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CHAPTER

practical chemistry

- Qualitative analysis deals with the identification of various constituents present in a given material. This analysis involves preliminary tests, wet tests for anions and cations, test for functional groups, etc.

INORGANIC

Preliminary tests:

- Colour : Blue (Cu^{2+}), green (Ni^{2+} or Cu^{2+}), deep green (Cr^{3+}), yellow or brown (Fe^{3+}), light pink (Mn^{2+}), pinkish violet (Co^{2+}).
- Smell : A pinch of mixture on rubbing with water gives characteristic smell. *e.g.* rotten eggs smell (sulphide), burning sulphur smell (some sulphites).

Analysis for acid radicals or anions

- ***Sulphite :*** Sulphite reacts with dilute H_2SO_4 producing SO_2 gas which turns acidified potassium dichromate solution green due to the reduction of dichromate to chromium sulphate which is green.

  $$K_2Cr_2O_7 + 3SO_2 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

  Sulphite reacts with barium chloride solution to produce barium sulphite (white ppt.) which is soluble in dilute HCl.
- ***Sulphide*** : Sulphide reacts with dilute H_2SO_4 liberating H_2S gas which turns lead acetate paper black due to the formation of black lead sulphide.

  $$Pb(CH_3COO)_2 + H_2S \rightarrow \underset{\text{Black ppt.}}{PbS} + 2CH_3COOH$$
- Soluble sulphide reacts with sodium nitroprusside to produce pink violet colour.

  $$Na_2S + \underset{\text{Sodium nitroprusside}}{Na_2[Fe(CN)_5NO]} \rightarrow \underset{\text{Pink violet colour}}{Na_4[Fe(CN)_5NOS]}$$
- ***Chloride*** : Chloride on heating with concentrated H_2SO_4 produces HCl gas which gives white precipitate of AgCl with $AgNO_3$ solution.

  $$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$$

  $$HCl + AgNO_3 \rightarrow AgCl\downarrow + HNO_3$$
- The gas evolved by heating chloride with H_2SO_4 forms white fumes of ammonium chloride with NH_4OH.

  $$NH_4OH + HCl \rightarrow \underset{\text{white fumes}}{NH_4Cl} + H_2O$$
- On heating chloride with $K_2Cr_2O_7$ and concentrated H_2SO_4 a reddish chromyl chloride (CrO_2Cl_2) gas is produced which gives yellow solution with NaOH due to sodium chromate and on adding acetic acid, lead acetate solution produces a yellow precipitate of $PbCrO_4$. This test is known as *chromyl chloride test.*

  $$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$$

$$K_2Cr_2O_7 + 2H_2SO_4 \rightarrow 2KHSO_4 + 2CrO_3 + H_2O$$

$$CrO_3 + 2HCl \rightarrow CrO_2Cl_2 + H_2O$$

$$CrO_2Cl_2 + 4NaOH \rightarrow \underset{\text{yellow colour}}{Na_2CrO_4} + 2NaCl + 2H_2O$$

$$Na_2CrO_4 + Pb(CH_3COO)_2 \rightarrow \underset{\text{yellow ppt.}}{PbCrO_4} + 2NaCl + 2H_2O$$

- ***Bromide*** : Bromide on heating with concentrated H_2SO_4 produces a reddish brown bromine gas which turns starch iodide paper blue due to the liberation of iodine from starch iodide. This iodine gives blue complex with starch.
- On adding $AgNO_3$ solution, a pale yellow precipitate of AgBr is formed which is hardly soluble in NH_4OH.

$$AgNO_3 + HBr \rightarrow AgBr\downarrow + HNO_3$$

$$AgBr + NH_4OH \rightarrow \underset{\text{Soluble silver ammonium bromide complex}}{[Ag(NH_3)_2]Br} + 2H_2O$$

- ***Iodide*** : Iodide on heating with concentrated H_2SO_4 gives a violet iodine gas which turns starch paper blue.
- On adding $AgNO_3$ solution, a yellow ppt. of AgI is formed which is insoluble in NH_4OH.

$$AgNO_3 + HI \rightarrow AgI\downarrow + HNO_3$$

Identification and separation of acidic radicals

- **Group I** : This group consists of radicals which are detected by dilute H_2SO_4 or dil. HCl. These are
  (i) carbonate (ii) sulphite (iii) sulphide (iv) nitrite (v) acetate.
- *Carbonate*

$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2$$

$$\underset{\text{lime water}}{Ca(OH)_2} + CO_2 \longrightarrow \underset{\text{white ppt.}}{CaCO_3} + H_2O$$

$$\underset{\text{white ppt.}}{CaCO_3} + H_2O + CO_2 \longrightarrow \underset{\text{soluble}}{Ca(HCO_3)_2}$$

- *Sulphite*

$$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + SO_2$$

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + \underset{\text{green}}{Cr_2(SO_4)_3} + H_2O$$

- *Sulphide*

$$Na_2S + H_2SO_4 \longrightarrow Na_2SO_4 + H_2S$$

$$Pb(CH_3COO)_2 + H_2S \longrightarrow \underset{\text{black ppt.}}{PbS} + 2CH_3COOH$$

- *Nitrite*

$$2NaNO_2 + H_2SO_4 \longrightarrow Na_2SO_4 + \underset{\text{nitrous acid}}{2HNO_2}$$

$$3HNO_2 \longrightarrow H_2O + 2NO + HNO_3$$

$$2NO + O_2 \longrightarrow \underset{\text{(brown coloured)}}{2NO_2}$$

- **Group II :** This group consists of radicals which are detected by concentrated H_2SO_4. These are
  (i) chloride (ii) bromide (iii) iodide (iv) nitrate (v) oxalate
- *Chloride*

