NEET|JEE ESSENTIALS

Class XII

Maximize your chance of success, and high rank in NEET, JEE (Main and Advanced) by reading this column. This specially designed column is updated year after year by a panel of highly qualified teaching experts well-tuned to the requirements of these Entrance Tests.

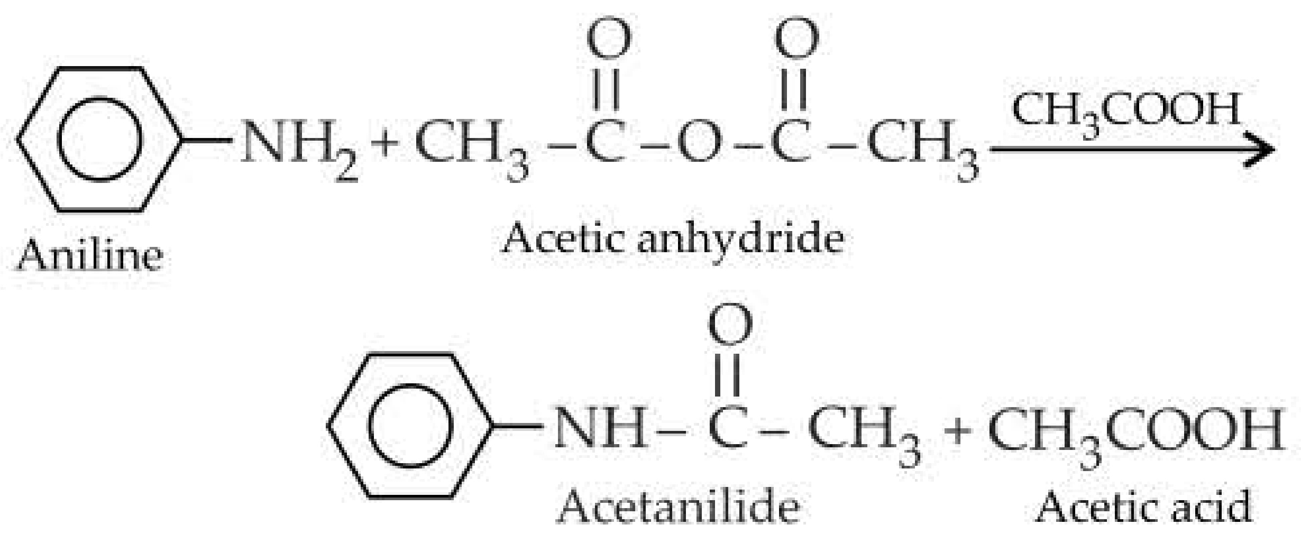
Unit 9

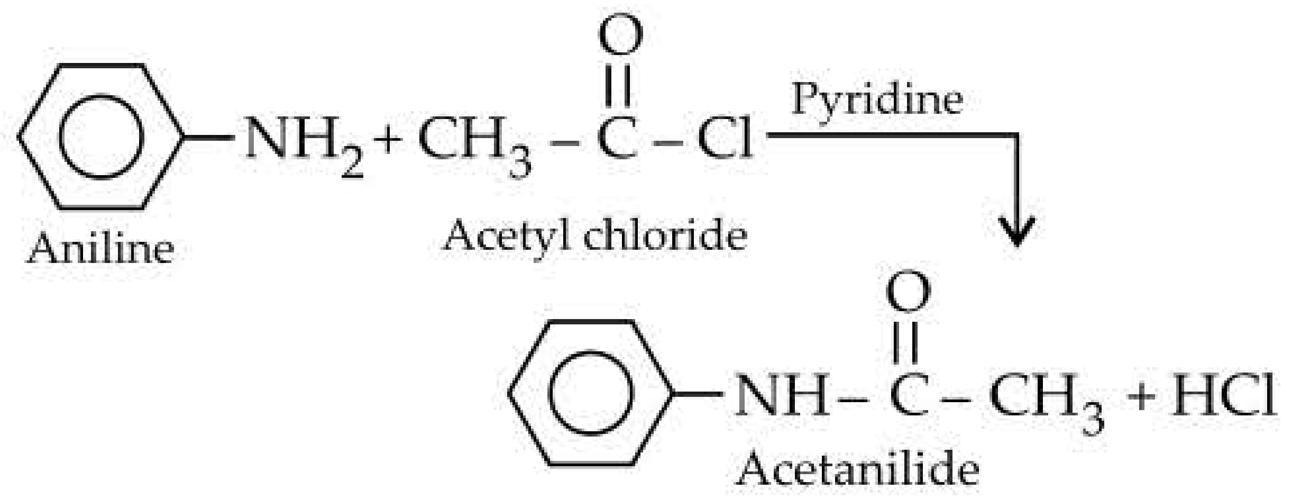
PRINCIPLES RELATED TO PRACTICAL CHEMISTRY

