Chapter 3

Analytical Chemistry: Uses of Ammonium Hydroxide and Sodium Hydroxide

- Key Difference – Qualitative vs Quantitative Analysis in Chemistry:-

• Qualitative vs Quantitative Analysis in Chemistry	
• Qualitative analysis in chemistry is a branch of chemistry that analyses the chemical	• Quantitative analysis in chemistry is a branch of chemistry that deals with the

composition of a sample.	quantities of different components in a sample.
• Details	
• Qualitative analysis in chemistry gives the presence or absence of different chemical components in a sample.	• Quantitative analysis in chemistry gives the amount of different chemical components present in a given sample.
• Techniques	

• Qualitative analysis in chemistry uses techniques such as distillation, extraction, and change in colour, chromatography, etc.	• Quantitative analysis in chemistry uses techniques such as titrations, gravimetric analysis, combustion analysis, AES, etc.

- Color of the salts:-
- Salts of the elements of the group IA to VIIA are generally colourless.
- Salts of the transition elements of group IB to VIIB and group VIII are generally coloured.

Colourless ions		Coloured ions		
Cation	***Symbol***	***Cation***	***Symbol***	***Colour***
Ammonium ion	NH_4^+	Cupric ion	Cu^{2+}	Blue
Sodium ion	Na^+	Ferrous ion	Fe^{2+}	Light green
Potassium ion	K^+			
Calcium ion	Ca^{2+}	Ferric ion	Fe^{3+}	Yellowish brown
Magnesium ion	Mg^{2+}			
Aluminium ion	Al^{3+}	Nickel ion	Ni^{2+}	Green
Lead ion	Pb^{2+}	Chromium ion	Cr^{3+}	Green
Zinc ion	Zn^{2+}	Manganese ion	Mn^{2+}	Pink
Anion	***Symbol***	***Anion***	***Symbol***	***Colour***
Chloride ion	Cl^-	Permanganate ion	MnO_4^-	Pink / Purple
Sulphate ion	SO_4^{2-}			
Carbonate ion	CO_3^{2-}	Dichromate ion	$Cr_2O_7^{2-}$	Orange
Hydrogen carbonate ion	HCO_3	Chromate ion	CrO_4^{2-}	Yellow
Sulphide ion	S^{2-}			
Bromide ion	Br^-			
Acetate ion	CH_3COO^-			

- Precipitation:-

- A precipitation reaction is a type of chemical reaction in which two soluble salts in aqueous solution combine and one of the products is an insoluble salt called a precipitate. The precipitate may stay in the solution as a suspension, fall out of solution on its own, or can be separated from the liquid using centrifugation, decantation, or filtration. The liquid that remains when a precipitate forms is called the supernate.
- The reaction between silver nitrate and potassium chloride is a precipitation reaction because solid silver chloride is formed as a product. $AgNO_3(aq) + KCl(aq) \rightarrow AgCl(s) + KNO_3(aq)$

- The reaction may be recognized as a precipitation because two ionic aqueous solutions (aq) react to yield a solid product (s).
- **Action of sodium hydroxide solution on certain metallic salt solutions:-**

1. CALCIUM SALTS [Ca^{2+} ion]

$Ca(NO_3)_2$	+	2NaOH	→	$Ca(OH)_2\downarrow$	+	$2NaNO_3$	SPARINGLY SOLUBLE
Calcium nitrate (colourless)	+	Caustic soda (colourless)	→	Calcium hydroxide (white precipitate)	+	Sodium nitrate (colourless)	

2. IRON :

(A) FERROUS SALTS [Fe^{2+} ion]

$FeSO_4$	+	2NaOH	→	$Fe(OH)_2\downarrow$	+	Na_2SO_4	INSOLUBLE
Ferrous sulphate (pale green)	+	Caustic soda (colourless)	→	Ferrous hydroxide (dirty green, gelatinous ppt.)	+	Sodium sulphate (colourless)	

