BRUSH UP for NEET/JEE CLASS-XI 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

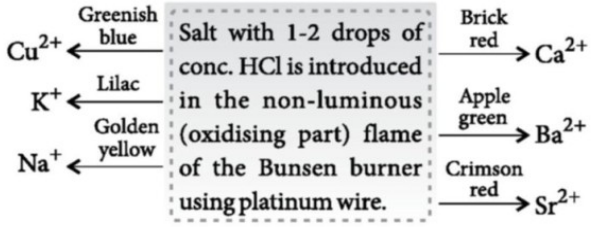
Principles Related to Practical Chemistry

Qualitative Salt Analysis

Identification of acidic and basic radicals in a salt can be carried out by performing various tests.

Preliminary Tests

Flame Test :



Borax bead test

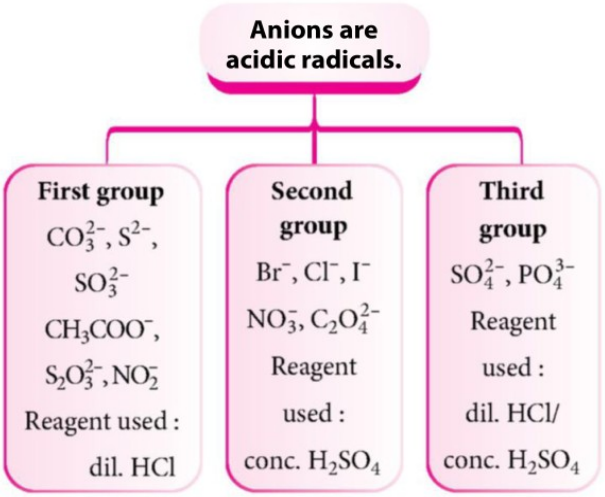
When borax is heated on a loop of Pt wire then colourless glassy bead of sodium metaborate and boric anhydride is formed.

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} \underbrace{2NaBO_2 + B_2O_3}_{\text{Glassy beads}}$$

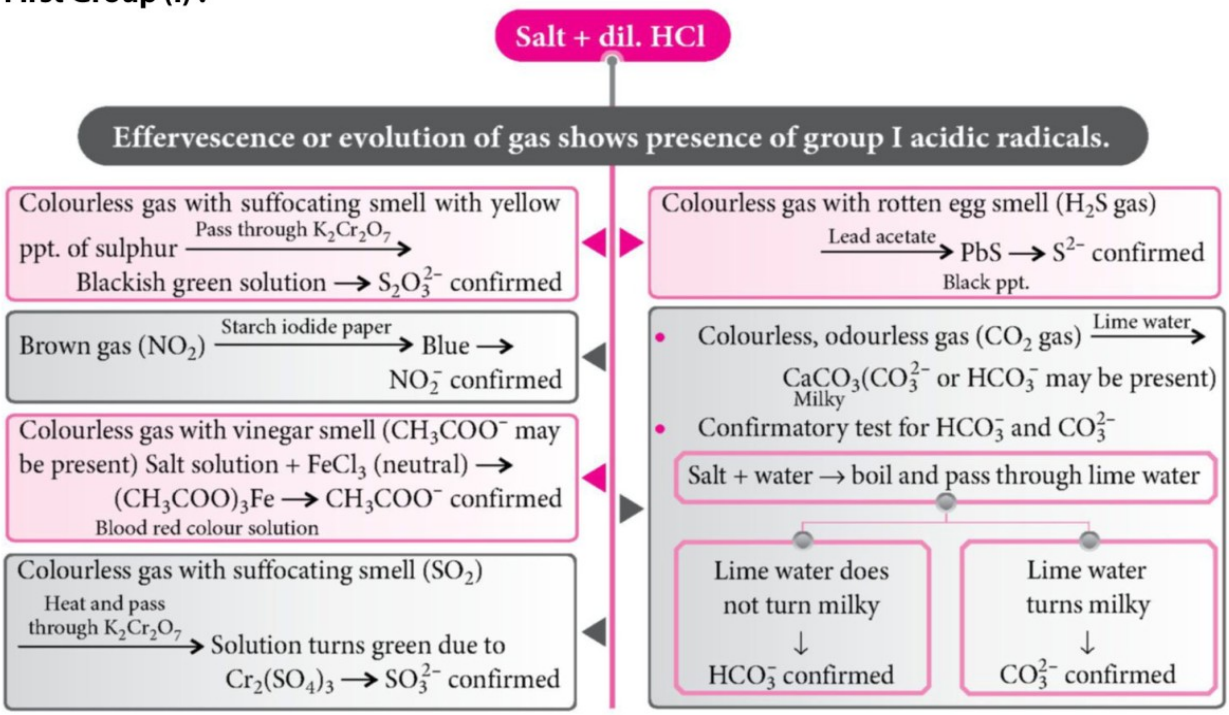
Coloured salts are then heated on the glassy bead to form coloured metaborate.

