

Chapter 21 Chemical Analysis

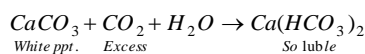
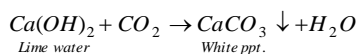
Analytical chemistry deals with qualitative and quantitative analysis of substances.

Qualitative analysis : A salt consists of two parts known as radicals. The positively charged part of a salt (cation) which has been derived from a base is termed as basic radical and the negatively charged part of salt (anion) which has been derived from an acid is termed as acidic radical. In qualitative inorganic analysis, the given compound is analysed for the basic and acid radicals (*i.e.*, the cations and the anions), that it contains. For example zinc blende is analysed for the Zn^{2+} and S^{2-} ions that it contains.

Test for Different Gases

(1) Colourless gases

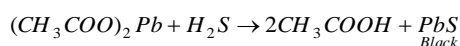
(i) **Tests for CO_2 :** It is colourless and odourless gas. It gives white ppt. with lime water which dissolves on passing excess of CO_2 .



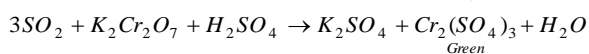
(ii) **Test for CO :** It is colourless and odourless gas. It burns with a blue flame. $2CO + O_2 \rightarrow 2CO_2$

(iii) **Test for O_2 :** It is colourless and odourless gas. It rekindles a glowing splinter.

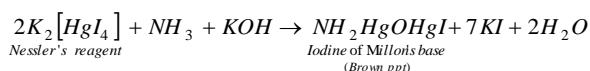
(iv) **Tests for H_2S :** It is a colourless gas with a smell of rotten eggs. It turns moist lead acetate paper black.



(v) **Tests for SO_2 :** It is a colourless gas with a suffocating odour of burning sulphur. It turns acidified $K_2Cr_2O_7$ solution green.

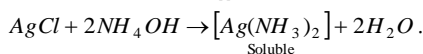
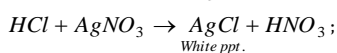


(vi) **Tests for NH_3 :** It is a colourless gas with a characteristic ammoniacal smell. It gives white fumes of NH_4Cl with HCl , $NH_3 + HCl \rightarrow NH_4Cl$. With Nessler's reagents, it gives brown ppt.



It gives deep blue colour with $CuSO_4$ solution, $CuSO_4 + 4NH_3 \rightarrow [Cu(NH_3)_4]SO_4$. NH_3 dissolves in water to give NH_4OH , which being basic, turns red litmus blue, $NH_3 + H_2O \rightarrow NH_4OH \rightleftharpoons NH_4^+ + OH^-$.

(vii) **Tests for HCl gas :** It is colourless gas with a pungent irritating smell. It turns moist blue litmus paper red *i.e.*, it is acidic in nature. It gives white ppt. with $AgNO_3$ solution. This white ppt. is soluble in NH_4OH .



(viii) **Test for CH_3COOH vapours :** These vapours are colourless with a vinegar like smell.

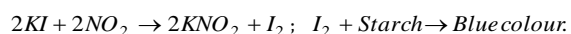
(2) Coloured gases

(i) **Tests for Cl_2 :** It is a greenish yellow gas with a pungent smell. In small quantity it appears almost colourless. It bleaches a moist litmus paper, $Cl_2 + H_2O \rightarrow 2HCl + [O]$; $Colour + [O] \rightarrow Colourless$ Blue litmus paper first turns red and then becomes colourless.

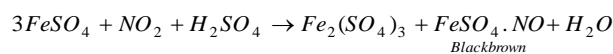
(ii) **Tests for Br_2 :** Brown vapours with a pungent smell. It turns moist starch paper yellow.

(iii) **Tests for I_2 :** Violet vapours with a pungent smell. It turns moist starch paper blue.

(iv) **Tests for NO :** Brown coloured pungent smelling gas. It turns moist starch KI paper blue



It turns ferrous sulphate solution black,



Systematic Procedure for Qualitative Analysis of Inorganic Salts

It involves the following steps : (1) Preliminary tests (2) Wet tests for acid radicals and (3) Wet tests for basic radicals.

(1) Preliminary tests

(i) **Physical examination** : It involves the study of colour, smell, density etc.

Table : 21.1 Colour

Colour	Salt
Black	Oxides : $MnO_2, FeO, CuO, Co_3O_4, Ni_2O_3$ Sulphides : $Ag_2S, CuS, Cu_2S, FeS, CoS, NiS, PbS, HgS, Bi_2S_3$ (blackish brown)
Blue	Hydrated $CuSO_4$, anhydrous $CoSO_4$
Orange	KO_2 , some dichromate ($K_2Cr_2O_7$), Sb_2S_3 , ferricyanides
Green	Nickel salts, hydrated ferrous salts, potassium permanganate ($KMnO_4$), some copper (II) salts
Brownish yellow	SnS
Dark brown	$PbO_2, Ag_2O, CdO, Fe_2O_3, CuCrO_4, FeCl_3$ (but yellow in aq. solution)
Pale brown	$MnCO_3$
Light pink	Hydrated manganese salts
Reddish pink	Hydrated cobalt (II) salts
Red	HgI_2, Pb_3O_4
Yellow	$CdS, PbI_2, AgBr, AgI$, chromates

(ii) **Dry heating** : Substance is heated in a dry test tube.

Table : 21.2

$2HgO \xrightarrow{\Delta} 2Hg + O_2$ (Red) (Silvery deposit)	$2Pb_3O_4 \xrightarrow{\Delta} 6PbO + O_2$ (Red) (Yellow)	$2PbO_2 \xrightarrow{\Delta} 2PbO + O_2$ (Brown)
$CuCO_3 \xrightarrow{\Delta} CuO + CO_2$ (Green)	$ZnO_3 \xrightarrow{\Delta} ZnO + CO_2$ (White) (Yellow (hot) White (cold))	$CuSO_4 \cdot 5H_2O \xrightarrow{\Delta} CuSO_4 + 5H_2O$ (Blue) (White)
$CuSO_4 \xrightarrow{\Delta} CuO + SO_3$	$2FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2 + SO_3$	$2Ag_2O \rightarrow 4Ag + O_2$
$2Zn(NO_3)_2 \xrightarrow{\Delta} 2ZnO + 4NO_2 + O_2$ (White) (Brown)	$2AgNO_3 \xrightarrow{450^\circ C} 2Ag + 2NO_2 + O_2$	$2Cu(NO_3)_2 \rightarrow 2CuO + 4NO_2 + O_2$

