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Unit 9 — Principles Related to Practical Chemistry

SURFACE CHEMISTRY

Preparation of Lyophilic Sol

- **Starch sol :** Starch is an intrinsic colloid, forms a hydrophilic sol directly when mixed with hot water. It is quite stable as it is electrically neutral.
- **Gum-arabic :** Gum-arabic is hydrophilic colloid and therefore, readily forms sol on shaking with water. The sol is stable as it is not affected by ionic impurities.
- **Egg albumin :** Egg albumin forms hydrophilic sol with water at room temperature. It is quite stable and not affected by the presence of any impurity.

#### Preparation of Lyophobic Sol

- **Hydrated ferric oxide sol :** It is prepared indirectly by the hydrolysis of ferric chloride with boiling water. Ferric ions produced from $FeCl_3$ solution are adsorbed on the surface of the particles of $Fe(OH)_3$.

$$FeCl_{3(aq)} + 3H_2O_{(l)} \xrightarrow{\Delta} Fe(OH)_{3(s)} + 3HCl_{(aq)}$$
<div align="center">Red sol</div>

- **Hydrated aluminium oxide sol :** It is prepared by hydrolysis of aluminium chloride.
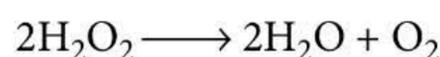
$$AlCl_{3(aq)} + 3H_2O_{(l)} \xrightarrow{\Delta} Al(OH)_{3(s)} + 3HCl_{(aq)}$$
<div align="center">White sol</div>

- **Arsenious sulphide sol :** It is prepared by passing hydrogen sulphide gas through a dilute aqueous solution of arsenious oxide.
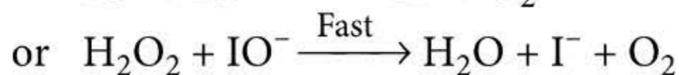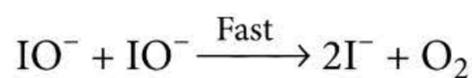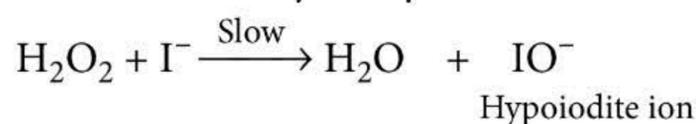
$$As_2O_{3(aq)} + 3H_2S_{(g)} \longrightarrow As_2S_{3(s)} + 3H_2O_{(l)}$$
<div align="center">Yellow sol</div>
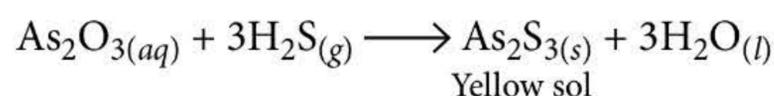
CHEMICAL KINETICS

Rate of Decomposition of H_2O_2 :

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

The reaction is catalysed by iodide ions.

$$H_2O_2 + I^- \xrightarrow{\text{Slow}} H_2O + IO^-$$
<div align="center">Hypoiodite ion</div>

$$IO^- + IO^- \xrightarrow{\text{Fast}} 2I^- + O_2$$

or $\quad H_2O_2 + IO^- \xrightarrow{\text{Fast}} H_2O + I^- + O_2$

Thus, rate law equation is

$$\text{Rate} = -\frac{1}{2}\frac{d[H_2O_2]}{dt} = k'\,[H_2O_2]\,[I^-]$$

If concentration of I^- ions remains constant, then the rate law equation is

$$\text{Rate} = -\frac{1}{2}\frac{d[H_2O_2]}{dt} = k\,[H_2O_2] \qquad (\because k'\,[I^-] = k)$$

i.e., it is a first order reaction.

Reaction of Iodide Ion with H_2O_2 at Room Temperature :

Here, reactions involved are

- **Main reaction :**

$$H_2O_2 + 2I^- + 2H^+ \xrightarrow{\text{Slow}} I_2 + 2H_2O$$

- **Monitor reaction :**

$$I_2 + 2S_2O_3^{2-} \xrightarrow{\text{Fast}} S_4O_6^{2-} + 2I^-$$

- **Indicator reaction :**

$$I_2 + \text{Starch} \longrightarrow \text{Blue colour complex}$$
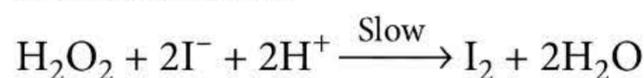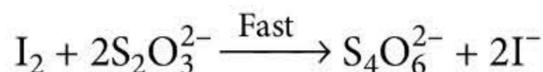
- As the concentration of thiosulphate ion is kept constant, the different time taken (t_c) for the appearance of blue colour with change in concentration of either reactant indicates the relative rate of reaction.

$$\text{Initial rate} \propto \frac{1}{t_c}$$

The rate of reaction decreases with decrease in the concentration of KI.