(B) FERRIC SALT [Fe^{3+} ion]

$FeCl_3$	+	3NaOH	→	$Fe(OH)_3\downarrow$	+	3NaCl	INSOLUBLE
Ferric chloride (yellow)	+	Caustic soda (colourless)	→	Ferric hydroxide (reddish brown ppt.)	+	Sodium chloride (colourless)	

3. COPPER SALTS [Cu^{2+} ion]

$CuSO_4$	+	2NaOH	→	$Cu(OH)_2\downarrow$	+	Na_2SO_4	INSOLUBLE
Copper sulphate (blue)	+	Caustic soda (colourless)	→	Copper (II) hydroxide (pale blue ppt.)	+	Sodium sulphate (colourless)	

4. ZINC SALTS [Zn^{2+} ion]

$ZnSO_4$	+	2NaOH	→	$Zn(OH)_2\downarrow$	+	Na_2SO_4	SOLUBLE
Zinc sulphate (colourless)	+	Caustic soda (colourless)	→	Zinc hydroxide (white, gelatinous ppt.)	+	Sodium sulphate (colourless)	$Zn(OH)_2 + 2NaOH$ (excess) $\rightarrow Na_2ZnO_2 + 2H_2O$ Sodium zincate (colourless)

5. LEAD SALTS [Pb^{2+} ion]

$Pb(NO_3)_2$	+	2NaOH	→	$Pb(OH)_2\downarrow$	+	$2NaNO_3$	SOLUBLE
Lead nitrate (colourless)	+	Caustic soda (colourless)	→	Lead hydroxide (white ppt.)	+	Sodium nitrate (colourless)	$Pb(OH)_2 + 2NaOH$ (excess) $\rightarrow Na_2PbO_2 + 2H_2O$ Sodium plumbite (colourless)

(White precipitate of lead hydroxide is readily soluble in acetic acid)

5. AMMONIUM SALTS [NH_4^+ ion]

When Sodium hydroxide (or any water soluble base) is heated with ammonium salts, ammonia gas is evolve

$$NH_4Cl + NaOH \xrightarrow{\Delta} NaCl + H_2O + NH_3$$

$$(NH_4)_2SO_4 + 2NaOH \xrightarrow{\Delta} Na_2SO_4 + 2H_2O + 2NH_3$$

1. CALCIUM SALTS

No precipitation of $Ca(OH)_2$ occurs even with addition of excess of NH_4OH. This is because the concentration of OH^- ions from the ionisation of NH_4OH is so low that it cannot precipitate the hydroxide of calcium.

2. IRON

(A) IRON (II) SALTS [Fe^{2+} ion]

$FeSO_4 + 2NH_4OH \rightarrow Fe(OH)_2\downarrow + (NH_4)_2SO_4$

(green) (dirty green ppt.) [colourless in solution] — INSOLUBLE

(B) IRON (III) SALTS [Fe^{3+} ion]

(i) $FeCl_3 + 3NH_4OH \rightarrow Fe(OH)_3\downarrow + 3NH_4Cl$

(yellow solution) (reddish brown ppt.) [colourless in solution] — INSOLUBLE

(ii) $Fe_2(SO_4)_3 + 6NH_4OH \rightarrow 2Fe(OH)_3\downarrow + 3(NH_4)_2SO_4$

(yellow solution) (reddish brown ppt.) (colourless in solution)

3. COPPER (II) SALTS [Cu^{2+} ion]

$CuSO_4 + 2NH_4OH \rightarrow Cu(OH)_2\downarrow + (NH_4)_2SO_4$

(blue) (Pale blue ppt.) (colourless in solution) — SOLUBLE

With excess of NH_4OH ppt. dissolves

$Cu(OH)_2 + (NH_4)_2SO_4 + 2NH_4OH \rightarrow [Cu(NH_3)_4]SO_4 + 4H_2O$

Tetrammine copper (II) sulphate (deep blue solution)

This reaction is a characteristic property of Cu^{2+} ion and is used for its detection in qualitative analysis.

