CLASS-XII

BRUSH UP for NEET/JEE 2020

Brush up your concepts to get 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

Practical Inorganic Chemistry

Identification and Separation of Acidic Radicals

- **Group I :** Salt + dil. H_2SO_4 or dil. HCl.
  - **Carbonate (CO_3^{2-}) :**

$$\underset{\text{Salt}}{Na_2CO_3} + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + \underset{\text{(Effervescence)}}{CO_2\uparrow}$$

$$\underset{\text{Lime water}}{Ca(OH)_2} + CO_2 \longrightarrow \underset{\text{White ppt. (milky)}}{CaCO_3} + H_2O$$

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

  - **Nitrite (NO_2^-) :**

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

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

$$2NO + O_2 \longrightarrow \underset{\text{(Brown coloured gas)}}{2NO_2\uparrow}$$

  - **Sulphite (SO_3^{2-}) :**

$$\underset{\text{Salt}}{Na_2SO_3} + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + SO_2\uparrow$$

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

$$\underset{\text{Salt}}{Na_2SO_3} + BaCl_2 \longrightarrow \underset{\text{White ppt.}}{BaSO_3\downarrow} + 2NaCl$$

$$\underset{\text{White ppt.}}{BaSO_3} + 2HCl \longrightarrow \underset{\text{Soluble}}{BaCl_2} + H_2O + SO_2\uparrow$$

  - **Sulphide (S^{2-}) :**

$$\underset{\text{Salt}}{Na_2S} + H_2SO_4 \longrightarrow Na_2SO_4 + H_2S\uparrow$$

$$\underset{\text{Salt}}{Pb(CH_3COO)_2} + H_2S \rightarrow \underset{\text{Black ppt.}}{PbS\downarrow} + 2CH_3COOH$$

Soluble sulphide reacts with sodium nitroprusside to produce pink violet colour.

$$\underset{\text{Sodium nitroprusside}}{Na_2S + Na_2[Fe(CN)_5NO]} \rightarrow \underset{\text{Pink violet colour}}{Na_4[Fe(CN)_5NOS]}$$

  - **Acetate (CH_3COO^-) :**

$$\underset{\text{Salt}}{2CH_3COONa} + H_2SO_4 \longrightarrow \underset{\text{Vinegar smell}}{2CH_3COOH} + Na_2SO_4$$

$$\underset{\text{Salt}}{3CH_3COONa} + FeCl_3 \longrightarrow \underset{\text{Blood red colour}}{(CH_3COO)_3Fe} + 3NaCl$$

- **Group II :** Salt + conc. H_2SO_4 or conc. HCl and heat.
  - **Chloride (Cl^-) :**

$$\underset{\text{Salt}}{2NaCl} + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$$

$$NH_4OH + HCl \rightarrow \underset{\text{White fumes}}{NH_4Cl} + H_2O$$

$$HCl + AgNO_3 \rightarrow \underset{\text{White ppt.}}{AgCl\downarrow} + HNO_3$$

  - **Chromyl chloride test :** On heating chloride with $K_2Cr_2O_7$ and conc. 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 $PbCrO_4$.

$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$

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

$CrO_3 + 2HCl \rightarrow \underset{\text{Chromyl chloride (Red vapours)}}{CrO_2Cl_2\uparrow} + H_2O$

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

$Na_2CrO_4 + (CH_3COO)_2Pb \longrightarrow \underset{\text{Yellow ppt.}}{PbCrO_4\downarrow} + 2CH_3COONa$

- **Bromide (Br^-) :**

$\underset{\text{Salt}}{NaBr} + H_2SO_4 \longrightarrow NaHSO_4 + HBr$

$2HBr + H_2SO_4 \longrightarrow \underset{\text{Brown}}{Br_2} + 2H_2O + SO_2$

Reddish brown bromine gas which turns starch iodide paper blue due to the liberation of iodine from starch iodide.

$AgNO_3 + HBr \rightarrow \underset{\text{Pale yellow ppt.}}{AgBr\downarrow} + HNO_3$

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

- **Iodide (I^-) :**

$\underset{\text{Salt}}{2KI} + 2H_2SO_4 \rightarrow 2KHSO_4 + 2HI$

$2HI + H_2SO_4 \rightarrow \underset{\text{Violet vapours}}{I_2\uparrow} + SO_2 + 2H_2O$

On adding $AgNO_3$ solution, a yellow ppt. of AgI is formed which is insoluble in NH_4OH.

