Analytical Chemistry—Use of Ammonium Hydroxide and Sodium Hydroxide

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CHAPTER AT A GLANCE

Analytical chemistry: $NaOH$ and NH_4OH

Colours of salts and their solutions
- Ferrous salt: Green
- Ferric salt: Yellow
- Cupric salt: Blue except $CuCO_3$ which is green
- Lead salt: Colourless
- Zinc salt: Colourless
- Calcium salt: Colourless

Action of NaOH on certain salt solutions

When NaOH is in little		When NaOH is in excess
• Dirty green ppt ←	• Ferrous salt	→ • Insoluble
• Reddish brown ppt ←	• Ferric salt	→ • Insoluble
• Pale blue ppt ←	• Cupric salt	→ • Insoluble
• White ppt ←	• Lead salt	→ • Soluble
• White ppt ←	• Zinc salt	→ • Soluble
• White ppt ←	• Calcium salt	→ • Soluble

Action of NH_4OH on certain salt solutions

When NH_4OH is in little quantity		When NH_4OH is in excess
• Dirty green ppt ←	• Ferrous salt	→ • Insoluble
• Reddish brown ppt ←	• Ferric salt	→ • Insoluble
• Pale blue ppt ←	• Cupric salt	→ • Soluble (deep blue solution)
• White ppt	• Lead salt	→ • Insoluble
• White ppt	• Zinc salt	→ • Soluble
• No visible reaction	• Calcium salt	→ • No visible reaction

Action of Alkalis

On metal oxides/Hydroxides
- $ZnO + 2NaOH \xrightarrow[\text{(conc.)}]{\Delta} Na_2ZnO_2 + H_2O$
- $ZnO + 2KOH \xrightarrow{\Delta} K_2ZnO_2 + H_2O$
- $Zn(OH)_2 + 2NaOH \xrightarrow[\text{(conc.)}]{\Delta} Na_2ZnO_2 + 2H_2O$
- $Zn(OH)_2 + 2KOH \xrightarrow[\text{(conc.)}]{\Delta} K_2ZnO_2 + 2H_2O$
- $Al_2O_3 + 2NaOH \xrightarrow[\text{(conc.)}]{\Delta} 2NaAlO_2 + H_2O$
- $2Al(OH)_3 + 2KOH \xrightarrow[\text{(conc.)}]{\Delta} 2KAlO_2 + 4H_2O$
- $Al_2O_3 + 2KOH \xrightarrow[\text{(conc.)}]{\Delta} 2KAlO_2 + H_2O$
- $Al(OH)_3 + NaOH \xrightarrow[\text{(conc.)}]{\Delta} NaAlO_2 + 2H_2O$

On certain metals
- $Zn + 2NaOH \xrightarrow[\text{(conc.)}]{\Delta} Na_2ZnO_2 + H_2$
- $Zn + 2KOH \xrightarrow[\text{(conc.)}]{\Delta} K_2ZnO_2 + H_2$
- $Pb + 2NaOH \xrightarrow[\text{(conc.)}]{\Delta} Na_2PbO_2 + H_2$
- $Pb + 2KOH \xrightarrow[\text{(conc.)}]{\Delta} K_2PbO_2 + H_2$
- $2Al + 2NaOH + 2H_2O \xrightarrow{\Delta} 2NaAlO_2 + 3H_2$

IMPORTANT TERMS, DEFINITIONS AND REACTIONS

1. **Alkalis,** i.e. sodium hydroxide and ammonium hydroxide react with the **soluble salts of metal** to precipitate **different coloured hydroxides.**
2. **Reaction of Sodium hydroxide and Ammonium hydroxide with the soluble salt of Zinc:**
   (*a*) **With NaOH:** On adding Sodium hydroxide drop by drop to a solution of Zinc salt, a **white precipitate** is formed which is **soluble** in excess of sodium hydroxide.