ORGANIC COMPOUNDS

PREPARATION

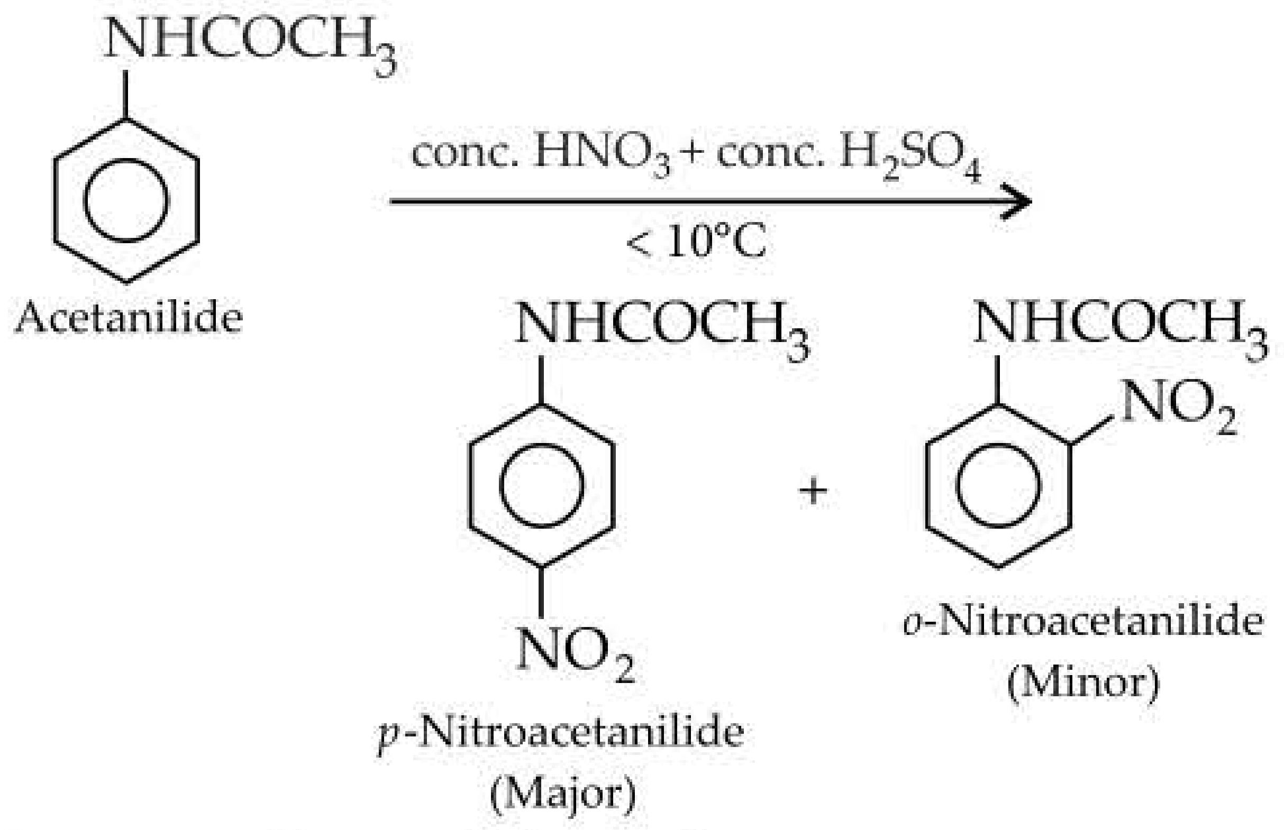
- **Acetanilide :** It is an acetyl derivative of aniline.
  - It is prepared by acetylation of aniline.





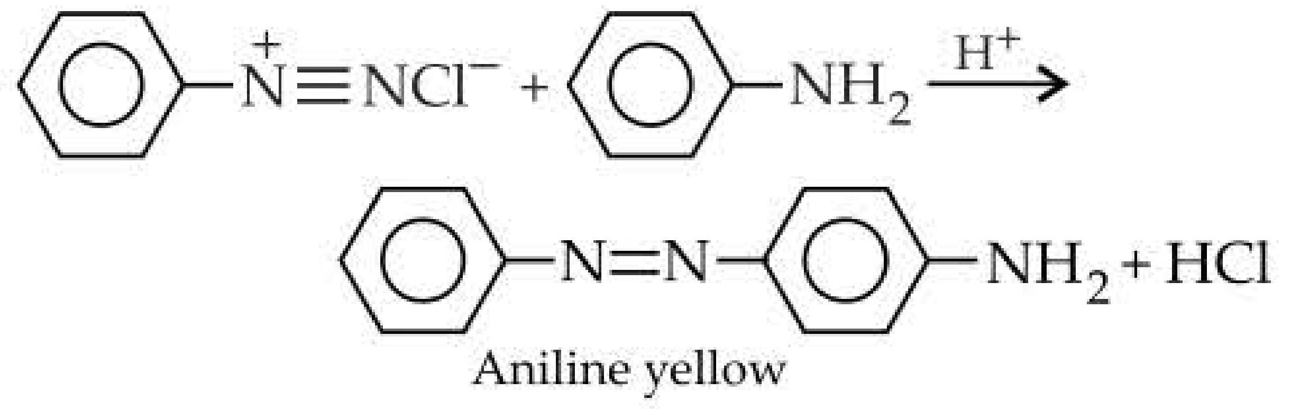
  - It is a nucleophilic acyl substitution reaction in which aniline acts as a nucleophile and acetic anhydride acts as an electrophile.

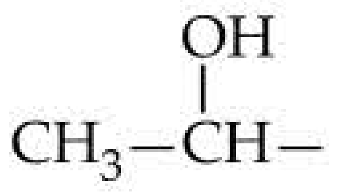
- ***p*-Nitroacetanilide :** It is a nitro derivative of acetanilide.
  - It is prepared by nitration of acetanilide with nitrating mixture.

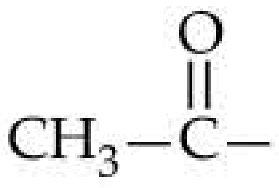


  - It is an electrophilic substitution reaction in which acetanilide acts as nucleophile and nitronium ion acts as an electrophile.

- **Aniline yellow :** It is an azo dye also known as *p*-aminoazobenzene.
  - It is prepared by coupling of benzenediazonium chloride with aniline in acidic medium.



- **Iodoform :** It is triiodomethane and is an iodine analogue of chloroform. It is used as a mild antiseptic and disinfectant.
  - It is prepared by treating an organic compound containing  $CH_3-\overset{\overset{\displaystyle OH}{|}}{C}H-$ group (ethanol,

propan-2-ol, butan-2-ol) or  $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-$ group (acetaldehyde, acetone, butan-2-one, acetophenone) with iodine in presence of sodium or potassium hydroxide.

