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SALT ANALYSIS

Analysis always does not mean breaking of substance into its ultimate constituents. Finding out the nature of substance and identity of its constituents is also analysis and is known as ***qualitative analysis.*** Qualitative analysis of inorganic salts means the identification of cations and anions present in the salt or a mixture of salts. Inorganic salts may be obtained by complete or partial neutralisation of acid with base or vice-versa. In the formation of a salt, the part contributed by the ***acid*** is called ***anion*** and the part contributed by the ***base*** is called ***cation***. For example, in the salts $CuSO_4$ and NaCl, Cu^{2+} and Na^+ ions are cations and SO_4^{2-} and Cl^- ions are anions. Qualitative analysis is carried out on various scales. Amount of substance employed in these is different. In macro analysis, 0.1 to 0.5 g of substance and about 20 mL of solution is used. For semimicro analysis, 0.05 g substance and 1 mL solution is needed while for micro analysis amount required is very small. Qualitative analysis is carried out through the reactions which are easily perceptible to our senses such as sight and smell. Such reactions involve:

(a) Formation of a precipitate

(b) Change in colour

(c) Evolution of gas etc.

Systematic analysis of an inorganic salt involves the following steps:

(i) Preliminary examination of solid salt and its solution.

(ii) Determination of anions by reactions carried out in solution (wet tests) and confirmatory tests.

(iii) Determination of cations by reactions carried out in solution (wet tests) and confirmatory tests.

Although these tests are not conclusive but sometimes they give quite important clues for the presence of certain anions or cations. These tests can be performed within 10^{-15} minutes. These involve noting the general appearance and physical properties, such as colour, smell, solubility etc. of the salt. These are named as ***dry tests.***

Heating of dry salt, blow pipe test, flame tests, borax bead test, sodium carbonate bead test, charcoal cavity test etc. come under dry tests.

Solubility of a salt in water and the pH of aqueous solutions give important information about the nature of ions present in the salt. If a solution of the salt is acidic or basic in nature, this means that it is being hydrolysed in water. If the solution is basic in nature then salt may be some carbonate or sulphide etc. If the solution shows acidic nature then it may be an acid salt or salt of weak base and strong acid. In this case it is best to neutralise the solution with sodium carbonate before testing it for anions.

Gases evolved in the preliminary tests with dil. H_2SO_4/dil. HCl and conc. H_2SO_4 also give good indication about the presence of acid radicals (See Tables 1 and 3). ***Preliminary tests should always be performed before starting the confirmatory tests for the ions.***

EXPERIMENT 1.1

Aim

To detect one cation and one anion in the given salt from the following ions:

Cations - Pb^{2+}, Cu^{2+}, As^{3+}, Al^{3+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mg^{2+},NH_4^+

Anions - CO_3^{2-} , S^{2-}, SO_4^{2-}, NO_2^- , NO_3^-, Cl^-, Br^-, I^-, PO_4^{3-}, CH_3COO^-.

(Insoluble salts to be excluded)

Theory

Two basic principles of great use in the analysis are:

(i) the Solubility product

(ii) the Common ion effect.

When ionic product of a salt exceeds its solubility product, precipitation takes place. Ionic product of salt is controlled by making use of common ion effect.

Material Required

• Boiling tube	:	As per need
• Test tubes	:	As per requirement
• Measuring cylinder	:	One
• Test tube stand	:	One
• Test tube holder	:	One
• Delivery tube	:	One
• Corks	:	As per need
• Filter paper	:	As per need
• Reagents	:	As per need

Step - I : Preliminary Test with Dilute Sulphuric Acid → In this test the action of dilute sulphuric acid (procedure is given below) on the salt is noted at room temperature and on warming.

Carbonate (CO_3^{2-}), sulphide (S^{2-}), sulphite (SO_3^{2-}), nitrite (NO_2^-) and acetate (CH_3COO^-) react with dilute sulphuric acid to evolve different gases. Study of the characteristics of the gases evolved gives information about the anions. Summary of characteristic properties of gases is given in Table 1.

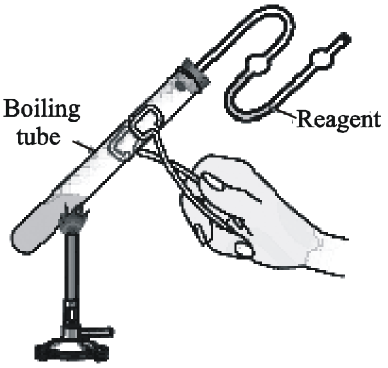


Fig. 7.1 - Testing a gas

Procedure

(a) Take 0.1 g of the salt in a test tube and add 1–2 mL of dilute sulphuric acid. Observe the change, if any, at room temperature. If no gas is evolved, warm the content of the test tube. If gas is evolved test it by using the apparatus shown in Fig.1 and identify the gas evolved (See Table 1).

