Common Ion Effect

In a solution wherein there are several species associating with each other via a chemical equilibrium process, an increase in the concentration of one of the ions dissociated in the solution by the addition of another species containing the same ion will lead to an increase in the degree of association of ions.
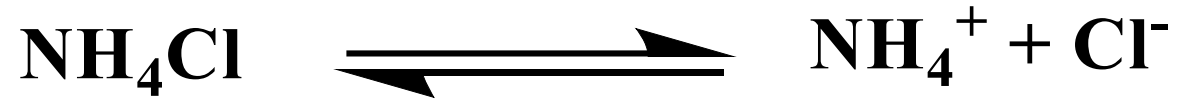
Consider the following reaction

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

Equilibrium constant

$$K= \frac{[NH_4^+][OH^-]}{NH_4OH}$$

Since equilibrium constant is fixed at for particular temperature, addition of NH_4Cl will increase the concentration of NH_4^+ ions which induced to increase concertation of NH_4OH keep K fixed.

Solubility product

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$$

$$K = \frac{[NH_4^+][Cl^-]}{NH_4Cl} \qquad\qquad K\,[NH_4Cl] = [NH_4^+][Cl^-]$$

1. If Solubility product is larger than the ionic product then no precipitate will form.

2. If Solubility product is smaller than the ionic product then excess solute will precipitate out because of the formation of super saturated solution.

3. If Solubility product is equal to the ionic product then saturated solution will form and addition of more solute will further precipitate out.

Group	Cations*	Group Reagent
Group zero	NH_4^+	None
Group-I	Pb^{2+}	Dilute HCl
Group-II	Pb^{2+}, Cu^{2+}, As^{3+}	H_2S gas in presence of dil. HCl
Group-III	Al^{3+}, Fe^{3+}	NH_4OH in presence of NH_4Cl
Group-IV	Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}	H_2S in presence of NH_4OH
Group-V	Ba^{2+}, Sr^{2+}, Ca^{2+}	$(NH_4)_2CO_3$ in presence of NH_4OH
Group-VI	Mg^{2+}	None

- Group I:
- $AgCl$-1.2×10^{-10}
- Hg_2Cl_2- 2.5×10^{-18}
- $PbCl_2$- 2×10^{-4}

Increasing temperature decreases the precipitation of $PbCl_2$

- Group II:
- BiS-10^{-72}
- CuS-10^{-44}
- CdS-10^{-29}
- PbS-10^{-49}

Presence of HCl decreases the $[S^{2-}]$ due to common ion effect and hence

- Group IV:
- BiS-10^{-24}
- CuS-10^{-23}
- CdS-10^{-22}
- PbS-10^{-15}

- Group III:
- $Cr(OH)_3$- 2.9×10^{-29}
- $Al(OH)_3$- 8.5×10^{-23}
- $Fe(OH)_3$- 3.8×10^{-36}

- Group V:
- $CaCO_3$- 3.3×10^{-9}
- $SrCO_3$- 5.6×10^{-10}
- $BaCO_3$- $2.58 \cdot 10^{-9}$

Buffer

A buffer solution is one which resists changes in pH when small quantities of an acid or an alkali are added to it.

An acidic buffer solution is simply one which has a pH less than 7. Acidic buffer solutions are commonly made from a weak acid and one of its salts - often a sodium salt.

An alkaline buffer solution has a pH greater than 7. Alkaline buffer solutions are commonly made from a weak base and one of its salts.

So how would you find the pH of a solution containing 0.100 mol dm^{-3} of ammonia and 0.0500 mol dm^{-3} of ammonium chloride? The value for K_a for the ammonium ion is 5.62 x 10^{-10} mol dm^{-3}.

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$$
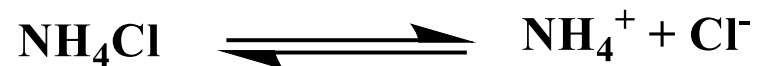
Assume this is the same as the concentration of the original ammonia solution.

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$$

Assume this is the same as the concentration of the ammonium chloride.

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$$

$$5.62 \times 10^{-10} = \frac{0.100 \times [H^+]}{0.0500}$$

$$[H^+] = \frac{0.0500}{0.100} \times 5.62 \times 10^{-10}$$

$$= 2.81 \times 10^{-10}$$

$$pH = -\log_{10}[H^+]$$

$$= 9.55$$

The presence of the ammonia in the mixture forces the equilibrium far to the left. That means that you can assume that the ammonium ion concentration is what you started off with in the ammonium chloride, and that the ammonia concentration is all due to the added ammonia solution.

