

Solvation Energy & Hydration Energy

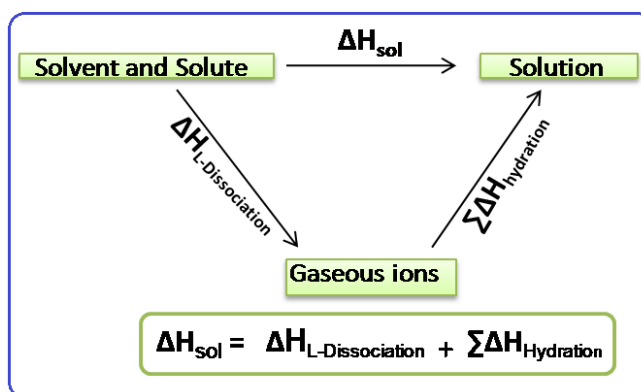
- Introduction:**

When a gaseous ion (cation or anion) is subjected to place in a solvent an interaction between this solvent and solute gaseous ion is established. This interaction is called solvation. The solvent molecule trend to stabilize the ion by such interaction. The energy is released in the process of solvation and the released energy is called solvation energy.

- **Solvation energy is defined as the energy released (exothermic process) when a gaseous cation or anion interacts with a liquid solvent in order to give a solution.**



- When the solvent is water (a good polar solvent having high dielectric constant), then the liberated energy for such interaction is called **hydration energy** and is represented as  $\Delta H_{hyd}$  as negative sign along with the unit of **K-Cal/mol or K-J/mol**.
- The enthalpy of solution can be calculated from the Enthalpy of lattice dissociation and the enthalpies of hydration using a **Hess's law cycle** given bellow:



- **Physical Basis:** Usually, solvation energies for most of the ions in water are largely negative (-Ve). When **a solid dissolves into ions the entropy increases ( $\Delta S = +ve$ )** as the disorder increases with the change from solid to solution and the number of particles increases. This will contribute towards making  **$\Delta G$  negative**. In that cases magnitude of **solvent-solute** interaction is **much higher than** the individual **solvent-**

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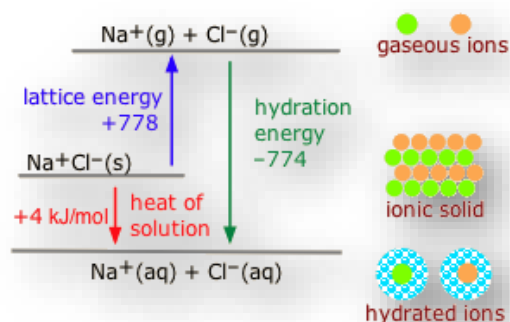
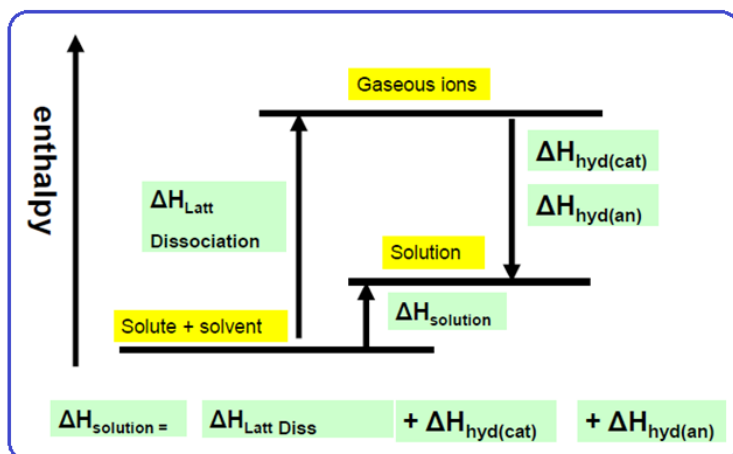
Dr. Tarun Mistri

Assistant Professor (UG & PG)

Jhargram Raj College

(9476107334)

**solvent** interaction & **solute-solute** interaction. This shows that the solvated ions are more stable than gaseous ions which is also supported from the corresponding potential energies graph given below:



- Considering hydration energy of cation and anion it is written as a function as follow:

$$\Delta H_{\text{hyd}} (\text{total}) = \Delta H_{\text{hyd}} (\text{cation}) + \Delta H_{\text{hyd}} (\text{anion}) = k_2 (1/r_+) + k_3 (1/r_-).$$

- **Solvated ions are in bigger size (radius)** than its gaseous species.

$$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+ \text{ (Gas phase or normal radius order)}$$

But  $r_+ (\text{aq.}): Li^+_{\text{aq}} > Na^+_{\text{aq}} > K^+_{\text{aq}} > Rb^+_{\text{aq}} > Cs^+_{\text{aq}}$  [solvated phase radius order (Reverse situation)].

Here the small size cation will be hydrated maximum due to high positive charge density on the small-cation and thereby its hydrated-radius (in Aq. Complex) will be maximum than that in gas-phase. Hence the ionic mobility (speed) of the most hydrated cation in solution become lower.

- **Ionic conductivity trends:** Electrical conductivity or ionic mobility (measure of speed of the ions) in solution inversely proportional to the size or radius of solvated ions.

This follows the reverse order of **solvated radius** of the corresponding ions.