$NH_4OH + HCl \longrightarrow \underset{\text{white fumes}}{NH_4Cl} + H_2O$

$AgNO_3 + HCl \longrightarrow \underset{\text{ppt.}}{AgCl} + HNO_3$

$AgCl + 2NH_4OH \longrightarrow \underset{\text{(soluble)}}{Ag(NH_3)_2Cl} + 2H_2O$

$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$

$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + \underset{\text{(yellowish green gas)}}{Cl_2\uparrow}$

Confirmatory test

$\text{Chloride} + K_2Cr_2O_7\text{ (solid)} + \text{conc. } H_2SO_4 \xrightarrow{\text{heat}} \underset{\text{(reddish brown vapours)}}{CrO_2Cl_2}$

$CrO_2Cl_2 \xrightarrow{NaOH} \underset{\text{yellow solution}}{Na_2CrO_4}$

$\downarrow CH_3COOH + (CH_3COO)_2Pb$

$PbCrO_4$ (yellow ppt.)

- *Bromide*

$NaBr + H_2SO_4 \longrightarrow NaHSO_4 + HBr$

$2HBr + H_2SO_4 \longrightarrow \underset{\text{(brown gas)}}{Br_2\uparrow} + 2H_2O + SO_2$

Confirmatory test

$NaBr + AgNO_3 \longrightarrow AgBr + NaNO_3$

$AgBr + 2NH_4OH \longrightarrow Ag(NH_3)_2Br + 2H_2O$

AgBr is sparingly soluble in NH_4OH solution.

- *Iodide*

$2KI + 2H_2SO_4 \longrightarrow 2KHSO_4 + 2HI$

$2HI + H_2SO_4 \longrightarrow \underset{\text{(violet vapours)}}{I_2\uparrow} + SO_2 + 2H_2O$

Violet vapours with starch produce blue colour.

$I_2 + \text{starch} \longrightarrow \text{blue colour}$

$NaI + AgNO_3 \longrightarrow \underset{\text{yellow ppt.}}{AgI} + NaNO_3$

$AgI + NH_4OH \longrightarrow \text{not soluble}$

- *Nitrate*

$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$

$4HNO_3 \longrightarrow 2H_2O + \underset{\text{(light brown fumes)}}{4NO_2} + O_2$

$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

Confirmatory test

$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$

$6FeSO_4 + 2HNO_3 + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2NO$

$[Fe(H_2O)_6]SO_4 \cdot H_2O + NO \longrightarrow \underset{\text{(brown ring)}}{[Fe(H_2O)_5NO]SO_4} + 2H_2O$

Ring test is not reliable in presence of nitrite, bromide and iodide.

- **Group III :** The radicals which do not give any characteristic gas with dilute acid and concentrated H_2SO_4. These are
(i) sulphate (ii) phosphate (iii) borate (iv) fluoride
- *Sulphate*

$Na_2SO_4 + BaCl_2 \xrightarrow{H^+} \underset{\text{white ppt.}}{BaSO_4} \downarrow + 2NaCl$

Identification of basic radicals

- Analysis of basic radicals includes the following steps.
  - Preparation of the original solution of the salt or mixture.
  - Separation of basic radicals into different groups.
  - Analysis of the precipitates obtained in different groups.
- *Separation of basic radicals into groups*

Group	Group reagent	Basic radical	Composition and colour of the precipitate	
I	Dilute HCl	Ag^+ Pb^{2+} Hg_2^{2+}	AgCl: white $PbCl_2$: white Hg_2Cl_2: white	Chloride insoluble in cold dilute HCl
II	H_2S in presence of dilute HCl	Hg^{2+} Pb^{2+} Bi^{3+} Cu^{2+} Cd^{2+} As^{3+} Sb^{3+} Sn^{2+} Sn^{4+}	HgS : black PbS: black Bi_2S_3: black CuS: black CdS: yellow As_2S_3: yellow Sb_2S_3: orange SnS: brown SnS_2: yellow	Sulphides insoluble in dilute HCl
III	NH_4OH in presence of NH_4Cl	Fe^{3+} Cr^{3+} Al^{3+}	$Fe(OH)_3$: reddish brown $Cr(OH)_3$:green $Al(OH)_3$: white	Hydroxides are insoluble in NH_4OH
IV	H_2S in presence of NH_4OH	Zn^{2+} Mn^{2+} Co^{2+} Ni^{2+}	ZnS: greenish white MnS: buff CoS: black NiS: black	Sulphides are insoluble in NH_4OH

V	$(NH_4)_2CO_3$ in presence of NH_4OH	Ba^{2+} Sr^{2+} Ca^{2+}	$BaCO_3$: white $SrCO_3$: white $CaCO_3$: white	Carbonates are insoluble
VI	Na_2HPO_4	Mg^{2+}	$Mg(NH_4)PO_4$: white	
Zero	NaOH	NH_4^+	Ammonia gas is evolved	

- ***Pb^{2+}* (lead)** : The sulphide is dissolved in dilute HNO_3, solution with dilute H_2SO_4 gives a white precipitate.

$$Pb(NO_3)_2 + H_2SO_4 \rightarrow PbSO_4\downarrow + 2HNO_3$$

- Lead sulphate is dissolved in concentrated ammonium acetate solution which gives a yellow precipitate of $PbCrO_4$ with K_2CrO_4 solution.
- ***Cu^{2+}* (copper)** : Sulphide on treatment with dilute HNO_3 and excess of NH_4OH, forms a deep blue coloured solution.