The graph of $1/t_c$ versus volume of KI solution is a straight line.
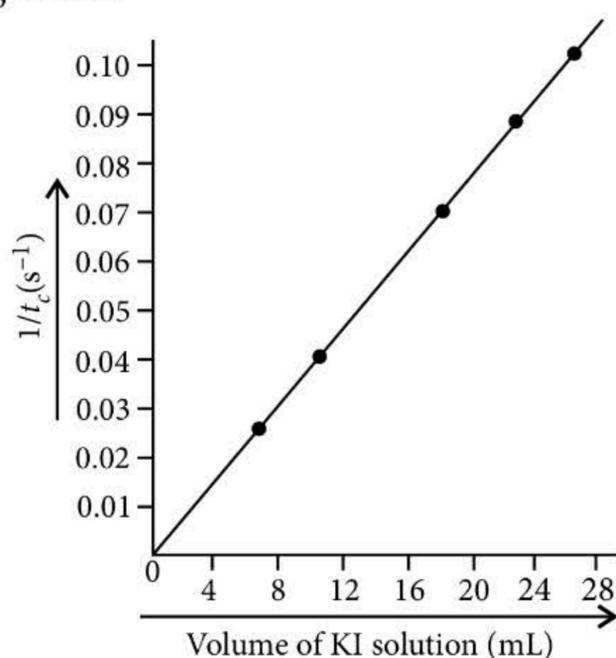
Rate of reaction ∝ Concentration of KI

Similarly, by keeping I^- ion concentration constant and taking different concentrations of H_2O_2, the rate $w.r.t.$ H_2O_2 can be found out.

THERMOCHEMISTRY

Enthalpy of Dissolution of Copper Sulphate

It is the amount of heat absorbed or evolved on dissolving one mole of substance in excess of solvent at a given temperature and pressure. It is +ve when heat is absorbed and –ve when heat is given out during dissolution.
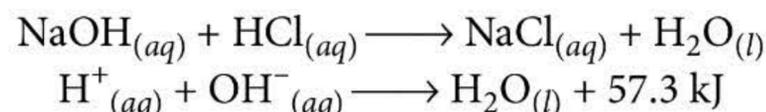
For copper sulphate :

$$CuSO_4 \cdot 7H_2O_{(s)} + H_2O_{(l)} \longrightarrow CuSO_{4(aq)} + \Delta H; \Delta H = ?$$

Heat gained or lost (Q) = Mass (m) × specific heat of the solution (s) × change in temperature (Δt)

Heat of the dissolution

$$= \frac{Q \times \text{Molecular weight of compound}}{\text{Weight of compound dissolved}}$$

Enthalpy of Neutralisation for a Strong Acid and a Strong Base

Heat of neutralisation is the heat evolved, when one mole of H^+ ions is completely neutralised by a base. The neutralisation reaction in case of HCl and NaOH is in accordance with Arrhenius theory of ionisation, can be written as

$$NaOH_{(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$$
$$H^+{}_{(aq)} + OH^-{}_{(aq)} \longrightarrow H_2O_{(l)} + 57.3 \text{ kJ}$$

Thus, the reaction between HCl and NaOH solution is, in fact, the reaction between $H^+_{(aq)}$ and $OH^-_{(aq)}$, therefore, the heat of neutralisation will be same for neutralisation of all strong acids with strong bases.

ELECTROCHEMISTRY

Variation of Cell Potential in $Zn|Zn^{2+}||Cu^{2+}|Cu$ with Change in Concentration of Electrolytes ($CuSO_4$ and $ZnSO_4$) at Room Temperature

Reduction potential of an electrode increases with increase in concentration of the electrolyte.

$$M^{n+}_{(aq)} + ne^- \longrightarrow M_{(s)}$$
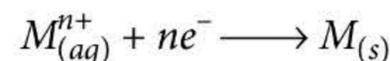
In the zinc-copper electrochemical cell, zinc electrode acts as anode while copper electrode acts as cathode.

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$$

E°_{cell} increases if $E^{\circ}_{cathode}$ increases and E°_{anode} decreases. Thus, higher conc. of Cu^{2+} and lower conc. of Zn^{2+} ions increase the E°_{cell} for $Zn | Zn^{2+} || Cu^{2+} | Cu$.

The relation between conc. of the eletrolyte and the standard electrode potential is given in the form of Nernst equation :

$$E_{cell} = E^{\circ}_{cell} - \frac{0.059}{n} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

iNFO SHOTS

Every therapeutic drug has a narrow range of optimal water content, which needs to be controlled to avoid potential adverse effect on patients. Recently, chemists have invented a method to quantify water content in solid pharmaceutical drugs that is faster, cheaper, more accurate and more precise than Karl Fischer titration method. In this method, water determination is done using ionic liquids and headspace gas chromatography.

CHROMATOGRAPHY

Chromatography is a modern and sensitive technique used for rapid and efficient analysis and separation of components of a mixture and purification of compounds.

Principle : This technique is based on the differential migration of individual components of a mixture through a stationary phase under the influence of moving phase.