$AgNO_3 + HI \rightarrow \underset{\text{Yellow ppt.}}{AgI\downarrow} + HNO_3$

- **Nitrate (NO_3^-) :** Light brown fumes of nitrogen dioxide are evolved on heating nitrates with conc. H_2SO_4 which intensify on adding Cu turnings.

$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$

$4HNO_3 \rightarrow 2H_2O + \underset{\text{Light brown fumes}}{4NO_2\uparrow} + O_2$

$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + \underset{\text{Dark brown fumes}}{2NO_2} + 2H_2O$

- **Oxalate ($C_2O_4^{2-}$) :**

$\underset{\text{Salt}}{Na_2C_2O_4} + H_2SO_4 \rightarrow Na_2SO_4 + H_2C_2O_4$

$H_2C_2O_4 + [H_2SO_4] \rightarrow \underset{\substack{\text{Burns with} \\ \text{blue flame}}}{CO} + \underset{\substack{\text{turns lime} \\ \text{water milky}}}{CO_2} + H_2O + [H_2SO_4]$

- **Group III :** For detection of this group radicals we need some specific test.
  - **Sulphate (SO_4^{2-}) :**

$\underset{\text{Salt}}{Na_2SO_4} + BaCl_2 \longrightarrow \underset{\substack{\text{White ppt.} \\ \text{(Insoluble in conc. } HNO_3\text{)}}}{BaSO_4\downarrow} + 2NaCl$

  - **Phosphate (PO_4^{3-}) :**

$\underset{\text{Salt}}{Ca_3(PO_4)_2} + 6HNO_3 \longrightarrow 3Ca(NO_3)_2 + 2H_3PO_4$

$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_{3(Conc.)} \longrightarrow \underset{\substack{\text{Ammonium} \\ \text{molybdate}}}{} (NH_4)_3PO_4 \cdot 12MoO_3\downarrow + 21NH_4NO_3 + 12H_2O$

Canary yellow ppt.

  - **Borate (BO_3^{3-}) :**

$\underset{\text{Salt}}{2Na_3BO_3} + 3H_2SO_4 \longrightarrow 3Na_2SO_4 + 2H_3BO_3$

$H_3BO_3 + 3C_2H_5OH \longrightarrow \underset{\substack{\text{Ethyl borate} \\ \text{(Burns with green edged flame)}}}{(C_2H_5)_3BO_3} + 3H_2O$

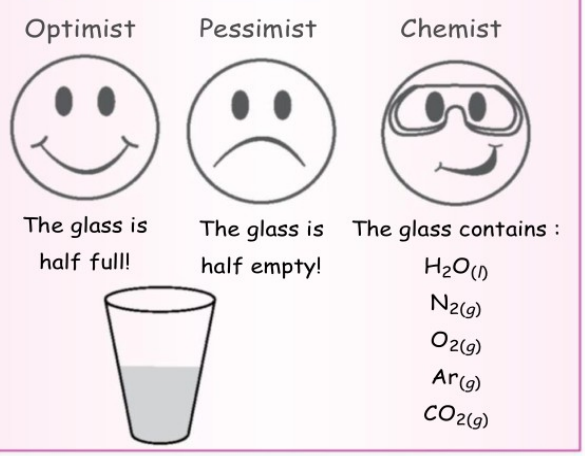
  - **Fluoride (F^-) :**

$\underset{\text{Salt}}{2NaF} + H_2SO_4 \longrightarrow Na_2SO_4 + \underset{\text{Hydrofluoric Acid}}{H_2F_2}$

