UNIT - II

Chemical Bonding

Lattice Energy

The stability of an ionic crystal is measured in terms of lattice energy.

Defintion :

Lattice energy of an ionic crystal is defined as the energy released when one mole of gaseous cations and one mole of gaseous anions, separated from each other by an infinite distance are brought to their equilibrium distances to form one mole of the ionic crystal.

Explanation :

The formation of a mole of an ionic solid $A^+B^-_{(s)}$ from its constituent gaseous ions $A^+_{(g)}$ and $B^-_{(g)}$ may be represented as follows

$$\underset{\text{one mole}}{A^+_{(g)}} + \underset{\text{one mole}}{B^-_{(g)}} \longrightarrow \underset{\text{one mole}}{A^+B^-_{(s)}} + \text{Energy released}$$

The energy released is called lattic energy.

Another definition :

Lattic energy is the energy required to move the ions of one mole of the ionic crystal which are at an equilibrium distance from each other, to an infinite distance.

Explanation :

The lattic energy of an ionic cystal is the energy required to convert one mole of an ionic crystal $A^+B^-_{(s)}$ into gaseous A^+ and B^- i,e.,

$$\underset{\text{One mole}}{A^+B^-_{(s)}} + \text{Energy absorbed} \longrightarrow A^+_{(g)} + B^-_{(g)}$$

The energy absorbed is numerically equal to the lattice energy.

Lattice energy is represented by - U. The negative sign indicates that the formation of an ionic solid from its gaseous cations and anions is an ***exothermic process***. ie., in the formation of the ionic solid, there is a release of energy and hence the energy of the system is lowered

This is because of the decrease in energy, the ionic solid is more stable than the individual ions of which the ionic solid is made of. Greater the value of lattice energy of an ionic solid, greater will be the stability of the ionic solid.

Example :

The melting points of NaCl, KCl and CsCl decrease in the same order. This is because their lattice energies decrease in the same order (184, 168 and 151 k.cals/mole respecively).

Applications of lattice energy :

1. With the help of lattice energy we can estimate electron affinities, proton affinities and heats of formation.
2. It is applied in the discussion of the special properties of fluorine in relation to other halogens.
3. It is applied to account for the stabilities of metal chlorides, hydrides, poly halides, peroxides and super oxides.
4. It is applied in the derivation of crystal field stablisation energies.
5. It is applied to account for the occurrence of high oxidation states of metals in their fluorides and low oxidation states in their iodides.

Born - Haber Cycle

The direct determination of the lattice energy of an ionic crystal has been carried out for only a few compounds. In many cases it is not possible to measure the lattice energy directly. Born and Haber devised a cyclic process to find the lattice energy.

Born - Haber cycle can be explained taking the formation of sodium chloride from elementary solid sodium and elementary gaseous chlorine. Let us make the following assumptions.

1. Sodium metal is evaporated to sodium atom, $Na_{(g)}$. The energy of sublimation is +S.
2. The diatomic chlorine gas is dissociated to chlorine atom $Cl_{(g)}$. The energy of dissociation for Cl_2 is + D.
3. The sodium atoms are ionised to form Na^+ The ionisation energy of sodium atom is +I.
4. The electrons obtained from sodium atoms are transferred to chlorine atoms to form negative chloride ions Cl^-. The electron affinity of chlorine atom is - E.

5. The latice energy of sodium chloride is $-U_0$.
6. The heat of formation 7of the crystals from its element is $-Q$.

All these changes can be represented by the Born - Heber cycle as follows.

$$\begin{tikzcd}
\mathrm{NaCl}_{(s)} & & \mathrm{Na}^{+}_{(g)} \arrow[ll, "-U_0"'] & + & \mathrm{Cl}^{-}_{(g)} \\
\mathrm{Na}_{(s)} + \frac{1}{2}\mathrm{Cl}_{2(g)} \arrow[u, "-Q"'] \arrow[rr, "+S+\frac{1}{2}D"] & & \mathrm{Na}_{(g)} \arrow[u, "+I"'] & + & \mathrm{Cl}_{(g)} \arrow[u, "-E"']
\end{tikzcd}$$

7. The total energy of formation of the crystal from is elementary components is given by the equation.

$$-Q = S + \tfrac{1}{2}D + I - E - U_0$$

So, $$U_0 = Q + S + \tfrac{1}{2}D + I - E$$

The values of Q are accurately known for many substances. Knowing the other thermochemical values, it is possible to calculate the lattice energy U_0.