$$3CuS + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 3S + 4H_2O$$

$$Cu(NO_3)_2 + 4NH_4OH \rightarrow \underset{\text{deep blue solution}}{[Cu(NH_3)_4](NO_3)_2} + 4H_2O$$

- On acidifying with acetic acid and adding potassium ferrocyanide, blue solution gives a chocolate coloured precipitate of $Cu_2[Fe(CN)_6]$.
- Fe^{3+}, Cr^{3+} and Al^{3+} comprise III group and the reagent is NH_4OH in presence of NH_4Cl.
- These radicals are precipitated as their hydroxides.
- ***Fe^{3+}* (iron)** : The brownish red precipitate of $Fe(OH)_3$ on treatment with dilute HCl and $K_4[Fe(CN)_6]$ solution, gives deep blue solution or precipitate.

$$Fe(OH)_3 + 3HCl \rightarrow FeCl_3 + 3H_2O$$

$$4FeCl_3 + 3K_4[Fe(CN)_6] \rightarrow \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3} + 12KCl$$

- Addition of potassium thiocyanate solution gives a blood red colouration.

$$FeCl_3 + 3KCNS \rightarrow \underset{\text{blood red colour}}{Fe(CNS)_3} + 3KCl$$

- ***Al^{3+}* (aluminium)** : The gelatinous precipitate of $Al(OH)_3$ on treatment with NaOH forms soluble $NaAlO_2$.

$$Al(OH)_3 + NaOH \rightarrow \underset{\text{sodium meta-aluminate}}{NaAlO_2} + 2H_2O$$

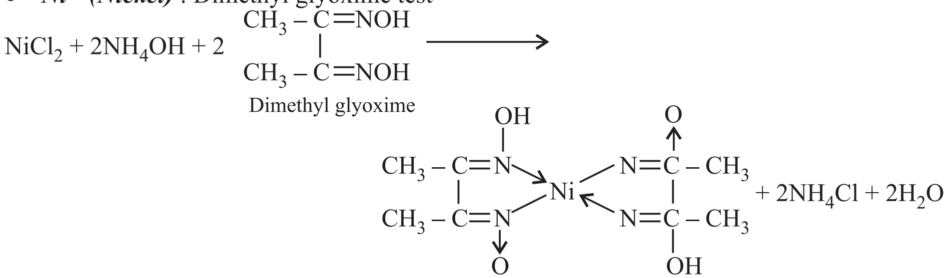
- Sodium meta aluminate on boiling with ammonium chloride gives $Al(OH)_3$ ppt.
- Zn^{2+} and Mn^{2+} are present in group IV and the reagent is H_2S in presence of NH_4OH.
- The radicals are obtained as their sulphides.
- ***Zn^{2+}* (zinc) :** The sulphide on treatment with HCl gives chloride, which gives a white precipitate with NaOH, which dissolves in excess of NaOH.

$$ZnS + 2HCl \rightarrow ZnCl_2 + H_2S$$

$$ZnCl_2 + 2NaOH \rightarrow Zn(OH)_2 + 2NaCl$$

$$Zn(OH)_2 + 2NaOH \rightarrow \underset{\text{(soluble)}}{Na_2ZnO_2} + 2H_2O$$

- ***Ni^{2+} (Nickel)*** : Dimethyl glyoxime test



Bright red complex (ppt)

- Sodium hydroxide-bromine water test

$$NiCl_2 + 2NaOH \rightarrow 2NaCl + Ni(OH)_2\downarrow$$
(green ppt.)

$$Br_2 + H_2O \rightarrow HBr + O$$
$$2Ni(OH)_2 + H_2O + O \rightarrow 2Ni(OH)_3\downarrow$$
(black ppt)

- ***Ba^{2+} (barium)*** : The acetate on treatment with potassium chromate solution gives yellow precipitate of barium chromate.

$$Ba(CH_3COO)_2 + K_2CrO_4 \rightarrow BaCrO_4\downarrow + 2CH_3COOK$$

- The yellow ppt. of $BaCrO_4$ is dissolved in concentrated HCl.
- ***Ca^{2+} (calcium)*** : The acetate on treatment with ammonium oxalate gives a white ppt. of calcium oxalate.

$$Ca(CH_3COO)_2 + (NH_4)_2C_2O_4 \rightarrow CaC_2O_4\downarrow + 2CH_3COONH_4$$

- The white ppt. is dissolved in dilute H_2SO_4 and a drop of $KMnO_4$ solution is added which immediately decolorises.
- ***Mg^{2+} (magnesium)*** : This is a member of group VI and the reagent is disodium hydrogen phosphate.
- The salts give a white precipitate of magnesium ammonium phosphate when disodium hydrogen phosphate is added to ammoniacal solution of Mg^{2+}.