The components of the mixture rise up at different rates and thus, get separated from one another and then the R_f value is calculated using the given formula :

$$R_f = \frac{\text{Distance travelled by the solute from the original line}}{\text{Distance travelled by the solvent from the original line}}$$
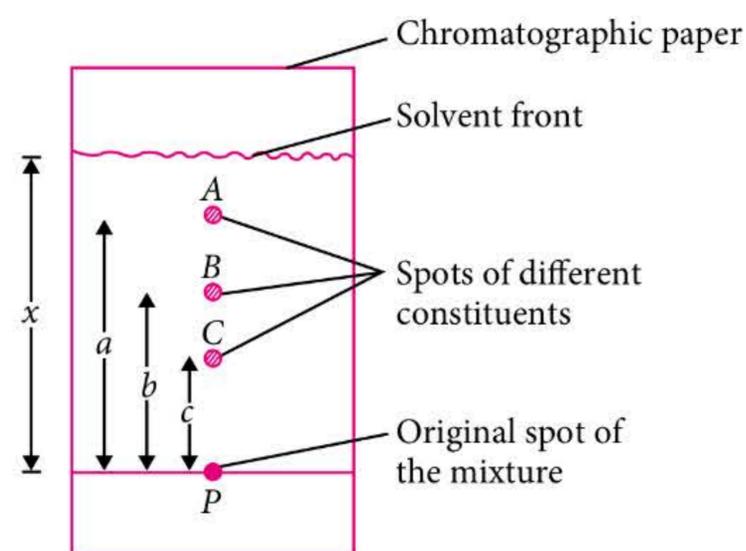
R_f value for $A = \dfrac{a}{x}$, for $B = \dfrac{b}{x}$ and for $C = \dfrac{c}{x}$

PREPARATION OF ORGANIC COMPOUNDS

p-Nitroacetanilide

p-Nitroacetanilide is prepared by nitration of acetanilide with a mixture of conc. HNO_3 and conc. H_2SO_4 (nitrating mixture).
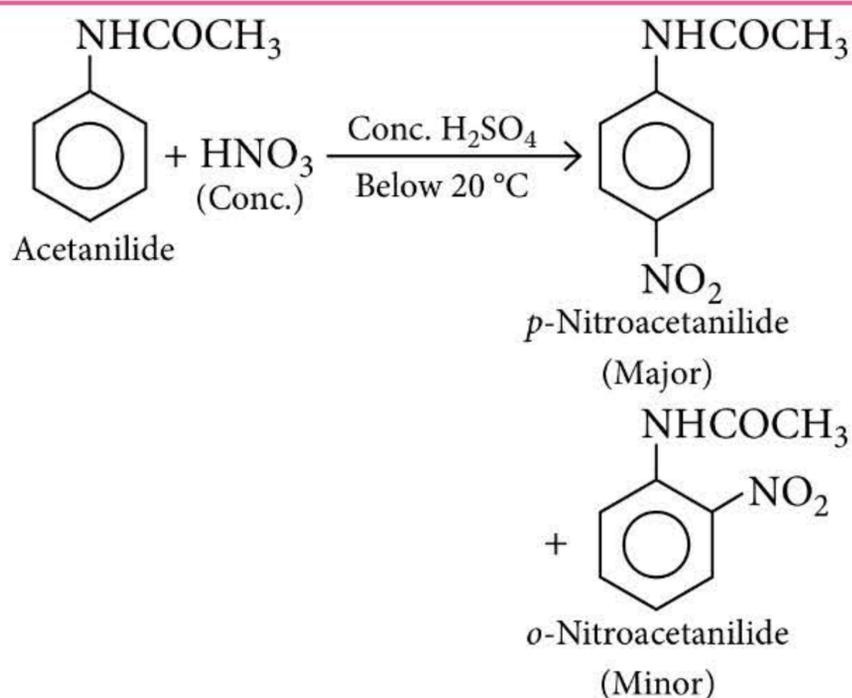
Acetanilide

It is prepared by acetylation of aniline with acetic anhydride in presence of glacial acetic acid and a small amount of zinc dust.
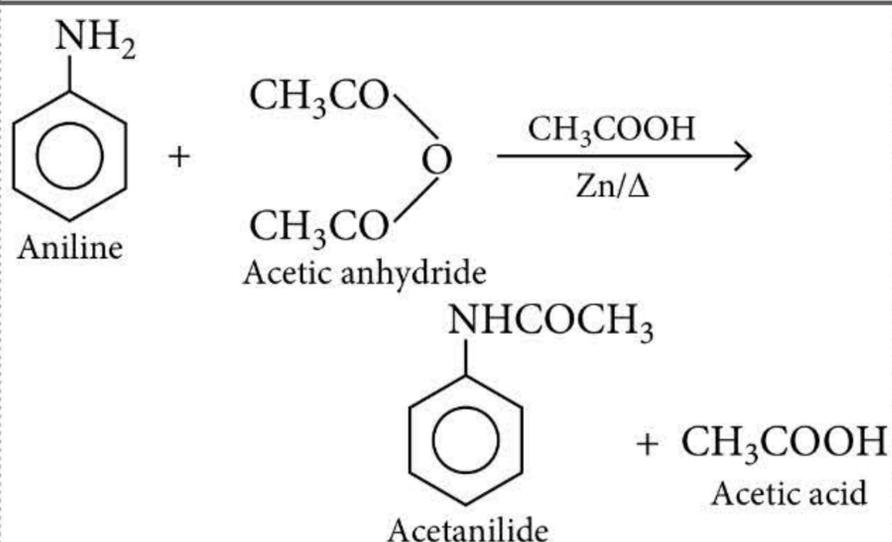
Aniline yellow