Observation	Result
(a) A gas or vapour is evolved.	Compounds with water of crystallisation
Vapour, evolved, test with litmus paper.	Ammonium salts, acid salts, and hydroxides. (usually accompanied by change of colour)
The vapour is alkaline.	Ammonium salts.
The vapour is acidic.	Readily decomposable salts of strong acids.
Oxygen is evolved	Nitrates, chlorates and certain oxides.
Dinitrogen oxide	Ammonium nitrate or nitrate mixed with an ammonium salt.
Dark-brown or reddish fumes (oxides of nitrogen), acidic in reaction.	Nitrates and nitrites of heavy metals.
CO_2 is evolved, lime water becomes turbid.	Carbonates or hydrogen carbonates.
NH_3 is evolved which turns red litmus blue.	Ammonium salts.
SO_2 is evolved, which turns acidified $K_2Cr_2O_7$ green, decolourises fuschin colour.	Sulphates and thiosulphates.
H_2S is evolved, turns lead acetate paper black, or cadmium acetate yellow.	Hydrates, sulphides or sulphides in the presence of water.
Cl_2 is evolved, yellowish green gas, bleaches litmus paper, turns KI - starch blue, poisonous.	Unstable chlorides e.g., copper chlorides in the presence of oxidising agents.
Br_2 is evolved (reddish brown, turns fluorescent paper red).	Bromides in the presence of oxidising agents.
I_2 is evolved, violet vapours condensing to black crystals	Free iodine and certain iodides
(b) A sublimate is formed	Ammonium and mercury salts.
White sublimate	As_2O_3, Sb_2O_3
Grey sublimate	Hg
Steel grey, garlic odour	As
Yellow sublimate	S, As_2S_3, HgI_2 (Red)

Action of heat on different compounds : Many inorganic salts decomposes on heating, liberating characteristic gases. A few such reactions are tabulated as follows,

Table : 21.3

$2Ag_2CO_3 \rightarrow 4Ag + 2CO_2 + O_2$	$2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$	$(NH_4)_2Cr_2O_7 \xrightarrow{\text{(Orange)}} N_2 + Cr_2O_3 + 4H_2O$ <small>(Green)</small>
$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$	$NH_4HCO_3 \rightarrow NH_3 + CO_2 + H_2O$	$CaCO_3 \rightarrow CaO + CO_2$
$2NaNO_3 \rightarrow 2NaNO_2 + O_2$	$MgCO_3 \rightarrow MgO + CO_2$	$2NH_3 \xrightarrow{\text{Red hot}} N_2 + 3H_2$
$2Mg(NO_3)_2 \rightarrow 2MgO + 4NO_2 + O_2$	$2Ca(NO_3)_2 \rightarrow 2CaO + 4NO_2 + O_2$	$Al_2(SO_4)_3 \xrightarrow{\text{Red hot}} Al_2O_3 + 3SO_3$
$2CaSO_4 \cdot 2H_2O \rightarrow 2CaSO_4 \cdot H_2O + 2H_2O$ <small>(Plaster of Paris)</small>	$2AlCl_3 \cdot 6H_2O \rightarrow Al_2O_3 + 6HCl + 9H_2O$	$2BeSO_4 \xrightarrow{\Delta} 2BeO + 2SO_2 + O_2$
$2AgNO_3 \xrightarrow{350^\circ C} 2AgNO_2 + O_2$	$2MgSO_4 \xrightarrow{\Delta} 2MgO + 2SO_2 + O_2$	$2ZnSO_4 \xrightarrow{\Delta} 2ZnO + 2SO_2 + O_2$
$(COO)_2Sn \xrightarrow{\Delta} SnO + CO_2 + CO$	$CaC_2O_4 \rightarrow CaCO_3 + CO$	$NH_4NO_2 \rightarrow N_2 + 2H_2O$
$NH_4NO_3 \rightarrow N_2O + 2H_2O$	$2KClO_3 \rightarrow 2KCl + 3O_2$	$2FeCl_3 \rightarrow 2FeCl_2 + Cl_2$
$Li_2CO_3 \rightarrow Li_2O + CO_2$	$(COO)_2Fe \rightarrow FeO + CO + CO_2$	$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$
$MgCl_2 \cdot 6H_2O \rightarrow HgCl_2 + Hg$	$NH_4Cl \rightarrow NH_3 + HCl$	$2LiNO_3 \rightarrow Li_2O + 2NO_2 + \frac{1}{2}O_2$
$Hg(NO_3)_2 \rightarrow Hg + 2NO_2 + O_2$	$2CuCl_2 \xrightarrow{\Delta} Cu_2Cl_2 + Cl_2$	$2Co(NO_3)_2 \xrightarrow{\Delta} 2CoO + 4NO_2 + O_2$
$4K_2Cr_2O_7 \rightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$	$2Mg(NH_4)PO_4 \xrightarrow{\Delta} Mg_2P_2O_7 + H_2O + 2NH_3$	
$2Zn(NH_4)PO_4 \xrightarrow{\Delta} Zn_2P_2O_7 + H_2O + 2NH_3$	$K_4Fe(CN)_6 \xrightarrow{\Delta} 4KCN + Fe + 2C + N_2$	
$ZnCl_2 \cdot 2H_2O \xrightarrow{\Delta} Zn(OH)Cl + HCl + H_2O$	$2(ZnCl_2 \cdot H_2O) \xrightarrow{\Delta} Zn_2OCl_2 + 2HCl + H_2O$	
$2[FeCl_3 \cdot 6H_2O] \xrightarrow{\Delta} Fe_2O_3 + 9H_2O + 6HCl$	$2ZnSO_4 \xrightarrow{800^\circ C} 2ZnO + 2SO_2 + O_2$	
$Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3$ <small>(Glassy bead)</small>		
$H_3BO_3 \xrightarrow{100^\circ C} HBO_2 \xrightarrow{160^\circ C} H_2B_4O_7 \xrightarrow{\text{Red hot}} B_2O_3$		
$ZnSO_4 \cdot 7H_2O \xrightarrow[-H_2O]{70^\circ C} ZnSO_4 \cdot 6H_2O \xrightarrow[-5H_2O]{100^\circ C} ZnSO_4 \cdot H_2O \xrightarrow{450^\circ C} ZnSO_4$		

(iii) Flame test

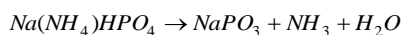
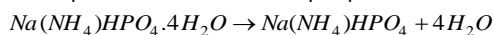
Characteristic flame colour : Certain metals and their salts impart specific colours to Bunsen burner flame.

- Pb* imparts pale greenish colour to the flame.
- Cu* and *Cu* salts impart blue or green colour to the flame.
- Borates also impart green colour to the flame.
- Ba* and its salts impart apple green colour to the flame.
- Sr* imparts crimson red colour to the flame.
- Ca* imparts brick red colour to the flame.
- Na* imparts yellow colour to the flame.
- K* imparts pink-violet (Lilac) colour to the flame.
- Li* imparts crimson-red, *Rb* imparts violet and *Cs* imparts violet colours to the flame.
- Livid- blue flame is given by *As*, *Sb* and *Bi*.
- (iv) **Borax bead test :** The transparent glassy bead ($NaBO_2 + B_2O_3$) when heated with inorganic salt and the colour produced gives some idea of cation present in it.