**Ionic Conductivity order of solvated ions:**  $Li^+_{\text{aq}} < Na^+_{\text{aq}} < K^+_{\text{aq}} < Rb^+_{\text{aq}} < Cs^+_{\text{aq}}$

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Dr. Tarun Mistri

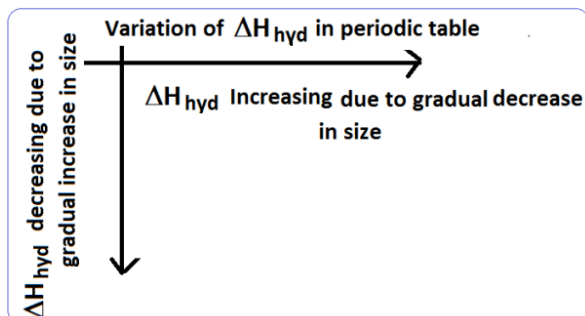
Assistant Professor (UG & PG)

Jhargram Raj College

(9476107334)

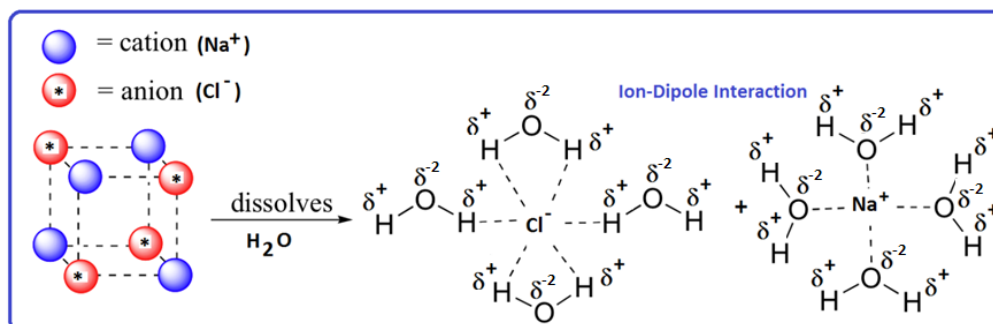
Ion	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>
Ionic radius (pm)	76	102	138	152	167
Hydrated radius (pm)	340	276	232	228	226
Ionic mobility (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )	33.5	43.5	64.5	67.5	68.0

- Hydration energy is a **periodic property** and it increases along a period due to



successive decrease of size or radius (with increasing  $Z_{\text{eff}}$ ) while it progressively decreases along a group due to successive increase of size or radius.

- In **polar solvent** (possessing a high dipole moment) **ion-dipole interaction** predominantly dissociates the ionic solid giving rise to a high value of solvation/hydration energy.



- Polar covalent compound like HCl dissolve in water by the mean of dipole-dipole interaction.
- The species belong to high hydration energy becomes highly hydrated in aqueous medium.
- Greater the dipole moment ( $\mu$ ) of the solvent greater will be the magnitude of hydration energy.
- Lanthanide ions [Ln(III)] have very high hydration energy.

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Dr. Tarun Mistri

Assistant Professor (UG & PG)

Jhargram Raj College

(9476107334)

## ■ \*\*Favorable condition for Hydration Energy /Solvation Energy:

For successful dissolution (solvation) of an ionic salt in a solvent, the hydration energy ( $\Delta H_{hyd}$ ) (solvation energy) should exceed the lattice energy ( $\Delta U$ ).

i.e.  $\Delta H_{hyd} \gg \Delta U$  [Dissolution condition]

This condition of favourable  $\Delta H_{hyd}$  will obtain when  $r_+ \neq r_-$  [i.e.  $r_+ \gg r_-$  or  $r_- \gg r_+$ ].

Such condition decreases both crystal backing energy as well as lattice energy of an ionic crystal by increasing the tendency of solvation process particularly in polar like solvent.

We should know that polar/ionic solvents dissolve polar/ionic solutes and non-polar solvents dissolve non-polar solutes (Like solvent like effect).

### • Relation of charge density or ionic potential with hydration energy:

It has been found that hydration energy of a system is directly **proportional to** the charge density or ionic potential ( $\Phi$ ) of the system.  $\Delta H_{hyd}$  may higher in some cases when **charge density or ionic potential ( $\Phi = \text{Charge} / \text{Radius}$ )** of the corresponding ions become higher. In that cases magnitude of **ion-dipole interaction** in solution will be high.

**The value of  $\Phi$  increases with:**

(a) The **increasing charge** on the relevant ion (cation) and hence  $\Delta H_{hyd}$  may also increases with the increase of charge of the ion.

e.g.  $\text{Na}^+ < \text{Mg}^{2+} < \text{Al}^{3+}$  (Increasing order of  $\Phi$  along with  $\Delta H_{hyd}$ ).

(b) The **decreasing size** (radius) of relevant ion and  $\Delta H_{hyd}$  increases with the decrease of the size (ionic radii) of the ion.

e.g. (i)  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$  (decreasing order of  $\Phi$  along with  $\Delta H_{hyd}$ ).

\*(ii)  $\text{Be}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$  (decreasing order of  $\Phi$  along with  $\Delta H_{hyd}$ ).

(iii)  $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$  (decreasing order of  $\Phi$  along with  $\Delta H_{hyd}$ ).

[For these above cases no counter anion or counter cation is taken]

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Dr. Tarun Mistri

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Jhargram Raj College

(9476107334)

## • Lattice Energy ( $\Delta U$ ) Vs. Solvation Energy ( $\Delta H_{hyd}$ ):

### ➤ Comparison:

	Parameters	Lattice Energy	Hydration Energy
1.	<b>Definition</b>	Amount of energy released generally when one mole ionic crystal is formed from the assembly of free gaseous ions. $M^+(g) + X^-(g) \longrightarrow MX(S) + U$	Hydration energy is defined as the energy released when a gaseous cation or anion interacts with water as a solvent in order to give a solution. $A^\pm(g) + H_2O \longrightarrow A^\pm(aq.) + \Delta H_{hyd}(total)$
2.	<b>Representation</b>	It is represented as $\Delta U$ with (-) <b>ve</b> sign (when crystal formation is taken into consideration).	It is represented as $\Delta H_{hyd}$ with (-) <b>ve</b> sign.
3.	<b>Unit</b>	K-Cal/mol <b>or</b> K-J/mol	K-Cal/mol <b>or</b> K-J/mol
4.	<b>*Mode of Writing</b>	$- U = k_1 [1/(r_+ + r_-)]$	$\Delta H_{hyd}(total) = \Delta H_{hyd}(cation) + \Delta H_{hyd}(anion)$ $= k_2 (1/r_+) + k_3 (1/r_-)$
5.	<b>**Favourable Condition</b>	$\Delta U$ will predominant over $\Delta H_{hyd}$ when counter ions have the <b>similar</b> sizes ( $r_+ \approx r_-$ ). Such condition increases crystal packing energy also.	$\Delta H_{hyd}$ will predominant over $\Delta U$ when counter ions belong to <b>different in sizes</b> ( $r_+ \gg r_-$ <b>or</b> $r_- \gg r_+$ ). Such condition leads to decrease crystal packing and facilitate solvation process.
6.	<b>**Dissolution Condition</b>	For successful dissolution of a salt in aqueous solvent, the $\Delta H_{hyd}$ must <b>exceed</b> the lattice energy ( $\Delta U$ ) of the system. i.e $\Delta H_{hyd} \gg \Delta U$ [Dissolution condition]. This situation will arrive when counter ions belong to <b>different in sizes</b> ( $r_+ \gg r_-$ <b>or</b> $r_- \gg r_+$ ).	
7.	<b>*Relation with ionic potential (<math>\Phi</math> = Cationic Charge/Cationic Radii)</b>	$\Delta H_{hyd}$ is directly proportional to charge-density or ionic potential of the system ( $\Phi$ ) while $\Delta U$ relates inversely with ionic potential.	