It is an azo dye, prepared by coupling benzenediazonium chloride with aniline in acidic medium.
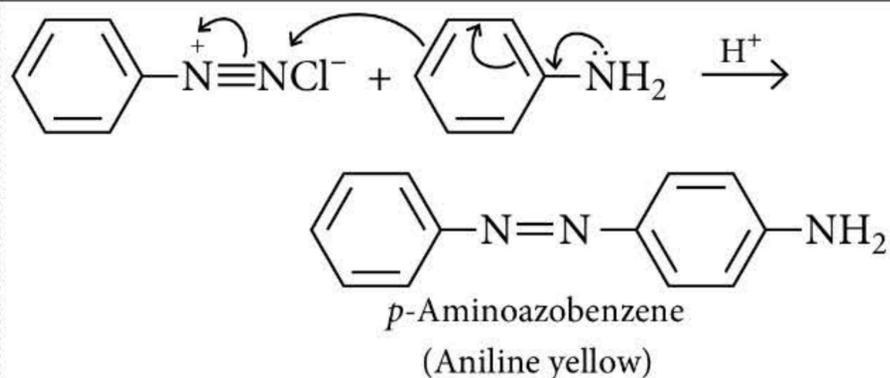
Dibenzalacetone

Dibenzalacetone is prepared by aldol condensation of acetone with two equivalents of benzaldehyde. It is a base catalysed aldol condensation.

DETECTION OF FUNCTIONAL GROUPS

Test for Unsaturation

Bromine test :

$$\text{C}=\text{C} + Br_2 \longrightarrow \text{CBr}-\text{CBr}$$

Alkene (Orange red)   Dibromoalkane (Colourless)

$$-C\equiv C- + 2Br_2 \longrightarrow -CBr_2-CBr_2-$$

Alkyne (Orange red)   Tetrabromoalkane (Colourless)

Baeyer's test or Permanganate test :

$$3CH_2=CH_2 + 2KMnO_4 + 4H_2O \longrightarrow$$

Ethene (Pink)

$$2KOH + 2MnO_2 + 3CH_2OH.CH_2OH$$

(Brown)   Glycol (Colourless)

$$CH\equiv CH + 2KMnO_4 + 2H_2O \longrightarrow$$

Ethyne (Pink)

$$2KOH + 2MnO_2 + (COOH)_2$$

(Brown)   Oxalic acid (Colourless)

Test for Alcoholic (–OH) Group

- **Sodium metal test :**

$$ROH_{(l)} + Na_{(s)} \longrightarrow RONa + 1/2H_{2(g)}\uparrow$$

Ethanol (sample)   Sodium   Sodium ethoxide   Hydrogen (effervescence)

- **Ceric ammonium nitrate test :**

$$2ROH + (NH_4)_2[Ce(NO_3)_6] \longrightarrow$$

Colourless (sample)   Ceric ammonium nitrate (yellow)

$$(ROH)_2Ce(NO_3)_4 + 2NH_4NO_3$$

(Pink or purple)   (Colourless)

- **Ester test :**

$$ROH + CH_3COOH \xrightarrow{\text{Conc. } H_2SO_4}$$

Ethanol (sample)   Acetic acid

$$CH_3COOR + H_2O$$
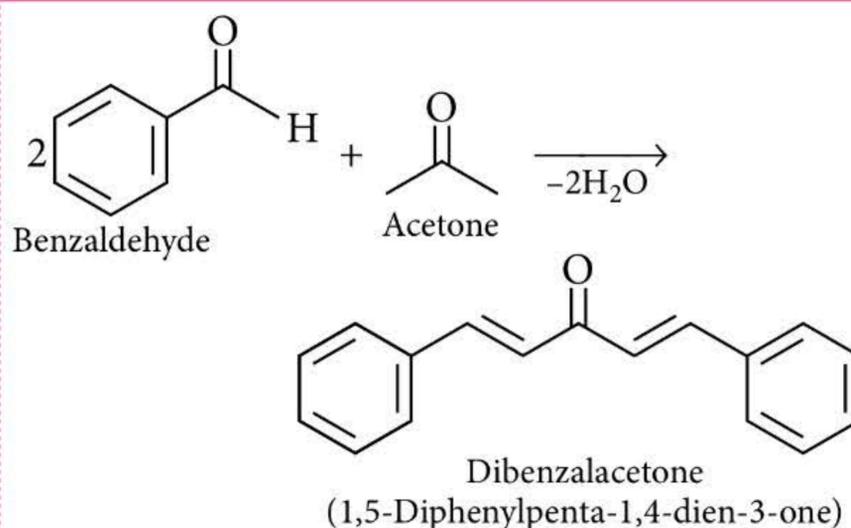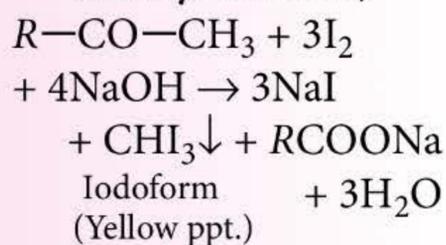
Ethyl acetate (fruity smell)   Water

- **Acetyl chloride test :**

$$R-OH + CH_3COCl \longrightarrow CH_3COOR + HCl\uparrow$$

Alcohol (sample)   Acetyl chloride   Ester

$$HCl\uparrow + NH_4OH \longrightarrow NH_4Cl\uparrow + H_2O$$

White dense fumes

- **Xanthate test :**

$$ROH + KOH \xrightarrow[\substack{(ii)\ \text{Cool}\\(iii)\ \text{Ether}}]{(i)\ \Delta} ROK + H_2O$$

Alcohol (Sample)

$$ROK + CS_2 \longrightarrow RO-C\begin{smallmatrix}S\\\\S^-K^+\end{smallmatrix}$$

Yellow ppt.