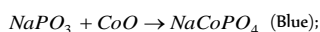
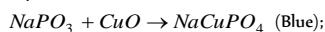
Table : 21.4

Colour of bead in oxidising flame	Colour of bead in reducing flame	Basic radical present
Greenish when hot, blue in cold.	Red and opaque	<i>Cu</i>
Dark green in hot and cold	Same	<i>Cr</i>
Deep - blue	Deep blue	<i>Co</i>
Yellow when hot	Green	<i>Fe</i>
Violet in hot and cold	Colourless	<i>Mn</i>
Brown in cold	Grey or black or opaque	<i>Ni</i>

Microcosmic salt bead test : Microcosmic salt, $Na(NH_4)HPO_4 \cdot 4H_2O$ is also used to identify certain cations just like borax. When microcosmic salt is heated in a loop of platinum wire, a colourless transparent bead of sodium metaphosphate is formed.



Now $NaPO_3$ reacts with metallic oxides to give coloured orthophosphates.

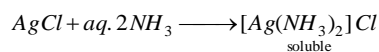
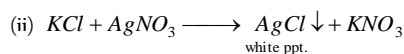
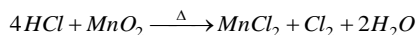
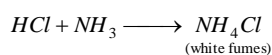
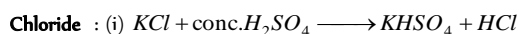


		$Ca(OH)_2 + SO_2 \longrightarrow CaSO_3$ (milky)
Solution gives smell of vinegar	CH_3COO^- (acetate)	Aq. Solution + neutral $FeCl_3 \rightarrow$ blood red colour $3CH_3COONa + FeCl_3 \longrightarrow Fe(CH_3COO)_3 + 3NaCl$ neutral (red)
White or yellowish white turbidity on warming	$S_2O_3^{2-}$ (thiosulphate)	Aq. Solution + $AgNO_3 \rightarrow$ white ppt. changing to black (viii) on warming $Na_2S_2O_3 + 2AgNO_3 \longrightarrow Ag_2S_2O_3 + 2NaNO_3$ white ppt. $Ag_2S_2O_3 + H_2O \longrightarrow Ag_2S + H_2SO_4$ black ppt.

Table : 21.8 Observation with concentrated H_2SO_4

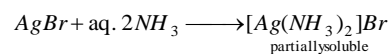
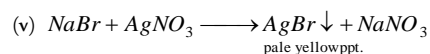
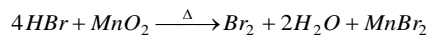
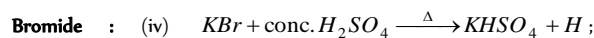
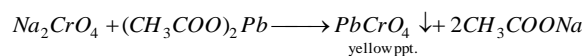
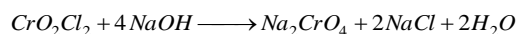
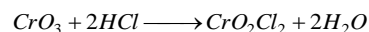
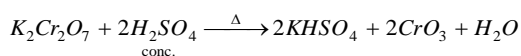
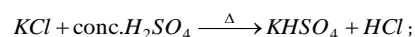
Observation	Acid Radical	Confirmatory Test
Colourless pungent gas giving white fumes with aq. NH_4OH	Cl^- (chloride)	Add MnO_2 in the same test tube and heat –pale green Cl_2 gas (i) $S.E. + HNO_3 + AgNO_3$ solution –white ppt. soluble in aq. NH_3 (ii) Chromyl chloride test (iii)
Reddish brown fumes	Br^- (bromide)	Add Mn_2O and heat –yellowish brown Br_2 gas (iv) $S.E. + HNO_3 + AgNO_3$ solution –pale yellow ppt. partially soluble aq. NH_3 (v) Layer test (vi)
Violet pungent vapours turning starch paper blue.	I^- (iodide)	$S.E. + HNO_3 + AgNO_3 \rightarrow$ yellow ppt. insoluble in aq. NH_3 (vii) Layer test (vi)
Brown pungent fumes intensified by the addition of Cu -turnings.	NO_3^- (nitrate)	Ring test (viii)
Colourless gases turning lime water milky and burning with blue flame.	$C_2O_4^{2-}$ (oxalate)	Acidified $KMnO_4$ solution is decolorised (ix) $S.E. + CH_3COOH + CaCl_2$ white ppt. decolorising acidified $KMnO_4$ solution (x)

Reactions

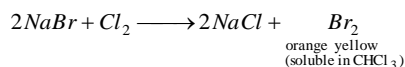


(iii) **Chromyl- chloride test :**

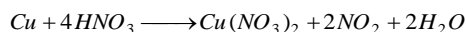
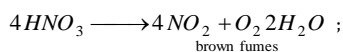
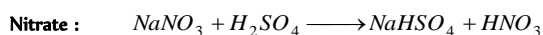
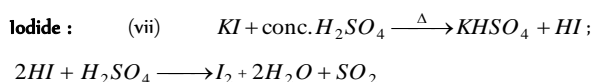
Chloride + $K_2Cr_2O_7$ (solid) + conc. $H_2SO_4 \xrightarrow{\text{heat}}$ reddish brown vapours of chromyl-chloride (CrO_2Cl_2). Pass these vapours into $NaOH$, when yellow Na_2CrO_4 solution is formed. On adding CH_3COOH and $(CH_3COO)_2 Pb$, yellow ppt. of lead chromate ($PbCrO_4$) is formed.



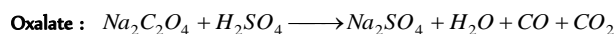
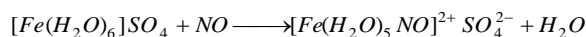
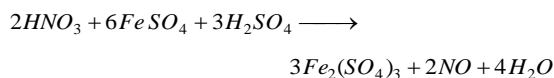
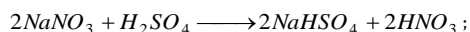
(vi) **Layer Test** : $S.E. + Cl_2$ water + $CHCl_3 \xrightarrow{\text{shake}}$ yellowish orange colour in $CHCl_3$ layer (CS_2 or CCl_4 can be taken instead of $CHCl_3$);



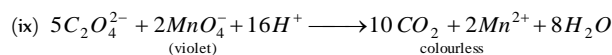
In case of I^- , violet colour of I_2 in $CHCl_3$ layer,
 $2NaI + Cl_2 \longrightarrow 2NaCl + I_2$ (violet)



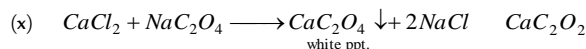
(viii) **Ring test** : To water extract (all NO_3^- are water soluble) add freshly prepared $FeSO_4$ solution and then conc. H_2SO_4 carefully by the side of the test-tube. A dark brown ring of $[Fe(H_2O)_5NO]^{2+} SO_4^{2-}$ at the interface between the two liquids is formed.



CO burns with blue flame and CO_2 turns lime water milky.