➤ **\*\*Remarks:**

For successful dissolution of a salt in aqueous solvent, the  $\Delta H_{hyd}$  must **exceed** the lattice energy ( $\Delta U$ ) of the system. i.e  $\Delta H_{hyd} \gg \Delta U$  [Dissolution condition]. This situation will arrive when counter ions belong to **different in sizes** ( $r_+ \gg r_-$  or  $r_- \gg r_+$ ). In this connection we should deal with two situations in order to determine the correct order of  $\Delta H_{hyd}$ :

1. **\*Case A ( $r_- \gg r_+$ ):** Salts containing **larger but similar type anion**:

With a bigger size anion, lattice energy decreases more rapidly than hydration energy in a series with decreasing cation size and **the condition of  $\Delta H_{hyd} \gg \Delta U$  easily establish because of mismatch of cationic & anionic radii ( $r_- \gg r_+$ )**. Additionally, high charge density or ionic-potential ( $\Phi$ ) value of smaller cation increases the magnitude of **ion-dipole** interaction with the water (solvent) molecule which facilitates the dissolution process. All of these factors will favour hydration process for the small size cation having common larger anion in a series of salt in the same group.

**Order of  $\Delta H_{hyd}$  and solubility in water** based on Case-A: Examples:

(i)  $\text{LiI}$  ( $r_- \gg r_+$ ,  $r_+ \neq r_-$ ;  $\Delta H_{hyd} \gg \Delta U$ , **most soluble due to low lattice energy**)  $> \text{NaI} > \text{KI} > \text{RbI} > \text{CsI}$  ( $r_+ \approx r_-$  (best fitting);  $\Delta U \gg \Delta H_{hyd}$ : high crystal packing as well as lattice energy making **least soluble**).

(ii)  $\text{LiClO}_4$  ( $r_- \gg r_+$ ,  $r_+ \neq r_-$ ;  $\Delta H_{hyd} \gg \Delta U$ , **most soluble due to low lattice energy**)  $> \text{NaClO}_4 > \text{KClO}_4 > \text{RbClO}_4 > \text{CsClO}_4$  ( $r_+ \approx r_-$ ;  $\Delta U \gg \Delta H_{hyd}$ : high crystal packing as well as lattice energy making **least soluble**).

(iii)  $\text{MgSO}_4$  ( $r_- \gg r_+$ ,  $r_+ \neq r_-$ ;  $\Delta H_{hyd} \gg \Delta U$ , **most soluble due to low lattice energy**)  $> \text{CaSO}_4 > \text{SrSO}_4 > \text{BaSO}_4$  ( $r_+ \approx r_-$ ;  $\Delta U \gg \Delta H_{hyd}$ : high crystal packing as well as lattice energy making **least soluble**).

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Dr. Tarun Mistri

Assistant Professor (UG & PG)

Jhargram Raj College

(9476107334)

2. \* **Case B ( $r_+ \gg r_-$ ):** Salts containing **smaller but similar type anion**:

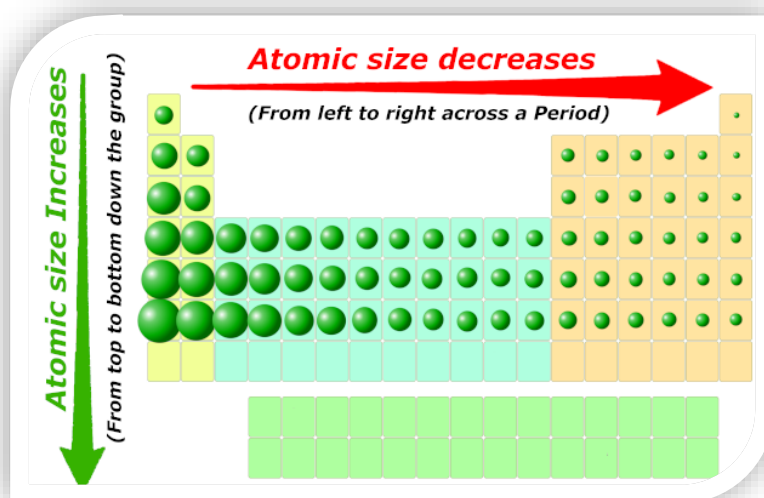
With a **smaller size anion**, lattice energy decreases more rapidly than hydration energy in a series with **increasing cation size** and the condition of  **$\Delta H_{hyd} \gg \Delta U$**  easily establish because of mismatch of cationic & anionic radii ( $r_+ \gg r_-$ ).

Order of  $\Delta H_{hyd}$  and solubility in water based on Case-B: Examples:

(i) LiF ( $r_+ \approx r_-$ ;  $\Delta U \gg \Delta H_{hyd}$ : high crystal packing as well as lattice energy making **least soluble**) < NaF < KF < RbF < CsF ( $r_+ \gg r_-$ ,  $r_+ \neq r_-$ ;  $\Delta H_{hyd} \gg \Delta U$ , **most soluble due to low lattice energy**).