- **Distinction between 1°, 2° and 3° alcohols :**
  Organic compound + Lucas reagent (Anhy. $ZnCl_2$ + conc. HCl) and shake :

- Separation of an insoluble layer at once confirms 3° alcohol.
- Appearance of cloudiness within 4-5 minutes confirms 2° alcohol.
- Clear solution confirms 1° alcohol.

Test for Phenolic Group

- **Ferric chloride test :**

$$6C_6H_5OH + FeCl_3 \longrightarrow [Fe(C_6H_5O)_6]^{3-} + 3HCl$$

Phenol (sample)   (Neutral)   (Green/Red/Violet colour)

- **Litmus test :** Sample solution + Blue litmus $\longrightarrow$ Red colour

- **Br₂-water test :**
  Gives white ppt. of 2,4,6-Tribromophenol.

- **Liebermann's test :**

Indophenol (Red)

Deep blue complex

- **Phthalein test :**

Phenol   Phthalic anhydride

Phenolphthalein (Colourless)

Pink Colour

Colourless

Tests for Carbonyl $\left(\diagdown C = O \right)$ group

For Ketones only

Sodium Nitroprusside Test

Sodium nitroprusside solution + NaOH + $RCOR$ → Appearance of wine-red colour.

Idoform Test (for methyl ketones)

R—CO—CH$_3$ + 3I$_2$ + 4NaOH → 3NaI + CHI$_3$↓ + RCOONa + 3H$_2$O
Iodoform (Yellow ppt.)

For both Aldehydes and Ketones

Sodium Bisulphite Test

$$\diagdown C = O + NaHSO_3 \rightarrow \diagup C \diagdown_{SO_3^-Na^+}^{OH}$$
Sample   (White ppt.)
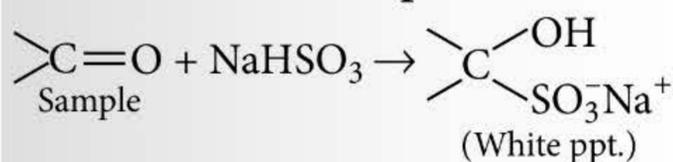
2, 4-DNP Test (Brady's reagent test)

$$\diagdown C = O + H_2NNH - \bigcirc - NO_2$$
$$O_2N$$
2, 4-Dinitrophenylhydrazine

↓

$$\diagdown C = NNH - \bigcirc \diagdown_{NO_2}^{NO_2} + H_2O$$
2,4-Dinitrophenylhydrazone
(Orange/red ppt.)

For Aldehydes only

Schiff's Test

RCHO + Schiff's reagent → Deep red/violet colour
(Sample)

Tollens' Test

RCHO + 2[Ag(NH$_3$)$_2$]OH →
(Sample)   Tollens' reagent
2Ag↓ + RCOONH$_4$ + 3NH$_3$ + H$_2$O
Silver mirror

Fehling Solution Test

RCHO + 2CuO → Cu$_2$O↓ + RCOOH
(Fehling   Red ppt.
solution
($A + B$))

Benedict's Test

RCHO + 2Cu(OH)$_2$ + NaOH →
Sample   Benedict solution
(Blue)
RCOONa + Cu$_2$O↓ + 3H$_2$O
Red ppt.

Tests for Amino (—NH$_2$) group

Carbylamine Test :

RNH$_2$ + CHCl$_3$ + 3KOH → RNC↑ + 3KCl + 3H$_2$O
(Sample)   Carbylamine
(Offensive odour)

Nitrous Acid Test :

RNH$_2$ + HNO$_2$ ⟶ ROH + H$_2$O + N$_2$↑
1° Amine   Brisk Effervescence

R_2NH + HONO ⟶ R_2N → NO + H$_2$O
2° Amine   Nitrosoamine, (Yellow oil)

