

NEET/JEE 2019

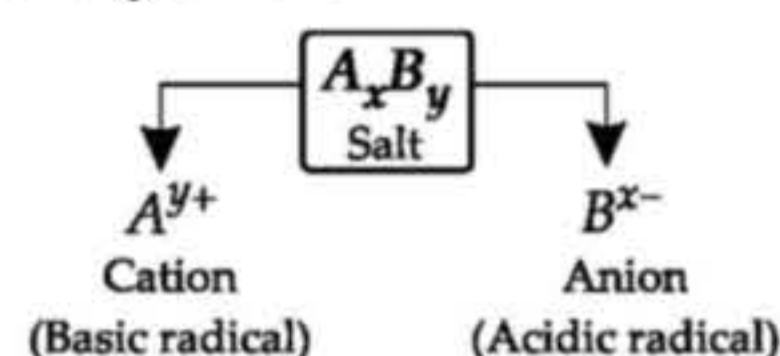
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UNIT - 9 : Principles Related to Practical Chemistry

INORGANIC CHEMISTRY

Qualitative Analysis

- Qualitative analysis deals with the identification of various constituents present in a given compound. This analysis involves preliminary tests, flame test, wet tests for anions and cations etc.
- In the salt, A_xB_y , A is positively charged ion and B is negatively charged ion.



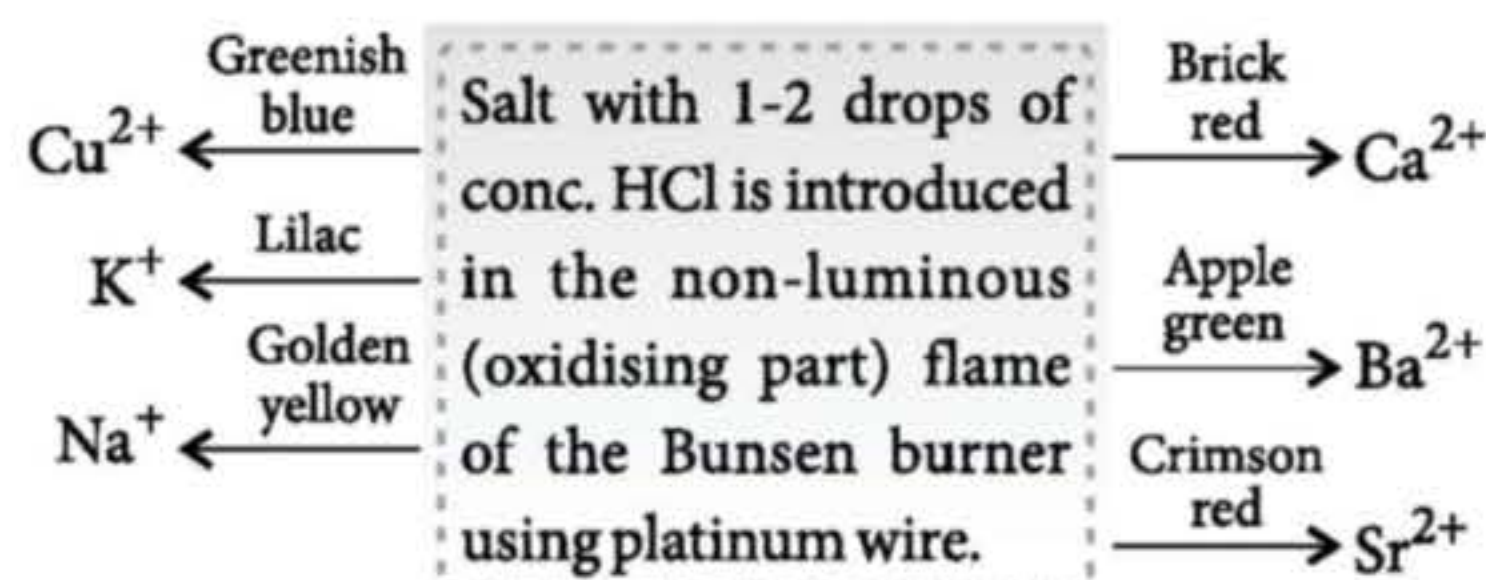
Preliminary Tests

- Physical examination**
 - Colour** : NH_4^+ , Pb^{2+} , Al^{3+} , Zn^{2+} , Ba^{2+} , Ca^{2+} , Sr^{2+} , Mg^{2+} (white); Cu^{2+} (blue); Ni^{2+} , Cr^{3+} (green); Fe^{2+} (light green); Fe^{3+} (brown); Co^{2+} (pink); Mn^{2+} (light pink or flesh colour)
 - Odour** : NH_4^+ (ammoniacal smell), CH_3COO^- (smell of vinegar), S^{2-} (smell of rotten eggs)
- Dry heating test**

| Observation | Radicals/Salts |
|---------------|---|
| (Gas evolved) | |
| Colourless | CO_3^{2-} , SO_3^{2-} , S^{2-} , Cl^- |
| Brown | Br^- , NO_3^- |
| Violet | I^- |