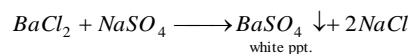
(3) **Wet tests for basic radicals** : Analysis of Basic Radicals



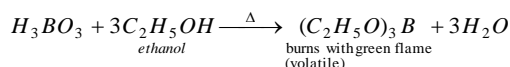
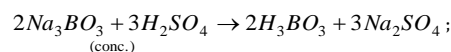
decolourises acidified $KMnO_4$.

Specific test in solution

(i) **Sulphate** : S.E. add dil. (to decompose CO_3^{2-} until reaction ceases). Add $BaCl_2$ solution. White ppt. insoluble in conc. HNO_3 ,

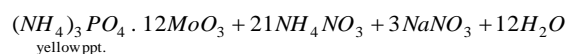


(ii) **Borate** : Ignite the mixture containing borate, conc. H_2SO_4 . And ethanol in a china-dish with a burning splinter –green edged flame of ethyl borate.



In presence of Cu^{2+} , perform this test in a test tube since Cu^{2+} salts are not volatile.

(iii) $S.E. + HNO_3 +$ ammonium molybdate solution. Heat, yellow crystalline ppt. confirms



Arsenic also gives this test. Hence presence of phosphate should also be checked after group II.

(iv) **Fluoride** : Sand + salt (F^-) + conc. H_2SO_4 ; heat and bring a water wetted rod in contact with vapours at the mouth of the test tube. A white deposit on the rod shows the presence to F^-

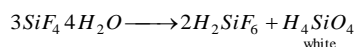
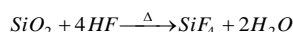
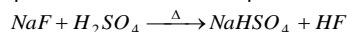


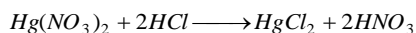
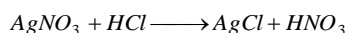
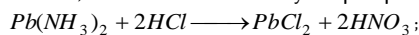
Table : 21.9

Group	Basic radicals	Group reagent	Ppt. as	Explanation
I	$Ag^+, Hg_2^{2+} (I), Pb^{2+}$	dil HCl	Chloride ($AgCl, Hg_2Cl_2, PbCl_2$)	K_{SP} values of chlorides are low, hence precipitated. Others have higher K_{SP} values hence not precipitated.
II	$Cu^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+} (II), Bi^{3+}, As^{3+}, Sb^{3+}, Sn^{2+}$	H_2S gas in presence of dil. HCl	Sulphides (CuS, As_2S_3 etc.)	K_{SP} values of sulphides are low hence precipitated by low $[S^{2-}]$ ion. HCl (with common H^+ ion) decreases ionization of H_2S which gives low $[S^{2-}]$. Hence II group is precipitated. Others with higher K_{SP} values not precipitated.
III	$Al^{3+}, Cr^{3+}, Fe^{3+}$	NH_4OH in presence of NH_4Cl	Hydroxide, $Al(OH)_3$ etc.	K_{SP} values of $Al(OH)_3$ etc. are low. NH_4Cl (with common NH_4^+ ion) decreases ionization of NH_4OH giving

				low $[OH^-]$. Hence group III is precipitated.
IV	$Zn^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+}$	H_2S in ammoniacal medium	Sulphides (ZnS etc.)	K_{SP} values of sulphides of group IV are high hence precipitation takes place in higher $[S^{2-}]$. Basic medium increases ionization of H_2S increasing $[S^{2-}]$ hence precipitation of group IV.
V	$Ca^{2+}, Ba^{2+}, Sr^{2+}$	$(NH_4)_2CO_3 + NH_4Cl$	Carbonates ($CaCO_3$ etc.)	K_{SP} values of carbonate are less than that of group VI (Mg^{2+}) hence precipitation before Mg^{2+} .
VI	$Mg^{2+}, (Na^+, K^+ \text{ also included})$	$NH_4OH + Na_2HPO_4$ (only for Mg^{2+})	White ppt. ($MgHPO_4$)	–
0 (Zero)	NH_4^+	–	–	Tested independently from original solution.

Chemical reactions involved in the tests of basic radicals

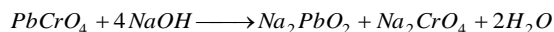
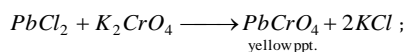
Group I : When dil. HCl is added to original solution, insoluble chlorides of lead, silver mercurous mercury are precipitated.



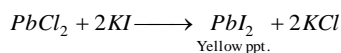
Pb (lead)

(i) $PbCl_2$ is soluble in hot water and on cooling white crystals are again formed.

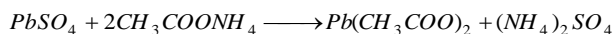
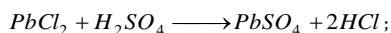
(ii) The solution of $PbCl_2$ gives a yellow precipitate with potassium chromate solution which is insoluble in acetic acid but soluble in sodium hydroxide.



(iii) The solution of $PbCl_2$ forms a yellow precipitate with potassium iodide solution.

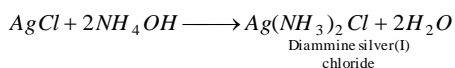


(iv) White precipitate of lead sulphate is formed with dilute H_2SO_4 . The precipitate is soluble in ammonium acetate,

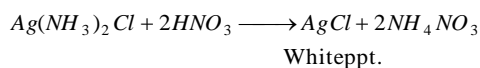


Ag (silver)

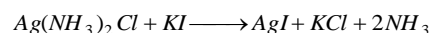
(i) $AgCl$ dissolves in ammonium hydroxide,



(ii) On adding dilute HNO_3 to the above solution, white precipitate is again obtained

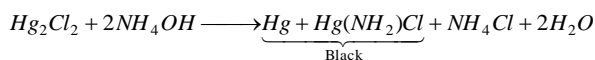


(iii) On adding KI to the complex solution, yellow precipitate is obtained.

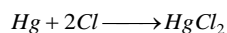
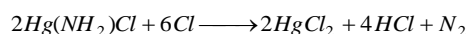
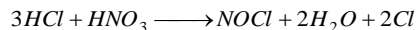


Hg₂²⁺ (mercurous)

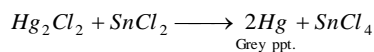
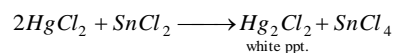
(i) Hg_2Cl_2 turns black with NH_4OH ,



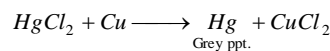
(ii) The black residue dissolves in aqua-regia forming mercuric chloride.



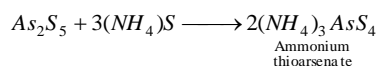
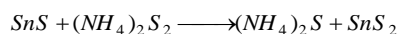
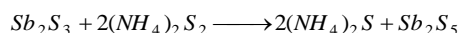
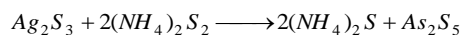
(iii) The solution of $HgCl_2$ forms white or slate-coloured precipitate with stannous chloride.

