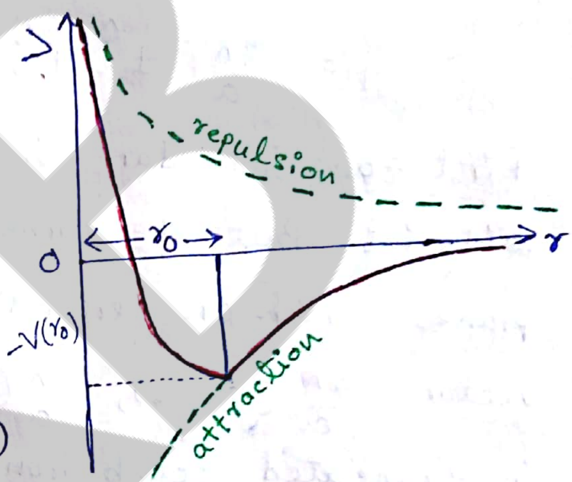
Crystal Bonding

The ability to hold the atoms / ions together is called bonding. Atoms vibrate in lattice & nucleus due to heavy mass is almost at rest. So electrostatic interaction happen between electron cloud & distribution of electron leads to 5 types of bonding due to ⓐ "attractive force" of negatively charged electron cloud of one atom with positive nuclear charge of other atom ⓑ "repulsive force" of overlapping negatively charged electron clouds & positively charged nucleus of two atoms.

"spring effect" → attraction → repulsion.



$F = -\dfrac{dV}{dr}$ attractive force = negative potential.

repulsive force = positive potential.

cohesive / binding energy $V(r_0)$ (negative)

dissociation energy $-V(r_0)$ (positive)

Cohesive energy of a solid is the energy that will be given out in forming a crystal by bringing neutral atoms from ∞ to equilibrium separation r_0.

Suppose $V_{attractive} \propto r^{-m}$ & $V_{repulsive} \propto r^{-n}$

$\therefore$ Cohesive energy $V = V_{attractive} + V_{repulsive} = -Ar^{-m} + Br^{-n}$

& force $F = -\dfrac{dV}{dr} = mAr^{-(m+1)} - nBr^{-(n+1)}$

at $r = r_0$, $F = 0 = mAr_0^{-(m+1)} - nBr_0^{-(n+1)}$.

or $r_0^{m-n} = \dfrac{A}{B}\dfrac{m}{n}$.

Then equilibrium potential energy $V(r_0) = -Ar_0^{-m} + Br_0^{-n}$

$= -Ar_0^{-m}\left(1 - \dfrac{B}{A}r_0^{m-n}\right) = -Ar_0^{-m}\left(1 - \dfrac{m}{n}\right)$.

For V to be minimum, it must be concave upwards curvature,

$$\left.\frac{d^2V}{dr^2}\right|_{r=r_0} > 0 \quad \text{or} \quad \left[-m(m+1)A r^{-(m+2)} + n(n+1)B r^{-(n+2)}\right]_{r=r_0} > 0$$

$$\text{or} \quad -m(m+1) + n(n+1)\frac{B}{A} r_0^{m-n} > 0$$

$$\text{or} \quad -\cancel{m}(m+\cancel{1}) + \cancel{n}(n+\cancel{1}) \frac{\cancel{m}}{\cancel{n}} \cancel{\frac{B}{A}} \cancel{\frac{A}{B}} > 0$$

or $n - m > 0$ or $n > m$. Thus to form a chemical bond, we always need repulsive force be of shorter range than attractive force.

<u>Types of bonding</u> 5 types of bonding exist

(a) Ionic bond (transfer of valence electron) : NaCl, LiF.

(b) Covalent bond (sharing of valence electrons) : Diamond, SiC.

