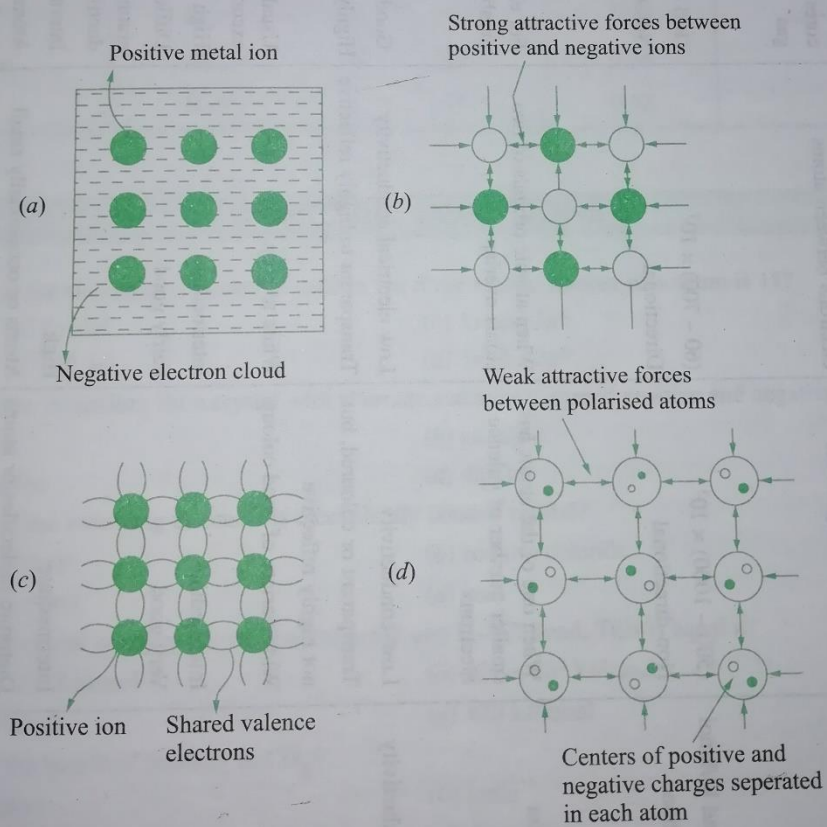


Fig. 3.18 The four types of chemical bonding in solids: (a) Metallic bonding, (b) Ionic bonding, (c) Covalent bonding, (d) van der Waals bonding