R_3N + HONO ⟶ R_3N$^+$HONO$^-$
3° Amine   Trialkyl ammonium nitrate
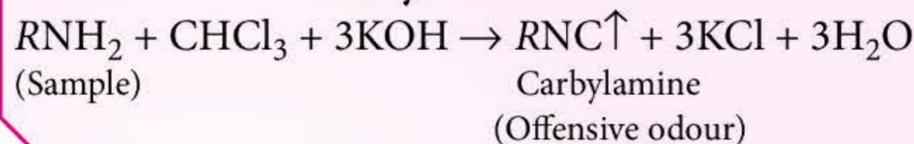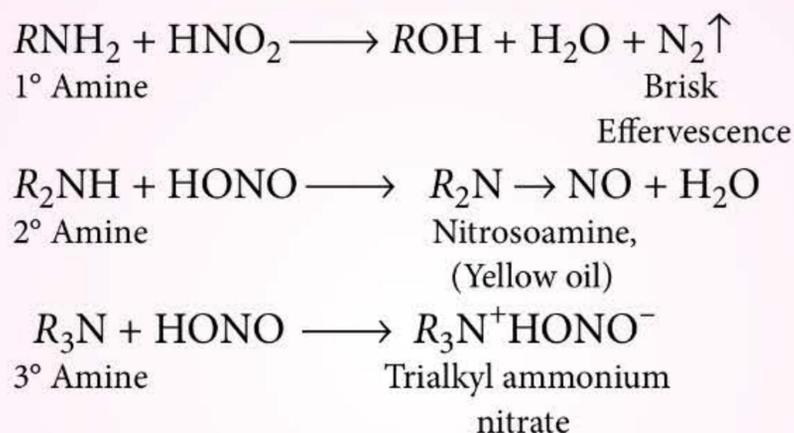
Azo-dye Test : (For Aromatic 1°Amine)

$$\bigcirc - NH_2 \xrightarrow{HONO + HCl/0\,°C} \bigcirc - \overset{+}{N}_2\overset{-}{Cl}$$

$$\bigcirc\bigcirc - OH \longrightarrow \bigcirc\bigcirc \diagdown_{OH}^{N=N-\bigcirc}$$
Orange/red ppt.
(2-Naphthol aniline dye)
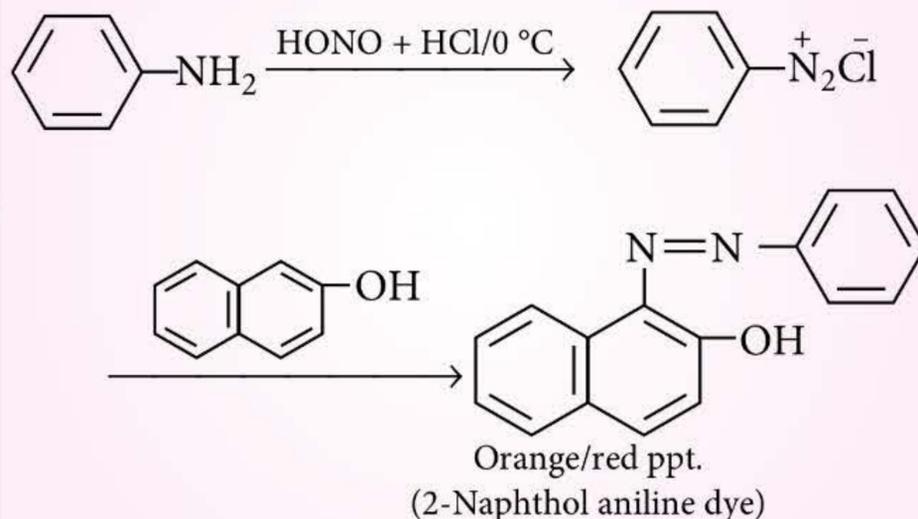
Distinction between 1°, 2° and 3° Amine (Hinsberg's Test)

Amine + NaOH + Benzene Sulphonyl Chloride

- Ppt. formed
  - Conc. HCl
    - Ppt. dissolved (3° Amine present)
    - Ppt. insoluble (2° Amine present)
- Clear solution
  - Conc. HCl
    - Insoluble mass formed (1° Amine)
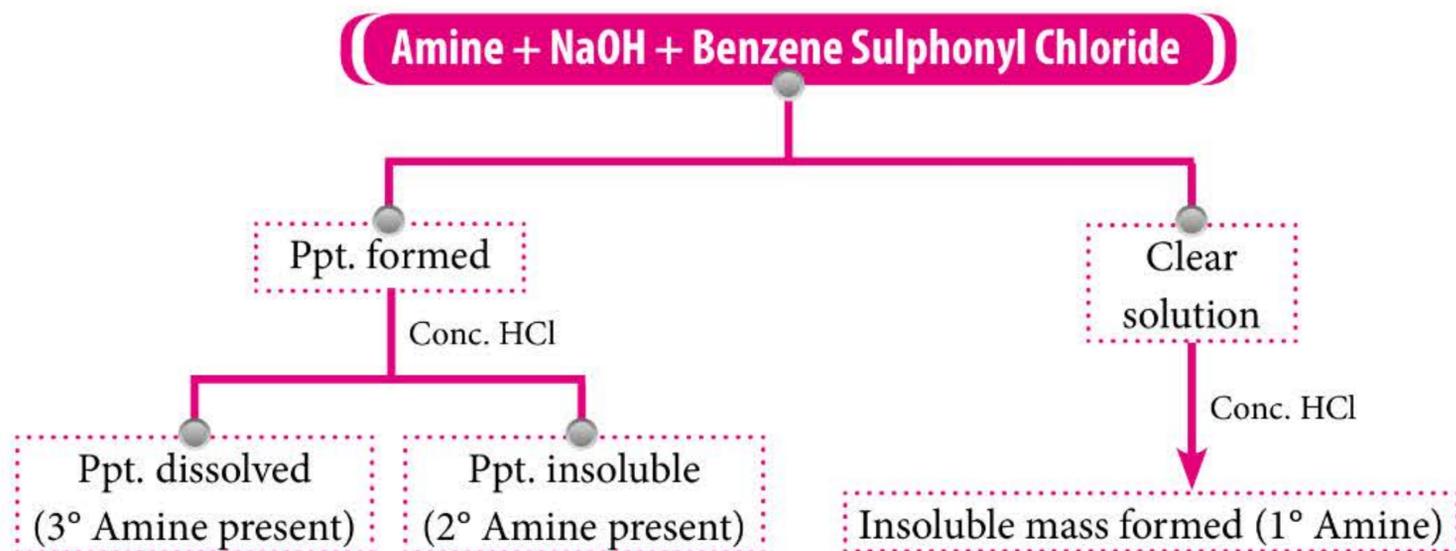
Test for Carboxylic (—COOH) Group

