LECTURE 2
INTERATOMIC FORCES
(Solid State physics S.O.Pillai)

http://202.141.40.218/wiki/index.php/
Unit-3:_Atomic_Cohesion_and_Crystal_Binding#FORCE_BETWEEN_ATOMS

Types of Bonding Mechanisms

It is conventional to classify the bonds between atoms into different types as

- Ionic,
- Covalent,
- Metallic,

Primary (interatomic)

- Van der Waals,
- Hydrogen.

Secondary (intermolecular)

1 - Ionic Bonding

- Ionic bonding is the electrostatic force of attraction between positively and negatively charged ions (between non-metals and metals).

- These ions have been produced as a result of a transfer of electrons between two atoms with a large difference in electro negativities.

Bond Energy of NaCl molecule

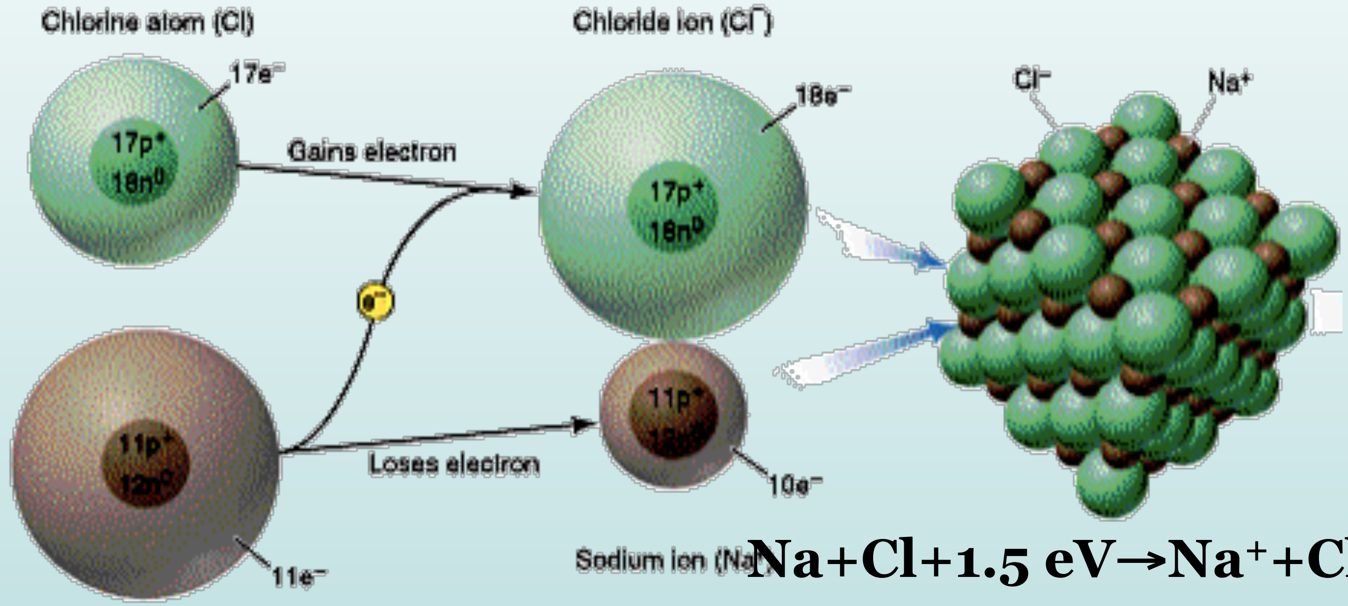
- Notice that when sodium loses its one valence electron it gets smaller in size, while chlorine grows larger when it gains an additional valance electron. After the reaction takes place, the charged Na+ and Cl- ions are held together by electrostatic forces, thus forming an ionic bond.

Electron affinity

$Cl + e^- \rightarrow Cl^- + 3.6eV$

$Na + 5.1eV \rightarrow Na^+ + e^-$

Ionization potential



$Na + Cl + 1.5\ eV \rightarrow Na^+ + Cl^-$

What happens when the electrostatic attraction between Na^+ and Cl^- ions brings them together to the equilibrium spacing r_o=0.24nm?

At the equilibrium potential energy will be the min.

$$V = -\frac{e^2}{4\pi\varepsilon_o r_o} = -6eV$$

and the energy released in the formation of NaCl molecule is called the bond energy of the molecule.

