

SOLUBILITY OF SALTS

Section - 5

[A] In Aqueous Solvent :

A solvent may be polar (having high dielectric constant such as water or mineral acids) or non-polar (having low dielectric constant such as benzene and tetrachloromethane). Ionic compounds are usually soluble in polar solvents while covalent compounds usually dissolve in covalent solvents. This rule may be stated as '*like dissolves like*'.

For a substance to dissolve in an aqueous solvent (water) the energy evolved when the ions are hydrated (hydration energy) must be larger than the energy required to break the crystal lattice (lattice enthalpy). Thus solubility in principle depends upon two major factors.

- (i) **Lattice Enthalpy :** The lattice enthalpy is inversely proportional to the distance between the cation and the anion (i.e. $r^+ + r^-$). Thus the lattice enthalpy decreases as we go down the group due to the increase in size of cation if the anion being considered is same.
- (ii) **Hydration Enthalpy :** Hydration enthalpy usually varies as the inverse of radius of cation (r^+). This is because as the size of cation increases, the polarising power of cation decreases and thus the tendency to attract water molecules decreases. (also known as *Dehydrating Capacity*). This decrease in dehydrating capacity decreases the hydration energy that is released when a molecule is hydrated.

The General Solubility Rules in Water are as follows :

1. All nitrates (NO_3^-) and chlorates (ClO_3^-) are soluble. All sulphates (SO_4^{2-}) are soluble except those of $[\text{Sr}^{2+}, \text{Ba}^{2+}$ and $\text{Pb}^{2+}]$ which are sparingly soluble and hence are used in qualitative analysis.
2. All the carbonates (CO_3^{2-}), sulphites (SO_3^{2-}), phosphates (PO_4^{3-}) and dichromates ($\text{Cr}_2\text{O}_7^{2-}$) are insoluble except of Group I, Na^+ , K^+ and NH_4^+ . Practically almost all salts of Group I, Na^+ , K^+ and NH_4^+ are soluble in water.
3. All simple salts of **Group I** metals dissolve in water producing ions. The solubility of most salts (NO_3^- , CO_3^{2-} , HCO_3^-) decreases down the group. This is because the decrease in hydration energy of metal ions is much more than the decrease in the lattice energy given.

Exception : The solubility of alkali metal fluorides, hydroxides and carbonates increases rapidly down the group. The reason is L.E. is proportional to $1/(r^+ + r^-)$ and thus the lattice energy will vary most when r^- is small (as in fluorides) and least when r^- is longer (with I^-). Thus the change in lattice enthalpy exceeds the change in hydration enthalpy in this case.

4. The solubility of most salts of *Group II* also decreases down the group. For example, $\text{BeSO}_4 > \text{MgSO}_4 \gg \text{CaSO}_4 > \text{SrSO}_4 > \text{BaSO}_4$. (As has been stated, all sulphates except these of Ca, Sr, Ba, Pb, Ag are very soluble).

Exception : The fluorides and hydroxide of *Group II* metals show an increase in solubility down the group. The reason is same as that for *Group I* salts.

5. All hydroxides are insoluble except those of alkali metals (*Group I*) leaving LiOH . Those of Ca^{2+} , Sr^{2+} and Ba^{2+} are moderately soluble.
6. All sulphides (S^{2-}) are insoluble except those of alkali metals, alkali earth metals and the ammonium (NH_4^+) ion.
7. All chlorides, bromides and iodides are soluble except those of Ag^+ , Hg_2^{2+} and Pb^{2+} which are used in qualitative analysis.

8. It has been noticed that compounds with large difference in radii of ions are generally soluble while the least soluble salts are those of ions with similar radii. Thus :



[Here the difference in size between the cation and anion increases down the group].

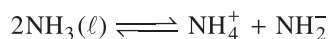
while, $\text{LiBr} > \text{NaBr} > \text{KBr} > \text{RbBr} > \text{CsBr}$.



[Here the difference in size between the cation and anion decreases down the group].

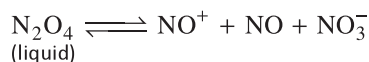
[B] In Non-aqueous Solvents :

Important non-aqueous solvents include liquid hydrofluoric acid(HF), liquid NO_2 and liquid ammonia (NH_3). Liquid ammonia is the most studied non aqueous solvent and it resembles the aqueous system quite closely.



Thus substances producing NH_4^+ are acids (like NH_4Cl) in liquid ammonia and those producing NH_2^- are bases (like NaNH_2)

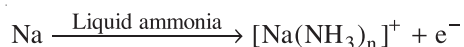
Similarly,



Thus in N_2O_4 substances containing NO^+ are acid (like NOCl) and those containing NO_3^- are bases (like NH_4NO_3). For HF we have :



Like in water, acid-base neutralisation and precipitation reactions also occur in liquid ammonia. Liquid ammonia is an extremely good solvent for the alkali metals and the heavier Group II metals Ca, Sr and Ba. The metals are very soluble and solutions in liquid ammonia have a conductivity comparable to that of pure metals. Thus solutions are very good reducing agents because of the presence of free electrons.



ANSWERS TO IN-CHAPTER EXERCISES

A	6. D	7. A	8. D	9. B	10. A	11. C	12. A	13. B	14. ABC	15. ACD	16. AD
B	6. C	7. B	8. B	9. B							
C	6. D	7. B	8. B	9. B	10. A	11. ABC					
D	2. A	3. C	4. A	5. AB							