Table 1 : Preliminary test with dilute sulphuric acid

Observations	Inference	
	Gas Evolved	**Possible Anion**
A colourless, odourless gas is evolved with brisk effervescence, which turns lime water milky.	CO_2	Carbonate (CO_3^{2-})
Colourless gas with the smell of rotten eggs is evolved which turns lead acetate paper black.	H_2S	Sulphide (S^{2-})
Colourless gas with a pungent smell, like burning sulphur which turns acidified potassium dichromate solution green.	SO_2	Sulphite (SO_3^{2-})
Brown fumes which turn acidified potassium iodide solution containing starch solution blue.	NO_2	Nitrite (NO_2^-)
Colourless vapours with smell of vinegar. Vapours turn blue litmus red.	CH_3COOH vapours	Acetate, (CH_3COO^-)

Confirmatory tests for CO_3^{2-} , S^{2-}, SO_3^{2-}, NO_2^- and CH_3COO^-

Confirmatory (wet) tests for anions are performed by using water extract when salt is soluble in water and by using sodium carbonate extract when salt is insoluble in water. Confirmation of CO_3^{2-} is done by using aqueous solution of the salt or by using solid salt as such because sodium carbonate extract contains carbonate ions. Water extract is made by dissolving salt in water. Preparation of sodium carbonate extract is given below.

Preparation of sodium carbonate extract

Take 1 g of salt in a porcelain dish or boiling tube. Mix about 3 g of solid sodium carbonate and add 15 mL of distilled water to it. Stir and boil the content for about 10 minutes. Cool, filter and collect the filtrate in a test tube and label it as sodium carbonate extract.

Confirmatory tests for acid radicals, which react with dilute sulphuric acid are given in Table 2.

Table 2 : Confirmatory tests for CO_3^{2-}, S^{2-}, SO_3^{2-}, NO_3^- , CH_3COO^-

Anion	Confirmatory Test
Carbonate (CO_3^{2-})	Take 0.1 g of salt in a test tube, add dilute sulphuric acid. CO_2 gas is evolved with brisk effervescence which turns lime water milky. On passing the gas for some more time, milkiness disappears.
Sulphide (S^{2-})	Take 1 mL of water extract and make it alkaline by adding ammonium hydroxide or sodium carbonate extract. Add a drop of sodium nitroprusside solution. Purple or violet colouration appears.
Sulphite (SO_3^{2-})	(a) Take 1 mL of water extract or sodium carbonate extract in a test tube and add barium chloride solution. A white precipitate is formed which dissolves in dilute hydrochloric acid and sulphur dioxide gas is also evolved (b) Take the precipitate of step (a) in a test tube and add a few drops of potassium permanganate solution acidified with dil. H_2SO_4. Colour of potassium permanganate solution gets discharged.
Nitrite (NO_2^-)	(a) Take 1 mL of water extract in a test tube. Add a few drops of potassium iodide solution and a few drops of starch solution, acidify with acetic acid. Blue colour appears. (b) Acidify 1 mL of water extract with acetic acid. Add 2-3 drops of sulphanilic acid solution followed by 2-3 drops of 1-naphthylamine reagent. Appearance of red colour indicates the presence of nitrite ion.
Acetate, (CH_3COO^-)	(a) Take 0.1 g of salt in a china dish. Add 1 mL of ethanol and 0.2 mL conc. H_2SO_4 and heat. Fruity odour confirms the presence of acetate ion. (b) Take 0.1 g of salt in a test tube, add 1-2 mL distilled water, shake well filter if necessary. Add 1 to 2 mL neutral ferric chloride solution to the filtrate. Deep red colour appears which disappears on boiling and a brown-red precipitate is formed.

Chemistry of Confirmatory Tests

1. Test for Carbonate ion [CO_3^{2-}]

If there is effervescence with the evolution of a colourless and odourless gas on adding dil. H_2SO_4 to the solid salt, this indicates the presence of carbonate ion.

The gas turns lime water milky due to the formation of $CaCO_3$

$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2$$

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

If CO_2 gas is passed in excess through lime water, the milkiness disappears due to the formation of calcium hydrogen carbonate which is soluble in water.

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2$$

2. Test for Sulphide ion [S^{2-}]

(a) With warm dilute H_2SO_4 a sulphide gives hydrogen sulphide gas which smells like rotten eggs. A piece of filter paper dipped in lead acetate solution turns black on exposure to the gas due to the formation of lead sulphide which is black in colour.

$$Na_2S + H_2SO_4 \longrightarrow Na_2SO_4 + H_2S$$

$$(CH_3COO)_2Pb + H_2S \longrightarrow \underset{\substack{\text{Lead sulphide}\\ \text{Black precipitate}}}{PbS} + 2CH_3COOH$$

(b) If the salt is soluble in water, take the solution of salt in water make it alkaline with ammonium hydroxide and add sodium nitroprusside solution. If it is insoluble in water take sodium carbonate extract and add a few drops of sodium nitroprusside solution. Purple or violet colouration due to the formation of complex compound $Na_4[Fe(CN)_5NOS]$ confirms the presence of sulphide ion in the salt.

$$Na_2S + \underset{\text{Sodium nitroprusside}}{Na_2[Fe(CN)_5NO]} \longrightarrow \underset{\text{Complex of Purple colour}}{Na_4[Fe(CN)_5NOS]}$$

3. Test for Sulphite ion [SO_3^{2-}]

(a) On treating sulphite with warm dil. H_2SO_4, SO_2 gas is evolved which is suffocating with the smell of burning sulphur.

$$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + SO_2$$

The gas turns potassium dichromate paper acidified with dil. H_2SO_4, green.