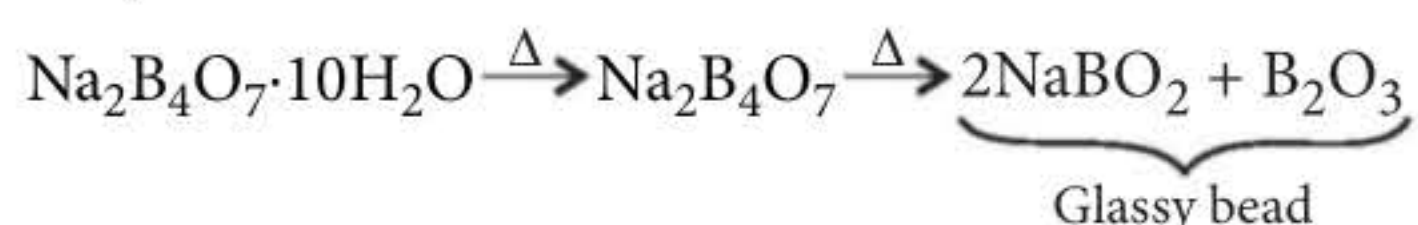
| Residue | |
|----------------------------------|---|
| Yellow when hot, white when cold | Zn^{2+} |
| Brown when hot, yellow when cold | Pb^{2+} |
| Reddish brown | Fe^{2+} |
| Black | Ni^{2+} , Co^{2+} , Mn^{2+} , Cu^{2+} |
| Change in colour of salt | |
| Blue to white | $CuSO_4 \cdot 5H_2O$ |
| Pink to blue | $CoCl_2$ |
| Green to yellow | Ni^{2+} salt |
| Blue/green to brown/black | Cu^{2+} salt |
| Sound produced | |
| Crackling sound | $NaCl$, KI , $Pb(NO_3)_2$, $Ba(NO_3)_2$ |

Flame Test



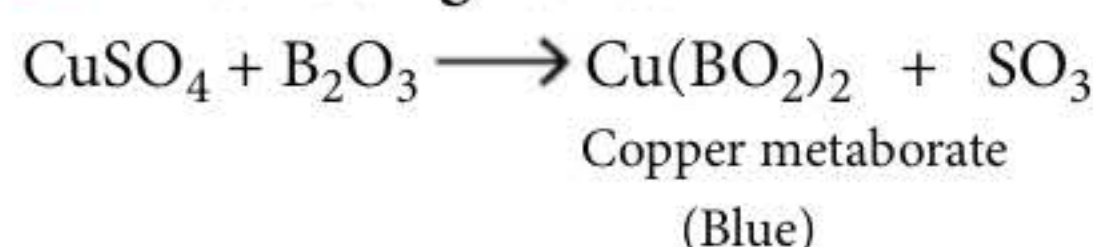
Borax Bead Test

- Borax is heated on a loop of Pt wire, colourless, glassy bead of sodium metaborate and boric anhydride is formed.

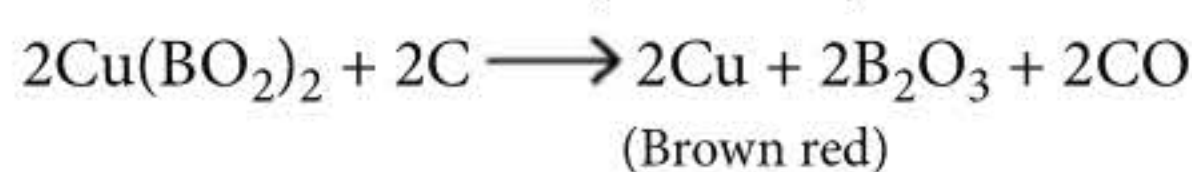
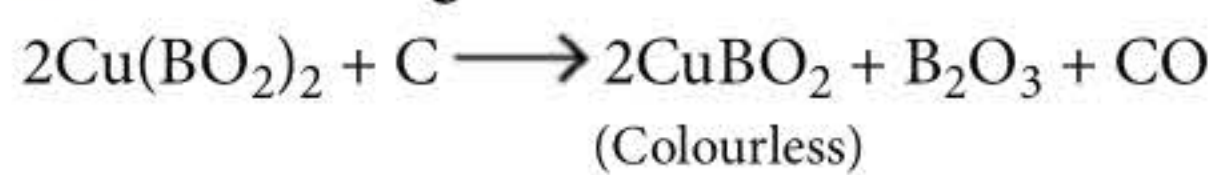


- Coloured salts are then heated on the glassy bead, coloured metaborate is formed in the oxidising flame.

– In oxidising flame :



– In reducing flame :



Hence, different colours appear in different flames.

| Metal | Colour of bead in | | | |
|-------|-------------------|--------------|----------------|--------------|
| | Oxidising flame | | Reducing flame | |
| | Hot | Cold | Hot | Cold |
| Cu | Green | Blue | Colourless | Brown red |
| Fe | Brown yellow | Pale yellow | Bottle green | Bottle green |
| Cr | Green | Green | Green | Green |
| Co | Blue | Blue | Blue | Blue |
| Mn | Violet | Amethyst red | Colourless | Colourless |
| Ni | Red brown | Brown | Grey | Grey |

Wet Tests

- Identification of Acidic Radicals

- Group I acidic radicals : Salt + dilute HCl or dilute H₂SO₄
Effervescence or evolution of gases indicates the presence of group I acidic radicals.