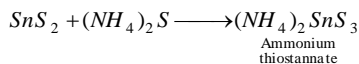
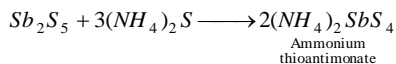


(iv) The solution of $HgCl_2$ with copper turning forms a grey deposit.



Group II : When hydrogen sulphide is passed in acidified solution, the radicals of second group are precipitated as sulphides. The precipitate is treated with yellow ammonium sulphide. The sulphides of IIB are first oxidised to higher sulphides which then dissolve to form thio-compounds.





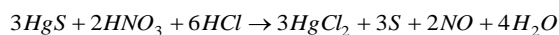
All the three are soluble.

In case, the precipitate does not dissolve in yellow ammonium sulphide, it may be either HgS or PbS or Bi_2S_3 or CuS or CdS . The precipitate is heated with dilute HNO_3 . Except HgS , all other sulphides of *IIA* are soluble.



Hg (mercuric)

HgS is dissolved in aqua-regia,



The solution is divided into two parts:

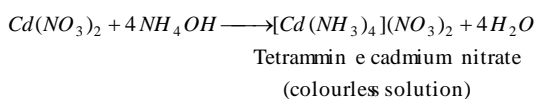
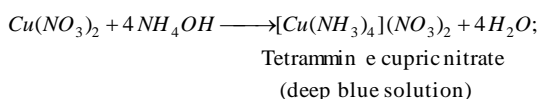
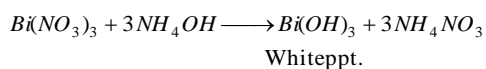
Part I : Stannous chloride solution reduces $HgCl_2$ first into white Hg_2Cl_2 and then to grey metallic mercury.

Part II : Copper displaces Hg from $HgCl_2$ which gets coated on copper turnings as a shining deposit.

Pb (lead)

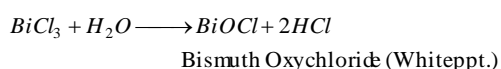
In case the sulphide dissolves in dilute HNO_3 , a small part of the solution is taken. Dilute H_2SO_4 is added. If lead is present, a white precipitate of lead sulphate appears, $Pb(NO_3)_2 + H_2SO_4 \rightarrow PbSO_4 + 2HNO_3$ (Whiteppt.)

In absence of lead, the remaining solution is made alkaline by the addition of excess of NH_4OH . Bismuth forms a white precipitate of $Bi(OH)_3$, copper forms a deep blue coloured solution while cadmium forms a colourless soluble complex,

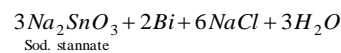


Bt (bismuth) : The precipitate dissolves in dilute HCl , $Bi(OH)_3 + 3HCl \longrightarrow BiCl_3 + 3H_2O$

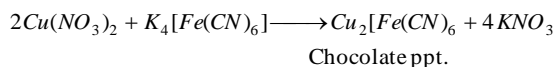
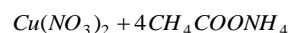
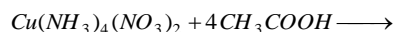
Part I : Addition of excess of water to $BiCl_3$ solution gives a white precipitate due to hydrolysis.



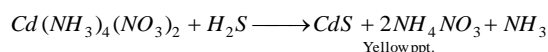
Part II : The solution of $BiCl_3$ is treated with sodium stannite when a black precipitate of metallic bismuth is formed, $2BiCl_3 + 3Na_2SnO_2 + 6NaOH \longrightarrow$



Cr (copper) : Blue coloured solution is acidified with acetic acid. When potassium ferrocyanide is added a chocolate coloured precipitate is formed,

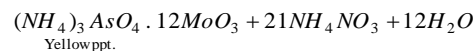
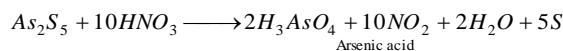


Cd (cadmium) : H_2S is passed through colourless solution. The appearance of yellow precipitate confirms the presence of cadmium,

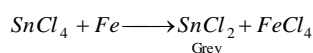
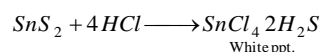


Group IIB : In case the precipitate dissolves in yellow ammonium sulphide, the tests of the radicals arsenic, antimony and tin are performed. The sulphide is treated with concentrated hydrochloric acid. Antimony and tin sulphide dissolve while arsenic sulphide remains insoluble.

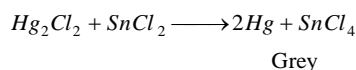
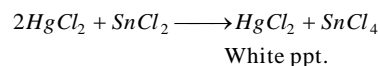
As (arsenic) : The insoluble sulphide is treated with concentrated nitric acid which is then heated with ammonium molybdate. Yellow precipitate of ammonium arsenomolybdate is formed.



Srr or Str (tin) : Solution of sulphide in concentrated HCl is reduced with iron filings or granulated zinc.

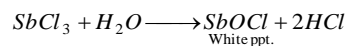


$HgCl_2$ solution is added to above solution which gives first a white precipitate that turns to grey.

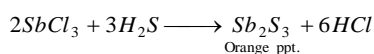


Sb (antimony) : Filtrate of sulphide in concentrated HCl is divided into two parts.

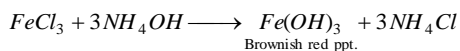
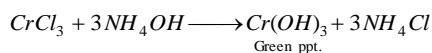
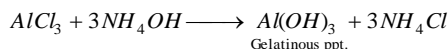
Part I : On dilution with excess of water, a white precipitate of antimony oxychloride is obtained.



Part II : H_2S is circulated. Orange precipitate is formed,

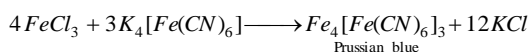
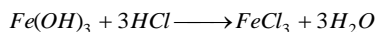


Group III : Hydroxides are precipitated on addition of excess of ammonium hydroxide in presence of ammonium chloride.

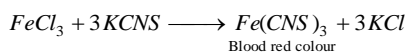


Fe (iron) : The brownish red precipitate dissolves in dilute *HCl*. The solution is divided into two parts.

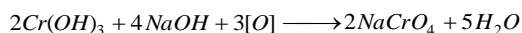
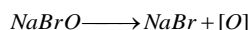
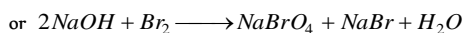
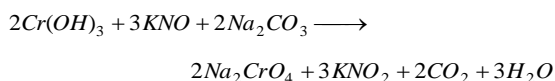
Part I : $K_4[Fe(CN)_6]$ solution is added which forms deep blue solution or precipitate.



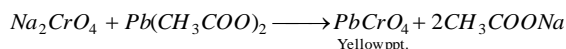
Part II : Addition of potassium thiocyanate solution gives a blood red colouration.