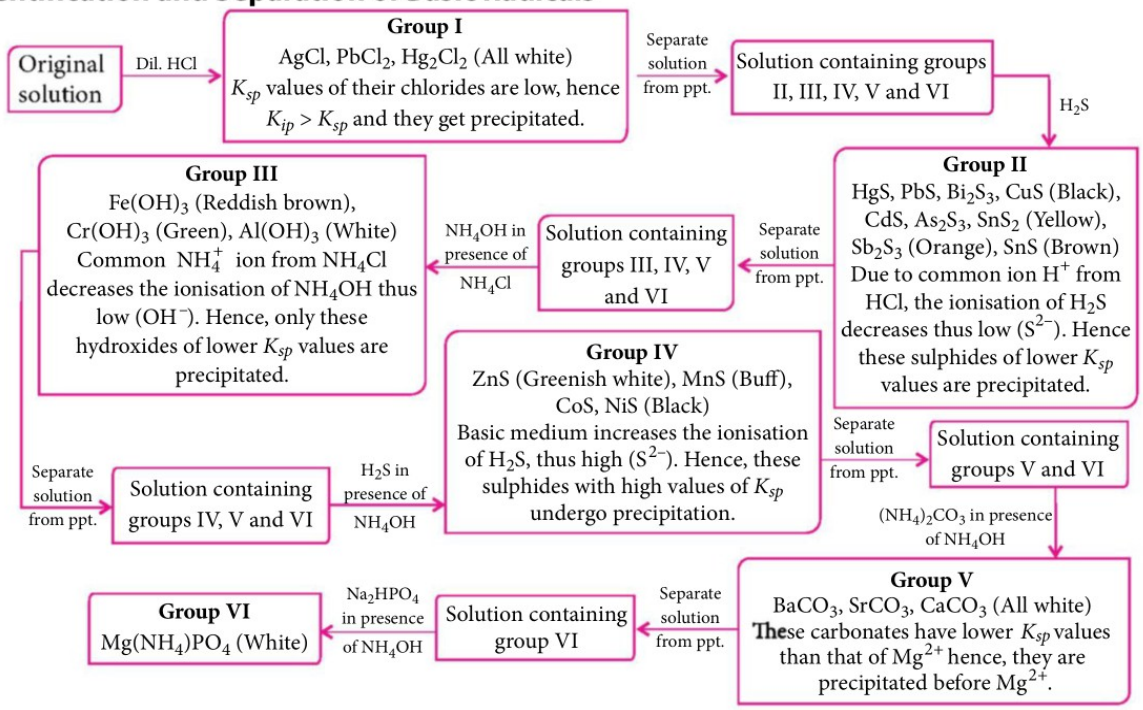
$\underset{\text{Silica}}{SiO_2} + 2H_2F_2 \longrightarrow \underset{\text{Silicon tetrafluoride}}{SiF_4} + 2H_2O$

$3SiF_4 + 4H_2O \longrightarrow \underset{\substack{\text{Silicic acid} \\ \text{(Gelatinous white)}}}{H_4SiO_4} + 2H_2SiF_6$

COMIC CAPSULE



Identification and Separation of Basic Radicals



Titrimetric Analysis

- Titrimetric or volumetric analysis is a method of finding the volume of one solution which reacts with a definite amount of another solution.
- **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**

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

Peep Into Previous Years

1. A solution containing a group-IV cation gives a precipitate on passing H_2S. A solution of this precipitate in dil. HCl produces a white precipitate with NaOH solution and bluish white precipitate with basic potassium ferrocyanide. The cation is

   (a) Co^{2+} (b) Ni^{2+} (c) Zn^{2+} (d) Mn^{2+}

   (JEE Main Online 2017)

2. A white sodium salt dissolves readily in water to give a solution which is neutral to litmus. When silver nitrate solution is added to the aforementioned solution, a white precipitate is obtained which does not dissolve in dil. nitric acid. The anion is

   (a) S^{2-} (b) SO_4^{2-} (c) CO_3^{2-} (d) Cl^-

   (JEE Main 2018)

Practical Organic Chemistry

Detection of the Functional Groups

Alcoholic group (—OH linked to aliphatic carbon chain)

- **Ceric ammonium nitrate test :**

$$2ROH + [(NH_4)_2Ce(NO_3)_6] \longrightarrow \underset{\text{Pink or red colour}}{[Ce(NO_3)_4R(OH)_2]} + 2NH_4NO_3$$

- **Sodium test :** $2ROH + 2Na \longrightarrow 2RONa + H_2\uparrow$
- **Ester test :**

$$RCOOH + 2R'OH \xrightarrow{\text{Conc. } H_2SO_4} 2RCOOR' + H_2O$$

- **Xanthate test :** $ROH + KOH \longrightarrow ROK + H_2O$

$$ROK + CS_2 \longrightarrow \underset{\text{Yellow ppt.}}{RO-C(=S)-\bar{S}K^+}$$

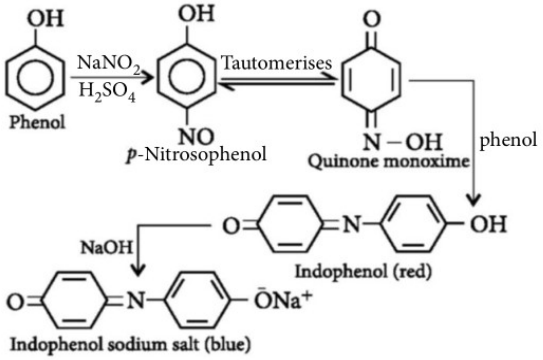
Phenolic group (–OH linked to benzene ring)