| Gas | Radical (Inference) | Confirmatory tests |
|--|---|---|
| CO ₂ (Brisk effervescence of colourless, odourless gas) | Carbonate (CO ₃ ²⁻) | $\text{Na}_2\text{CO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{CO}_2 \uparrow$ <p style="text-align: center;">Salt</p> $\text{Ca}(\text{OH})_2 + \text{CO}_2 \longrightarrow \text{CaCO}_3 \downarrow + \text{H}_2\text{O}$ <p style="text-align: center;">Lime water White ppt. (milky)</p> $\text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \longrightarrow \text{Ca}(\text{HCO}_3)_2$ <p style="text-align: center;">Soluble</p> |
| H ₂ S (Colourless gas with smell of rotten eggs) | Sulphide (S ²⁻) | $\text{Na}_2\text{S} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{S} \uparrow$ <p style="text-align: center;">Salt</p> $(\text{CH}_3\text{COO})_2\text{Pb} + \text{H}_2\text{S} \longrightarrow \text{PbS} \downarrow + 2\text{CH}_3\text{COOH}$ <p style="text-align: center;">Black ppt.</p> $\text{Na}_2\text{S} + \text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \longrightarrow \text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$ <p style="text-align: center;">Salt Sodium nitroprusside Violet</p> |
| SO ₂ (Colourless gas with suffocating odour having smell of burning sulphur) | Sulphite (SO ₃ ²⁻) | $\text{Na}_2\text{SO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{SO}_2 \uparrow$ <p style="text-align: center;">Salt</p> $\text{K}_2\text{Cr}_2\text{O}_7 + 3\text{SO}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$ <p style="text-align: center;">Green</p> $\text{Na}_2\text{SO}_3 + \text{BaCl}_2 \longrightarrow \text{BaSO}_3 \downarrow + 2\text{NaCl}$ <p style="text-align: center;">Salt White ppt.</p> $\text{BaSO}_3 + 2\text{HCl} \longrightarrow \text{BaCl}_2 + \text{H}_2\text{O} + \text{SO}_2 \uparrow$ <p style="text-align: center;">Soluble</p> |

| | | |
|--|--|--|
| NO_2 (Brown gas) | Nitrite (NO_2^-) | $2\text{NaNO}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{HNO}_2$ Salt Nitrous acid $3\text{HNO}_2 \longrightarrow \text{H}_2\text{O} + 2\text{NO} + \text{HNO}_3$ $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2 \uparrow$ Brown $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} + \text{NO} \longrightarrow [\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4 + 2\text{H}_2\text{O}$ Brown |
| CH_3COOH (Colourless gas with smell of vinegar) | Acetate (CH_3COO^-) | $2\text{CH}_3\text{COONa} + \text{H}_2\text{SO}_4 \longrightarrow 2\text{CH}_3\text{COOH} + \text{Na}_2\text{SO}_4$ Salt $3\text{CH}_3\text{COONa} + \text{FeCl}_3 \longrightarrow (\text{CH}_3\text{COO})_3\text{Fe} + 3\text{NaCl}$ Salt Blood red $2\text{CH}_3\text{COONa} + \begin{array}{c} \text{COOH} \\ \\ \text{COOH} \end{array} \longrightarrow \begin{array}{c} \text{COONa} \\ \\ \text{COONa} \end{array} + 2\text{CH}_3\text{COOH}$ Salt Smell of vinegar |

Carbonates of Bi and Ba are not easily decomposed by dil. H_2SO_4 hence, dil. HCl should be used.

- **Group II acidic radicals** : Salt + conc. H_2SO_4 or conc. HCl and heat (if necessary)

Effervescence or evolution of gases indicates the presence of group II acidic radicals.

| Gas | Radical | Observations and Reactions | Confirmatory tests |
|--|-------------------------------|--|--|
| HCl (Colourless gas with pungent smell) Cl_2 (Yellowish green, suffocating odour) | Chloride (Cl^-) | $\text{NaCl} + \text{H}_2\text{SO}_4 \longrightarrow \text{NaHSO}_4 + \text{HCl} \uparrow$ Salt $\text{NH}_4\text{OH} + \text{HCl} \longrightarrow \text{NH}_4\text{Cl} \uparrow + \text{H}_2\text{O}$ White dense fumes $\text{HCl} + \text{AgNO}_3 \longrightarrow \text{AgCl} \downarrow + \text{HNO}_3$ White ppt. $\text{AgCl} + 2\text{NH}_4\text{OH} \longrightarrow$ $[\text{Ag}(\text{NH}_3)_2]\text{Cl} + 2\text{H}_2\text{O}$ Soluble $2\text{NaCl} + \text{MnO}_2 + 3\text{H}_2\text{SO}_4 \longrightarrow$ Salt $2\text{NaHSO}_4 + \text{MnSO}_4 + 2\text{H}_2\text{O} + \text{Cl}_2 \uparrow$ | Chromyl chloride test : $\text{NaCl} + \text{H}_2\text{SO}_4 (\text{Conc.}) \longrightarrow \text{NaHSO}_4 + \text{HCl}$ Salt $\text{K}_2\text{Cr}_2\text{O}_7 + 2\text{H}_2\text{SO}_4 \longrightarrow 2\text{KHSO}_4 + 2\text{CrO}_3 + \text{H}_2\text{O}$ $\text{CrO}_3 + 2\text{HCl} \longrightarrow \text{CrO}_2\text{Cl}_2 \uparrow + \text{H}_2\text{O}$ Chromyl chloride (Deep red vapours) $\text{CrO}_2\text{Cl}_2 + 4\text{NaOH} \longrightarrow$ $\text{Na}_2\text{CrO}_4 + 2\text{NaCl} + 2\text{H}_2\text{O}$ Yellow solution $\text{Na}_2\text{CrO}_4 + (\text{CH}_3\text{COO})_2\text{Pb} \longrightarrow$ $\text{PbCrO}_4 \downarrow + 2\text{CH}_3\text{COONa}$ Yellow ppt. |
| Br_2 (Brown gas, intensify on addition of MnO_2) | Bromide (Br^-) | $\text{NaBr} + \text{H}_2\text{SO}_4 \longrightarrow \text{NaHSO}_4 + \text{HBr}$ Salt $2\text{HBr} + \text{H}_2\text{SO}_4 \longrightarrow \text{Br}_2 \uparrow + 2\text{H}_2\text{O} + \text{SO}_2$ Brown $\text{AgNO}_3 + \text{NaBr} \longrightarrow \text{AgBr} \downarrow + \text{NaNO}_3$ Pale yellow ppt. $\text{AgBr} + 2\text{NH}_4\text{OH} \longrightarrow$ $[\text{Ag}(\text{NH}_3)_2]\text{Br} + 2\text{H}_2\text{O}$ Soluble $2\text{NaBr} + \text{MnO}_2 + 3\text{H}_2\text{SO}_4 \longrightarrow$ $2\text{NaHSO}_4 + \text{MnSO}_4 + 2\text{H}_2\text{O} + \text{Br}_2 \uparrow$ | Layer test : On treating salt with dil. H_2SO_4 , CHCl_3 or CCl_4 and chlorine water, brown coloured layer is formed. $\text{NaBr} + \text{Cl}_2 \text{ water} \longrightarrow 2\text{NaCl} + \text{Br}_2$ Salt $\text{Br}_2 + \text{CHCl}_3 \longrightarrow$ Brown coloured layer or CCl_4 |