$$\underset{\text{Zinc nitrate}}{Zn(NO_3)_2} + \underset{\text{Sodium hydroxide}}{2NaOH} \longrightarrow \underset{\text{Zinc hydroxide (White ppt.)}}{Zn(OH)_2\downarrow} + \underset{\text{Sodium nitrate}}{2NaNO_3}$$

$$\underset{\text{Zinc hydroxide}}{Zn(OH)_2} + \underset{\text{Sodium hydroxide (excess)}}{2NaOH} \longrightarrow \underset{\text{Sodium zincate (Soluble salt)}}{Na_2ZnO_2} + \underset{\text{Water}}{2H_2O}$$

   (*b*) **With NH_4OH:** On adding ammonium hydroxide drop by drop to a solution of zinc salt, a **white precipitate** is formed which is **soluble** in excess of ammonium hydroxide.

$$\underset{\text{Zinc nitrate}}{Zn(NO_3)_2} + \underset{\text{Sodium hydroxide}}{2NH_4OH} \longrightarrow \underset{\text{Zinc hydroxide (White ppt.)}}{Zn(OH)_2\downarrow} + \underset{\text{Ammonium nitrate}}{2NH_4NO_3}$$

$$\underset{\text{Zinc hydroxide}}{Zn(OH)_2} + \underset{\text{Ammonium hydroxide}}{4NH_4OH} \longrightarrow \underset{\text{Tetraamine zinc hydroxide (Soluble salt)}}{[Zn(NH_3)_4](OH)_2} + \underset{\text{Water}}{4H_2O}$$

3. **Reaction of sodium hydroxide and ammonium hydroxide with the soluble salt of lead:**
   (*a*) **With NaOH:** On adding Sodium hydroxide drop by drop to a solution of Lead salt, a **white precipitate** is formed which is **soluble** in excess of Sodium hydroxide.

$$\underset{\text{Lead nitrate}}{Pb(NO_3)_2} + \underset{\text{Sodium hydroxide}}{2NaOH} \longrightarrow \underset{\text{Lead hydroxide (White ppt.)}}{Pb(OH)_2\downarrow} + \underset{\text{Sodium nitrate}}{2NaNO_3}$$

$$\underset{\text{Lead hydroxide}}{Pb(OH)_2} + \underset{\text{Sodium hydroxide}}{2NaOH} \longrightarrow \underset{\text{Sodium plumbite (Soluble salt)}}{Na_2PbO_2} + \underset{\text{Water}}{2H_2O}$$

   (*b*) **With NH_4OH:** On adding ammonium hydroxide drop by drop to a solution of lead salt, a **white precipitate** is formed which is **insoluble** in excess of ammonium hydroxide.

$$\underset{\text{Lead nitrate}}{Pb(NO_3)_2} + \underset{\text{Ammonium hydroxide}}{2NH_4OH} \longrightarrow \underset{\text{Lead hydroxide (White ppt.)}}{Pb(OH)_2\downarrow} + \underset{\text{Ammonium nitrate}}{2NH_4NO_3}$$

4. **Reaction of sodium hydroxide and ammonium hydroxide with the soluble salt of copper:**
   (*a*) **With NaOH:** On adding sodium hydroxide drop by drop to a solution of copper salt, a **bluish white precipitate** is formed which is **insoluble** in excess of Sodium hydroxide.

$$\underset{\text{Copper sulphate}}{CuSO_4} + \underset{\text{Sodium hydroxide}}{2NaOH} \longrightarrow \underset{\text{Copper hydroxide (Bluish white ppt.)}}{Cu(OH)_2\downarrow} + \underset{\text{Sodium sulphate}}{Na_2SO_4}$$