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

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

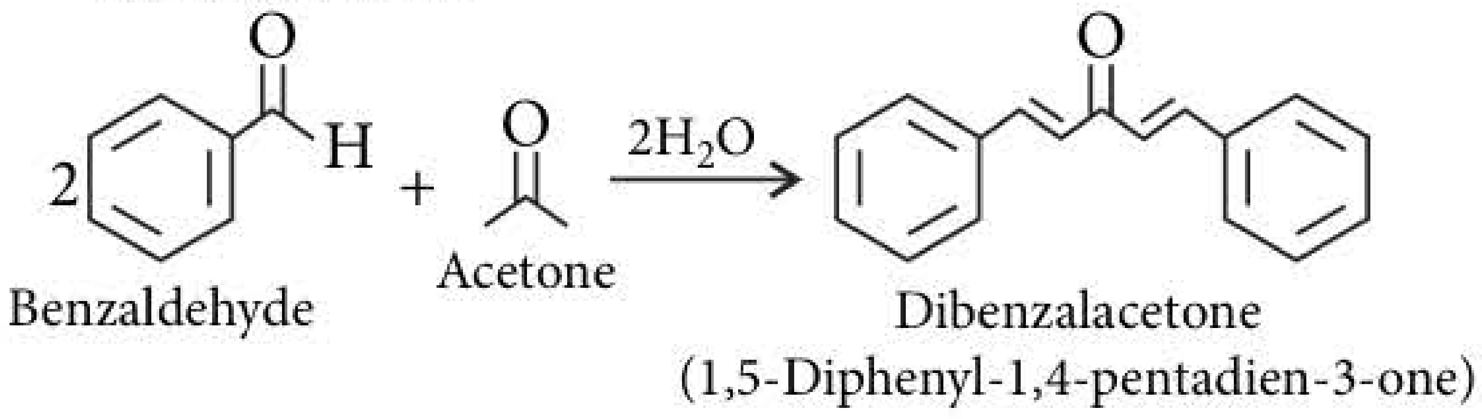
$$CI_3CHO + NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + HCOONa \quad \text{(Hydrolysis)}$$

- With acetone no initial oxidation takes place.

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

$$CI_3COCH_3 + NaOH \xrightarrow{\text{Hydrolysis}} CHI_3 + CH_3COONa$$

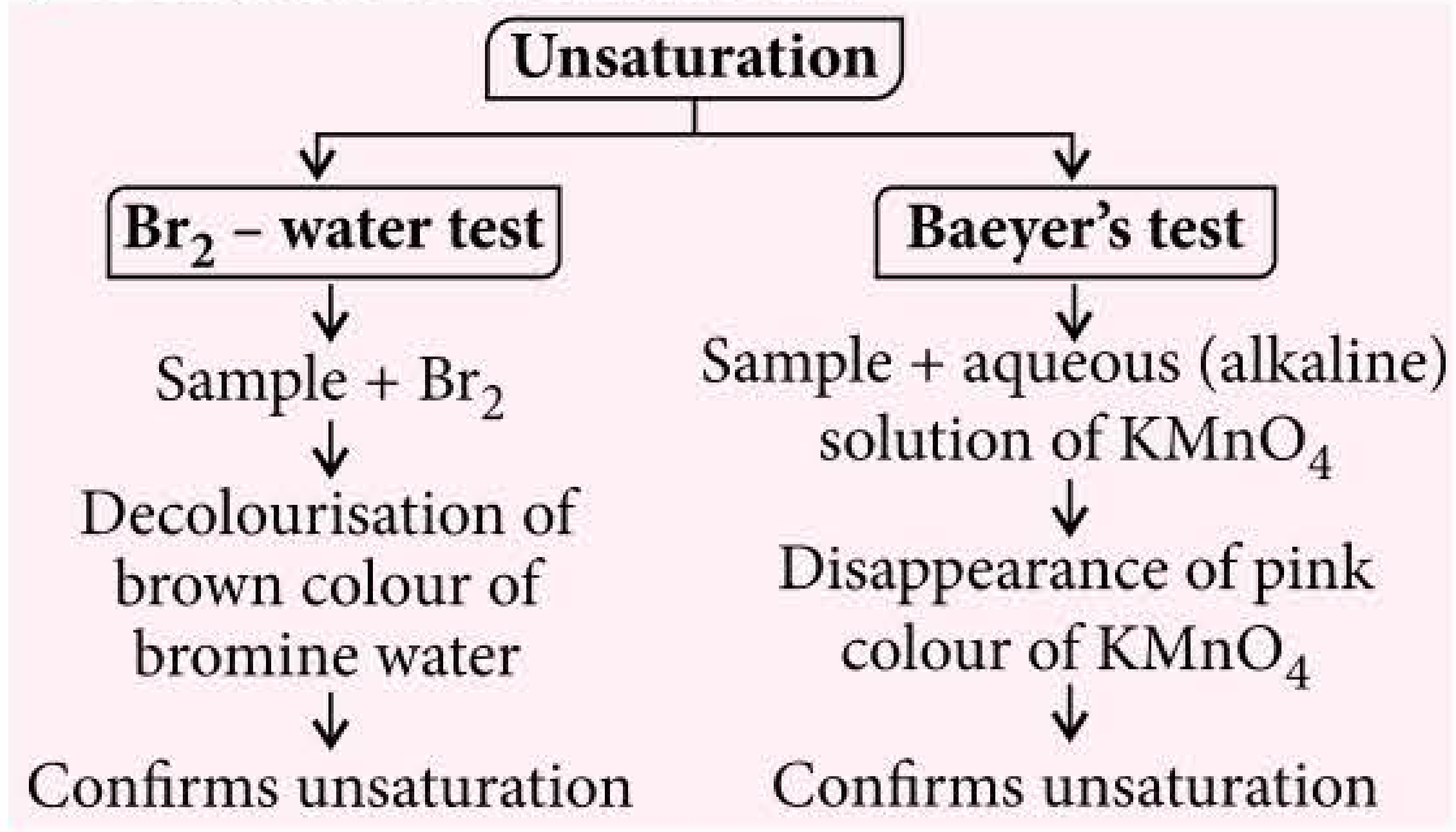
Dibenzalacetone : Dibenzalacetone is prepared by aldol condensation of acetone with two equivalents of benzaldehyde. It is a base catalysed aldol condensation.