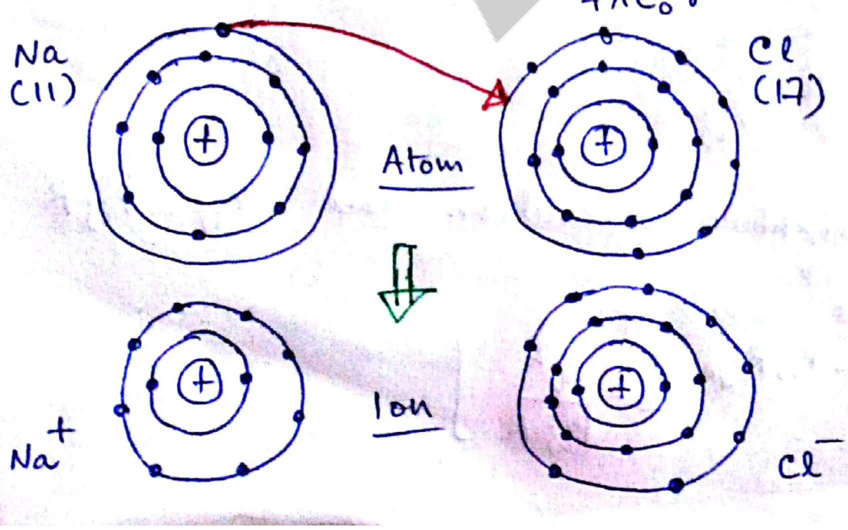
(c) Metallic bond (free nature of valence electron) : Cu, Ag, Fe

(d) Hydrogen bond ($V \propto -r^{-2}$) : Ice

(e) van der Waal's bonding (dipole-dipole interaction)

Ionic / Electrovalent Bonding

Transfer of electrons from an electropositive element to electronegative element, to create +− ion. Electronegative element of large electron affinity accomodate extra added electron to complete outermost valence orbit to stabilize. Oppositely charged ions attract $V_{attraction} = -\frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 r}$



$Na + \text{ionisation energy } (5.1\text{ eV}) \rightarrow Na^+ + e^-$

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

$\therefore Na + Cl + 1.5\text{ eV} \rightarrow Na^+ + Cl^-$

$Z_1 = Z_2 = 1.$

So potential energy $V = -\frac{e^2}{4\pi\epsilon_0 r_0} = \frac{-(1.6\times10^{-19})^2}{4\pi\times8.85\times10^{-12}\times2.4\times10^{-10}}$
$(r_0 = 2.4\ \text{Å})$

$$= -\frac{9.6\times10^{-19}}{1.6\times10^{-19}}\ eV = -6\ eV.$$

So net energy released $= 5.1 - 3.6 - 6 = -4.5\ eV$.

Cohesive energy   Binding energy calculated by Born & Madelung in 1910 extended by Mayer.

assumptions : (a) Ionic crystals are formed by positive & negative ions with spherical charge distribution. (b) Force of attraction depends on inter-ionic distance & isotropic (orientation independent), (c) Electrostatic interaction (Madelung energy $V_a = -\frac{\alpha q^2}{4\pi\epsilon_0 r}$, α = Madelung constant) contributes to cohesive energy

According to Born-Madelung theory interaction energy U_i on ion i due to all j other ions, $U_i = \sum_{j\neq i} U_{ij}$

U_i consists of two parts :

1. Short range central field repulsive potential βr_{ij}^{-n} between + & − ions which was modified by $\lambda e^{-r_{ij}/\rho}$, λ = strength, ρ = range of interaction (screened Coulomb)

2. Attractive or repulsive long ranged coulomb force with energy $\pm\frac{q^2}{r_{ij}}$

$$\therefore\ U_i = \sum_{j\neq i}\left[\lambda e^{-r_{ij}/\rho} \pm \frac{q^2}{r_{ij}}\right]$$

If R is the nearest neighbour separation then $r_{ij} = P_{ij}R$ where P_{ij} is a dimensionless quantity.