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + \underset{\substack{\text{Chromium}\\ \text{sulphate (green)}}}{Cr_2(SO_4)_3} + H_2O$$

(b) An aqueous solution or sodium carbonate extract of the salt produces a white precipitate of barium sulphite on addition of barium chloride solution.

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

This precipitate gives following tests.

(i) This precipitate on treatment with dilute HCl, dissolves due to decomposition of sulphite by dilute HCl. Evolved SO_2 gas can be tested.

$$BaSO_3 + 2HCl \longrightarrow BaCl_2 + H_2O + SO_2$$

(ii) Precipitate of sulphite decolourises acidified potassium permanganate solution.

$$BaSO_3 + H_2SO_4 \longrightarrow BaSO_4 + H_2O + SO_2$$

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

$$SO_2 + H_2O + [O] \longrightarrow H_2SO_4$$

4. Test for Nitrite ion [NO_2^-]

(a) On treating a solid nitrite with dil. H_2SO_4 and warming , reddish brown fumes of NO_2 gas are evolved. Addition of potassium iodide solution to the salt solution followed by freshly prepared starch solution and acidification with acetic acid produces blue colour. Alternatively, a filter paper moistened with potassium iodide and starch solution and a few drops of acetic acid turns blue on exposure to the gas, due to the interaction of liberated iodine with starch.

(i) $2NaNO_2 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HNO_2$

$3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O$ (disproportionation)

$2NO + O_2 \longrightarrow \underset{\text{Brown gas}}{2NO_2}$

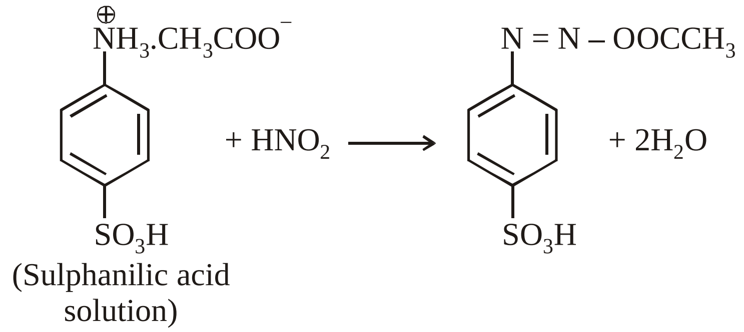
(ii) $NO_2^- + CH_3COOH \longrightarrow HNO_2 + CH_3COO^-$

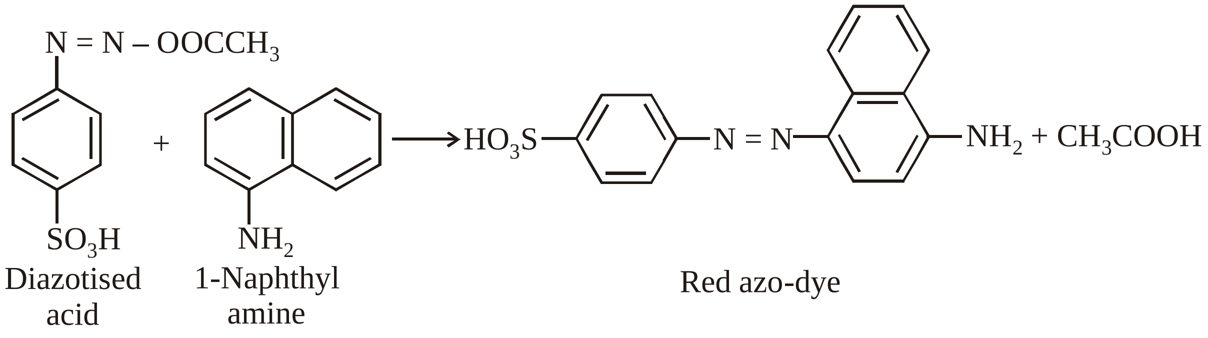
$2HNO_2 + 2KI + 2CH_3COOH \longrightarrow 2CH_3COOK + 2H_2O + 2NO + I_2$

I_2 + Starch ⟶ Blue complex

(b) **Sulphanilic acid — 1-naphthylamine reagent test (Griess-llosvay test) :** On adding sulphanilic acid and 1-naphthylamine reagent to the water extract or acidified with acetic acid, sulphanilic acid is diazotised in the reaction by nitrous acid formed. Diazotised acid couples with 1-naphthylamine to form a red azo-dye.