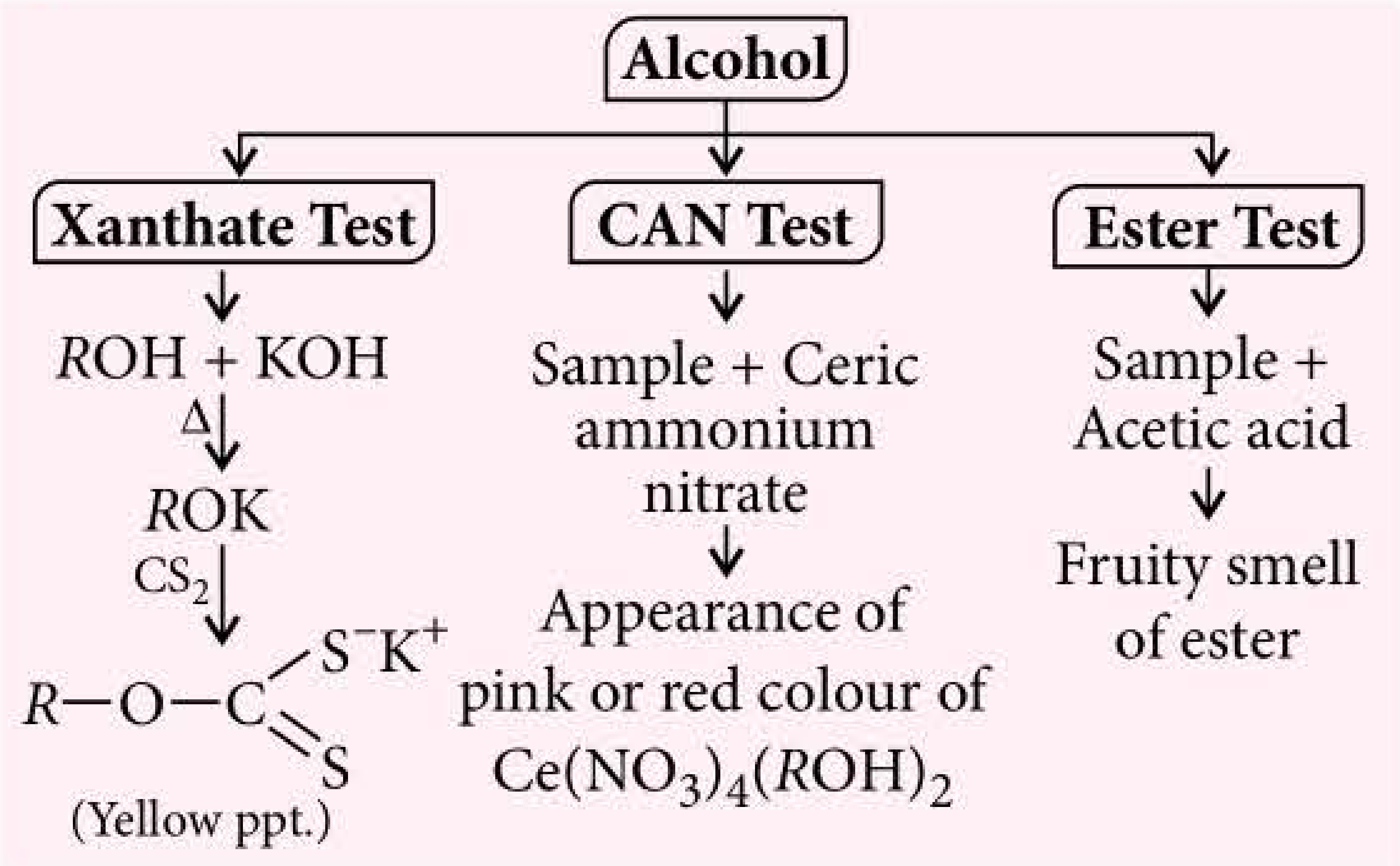
Benzaldehyde Acetone Dibenzalacetone (1,5-Diphenyl-1,4-pentadien-3-one)

DETECTION OF FUNCTIONAL GROUPS

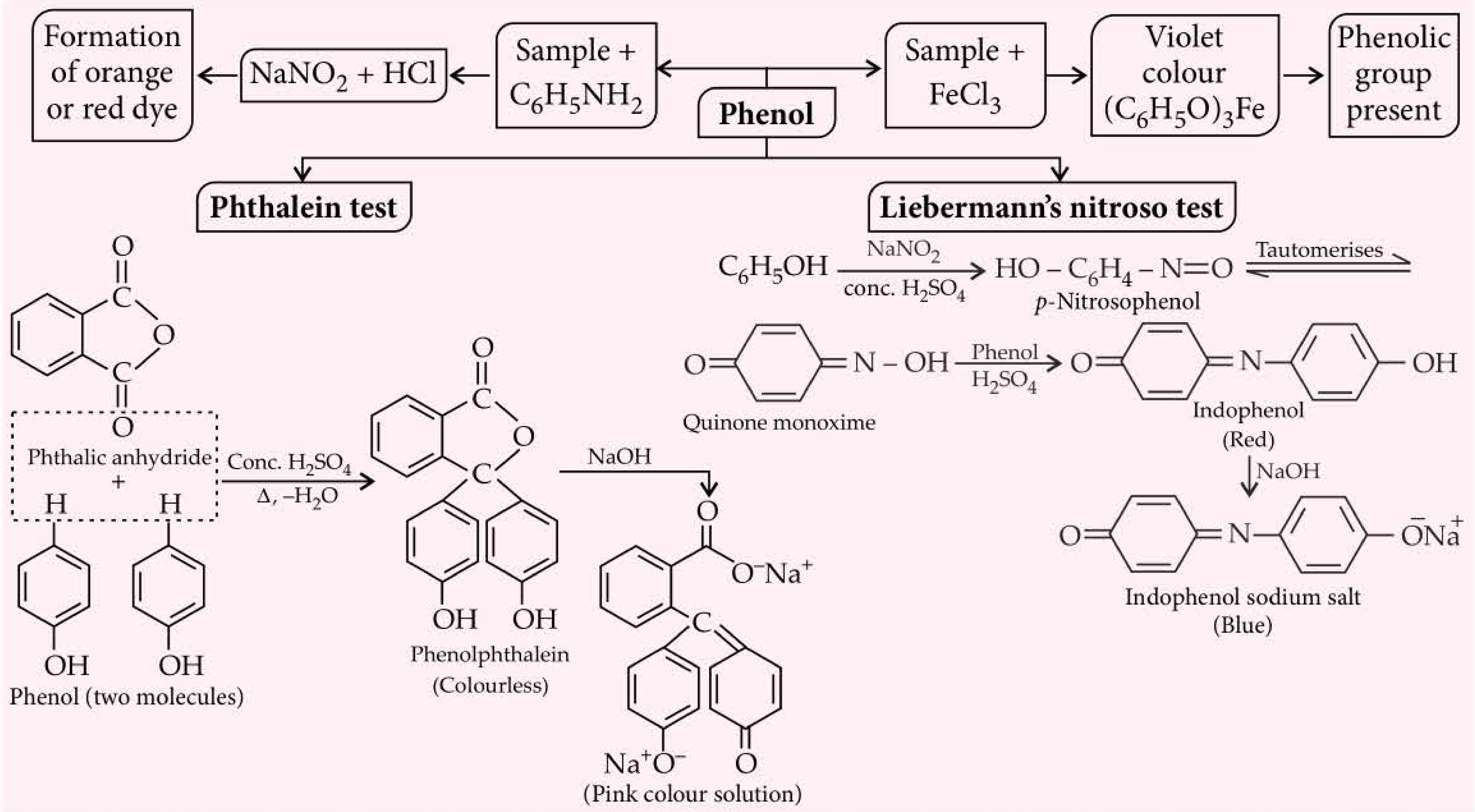
Detection of unsaturation :