Metal	Colour in			
	Oxidising flame		Reducing flame	
Copper	Hot	Cold	Hot	Cold
	Green	Blue	Colourless	Brown red
Iron	Brown-yellow	Pale yellow	Bottle green	Bottle green
Chromium	Green	Green	Green	Green
Cobalt	Blue	Blue	Blue	Blue
Manganese	Violet	Amethyst red	Colourless	Colourless
Nickel	Red-brown	Brown	Grey	Grey

Identification of Acidic Radicals



First Group (I) :



Second Group (II) :

Salt + conc. H_2SO_4

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

Gas	Radical	Observations and Reactions
HCl (Colourless gas, pungent smell)	Chloride (Cl^-)	$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl\uparrow$ (Salt) $NH_4OH + HCl \rightarrow NH_4Cl\uparrow + H_2O$ (White dense fumes)
Br_2 (Brown fumes)	Bromide (Br^-)	$NaBr + H_2SO_4 \rightarrow NaHSO_4 + HBr$ (Salt) $2HBr + H_2SO_4 \rightarrow Br_2\uparrow + 2H_2O + SO_2$ (Brown)
I_2 (Deep violet gas)	Iodide (I^-)	$2KI + 2H_2SO_4 \rightarrow 2KHSO_4 + 2HI$ (Salt) $2HI + H_2SO_4 \rightarrow I_2\uparrow + SO_2 + 2H_2O$ (Violet)
NO_2 (Light brown gas, pungent smell)	Nitrate (NO_3^-)	$NaNO_3 + H_2SO_4 \rightarrow$ (Salt) $NaHSO_4 + HNO_3$ $4HNO_3 \rightarrow 2H_2O + 4NO_2\uparrow + O_2\uparrow$ (Light brown fumes)
CO + CO_2 (Colourless, odourless gas)	Oxalate ($C_2O_4^{2-}$)	$Na_2C_2O_4 + H_2SO_4 \rightarrow$ (Salt) $Na_2SO_4 + H_2C_2O_4$ $H_2C_2O_4 + H_2SO_4 \rightarrow$ CO (Burns with blue flame) + CO_2 (Turns lime water milky) + H_2O

- **Confirmatory Tests for Group II :**

Nitrate (NO_3^-)

Brown ring test : On treating aqueous solution of salt with freshly prepared solution of ferrous sulphate and concentrated sulphuric acid, gives a brown ring at the junction of two liquids.

$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$
Salt

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

$[Fe(H_2O)_6]SO_4 + NO \longrightarrow [Fe(H_2O)_5NO]SO_4 + H_2O$
Brown ring

Oxalate ($C_2O_4^{2-}$)

On acidifying salt solution or sodium carbonate extract with acetic acid and on adding calcium chloride solution gives white precipitate.

$Na_2C_2O_4 + CaCl_2 \longrightarrow CaC_2O_4\downarrow + 2NaCl$
Salt — White ppt.

Filter and dissolve the precipitate in dilute sulphuric acid and add few drops of potassium permanganate solution.