Pauling's scale of electronegativity

On the basis of bond energies, Pauling devised a scale for electronegativity. Bond energy of a compound A – B for pure covalency is geometric mean of the bond energies of A – A and B – B.

That is, $E_{A-B} = [E_{A-A} \times E_{B-B}]^{1/2}$

But actual experimental value is found to be greater than this expected value. Let the difference between the two be D.

i.e., $D = E_{A-B} - [E_{A-A} \times E_{B-B}]^{1/2}$

D is a measure of the polarity of the bond A – B. It depends on the difference in the electronegative character of A and B.

Let X_A and X_B represent the electronegativity of A and B. According to Pauling, the relationship between Δ and the electronegativity difference is

$$X_A - X_B = 0.088\sqrt{\Delta}$$

The factor 0.088 converts Δ from kJ $mole^{-1}$ to eV (electron volts) units.

Pauling gave an arbitrary value of electronegativity to hydrogen as $X_H = 2.1$. This is used as reference standard for calculating the electronegativities of other elements.

Mulliken scale of electronegativity

According to Mulliken, the electronegativity is related to its ionisation potential and its electron affinity. Ionisation potential measures an element's tendency to lose its valence electron while electron affinity measures its tendency to attract an extra electron. Thus elements having high values of ionisation potential and electron affinity will also have a high value of electronegativity, Thus

$$\chi = \frac{IP + EA}{2}$$

Where χ = Electronegativity ; IP = ionisation potential in eV and EA = Electron affinity in eV.

Mulliken's value of electronegativities are about 2.8 times larger than Pauling's value. Hence to make both values approximately equal, Mulliken's value is divided by 2.8. Thus,

$$\chi = \frac{IP + EA}{2 \times 2.8} = \frac{IP + EA}{5.6}$$

The constant $\frac{1}{5.6}$ is called ***scale adjustment factor***. This factor is used when IP and EA are expressed in eV. If they are expressed in k.cals, the following scale is used.

$$\chi = \frac{IP + EA}{2 \times 62.5}$$

Example :

Calculate the electronegativity value of chlorine on Mulliken's scale Given that $(IP)_{Cl}$ = 13 eV / atom and $(EA)_{Cl}$ = 4eV / atom.

Solution :

$$\chi_{Cl} = \frac{(IP)_{Cl} + (EA)_{Cl}}{5.6} = \frac{13 + 4}{5.6} = \frac{17}{5.6} = 3.03$$

$$\therefore \chi_{Cl} = 3.03$$

Disadvantages of Mulliken's scale :

1. Electron affinity values are accurately known for only a few elements.
2. The values of IP and EA refer to the transfer of electrons between the atomic orbitals. We do not know whether these can be rightly applied to the electrons is a bond.
3. The values of IP and EA vary with the nature of shell in which the concerned electrons are situated. So values on Mulliken scale will also vary accordingly.

Polarising Power

The ability of a cation to polarize a nearby anion is called polarising power or polarising ability.

Polarizability

The tendency of an anion to get polarised or distorted by a cation is called its polarizability.

Thus in ion polarisation, the role of cation is to distort the electronic cloud of the anion because of the its polorising power. The role of anion is to get distorted by the cation because of its nature of polarizability.

Effects of ion polarization :

i. Due to ion polarisation, some covalent character is introduced in an otherwise ionic bond.

ii. Ion polarisation accounts for variation of melting points in ionic crystals.

Partial ionic character from electro negativity :

We have seen that a covalent bond is set up by sharing of electrons between atoms. If the electron pair is shared equaly the bond is non - polar. If the electron pair is shared unequally the bond is polar. For example, the covalent bonds in H_2 and Cl_2 are called pon - polar. In the case of hydrogen fluoride the bond is polar as the electron pair is unequaly shared. Fluorine has a greater attraction for electrons (higher electronegativity than hydrogen). So the shared pair of electrons is nearer to fluorine atom than hydrogen. This makes the covalent bond polar in nature. This is called the partial ionic character.