(ii) Mg(OH)<sub>2</sub> ( $r_+ \approx r_-$ ;  $\Delta U \gg \Delta H_{hyd}$ : high crystal packing as well as lattice energy making **least soluble**) < Ca(OH)<sub>2</sub> < Sr(OH)<sub>2</sub> < Ba(OH)<sub>2</sub> ( $r_+ \gg r_-$ ,  $r_+ \neq r_-$ ;  $\Delta H_{hyd} \gg \Delta U$ , **most soluble due to low lattice energy**).

$$\text{solubility} \propto \frac{1}{\text{Lattice energy}}$$



❖ \* **Exceptional Case regarding Solubility:** Concept comes from Fajan's rule:

**Case-a:** For the presence of very high polarizing cation (high ionic potential system):

The concept of ionic protentional correlating the hydration energy is not always runs parallel because with increasing ionic potential (by either increasing charge of the cation or decreasing the radius of the cation) of cations, the increased polarizing power of cation

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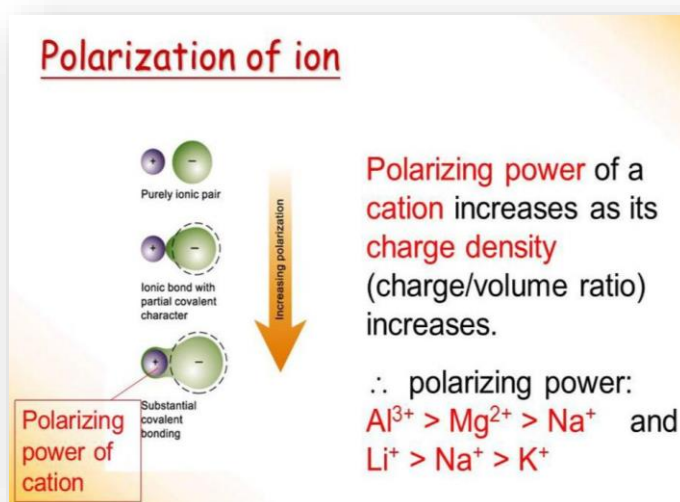
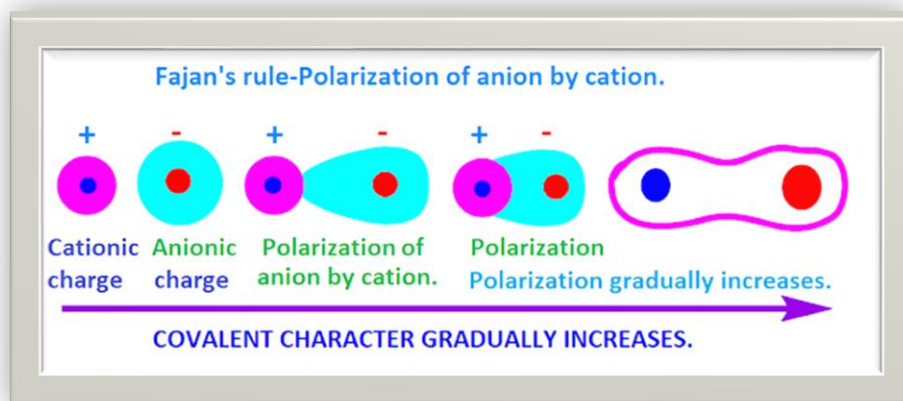
Dr. Tarun Mistri

Assistant Professor (UG & PG)

Jhargram Raj College

(9476107334)

leads to shell deformation of the outermost electrons of polarizable anion developing a covalent character within the ionic system based on Fajan's rule. Due to this covalent character the solubility of that system may decreases in ionic (polar) solvent.



\*\*\* **Case-b:** Presence of pseudo noble gas type cation (along with the presence of additional 4d and 4f-poor shielding electrons):

The development of covalent character (Based on Fajan's Rule) is also favourable for pseudo-noble gas system cation (having 18 valence electron system) like  $Ag^{+}$ :  $[Kr] 5s^1 4d^9$  where the presence of additional 4d-electrons [less penetrating and less shielding causing higher  $Z_{eff}$  (due to diffused nature of the 4d orbital ;  $Z_{eff} = Z - \sigma$ )] makes the cation highly



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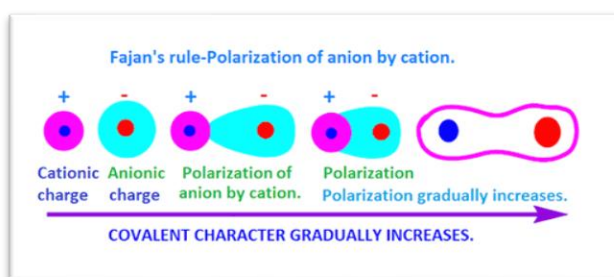
Assistant Professor (UG & PG)

Jhargram Raj College

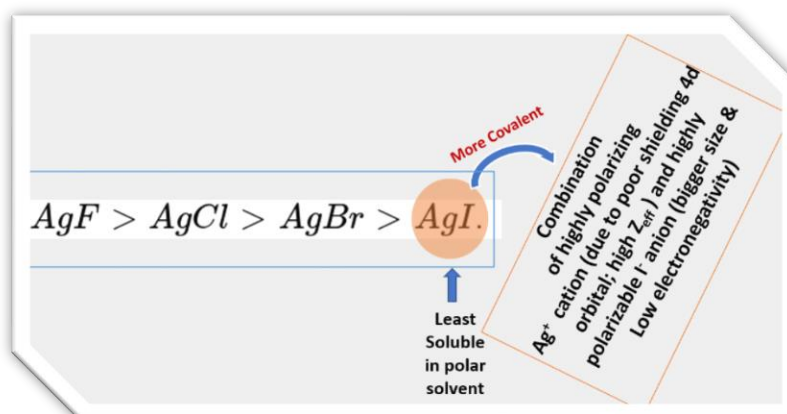
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polarizing towards the anion's outermost shell deformation leading to develop a covalent character within the system.