| | | | |
|--|----------------------|---|---|
| I_2 (Deep violet vapour, intensify on addition of MnO_2) | Iodide (I^-) | $2KI + 2H_2SO_4 \longrightarrow 2KHSO_4 + 2HI$ Salt $2HI + H_2SO_4 \longrightarrow I_2 \uparrow + SO_2 + 2H_2O$ Violet $AgNO_3 + KI \longrightarrow AgI \downarrow + KNO_3$ Yellow ppt. $AgI + NH_4OH \longrightarrow$ Not soluble $2KI + MnO_2 + 3H_2SO_4$ Salt $\longrightarrow 2KHSO_4 + MnSO_4 + 2H_2O + I_2 \uparrow$ | Layer test : $2K + Cl_2 \longrightarrow 2KCl + I_2$ Salt $I_2 + \text{Chloroform} \longrightarrow$ Violet coloured layer Starch paper test : $I_2 + \text{Starch} \longrightarrow I_2\text{-starch complex}$ Violet vapours Blue colour |
| NO_2 (Light brown gas having pungent smell, intensify on adding Cu turning) | Nitrate (NO_3^-) | $NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$ Salt $4HNO_3 \longrightarrow 2H_2O + 4NO_2 \uparrow + O_2$ Light brown fumes $Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 \uparrow + 2H_2O$ | Brown ring test : $NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$ Salt $6FeSO_4 + 2HNO_3 + 3H_2SO_4(\text{conc.}) \longrightarrow$ Ferrous sulphate $3Fe_2(SO_4)_3 + 4H_2O + 2NO$ $[Fe(H_2O)_6]SO_4 \cdot H_2O + NO \longrightarrow$ $[Fe(H_2O)_5NO]SO_4 + 2H_2O$ Brown ring |

- **Group III acidic radicals :** These radicals cannot be detected by either dil. H_2SO_4 or conc. H_2SO_4 . For detection of these acidic radicals we need some specific tests.

| Radical | Observations and Reactions |
|---------------------------|---|
| Sulphate (SO_4^{2-}) | $Na_2SO_4 + BaCl_2 \longrightarrow BaSO_4 \downarrow + 2NaCl$ Salt White ppt. |
| Phosphate (PO_4^{3-}) | $Ca_3(PO_4)_2 + 6HNO_3 \xrightarrow{H^+} 3Ca(NO_3)_2 + 2H_3PO_4$ Salt $H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3(\text{Conc.}) \longrightarrow (NH_4)_3PO_4 \cdot 12MoO_3 \downarrow + 21NH_4NO_3 + 12H_2O$ Ammonium molybdate Canary yellow ppt. |
| Borate (BO_3^{3-}) | $2Na_3BO_3 + 3H_2SO_4 \longrightarrow 3Na_2SO_4 + 2H_3BO_3$ Salt $H_3BO_3 + 3C_2H_5OH \longrightarrow (C_2H_5)_3BO_3 \uparrow + 3H_2O$ Ethyl borate (burns with green edged flame) |
| Fluoride (F^-) | $2NaF + H_2SO_4 \longrightarrow Na_2SO_4 + H_2F_2$ Salt $SiO_2 + 2H_2F_2 \longrightarrow SiF_4 + 2H_2O$ $3SiF_4 + 4H_2O \longrightarrow H_4SiO_4 + 2H_2SiF_6$ Silicic acid (Gelatinous white) |