Then $$U_i = \sum_{j\neq i}\left[\lambda e^{-P_{ij}R/\rho} \pm \frac{q^2}{P_{ij}R}\right]$$

$$= Z\lambda e^{-R/\rho} \pm \sum_{j\neq i} \frac{q^2}{p_{ij}R} = Z\lambda e^{-R/\rho} - \frac{\alpha q^2}{R}$$

where Z is number of nearest neighbour of i^{th} ion & $\alpha = \pm \sum \frac{1}{p_{ij}}$ is called Madelung constant

If the crystal contain $2N$ ions or N molecules, then

$$U_{total} = NU_i = N\left[Z\lambda e^{-R/\rho} - \frac{\alpha q^2}{R}\right]$$

at equilibrium distance $R = R_0$, $\frac{dU_{total}}{dR} = 0$

$$\text{or } -\frac{Z\lambda}{\rho} e^{-R_0/\rho} + \frac{\alpha q^2}{R_0^2} = 0 \quad \text{or} \quad \boxed{e^{-R_0/\rho} = \frac{\rho\alpha q^2}{Z\lambda R_0^2}}$$

$$\therefore U_{total} = N\left[\cancel{Z\lambda}\frac{\rho\alpha q^2}{\cancel{Z\lambda}R_0^2} - \frac{\alpha q^2}{R_0}\right] = \underbrace{-\frac{N\alpha q^2}{R_0}}_{\text{Madelung energy}}\underbrace{\left(1 - \frac{\rho}{R_0}\right)}_{\text{contribution from short range repulsion}}$$

$$U_i = -\frac{\alpha q^2}{R_0}\left(1 - \frac{\rho}{R_0}\right),$$

or in SI units, $\boxed{U_i = -\frac{\alpha q^2}{4\pi\epsilon_0 R_0}\left(1 - \frac{\rho}{R_0}\right)}$

as $\frac{\rho}{R_0} \to 0$ repulsive interaction is very short range.

In $\alpha = \sum \pm \frac{1}{p_{ij}}$, $+$ is used for +ive ion & $-$ for $-$ive ion if i^{th} ion is $-$ive. & we consider repulsive interaction effective for nearest neighbours only.

Madelung constant for a 1D lattice

R

$+ \; - \; + \; - \; + \; (-) \; + \; - \; + \; - \; + \; -$

reference

$$\alpha = \sum_{j\neq i} \pm \frac{1}{p_{ij}}, \quad \frac{\alpha}{R} = \sum_{j\neq i} \pm \frac{1}{p_{ij}R} = \pm \sum_{j\neq i} \frac{1}{r_{ij}}$$

$$\text{or } \frac{\alpha}{R} = 2\left[\frac{1}{R} - \frac{1}{2R} + \frac{1}{3R} - \frac{1}{4R} + \cdots\right]$$

$\therefore \alpha = 2\left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \cdots\right]$

↑ due to both side of reference ion

but $\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \cdots$

if $x = 1$, $\ln 2 = 1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \cdots$

$\therefore \alpha = 2\ln 2 = 1.38$

Madelung constant for NaCl crystal

Nearest neighbour to −ive (reference) ion = 6 +ive ions with $p_{ij} = p = 1$. 12 −ive ions at $p = \sqrt{2}$. 8 +ive ions at $p = \sqrt{3}$. 6 −ive ions at $p = \sqrt{4}$ & so on

$$\alpha = \frac{6}{1} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \cdots = 1.748$$

Bigger α, more cohesive energy, greater stability of structure

Cohesive energy for repulsive core potential $\propto r^{-n}$

$$V_i = V_{attractive} + V_{repulsive} = -\frac{\alpha q^2}{4\pi\epsilon_0 r} + \frac{B}{r^n}$$

at $r = r_0$, V is minimum, $\left.\frac{dV}{dr}\right|_{r=r_0} = 0 = \frac{\alpha q^2}{4\pi\epsilon_0 r_0^2} - \frac{nB}{r_0^{n+1}}$

$$\therefore B = \frac{\alpha q^2 r_0^{n-1}}{4\pi\epsilon_0 n}$$

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

& for 2N molecules, $V_{tot} = -\frac{N\alpha q^2}{4\pi\epsilon_0 r_0}\left(1 - \frac{1}{n}\right)$

for NaCl, $\alpha = 2\ln 2$, $\boxed{V_{tot} = -\frac{2Nq^2\ln 2}{4\pi\epsilon_0 r_0}\left(1 - \frac{1}{n}\right)}$