$NO_2^- + CH_3COOH \rightarrow HNO_2 + CH_3COO^-$





The test solution should be very dilute. In concentrated solutions reaction does not proceed beyond diazotisation.

5. Test for Acetate ion [CH_3COO^-]

(a) If the salt smells like vinegar on treatment with dil. H_2SO_4, this indicates the presence of acetate ions. Take 0.1 g of salt in a china dish and add 1 mL of ethanol. Then add about 0.2 mL of conc. H_2SO_4 and heat. Fruity odour of ethyl acetate indicates the presence of CH_3COO^- ion.

$$2CH_3COONa + H_2SO_4 \longrightarrow Na_2SO_4 + 2CH_3COOH$$

$$CH_3COOH + C_2H_5OH \longrightarrow \underset{\substack{\text{Ethylacetate}\\ \text{(Fruity odour)}}}{CH_3COOC_2H_5} + H_2O$$

(b) Acetate gives deep red colour on reaction with neutral ferric chloride solution due to the formation of complex ion which decomposes on heating to give Iron (III) dihydroxyacetate as brown red precipitate.

$$6CH_3COO^- + 3Fe^{3+} + 2H_2O \longrightarrow [Fe_3(OH)_2(CH_3COO)_6]^+ + 2H^+$$

$$[Fe_3(OH)_2(CH_3COO)_6]^+ + 4H_2O \longrightarrow \underset{\substack{\text{Iron(III)dihydroxyacetate}\\ \text{(Brown-red precipitate)}}}{3[Fe(OH)_2(CH_3COO)]} + 3CH_3COOH + H^+$$

Step-II : Preliminary Test with Concentrated Sulphuric Acid If no positive result is obtained from dil. H_2SO_4 test, take 0.1 g of salt in a test tube and 3-4 drops of conc. H_2SO_4. Observe the change in the reaction mixture in cold and then warm it. Identify the gas evolved on heating (see Table 3).

Table 3 : Preliminary examination with concentrated sulphuric acid

Observations	Inference	
	Gas/Vapours Evolved	**Possible Anion**
A colourless gas with pungent smell, which gives dense white fumes when a rod dipped in ammonium hydroxide is brought near the mouth of the test tube.	HCl	Chloride, (Cl^-)
Reddish brown gas with a pungent odour is evolved. Intensity of reddish gas increases on heating the reaction mixture after addition of solid MnO_2 to the reaction mixture. Solution also acquires red colour.	Br_2 vapours	Bromide, (Br^-)
Violet vapours, which turn starch paper blue and a layer of violet sublimate is formed on the sides of the tube. Fumes become dense on adding MnO_2 to the reaction mixture.	I_2 vapours	Iodide, (I^-)
Brown fumes evolve which become dense upon heating the reaction mixture after addition of copper turnings and the solution acquires blue colour.	NO_2	Nitrate, (NO_3^-)
Colourless, odourless gas is evolved which turns lime water milky and the gas coming out of lime water burns with a blue flame, if ignited.	CO and CO_2	Oxalate, ($C_2O_4^{2-}$)

Table 4 : Confirmatory tests for Cl^-, Br^-, I^-, NO_3^- and $C_2O_4^{2-}$

Anion	Confirmatory Test
Chloride (Cl^-)	(a) **Take 0.1 g of salt in a test tube, add a pinch of manganese dioxide and 3-4 drops of conc. sulphuric acid. Heat the reaction mixture. Greenish yellow chlorine gas is evolved which is detected by its pungent odour and bleaching action.** (b) **Take 1 mL of sodium carbonate extract in a test tube, acidify it with dil. HNO_3 or take water extract and add silver nitrate solution. A curdy white precipitate is obtained which is soluble in ammonium hydroxide solution.** (c) **Take 0.1 g salt and a pinch of solid potassium dichromate in a test tube, add conc. H_2SO_4, heat and pass the gas evolved through sodium hydroxide solution. It becomes yellow. Divide the solution into two parts. Acidify one part with acetic acid and add lead acetate solution. A yellow precipitate is formed. Acidify the second part with dilute sulphuric acid and add 1 mL of amyl alcohol followed by 1 mL of 10% hydrogen peroxide. After gentle shaking the organic layer turns blue.**
Bromide (Br^-)	(a) **Take 0.1 g of salt and a pinch of MnO_2 in a test tube. Add 3-4 drops conc.sulphuric acid and heat. Intense brown fumes are evolved.** (b) **Neutralise 1 mL of sodium carbonate extract with hydrochloric acid (or take the water extract). Add 1 mL carbon tetrachloride (CCl_4)/ chloroform ($CHCl_3$)/ carbon disulphide. Now add an excess of chlorine water dropwise and shake the test tube. A brown colouration in the organic layer confirms the presence of bromide ion.** (c) **Acidify 1 mL of sodium carbonate extract with dil. HNO_3 (or take 1 mL water extract) and add silver nitrate solution. A pale yellow precipitate soluble with difficulty in ammonium hydroxide solution is obtained.**
Iodide (I^-)	(a) **Take 1 mL of salt solution neutralised with HCl and add 1 mL chloroform/carbon tetrachloride/carbon disulphide. Now add an excess of chlorine water drop wise and shake the test tube. A violet colour appears in the organic layer.** (b) **Take 1 mL of sodium carbonate extract acidify it with dil. HNO_3 (or take water extract). Add, silver nitrate solution. A yellow precipitate insoluble in NH_4OH solution is obtained.**

