4 Analytical Chemistry : Units of Ammonium Hydroxide and Sodium Hydroxide

SYLLABUS

Analytical Chemistry – Use of Ammonium Hydroxide and Sodium Hydroxide.

(i) On solution of salts: colour of salt and its solution; formation and colour of hydroxide precipitated for solutions of salts of Ca, Fe, Cu, Zn and Pb; special action of ammonium hydroxide on solutions of copper salt and sodium hydroxide on ammonium salts.

On solution of salts :

- *Colour of salt and its solution.*
- *Action on addition of Sodium Hydroxide to solution of Ca, Fe, Cu, Zn and Pb salts drop by drop in excess. Formation and colour of hydroxide precipitated to be highlighted with the help of equations.*
- *Action on addition of Ammonium Hydroxide to solution of Ca, Fe, Cu, Zn and Pb salts drop by drop in excess. Formation and colour of hydroxide precipitated to be highlighted with the help of equations.*
- *Special action of Ammonium Hydroxide on solutions of copper salts and sodium hydroxide on ammonium salts.*

(ii) On certain metals and their oxides (relevant laboratory work is essential).

The metals must include zinc and aluminium, their oxides and their hydroxides, which react with caustic alkalis (NaOH, KOH), showing the amphoteric nature of these substances.

INTRODUCTION

Determination of the chemical components in a given sample is called **Analysis**. In chemistry, we study two types of analysis, ***Qualitative analysis*** which involves the identification of the unknown substances, and ***Quantitative analysis*** which involves the determination of composition of a mixture.

Qualitative analysis, *i.e.,* identification of an unknown substance is done by carrying out chemical tests with the help of *reagents*. A ***reagent*** is a substance that reacts with another substance.

Alkalis are important laboratory reagents. When they are added to certain salt solution characteristic coloured precipitates of metallic hydroxides are formed. Thus a metal ion is identified.

4.1 COLOURS OF THE SALTS AND THEIR SOLUTIONS

The salts of **'representative elements'** of the periodic table, *i.e.,* the elements of the Groups 1, 2, and 13 to 17 are generally **colourless**, while those of the **'transition elements'**, *i.e.,* salts of elements of Groups 3 to 12 are generally coloured.

Different colours of coloured salts help in their identification during qualitative analysis. Some examples of colourless and coloured ions are given below :

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 or Purple
Sulphate ion	SO_4^{2-}			
Carbonate ion	CO_3^{2-}	Dichromate ion	$Cr_2O_7^{2-}$	Orange
Nitrate	NO_3^-			
Hydrogen carbonate ion	HCO_3^-	Chromate ion	CrO_4^{2-}	Yellow
Sulphide ion	S^{2-}			
Bromide ion	Br^-			
Acetate ion	CH_3COO^-			

Action of alkali on metal cations results in the formation of their hydroxides which often appear as precipitates.

Precipitation is the process of formation of an insoluble solid when solutions are mixed. The solid thus formed is called precipitate. Only those compounds form precipitates which are insoluble in water.

4.2 ACTION OF SODIUM HYDROXIDE SOLUTION ON CERTAIN METALLIC SALT SOLUTIONS

When the sodium hydroxide (caustic soda) solution is added drop by drop to the solution of metallic salts, the metal hydroxide formed gets precipitated. Colour of the precipitate identifies the metal ion. Some precipitated metallic hydroxides dissolve in excess of sodium hydroxide solution to give soluble complexes.