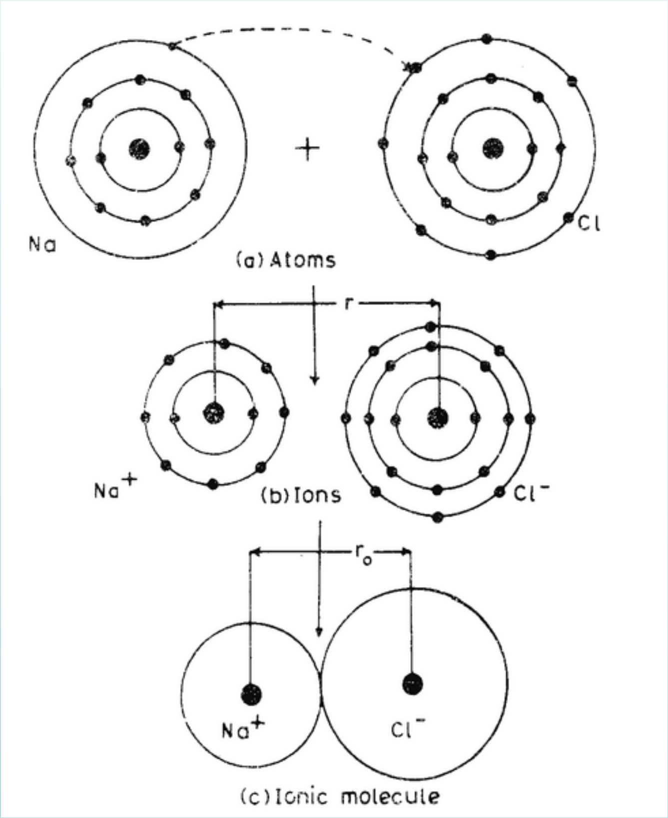
$1eV = 1.6 \times 10^{-19}$ J

Thus 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)=-4.5eV.

$$\mathbf{Na+Cl} \rightarrow \mathbf{Na^{+} + Cl^{-}} \rightarrow \mathbf{NaCl + 4.5eV}$$

$\underset{\infty}{\longleftrightarrow}$ $\underset{0.24\text{nm}}{\longleftrightarrow}$

Energy released

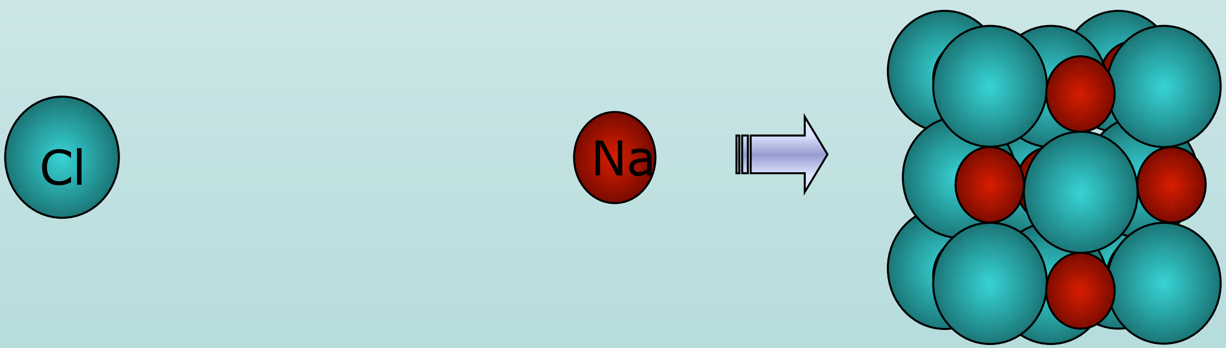


Cohesive or Dissociation Energy released

Calculation of Lattice Energy of Ionic Crystal

BOND ENERGY → *for particular molecule (making bond), Energy liberated by the formation of the crystal from individual neutral atom.*

LATTICE ENERGY → *for particular crystal. (chain of molecules with bond)*



NaCl

Bond Energy

Lattice energy

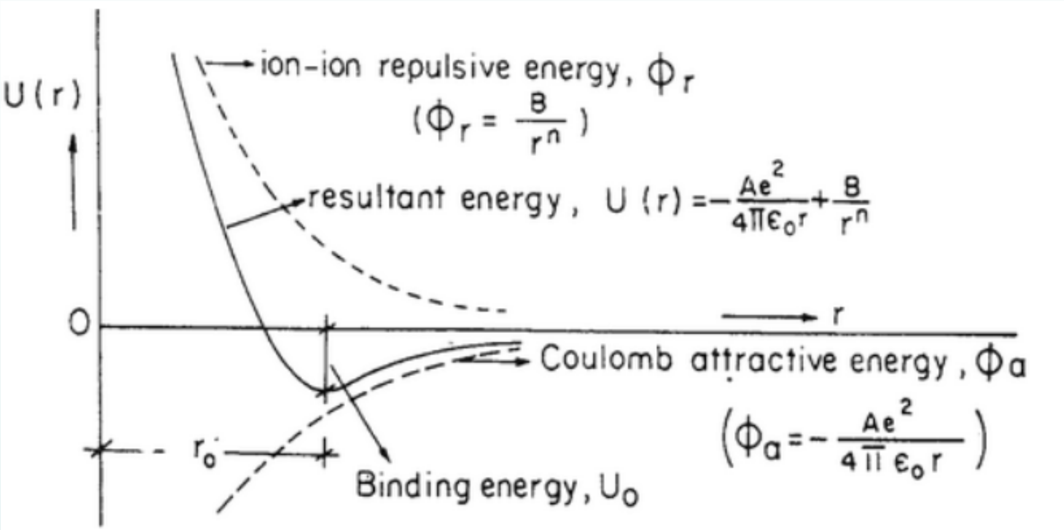
Calculation of Lattice Energy of Ionic Crystal