4. ZINC SALTS [Zn^{2+} ion]

(i) $ZnSO_4 + 2NH_4OH \rightarrow Zn(OH)_2\downarrow + (NH_4)_2SO_4$

(colourless solution) (white, gelatinous ppt.) (colourless in solution) — SOLUBLE

With excess of NH_4OH ppt. dissolves.

$Zn(OH)_2 + (NH_4)_2SO_4 + 2NH_4OH \rightarrow [Zn(NH_3)_4]SO_4 + 4H_2O$

Zinc hydroxide (excess) Tetrammine zinc (II) sulphate (colourless solution)

(ii) $ZnCl_2 + 2NH_4OH \rightarrow Zn(OH)_2\downarrow + 2NH_4Cl$

(colourless solution) (white, gelatinous ppt.) (colourless in solution)

With excess of NH_4OH ppt. dissolves

$Zn(OH)_2 + 2NH_4Cl + 2NH_4OH \rightarrow [Zn(NH_3)_4]Cl_2 + 4H_2O$

(excess) Tetrammine zinc (II) chloride (colourless solution)

5. LEAD SALTS [Pb^{2+} ion]

$Pb(NO_3)_2 + 2NH_4OH \rightarrow Pb(OH)_2\downarrow + 2NH_4NO_3$

(white) (chalky white ppt.) — INSOLUBLE

- **Action of ammonium hydroxide on**

certain salt solutions:-

METAL		ALKALI		SALT		HYDROGEN
1. ZINC						
(i) Zn	+	2NaOH (Hot and conc.)	→	Na_2ZnO_2 Sodium zincate (colourless)	+	H_2
(ii) Zn	+	2KOH (Hot and conc.)	→	K_2ZnO_2 Potassium zincate (colourless)	+	H_2
2. ALUMINIUM						
Aluminium reacts only with boiling and dilute alkalis						
(i) 2Al + 2NaOH	+	$2H_2O$	→	$2NaAlO_2$ Sodium aluminate (colourless)	+	$3H_2$
(ii) 2Al + 2KOH	+	$2H_2O$	→	$2KAlO_2$ Potassium aluminate	+	$3H_2$
3. LEAD						
(i) Pb	+	2NaOH	→	Na_2PbO_2 Sodium plumbite (colourless)	+	H_2
(ii) Pb	+	2KOH	→	K_2PbO_2 Potassium plumbite (colourless)	+	H_2

- **Action of alkalis on certain metals:-**
- **Oxides and hydroxides:-**

- OXIDES OF ALKALINE EARTH METALS - DEFINITION
- All the elements of group 2 burns with oxygen gas to produce metallic oxide. The oxides of alkaline earth metals are less basic. Oxides become more basic on increas in electropositive character.

- HYDROXIDES OF ALKALINE EARTH METAL - DEFINITION
- Alkaline earth metals have tendency to form hydroxides which decrease as moving down in the group. All the hydroxides are basic in nature which decreases on moving down the group.

- **What are Oxides?**
- The classification of oxides is done into neutral, amphoteric and basic or acidic based on their acid-base characteristics.
- An acidic oxide is an oxide which when combined with water gives off an acid.

- A basic oxide is an oxide which when combined with water gives off a base.