Anion	Confirmatory Test
***Nitrate (NO_3^-)**	**Take 1 mL of salt solution in water in a test tube. Add 2 mL of conc. H_2SO_4 and mix thoroughly. Cool the mixture under the tap. Add freshly prepared ferrous sulphate along the sides of the test tube without shaking. A dark brown ring is formed at the junction of the two solutions.**
Oxalate ($C_2O_4^{2-}$)	**(a) Take 1 mL of water extract or sodium carbonate extract acidified with acetic acid and add calcium chloride solution. A white precipitate insoluble in ammonium oxalate and oxalic acid solution but soluble in dilute hydrochloric acid and dilute nitric acid is formed.** **(b) Take the precipitate from test (a) and dissolve it in dilute H_2SO_4. Add very dilute solution of $KMnO_4$ and warm. Colour of $KMnO_4$ solution is discharged. Pass the gas coming out through lime water. The lime water turns milky.**

Chemistry of Confirmatory Tests

1. Test for Chloride ion [Cl⁻]

(a) If on treatment with warm conc. H_2SO_4 the salt gives a colourless gas with pungent smell or if the gas which gives dense white fumes with ammonia solution, then the salt may contain Cl^- ions and the following reaction occurs.

$$NaCl + H_2SO_4 \longrightarrow \underset{\substack{\text{Sodium}\\\text{hydrogen sulphate}}}{NaHSO_4} + \underset{\substack{\text{Hydrogen chloride}\\\text{Colourless gas}}}{HCl}$$

$$HCl + NH_3 \longrightarrow \underset{\substack{\text{Ammonium chloride}\\\text{White fumes}}}{NH_4Cl}$$

(b) If a salt gives effervescence on heating with conc. H_2SO_4 and MnO_2 and a light greenish yellow pungent gas is evolved, this indicates the presence of Cl^-ions.

$$MnO_2 + 2NaCl + 2H_2SO_4 \longrightarrow Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2$$

(c) Salt solution acidified with dilute HNO_3 on addition of silver nitrate solution gives a curdy white precipitate soluble in ammonium hydroxide solution. This indicates the presence of Cl^- ions in the salt.

$$NaCl + AgNO_3 \longrightarrow NaNO_3 + \underset{\substack{\text{Silver chloride}\\\text{(White precipitate)}}}{AgCl}$$

$$AgCl + 2NH_4OH \longrightarrow \underset{\substack{\text{Diammine silver (I)}\\\text{chloride}}}{[Ag(NH_3)_2]Cl} + 2H_2O$$

(d) Mix a little amount of salt and an equal amount of solid potassium dichromate ($K_2Cr_2O_7$) in a test tube and add conc. H_2SO_4 to it. Heat the test tube and pass the evolved gas through sodium hydroxide solution. If a yellow solution is obtained, divide the solution into two parts. Acidify the first part with acetic acid and then add lead acetate solution. Formation of a yellow precipitate of lead chromate confirms the presence of chloride ions in the salt. This test is called ***chromyl chloride test.***

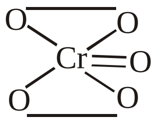
$$4NaCl + K_2Cr_2O_7 + 6H_2SO_4 \longrightarrow 2KHSO_4 + \underset{\substack{\text{(Chromyl}\\\text{chloride)}}}{2CrO_2Cl_2} + 4NaHSO_4 + 3H_2O$$

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

$$(CH_3COO)_2Pb + \underset{\substack{\text{Sodium}\\\text{chromate}}}{Na_2CrO_4} \longrightarrow \underset{\substack{\text{Lead chromate}\\\text{(Yellow precipitate)}}}{PbCrO_4} + 2CH_3COONa$$

Acidify the second part with dilute sulphuric acid and add small amounts of amyl alcohol and then 1 mL of 10% hydrogen peroxide solution. On gentle shaking organic layer turns blue. CrO_4^{2-} ion formed in the reaction of chromyl chloride with sodium hydroxide reacts with hydrogen peroxide to form chromium pentoxide (CrO_5) (See structure) which dissolves in amyl alcohol to give blue colour.

$$CrO_4^{2-} + 2H^+ + 2H_2O_2 \longrightarrow \underset{\substack{\text{Chromium}\\\text{pentoxide}}}{CrO_5} + 3H_2O$$