Calculation of percent ionic nature from electronegativity :

Electronegativity can b used to calculate the percentage of ionic character in a polar covalent bond. If two atoms A and B are linked by a polar covalent bond A – B, the amount of ionic character in this bonc depends on the difference of electronegativity values of A and B. If the differnce of electronegativity value is $X_A - X_B$, the greater the value o $X_A - X_B$ greater is the percentage of ionic character in A – ←B bond Here the electronegativity of ionic atom A (X_A) is assumed to be greate than that of B(X_B). Pauling has estimated the percentage of ionic character in various polar covalent bonds from $X_A - X_B$ values and has derived the following conclusions.

Value of $X_A - X_B$	Percentage ionic Character	Nature of A – B bond
1.7	50%	50% covalent 50% ionic
< 1.7	< 50% Written as A – B	Predominantly covalent
> 1.7	> 50% Written as A – B.	Predominantly ionic

Transition from ionic to covalent character and vice - versa

From the above discussion we come to know that a compound neither 100% covalent nor 100% ionic. When there is a difference electronegativities between two covalently bound atoms, the covale bond present in it develops a partial ionic character. In an io compound, there may be ion polarisation causing a partial covale character. Thus there is a transition between ionic and covale characters.

Fajan's Rules :

The various factors that affect the magnitude of the polarising powe of a a cation and the polarizability of the anion are suggested by Fajans These are called Fajan's rules.

1. ***Size of cation :***

   If the cation is small, it will have greater polarising power on anion

2. ***Size of anion :***

   If the anion is large, in will have greater tendency to get polarised by cations. When an anion is small, the valency electrons are nearer t the nucleus and hence the tendency to get polarised by the cation wi be less. But when an anion is large, it is polarised easily.

3. ***Charge on ions :***

   As the ionic charge on cation increases the polarising capaci also increases.

Explanation with examples :

i. Let us consider Ag^+ and K^+. Whose ionic radii are 1.13Å and 1.33 Å respectively. Because of smaller size Ag^+ will have greater polarising power.

ii. Let us consider Na^+ and Al^{3+}. Since Al^{3+} has got more ionic charge it will have greater polarising power.

Effects of transition from ionic to covalent charater and vice versa

Decrease in melting points :

During the transition from ionic to covalent bonding, melting point decrease. e.g.,

i. The melting points of NaCl, KCl and CsCl are 801°C, 770°C and 650°C. As we go from $Na^+ \rightarrow K^+ \rightarrow Cs^+$ the sizes increase because their atomic numbers increase. Their polarizing powers decrease. Thus the ionic characters decrease in the above other. Therefore their melting points also decrease in the same order because ionic character and melting point are directly related to each other e.g.,

ii. The melting points of CaF_2 and $CaCl_2$ are 1329°C and 772°C respectively. Reason : Between F^- and Cl^-, the ionic size of Cl^- is greater than that of F^- because the atomic number of Cl^- is more than that of F. So Cl^- is more polarizable than F^-. This makes $CaCl_2$ less ionic than CaF_2. So its melting point is also less than that CaF_2. e.g.,

iii. The melting point of aluminium chloride is less than that of sodium chloride. Between Al^{3+} and Na^+, Al^{3+} will have more polarising power than Na^+ because it has more nuclealr charge. So $AlCl_3$ will be less ionic that NaCl. Therefore $AlCl_3$ has less melting point.

b. ***Decrease in ionic character :***

The ionic or polar characters of the following pairs are as follows;

HF > HI ; NaF > NaCl ;

$PbF_4 > PbCl_4$; $MaCl_2 > AlCl_3$;

Between HF and HI, the more ionic will be HF. This is because I^- is more polarizable than F^- due the large size of I^-.

Between NaF and $NaCl$, the more ionic will be NaF. This is because Cl^- is more polarizable than F^- due to the larger size of Cl^-. Similary, for the some reason, PbF_4 will more ionic than $PbCl_4$.

Between $MgCl_2$ and $AlCl_3$ the more ionic will be $MgCl_2$. This is because Al^{3+} will have more polarizing power than Mg^{2+} due to the fact that Al^{3+} has more nuclear charge than Mg^{2+}

c. ***Increase in covalent character :***

i. Amongest NaI, $NaCl$ and LiI, the covalent character increases in the order:

$NaCl < NaI < LiI$

Thus LiI will have maximum covalent character. This is because between $NaCl$ and NaI, the more covalent will be NaI. This is because I^- is more polarizable, than Cl^- due to the larger size of I^-. Between NaI and LiI, the more covalent will be LiI. This is because Li^+ is smaller than Na^+ So Li^+ will have more polarizing power than Na^+

ii. Between $BeCl_2$ and $BaCl_2$, the more covalent wil be $BeCl_2$. This is because Be^{2+} is smaller than Ba^{2+}. So it will have more polarising power. So it polarises the electronic cloud of Cl^- more than Ba^{2+}. So tha transition from electrovalency into covalency is more in $BeCl_2$ than in $BaCl_2$.