SALT SOLUTION	+ ALKALI	→ METAL HYDROXIDE [PPT.]	+ SALT FORMED IN SOLUTION	COLOUR OF PPT AND ITS SOLUBILITY IN EXCESS OF ALKALI
1. CALCIUM SALTS [Ca^{2+} ion]				WHITE SPARINGLY SOLUBLE
$Ca(NO_3)_2$	+ **2NaOH**	→ **$Ca(OH)_2\downarrow$**	+ **$2NaNO_3$**	
Calcium nitrate (colourless)	+ Caustic soda (colourless)	→ Calcium hydroxide (white precipitate)	+ Sodium nitrate (colourless)	
2. IRON :				
(A) FERROUS SALTS [Fe^{2+} ion]				DIRTY GREEN INSOLUBLE
$FeSO_4$	+ **2NaOH**	→ **$Fe(OH)_2\downarrow$**	+ **Na_2SO_4**	
Ferrous sulphate (pale green)	+ Caustic soda (colourless)	→ Ferrous hydroxide (dirty green, gelatinous ppt.)	+ Sodium sulphate (colourless)	
(B) FERRIC SALT [Fe^{3+} ion]				REDDISH BROWN INSOLUBLE
$FeCl_3$	+ **3NaOH**	→ **$Fe(OH)_3\downarrow$**	+ **3NaCl**	
Ferric chloride (yellow)	+ Caustic soda (colourless)	→ Ferric hydroxide (reddish brown ppt.)	+ Sodium chloride (colourless)	
3. COPPER SALTS [Cu^{2+} ion]				PALE BLUE INSOLUBLE
$CuSO_4$	+ **2NaOH**	→ **$Cu(OH)_2\downarrow$**	+ **Na_2SO_4**	
(blue)	(colourless)	(pale blue ppt.)	(colourless)	
4. ZINC SALTS [Zn^{2+} ion]				GILATINOUS WHITE SOLUBLE
$ZnSO_4$	+ **2NaOH**	→ **$Zn(OH)_2\downarrow$**	+ **Na_2SO_4**	
(colourless)	(colourless)	(white, gelatinous ppt.)	(colourless)	
(With excess of NaOH ppt dissolves)				
$Zn(OH)_2$	+ **2NaOH** (excess)	→ **Na_2ZnO_2** Sodium zincate (colourless)	+ **$2H_2O$**	
5. LEAD SALTS [Pb^{2+} ion]				CHALKY WHITE SOLUBLE
$Pb(NO_3)_2$	+ **2NaOH**	→ **$Pb(OH)_2\downarrow$**	+ **$2NaNO_3$**	
(colourless)	(colourless)	(white ppt.)	(colourless)	
(With excess of NaOH ppt dissolves)				
$Pb(OH)_2$	+ **2NaOH** (excess)	→ **Na_2PbO_2** Sodium plumbite (colourless)	+ **$2H_2O$**	
(White precipitate of lead hydroxide is readily soluble in acetic acid)				
6. AMMONIUM SALTS [NH_4^+ ion]				
When Sodium hydroxide (or any water soluble base) is heated with ammonium salts, ammonia gas is evolved.				
NH_4Cl	+ **NaOH**	$\xrightarrow{\Delta}$ **NaCl**	+ **$H_2O + NH_3$**	
$(NH_4)_2SO_4$	+ 2NaOH	$\xrightarrow{\Delta}$ Na_2SO_4	+ $2H_2O + 2NH_3$	

Note : Potassium hydroxide (caustic potash) solution also shows similar behaviour.

4.3 ACTION OF AMMONIUM HYDROXIDE ON CERTAIN SALT SOLUTIONS

When ammonium hydroxide solution is added dropwise to the solutions of metallic salts, precipitates of their hydroxides are formed, which are identified by their distinct colours. Some precipitated metallic hydroxides are soluble in excess of ammonium hydroxide, because of the formation of soluble amino complexes on further reaction with excess of NH_4OH.