- **Sodium bicarbonate test :**

  $$RCOOH + NaHCO_3 \rightarrow RCOONa + H_2O + CO_2\uparrow$$
  (Sample)   (Effervescence)

- **Litmus test :**

  $$RCOOH + \text{Blue litmus} \rightarrow \text{Red}$$
  (Sample)

  Note : Phenols also give this test.

- **Ester test :**

  $$RCOOH + C_2H_5OH \xrightarrow[\Delta]{\text{conc. } H_2SO_4} RCOOC_2H_5 + H_2O$$
  Ester
  (Fruity smell)
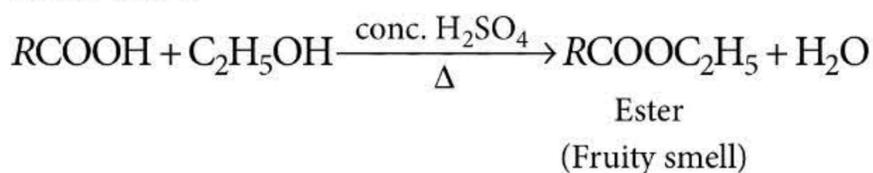
Characteristic Tests for Carbohydrates, Fats and Proteins

- **Tests for carbohydrates :**

  Tests for carbohydrates

  - Simple carbohydrates
    - Monosaccharides or disaccharides + Benedict's solution (Blue coloured)
      - Changes to orange red or brick red
  - Complex sugar
    - Starch + I_2 solution (Lugol's reagent) (Yellowish-brown)
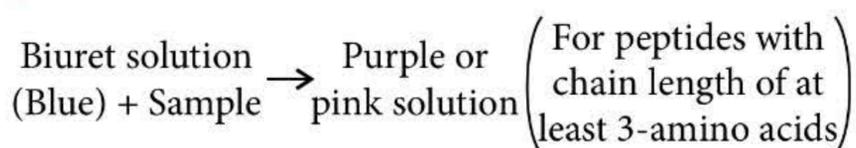   - Changes to dark purple/black
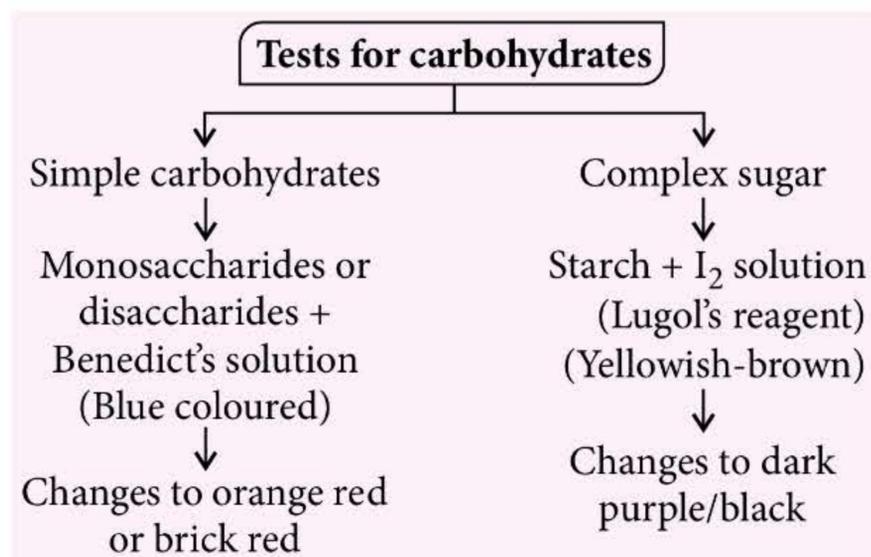
- **Tests for lipids :**

  ➢ **Grease spot test :** Lipid leaves translucent spot on unglazed brown paper bags.

  ➢ **Sudan red test :** Sudan red is a fat soluble dye that stains lipids red.