ORGANIC

Colour		**ODOUR**	
(A) Solids	Compounds	Mousy	acetamide, acetonitrile
Yellow	iodoform, nitro compounds and quinones	Fruity	esters
		Penetrating smell	HCHO, CH_3CHO and HCOOH
Orange	*o*-nitroaniline		
Brown-red	azo compounds, diamines, aromatic amines, amino-phenol	Pleasant	ketones (aliphatic and aromatic)
		Smell of bitter almonds	C_6H_5CHO, nitrobenzene, nitrotoluene
Pink	naphthols		
Colourless	simple phenols, carbohydrates	Vinegar smell	CH_3COOH
		Garlic smell	thiophenol, thioalcohol
		Wine like	alcohol

(B) Liquids		Fishy smell	aliphatic and aromatic amines
Brown-red	amines	Carbolic smell	phenols, cresols, naphthols
Yellow-orange	nitrocompounds, diketones	Ammonical smell	tertiary amines
Colourless	alcohols, aldehydes, ketones, lower aliphatic acid and their anhydrides	Sweet smell	chloroform
		Oil of winter green	methyl salicylate
		Characteristic aromatic smell	benzene, toluene

- ***Detection of nitrogen, sulphur and halogens***
- Nitrogen, sulphur and halogens in any organic compounds are detected by 'Lassaigne's test'.
- ***Preparation of Lassaigne's Extract (or Sodium Extract)***
- A small piece of sodium is heated gently in an ignition tube till the sodium melts. About 50 - 60 mg of the organic compound is added to this and the tube heated strongly for 2-3 minutes to fuse the material inside it. After cooling, the tube is carefully broken in a china dish containing about 20 to 30 mL of distilled water. The fused material along with the pieces of ignition tube is crushed with the help of a glass rod and the contents of the china dish are boiled for a few minutes. The sodium salts formed in the above reactions (*i.e.* NaCN, Na_2S, NaX or NaSCN) dissolve. Excess of sodium reacts with water to give sodium hydroxide. This alkaline solution is called Lassaigne's extract or sodium extract. The solution is then filtered to remove the insoluble materials and the filtrate is used for making the tests for nitrogen, sulphur and halogens.
- ***Reactions***
- An organic compound containing C, H, N, S and halogens when fused with sodium metal gives the following reactions.

$$\underset{\text{present in organic compound}}{C + N + Na} \xrightarrow{\text{Fusion}} \underset{\text{sodium cyanide}}{NaCN}$$

$$X(Cl, Br, I) + Na \xrightarrow{\text{Fusion}} NaX\ (X = Cl, Br, I)$$

$$S + 2Na \xrightarrow{\text{Fusion}} Na_2S$$

(NaSCN) is formed during fusion, which in the presence of excess sodium forms sodium cyanide and sodium sulphide.

$$Na + C + N + S \xrightarrow{\text{Fusion}} NaCNS$$

$$NaCNS + 2Na \xrightarrow{\text{Fusion}} NaCN + Na_2S$$

Element	Sodium extract	Confirmatory test
Nitrogen	$Na + C + N \xrightarrow{\Delta} NaCN$	$(NaCN + FeSO_4 + NaOH) + FeCl_3 + \text{conc.}HCl$ boil and cool $\longrightarrow$ Blue or green colour.
Sulphur	$2Na + S \xrightarrow{\Delta} Na_2S$	(i) Na_2S + sodium nitroprusside $\longrightarrow$ A deep violet colour. (ii) $Na_2S + CH_3COOH + (CH_3COO)_2Pb \longrightarrow$ A black ppt.

Halogen	$Na + X \xrightarrow{\Delta} NaX$	$NaX + HNO_3 + AgNO_3$ (i) White ppt. soluble in aq. NH_3 confirms Cl. (ii) Yellow ppt. partially soluble in aq. NH_3 confirms Br. (iii) Yellow ppt. insoluble in aq. NH_3 confirms I.
Nitrogen and sulphur together	$Na + C + N + S \xrightarrow{\Delta} NaCNS$	As in test for nitrogen ; instead of green or blue colour, blood red colouration confirms presence of N and S both.

Detection of organic functional groups

- **Alcoholic group** (– OH) (linked to aliphatic carbon chain)
  - *Sodium metal test*

$$2R-OH + 2Na \longrightarrow 2R-ONa + H_2\uparrow$$

  - *Ester test*

$$R-OH + R'-COOH \overset{H^+}{\rightleftharpoons} \underset{\text{ester}}{R'-COOR} + H_2O$$

  - $$2R-OH + \underset{\text{ceric ammonium nitrate}}{(NH_4)_2Ce(NO_3)_6} \longrightarrow \underset{\text{pink or red}}{(ROH)_2Ce(NO_3)_4} + 2NH_4NO_3$$

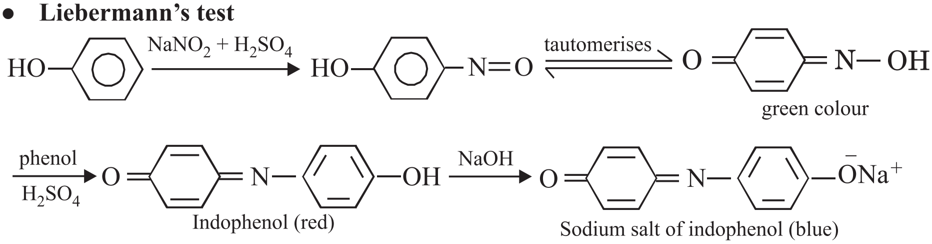
  - *Acetyl chloride test*

$$R-OH + CH_3COCl \longrightarrow CH_3COOR + HCl_{(g)}$$

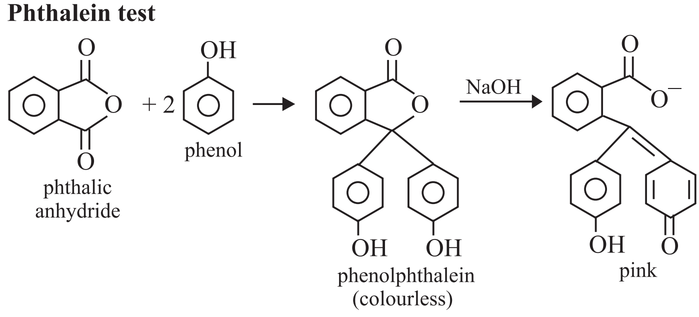
$$HCl + NH_3 \longrightarrow \underset{\text{(white fumes)}}{NH_4Cl}$$

Test for phenolic (– OH) group

- **Liebermann's test**



- **Phthalein test**



This test is also called fluorescein test.