- **Identification of Basic Radicals**

- **Separation of basic radicals into different groups :**

| Basic radicals of | Group reagent | Precipitated as | Explanation |
|--|---------------|---|--|
| Group I Ag^+, Pb^{2+}, Hg_2^{2+} | dil. HCl | $AgCl, PbCl_2, Hg_2Cl_2$ (All white) | K_{sp} values of their chlorides are low, hence $K_{ip} > K_{sp}$ and they get precipitated. |

| | | | |
|---|---|---|--|
| Group II Hg ²⁺ , Pb ²⁺ , Bi ³⁺ , Cu ²⁺ , Cd ²⁺ , As ³⁺ , Sb ³⁺ , Sn ²⁺ , Sn ⁴⁺ | H ₂ S in presence of dil. HCl | HgS, PbS, Bi ₂ S ₃ , CuS (Black); CdS, As ₂ S ₃ , SnS ₂ (Yellow); Sb ₂ S ₃ (Orange); SnS (Brown) | HCl (with common H ⁺ ion) decreases the ionization of H ₂ S which gives low [S ²⁻]. Hence, only group II sulphides having low K _{sp} values are precipitated. |
| Group III Fe ³⁺ , Cr ³⁺ , Al ³⁺ | NH ₄ OH in presence of NH ₄ Cl | Fe(OH) ₃ (Reddish brown), Cr(OH) ₃ (Green), Al(OH) ₃ (White) | NH ₄ Cl (with common NH ₄ ⁺ ion) decreases the ionization of NH ₄ OH giving low [OH ⁻]. Hence, only group III hydroxides having low K _{sp} values are precipitated. |
| Group IV Zn ²⁺ , Mn ²⁺ , Co ²⁺ , Ni ²⁺ | H ₂ S in presence of NH ₄ OH | ZnS (Greenish white), MnS (Buff), CoS, NiS (Black), | Basic medium increases the ionization of H ₂ S, thus increasing [S ²⁻], hence precipitation of group IV sulphides having high K _{sp} values occurs. |
| Group V Ba ²⁺ , Sr ²⁺ , Ca ²⁺ | (NH ₄) ₂ CO ₃ in presence of NH ₄ OH | BaCO ₃ , SrCO ₃ , CaCO ₃ (All white) | K _{sp} values of their carbonates are less than that of group VI (Mg ²⁺) hence, group V is precipitated before Mg ²⁺ . |
| Group VI Mg ²⁺ | Na ₂ HPO ₄ in presence of NH ₄ OH | Mg(NH ₄)PO ₄ (White) | — |
| Zero NH ₄ ⁺ | NaOH | Ammonia gas is evolved. | Tested independently from original solution. |

ORGANIC CHEMISTRY

Qualitative Analysis

- In addition to carbon and hydrogen, organic compounds may also contain oxygen, nitrogen, sulphur, halogens and phosphorus.
- The qualitative analysis of organic compounds involves the detection of all these major elements present in it with the help of suitable chemical tests.

Detection of Extra Elements (N, S, halogens) in Organic Compounds

- The elements other than C, H and O are called extra elements.
- The elements are usually tested in the form of ions. Since organic compounds are covalent in nature, they do not ionize. Therefore, to convert elements present in organic compounds into ions, the organic compound is fused with sodium metal which is plunged in distilled water, boiled and filtered.
- The filtrate is called Lassaigne's extract (L.E.) or sodium extract.

| Element | Detection | Confirmatory test | Reactions |
|----------|---|--|---|
| Nitrogen | Lassaigne's extract (L.E.) Na + C + N $\xrightarrow{\Delta}$ NaCN (L.E.) | L.E. + FeSO ₄ + NaOH, boil and cool + FeCl ₃ + conc. HCl Gives blue or green colour. | FeSO ₄ + 2NaOH \longrightarrow Fe(OH) ₂ + Na ₂ SO ₄ Fe(OH) ₂ + 6NaCN \longrightarrow Na ₄ [Fe(CN) ₆] + 2NaOH 3Na ₄ [Fe(CN) ₆] + 4FeCl ₃ \longrightarrow Fe ₄ [Fe(CN) ₆] ₃ + 12NaCl Prussian blue |
| Sulphur | 2Na + S $\xrightarrow{\Delta}$ Na ₂ S (L.E.) | (i) L.E. + sodium nitroprusside A deep violet colour. (ii) L.E. + CH ₃ COOH + (CH ₃ COO) ₂ Pb Gives a black ppt. | (i) Na ₂ S + Na ₂ [Fe(CN) ₅ NO] \longrightarrow Sodium nitroprusside Na ₄ [Fe(CN) ₅ NOS] Deep violet (ii) Na ₂ S + (CH ₃ COO) ₂ Pb $\xrightarrow{\text{CH}_3\text{COOH}}$ PbS↓ + 2CH ₃ COONa Black ppt. |

| | | | |
|-------------------------------------|--|---|--|
| Halogens | $\text{Na} + \text{X} \xrightarrow{\Delta} \text{NaX}$ (L.E.) | L.E. + HNO_3 + AgNO_3 (i) White ppt. soluble in aq. NH_3 (or NH_4OH) confirms Cl. (ii) Yellow ppt. partially soluble in aq. NH_3 (or NH_4OH) confirms Br. (iii) Yellow ppt. insoluble in aq. NH_3 (or NH_4OH) confirms I. | $\text{NaX} + \text{AgNO}_3 \xrightarrow{\text{HNO}_3} \text{AgX} \downarrow$ White ppt. $\text{AgCl} + 2\text{NH}_3(\text{aq.}) \longrightarrow [\text{Ag}(\text{NH}_3)_2]\text{Cl}$ Soluble |
| Nitrogen and sulphur together | $\text{Na} + \text{C} + \text{N} + \text{S} \xrightarrow{\Delta} \text{NaSCN}$ (L.E.) | As in test for nitrogen; instead of green or blue colour, blood red colouration confirms presence of N and S both. | $3 \text{NaSCN} + \text{FeCl}_3 \longrightarrow \text{Fe}(\text{SCN})_3$ Blood red colour + 3NaCl |