Structure of chromium pentoxide

2. Test for Bromide ion (Br^-)

If on heating the salt with conc. H_2SO_4 reddish brown fumes of bromine are evolved in excess, this indicates the presence of Br^- ions. The fumes get intensified on addition of MnO_2. Bromine vapours turn starch paper yellow.

$$2NaBr + 2H_2SO_4 \longrightarrow Br_2 + SO_2 + Na_2SO_4 + 2H_2O$$
$$2NaBr + MnO_2 + 2H_2SO_4 \longrightarrow Na_2SO_4 + MnSO_4 + 2H_2O + Br_2$$

(a) Add 1 mL of carbon tetrachloride (CCl_4)/chloroform ($CHCl_3$) and excess of freshly prepared chlorine water dropwise to the salt solution in water or sodium carbonate extract neutralised with dilute HCl. Shake the test tube vigorously. The appearance of an orange brown colouration in the organic layer due to the dissolution of bromine in it, confirms the presence of bromide ions.

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

(b) Acidify the sodium carbonate extract of the salt with dil. HNO_3. Add silver nitrate ($AgNO_3$) solution and shake the test tube. A pale yellow precipitate is obtained which dissolves in ammonium hydroxide with difficulty.

$$NaBr + AgNO_3 \longrightarrow NaNO_3 + \underset{\substack{\text{Silver bromide} \\ \text{Pale yellow precipitate}}}{AgBr}$$

3. Test for Iodide ion (I^-)

(a) If on heating the salt with conc. H_2SO_4 , deep violet vapours with a pungent smell are evolved. These turns starch paper blue and a violet sublimate is formed on the sides of the test tube, it indicates the presence of I^- ions. Some HI, sulphur dioxide, hydrogen sulphide, and sulphur are also formed due to the following reactions.

$$2NaI + 2H_2SO_4 \longrightarrow Na_2SO_4 + SO_2 + 2H_2O + I_2$$
$$I_2 + \underset{\text{solution}}{\text{Starch}} \longrightarrow \text{Blue colour}$$
$$NaI + H_2SO_4 \longrightarrow NaHSO_4 + HI$$
$$2HI + H_2SO_4 \longrightarrow 2H_2O + I_2 + SO_2$$
$$6NaI + 4H_2SO_4 \longrightarrow 3I_2 + 4H_2O + S + 3Na_2SO_4$$
$$8NaI + 5H_2SO_4 \longrightarrow 4I_2 + H_2S + 4Na_2SO_4 + 4H_2O$$

On adding MnO_2 to the reaction mixture, the violet vapours become dense.

$$2NaI + MnO_2 + 2H_2SO_4 \longrightarrow I_2 + MnSO_4 + Na_2SO_4 + 2H_2O$$

(b) Add 1 mL of $CHCl_3$ or CCl_4 and chlorine water in excess to the salt solution in water or sodium carbonate extract neutralised with dil.HCl and shake the test tube vigorously. Presence of violet colouration in the organic layer confirms the presence of iodide ions.

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

Iodine dissolves in the organic solvent and the solution becomes violet.

(c) Acidify sodium carbonate extract of the salt with dil.HNO_3 and add $AgNO_3$ solution. Appearance of a yellow precipitate insoluble in excess of NH_4OH confirms the presence of iodide ions.

$$NaI + AgNO_3 \longrightarrow \underset{\substack{\text{silver iodide} \\ \text{(Yellow precipitate)}}}{AgI} + NaNO_3$$

(a) If on heating the salt with conc. H_2SO_4 light brown fumes are evolved then heat a small quantity of the given salt with few copper turnings or chips and conc. H_2SO_4. Evolution of excess of brown fumes indicates the presence of nitrate ions. The solution turns blue due to the formation of copper sulphate.

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

$$4HNO_3 \longrightarrow 4NO_2 + O_2 + 2H_2O$$

$$2NaNO_3 + 4H_2SO_4 + 3Cu \longrightarrow \underset{\substack{\text{Copper sulphate}\\ \text{(Blue)}}}{3CuSO_4} + Na_2SO_4 + 4H_2O + 2NO$$

$$2NO + O_2 \longrightarrow \underset{\text{(Brown fumes)}}{2NO_2}$$

(b) Take 1 mL of an aqueous solution of the salt and add 2 mL conc. H_2SO_4 slowly. Mix the solutions thoroughly and cool the test tube under the tap. Now, add freshly prepared ferrous sulphate solution along the sides of the test tube dropwise so that it forms a layer on the top of the liquid already present in the test tube. A dark brown ring is formed at the junction of the two solutions due to the formation of nitroso ferrous sulphate (Fig. 1.2). Alternatively first ferrous sulphate is added and then concentrated sulphuric acid is added.