Cr (chromium) : The green precipitate is fused with fusion mixture ($Na_2CO_3 + KNO_3$). The fused product is extracted with water or the precipitate is heated with *NaOH* and bromine water.



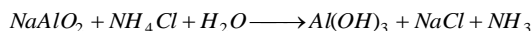
The solution thus obtained contains sodium chromate. The solution is acidified with acetic acid and treated with lead acetate solution. A yellow precipitate appears.



Al (aluminium) : The gelatinous precipitate dissolves in *NaOH*, $Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$

Soluble

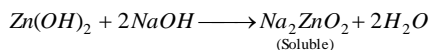
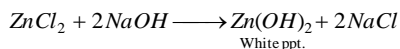
The solution is boiled with ammonium chloride when $Al(OH)_3$ is again formed.



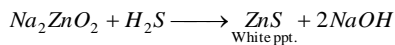
Group IV : On passing H_2S through the filtrate of the third group, sulphides of fourth group are precipitated. *NiS* and *CoS* are black and insoluble in concentrated *HCl* while *MnS* (buff coloured), *ZnS* (colourless) are soluble in conc. *HCl*.

Zn (zinc) : The sulphide dissolves in *HCl*. $ZnS + 2HCl \longrightarrow ZnCl_2 + H_2S$

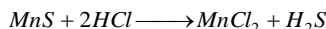
When the solution is treated with *NaOH*, first a white precipitate appears which dissolves in excess of *NaOH*



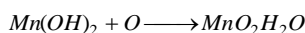
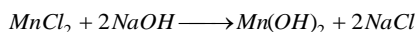
On passing H_2S , white precipitate of zinc sulphide is formed



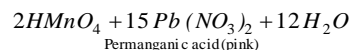
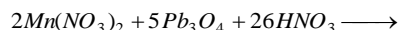
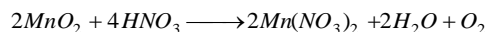
Mn (manganese) : Manganese sulphide dissolves in *HCl*



On heating the solution with *NaOH* and Br_2 -water, manganese dissolve gets precipitated.



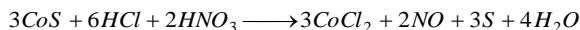
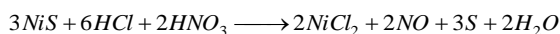
The precipitate is treated with excess of nitric acid and PbO_2 or Pb_3O_4 (red lead). The contents are heated. The formation of permanganic acid imparts pink colour to the supernatant liquid.



The above test fails in presence of *HCl*.

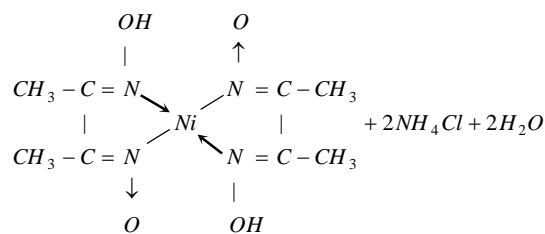
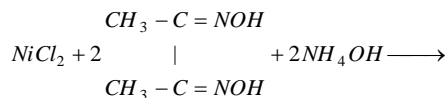
Ni (nickel) and Co (cobalt)

The black precipitate is dissolved in aqua-regia.

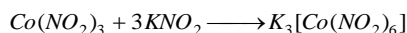
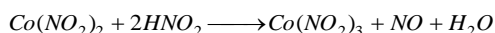
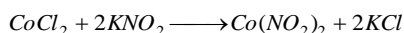
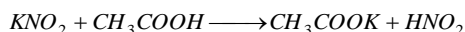


The solution is evaporated to dryness and residue extracted with dilute *HCl*. It is divided into three parts.

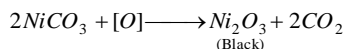
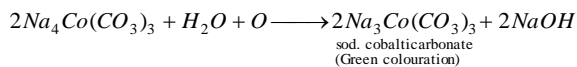
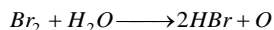
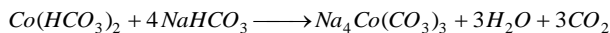
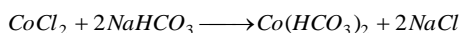
Part I : Add NH_4OH (excess) and dimethyl glyoxime. A rosy red precipitate appears, if nickel is present,



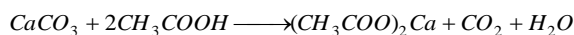
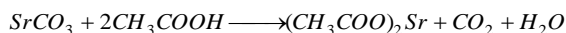
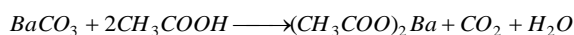
Part II : Add CH_3COOH in excess and KNO_2 . The appearance of yellow precipitate confirms the presence of cobalt.



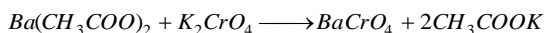
Part III : Solution containing either nickel or cobalt is treated with NaHCO_3 and bromine water. Appearance of apple green colour is observed, the solution is heated when black precipitated is formed, which shows the presence of nickel,



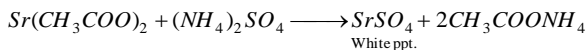
Group V : Ammonium carbonate precipitates V group radicals in the form of carbonates are soluble in acetic acid.



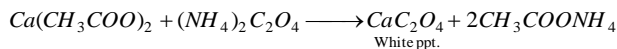
Ba (barium) : Barium chromate is insoluble and precipitated by the addition of potassium chromate solution,



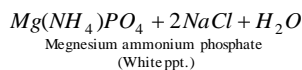
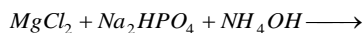
Sr (Strontium) : Strontium sulphate is insoluble and precipitated by the addition of ammonium sulphate solution,



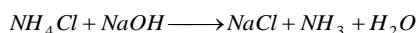
Ca (calcium) : Calcium oxalate is insoluble and precipitated by the addition of ammonium oxalate.



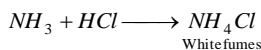
Group VI : In the filtrate of V group, some quantity of ammonium oxalate is added as to remove Ba , Ca and Sr completely from the solution. The clear solution is concentrated and made alkaline with NH_4OH . Disodium hydrogen phosphate is now added, a white precipitate is formed.



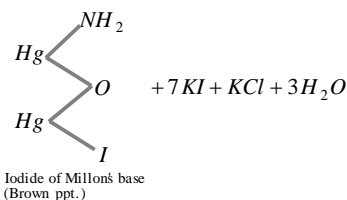
Zero group NH_4^+ (ammonium) : The substance (salt or mixture) when heated with NaOH solution evolves ammonia.



When a rod dipped in HCl is brought on the mouth of the test tube, white fumes of ammonium chloride are formed,



To the aqueous solution of ammonium salt when Nessler's reagents is added, brown coloured precipitate is formed.



Volumetric analysis

Volumetric analysis is a quantitative analysis. It involves the measurement of the volume of a known solution required to bring about the completion of the reaction with a measured volume of the unknown solution.