Detection of alcohol :



Detection of phenol :



Note : These tests of phenol, can be used to distinguish between alcohols and phenols, as these tests cannot be given by alcohols.

Detection of carbonyl groups

For ketones only

Iodoform test (for methyl ketones)

$R{-}CO{-}CH_3 + 3I_2 + 4NaOH \rightarrow 3NaI + CHI_3\downarrow + RCOONa + 3H_2O$

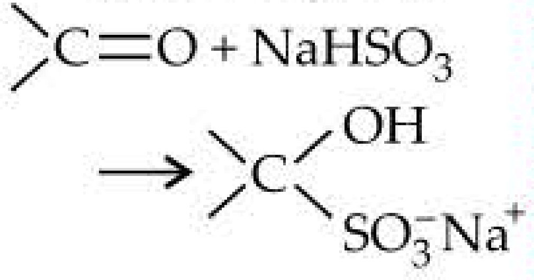
Yellow ppt.

Sodium nitroprusside test

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

For both aldehydes/ketones

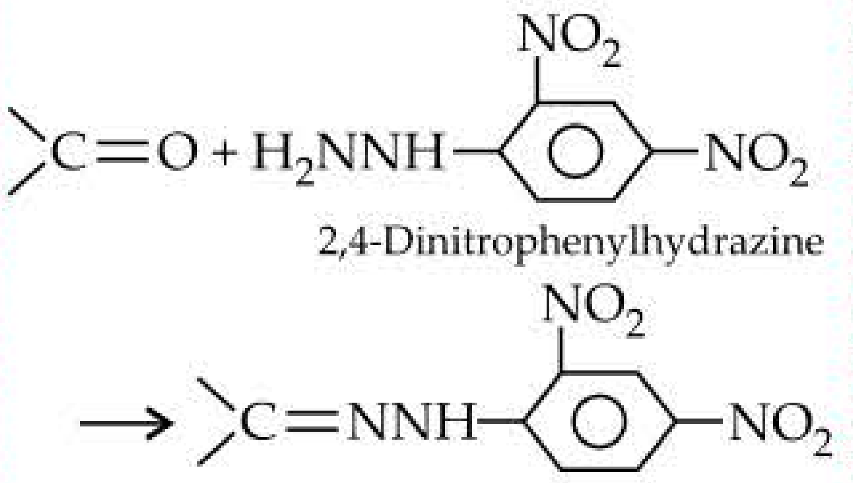
$NaHSO_3$ test



$>C{=}O + NaHSO_3 \rightarrow >C(OH)(SO_3^-Na^+)$

(White ppt.)

Brady's reagent test (2, 4-DNP)



2,4-Dinitrophenylhydrazine

(Orange or red ppt.)

For aldehydes only

Schiff's test

Schiff's reagent + $R{-}CHO$ ↓ Deep red or violet colour complex

(Colourless)

Benedict's test (Cu^{2+} ions complexed with citrate ions)

$RCHO + 2Cu(OH)_2 + NaOH \rightarrow RCOONa + Cu_2O\downarrow + 3H_2O$

Red ppt.

Fehling's test (Cu^{2+} ions complexed with tartarate ions)

$RCHO + 2Cu^{2+} + 3OH^- \rightarrow 2Cu^+\downarrow + RCOO^- + 2H_2O$

Red ppt.

Tollens' test

$RCHO + 2[Ag(NH_3)_2]OH \downarrow RCOONH_4 + 3NH_3 + H_2O + 2Ag_{(s)}\downarrow$

Silver mirror

Detection of amino group :

Amino group

Nitrous acid test

Sample + HNO_2

- Evolution of N_2 gas indicates 1° amine group
- Formation of yellow oily compound indicates 2° amine group
- Formation of water soluble nitrite salts indicates 3° amine group

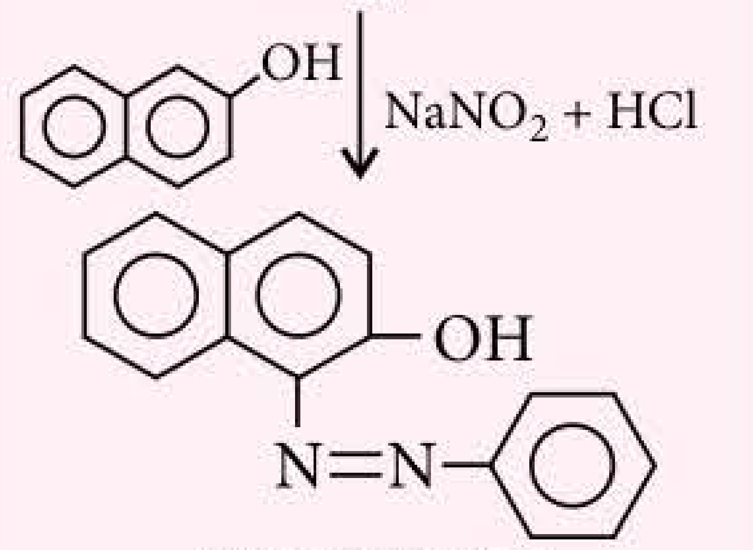
Isocyanide test

Sample + $CHCl_3$ + KOH

Offensive smell of isocyanide confirms the presence of 1° aliphatic or aromatic amine

Azo dye test

Sample



Orange azo dye

(1° Aromatic amine group present)

Detection of carboxylic acid group :

Test	Experiment	Inference
Litmus test	Few drops of sample on blue litmus	Blue litmus paper turns red.
$NaHCO_3$ test	Sample + $NaHCO_3$ solution	Brisk effervescence of CO_2 indicates presence of $-COOH$ group.
Ester test	Sample + Alcohol + conc. H_2SO_4	Fruity smell of ester inferes the presence of $-COOH$ group.