- **Test for proteins :**

  ➢ **Biuret test :**

  Biuret solution (Blue) + Sample $\rightarrow$ Purple or pink solution $\begin{pmatrix} \text{For peptides with} \\ \text{chain length of at} \\ \text{least 3-amino acids} \end{pmatrix}$

VOLUMETRIC ANALYSIS

- In a titration, a volume of a standardized solution containing a known concentration of reactant 'A' is added incrementally to a sample containing an unknown concentration of reactant 'B' till reactant 'B' is just consumed (stoichiometric completion). This is known as the equivalence point.
  At this point we have, $N_1V_1 = N_2V_2$.
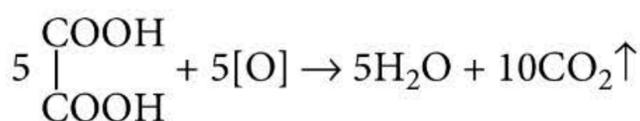
- Strength = Normality × Equivalent weight
  Relation between normality and molarity :
  Normality = n × Molarity
  where, n = number of equivalents in 1 mole.

Titration of Oxalic Acid with KMnO₄

- $$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$
  $$5\,\overset{\text{COOH}}{\underset{\text{COOH}}{|}} + 5[O] \rightarrow 5H_2O + 10CO_2\uparrow$$

- **Indicator :** KMnO₄ is self indicator.

- **End point :** Appearance of light pink colour.

- **Observations :**

S.No.	Initial burette reading (R_1)	Final burette reading (R_2)	Volume of KMnO₄ used $V_1 = (R_2 - R_1)$
1			
2			

- **Calculation :** $n_1 \times M_1 \times V_1 = n_2 \times M_2 \times V_2$
  (KMnO₄)   (Oxalic acid)

Molarity of $KMnO_4$ (M_1) = $\dfrac{n_2 \times M_2 \times V_2}{n_1 \times V_1}$

where, $n_1 = 5$ and $n_2 = 2$

Titration of Mohr's Salt vs KMnO₄

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

- **Indicator :** $KMnO_4$ is self indicator.
- **End Point :** Appearance of light pink colour.
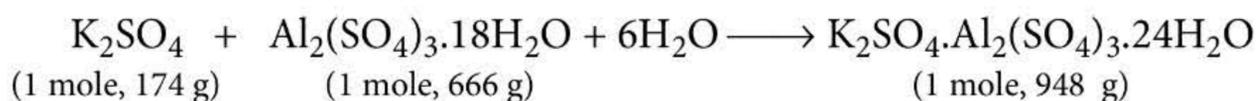
PREPARATION OF INORGANIC COMPOUNDS

▶ **Ferrous Ammonium Sulphate (Mohr's Salt)**

It is a double salt, prepared by dissolving equimolar quantities of iron(II) sulphate and ammonium sulphate in water containing a little amount of sulphuric acid, and then subjecting the resulting solution to crystallization.

$$FeSO_4.7H_2O + (NH_4)_2SO_4 \longrightarrow FeSO_4.(NH_4)_2SO_4.6H_2O + H_2O$$
(1 mole, 278 g) (1 mole, 132 g) (1 mole, 392 g)
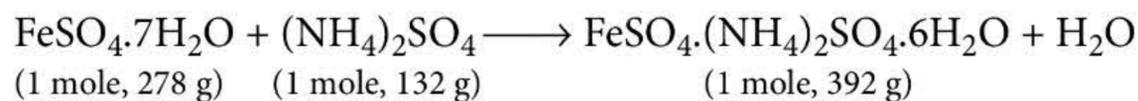
▶ **Potash alum (*Phitkari*)**

It is a double salt of potassium sulphate and aluminium sulphate prepared by concentrating a solution containing equimolar quantities of K_2SO_4 and $Al_2(SO_4)_3.18H_2O$ to crystallization point followed by cooling.

$$K_2SO_4 + Al_2(SO_4)_3.18H_2O + 6H_2O \longrightarrow K_2SO_4.Al_2(SO_4)_3.24H_2O$$
(1 mole, 174 g) (1 mole, 666 g) (1 mole, 948 g)

- **Observation :**

S.No.	Initial burette reading (R_1)	Final burette reading (R_2)	Volume of KMnO₄ used $V_1 = (R_2 - R_1)$
1			
2			

- **Calculation :** $n_1 \times M_1 \times V_1 = n_2 \times M_2 \times V_2$
  (KMnO₄)   (Mohr's salt)

Molarity of $KMnO_4 (M_1)$ = $\dfrac{n_2 \times M_2 \times V_2}{n_1 \times V_1}$

where, $n_1 = 5$ and $n_2 = 1$

SPEED PRACTICE

1. Liebermann's test is used for identification of which functional group in organic compounds?
   (a) Alcohol
   (b) 1° Amine
   (c) Phenolic
   (d) Aldehyde

2. Which of the following statements is not correct regarding preparation of *p*-nitroacetanilide?
   (a) Nitration of acetanilide gives a mixture of *o*- and *p*-nitroacetanilide in which *p*-isomer predominates.
   (b) Nitration is carried out with a mixture of conc. HNO_3 + conc. H_2SO_4
   (c) During crystallisation of the crude product, *p*-nitroacetanilide crystallises out leaving *o*-nitroacetanilide in the mother liquor.
   (d) *o*-Nitroacetanilide is colourless but *p*-nitroacetanilide is yellow coloured

3. The purpose of adding dilute sulphuric acid in the preparation of Mohr's salt is to
   (a) prevent the hydrolysis of ferrous sulphate
   (b) increase the solubility of the salts used
   (c) prevent the precipitation of carbonates of metals
   (d) neutralize ammonium salts.