- **Tests for aldehyde group**

  The presence of a carbonyl group can be confirmed by treating the organic compound with hydrazine and observing the formation of hydrazones.

  $$>C=O + H_2N-NH_2 \longrightarrow >C=N-NH_2$$

  Aldehyde/Ketone → Hydrazone

  To identify aldehydic group, the following tests are performed:

  - *Tollen's test :* To about 5-10 ml of Tollen's reagent (ammoniacal $AgNO_3$), a small quantity of organic compound is added and it is heated on a water bath. A shining silver mirror or grey deposit on the inner wall of the test tube indicates the presence of – CHO group.

  $$R-CHO + 2[Ag(NH_3)_2]OH + H_2O \longrightarrow RCOONH_4 + 3NH_3 + H_2O + \underset{\text{(silver mirror)}}{2Ag\downarrow}$$

    Formic acid and α-hydroxy ketones also give the test.

  - *Fehling's test* : A small amount of the organic compound is boiled with some Fehling solution (alkaline solution of cupric ions complexed with sodium potassium tartarate), it gives red precipitate of Cu_2O.

    Salicylaldehyde does not reduce Fehling's solution.

  - *Benedict's test* : To 4-5 ml of Benedict's reagent (cupric ion complexed with citrate ion) a small quantity of the organic compound is added and the solution is heated to boiling. Formation of red precipitate indicates the presence of –CHO group.
  - *Schiff's test* : 5 ml of Schiff's reagent is taken in a test tube and shaken with organic compound (without heating). A pink colour is formed within two minutes.

- **Tests for ketones**

  Ketones do not respond to Fehling's, Tollen's and Benedict's tests. However, the following tests can be used to confirm the presence of a keto group:

  - *Iodoform test* : Ketones with $CH_3CO–$ group react with I_2 in alkali to give yellow precipitate of CHI_3. Carboxylic acid, its derivatives and active methylene compounds (except β-keto acids) do not respond to this test.

  $$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + I_2 \xrightarrow{OH^-} \underset{\text{yellow}}{CHI_3\downarrow} + CH_3COO^-$$

  - *Nitroprusside test* : 1 ml of the organic compound is treated with 1 ml of freshly prepared solution of sodium nitroprusside followed by addition of excess of NaOH solution. A wine-red colour is obtained.

- **Tests for carboxylic group**

  Aliphatic acids are soluble in cold water and aromatic acids are soluble in hot water. Dicarboxylic acids, phenolic acids are more soluble than simple carboxylic acids.

  - *Litmus test* : A small amount of organic compound or its aqueous solution is added to a blue litmus paper. If the paper turns red, the acidic carboxylic group may present.
  - *Sodium bicarbonate test* : A small quantity of the organic compound is added to an aqueous solution of sodium bicarbonate solution. CO_2 effervescence confirms the presence of –COOH (picric acid, 2,4,6-trinitrophenol also gives a positive test).

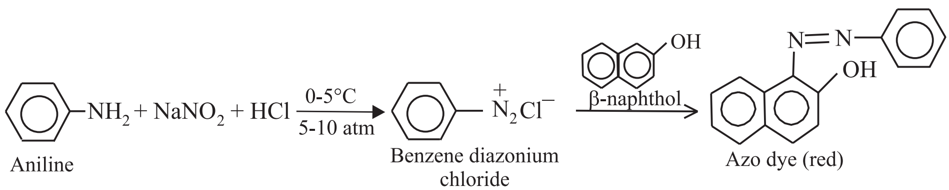
- **Tests for primary amines**

  Amines are basic in nature, soluble in water and dilute HCl but insoluble in NaOH or Na_2CO_3.

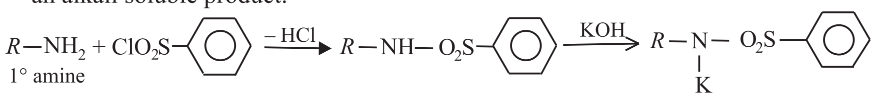
- *Carbylamine test* : The organic compound is heated with alc. KOH and $CHCl_3$ in a test tube. A highly offensive smell is evolved due to the formation of isocyanides.

$$RNH_2 + CHCl_3 + 3KOH \longrightarrow \underset{\text{foul smell}}{R - N \equiv C} + 3KCl + 3H_2O$$

  Aromatic amines like $C_6H_5 - NH_2$ also give this test.
- *Azo dye test* : This test is applicable for aromatic amines. The test involves the additioin of a small amount of the organic compound in dil. HCl and $NaNO_2$ (at 0-5°C) and alkaline β-naphthol (at 0-5°C) with constant shaking, a red dye is obtained.



- *Hinsberg test* : With benzene sulphonyl chloride in alkaline medium, 1° amines give an alkali soluble product.