$CaC_2O_4 + H_2SO_4 \longrightarrow H_2C_2O_4 + CaSO_4$

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

$\begin{matrix}COOH\\|\\COOH\end{matrix} + [O] \longrightarrow 2CO_2 + H_2O$

Pink colour discharge of $KMnO_4$ confirming presence of oxalate ion.

Chloride (Cl^-)

Chromyl chloride test :

$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$
Salt

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

$CrO_3 + 2HCl \longrightarrow CrO_2Cl_2\uparrow + H_2O$
Chromyl chloride (Red vapours)

These vapours on passing through sodium hydroxide solution give yellow solution of sodium chromate.

$CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O$
Yellow colour

The yellow solution on neutralising with acetic acid and on addition of lead acetate gives yellow precipitate of lead chromate.

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

Confirmatory tests for acid radicals of group II

Iodide (I^-)

Layer test : On treating salt with dilute sulphuric acid, chloroform or carbon tetrachloride and chlorine water, gives violet coloured layer.

$2NaI + Cl_2 \longrightarrow 2NaCl + I_2$
Salt

I_2 + Chloroform $\longrightarrow$ Violet coloured layer

Starch paper test :

I_2 + Starch $\longrightarrow$ I_2-starch complex
Blue colour

Bromide (Br^-)

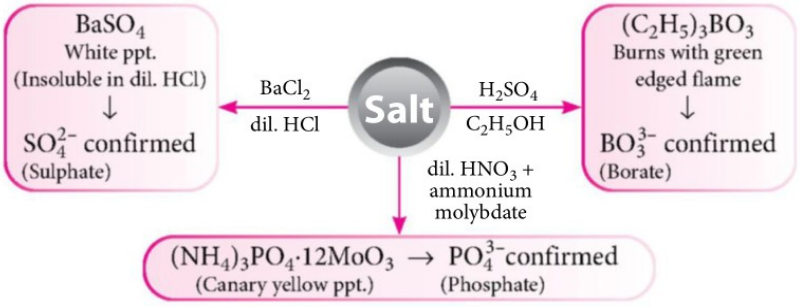
Layer test : On treating salt with dilute sulphuric acid, chloroform or carbon tetrachloride and chlorine water gives brown coloured layer.

$2NaBr + Cl_2 \longrightarrow 2NaCl + Br_2$
Salt

Br_2 + Chloroform $\longrightarrow$ Brown coloured layer

Third Group (III) :

These anions are identified by their characteristic chemical reactions.



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_2S in presence of dil. HCl	HgS, PbS, Bi_2S_3, CuS (Black); CdS, As_2S_3, SnS_2 (Yellow); Sb_2S_3 (Orange); SnS (Brown)	HCl (with common H^+ ion) decreases the ionization of H_2S 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_4OH in presence of NH_4Cl	$Fe(OH)_3$ (Reddish brown), $Cr(OH)_3$ (Green), $Al(OH)_3$ (White)	NH_4Cl (with common NH_4^+ ion) decreases the ionization of NH_4OH 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_2S in presence of NH_4OH	ZnS (Greenish white), MnS (Buff), CoS, NiS (Black),	Basic medium increases the ionization of H_2S, thus increasing $[S^{2-}]$, hence precipitation of group IV sulphides having high K_{sp} values occurs.
Group V Ba^{2+}, Sr^{2+}, Ca^{2+}	$(NH_4)_2CO_3$ in presence of NH_4OH	$BaCO_3$, $SrCO_3$, $CaCO_3$ (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_2HPO_4 in presence of NH_4OH	$Mg(NH_4)PO_4$ (White)	—
Zero NH_4^+	NaOH	Ammonia gas is evolved.	Tested independently from original solution.

Quantitative Analysis

Titration

The process of addition of the known solution from the burette to the measured volume of solution of the substance to be estimated until the reaction between the two is just complete.