SALT SOLUTION + AMMONIUM HYDROXIDE → METAL HYDROXIDE + SALT FORMED IN SOLUTION	COLOUR OF PPT AND ITS SOLUBILITY IN EXCESS OF AMMONIUM HYDROXIDE
1. CALCIUM SALTS **No precipitation** 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]** $FeSO_4$ + $2NH_4OH$ → $Fe(OH)_2\downarrow$ + $(NH_4)_2SO_4$ (green) (dirty green ppt.) [colourless in solution]	DIRTY GREEN PPT INSOLUBLE
(B) IRON (III) SALTS [Fe^{3+} ion]	REDDISH BROWN PPT
(i) $FeCl_3$ + $3NH_4OH$ → $Fe(OH)_3\downarrow$ + $3NH_4Cl$ (yellow solution) (reddish brown ppt.) [colourless in solution]	INSOLUBLE
(ii) $Fe_2(SO_4)_3$ + $6NH_4OH$ → $2Fe(OH)_3\downarrow$ + $3(NH_4)_2SO_4$ (yellow solution) (reddish brown ppt.) (colourless in solution)	
3. COPPER (II) SALTS [Cu^{2+} ion] $CuSO_4$ + $2NH_4OH$ → $Cu(OH)_2\downarrow$ + $(NH_4)_2SO_4$ (blue) (Pale blue ppt.) (colourless in solution)	PALE BLUE PPT
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 or $Cu(OH)_2 + 4NH_4OH \rightarrow [Cu(NH_3)_4](OH)_2 + 4H_2O$ Tetrammine copper hydroxide	SOLUBLE in excess of NH_4OH and forms 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] $ZnSO_4$ + $2NH_4OH$ → $Zn(OH)_2\downarrow$ + $(NH_4)_2SO_4$ (colourless solution) (white, gelatinous ppt.) (colourless in solution)	GELATINOUS WHITE PPT
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) OR $Zn(OH)_2 + 4NH_4OH \rightarrow [Zn(OH_3)_4](OH)_2 + 4H_2O$ Tetrammine zinc hydroxide	SOLUBLE in excess of NH_4OH
5. LEAD SALTS [Pb^{2+} ion] $Pb(NO_3)_2$ + $2NH_4OH$ → $Pb(OH)_2\downarrow$ + $2NH_4NO_3$ (colourless) (white ppt.)	CHALKY WHITE PPT INSOLUBLE

Intext Questions

1. What do you understand by the following :
   (i) Analysis, (ii) Qualitative analysis, (iii) Reagent, (iv) Precipitation ?
2. Write the probable colour of the following salts :
   (i) Iron (III) chloride, (ii) Potassium nitrate, (iii) Ferrous sulphate, (iv) Aluminium acetate,
3. Name the probable cation present based on the following observations :
   (i) White precipitate insoluble in NH_4OH but soluble in NaOH (ii)Blue coloured solution,
4. Name the metal hydroxides which are :
   (i) Insoluble, (ii) Soluble,
   in (a) Caustic soda solution (b) Ammonium hydroxide solution.
5. What do you observe when ammonium salt is heated with caustic soda solution ? Write the word equation.
6. How will you distinguish NH_4OH solution from NaOH solution ?
7. Why the alkali is added drop by drop to the salt solution.
   Ans: If alkali is added too quickly, it is easy to miss a precipitate that redissolves in excess.

4.4 ACTION OF ALKALIS ON CERTAIN METALS

Certain metals like zinc, aluminium and lead react with hot concentrated caustic alkalis (NaOH, KOH) to give the corresponding soluble salt and liberate hydrogen.

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 with boiling caustic alkalis solution						
(i) 2Al + 2NaOH +		$2H_2O$	→	$2NaAlO_2$ Sodium meta aluminate (colourless)	+	$3H_2$
(ii) 2Al + 2KOH +		$2H_2O$	→	$2KAlO_2$ Potassium meta 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

4.5 ACTION OF ALKALIS ON METAL OXIDES

Oxides of most of the metals are basic in nature. They dissolve in water forming hydroxides (or alkalis). These metal oxides and hydroxides neutralize acids but *do not react with bases.*

For example :

Na_2O (Sodium oxide) + H_2O → 2NaOH (Sodium hydroxide)

$Na_2O + 2HCl \rightarrow 2NaCl + H_2O$

$NaOH + HCl \rightarrow NaCl + H_2O$

A few metallic oxides and hydroxides exhibit dual character, *i.e.,* they show acidic as well as basic character. They are said to be **amphoteric** in nature.

For example :

Zinc oxide and zinc hydroxide react with both acids and concentrated alkalis (NaOH and KOH) forming salt and water.

ZnO (Zinc oxide) + $2HCl$ (Hydrochloric acid) → $ZnCl_2$ (Zinc chloride) + H_2O (Water)

$Zn(OH)_2$ (Zinc hydroxide) + $2HCl \rightarrow ZnCl_2 + 2H_2O$

ZnO (Zinc oxide) + $2NaOH$ (Sodium hydroxide) → Na_2ZnO_2 (Sodium zincate) + H_2O (Water)

$Zn(OH)_2$ (Zinc hydroxide) + $2NaOH$ (Alkali) → Na_2ZnO_2 (Sodium zincate) + $2H_2O$ (Water)

Amphoteric oxides and hydroxides are those compounds which react with both acids and alkalis to form salt and water.