Functional Group

- An atom or group of atoms that largely determines the properties of an organic compound.
- Detection of functional groups :** Hydroxyl (alcoholic and phenolic), carbonyl (aldehyde and ketone), carboxyl, amino and nitro groups in organic compounds.

| Test | Reaction | Confirmation |
|---|--|---|
| (A) Detection of unsaturation | | |
| (i) Baeyer's or KMnO_4 test | $2\text{KMnO}_4 + \text{H}_2\text{O} \longrightarrow 2\text{KOH} + 2\text{MnO}_2 + 3[\text{O}]$ $>\text{C}=\text{C}< + \text{H}_2\text{O} + [\text{O}] \longrightarrow \begin{array}{c} >\text{C}-\text{C}< \\ \quad \\ \text{OH} \quad \text{OH} \end{array}$ | Disappearance of pink colour of KMnO_4 . |
| (ii) $\text{Br}_2 - \text{CCl}_4$ test | $>\text{C}=\text{C}< + \text{Br}_2 \xrightarrow{\text{CCl}_4} \begin{array}{c} \text{Br} \\ \\ >\text{C}-\text{C}< \\ \\ \text{Br} \end{array}$ Red brown | Disappearance of brown colour. |
| (B) Detection of alcoholic group | | |
| (i) Acetyl chloride test | $\text{R}-\text{OH} + \text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl} \longrightarrow \begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{C}-\text{O}-\text{R} \end{array} + \text{HCl} \uparrow$ | Evolution of HCl gas and fruity smell |
| (ii) Ceric ammonium nitrate test | $2\text{ROH} + (\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6] \longrightarrow [(\text{ROH})_2\text{Ce}(\text{NO}_3)_4] + 2\text{NH}_4\text{NO}_3$ Pink or red | Appearance of pink or red colour. |
| (C) Detection of phenolic group | | |
| (i) FeCl_3 test | $\text{FeCl}_3 + 6\text{C}_6\text{H}_5\text{OH} \longrightarrow [\text{Fe}(\text{OC}_6\text{H}_5)_6]^{3-} + 3\text{H}^+ + 3\text{HCl}$ Violet | Appearance of violet colouration. |
| (ii) Azo dye test | $\text{C}_6\text{H}_5\text{NH}_2 + \text{NaNO}_2 + \text{HCl} \longrightarrow \text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$ $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^- + \text{C}_6\text{H}_5\text{OH} \xrightarrow[\text{p-Hydroxyazobenzene}]{\text{pH 9-10, } 0-5^\circ\text{C}}$ | Formation of orange or red dye. |

| (D) Detection of carbonyl group | | | |
|--|------------------------------------|--|--|
| Aldehydic/Ketonic group | | | |
| (i) | Brady's reagent (2, 4-DNP) test | $\begin{array}{c} \text{NO}_2 \\ \\ \text{>C=O} + \text{H}_2\text{NNH}-\text{C}_6\text{H}_3(\text{NO}_2)_2 \\ \\ \text{2,4-Dinitrophenylhydrazine} \\ \downarrow \\ \text{>C=NNH}-\text{C}_6\text{H}_3(\text{NO}_2)_2 \\ \\ \text{Yellow, orange or red ppt.} \end{array}$ | Appearance of yellow, orange or red ppt. |
| (ii) | Sod. bisulphite test | $\text{>C=O} + \text{NaHSO}_3 \rightarrow \begin{array}{c} \text{OH} \\ \\ \text{>C} \\ \\ \text{SO}_3^- \text{Na}^+ \end{array}$ <p style="text-align: center;">White ppt.</p> | Appearance of white ppt. |
| Aldehydic group | | | |
| (i) | Tollens' test | $\text{RCHO} + 2[\text{Ag}(\text{NH}_3)_2]\text{OH} \rightarrow \text{RCOONH}_4 + 3\text{NH}_3 + \text{H}_2\text{O} + 2\text{Ag}_{(s)} \downarrow$ <p style="text-align: center;">(Silver mirror)</p> | Formation of silver mirror along the sides of the test tube. |
| (ii) | Fehling's test | $\text{RCHO} + 2\text{Cu}^{2+} + 3\text{OH}^- \rightarrow 2\text{Cu}^+ \downarrow + \text{RCOO}^- + 2\text{H}_2\text{O}$ <p style="text-align: center;">Red ppt.</p> | A red ppt. is formed (only by aliphatic aldehydes). |
| (iii) | Benedict's test | $\text{RCHO} + 2\text{Cu}(\text{OH})_2 + \text{NaOH} \rightarrow \text{RCOONa} + \text{Cu}_2\text{O} \downarrow + 3\text{H}_2\text{O}$ <p style="text-align: center;">Red ppt.</p> | Appearance of red ppt. |
| Ketonic group | | | |
| (i) | Iodoform test | $\text{R}-\text{CO}-\text{CH}_3 + 3\text{I}_2 + 4\text{NaOH} \rightarrow 3\text{NaI} + \text{CHI}_3 \downarrow + \text{RCOONa} + 3\text{H}_2\text{O}$ <p style="text-align: center;">Yellow ppt.</p> | Formation of yellow ppt. of CHI_3 (for methyl ketones only). |
| (ii) | Sodium nitroprusside test | $\text{RCOR} + \text{sod. nitroprusside solution} + \text{NaOH} \rightarrow \text{Wine-red coloured complex}$ | Appearance of wine-red colour. |
| (E) Detection of carboxylic group | | | |
| (i) | NaHCO_3 test | $\text{RCOOH} + \text{NaHCO}_3 \rightarrow \text{RCOONa} + \text{H}_2\text{O} + \text{CO}_2 \uparrow$ | Brisk effervescence of CO_2 indicates $-\text{COOH}$ group. |
| (ii) | Ester test | $\text{RCOOH} + \text{C}_2\text{H}_5\text{OH} \xrightarrow[\Delta]{\text{Conc. H}_2\text{SO}_4} \text{RCOOC}_2\text{H}_5 + \text{H}_2\text{O}$ | Fruity smell of esters formed. |
| (iii) | FeCl_3 test | $\begin{array}{l} 3\text{RCOOH} + 3\text{NH}_4\text{OH} + \text{FeCl}_3 \rightarrow (\text{RCOO})_3\text{Fe} + 3\text{NH}_4\text{Cl} + 3\text{H}_2\text{O} \\ \downarrow \text{H}_2\text{O} \\ \text{Fe}(\text{OH})(\text{OOCR})_2 + \text{RCOOH} \\ \text{Basic iron salt} \end{array}$ | Red : acetic acid, formic acid No colour change : oxalic acid Violet : salicylic acid Buff : benzoic acid |
| (F) Detection of amino group | | | |
| Primary amines | | | |
| (i) | Carbylamine test | $\text{R}-\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH} \xrightarrow{\Delta} \text{R}-\text{N} \equiv \text{C} + 3\text{KCl} + 3\text{H}_2\text{O}$ <p style="text-align: center;">Isocyanide</p> | Offensive smell of isocyanide indicates 1° aliphatic or aromatic amino group. |