Acid-Base Titration

- When the strength of an acid is determined with the help of a standard solution of base, it is known as acidimetry.
- When the strength of a base is determined with the help of a standard solution of an acid, it is known as alkalimetry.

These titrations involve neutralisation of an acid with an alkali.

$$\underset{\text{Acid}}{HA} + \underset{\text{Alkali}}{BOH} \longrightarrow \underset{\text{Salt}}{BA} + \underset{\text{Water}}{H_2O}$$

Calculations Involving in Volumetric Analysis

Number of equivalents = Normality (N) × Volume (V) (in L)

Number of equivalents of titrate *i.e.*,

$N_1V_1 = N_2V_2$ = Number of equivalents of titrant

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 : $M_1V_1n_1 = M_2V_2n_2$

Indicator

A substance which helps in physical detection of completion of the titration is called 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	3.2 – 4.4	Weak base *vs* strong acid titration
Methyl red (red ⇒ yellow)	5.1	4.2 – 6.3	Weak base *vs* strong acid titration
Phenol red (yellow ⇒ red)	7.9	6.4 – 8.2	Strong acid *vs* strong base titration
Phenolphthalein (colourless ⇒ pink)	9.3	8.3 – 10.0	Weak acid *vs* strong base titration

Peep Into Previous Years

1. The cation that will not be precipitated by H_2S in the presence of dil. HCl is
   (a) Cu^{2+} (b) Pb^{2+}
   (c) As^{3+} (d) Co^{2+}
   (Online JEE Main 2015)

2. For standardising NaOH solution, which of the following is used as a primary standard?
   (a) Oxalic acid
   (b) Ferrous ammonium sulphate
   (c) Sodium tetraborate
   (d) Dil. HCl ***(Online JEE Main 2018)***

3. An alkali is titrated against an acid with methyl orange as indicator, which of the following is a correct combination?

	Base	Acid	End point
(a)	Weak	Strong	Colourless to pink
(b)	Strong	Strong	Pinkish red to yellow
(c)	Weak	Strong	Yellow to pinkish red
(d)	Strong	Strong	Pink to colourless

(JEE Main 2018)

4. Which will make basic buffer?
   (a) 100 mL of 0.1 M HCl + 100 mL of 0.1 M NaOH
   (b) 50 mL of 0.1 M NaOH + 25 mL of 0.1 M CH_3COOH
   (c) 100 mL of 0.1 M CH_3COOH + 100 mL of 0.1 M NaOH
   (d) 100 mL of 0.1 M HCl + 200 mL of 0.1 M NH_4OH ***(NEET 2019)***

Qualitative Analysis of Organic Compounds

Detection of N, S, Cl in Organic Compounds

Lassaigne's extract : A small pellet of metallic sodium together with a little amount of the substance is heated to red hot in an ignition tube. It is then suddenly plunged into about 10 mL of distilled water in a China dish. The mixture is boiled well and filtered. Filtrate is known as Lassaigne's extract (L.E.).

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.	$FeSO_4 + 2NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4$ $Fe(OH)_2 + 6NaCN \longrightarrow Na_4[Fe(CN)_6] + 2NaOH$ $Na_4[Fe(CN)_6] + FeCl_3 \xrightarrow{HCl} NaFe[Fe(CN)_6] + 3NaCl$ Prussian blue or $3Na_4[Fe(CN)_6] + 4FeCl_3 \longrightarrow Fe_4[Fe(CN)_6]_3 + 12NaCl$ Prussian blue
Sulphur	$2Na + S \xrightarrow{\Delta} Na_2S$ (L.E.)	(i) L.E. + sodium nitroprusside A deep violet colour. (ii) L.E. + CH_3COOH + $(CH_3COO)_2Pb$ Gives a black ppt.	(i) $Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow$ Sodium nitroprusside $Na_4[Fe(CN)_5NOS]$ Deep violet (ii) $Na_2S + (CH_3COO)_2Pb \xrightarrow{CH_3COOH}$ $PbS\downarrow + 2CH_3COONa$ Black ppt.
Halogens	$Na + X \xrightarrow{\Delta} NaX$ (L.E.) (X = Cl, Br, I)	L.E. + HNO_3 + $AgNO_3$ (i) White ppt. soluble in aq. NH_3 (or NH_4OH) confirms Cl. (ii) Pale 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.	$NaX + AgNO_3 \xrightarrow{HNO_3} AgX\downarrow + NaNO_3$ White ppt. $AgCl + 2NH_4OH_{(aq.)} \longrightarrow [Ag(NH_3)_2]Cl + 2H_2O$ Soluble
Nitrogen and sulphur together	$Na + C + N + S \xrightarrow{\Delta} NaSCN$ (L.E.) Sodium thiocyanate	As in test for nitrogen; instead of green or blue colour, blood red colouration confirms the presence of N and S both.	$3NaSCN + FeCl_3 \longrightarrow [Fe(SCN)_3] + 3NaCl$ Blood red colour