For two ions Z_1e and Z_2e separated by a distance r, the attractive energy is

$$-\frac{Z_1 Z_2}{4\pi\varepsilon_o}\frac{e^2}{r}$$

For the whole crystal , the Coulomb potential energy may be written as

$$-\frac{A Z_1 Z_2}{4\pi\varepsilon_o}\frac{e^2}{r}$$



The minus sign shows that the net Coulomb energy is attractive. The constant 'A' is MADELUNG constt.

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

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

Repulsive energy of this ion due to presence of all other ions in the crystal.

n → repulsive exponent.

Calculation of Lattice Energy of Ionic Crystal

For univalent alkali halides

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

The total energy per mol of the crystal is

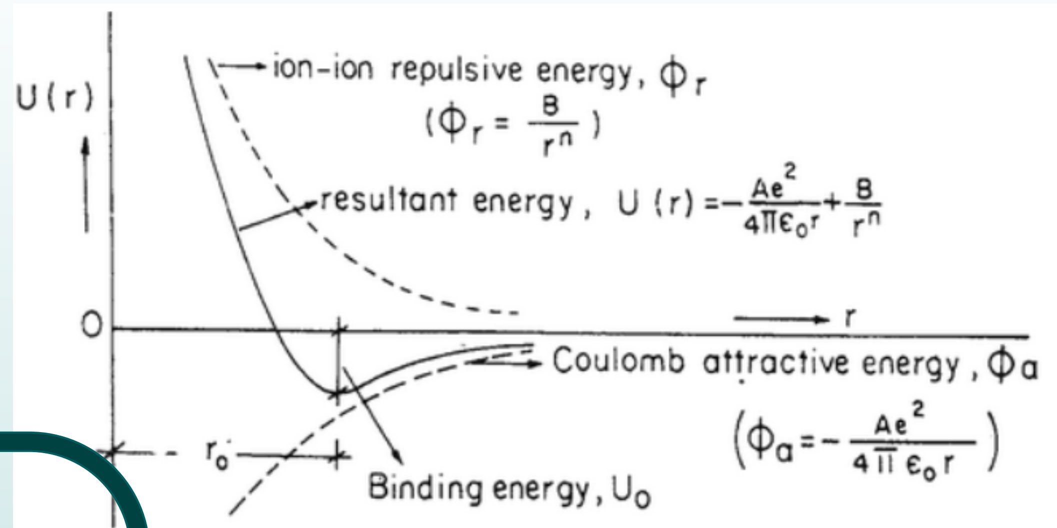
$$U(r) = N_A\left[\frac{B}{r^n} - \frac{A}{4\pi\varepsilon_o}\frac{e^2}{r}\right]$$

The potential energy is the min. at the equilibrium spacing r_o . Thus,

$$\left[\frac{dU(r)}{dr}\right]_{r=r_o} = N_A\left[\frac{A}{4\pi\varepsilon_o}\frac{e^2}{r_o^2} - \frac{Bn}{r_o^{n+1}}\right] = 0$$

$$\frac{A}{4\pi\varepsilon_o}\frac{e^2}{r_o^2} = \frac{Bn}{r_o^{n+1}}$$

$$B = \frac{A}{4\pi\varepsilon_o}\frac{e^2 r_o^{n-1}}{n}$$



$N_A = 6.022140857 \times 10^{23}$

$$\left[U(r)\right]_{r=r_o} = U_o = N_A\left[-\frac{A}{4\pi\varepsilon_o}\frac{e^2}{r_o} + \frac{A}{4\pi\varepsilon_o}\frac{e^2}{nr_o}\right]$$

$$U_o = -U_1 + U_2$$

Where U_1 and U_2 represent the net coulomb attractive energy and repulsive energy.