Titration : The process of addition of the known solution from the burette to the measured volume of solution of the substance to be estimated until the reaction between the two is just complete, is termed as titration. Thus, a titration involves two solutions;

(i) **Unknown solution :** The solution consisting the substance to be estimated is termed unknown solution. The substance is termed titrate.

(ii) **Standard solution :** The solution in which an accurately known amount of the reagent (titrant) has been dissolved in a known volume of the solution is termed standard solution. There are two types of reagents (titrants) :

(a) **Primary standards :** These can be accurately weighed and their solutions are not to be standardised before use. Oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), silver nitrate (AgNO_3), copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), ferrous ammonium sulphate [$\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$], sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), etc., are the examples of primary standards.

(b) **Secondary standards :** The solutions of these reagents are to be standardised before use as these cannot be weighed accurately. The examples are sodium hydroxide (NaOH), potassium hydroxide (KOH), hydrochloric acid (HCl), sulphuric acid (H_2SO_4), potassium permanganate (KMnO_4), iodine, etc.

Law of equivalence : It is applied in all volumetric estimations. According to it, the chemical substances react in the ratio of their chemical equivalent masses.

$$\frac{\text{Mass of substance A}}{\text{Mass of substance B}} = \frac{\text{Chemical equivalent mass of A}}{\text{Chemical equivalent mass of B}}$$

$$\text{or } \frac{\text{Mass of substance A}}{\text{Chemical equivalent mass of A}}$$

$$= \frac{\text{Mass of substance B}}{\text{Chemical equivalent mass of B}}$$

or gram equivalent of A = gram equivalent of B

or milli-gram equivalent of A = milli-gram equivalent of B

The point at which the amounts of the two reactants are just equivalent is known as equivalence point or end point. An auxiliary substance which helps in the usual detection of the completion of the titration or equivalence point or end point is termed as indicator, i.e., substances which undergo some easily detectable changes at the equivalence point are used as indicators.

Methods of expressing concentrations of solutions

The concentration of a solution can be expressed in various ways.

- (1) Percent by mass
- (2) Molarity
- (3) molality

(4) Mole fraction

(5) Normality

Types of titrations : Titrations can be classified as :

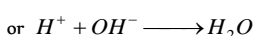
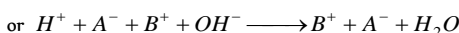
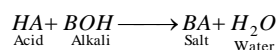
(1) Acid base titrations or acidimetry and alkalimetry

(2) Oxidation reduction titrations or redox titrations

(3) Precipitation titrations

(4) Complexometric titrations.

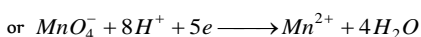
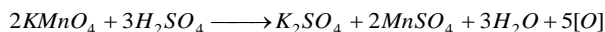
(1) **Acid-base titrations :** When the strength of an acid is determined with the help of a standard solution of base, it is known as **acidimetry**. Similarly, when the strength of a base (alkali) is determined with the help of a standard solution of an acid, it is known as **alkalimetry**. Both these titrations involve neutralisation of an acid with an alkali. In these titrations H^+ ions of the acid combine with OH^- ions of the alkali to form unionised molecules of water.



The end point in these titrations is determined by the use of organic dyes which are either weak acids or weak bases. These change their colours within a limited range of hydrogen ion concentrations, *i.e.*, *pH* of the solution. Phenolphthalein is a suitable indicator in the titrations of strong alkalis (free from carbonate) against strong acids or weak acids. Methyl orange is used as an indicator in the titrations of strong acids against strong and weak alkalis. As no indicator gives correct results in the titrations of weak acids against weak bases, such titrations are performed by some other methods (physical methods).

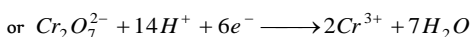
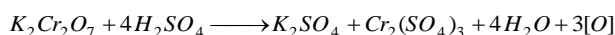
(2) **Oxidation reduction titrations :** The titrations based on oxidation-reduction reactions are called redox titrations. The chemical reactions proceed with transfer of electrons (simultaneous loss or gain of electrons) among the reacting ions in aqueous solutions. Sometimes these titrations are named after the reagent used, as:

(i) **Permanganate titrations :** These are titrations in which potassium permanganate is used as an oxidising agent in acidic medium. The medium is maintained by the use of dilute sulphuric acid. Potassium permanganate acts as a self-indicator. The potential equation, when potassium permanganate acts as an oxidising agent, is :



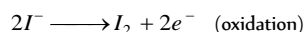
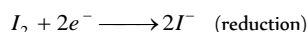
Before the end point, the solution remains colourless (when $KMnO_4$ solution is taken in burette) but after the equivalence point only one extra drop of $KMnO_4$ solution imparts pink colour, *i.e.*, appearance of pink colour indicates the end point. Potassium permanganate is used for the estimation of ferrous salts, oxalic acid, oxalates, hydrogen peroxide, etc. The solution of potassium permanganate is always first standardised before its use.

(ii) **Dichromate titrations :** These are titrations in which, potassium dichromate is used as an oxidising agent in acidic medium. The medium is maintained acidic by the use of dilute sulphuric acid. The potential equation is



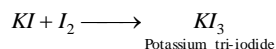
The solution of potassium dichromate can be directly used for titrations. It is mainly used for the estimation of ferrous salts and iodides. In the titration of $K_2Cr_2O_7$ versus ferrous salt either an external indicator (potassium ferricyanide) or an internal indicator (diphenyl amine) can be used.

(iii) **Iodimetric and iodometric titrations :** The reduction of free iodine to iodide ions and oxidation of iodide ions to free iodine occurs in these titrations.



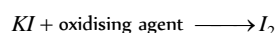
These are divided into two types :

(a) **Iodimetric titrations :** These are the titrations in which free iodine is used. As it is difficult to prepare the solution of iodine (volatile and less soluble in water), it is dissolved in potassium iodide solution.

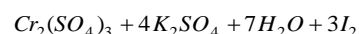
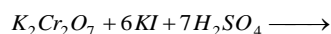
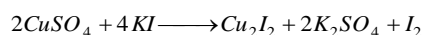
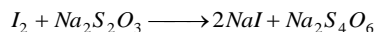


This solution is first standardised before use. With the standard solution of I_2 . Substances such as sulphite, thiosulphate, arsenite, etc., are estimated.

(b) **Iodometric titrations :** In iodometric titrations, an oxidising agent is allowed to react in neutral medium or in acidic medium, with excess of potassium iodide to liberate free iodine.

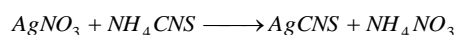
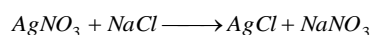


Free iodine is titrated against a standard reducing agent usually with sodium thiosulphate. Halogens, oxyhalogens, dichromates, cupric ion, peroxides, etc., can be estimated by this method.