   (*b*) **With NH_4OH:** On adding ammonium hydroxide drop by drop to a solution of copper salt, a **pale blue** or **bluish white precipitate** is formed which dissolves in excess of ammonium hydroxide to give **deep blue** or **inky blue** or **prussian blue solution.**

$$\underset{\text{Copper sulphate}}{CuSO_4} + \underset{\text{Ammonium hydroxide}}{2NH_4OH} \longrightarrow \underset{\text{Copper hydroxide (Bluish white ppt.)}}{Cu(OH)_2 \downarrow} + \underset{\text{Ammonium sulphate}}{(NH_4)_2SO_4}$$

$$\underset{\text{Copper hydroxide}}{Cu(OH)_2} + \underset{\text{Ammonium hydroxide}}{4NH_4OH} \longrightarrow \underset{\text{Tetraamine copper hydroxide (Prussian blue solution)}}{[Cu(NH_3)_4](OH)_2} + \underset{\text{Water}}{4H_2O}$$

5. **Reaction of sodium hydroxide and ammonium hydroxide with the soluble salt of calcium:**
   (*a*) **With NaOH:** On adding sodium hydroxide drop by drop to a solution of calcium salt, a **white precipitate** is formed which is **insoluble** in excess of sodium hydroxide.

$$\underset{\text{Calcium nitrate}}{Ca(NO_3)_2} + \underset{\text{Sodium hydroxide}}{2NaOH} \longrightarrow \underset{\text{Calcium hydroxide (White ppt.)}}{Ca(OH)_2 \downarrow} + \underset{\text{Sodium nitrate}}{2NaNO_3}$$

   (*b*) **With NH_4OH:** No visible reaction.

6. **Reaction of Sodium hydroxide and Ammonium hydroxide with soluble salt of Ferrous:**
   (*a*) **With NaOH:** On adding sodium hydroxide drop by drop to a solution of ferrous salt, a **dirty green precipitate** is formed which turns **reddish brown** after sometime and is **insoluble** in excess of sodium hydroxide.

$$\underset{\text{Ferrous chloride}}{FeCl_2} + \underset{\text{Sodium hydroxide}}{2NaOH} \longrightarrow \underset{\text{Ferrous hydroxide (Dirty green ppt.)}}{Fe(OH)_2 \downarrow} + \underset{\text{Sodium chloride}}{2NaCl}$$

   (*b*) **With NH_4OH:** On adding ammonium hydroxide drop by drop to a solution of ferrous salt, a **dirty green precipitate** is formed which turns **reddish brown** after sometime and is **insoluble** in excess of ammonium hydroxide.

$$\underset{\text{Ferrous chloride}}{FeCl_2} + \underset{\text{Ammonium hydroxide}}{2NH_4OH} \longrightarrow \underset{\text{Ferrous hydroxide (Dirty green ppt.)}}{Fe(OH)_2 \downarrow} + \underset{\text{Ammonium chloride}}{2NH_4Cl}$$

7. **Reaction of sodium hydroxide and ammonium hydroxide with the soluble salt of ferric:**
   (*a*) **With NaOH:** On adding sodium hydroxide drop by drop to a solution of ferric salt, a **reddish brown precipitate** is formed which is **insoluble** in excess of sodium hydroxide.

$$\underset{\text{Ferric chloride}}{FeCl_3} + \underset{\text{Sodium hydroxide}}{3NaOH} \longrightarrow \underset{\text{Ferric hydroxide (Reddish brown ppt.)}}{Fe(OH)_3 \downarrow} + \underset{\text{Sodium chloride}}{3NaCl}$$

   (*b*) **With NH_4OH:** On adding ammonium hydroxide drop by drop to a solution of ferric salt, a **reddish brown precipitate** is formed which is **insoluble** in excess of ammonium hydroxide.

$$\underset{\text{Ferric chloride}}{FeCl_3} + \underset{\text{Ammonium hydroxide}}{3NH_4OH} \longrightarrow \underset{\text{Ferric hydroxide (Reddish brown ppt.)}}{Fe(OH)_3 \downarrow} + \underset{\text{Ammonium chloride}}{3NH_4Cl}$$

8. **Reaction of Sodium hydroxide and Ammonium hydroxide with soluble salt of Magnesium:**
   (*a*) **With NaOH:** On adding sodium hydroxide drop by drop to a solution of magnesium salt, a **white precipitate** appears which is **insoluble** in excess of sodium hydroxide.