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 meta aluminate	+	H_2O
	$Al(OH)_3 + NaOH$	⟶	$NaAlO_2$	+	$2H_2O$
	(ii) Al_2O_3 (white) + $2KOH$	⟶	$2KAlO_2$ Potassium meta aluminate	+	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	+	$2H_2O$

EXERCISE

1. Write the probable colour of the following salts :
   (a) Ferrous salts (b) Ammonium salts
   (c) Cupric salts (d) Calcium salts
   (e) Aluminium salts.

2. Name :
   (a) a metallic hydroxide soluble in excess of NH_4OH.
   (b) a metallic oxide soluble in excess of caustic soda solution.
   (c) a strong alkali.
   (d) a weak alkali.
   (e) two colourless metal ions.
   (f) two coloured metal ions.
   (g) a metal that evolves a gas which burns with a pop sound when boiled with alkali solutions.
   (h) two bases which are not alkalis but dissolve in strong alkalis.
   (i) a coloured metallic oxide which dissolves in alkalis to yield colourless solutions.
   (j) a colourless cation not a representative element.

3. Write balanced equations for Q. 2 (g) and (i).

4. What happens when ammonia solution is added first dropwise and then in excess to the following solutions :
   (i) $CuSO_4$ (ii) $ZnSO_4$ (iii) $FeCl_3$.
   Write balanced equations for these reactions.

5. What do you observe when caustic soda solution is added to the following solution, first a little and then in excess:
   (a) $FeCl_3$, (b) $ZnSO_4$,
   (c) $Pb(NO_3)_2$, (d) $CuSO_4$?
   Write balanced equations for these reactions.

6. Name the chloride of a metal which is soluble in excess of ammonium hydroxide. Write equation for the same.

7. On adding dilute ammonia solution to a colourless solution of a salt, a white gelatinous precipitate appears. This precipitate however dissolves on addition of excess of ammonia solution. Identify (choose from Na, Al, Zn, Pb, Fe)
   (a) Which metal salt solution was used ?
   (b) What is the formula of the white gelatinous precipitate obtained ?

8. Name :
   (a) a yellow monoxide that dissolves in hot and concentrated caustic alkali.
   (b) a white, insoluble oxide that dissolves when fused with caustic soda or caustic potash.
   (c) a compound containing zinc in the anion.

9. Select the correct answers :
   (a) Colour of an aqueous solution of copper sulphate is
      (i) Green (ii) Brown
      (iii) Blue (iv) Yellow
   (b) Colour of the precipitate formed on adding NaOH solution to iron (II) sulphate solution is
      (i) White (ii) Brown
      (iii) Green (iv) Pale blue
   (c) A metal which produces hydrogen on reactng with alkali as well as with acid.
      (i) Iron (ii) Magnesium
      (iii) Zinc (iv) Copper

10. What do you observe when freshly precipitated aluminium hydroxide reacts with caustic soda solution ? Give balanced equation.

11. You are provided with two reagent bottles marked A and B. One of which contains NH_4OH solution and the other contains NaOH solution. How will you identify them by a chemical test ?

12. Distinguish by adding :
   (a) Sodium hydroxide solution and
   (b) Ammonium hydroxide solution to
      (i) Calcium salt solution and lead salt solution .
      (ii) Lead salt solution and zinc salt solution.
      (iii) Copper salt solution and ferrous salt solution.
      (iv) Fe(II) salt solution and Fe(III) salt solution.
      (v) Ferrous nitrate and lead nitrate

13. How will you distinguish lead carbonate and zinc carbonate in solution ?

14. What is observed when hot concentrated caustic soda solution is added to (a) Zinc (b) Aluminium. Write balanced equations.

15. (a) What do you understand by amphoteric oxide ?
   (b) Give the balanced equations for the reaction with two different amphoteric oxides with a caustic alkali.
   (c) Name the products formed.

16. Write balanced equations for the following conversions
   (a) $ZnSO_4 \xrightarrow{A} Zn(OH)_2 \xrightarrow{B} Na_2ZnO_2$.
   (b) $CuSO_4 \xrightarrow{A} Cu(OH)_2 \xrightarrow{B} [Cu(NH_3)_4]SO_4$

For I.C.S.E. questions see Chapter 13