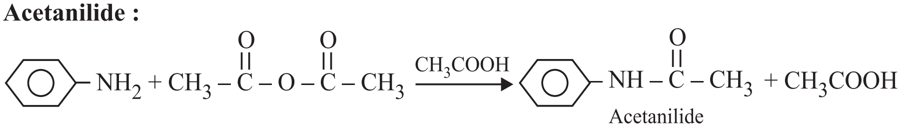
Test for Functional Groups

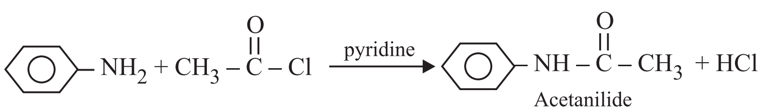
No.	Experiment	Observation	Inference
1.	O.C. + 3 cc saturated soln. of $NaHCO_3$	effervescences of CO_2 which changes lime water milky	–COOH (carboxylic)
2.	5 cc O.C. + 2 – 3 drops of ceric ammonium nitrate	a red colour	–OH (alcoholic)
3.	2 cc aq. or alc. soln. of O.C. + 1 – 2 drops neutral $FeCl_3$ soln	blue violet, red or deep green colour	–OH (phenolic)
4.	1 cc Schiff's reagent + 2 – 3 drops O.C. and shake	violet or red colour	–CHO (aldehydic)
5.	1 – 2 cc of sodium nitroprusside + 1 – 2 drops O.C. + NaOH	red or violet colour	> C = O (ketonic)
6.	2 cc aq. soln. of O.C. + 2 drops Molisch reagent + pour it in another test tube containing 1 – 2 c.c. conc. H_2SO_4	formation of red ring at the junction	Carbohydrate
7.	O.C. + 2 cc conc. H_2SO_4 & shake	insoluble or immiscible	Hydrocarbon
8.	0.5 g O.C. in 2 cc alcohol + 1 drop NaOH + 1 drop phenolphthalein	disappearance of pink colour	–COOR (ester)

9.	0.3 g O.C. + 5 cc H_2O + 1 cc acetone + few drops sodium nitroprusside	formation of violet red colour	$-NH_2$ (amino)
10.	0.2 g O.C. + 1 c.c. NaOH + heat	smell of NH_3, red litmus changes to blue	$-CONH_2$ (amide)
11.	O.C. + 2 c.c alcoholic $AgNO_3$ + heat	(a) ppt. formed (b) no ppt.	aliphatic halogen aromatic halogen (means halogen attached to benzene nucleus)
12.	O.C. + caustic alkali (1 : 1) + dilute HCl	penetrating smell of SO_2 which on passing into acidic $K_2Cr_2O_7$ soln. produces green colour	$-SO_3H$ (sulphonic acid)

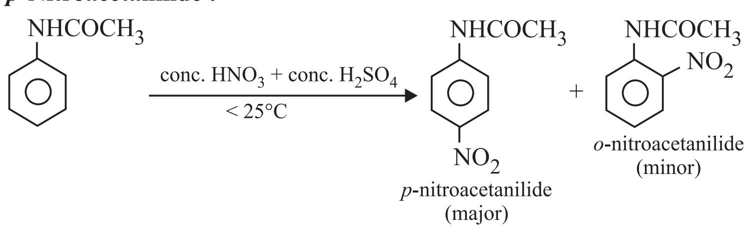
Chemistry involved in the preparation of some organic compounds

- **Acetanilide :**





- ***p*-Nitroacetanilide :**



- **Iodoform :**

Compounds containing $CH_3-\underset{}{CH}(OH)$ group or CH_3CO- group can form iodoform on reaction with sodium hypoiodide. *e.g.* ethanol, acetaldehyde, acetone, etc.

$$CH_3CH_2OH \xrightarrow[\text{or NaOI}]{\text{KOI}} CH_3CHO \quad \text{(oxidation)}$$

$$CH_3CHO \xrightarrow[\text{or NaOI}]{\text{KOI}} CI_3CHO \quad \text{(iodination)}$$

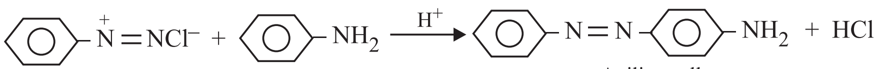
$$CI_3CHO + NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + HCOONa \text{ (hydrolysis)}$$

With acetone no initial oxidation takes place.

$$CH_3COCH_3 \xrightarrow[\text{(iodination)}]{\text{NaOI}} CI_3COCH_3$$

$$CI_3COCH_3 + NaOH \xrightarrow[\text{(hydrolysis)}]{} CHI_3 + CH_3COONa$$

- **Aniline yellow :**



Aniline yellow

PHYSICAL

Volumetric analysis

- Volumetric analysis is a process by which the concentration or strength of a chemical substance is measured by measuring the volume of its solution taking part in a given chemical reaction. The main process of this analysis is called titration.

Titration

- Determination of strength of one solution using another solution of known strength under volumetric conditions is known as titration.

Some important terms

(i) Analyte : The substance being analyzed is known as analyte or titre.

(ii) Titrant : The substance added to the analyte in a titration is known as titrant.

(iii) Equivalence point : It is the point where reaction between two solutions is just complete or the point in a titration at which the quantity of titrant is exactly sufficient for stoichiometric reaction to be complete with the analyte.
At this point there is a sudden change in a physical property, such as indicator colour, pH, conductivity, or absorbance. It is also known as end point.

(iv) Indicator : A compound having a physical property (usually colour) that changes abruptly near the equivalence point of a chemical reaction is known as indicator. It indicates the attainment of end point.