If highly polarizable anions (Like  $I^-$ ) (loosely bound outermost electrons due to higher size and lower electro negativity) are present then effective polarization (easy distortion of outermost electron cloud of anion) by such highly polarizing cation like  $Ag^+$  will much pronounced making the entire system much covalent for which their solubility in polar solvent will decrease.



For this particular case (b) the condition of favourable  $\Delta H_{hyd}$  [i.e.  $r_+ \neq r_-$ ;  $r_+ >> r_-$  or  $r_- >> r_+$ ] is not necessary to be obeyed and these systems behave oppositely wrt the general concept of favorable hydration energy. Solubility order of  $AgX$  in water is found to be exceptional than alkali metal and alkali earth metal halides ( $MX$  &  $MX_2$ ) due to the above-mentioned reason (case-b). The actual order of solubility of covalent  $AgX$  in water (polar solvent) is given below:



However, in non-polar solvent ( $\text{CCl}_4$ ) the solubility of  $\text{AgX}$  will reverse than in polar solvent where most covalent AgI will be maximum soluble in non-polar  $\text{CCl}_4$  solvent due to like-solvent-like effect.

Such situation (development of covalent character) may also come for the cation where additional more diffused 4f-electrons present [ $Z_{\text{eff}}$  become very high due to lanthanide like contraction as well as relativistic effect].

However, the solubility of a covalent compound is higher in non-polar solvent (like  $\text{CCl}_4$ ) than polar solvent due to like-solvent-like effect.

- **Factor Affecting Hydration Energy:**

- a. Lattice energy
- b. Charge density or Ionic potential
- c. Dielectric constant ( $\epsilon$ ) of the medium and dipole moment ( $\mu$ ) of the medium
- d. Ion-dipole interaction
- e. Dipole-dipole interaction
- f. H-bonding
- g. Molecular Weight
- h. Compact volume / Surface area

- **Effect of Hydration Energy On:**

1. Size of hydrated ion
2. Electrical Conductivity
3. Solubility of ionic solid
4. Formation of hydrated salt of alkaline earth metal

- **Utility of Hydration Energy:**

It can explain several usual & unusual facts like:

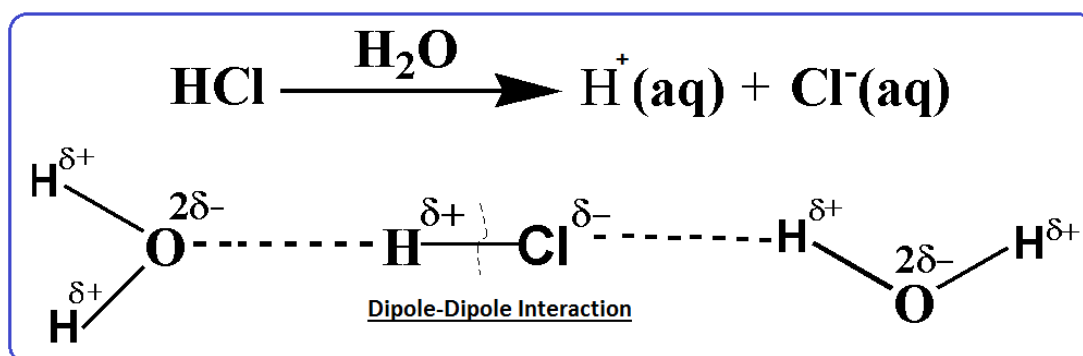
1. Solubility of covalent compound in water.
2. Highly hydrated  $\text{Li}^+$  ion than the other group member
3. Stability of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  (ionic) over anhydrous  $\text{AlCl}_3$ .
4. Higher Oxidizing character of  $\text{F}_2$  than  $\text{Cl}_2$ .

5. Inert nature of Pt, Ag, Au etc.
6. Higher solubility of  $\text{MgSO}_4$  than  $\text{BaSO}_4$ .

• Some Problems and Solutions Related to  $\Delta H_{\text{hyd}}$ :

1. Why covalent HCl molecules dissolve in water?

**Ans.** Although HCl is covalent compound but due to the electronegativity of Cl atom, there is a charge separation in this molecule as  $\text{H}^{\delta+}\text{Cl}^{\delta-}$  introducing some extend polar character. When it is placed in polar water solvent, there is an attractive dipole-dipole interaction between the opposite dipoles of HCl and  $\text{H}_2\text{O}$  molecules.



The polar  $\text{H}^{\delta+}$  ends of HCl moves close to the negative  $\text{O}^{\delta-}$  end of  $\text{H}_2\text{O}$  and  $\text{Cl}^{\delta-}$  end orients itself towards  $\text{H}^{\delta+}$  end of  $\text{H}_2\text{O}$ . In this case combined hydration energies of  $\text{H}^+$  &  $\text{Cl}^-$  is so high that it easily splits the covalent bond in HCl and help hydration process.

2. Why  $\text{Li}^+$  salts are highly hydrated than other group members?

**Ans.** Following reasons are responsible to make the  $\text{Li}^+$  for its highly hydrated nature than its other **uni-positive** group member's ions.

- i. High ionic potential value ( $\Phi$ ) of  $\text{Li}^+$  due to very **smaller size** factor.
- ii. High charge density of  $\text{Li}^+$  due to its smaller ionic size ( $r_{\text{Li}^+}$  is very small).

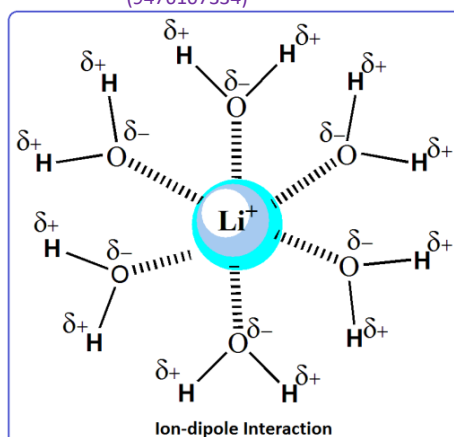
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Dr. Tarun Mistri

Assistant Professor (UG & PG)

Jhargram Raj College

(9476107334)



As a result of these factors a large number of water molecules are associated with smaller  $\text{Li}^+$  ion by the mean of **ion-dipole interaction** (electrostatic attraction) which increases the  $\Delta H_{\text{hyd}}$  of the entire system.

