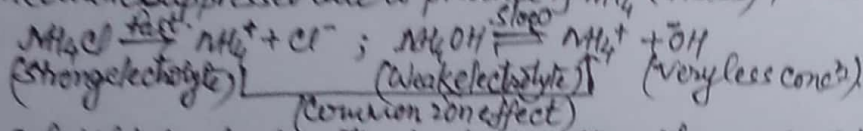


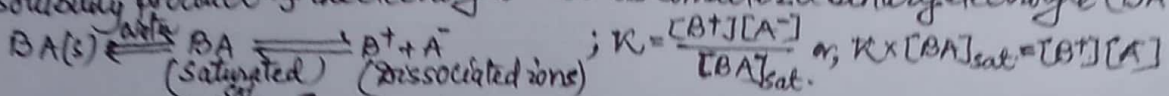
(b) Theory Behind the group Separation in Inorganic Qualitative Analysis

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 M_1Cl is added to M_2OH solution, ionisation of M_2OH in aqueous medium suppressed due to presence of M_1^+ (excess) produced by M_1Cl , hence $[OH^-]$ 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).



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

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

* When $[B^+][A^-] < K_{sp}$, 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).

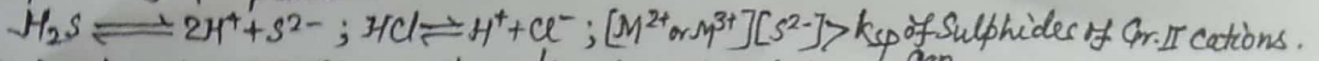
Analytical table

Group	Group Reagent	Cations/Basic radicals	Form of precipitate
I	Dilute HCl	Pb^{2+}, Hg_2^{2+}, Ag^+	Chlorides ($PbCl_2, Hg_2Cl_2, AgCl$)
II	H_2S gas in presence of H^+ (acidic medium)	$Hg^{2+}, Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}, As^{3+}, Sb^{3+}, Sn^{2+} \& Sn^{4+}$	Sulphides ($HgS, PbS, Bi_2S_3, CuS, CdS, As_2S_3, Sb_2S_3, SnS \& SnS_2$)
III	$NH_4OH(aq) + NH_4Cl(s)$	$Fe^{3+}, Al^{3+}, Cr^{3+}$	Hydroxides ($Fe(OH)_3, Al(OH)_3, Cr(OH)_3$)
IV	H_2S in presence of $NH_4OH \& NH_4Cl$ (alkaline)	$Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}$	Sulphides (MnS, CoS, NiS, ZnS)
V	$(NH_4)_2CO_3$ in presence of $NH_4OH \& NH_4Cl(s)$	$Ca^{2+}, Ba^{2+}, Sr^{2+}$	Carbonates ($CaCO_3, BaCO_3, SrCO_3$)
VI	No specific common reagent	$Mg^{2+}, Na^+, K^+, NH_4^+$	Remains as soluble salt.

* Group-I Cations ($Ag^+, Pb^{2+} \& Hg_2^{2+}$): These are precipitated as chlorides because the solubility products of these chlorides ($AgCl, PbCl_2 \& Hg_2Cl_2$) is less than the solubility products of chloride 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 ($Hg^{2+}, Cu^{2+}, Pb^{2+}, Bi^{3+}, Cd^{2+}, As^{3+}, Sb^{3+}, Sn^{2+} \& Sn^{4+}$) are precipitated by H_2S gas in presence of HCl as sulphides ($MS \& M_2S_3$ 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.

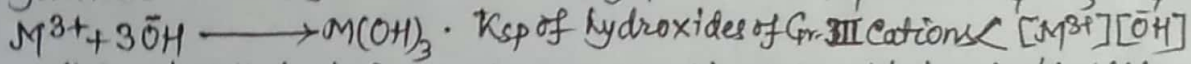
Sulphides of Group-II cations.



It is noted H_2SO_4 & HNO_3 are not used in place of HCl . Former ^{can} precipitate sulphate of Gr. V cations, while latter can oxidise H_2S into yellow S , causing confusion with As_2S_3 & Sb_2S_3 (yellow) even ^{they} absent.

* Group-III cations: Group III cations (Al^{3+} , Cr^{3+} , Fe^{3+}) are precipitated as hydroxides by $NH_4OH(aq)$ &

The $NH_4Cl(s)$ suppress the ionisation of NH_4OH so that only the gr. III cations are precipitated as hydroxides because of their low solubility products. $NH_4OH \rightleftharpoons NH_4^+ + OH^-$; $NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$



It is noted that: (i) Excess of NH_4Cl should not be added, as M^{3+} will precipitate as $MnO_2 \cdot xH_2O$

(ii) $(NH_4)_2SO_4$ cannot be used in place of NH_4Cl because SO_4^{2-} will precipitate Gr. V cations as sulphate

(iii) NH_4NO_3 cannot be used in place of NH_4Cl as NO_3^- ion will oxidise Mn^{2+} to Mn^{3+} and thus, $Mn(OH)_3$

will be precipitated in group-III (iv) In place of NH_4OH , $NaOH$ solution cannot be used for the precipitation as their hydroxides because of it (in excess) we get soluble complex of Al^{3+} & Cr^{3+} .

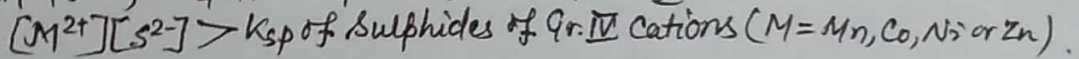
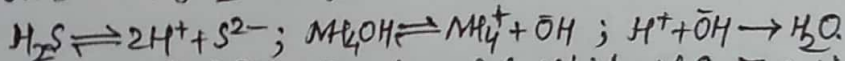
(v) If medium remains acidic the hydroxides do not precipitate and we would think that Fe^{3+} , Al^{3+} & Cr^{3+} are absent even though they may be present.

* Group-IV cations: Group-IV cations (Co^{2+} , Ni^{2+} , Mn^{2+} & Zn^{2+}) are precipitated as sulphides by H_2S

in the presence of $NH_4OH(aq)$ & NH_4Cl (alkaline medium). Here NH_4OH increases the ionisation of H_2S , since OH^- ions by dissociation of NH_4OH combine with the H^+ from H_2S forming undissociated H_2O .

The increased concⁿ of S^{2-} is now sufficient to exceed the solubility products of the group-IV metal sulphides, and will be precipitated. When H_2S gas is passed through a neutral solution,

incomplete precipitation will take place due to the formation of HCl , which decreases the ionisation of H_2S . e.g; $MnCl_2 + H_2S \longrightarrow MnS + 2HCl$.



* Group-V cations: Group-V cations (Ca^{2+} , Sr^{2+} & Ba^{2+}) are precipitated as carbonates by ammonium carbonate solution in the presence of NH_4Cl & NH_4OH . Here NH_4OH & NH_4Cl decreases

the ionisation of $(NH_4)_2CO_3$ / NH_4OH respectively. Due to common ion effect, very less concentration of CO_3^{2-} / OH^- ion produced which does not exceed the solubility product of

carbonate/hydroxide of Group-VI cation (Mg^{2+}), remains in the solution. Very low concentration of CO_3^{2-} ion precipitate cations of group-V, because ionic product exceeds

the solubility products of carbonates of Group-V cations only.