(v) Standard solution : A solution whose concentration is known is called standard solution.

(vi) Standardization : It is the process in which concentration of a reagent is determined by reaction with a known quantity of second reagent whose concentration is known.

(vii) Primary standard substance : A reagent that is pure enough so that its standard solution can be prepared directly by dissolving a definite weight of it in a definite volume of solvent is known as primary standard, *e.g.*, crystalline oxalic acid, anhydrous Na_2CO_3, Mohr's salt, etc.

(viii) Secondary standard substance : The substance or reagent whose standard solution can not be prepared directly is called secondary standard, *e.g.* $KMnO_4$, NaOH, KOH, etc.

Number of equivalents = Normality × Volume (L)

Number of equivalents of titre = Number of equivalents of titrant

$$\boxed{N_1V_1 = N_2V_2}$$

Where N_1 = Normality of titre, V_1 = Volume of titre
N_2 = Normality of titrant, V_2 = Volume of titrant

If volume is taken in ml

Then, Number of milliequivalents (m.eq.)

= Normality × Volume (in ml)

then also, $\boxed{N_1V_1 = N_2V_2}$

The above equation is known as normality equation.

Similarly molarity equation is also given but it is usually applicable for dilution of a solution.

$M_1V_1 = M_2V_2$

Normality = Molarity × n, where n = valency factor

Thus $N_1V_1 = N_2V_2$ can be written as

or $M_1V_1n_1 = M_2V_2n_2$

or $\boxed{\dfrac{M_1V_1}{M_2V_2} = \dfrac{n_2}{n_1}}$

Redox titrations

- Redox titrations involving $KMnO_4$ as oxidising agent are called *permanganometric titrations*. In these titrations reducing agents like Mohr's salt, $(NH_4)_2SO_4$. $FeSO_4 \cdot 6H_2O$, $FeSO_4$, H_2O_2, oxalic acid and oxalates are directly titrated against $KMnO_4$ as oxidising agent in acidic medium.

Indicator

- In these titrations, $KMnO_4$ acts as self indicator. In acidic medium, $KMnO_4$ reacts with reducing agent (like oxalic acid or Mohr's salt), when whole of the reducing agent has been oxidised the remaining $KMnO_4$ is not decomposed and imparts pink colour to the solution and thus acts as an indicator.

End point

- In $KMnO_4$ titration end point is from colourless to permanent light pink colour.

Titration of oxalic acid *vs* $KMnO_4$

- ***Indicator***

  $KMnO_4$ is a self indicator.
- ***End point***

  Colourless to permanent pink colour ($KMnO_4$ in burette).
- ***Chemistry of experiment***

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

$$\left[\begin{array}{l}COOH\\ |\\ COOH_{(aq)}\end{array} \cdot 2H_2O + [O] \xrightarrow{60\text{-}70°C} 2CO_2 + 3H_2O\right] \times 5$$

$$2KMnO_4 + 3H_2SO_4 + 5\begin{array}{l}COOH\\ |\\ COOH\end{array} \cdot 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 18H_2O + 10CO_2$$

or $[MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$

$[C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-] \times 5$

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+}\ 8H_2O + 10CO_2$$

It is clear from the above reactions that two moles of $KMnO_4$ react with five moles of oxalic acid.

- $KMnO_4$ accepts five electrons and gets reduced from MnO_4^- to Mn^{2+} whereas oxalic acid releases two electrons and gets oxidised from $H_2C_2O_4.2H_2O$ to CO_2.
- Oxalic acid solution is heated to 60-70°C before titrating with $KMnO_4$ because in cold, reaction is very slow due to slow formation of Mn^{2+}. When the solution is heated, liberation of Mn^{2+} speeds up which autocatalyses the reaction and therefore reaction proceeds rapidly. Heating of oxalic acid solution also expels the CO_2 evolved during the reaction which otherwise does not allow the reaction to go to completion.

- ***Autocatalysis***

  It is the process in which one of the reaction product catalyses the further reaction of the reactants.

- ***Calculations***

  We can apply normality equation to this titration as

$$\underset{\text{(Oxalic acid)}}{N_1V_1} = \underset{(\text{KMnO}_4)}{N_2V_2}$$

Volume of both the solutions are known in the experiment. By knowing normality of one solution, normality of other solution can be calculated.

We can also apply molarity equation to this titration. Since two moles of $KMnO_4$ react with 5 moles of oxalic acid

$$\frac{M_{\text{KMnO}_4} \times V_{\text{KMnO}_4}}{M_{\text{Oxalic acid}} \times V_{\text{Oxalic acid}}} = \frac{2}{5}$$

By knowing the molarity of one solution that of the other solution can be calculated.

Normality and molarity of a solution are related as

Normality = Molarity × number of electrons gained or lost

- Strength of any solution can be calculated as

Strength = Normality × Equivalent mass

or Strength(g/L) = Molarity × Molecular mass

Equivalent mass of oxalic acid

$$= \frac{\text{Molecular mass}}{2} = \frac{126}{2} = 63$$

Equivalent mass of $KMnO_4$

$$= \frac{\text{Molecular mass}}{5} = \frac{158}{5} = 31.6$$

- Percentage purity of a given salt can also be calculated

$$\text{Percentage purity} = \frac{\text{Strength of pure sample}}{\text{Strength of given sample}} \times 100$$

Titration of Mohr's salt *vs* $KMnO_4$

- ***Indicator***

  $KMnO_4$ is a self indicator.