## 3. Compare the solubility of $\text{MgSO}_4$ & $\text{BaSO}_4$ in water.

**Ans.** Solubility  $\text{MgSO}_4$  is very high than  $\text{BaSO}_4$  in water. In this concern case following comparison table has been shown:

Cation having same ( $Z^+ = 2$ ) charge	Anion (common)	Size order of cations	Ionic Potential order of cation ( $\Phi = \text{charge}/\text{radius}$ )	Charge Density order	Ion-dipole Interaction in $\text{H}_2\text{O}$	Crystal Packing energy or Lattice Energy ( $\Delta U$ )	Hydration Energy ( $\Delta H_{\text{hyd}}$ )
$\text{Mg}^{2+}$	$\text{SO}_4^{2-}$	$r_{\text{Mg}^{2+}} < r_{\text{Ba}^{2+}}$	$\Phi_{\text{Mg}^{2+}} > \Phi_{\text{Ba}^{2+}}$	$\text{Mg}^{2+} > \text{Ba}^{2+}$	High for $\text{Mg}^{2+}$ due to its high $\Phi$ -value or charge density factor.	High for $\text{BaSO}_4$ as $r_{\text{Ba}^{2+}} \approx r_{\text{SO}_4^{2-}}$ so $(\Delta U \gg \Delta H_{\text{hyd}})$ (Least Soluble)	High for $\text{MgSO}_4$ as $r_{\text{Mg}^{2+}} < r_{\text{SO}_4^{2-}}$ so $(\Delta H_{\text{hyd}} \gg \Delta U)$ (more soluble)
$\text{Ba}^{2+}$							

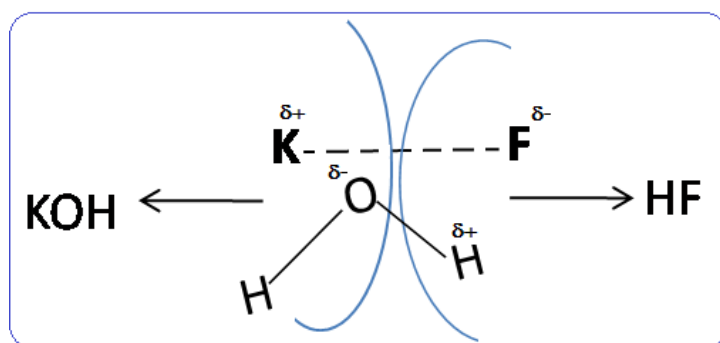
Considering size factor  $\Delta H_{\text{hyd}} \gg \Delta U$  is established for  $\text{MgSO}_4$  than  $\text{BaSO}_4$  which satisfy the dissolution condition for  $\text{MgSO}_4$ . Additionally, considering ' $\Phi$ ' value for cation, ion-dipole interaction in water is also

high for  $\text{Mg}^{2+}$  than  $\text{Ba}^{2+}$ . All of these findings indicate the higher solubility of  $\text{MgSO}_4$  over  $\text{BaSO}_4$  (insoluble) in water.

**4. On hydrolysis KF produces KOH and HF- Ration the fact.**

Or **hydration energy of  $\text{K}^+$  &  $\text{F}^-$  is different although then belongs to almost same ionic radii- Explain.**

**Ans.** Although  $\text{K}^+$  and  $\text{F}^-$  belongs to almost same ionic radii but their hydration energies are different. H.E. ( $\Delta H_{\text{hyd}}$ ) of  $\text{F}^-$  is much greater than  $\text{K}^+$ . This can be understood by the following hydrolysis reaction of KF lattice in water:



During hydrolysis small size & high charge-dense  $\text{F}^-$  interacts with the **small  $\text{H}^+$**  ion giving rise to **HF** molecule which is **stabilized** through '**H-bonding**' (symmetrical type). Here hydration energy becomes predominating factor. While  $\text{K}^+$  ion interacts with comparatively large  $\text{O}^{\delta-}$  atom of the water dipoles giving rise to KOH **lattice** where **lattice energy** predominating factor.

**5. Why Pt, Ag, Au metals are found to be inert while alkali metals and alkaline are reactive?**

**Ans.** Whenever a metal will be reactive or not this can be explained with the help of Born-Haber cycle associated with lattice energy and hydration energy. In this case following type BHC (Born Haber Cycle) has to be considered.

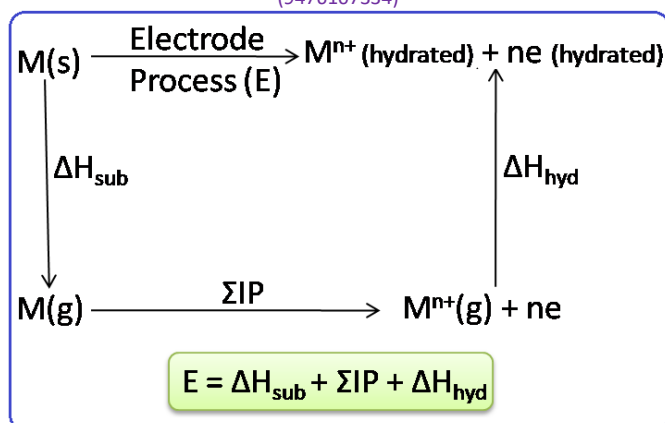
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Jhargram Raj College

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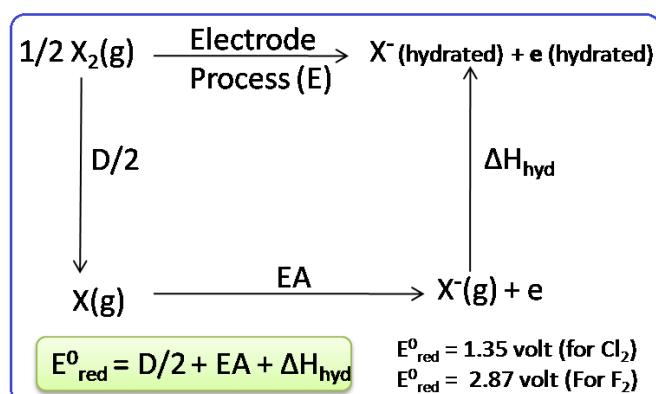