- **$FeCl_3$ test :**

$FeCl_3 + 6C_6H_5OH \longrightarrow 3H^+ + [Fe(OC_6H_5)_6]^{3-} + 3HCl$

Neutral Phenol Violet complex

- **Liebermann's nitroso test :**

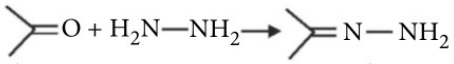


- **Phthalein test :**

Organic compound + phthalic anhydride + conc. $H_2SO_4 \longrightarrow$ phenolphthalein $\xrightarrow{NaOH}$ pink cololur complex

Carbonyl group (>C = O)

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



Aldehyde/Ketone Hydrazone

- **Tests for aldehyde group :**
  - **Tollen's test :** $RCHO + 2[Ag(NH_3)_2]OH$

Aldehyde

$\longrightarrow RCOONH_4 + 3NH_3 + H_2O + 2Ag$

Silver mirror

  - **Fehling's test :** $RCHO + 2Cu^{2+} + 5OH^- \longrightarrow$

Aldehyde Fehling's solution

$Cu_2O_{(s)}\downarrow + RCOO^- + 3H_2O$

Red ppt.

  - **Benedict's test :** $RCHO + 2Cu(OH)_2 + NaOH \longrightarrow RCOONa + Cu_2O\downarrow + 3H_2O$

Red ppt.

  - **Schiff's test :**

$RCHO$ + p-Rosaniline hydrochloride $\longrightarrow$

(Schiff's reagent, colourless)

Pink colour

- **Tests for ketonic group :**
  - **Iodoform test :**

$RCOCH_3 + 3I_2 + 4NaOH \longrightarrow 3NaI + CHI_3\downarrow$

Yellow ppt.

$+ RCOONa + 3H_2O$

  - **Nitroprusside test :**

$RCOR$ + Sod.nitroprusside solution + NaOH $\longrightarrow$ Wine red colour complex

Carboxylic group (—COOH)

- **Ester test :**

$R - COOH + CH_3CH_2OH \xrightarrow[-H_2O]{\text{Conc. } H_2SO_4} RCOOCH_2CH_3$

Carboxylic acid Ethyl alcohol Ethyl carboxylate (Ester-fruity smell)

- **Sodium bicarbonate test :**

$RCOOH + NaHCO_3 \rightarrow RCOONa + CO_2\uparrow + H_2O$

Carboxylic acid Effervescence

Amino group (—NH_2, Primary)

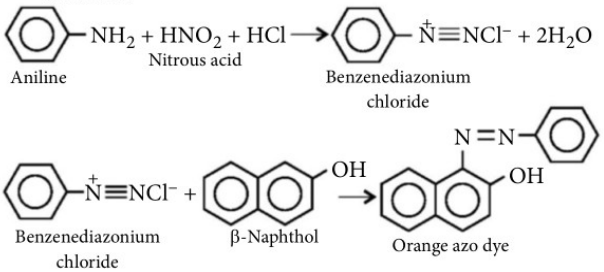
- **Carbylamine test :**

$RNH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} RNC + 3KCl + 3H_2O$

Carbylamine offensive odour

Aromatic or aliphatic 1° amines give this test.

- **Azo-dye test :** This test is given by primary aromatic amines.



Nitro group ($-NO_2$)

- **Mulliken Barker test :**

$RNO_2 + 4[H] \xrightarrow{Zn + NH_4Cl} RNHOH + H_2O$

$RNHOH + 2[Ag(NH_3)_2]OH \longrightarrow RNO + 2H_2O + 4NH_3 + 2Ag\downarrow$

Grey black ppt.

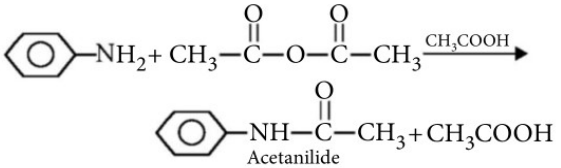
- **Ferrous hydroxide test :**

$RNO_2 + 6Fe(OH)_2 + 4H_2O \longrightarrow RNH_2 + 6Fe(OH)_3\downarrow$

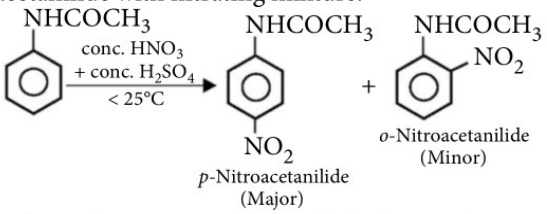
Light green Brown ppt.