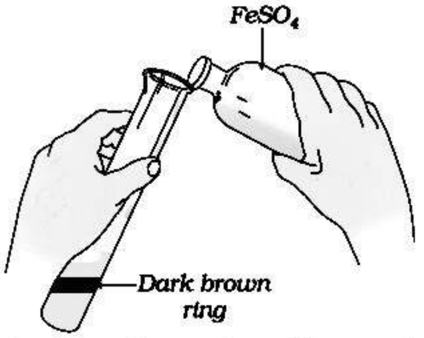


Fig. 1.2 : *Formation of brown ring*

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

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

$$FeSO_4 + NO \longrightarrow \underset{\substack{\text{Nitroso ferrous sulphate}\\ \text{(Brown)}}}{[Fe(NO)]SO_4}$$

5. Test for Oxalate ion $[C_2O_4^{2-}]$

If carbon dioxide gas along with carbon monoxide gas is evolved in the preliminary examination with concentrated sulphuric acid, this gives indication about the presence of oxalate ion.

$$Na_2C_2O_4 + \text{Conc.}H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2\uparrow + CO\uparrow$$

Oxalate is confirmed by the following tests:

(a) Acidify sodium carbonate extract with acetic acid and add calcium chloride solution. A white precipitate of calcium oxalate, insoluble in ammonium oxalate and oxalic acid solution indicates the presence of oxalate ion.

$$CaCl_2 + Na_2C_2O_4 \longrightarrow \underset{\substack{\text{Calcium oxalate}\\ \text{(White precipitate)}}}{CaC_2O_4} + 2NaCl$$

(b) $KMnO_4$ test

Filter the precipitate from test (a). Add dil. H_2SO_4 to it followed by dilute $KMnO_4$ solution and warm. Pink colour of $KMnO_4$ is discharged:

$$CaC_2O_4 + H_2SO_4 \longrightarrow \underset{\text{Calcium sulphate}}{CaSO_4} + \underset{\text{Oxalic acid}}{H_2C_2O_4}$$

$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 10CO_2$$

Pass the gas evolved through lime water. A white precipitate is formed which dissolves on passing the gas for some more time.

Step-III : Test for Sulphate and Phosphate

If no positive test is obtained in Steps-I and II, then tests for the presence of sulphate and phosphate ions are performed. These tests are summarised in Table 5.

Table 5 : Confirmatory tests for Sulphate and Phosphate

Ion	Confirmatory Test
Sulphate (SO_4^{2-})	(a) Take 1 mL water extract of the salt in water or sodium carbonate and after acidifying with dilute hydrochloric acid add $BaCl_2$ solution. White precipitate insoluble in conc. HCl or conc. HNO_3 is obtained. (b) Acidify the aqueous solution or sodium carbonate extract with acetic acid and add lead acetate solution. Appearance of white precipitate confirms the presence of SO_4^{2-} ion.
Phosphate (PO_4^{3-})	(a) Acidify sodium carbonate extract or the solution of the salt in water with conc. HNO_3 and add ammonium molybdate solution and heat to boiling. A canary yellow precipitate is formed.

1. **Test of Sulphate ions [SO_4^{2-}]**

(a) Aqueous solution or sodium carbonate extract of the salt acidified with acetic acid on addition of barium chloride gives a white precipitate of barium sulphate insoluble in conc. HCl or conc. HNO_3.

$$Na_2SO_4 + BaCl_2 \longrightarrow \underset{\substack{\text{Barium sulphate}\\ \text{(White precipitate)}}}{BaSO_4} + 2NaCl$$

(b) Sulphate ions give white precipitate of lead sulphate when aqueous solution or sodium carbonate extract neutralised with acetic acid is treated with lead acetate solution.

$$Na_2SO_4 + (CH_3COO)_2Pb \longrightarrow \underset{\substack{\text{Lead sulphate}\\ \text{(White precipitate)}}}{PbSO_4} + 2CH_3COONa$$

2. **Test for Phosphate ion [PO_4^{3-}]**

(a) Add conc. HNO_3 and ammonium molybdate solution to the test solution containing phosphate ions and boil. A yellow colouration in solution or a canary yellow precipitate of ammonium-phosphomolybdate, $(NH_4)_3[P(Mo_3O_{10})_4]$ is formed. Each oxygen of phosphate has been replaced by Mo_3O_{10} group.

$$Na_2HPO_4 + 12(NH_4)_2MoO_4 + 23HNO_3 \longrightarrow \underset{\substack{\text{Canary yellow}\\ \text{precipitate}}}{(NH_4)_3[P(Mo_3O_{10})_4]} + 2NaNO_3 + 21NH_4NO_3 + 12H_2O$$

HEATING DEVICES

Heating during the laboratory work can be done with the help of a gas burner, spirit lamp or a kerosene lamp. The gas burner used in the laboratory is usually Bunsen burner . Various parts of Bunsen burner are shown in Fig. The description of these parts is as follows :

(A) Parts of Bunsen Burner

1. The Base

Heavy metallic base is connected to a side tube called gas tube. Gas from the source enters the burner through the gas tube and passes through a small hole called Nipple or Nozzle and enters into the burner tube under increased pressure and can be burnt at the upper end of the burner tube.