- ***End point***

  Colourless to permanent light pink ($KMnO_4$ in burette).

- ***Chemistry of experiment***

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

$$[2FeSO_4.(NH_4)2SO_4.6H_2O + H_2SO_4 + [O] \longrightarrow Fe_2(SO_4)_3 + 2(NH_4)2SO_4 + 13H_2O] \times 5$$

$$2KMnO_4 + 8H_2SO_4 + 10FeSO_4.(NH_4)2SO_4.6H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 10(NH_4)_2SO_4 + 68H_2O$$

or $$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

$$[Fe^{2+} \longrightarrow Fe^{3+} + e^-] \times 5$$

$$MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

It is clear from the above reactions that one mole of $KMnO_4$ reacts with five moles of Mohr's salt.

$KMnO_4$ accepts five electrons and reduces from MnO_4^- to Mn^{2+} whereas in Mohr's salt one electron is released so that Fe^{2+} is oxidised to Fe^{3+}.

- ***Calculations***

According to normality equation

$$\underset{\text{(Mohr's salt)}}{N_1V_1} = \underset{(KMnO_4)}{N_2V_2}$$

Volume of both solutions are known in the experiment. By knowing normality of one solution, that of other solution can be calculated.

Molarity equation can also be applied to this titration. Since one mole of $KMnO_4$ reacts with five moles of Mohr's salt, $\frac{M_{KMnO_4} \times V_{KMnO_4}}{M_{\text{Mohr's salt}} \times V_{\text{Mohr's salt}}} = \frac{1}{5}$

where M_{KMnO_4} = Molarity of $KMnO_4$ solution, V_{KMnO_4} = Volume of $KMnO_4$ solution

$M_{\text{Mohr's salt}}$ = Molarity of Mohr's salt, $V_{\text{Mohr's salt}}$ = Volume of Mohr's salt

By knowing the normality of one solution, that of other solution can be calculated.

– Strength of a solution can be calculated as

Strength(g/L) = Normality × Equivalent mass

or Strength(g/L) = Molarity × Molecular mass

Eq. mass of Mohr's salt $= \frac{\text{Molecular mass}}{1} = 392$

Eq. mass of $KMnO_4$ $= \frac{158}{5} = 31.6$

– Percentage purity of a given salt can also be calculated

$$\text{Percentage purity} = \frac{\text{Strength of pure sample}}{\text{Strength of given sample}} \times 100$$

Acid-Base titrations

In acid-base titration the amount of an acid or base is determined by titrating it against a standard solution of base or acid respectively.

Acid-base titration involves neutralization reaction.

$$\underset{\text{(from acid)}}{H^+} + \underset{\text{(from base)}}{OH^-} \longrightarrow \underset{\text{(water)}}{H_2O}$$

In acid base titration there is a sudden change in pH at the end point.

The point at which there is sudden change in pH with addition of very small amount of the titrant to the titrate (titre) is called point of inflection.

Indicator

Acid-base indicators are generally complex organic molecules which are either weak acids or weak bases, *e.g.* phenolphthalein is a weak organic acid (represented as HPh) and methyl orange is a weak organic base (represented as MeOH). These indicators dissociate in aqueous solution such that the unionised indicator and its conjugate part (*i.e.* either conjugate acid or conjugate base) have different colours.

$$\underset{\text{(Colourless)}}{HPh} \rightleftharpoons \underset{\text{(Colourless)}}{H^+} + \underset{\text{(Pink)}}{Ph^-} \qquad \underset{\text{(Yellow)}}{MeOH} \rightleftharpoons \underset{\text{(Red)}}{Me^+} + \underset{\text{(Colourless)}}{OH^-}$$

The choice of an indicator for a particular acid-base titration should be made in such a way that indicator used shows change in colour in the same pH range as developed around the equivalence point.

To show the colour change by an indicator, $\boxed{pK \text{ indicator} = \text{pH at equivalence point}}$

- For strong acid and strong base titration, methyl orange, thymol blue or phenolphthalein can be used.
- For strong acid and weak base titration, methyl orange or methyl red can be used as an indicator.
- For weak acid and strong base titration, phenolphthalein is best suited indicator.

Some common acid-base indicators

Indicator colour change, from acidic to alkaline medium	**pK(ind)**	**pH range**	**Example of titration**
Methyl orange (red ⇒ yellow)	3.7	3.1 – 4.4	Weak base *vs* strong acid titration *e.g.* Ammonia titrated with hydrochloric acid
Bromocresol green (yellow ⇒ blue)	4.0	3.8 – 4.6	Weak base *vs* strong acid titration
Methyl red (red ⇒ yellow)	5.1	4.2 – 6.3	Weak base *vs* strong acid titration
Bromothymol blue (yellow ⇒ blue)	7.0	6.0 – 7.6	Strong acid *vs* strong base titration *e.g.* Hydrochloric acid with sodium hydroxide
Phenol red (yellow ⇒ red)	7.9	6.4 – 8.2	Strong acid *vs* strong base titration *e.g.* Hydrochloric acid with sodium hydroxide
Thymol blue (basic form), (yellow ⇒ blue)	8.9	8.0 – 9.6	Weak/strong acid *vs* strong base titration
Phenolphthalein (colourless ⇒ pink)	9.3	8.3 – 10.0	Weak acid vs strong base titration *e.g.* Ethanoic acid titrated with sodium hydroxide
Alizarin yellow (yellow ⇒ violet)	–	10.1 – 12.0	Weak acid *vs* strong base titration

End