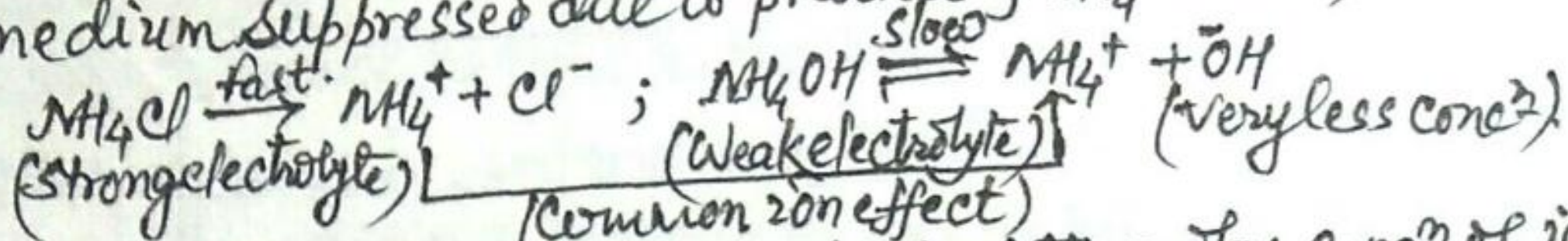


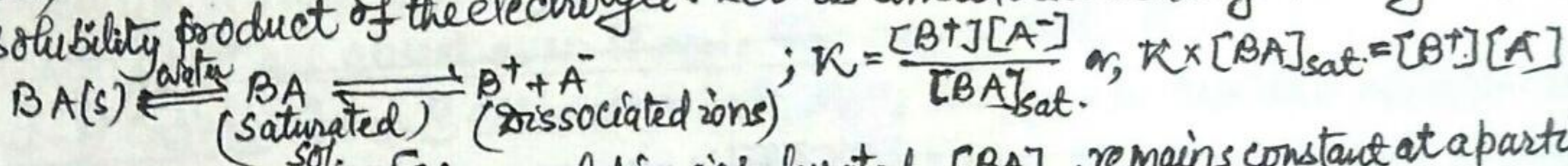
(b) Theory behind the group separation in Inorganic Qualitative Analysis

The separation of cations (basic radicals) into various analytical groups depends on two theories: 1. Common ion effect 2. Solubility product. The brief knowledge of these theories are essential for study of group separation of different cations during wet test of basic radicals.

* Common ion effect: The dissociation/ionisation of an electrolyte can be suppressed considerably by adding a strong electrolyte having an ion common is called common ion effect. For example, if some NH_4Cl is added to NH_4OH solution, ionisation of NH_4OH in aqueous medium suppressed due to presence of NH_4^+ (excess) produced by NH_4Cl , hence $[\text{OH}^-]$ decreases.



* Solubility product: The product of the molar concⁿ of ions of a binary electrolyte (sparingly soluble) in its saturated solution is a constant quantity at a particular temperature, known as solubility product of the electrolyte. Let us consider a binary electrolyte (BA).



$\therefore K_{sp} = [\text{B}^+][\text{A}^-]$ [Since solution is saturated, $[\text{BA}]_{\text{sat}}$ remains constant at a particular temp. so, $[\text{BA}]_{\text{sat}} \times K = K_{sp}$ (solubility product of BA)]

* When $[\text{B}^+][\text{A}^-] > K_{sp}$, precipitation will occur as super saturation of BA in solution.

* When $[\text{B}^+][\text{A}^-] < K_{sp}$, no precipitation occurs, i.e; B^+A^- remains in the solution (unsaturation)

This is main basis of separation of different cations in analytical groups (as shown in following table, and principles discussed later on.

Analytical table

Group	Group Reagent	Cations/Basic radicals	Form of precipitate
I	Dilute HCl	$\text{Pb}^{2+}, \text{Hg}_2^{2+}, \text{Ag}^+$	Chlorides ($\text{PbCl}_2, \text{Hg}_2\text{Cl}_2, \text{AgCl}$)
II	H_2S gas in presence of H^+ (acidic medium)	$\text{Hg}^{2+}, \text{Pb}^{2+}, \text{Bi}^{3+}, \text{Cu}^{2+}, \text{Cd}^{2+}, \text{As}^{3+}, \text{Sb}^{3+}, \text{Sn}^{2+} \& \text{Sn}^{4+}$	Sulphides ($\text{HgS}, \text{PbS}, \text{Bi}_2\text{S}_3, \text{CuS}, \text{CdS}, \text{As}_2\text{S}_3, \text{Sb}_2\text{S}_3, \text{SnS} \& \text{SnS}_2$)
III	NH_4OH (aq) + NH_4Cl (s)	$\text{Fe}^{3+}, \text{Al}^{3+}, \text{Cr}^{3+}$	Hydroxides; $\text{Fe}(\text{OH})_3, \text{Al}(\text{OH})_3, \text{Cr}(\text{OH})_3$
IV	H_2S in presence of $\text{NH}_4\text{OH} \& \text{NH}_4\text{Cl}$ (alkaline)	$\text{Mn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}$	Sulphides ($\text{MnS}, \text{CoS}, \text{NiS}, \text{ZnS}$)
V	$(\text{NH}_4)_2\text{CO}_3$ in presence of $\text{NH}_4\text{OH} \& \text{NH}_4\text{Cl}$ (s)	$\text{Ca}^{2+}, \text{Ba}^{2+}, \text{Sr}^{2+}$	Carbonates ($\text{CaCO}_3, \text{BaCO}_3, \text{SrCO}_3$)
VI	No specific common reagent	$\text{Mg}^{2+}, \text{Na}^+, \text{K}^+, \text{NH}_4^+$	Remains as soluble salt.

* Group-I Cations ($\text{Ag}^+, \text{Pb}^{2+} \& \text{Hg}_2^{2+}$): These are precipitated as chlorides because the solubility products of these chlorides ($\text{AgCl}, \text{PbCl}_2 \& \text{Hg}_2\text{Cl}_2$) is less than the solubility products of chlorides of other cations, which remain in solution. PbCl_2 is slightly soluble in water and therefore, lead (Pb^{2+}) is never completely precipitated by adding dilute HCl to a sample, the rest of the lead ions (Pb^{2+}) are precipitated with H_2S in acidic medium together with cations of Gr. II.

* Group-II Cations: Group-II Cations ($\text{Hg}^{2+}, \text{Cu}^{2+}, \text{Pb}^{2+}, \text{Bi}^{3+}, \text{Cd}^{2+}, \text{As}^{3+}, \text{Sb}^{3+}, \text{Sn}^{2+} \& \text{Sn}^{4+}$) are precipitated by H_2S gas in presence of HCl as sulphides (MS or M_2S_3 type) because of their low solubility products whereas sulphides of other metals remain in solution due to high solubility products. HCl acts as a source of H^+ which decreases the concentration of S^{2-} (Common ion effect). Hence, the concentration of S^{2-} is too low that it exceeds the solubility products of metal.