Thus,

$$U_o = -\left[\frac{Ae^2 N_A}{4\pi\varepsilon_o r_o}\right]\left[\frac{n-1}{n}\right]$$

This equilibrium energy U_o is **lattice energy**

$$U_o = -\left[\frac{Ae^2 N_A}{4\pi\varepsilon_o r_o}\right]\left[\frac{n-1}{n}\right]$$

This equilibrium energy U_o 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.

***Example**: In a NaCl crystal , the equilibrium distance r_o between ions is 0.281 nm. Find the cohesive energy in NaCl. Given A=1.748 and n=9.*

Solution:

$$U_o = -\left[\frac{Ae^2 N_A}{4\pi\varepsilon_o r_o}\right]\left[\frac{n-1}{n}\right] = -7.96 \text{ eV}$$

Energy spent in ionization (atom→ion) =5.13eV-3.6 0eV= 1.53 eV

Cohesive energy (in crystal) per NaCl molecule=(-7.96+1.53)=-6.42 eV

And, Cohesive energy (in crystal)per atom=-6.42/2=-3.21 eV

Experimental value=-3.28 eV

$N_A = 6.022140857 \times 10^{23}$

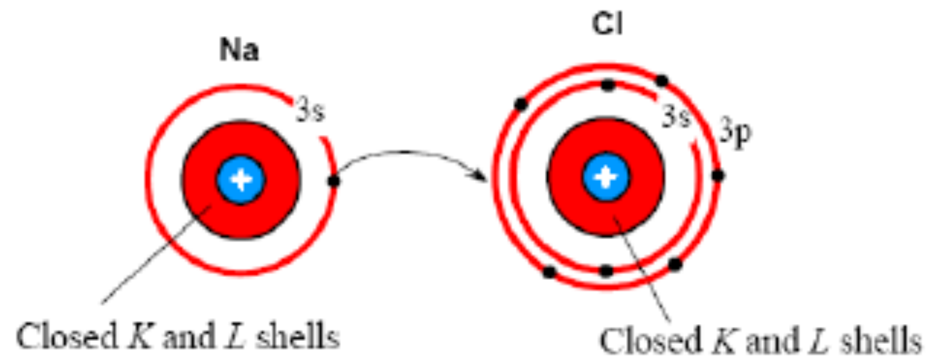
Ionic bonding – example of NaCl

The ionic bond results from electrostatic interaction of oppositely charged ions. Let us take NaCl as an example. In the crystalline state, each Na atom loses its single valence electron to a neighboring Cl atom (a), producing Na^+ and Cl^- ions which have filled electronic shells (b). As a result, an ionic crystal is formed containing positive and negative ions coupled by a strong electrostatic interaction (c).

$Na + 5.1\ eV$ (ionization energy) $\rightarrow Na^+ + e^-$

$e^- + Cl \rightarrow Cl^- + 3.6\ eV$ (electron affinity)

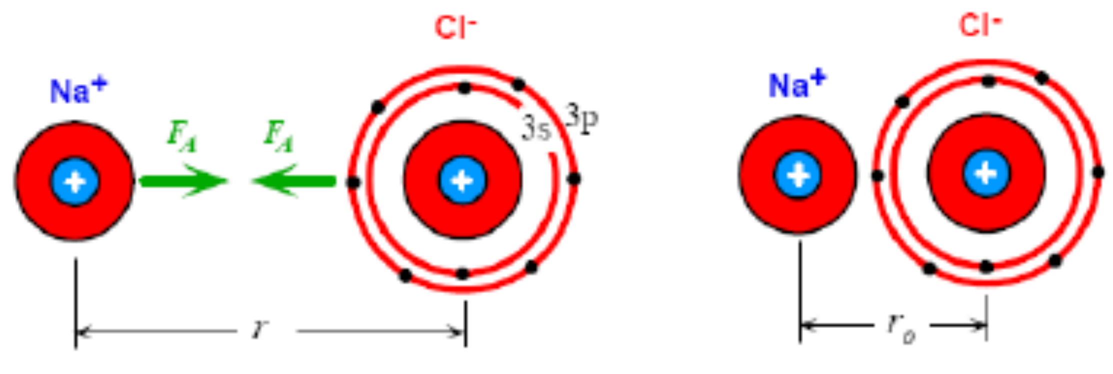
$Na^+ + Cl^- \rightarrow NaCl + 7.9\ eV$ (electrostatic energy)



(a)

The cohesive energy with respect to neutral atoms can be calculated as 7.9 eV - 5.1 eV + 3.6 eV, i.e.

$Na + Cl \rightarrow NaCl + 6.4\ eV$ (cohesive energy).



(b) (c)