| | | | |
|-------------------------------------|---------------------------|---|---|
| (ii) | Azo dye test | $\text{C}_6\text{H}_5\text{NH}_2 + \text{NaNO}_2 + \text{HCl} \xrightarrow[5-10 \text{ atm}]{0-5^\circ\text{C}} \text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$ | A red or orange coloured dye confirms 1° aromatic amino group. |
| Secondary amines | | | |
| | Liebermann's nitroso test | $\text{C}_6\text{H}_5 - \underset{\text{CH}_3}{\text{N}} - \text{H} + \text{HNO}_2 \longrightarrow \text{C}_6\text{H}_5 - \underset{\text{CH}_3}{\text{N}} - \text{N} = \text{O} + \text{H}_2\text{O}$ <p style="text-align: center;">Nitrosoamine</p> | Formation of a yellow oily nitrosoamine indicates 2° aliphatic or aromatic amino group. |
| (G) Detection of nitro group | | | |
| (i) | Mulliken Barker test | $\text{RNO}_2 + 4[\text{H}] \xrightarrow{\text{Zn} + \text{NH}_4\text{Cl}} \text{RNHOH} + \text{H}_2\text{O}$ $\text{RNHOH} + 2[\text{Ag}(\text{NH}_3)_2]\text{OH} \longrightarrow \text{RNO} + 2\text{H}_2\text{O} + 4\text{NH}_3 + 2\text{Ag}\downarrow$ <p style="text-align: center;">Grey-black ppt.</p> | Appearance of grey-black ppt. |
| (ii) | Ferrous hydroxide test | $\text{RNO}_2 + 6\text{Fe}(\text{OH})_2 + 4\text{H}_2\text{O} \longrightarrow \text{RNH}_2 + 6\text{Fe}(\text{OH})_3\downarrow$ <p style="text-align: center;">Light green Brown ppt.</p> | Appearance of brown ppt. |

Distinction Tests

| Test | Phenol | Alcohol |
|-----------------------------|--|---------|
| Blue litmus test | Turns red | × |
| FeCl ₃ test | Gives blue, violet, green or red colouration | × |
| Azo dye test | Forms orange-red colour dye | × |
| Br ₂ -water test | Gives white ppt. | × |

| Test | Phenol | Carboxylic acid |
|-------------------------|--------|---------------------------|
| NaHCO ₃ test | × | Gives brisk effervescence |

| Test | Aldehyde | Ketone |
|--|---------------------------|-----------------------|
| Tollens' test | Gives shiny silver mirror | × |
| Fehling's solution test | Gives red ppt. | × |
| Schiff's reagent test | Gives pink colour | × |
| Reduction with LiAlH ₄ | Reduced to 1° alcohol | Reduced to 2° alcohol |
| Peroxy acid (Caro's acid, peroxy benzoic acid) | Acid is formed. | Ester is formed. |

PHYSICAL CHEMISTRY

Quantitative Analysis

- A quantitative analysis is one in which the amount or concentration of a particular species in a sample is determined accurately and precisely.

Volumetric Analysis

- Volumetric analysis is a process by which the concentration or strength of an unknown chemical solution 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 used in volumetric analysis

- Titrant** : The solution of known strength (which is taken in burette) is called titrant.
- Titrate** : The substance whose concentration is to be determined by titration is called titrate.
- 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