Preparation of Organic Compounds

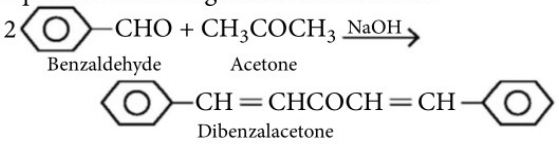
- **Acetanilide :** It is prepared by acetylation of aniline.



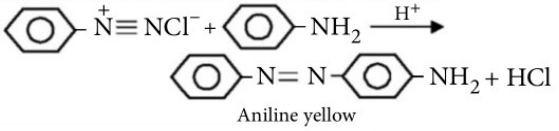
- ***p*-Nitroacetanilide :** It is prepared by nitration of acetanilide with nitrating mixture.



- **Dibenzalacetone :** Benzaldehyde undergoes condensation with acetone in the presence of aqueous NaOH to give dibenzalacetone.



- **Aniline yellow :** It is prepared by reaction of benzendiazonium chloride with aniline.



Peep Into Previous Years

3. Compound *A*, $C_8H_{10}O$, is found to react with NaOI (produced by reacting *Y* with NaOH) and yields a yellow precipitate with characteristic smell. *A* and *Y* are respectively

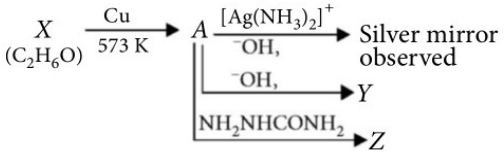
(a) H_3C–C$_6$H$_4$–CH_2–OH and I_2

(b) C$_6$H$_5$–CH_2–CH_2–OH and I_2

(c) C$_6$H$_5$–CH(OH)–CH_3 and I_2

(d) CH_3–C$_6$H$_3$(CH_3)–OH and I_2 ***(NEET 2018)***

4. Consider the reactions,



Identify *A*, *X*, *Y* and *Z*.

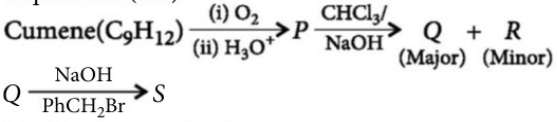
(a) *A*-Methoxymethane, *X*-Ethanol, *Y*-Ethanoic acid, *Z*-Semicarbazide

(b) *A*-Ethanal, *X*-Ethanol, *Y*-But-2-enal, *Z*-Semicarbazone

(c) *A*-Ethanol, *X*-Acetaldehyde, *Y*-Butanone, *Z*-Hydrazone

(d) *A*-Methoxymethane, *X*-Ethanoic acid, *Y*-Acetate ion, *Z*-Hydrazine ***(NEET 2017)***

5. The correct statement(s) about the following reaction sequence is(are)



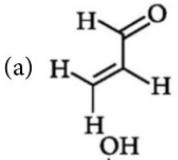
(a) *R* is steam volatile

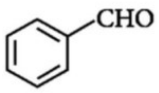
(b) *Q* gives dark violet colouration with 1% aqueous $FeCl_3$ solution

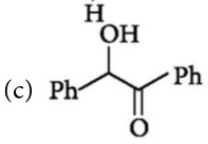
(c) *S* gives yellow precipitate with 2,4-dinitrophenyl-hydrazine

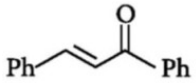
(d) *S* gives dark violet colouration with 1% aqueous $FeCl_3$ solution. ***(JEE Advanced 2016)***

6. Positive Tollens' test is observed for

(a) 

(b) 

(c) 

(d) 

(JEE Advanced 2016)

Practical Physical Chemistry

Preparation of Lyophilic and Lyophobic sols

Lyophilic sols are prepared by direct mixing of dispersed phase with dispersion medium, *e.g.*, starch sol is prepared by mixing starch in finely powdered form with boiling water. Colloidal solution of egg albumin is prepared in cold water because in hot water precipitation of egg albumin takes place. Lyophilic sols are quite stable and are not affected by presence of any electrolytic impurity.