Electrode potential is determined by the sum of **sublimation energy**, **ionization energy** & hydration energy. Here both  $\Delta H_{\text{sub}}$  & IP are highly endothermic. Hence favorable condition will attain when  $\Delta H_{\text{hyd}}$  (exothermic) becomes extremely high enough. The metals like **Pt, Ag, Au** etc have very high value of sublimation & ionization energy and hence they are found to be inert (noble). While low value of  $\Delta H_{\text{sub}}$  & IP makes alkali & alkaline earth metals very reactive.

### 6. Why oxidation character of $\text{F}_2$ is higher than $\text{Cl}_2$ although EA of $\text{Cl}_2$ is very high?

**Ans.** Although EA of  $\text{Cl}_2$  is very high than  $\text{F}_2$ , but oxidation character of them follows the reversed order. Electron affinity alone can't explain the oxidizing character of  $\text{F}_2$  &  $\text{Cl}_2$ . The relative reduction potential (Electrode process) of  $\text{F}_2$  &  $\text{Cl}_2$  depend of the three thermodynamical parameters based on Born-Haber Cycle (BHC):

- i) B.D (Bond dissociation energy) ii) E.A (Electron affinity) iii)  $\Delta H_{\text{hyd}}$  (H.E)



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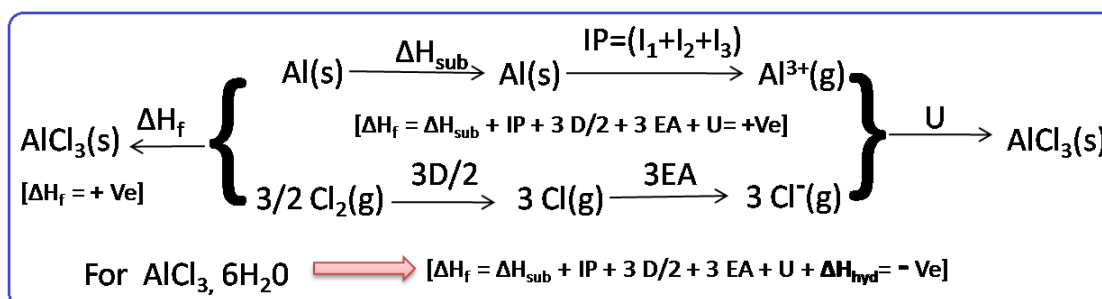
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Bond dissociation energy of  $F_2$  much less endothermic (*due to maximum electron-electron repulsion due to its very small size factor*) than  $Cl_2$  besides that  $\Delta H_{hyd}$  of  $F^-$  is much higher than  $Cl^-$  because of smaller size factor in case of  $F^-$ . Hence, algebraic sum of B.D & H.E far out way of (overcome) E.A. factor making the electrode process more favorable for  $F_2$ . So,  $F_2$  is higher oxidant than  $Cl_2$ .

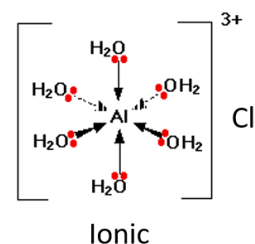
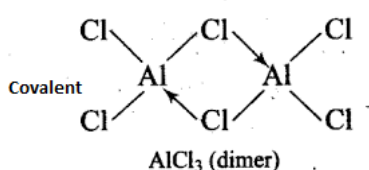
(Unit = $kJ\ mol^{-1}$ )	$\Delta_{bond\ diss}\ H$	$\Delta_{elec\ gain}\ H$	$\Delta_{hydr}\ H$
$F_2$	158.8	- 333	515
$Cl_2$	242.6	- 349	381

7.  $AlCl_3, 6H_2O$  is more ionic than anhydrous  $AlCl_3$ . Explain.

**Ans.** This can be explained on the basis of B.H.C. Anhydrous  $AlCl_3$  is less stable (covalent like compound) due to the **high IP** value of tri-positive  $Al^{3+}(g)$  ion which make overall formation energy  $\Delta H_f(AlCl_3)$  **positive** i.e thermodynamically unstable as an ionic solid.



But in case of  $AlCl_3, 6H_2O$  overall  $\Delta H_f(AlCl_3, 6H_2O)$  additionally contain  $\Delta H_{hyd}$  portion which is so **high (exothermic: - Ve)** that it **compensates** the high I.P factor of  $Al^{3+}$  ion making the  **$\Delta H_f$  negative**. Hence  $AlCl_3, 6H_2O$  is more ionic and stable.



# SOLVATION AND HYDRATION ENERGY

Dr. Tarun Mistri

Assistant Professor (UG & PG)

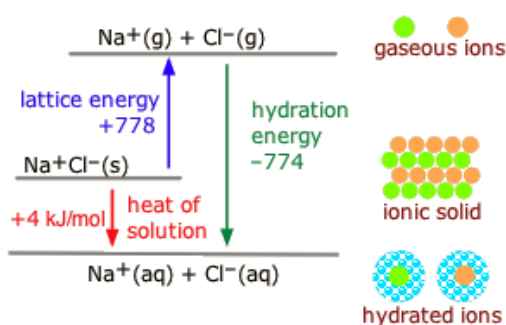
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8. The lattice energy of NaCl calculated using the **Madelung constant** of the NaCl structure type is +788 kJ/mol. The estimated enthalpy of hydration for sodium and chloride ions are -406 and -363 kJ/mol respectively. Estimate the enthalpy of solvation for NaCl.