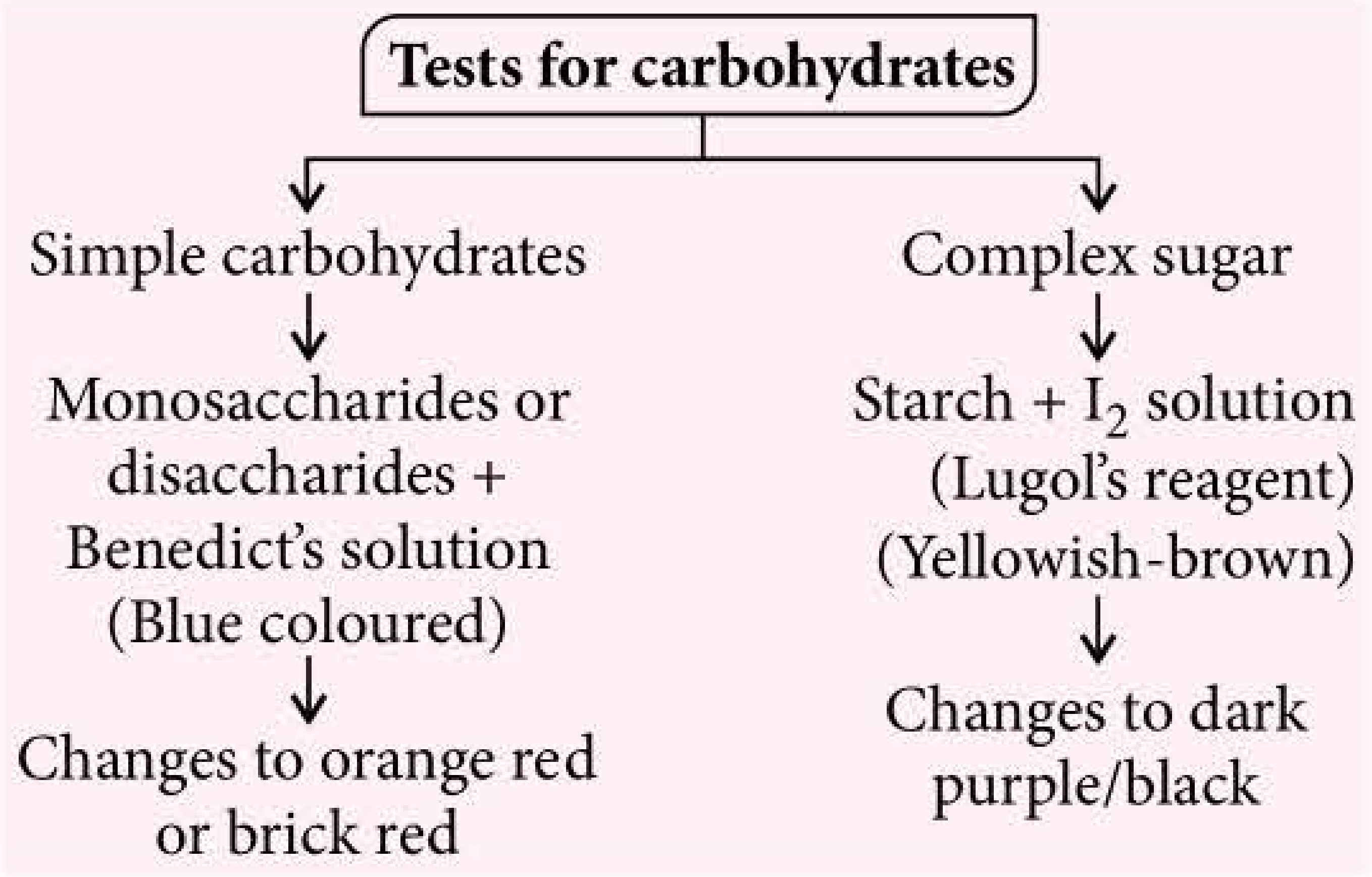
$FeCl_3$ test	$3RCOOH + FeCl_3 \rightarrow \underset{\text{(Coloured ppt.)}}{(RCOO)_3Fe} + 3HCl$	Wine red ppt. : acetic acid Red colour changes to brown ppt. : formic acid No colour change or light yellow colour : oxalic acid Violet coloured ppt. : salicylic acid Buff coloured ppt. : benzoic acid

Detection of nitro group :

Mulliken Barker test	$RNO_2 + 4[H] \xrightarrow{Zn + NH_4Cl} RNHOH + H_2O$ $RNHOH + 2[Ag(NH_3)_2]OH \rightarrow RNO + 2H_2O + 4NH_3 + \underset{\text{Grey black ppt.}}{2Ag\downarrow}$	Appearance of greyish black ppt. indicates the presence of $-NO_2$ group.
Ferrous hydroxide test	$RNO_2 + \underset{\text{Light green}}{6Fe(OH)_2} + 4H_2O \rightarrow RNH_2 + \underset{\text{Red brown ppt.}}{6Fe(OH)_3\downarrow}$	Appearance of brown ppt. indicates the presence of $-NO_2$ group.

CHARACTERISTICS TESTS OF CARBOHYDRATES, FATS AND PROTEINS

Tests for carbohydrates :



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 :**

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

PHYSICAL CHEMISTRY

TITRIMETRIC EXERCISES

Strength of a solution : It is the amount of solute in grams present per litre of the solution.