Decrease in electrical conductivity :

Fused $BeCl_2$ shows poor electrical conductivity ; but fused $MgCl_2$ is a good electrical conductor. This is because Be^{2+} is smallar than Mg^{2+}. So it will have more polarising power tha Mg^{2+}. Because of this, it polarises the lectronic cloud of Cl^- more than Mg^{2+}. So $BeCl_2$ becomes less ionic and more covalent. So its electrical conductivity is less.

So far we have discussed various examples in the light of the transition from ionic to covalent character. If we discuss the reverse case, viz., transition from covalent to ionic character, the whole discussion will be in the reverse direction.

Summary :

i. - Between two cations with similar nuclear charge, the smaller cation will polarise more.

ii. Between two anions with similar charge the bigger anion will get polarised more.

iii. Between cations with different nuclear charges, the cation with more charge will polarise more.

iv. Polarisation more means that covalent character is more,, ionic character is less, melting point is less and electrical conductivity is less.

Anomalous behaviour of HCl :

The behaviour of hydrogen chloride is remarkable. According to Fajans rule HCl must be a covalent compound since its cation is very small. This is borne by the fact that hydrogen cloride is a non - conductor and has very low melting and boiling points. Therefore in hydrogen chloride the electrons are shared between the two atoms. But a solution of hydrogen chlorine in water is an excellent conductor. So the covalent bond has now been transformed into electrovalent bond.

$$H\!:\!\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}} \longrightarrow H^{+} + Cl^{-}$$

The dielectric constant of wateris an important factor in ionisation. Accoridng to Lowry and Bronsted, hydrogen ion (H^+) must be considered different from any other cation since it has no shielding electron. On account of its small size, it cannot exist in the free state in any solution. It exists as hydronium ion, (H_3O^+) in water.

Hard and Soft Acids and Bases :

In 1963 R.G. Pearson clssified the Lew's acids and bases as and soft acids and bases.

Soft and Hard Bases :

Soft Lewis bases are those in which the donor atoms are ea polarised and have low electro - negativity. Hard Lewis bases those in which the donor atoms have low polarisabilities and h electro - negativities.

It will be seen that within a group of the periodic table softness the Lewis bases increases with the increase in the size of the do atom. Thus, among the halide ions, softness increases in the order $< Cl^- < Br^- < I^-$. Thus F^- is the hardest and I^- is the softest Lewis ba

Hard bases :

E.g., : H_2O, OH^-, F^-, CH_3COO^-

Boderline (i.e., intermediate) bases :

E.g., : $C_6H_5NH_2$, C_6H_5N, Br^-

Soft bases :

E.g., : R_2S, RSH, RS^-, I^-, SCN^-

Soft and Hard Acids :

A hard acid, like a hard base, is difficult to polarise. A cationic har acid, such as Al^{3+}, generally has

i. a small size

ii. a high positive charge and

iii. a noble gas electronic configuration.

Hard Acids :

E.g., : H^+, Li^+, Na^+, K^+, Be^{2+}, Ca^{2+}

Boderline (i.e., intermediate) Acids :

E.g, : Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}

Soft Acids :

E.g.; : Cu^+, Ag^+, Au^+, Tl^+, Hg^+

HSAB principle and stability of the complex A : B

The typical Lewis acid - base reaction can be generalised as :

A	+	: B	⟶	A : B
Lewis acid		Lewis base		Adduct or complex
(acceptor)		(donor)		

A concept known as **Principle of Soft and Hard Acids and Bases** (abbreviated to HSAB principle) is very helpful in making a prediction of the stability of the complex A : B. This principle was proposed by Ralph G. Pearson (1963).

According to this principle the complex A : B is most stable when A and B are either both soft or both hard. The complex is least stable when one of the reactants (namely A and B) is very hard and the other one is very soft.

This principle also means that if there is a choice of reaction between an acid and two bases, or between a base and two acids, a hard acid will prefer to combine with a hard base and a soft acid will prefer to combine with a soft base and thus a more stable product will be obtained.