Quantitative Analysis of Organic Compounds

Element	Method
Carbon and Hydrogen	**Liebig's Combustion method :** A known mass of an organic compound is burnt in the presence of excess of O_2 and CuO. $C_xH_y + \left(x + \frac{y}{4}\right)O_2 \xrightarrow{\Delta} xCO_2 + \frac{y}{2}H_2O$ CO_2 evolved is absorbed by conc. solution of KOH or ascarite (NaOH + CaO). H_2O produced is absorbed by anhydrous $CaCl_2$ or $Mg(ClO_4)_2$. Increase in masses of these absorbing compounds gives the masses of CO_2 and H_2O produced. $\%\text{ of C} = \frac{12}{44} \times \frac{\text{Mass of } CO_2 \text{ formed}}{\text{Mass of compound taken}} \times 100$, $\%\text{ of H} = \frac{2}{18} \times \frac{\text{Mass of } H_2O \text{ formed}}{\text{Mass of compound taken}} \times 100$
Nitrogen	(i) **Dumas method :** Nitrogen containing organic compound is heated with CuO in an atmosphere of CO_2. $C_xH_yN_z + \left(2x + \frac{y}{2}\right)CuO \longrightarrow xCO_2 + \frac{y}{2}H_2O + \frac{z}{2}N_2 + \left(2x + \frac{y}{2}\right)Cu$ N_2 evolved gets collected over conc. KOH solution which absorbs all other gases. $\%\text{ of N} = \frac{28}{22400} \times \frac{\text{Vol. of } N_2 \text{ at STP}}{\text{Mass of compound taken}} \times 100$, $\%\text{ of N} = \frac{1.4 \times \text{Normality of acid} \times \text{Vol. of acid used}}{\text{Mass of compound taken}}$ (ii) **Kjeldahl's method :** $\text{Organic compound} + H_2SO_{4\,(conc.)} \longrightarrow (NH_4)_2SO_4 \xrightarrow{2NaOH} Na_2SO_4 + 2NH_3 + 2H_2O$ $2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$ $\%\text{ of N} = \frac{1.4 \times \text{Molarity of acid} \times \text{Vol. of acid used} \times \text{Basicity of acid}}{\text{Mass of compound taken}}$
Halogens	**Carius method :** Halogen in organic compound is precipitated as silver halide by boiling with conc. HNO_3 and then adding $AgNO_3$. $X \xrightarrow[AgNO_3]{HNO_3, \Delta} AgX\downarrow$ $\%\text{ of Cl} = \frac{35.5}{143.5} \times \frac{\text{Mass of AgCl formed}}{\text{Mass of compound taken}} \times 100$ $\%\text{ of Br} = \frac{80}{188} \times \frac{\text{Mass of AgBr formed}}{\text{Mass of compound taken}} \times 100$, $\%\text{ of I} = \frac{127}{235} \times \frac{\text{Mass of AgI formed}}{\text{Mass of compound taken}} \times 100$
Sulphur	**Carius method :** Sulphur in organic compound is converted into H_2SO_4 by boiling with Na_2O_2 or conc. HNO_3 and is precipitated as $BaSO_4$ by adding excess of $BaCl_2$ solution in water. $S \xrightarrow[(ii)\ BaCl_2]{(i)\ HNO_3, \Delta} \underset{\text{White ppt.}}{BaSO_4\downarrow}$ $\%\text{ of S} = \frac{32}{233} \times \frac{\text{Mass of } BaSO_4 \text{ formed}}{\text{Mass of compound taken}} \times 100$