- Strength (g/L) = Normality × Eq. wt.
- Strength (g/L) = Molarity × Mol. mass

Normality equation : $\underset{\text{(Solution 1)}}{N_1V_1} = \underset{\text{(Solution 2)}}{N_2V_2}$

Molarity equation : $\underset{\text{(Solution 1)}}{M_1V_1n_1} = \underset{\text{(Solution 2)}}{M_2V_2n_2}$

[$\because N = M \times n$, where n = valency factor]

Percentage purity of a given salt

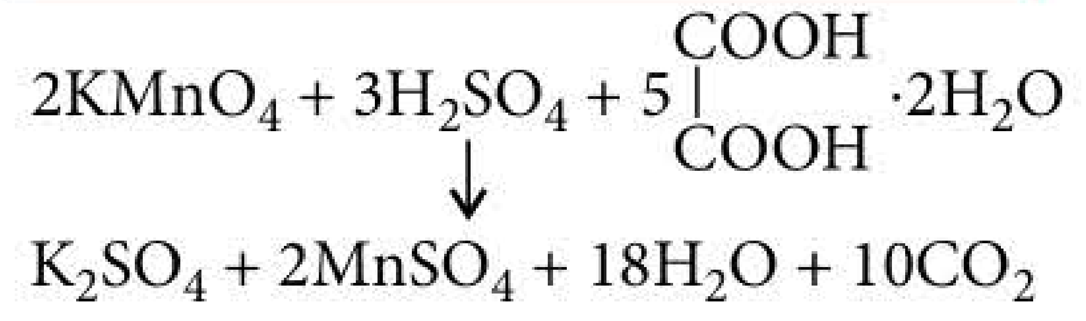
$$= \frac{\text{Strength of pure sample}}{\text{Strength of given sample}} \times 100$$

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

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

$$\frac{M_{KMnO_4} \times V_{KMnO_4}}{M_{\text{Mohr's salt}} \times V_{\text{Mohr's salt}}} = \frac{1}{5}$$

Titration of oxalic acid *vs* $KMnO_4$



- $2KMnO_4 + 3H_2SO_4 + 5\begin{matrix}COOH\\ |\\ COOH\end{matrix} \cdot 2H_2O \downarrow K_2SO_4 + 2MnSO_4 + 18H_2O + 10CO_2$
- *Calculation :*

$$\frac{M_{KMnO_4} \times V_{KMnO_4}}{M_{\text{Oxalic acid}} \times V_{\text{Oxalic acid}}} = \frac{2}{5}$$

Redox titrations

Proceed with transfer of electrons

THERMOCHEMISTRY

- **Enthalpy of dissolution of copper sulphate :** It is the heat change involved during the dissolution of one mole of a solute in such a large excess of solvent so that no further heat change occurs on dilution.

  $CuSO_{4(s)} + H_2O \rightarrow CuSO_{4(aq)}$

  - Dissolution of $CuSO_4$ in water is exothermic. The enthalpy of solution of $CuSO_{4(s)}$ is calculated from the highest temperature attained during its dissolution.
  - *Calculation* : If dissolution of w g of $CuSO_4$ in 200 g solvent (water) causes Δt°C change in temperature, then

    Heat evolved (q) = Mass × Specific heat × Change in temperature

    $q = (200 + W) \times 4.2 \times \Delta t$ J

    where, W is water equivalent of calorimeter (given).

    Enthalpy of dissolution of $CuSO_4$ in water

    $$= \frac{q \times 159.5 \times 10^{-3}}{w} \text{ kJ}$$

    [$\because$ Molar mass of $CuSO_4$ = 159.5 g]

- **Enthalpy of neutralisation of strong acid and strong base :** It is the enthalpy change accompanying the neutralisation of one gram equivalent of a base by an acid in dilute solution at a given temperature.

  $NaOH_{(aq)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$

  It is an exothermic reaction.

  - The heat of neutralisation of a strong acid by a strong base in their dilute solutions is generally 57.3 kJ. The reaction may be represented as :

    $H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O; \Delta H = -57.3$ kJ
  - *Calculation* : Heat evolved during neutralisation of 100 mL of 0.5 N HCl,

    $q = (200 + W) \times \Delta t \times 4.2$ J where, W is water equivalent of calorimeter (given).

    Thus, enthalpy of neutralisation of 1000 mL of 1 N HCl and NaOH $= \dfrac{q}{0.5 \times 100}$ kJ

MPP CLASS XI ANSWER KEY

1.	(b)	**2.**	(c)	**3.**	(c)	**4.**	(d)	**5.**	(d)
6.	(c)	**7.**	(b)	**8.**	(a)	**9.**	(b)	**10.**	(a)
11.	(a)	**12.**	(b)	**13.**	(b)	**14.**	(b)	**15.**	(b)
16.	(b)	**17.**	(c)	**18.**	(b)	**19.**	(b)	**20.**	(a,c,d)
21.	(a,c)	**22.**	(a,b)	**23.**	(a,b,d)	**24.**	(4)	**25.**	(2)
26.	(4)	**27.**	(a)	**28.**	(a)	**29.**	(b)	**30.**	(d)

- **Kinetic study of reaction of iodide ion with hydrogen peroxide at room temperature :**

Overall reaction(Clock reaction)

Main reaction

$H_2O_{2(aq)} + 2I^-_{(aq)} + 2H^+_{(aq)} \xrightarrow{\text{Slow}} I_{2(aq)} + 2H_2O_{(l)}$

Monitor reaction

$2S_2O^{2-}_{3(aq)} + I_{2(aq)} \xrightarrow{\text{Fast}} S_4O^{2-}_{6(aq)} + 2I^-_{(aq)}$