**Solution**

Using the given cycle:



$$\Delta H_{\text{Hyd}} = \Delta H_{\text{Lattice}} + \Delta H_{\text{Sol}}$$

$$\Delta H_{\text{Sol}} = -769 - (788) \text{ kJ} = -19 \text{ kJ/mol}$$

Dr. Tarun Mistri

Assistant Professor

Dept. of Chemistry (UG & PG)

Jhargram Raj College

9476107334



- **Tropic Questions**

1. Define hydration energy and discuss the favorable condition of dissolution process of an ionic solid in solution with example.
2. Give a comparative statement between lattice energy and hydration energy.
3. Explain the order of ionic mobility as well as conductivity of alkali metal ions in water.
4. **\*\*Li-salts are highly hydrated. Why?**
5. **\*\*Explain the solubility order of AgX type system:**  
$$\text{AgI} < \text{AgBr} < \text{AgCl} < \text{AgF}$$
6. **\*Explain the order of solubility:**  
$$\text{LiI} > \text{NaI} > \text{KI} > \text{RbI} > \text{CsI}$$
7. **\*\*Explain why  $\text{BaSO}_4$  less soluble than  $\text{MgSO}_4$ ?**
8. **\*\* $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  is more ionic than anhydrous  $\text{AlCl}_3$ -Explain.**
9. **\*\*Why oxidation character of  $\text{F}_2$  is higher than  $\text{Cl}_2$  although EA of  $\text{Cl}_2$  is very high?**
10. **\*Why Pt, Ag, Au metals are found to be inert while alkali metals and alkaline are reactive?**
11. **\*\*Hydration energy of  $\text{K}^+$  &  $\text{F}^-$  is different although then belongs to almost same ionic radii- Explain.**
12. Why covalent HCl molecules dissolve in water?
13. **\*Explain the solubility order:**  
$$\text{Mg}(\text{OH})_2 < \text{Ca}(\text{OH})_2 < \text{Sr}(\text{OH})_2 < \text{Ba}(\text{OH})_2$$
14. What are the factors that affect hydration energy?
15. Explain the concept of hydration energy with respect to physical concept.
16. How hydration energy relates with ionic potential ( $\Phi$ ).
17. Describe the favorable condition of lattice energy and hydration energy.
18. **\*Why AgI is highly soluble in  $\text{CCl}_4$  but less soluble in water?**
19. **\* $\text{LiClO}_4$  is highly soluble in water. Explain.**
20.  $\text{Li}^+$  salts are covalent mostly. Why?

# SOLVATION AND HYDRATION ENERGY

Dr. Tarun Mistri

Assistant Professor (UG & PG)

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Solubility Table

	Na <sup>+</sup>	K <sup>+</sup>	Sr <sup>2+</sup>	Al <sup>3+</sup>	Cr <sup>3+</sup>	Ag <sup>+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>
F <sup>-</sup>	sol	sol	insol	sol	insol	sol	sol	insol
Cl <sup>-</sup>	sol	sol	sol	sol	sol	insol	sol	sol
Br <sup>-</sup>	sol	sol	sol	sol	insol	insol	sol	sol
I <sup>-</sup>	sol	sol	sol	sol	insol	insol	sol	insol
SO <sub>4</sub> <sup>2-</sup>	sol	sol	insol	sol	sol	sl sol	sol	insol
NO <sub>3</sub> <sup>-</sup>	sol	sol	sol	sol	sol	sol	sol	sol
PO <sub>4</sub> <sup>3-</sup>	sol	sol	insol	insol	insol	insol	insol	insol
CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	sol	sol	sol	sol	sol	sol	sol	sol

sol - soluble; sl sol - slightly soluble; insol - insoluble

Solubility (molar value first, g/100 g H<sub>2</sub>O given in brackets).

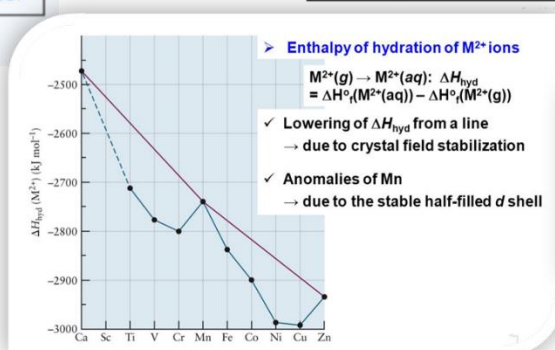
	MF	MCl	MBr	MI
Li	0.1 (0.27)	19.6 (830)	20.4 [177]	8.8 [165]
Na	1.0 (4.22)	6.2 (36)	8.8 [91]	11.9 [179]
K	15.9 (92.3)	4.8 (34.7)	7.6 [67]	8.7 [144]
Rb	12.5 (130.6)	7.5 [91]	6.7 [110]	7.2 [152]
Cs	24.2 (367)	11.0 [186]	5.1 [108]	3.0 [79]

## Overview

Mg(OH) <sub>2</sub>	Least soluble	MgSO <sub>4</sub>	Most soluble
Ca(OH) <sub>2</sub>		CaSO <sub>4</sub>	
Sr(OH) <sub>2</sub>		SrSO <sub>4</sub>	
Ba(OH) <sub>2</sub>	Most soluble	BaSO <sub>4</sub>	Least soluble

Metal	Hydroxide Solubility
Mg	0.0001
Ca	1.2
Sr	10
Ba	47

Halide Ion	Colour of Silver Halide Solution	Effect of Adding Dilute Ammonia Solution to Precipitate	Effect of Adding Concentrated Ammonia Solution to Precipitate
Cl <sup>-</sup> (aq)	White	Dissolves	Dissolves
Br <sup>-</sup> (aq)	Cream	Remains insoluble	Dissolves
I <sup>-</sup> (aq)	Pale yellow	Remains insoluble	Remains insoluble



Strongly Hydrated (small)	Li <sup>+</sup>	F <sup>-</sup>
	Na <sup>+</sup>	
Weakly Hydrated (large)	K <sup>+</sup>	Cl <sup>-</sup>
	Rb <sup>+</sup>	Br <sup>-</sup>
	Cs <sup>+</sup>	I <sup>-</sup>

Water