Lyophobic sols require special methods of preparation, *e.g.*, ferric hydroxide sol and aluminium hydroxide sol are prepared by hydrolysis of their respective chlorides with boiling water.

$$FeCl_{3(aq.)} + 3H_2O_{(l)} \xrightarrow{\text{Boil}} \underset{\text{Red or Brown sol}}{Fe(OH)_{3(s)}} + 3HCl_{(aq.)}$$

$$AlCl_{3(aq.)} + 3H_2O_{(l)} \rightarrow \underset{\text{Colourless}}{Al(OH)_{3(aq.)}} + 3HCl_{(aq.)}$$

Kinetic Study of Reaction of Iodide Ion with Hydrogen Peroxide at Room Temperature

Hydrogen peroxide oxidises iodide ions to iodine in acidic medium.

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

The reaction is observed by adding a known volume of sodium thiosulphate solution and starch solution to the reaction mixture. Iodine liberated from KI reacts with sodium thiosulphate solution and is reduced to iodide ions.

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

When thiosulphate ions get completely consumed, liberated iodine reacts with starch solution to give blue colour.

$$I_2 + \text{Starch} \longrightarrow \text{Blue complex}$$

The time elapsed before the appearance of blue colour gives an idea about the rate of reaction.

If we prepare a number of reaction mixtures with different concentrations of KI solution, the blue colour appears first in reaction mixture with highest concentration of KI which indicates that rate of reaction is directly proportional to concentration of reactants.

Enthalpy of Neutralisation of Strong acid and Strong base.

Enthalpy of neutralization of strong acid and strong base is measured using simple calorimeter consisting of polythene bottle. Known volumes of standard solution of an acid and alkali are mixed and change in temperature is recorded.

Now enthalpy of neutralization can be calculated as :

$$\text{Heat of neutralization} = \frac{(W+m) \times \Delta t \times 4.2}{N \times V_{(mL)}} \text{ kJ}$$

or $$\text{Heat of neutralization} = \frac{(W+m) \times \Delta t}{N \times V_{(mL)}} \text{ cal}$$

where, W = water equivalent of calorimeter

m = mass of mixture of solution after neutralization

Δt = change in temperature

N = normality of acid or base under investigation

V = volume of acid or base under investigation in mL.

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 $Zn \mid Zn^{2+} \| Cu^{2+} \mid Cu$.
- The relation between concentration of the eletrolyte and the standard electrode potential, is given in the form of Nernst equation :

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

Peep Into Previous Years

7. The most appropriate method of making egg-albumin sol is
   (a) break an egg carefully and transfer the transparent part of the content to 100 mL of 5% *w*/*V* saline solution and stir well.
   (b) keep the egg in boiling water for 10 minutes. After removing the shell, transfer the yellow part of the content to 100 mL of 5% *w*/*V* saline solution and homogenize with a mechanical shaker.
   (c) keep the egg in boiling water for 10 minutes. After removing the shell, transfer the white part of the content to 100 mL of 5% *w*/*V* saline solution and homogenize with a mechanical shaker.
   (d) break an egg carefully and transfer only the yellow part of the content to 100 mL of 5% *w*/*V* saline solution and stir well.

   (JEE Main Online 2016)

8. Which mixture of the solutions will lead to the formation of negatively charged colloidal $[AgI]I^-$ sol?
   (a) 50 mL of 0.1 M $AgNO_3$ + 50 mL of 0.1 M KI
   (b) 50 mL of 1 M $AgNO_3$ + 50 mL of 1.5 M KI
   (c) 50 mL of 1 M $AgNO_3$ + 50 mL of 2 M KI
   (d) 50 mL of 2 M $AgNO_3$ + 50 mL of 1.5 M KI

   (NEET 2019)

Points For Extra Scoring

- Oxidation of methyl ketones with sodium hypohalite gives carboxylic acids with one carbon atom less than the corresponding ketones-haloform reaction.
- Acidified potassium dichromate solution is used by police to test that a person is drunk or not which has inorganic colour. The person is asked to breathe into the solution taken in a test tube. If the person has consumed alcohol, the orange colour will change into green colour due to oxidation of alcohol and reduction of acidified potassium dichromate to green colour chromium sulphate.
- Tests for Fe^{2+} and Fe^{3+} ions : Ferric salts react with potassium ferrocyanide to give blue ppt. or colourations due to the formation of ferri-ferrocyanide or prussian blue.