Interfering Radical

In acidic medium, salts produce their corresponding acids like oxalic acid, phosphoric acid, hydrofluoric acid, boric acid and tartaric acid. For example, barium oxalate reacts with HCl and produces oxalic acid.

$$BaC_2O_4 + 2HCl \rightarrow BaCl_2 + H_2C_2O_4$$
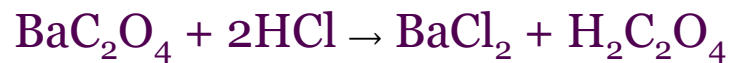
These interfering acids are weak acids so they do not dissociate completely and remain in solution in their unionised form. Equilibrium is developed between dissociated and un-dissociated acid.

$$H_2C_2O_4 \rightleftharpoons 2H^+ + C_2O_4^{2-}$$
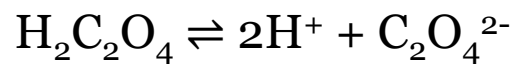
Ionic product of $C_2O_4^{2-}$ and Ba^{2+} doesn't exceed the solubility product of barium oxalate which is why Ba^{2+} remains in the solution as barium oxalate. That's how interfering radicals do not interfere as long as the medium remains acidic enough. But when we make the medium alkaline by adding 3rd group reagent ammonium hydroxide NH_4OH, OH^- ions combine with H^+ and neutralise them. This decreases the concentration of H^+ ions which shifts the equilibrium of dissociation of interfering acid forward and increases the concentration of $C_2O_4^{2-}$. Thus the ionic product of $C_2O_4^{2-}$ and Ba^{2+} exceeds the solubility product of barium oxalate and Ba^{2+} gets precipitated in the 3rd group, which actually belongs to the 4th group.

One or more interfering radicals can be present in the solution. They have to be removed in the following order: first we remove oxalate and tartrate, then borate and fluoride, then silicate and in the last phosphate.
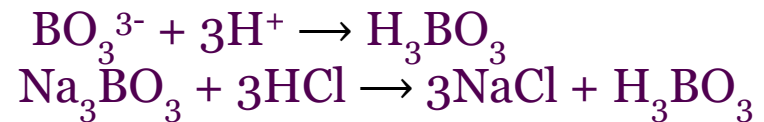
Removal of Interfering radical

Oxalate and tartrate of metals are soluble in acid and they decompose on heating. Take the filtrate of 2nd group and boil off H_2S gas from it. Add 4-5ml concentrated nitric acid HNO_3 and heat it till it is almost dry. Repeat this treatment for 2-3 times.

$$(COO)_2{}^{2-} + H^+ \rightarrow (COOH)_2$$
$$(COOH)_2 \rightarrow HCOOH + CO_2\uparrow$$
$$HCOOH \rightarrow CO\uparrow + H_2O\uparrow$$
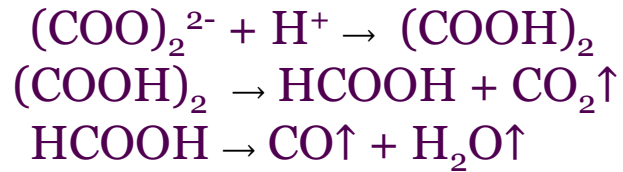
Take the filtrate and evaporate it to dryness. Add concentrated HCl and again evaporate to dryness.

$$F^- + H^+ \longrightarrow HF$$

$$CaF_2 + 2HCl \longrightarrow CaCl2 + 2HF$$
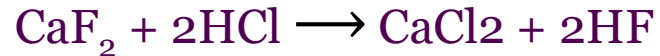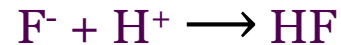
On heating with Borate forms orthoboric acid which evaporate on heating.

$$BO_3{}^{3-} + 3H^+ \longrightarrow H_3BO_3$$
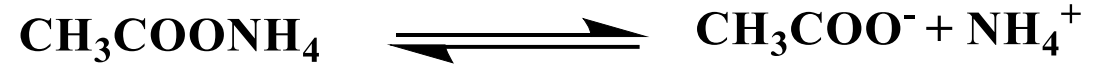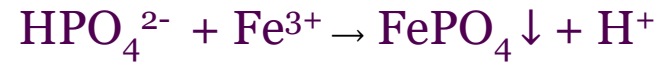$$Na_3BO_3 + 3HCl \rightarrow 3NaCl + H_3BO_3$$

Extract the residue with dilute HCl and filter. Use this filtrate for analysis of 3rd group or use for removal of other interfering radicals.

If borate is present then residue use a mixture of 5ml ethyl alcohol and 10ml conc. HCl and evaporate to dryness.
$$BO_3{}^{3-} + 3H^+ \longrightarrow H_3BO_3$$
$$H_3BO_3 + 3C_2H_5OH \rightarrow (C_2H_5O)_3B\uparrow + H_2O$$
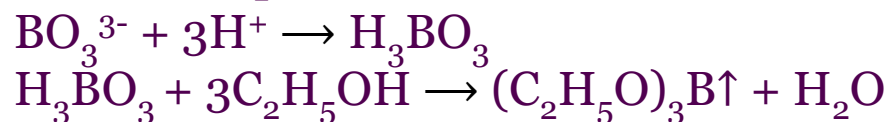
Procedure for the removal of phosphate

Ferric chloride is generally used for the removal of phosphate. Fe(III) combines with phosphate and removes all phosphate as insoluble $FePO_4$. Fe(III) is also a member of 3rd group so first we have to test its presence in the filtrate of 2nd group then we can proceed for the removal of phosphate.

$$HPO_4{}^{2-} + Fe^{3+} \rightarrow FePO_4\downarrow + H^+$$

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \qquad\qquad CH_3COONH_4 \rightleftharpoons CH_3COO^- + NH_4{}^+$$

The group III radicals are precipitated as phosphate.
If group III absent, no precipitate will form. Now on adding neutral ferric chloride, drop by drop, Fe^{3+} will react with $PO_4{}^{3-}$ to form insoluble $FePO_4$.