Oxygen	**Iodine method :** Organic compound $\xrightarrow{\Delta} O_2$ + Other gaseous products $[2C + O_2 \xrightarrow{1373\ K} 2CO] \times 5$ $[I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2] \times 2$ $10C + 5O_2 + 2I_2O_5 \longrightarrow 10CO_2 + 2I_2$ $\%\ \text{of O} = \frac{32}{88} \times \frac{\text{Mass of } CO_2 \text{ formed}}{\text{Mass of compound taken}} \times 100$; $\%\ \text{of O} = \frac{5 \times 16}{2 \times 127} \times \frac{\text{Mass of } I_2 \text{ formed}}{\text{Mass of compound taken}} \times 100$

Peep Into Previous Years

5. In Carius method of estimation of halogens, 250 mg of an organic compound gave 141 mg of AgBr. The percentage of bromine in the compound is (At. mass of Ag = 108; Br = 80)
   (a) 48 (b) 60
   (c) 24 (d) 36 ***(JEE Main 2015)***

6. Sodium extract is heated with concentrated HNO_3 before testing for halogens because
   (a) Ag_2S and AgCN are soluble in acidic medium
   (b) silver halides are totally insoluble in nitric acid
   (c) S^{2-} and CN^-, if present, are decomposed by conc. HNO_3 and hence do not interfere in the test
   (d) Ag reacts faster with halides in acidic medium.
   (Online JEE Main 2016)

Points For Extra Scoring

- Blood is a buffer containing carbonic acid (H_2CO_3) and bicarbonate ions (HCO_3^-), small amounts of the acid or base produced from the spicy food do not disturb its pH.
- Indicator used in acid-base titration should be such that $pK_{Indicator}$ = pH at the equivalent point.
- For a colour change of an indicator, pH = $pK_{Indicator}$ +1, *i.e.*, indicator have a useful colour change over a pH range of 2 units.
- In the titration of a weak acid, at half the equivalence point (half-neutralisation), pH = pK_a.
- Messenger's method is used for estimation of sulphur. It this method, the organic compound is heated with alkaline $KMnO_4$ solution when sulphur present in the organic compound is oxidised to K_2SO_4 which is then estimated as $BaSO_4$.
- Rectified spirit contains about 95% alcohol (b.p. 351 K) and 5% water (b.p. 373 K) but alcohol and water cannot be separated from this mixture even though their boiling points to differ by 22 K. To remove water from such mixture (alcohol and water) azeotropic distillation is used.

Answer Key For Peep Into Previous Years

1.	(d)	2.	(a)	3.	(c)	4.	(d)	5.	(c)	6.	(c)

WRAP it up!

1. Which of the following does not give borax bead test?
   (a) Cr^{3+} (b) Cu^{2+} (c) Mn^{2+} (d) Pb^{2+}

2. In the test of basic radicals, which reagent is used in IVth group?
   (a) H_2S + HCl
   (b) $NH_4OH + NH_4Cl$
   (c) $NH_4OH + NH_4Cl + H_2S$ gas
   (d) $NH_4OH + NH_4Cl + (NH_4)_2CO_3$

3. Which of the following groups constitute basic radicals of fourth group?
   (a) Pb^{2+}, Hg^{2+}, Cd^{2+} (b) Zn^{2+}, Mn^{2+}, Ni^{2+}
   (c) Al^{3+}, Fe^{3+}, Cr^{3+} (d) Ca^{2+}, Sr^{2+}, Ba^{2+}