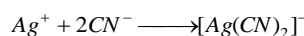
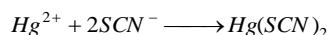
In iodimetric and iodometric titrations, starch solution is used as an indicator. Starch solution gives blue or violet colour with free iodine. At the end point the blue or violet colour disappears when iodine is completely changed to iodide.

(3) **Precipitation titrations :** The titrations which are based on the formation of insoluble precipitates, when the solutions of two reacting substances are brought in contact with each other, are called **precipitation titrations**. For example, when a solution of silver nitrate is added to a solution of sodium chloride or a solution of ammonium thiocyanate, a white precipitate of silver chloride or silver thiocyanate is formed.



Such titrations involving silver nitrate are called argentometric titrations.

(4) **Complexometric titrations :** A titration, in which an undissociated complex is formed at the equivalence point, is called **complexometric titration**. These titrations are superior to precipitation titrations as there is no error due to co-precipitation.



EDTA (ethylenediamine tetra-acetic acid) is a useful reagent which forms complexes with metals. In the form of disodium salt, it is used to estimate Ca^{2+} and Mg^{2+} ions in presence of eriochrome black-*T* as an indicator.

Equivalent masses of acids and bases : Equivalent masses of some acids and bases are given in the following table

Table : 21.10

Acid	Basicity	Mol. Mass	Eq. Mass
HCl	1	36.5	$\frac{36.5}{1} = 36.5$
HNO ₃	1	63	$\frac{63}{1} = 63.0$
H ₂ SO ₄	2	98	$\frac{98}{2} = 49.0$
CH ₃ COOH	1	60	$\frac{60}{1} = 60.0$
H ₂ CO ₃	2	126	$\frac{126}{2} = 63.0$
H ₃ PO ₄	3	98	$\frac{98}{3} = 32.7$
H ₂ PO ₄	2	82	$\frac{82}{2} = 41.0$
HPO ₄	1	66	$\frac{66}{1} = 66.0$

Table : 21.11

Alkali	Acidity	Mol. Mass	Eq. Mass
NaOH	1	40	$\frac{40}{1} = 40$
KOH	1	56	$\frac{56}{1} = 56$
Ca(OH) ₂	2	74	$\frac{74}{2} = 37$
NH ₄ OH	1	35	$\frac{35}{1} = 35$

Calculations of Volumetric analysis

The following points should be kept in mind while making calculations of volumetric exercises.

(i) 1g equivalent mass of a substance reacts completely with 1g equivalent mass of any other substance. 1g equivalent mass of a substance means equivalent mass of the substance in grams. For example,

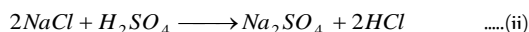
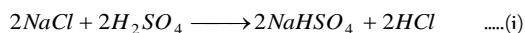
1g equivalent mass of NaOH = 40g of NaOH

1g equivalent mass of H₂SO₄ = 49g of H₂SO₄

1g equivalent mass of KMnO₄ in acidic medium
= 31.6g of KMnO₄

1g equivalent mass of hydrated oxalic acid
= 63g of hydrated oxalic acid

Note : Equivalent mass is a variable quantity and depends on the reaction in which the substance takes part. The nature of the reaction should be known before writing the gram equivalent mass of the substance. For example in the reactions.



The value of g equivalent mass of H₂SO₄ in reaction (i) is 98g and in reaction (ii) 49g.

(ii) Number of g equivalents

$$= \frac{\text{Mass of the substance in g}}{\text{Equivalent mass of the substance}}$$

$$\text{Number of g moles} = \frac{\text{Mass of the substance in g}}{\text{Molecular mass of the substance}} \\ = \frac{\text{Volume in litres of the substance at N.T.P.}}{22.4} \quad (\text{only for gases})$$

$$\text{Number of milli-equivalent} = \frac{\text{Mass in g} \times 1000}{\text{Equivalent mass}}$$

$$\text{Number of milli-moles} = \frac{\text{Mass in g} \times 1000}{\text{Molecular mass}}$$

$$(iii) \text{ Molarity} = \frac{\text{No. of moles of the solute}}{\text{No. of litres of the solution}} = \frac{w}{m \times V}$$

Molarity \times molecular mass = strength of the solution (g/L) No. of moles of the solute = Molarity \times No. of litres of solution Mass of the solute in g(w) = molarity \times No. of litres of solution \times mol. mass of solute

$$\text{Normality} = \frac{\text{No. of g equivalent of the solute}}{\text{No. of litres of the solution}} = \frac{w}{E \times V}$$

Normality \times equivalent mass = strength of the solution (g/L)

No. of equivalents of the solute = Normality \times No. of litres of solution

Mass of the solute in g(w) = Normality \times No. of litres of solution \times Eq. mass of the solute

$$\frac{\text{Molecular mass}}{\text{Equivalent mass}} = n = \frac{\text{Normality}}{\text{Molarity}}$$

Normality = n \times Molarity

(iv) **Normality equation :** When solutions A and B react completely.

$$N_A V_A = N_B V_B$$

Normality of A \times volume of A = Normality of B \times volume of B

$$\text{or } \frac{\text{Strength A}}{\text{Eq. mass A}} \times V_A = \frac{\text{Strength B}}{\text{Eq. mass B}} \times V_B$$

$$\frac{\text{Wt. of metal hydroxide}}{\text{wt. of metal oxide}} = \frac{\text{Eq. wt. of metal hydroxide}}{\text{Eq. wt. of metal oxide}}$$

$$= \frac{\text{Eq. wt of metal} + \text{Eq. wt of OH}}{\text{Eq. wt. of metal} + \text{Eq. wt of O}^{2-}}$$

(v) When the solution is diluted, the following formulae can be applied :

$$N_1 V_1 = N_2 V_2 \quad \text{or} \quad M_1 V_1 = M_2 V_2 \quad \text{or} \quad S_1 V_1 = S_2 V_2$$

Before dilution = After dilution

(vi) If a number of acids are mixed, the combined normality of the mixture, N_x, is given

$$N_x V_x = N_1 V_1 + N_2 V_2 + N_3 V_3 + \dots$$

Where V_x is the total volume of the mixture, N₁ and V₁ are the normality and volume respectively of one acid, N₂ and V₂ of the second acid and so on.

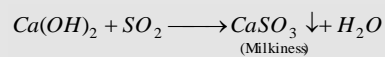
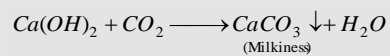
T Tips & Tricks

✍ Glass rod should never be used in flame test as it gives a golden yellow colour due to sodium present in it. An asbestos fibre can be safely used in place of platinum wire.

✍ The transparent bead in borax bead test is made of $NaBO + BO$.

✍ Filter ash test is an alternative to cobalt nitrate test and gives better results.

✍ Both CO_2 and SO_2 turn lime water milky.



✍ Eq. wt. of $KMnO_4$ is different in acidic, alkaline and neutral medium i.e., 31.6, 158 and 52.67 respectively.