AMPHOTERIC OXIDE / HYDROXIDE	OXIDE / HYDROXIDE	+ ALKALI		SALT	+ WATER
1. Zinc oxide / Zinc hydroxide	(i) ZnO (white)	+ $2NaOH$	⟶	Na_2ZnO_2 Sodium zincate (colourless, soluble)	+ H_2O
	$Zn(OH)_2$	+ $2NaOH$	⟶	Na_2ZnO_2	+ $2H_2O$
	(ii) ZnO (white)	+ $2KOH$	⟶	K_2ZnO_2 Potassium zincate (colourless, soluble)	+ H_2O
	$Zn(OH)_2$	+ $2KOH$	⟶	K_2ZnO_2	+ $2H_2O$
2. Aluminium oxide / Aluminium hydroxide	(i) Al_2O_3 (white)	+ $2NaOH$	⟶	$2NaAlO_2$ Sodium aluminate (white)	+ H_2O
	$Al(OH)_3$	+ $NaOH$	⟶	$NaAlO_2$	+ $2H_2O$
	(ii) Al_2O_3 (white)	+ $2KOH$	⟶	$2KAlO_2$ Potassium aluminate (white)	+ H_2O
	$Al(OH)_3$	+ KOH	⟶	$KAlO_2$	+ $2H_2O$
3. Lead oxide / Lead hydroxide	(i) PbO (yellow)	+ $2NaOH$	⟶	Na_2PbO_2 Sodium plumbite (colourless, soluble)	+ H_2O
	$Pb(OH)_2$	+ $2NaOH$	⟶	Na_2PbO_2	+ $2H_2O$
	(ii) PbO (yellow)	+ $2KOH$	⟶	K_2PbO_2 Potassium plumbite (colourless, soluble)	+ H_2O
	$Pb(OH)_2$	+ $2KOH$	⟶	K_2PbO_2	+ $2H_2O$

- When a substance reacts chemically, both as a base or acid it termed as an amphoteric solution.
- Neutral Oxide is one which neither has an acidic characteristic or a basic one.

- Metal Oxides have an oxidation number of -2 and generally comprise of an oxygen anion. The Earth’s crust is mostly made up of oxides that are solid. Oxide coatings can get formed over pure elements too, for instance, a foil made of aluminum gets covered by a thin skin of Al_2O_3, and this skin defends the rest of the foil from corrosion.
- **Classification Of Oxides**
- Depending upon nature and the properties exhibited by compounds, they are classified into
- Acidic oxides
- Basic oxides
- Amphoteric oxides
- Neutral oxides

- **Basic oxide:**
- Metals react with oxygen to give basic compounds of oxygen. These compounds are usually ionic in nature. Group 1, 2 and lanthanides form basic compounds of oxygen when they react with dioxygen. During the formation of these compounds, a large amount of energy is released. These compounds readily react with water except few exceptions.
- Examples: M_2O_3, MO_2, ThO_2
- $Na_2O + H_2O \rightarrow 2NaOH$
- **Acidic oxide:**
- Non-metals react with oxygen to form acidic compounds of oxides which are held together by covalent bonds. These compounds can also be called

as acid anhydrides. Acid anhydrides usually have a low melting and boiling point except for compounds like B_2O_3 and SiO_2 which have high melting points and form giant molecules.

- Examples: NO, CO_2
- $SO_3 + H_2O \rightarrow H_2SO_4$
- $B_2O_3 + H_2O \rightarrow 2H_3BO_3$
- **Amphoteric oxide:**
- Amphoteric oxides are compounds of oxygen which exhibits both acidic as well as basic characteristics. These oxides when reacting with acid undergoes a neutralization reaction to form water and salt. This exhibits the basic property of the compounds. Similarly reacts with the alkali to form

salt and water, exhibiting acidic property. Example: aluminium oxide

- Acidic characteristics:
- $AL_2O_3 + 6HCl \rightarrow 2Al_3+ + 6Cl– + 3H_2O$
- Basic characteristics:
- $Al_2O_3 +2OH– + 3H_2O \rightarrow 2[Al (OH)_4]–$
- **Neutral Oxides:**
- Some compounds react with oxygen to form oxides which do not exhibit acidic nor basic characteristics. Such compounds are called as neutral compounds of oxygen.
- Example: NO, CO.
- ***QUESTIONS:-***