Indicator reaction

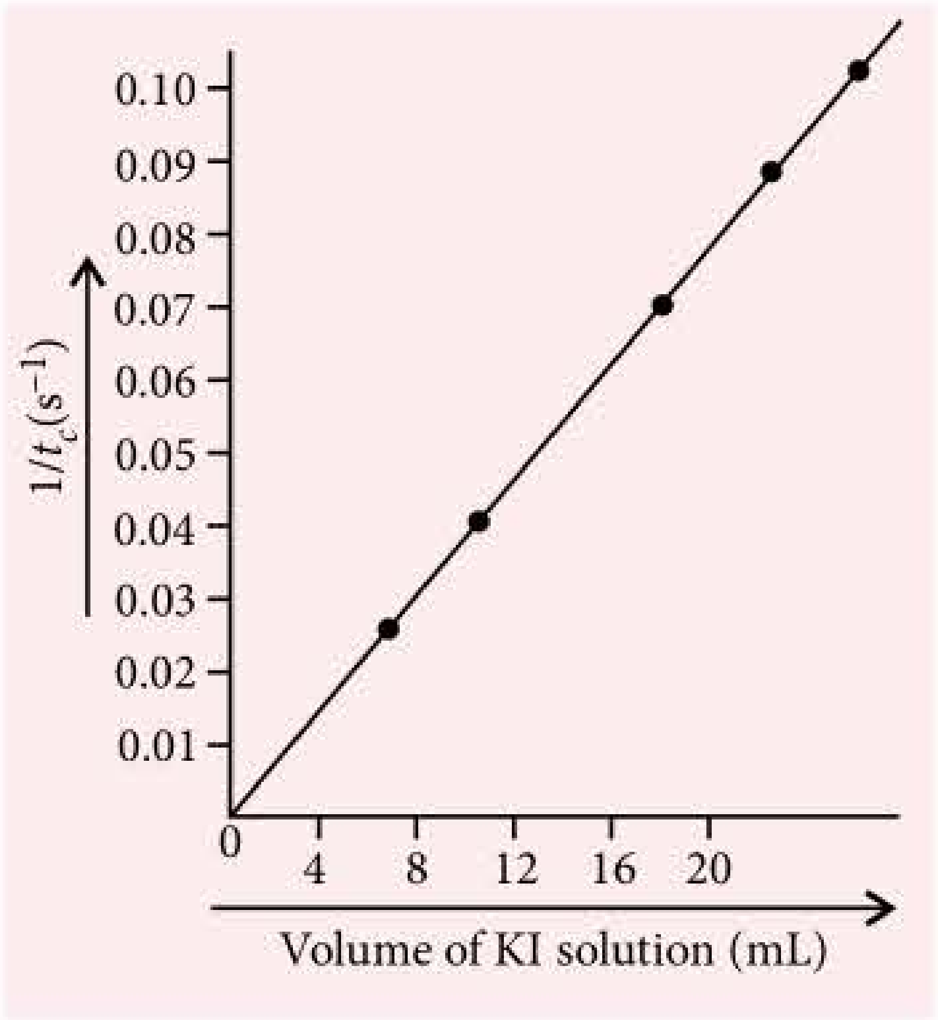
$I_{2(aq)} + \text{starch}_{(aq)} \longrightarrow$ Blue colour

- 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.

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 :**

Theory

- **Nernst equation :**

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{2.303RT}{nF}\log\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \qquad \text{...(i)}$$

$R = 8.314$ J K^{-1} mol^{-1}, $T = 298$ K and $F = 96500$ C

At anode :

$\text{Zn}_{(s)} \rightarrow \text{Zn}^{2+}_{(aq)} + 2e^-$

At cathode :

$\text{Cu}^{2+}_{(aq)} + 2e^- \rightarrow \text{Cu}_{(s)}$

Thus, $n = 2$,

$$E^\circ_{\text{cell}} = E^\circ_{\text{Cu}^{2+}/\text{Cu}} - E^\circ_{\text{Zn}^{2+}/\text{Zn}} = +0.34 - (-0.76) = 1.10 \text{ V}$$

Substituting E°_{cell}, n, R, T and F in eq. (i)

$$E_{\text{cell}} = 1.10 - \frac{0.059}{2}\log\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

Procedure :

- Clean the electrodes of copper and zinc using a sand paper.
- Put the solution of copper sulphate in beaker and the solution of zinc sulphate in a porous pot.
- Connect the voltmeter with electrodes, close the circuit and note down the cell potentials.
- Repeat the experiment by taking the solutions of $CuSO_4$ and $ZnSO_4$ at different concentrations.

Observation :

Concentration of $[Zn^{2+}]$	Concentration of $[Cu^{2+}]$	Theoretical E_{cell}
1 M	1 M	1.10 V
0.1 M	1 M	1.1295 V
0.01 M	1 M	1.1591 V
0.001 M	1 M	1.1886 V
1 M	0.1 M	1.0705 V
1 M	0.01 M	1.0409 V
1 M	0.001 M	1.0114 V

Result :

- E_{cell} decreases with increase in concentration of Zn^{2+} in $ZnSO_4$.
- E_{cell} increases with increase in concentration of Cu^{2+} in $CuSO_4$.

INORGANIC COMPOUNDS

PREPARATION

Mohr's salt (Ferrous ammonium sulphate) :

- It is a double salt containing ferrous sulphate and ammonium sulphate in equimolar amounts.
- It is prepared by dissolving an equimolar mixture of hydrated ferrous sulphate and ammonium sulphate in water containing a little amount of sulphuric acid to prevent the hydrolysis.

$$FeSO_4\cdot 7H_2O + (NH_4)_2SO_4 \rightarrow \underset{\text{(Mohr's salt)}}{FeSO_4\cdot(NH_4)_2SO_4\cdot 6H_2O} + H_2O$$

Potash alum (*Phitkari*) :

- It is a double salt containing potassium sulphate and aluminium sulphate in equimolar amounts.
- It is prepared by dissolving an equimolar mixture of hydrated aluminium sulphate and potassium sulphate in water containing a little amount of sulphuric acid to prevent the hydrolysis.

$$K_2SO_4 + Al_2(SO_4)_3\cdot 18H_2O + 6H_2O \rightarrow \underset{\text{(Potash alum)}}{K_2SO_4\cdot Al_2(SO_4)_3\cdot 24H_2O}$$

INFO SHOTS

Fluorescent sensor provides low-cost diagnosis of cystic fibrosis!

Scientists have developed a new diagnostic test for cystic fibrosis. The new device provides a cheaper, easier way to detect levels of chloride in sweat, which are elevated in cystic fibrosis patients. Cystic fibrosis is caused by two faulty copies of a gene that affects the flow of chloride in and out of cells, leading to damage to the lungs and digestive system. Testing chloride levels in sweat is done by manual titration–a labour-intensive technique that is subject to human error and can miss cases. But a new system is based on a fluorescent dye that decreases in the presence of chloride, allowing the test to be automated. To create the sensor, the researchers first developed a citrate-based dye that emits fluorescent light. In the presence of chloride, however, the amount of light given off by the molecule diminishes: the more chloride, the less fluorescence. The new test can detect chloride over a wider range of concentrations and, because it's automated, it avoids the problem of human error. Besides detecting chloride, the new fluorescence-based system can also tell the difference between three ions: chloride, bromide, and iodide.