$$\underset{\text{Magnesium nitrate}}{Mg(NO_3)_2} + \underset{\text{Sodium hydroxide}}{2NaOH} \longrightarrow \underset{\text{Magnesium hydroxide (White ppt.)}}{Mg(OH)_2} + \underset{\text{Sodium nitrate}}{2NaNO_3}$$

(*b*) **With NH_4OH:** On adding ammonium hydroxide drop by drop to a solution of magnesium salt, a **white precipitate** appears which is **insoluble** in excess of ammonium hydroxide.

$$\underset{\text{Magnesium nitrate}}{Mg(NO_3)_2} + \underset{\text{Ammonium hydroxide}}{2NH_4OH} \longrightarrow \underset{\text{Magnesium hydroxide (White ppt.)}}{Mg(OH)_2} + \underset{\text{Ammonium nitrate}}{2NH_4NO_3}$$

9. **Colour of salt solutions:** The salts on dissolving in water form different coloured salt solutions.

Name of the salt	Colour of the salt solution
(*i*) Ferrous salt	Pale green
(*ii*) Ferric salt	Yellow
(*iii*) Cupric salt	Blue (except $CuCO_3$ which is a green coloured insoluble salt)
(*iv*) Lead salt	Colourless solution (only two salts of lead are soluble in water: (*i*) lead nitrate (*ii*) lead acetate)
(*v*) Zinc salt	Colourless solutions
(*vi*) Calcium salt	Colourless solutions

10. **The acid radicals are divided in three main categories:**
   (*i*) The acid radicals or anions detected by **dilute Sulphuric acid** are
   (*a*) Carbonate – CO_3^{2-} (*b*) Sulphite – SO_3^{2-} (*c*) Sulphide – S^{2-}
   (*ii*) The acid radicals or anions detected by **concentrated Sulphuric acid** are
   (*a*) Chloride – Cl^- (*b*) Nitrate – NO_3^-
   (*iii*) The acid radical or anion **neither** detected by **dilute Sulphuric acid nor** by **concentrated Sulphuric acid** is
   Sulphate – SO_4^{2-}

11. **Detection of Carbonate**: On adding dilute Sulphuric acid to a metallic Carbonate a **colourless** and **odourless gas** evolved with **brisk effervescence** which turns Lime water **milky**.

$$\underset{\text{Sodium carbonate}}{Na_2CO_3} + \underset{\text{Sulphuric acid}}{H_2SO_4(dil.)} \longrightarrow \underset{\text{Sodium sulphate}}{Na_2SO_4} + \underset{\text{Water}}{H_2O} + \underset{\text{Carbon dioxide (Colourless, odourless gas with brisk effervescence)}}{CO_2\uparrow}$$

$$\underset{\text{Lime water}}{Ca(OH)_2} + CO_2 \longrightarrow \underset{\text{(White ppt.)}}{CaCO_3\downarrow} + H_2O$$

12. **Detection of Sulphite**: On adding dilute Sulphuric acid to a metallic Sulphite a **colourless gas** having **burning sulphur smell** evolves which turns acidified Potassium dichromate solution from **orange** to **green** and Potassium permanganate solution from **purple** to **colourless**, *i.e*, it decolourizes.

$$\underset{\text{Sodium sulphite}}{Na_2SO_3} + \underset{\text{Sulphuric acid}}{H_2SO_4(dil.)} \longrightarrow \underset{\text{Sodium sulphate}}{Na_2SO_4} + \underset{\text{Water}}{H_2O} + \underset{\text{Sulphur dioxide (milkiness)}}{SO_2\uparrow}$$

$$\underset{\text{Potassium dichromate (Orange)}}{K_2Cr_2O_7} + \underset{\text{Sulphur dioxide}}{3SO_2} + \underset{\text{Sulphuric acid}}{H_2SO_4} \longrightarrow \underset{\text{Potassium sulphate}}{K_2SO_4} + \underset{\text{Chromium sulphate (Green)}}{Cr_2(SO_4)_3} + \underset{\text{Water}}{H_2O}$$

$$\underset{\text{Potassium permanganate (Purple)}}{2KMnO_4} + \underset{\text{Water}}{2H_2O} + \underset{\text{Sulphur dioxide}}{5SO_2} \longrightarrow \underset{\text{Potassium sulphate}}{K_2SO_4} + \underset{\text{Manganese sulphate}}{2MnSO_4} + \underset{\text{Sulphuric acid}}{2H_2SO_4}$$