- *Short Answer Questions*

- **Write the balanced equations for the reaction between aluminum oxide and sodium hydroxide.**
- **What do you observe when excess of NH3 is passed through an aqueous solution of lead nitrate?**
- **From the list of metals given below, select a metal whose hydroxide is soluble in sodium hydroxide solution: Ca, Mg, Fe and Zn.**
- **Write balanced equations for (a) Al and (b) Zn, when warmed with caustic soda solution.**
- **What would you observe when NH4OH solution is added to iron(III)sulphate solution?**

- Write a balanced equation for the following: iron (III) chloride solution with NaOH solution.
- Long Answer Questions
- NaOH solution is added to the solutions containing the ions mentioned in List X. List Y gives the details of the precipitate. Match the ions with their coloured precipitates
- List X List Y
  - a. Pb^{+2}
    i. Reddish brown
  - b. Fe^{+2}
    ii. White insoluble in excess
  - c. Zn^{+2}
    iii. Dirty green

- d. Fe+3
  iv. White soluble in excess
- e. Cu+2
  v. White soluble in excess
- f. Ca+2
  vi. Blue

- Write the equation for the following reactions:

- a. ZnO is treated with NaOH solution. b. NH_4Cl is heated with NaOH.
- Identify the substances P, Q and R in each case based in the information given below:
  - The deliquescent salt P, turns yellow on dissolving in water, and gives a reddish brown

precipitate with NaOH solution.

- The white crystalline solid Q is soluble in water. It liberates a pungent smelling gas when heated with sodium hydroxide solution.

- The pale green solid R turns reddish brown on heating. Its aqueous solution gives a white precipitate with barium chloride solution. The precipitate is soluble in mineral acids.

- Give one chemical test to distinguish between the following pairs of compounds iron (II) chloride, solution and iron (III) chloride solution.

- Give one test each to distinguish between the following pairs of chemicals:
  - Zinc nitrate solution and Calcium nitrate solution.
  - Iron(III) chloride solution and copper chloride solution.
- The questions (a) and (b) given below refer to the following salt solutions listed A to F:
- A: $Cu(NO_3)_2$ B: $FeSO_4$ C: $FeCl_3$ D: $Pb(NO_3)_2$ E: $MgSO_4$ F: $ZnCl_2$
  - Which salt solution becomes deep inky blue in colour when excess of ammonium hydroxide solution is added to it?

- Which salt solution gives a white precipitate with excess of NH_4OH solution?

- 7. NaOH solution is added first in a small quantity and then in excess to each of the aqueous salt solutions given below: $CuSO_4$, $Zn(NO_3)_2$, $Pb(NO_3)_2$, $CaCl_2$ and $Fe_2(SO_4)_3$. Copy the following table.
- Also, write the color of the precipitate obtained in (A) to (E) and the nature of the precipitate (soluble or insoluble) in (F) to (J):

• Aqueous salt solution	• Ppt col or	• Nature of ppt with

	with little NaOH	excess NaOH (Soluble or Insoluble)
• Copper(II)sulphate	• A	• F
• Zinc nitrate	• B	• G
• Lead nitrate	• C	• H
• Calcium chloride	• D	• I
• Iron(III)sulphate	• E	• J

- What do you observe when NH4OH solution is added in excess to CuSO4 solution?
- What do you observe when NaOH solution is added to Zinc sulphate solution is excess?
- a. How would you distinguish between Zn+2 and Pb+2 ions using NH4OH solution?
- b. The following table shows the tests a student performed on aqueous solution of A and B. What are his observations?

• Test	• Observations	• Conclusions

• To solution A, NaOH was added	•	• A contains Fe+3 ions
• To solution B, NH4OH was added slowly till it was in	•	• B contains Cu+2 ions.

excess		

- State the effect of adding to small amount of
- (i) NaOH (ii) NH4OH – followed by an excess of (a) Ca(NO3)2 (b) Zn(NO3)2 (c) Pb(NO3)2 solutions.