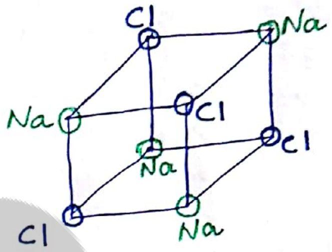
Bulk modulus of Ionic crystals

Volume strain $= \frac{dV}{V}$, change in pressure dp, Bulk moduleus

$$B = -\left.\frac{dp}{dV/V}\right|_{R=R_0}. \quad \text{Using } 1^{st} \text{ law of thermodynamics, } dQ = dU + pdV$$

$$\text{or } \frac{dU}{dV} = -p \quad (dQ = 0) \quad \text{or} \quad \frac{d^2U}{dV^2} = -\frac{dp}{dV}.$$

$$\therefore \quad B = V \left.\frac{d^2U}{dV^2}\right|_{R=R_0}$$



Volume occupied by $\frac{1}{2}$ molecule $\rightarrow R_0^3$

volume occupied by 1 molecule $\rightarrow 2R_0^3$ (equilibrium separation)

volume occupied by N molecule $\rightarrow 2NR_0^3$.
(2N ions)

volume of unit cell $\rightarrow (2R_0)^3 = 8R_0^3$ because $a = 2R_0$

$$V = 2NR^3, \quad \frac{dV}{dR} = 6NR^2 \quad \text{and} \quad \left.\frac{dU}{dR}\right|_{R=R_0} = 0$$

$$\therefore \frac{d^2U}{dV^2} = \frac{d}{dV}\left(\frac{dU}{dV}\right) = \frac{d}{dV}\left(\frac{dU}{dR}\cdot\frac{dR}{dV}\right) = \frac{d}{dV}\left(\frac{dU}{dR}\right)\cdot\frac{dR}{dV} + \frac{dU}{dR}\cdot\frac{d^2R}{dV^2}$$

$$= \frac{d}{dR}\left(\frac{dU}{dR}\right)\frac{dR}{dV}\cdot\frac{dR}{dV} + \frac{dU}{dR}\cdot\frac{d^2R}{dV^2} = \frac{d^2U}{dR^2}\cdot\left(\frac{dR}{dV}\right)^2 + \cancel{\frac{dU}{dR}}^{\,0}\cdot\frac{d^2R}{dV^2}$$

$R = R_0$

$$\therefore \left.\frac{d^2U}{dV^2}\right|_{R=R_0} = \frac{d^2U}{dR^2}\cdot\left(\frac{dR}{dV}\right)^2 = \frac{1}{(6NR_0^2)^2}\left.\frac{d^2U}{dR^2}\right|_{R=R_0}$$

$$\therefore B = V\left.\frac{d^2U}{dV^2}\right|_{R=R_0} = 2NR_0^3\,\frac{1}{36N^2R_0^4}\left.\frac{d^2U}{dR^2}\right|_{R=R_0} = \frac{1}{18NR_0}\left.\frac{d^2U}{dR^2}\right|_{R=R_0}$$

We learned that $U_{total} = N\left[Z\lambda\, e^{-R/\rho} - \frac{\alpha q^2}{R}\right]$

$$\therefore \frac{dU_{total}}{dR} = -\frac{NZ\lambda}{\rho}\, e^{-R/\rho} + \frac{N\alpha q^2}{R^2}$$

$$\frac{d^2U_{total}}{dR^2} = \frac{NZ\lambda}{\rho^2}\, e^{-R/\rho} - \frac{2N\alpha q^3}{R^3}, \quad \text{also } e^{-R_0/\rho} = \frac{\rho\alpha q^2}{Z\lambda R_0^2}$$

$$\therefore B = \frac{1}{18NR_0}\left[\frac{NZ\lambda}{\rho^2}\, e^{-R_0/\rho} - \frac{2N\alpha q^3}{R_0^3}\right] = \frac{1}{18\cancel{N}R_0}\left[\frac{\cancel{NZ\lambda}}{\cancel{\rho^2}}\,\frac{\cancel{\rho}\alpha q^2}{\cancel{Z\lambda}R_0^2} - \frac{2\cancel{N}\alpha q^3}{R_0^3}\right]$$

$$\boxed{B = \frac{\alpha q^2}{18R_0^4}\left(\frac{R_0}{\rho} - 2\right)}$$

From B & R_0, range of repulsive interaction can be calculated.