13. **Detection of Sulphide**: On adding dilute Sulphuric acid to metallic Sulphide a **colourless gas** having **rotten egg smell** evolves which turns lead acetate solution **black**.

$$\underset{\text{Ferrous sulphide}}{FeS} + \underset{\text{Sulphuric acid}}{H_2SO_4(dil.)} \longrightarrow \underset{\text{Ferrous sulphate}}{FeSO_4} + \underset{\text{Hydrogen sulphide (Colourless gas with rotten egg smell)}}{H_2S\uparrow}$$

$$\underset{\text{Lead acetate}}{(CH_3COO)_2Pb} + \underset{\text{Hydrogen sulphide}}{H_2S} \longrightarrow \underset{\text{Acetic acid}}{2CH_3COOH} + \underset{\text{Lead sulphide (Black ppt.)}}{PbS\downarrow}$$

14. **Detection of Chloride:** On adding concentrated Sulphuric acid to metallic Chlorides a **colourless gas** having **pungent suffocating smell** which **fumes in moist air** evolves which gives **white ppt.** with silver nitrate solution which is **soluble** in excess of Ammonium hydroxide and **dense white fumes** with Ammonium hydroxide.

$$\underset{\text{Sodium chloride}}{NaCl} + \underset{\text{Sulphuric acid}}{H_2SO_4(conc.)} \longrightarrow \underset{\text{Sodium bisulphate}}{NaHSO_4} + \underset{\text{Hydrogen chloride (Colourless gas with pungent suffocating smell)}}{HCl}$$

$$\underset{\text{Silver nitrate}}{AgNO_3} + \underset{\text{Hydrogen chloride}}{HCl} \longrightarrow \underset{\text{Silver chloride (White ppt.)}}{AgCl\downarrow} + \underset{\text{Nitric acid}}{HNO_3}$$

$$\underset{\text{Silver chloride}}{AgCl} + \underset{\text{Ammonium hydroxide}}{2NH_4OH} \longrightarrow \underset{\text{Diamminesilver chloride (Soluble)}}{[Ag(NH_3)_2]Cl} + \underset{\text{Water}}{2H_2O}$$

$$\underset{\text{Ammonium hydroxide}}{NH_4OH} + \underset{\text{Hydrogen chloride}}{HCl} \longrightarrow \underset{\text{Ammonium chloride (Dense white fumes)}}{NH_4Cl} + \underset{\text{Water}}{H_2O}$$

15. **Detection of Nitrate:** On adding concentrated Sulphuric acid to metallic Nitrate in presence of Copper turnings and heated strongly a **reddish brown gas** having **pungent suffocating smell** evolves which turns freshly prepared acidified Ferrous sulphate solution **brown black.**

$$\underset{\text{Potassium nitrate}}{KNO_3} + \underset{\text{Sulphuric acid}}{H_2SO_4(conc.)} \longrightarrow \underset{\text{Potassium bisulphate}}{KHSO_4} + \underset{\text{Nitric acid}}{HNO_3}$$

$$\underset{\text{Copper turnings}}{Cu} + \underset{\text{Nitric acid}}{4HNO_3} \longrightarrow \underset{\text{Cuprous nitrate}}{Cu(NO_3)_2} + \underset{\text{Water}}{2H_2O} + \underset{\text{Nitrogen dioxide (Reddish brown gas)}}{2NO_2\uparrow}$$