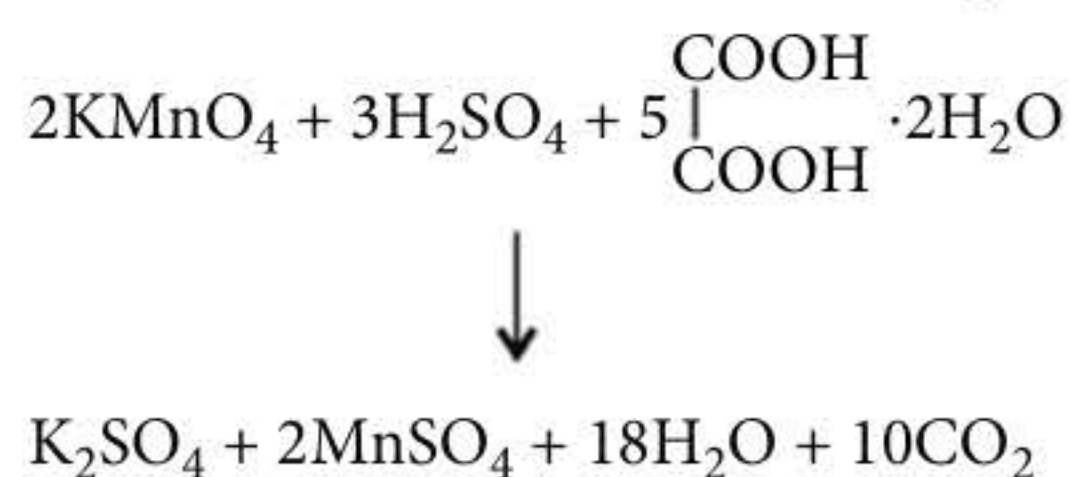
sufficient for the completion of stoichiometric reaction to be completed with titrate. At this point, there is a sudden change in a physical property, such as indicator colour, pH, conductivity.

- **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.
- **Standard solution** : A solution whose concentration is known is called standard solution.
- **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.
- **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.
- **Secondary standard substance** : The substance or reagent whose standard solution cannot be prepared directly is called secondary standard, e.g. KMnO_4 , NaOH , KOH , etc.

| Acid | Alkali | Indicator | End point |
|---|--|----------------------------------|---|
| Strong acid (HCl , H_2SO_4 , HNO_3) | Strong alkali (NaOH , KOH) | Phenolphthalein or methyl orange | Pink to colourless or yellow/orange to red, <i>vice versa</i> |
| Weak acid (oxalic acid, acetic acid) | Strong alkali (NaOH , KOH) | Phenolphthalein | Pink to colourless, <i>vice versa</i> |
| Strong acid (HCl , H_2SO_4 , HNO_3) | Weak alkali (Na_2CO_3 , NaHCO_3 , KHCO_3 , NH_4OH) | Methyl orange | Yellow/orange to red, <i>vice versa</i> |

- **Redox titrations** : These titrations proceed with transfer of electrons among the reacting ions in aqueous solutions.

- **Titration of oxalic acid vs KMnO_4** :



Calculation involving in volumetric analysis

Number of equivalents = Normality \times Volume (in L)

Number of equivalents of titrant = Number of equivalents of titrate, i.e., $N_1V_1 = N_2V_2$

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 $\times n$; where, n = valency factor

Thus, $N_1V_1 = N_2V_2$ can be written as

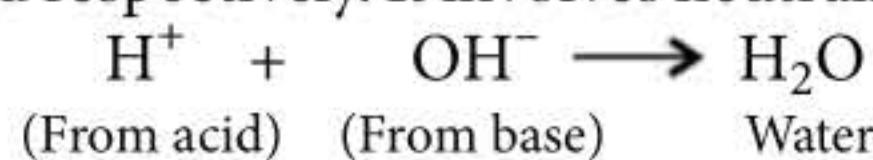
$$M_1V_1n_1 = M_2V_2n_2$$

$$\text{or } \frac{M_1V_1}{M_2V_2} = \frac{n_2}{n_1}$$

Strength (in g/litre) = Molarity \times Molecular mass

Types of titrations

- **Acid-base titrations** : In acid-base titration, the strength of an acid or base is determined by titrating it against a standard solution of base or acid respectively. It involves neutralisation reaction.

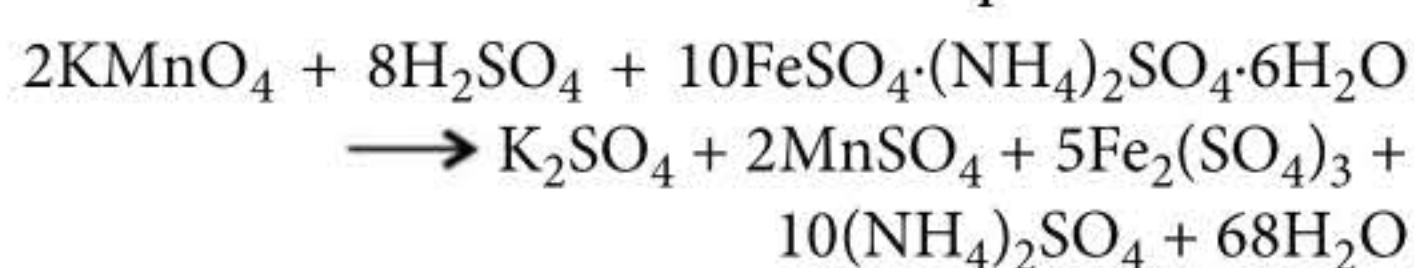


- **Choice of indicators** : The choice of an indicator should be made in such a way that indicator used shows change in colour in the same pH range as developed around the equivalence point.

- Calculations:

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

- **Titration of Mohr's salt vs KMnO_4** :



Calculations :

$$\frac{M_{\text{KMnO}_4} \times V_{\text{KMnO}_4}}{M_{\text{Mohr's salt}} \times V_{\text{Mohr's salt}}} = \frac{1}{5}$$