2. The Burner Tube

It is a long metallic tube having two holes diametrically opposite to each other near the lower end which form the air vent. The tube can be screwed at the base. The gas coming from the nozzle mixes with the air coming through the air vent and burns at its upper end.

3. The Air Regulator

It is a short metallic cylindrical sleeve with two holes diametrically opposite to each other. When it is fitted to the burner tube, it surrounds the air vent of the burner tube. To control the flow of air through the air vent, size of its hole is adjusted by rotating the sleeve.

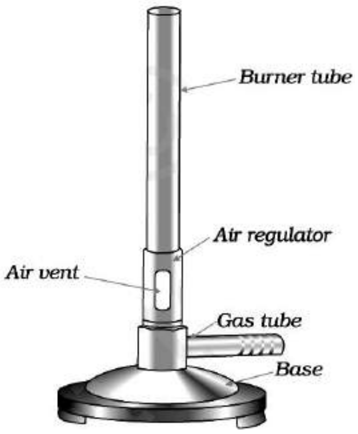


Fig. Bunsen burner

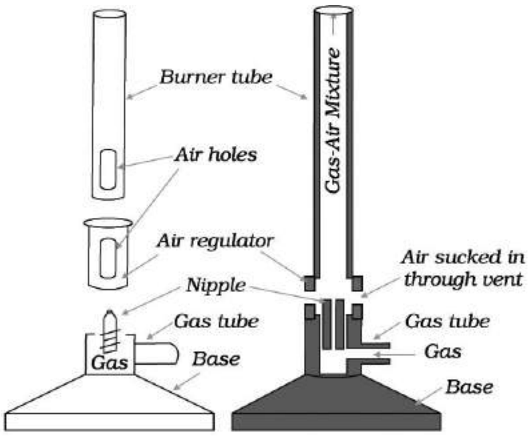


Fig. Parts of Bunsen barner

If the air vent is closed and the gas is ignited, the flame will be large and luminous (smoky and yellow in colour). The light emitted by the flame is due to the radiations given off by the hot carbon particles of partially burnt fuel. The temperature of the flame in this situation is low. If adjustment of sleeve on vent is such that gas mixed with air is fed into the flame, the flame becomes less luminous and finally turns blue. When the flow of air is correctly adjusted, the temperature of the flame becomes quite high. This is called non-luminous flame. Various zones of flame are shown below in Fig.

Three distinctly visible parts of the Bunsen flame are described below :

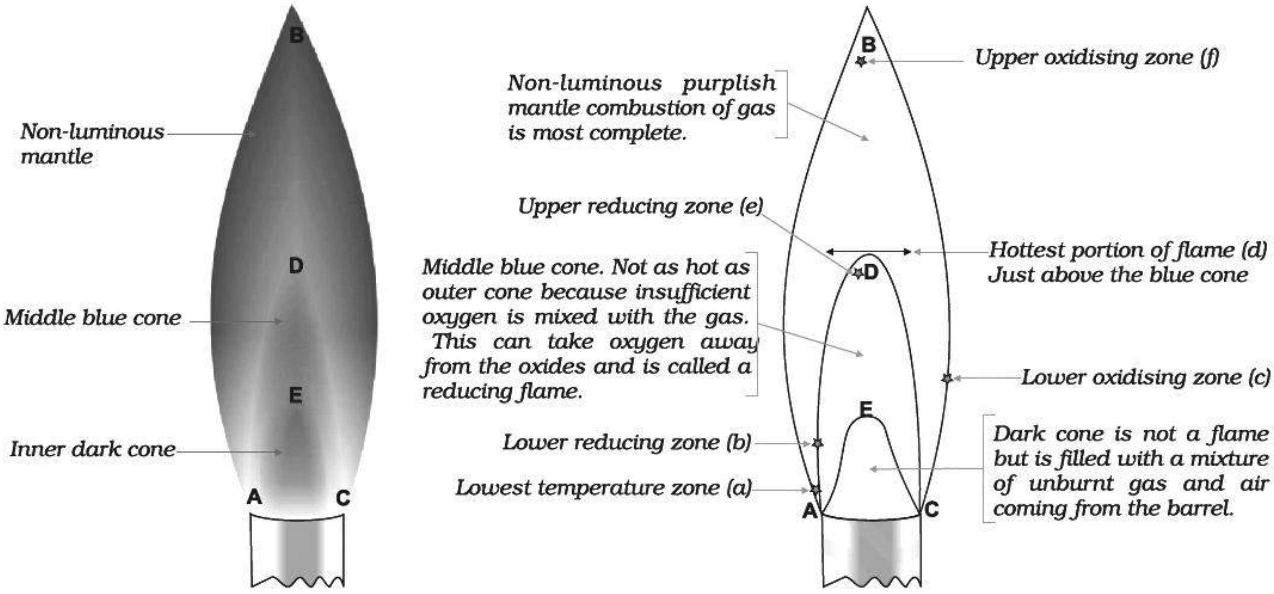


Fig. 1.13 : *Zones of flame of Bunsen burner*

(B) PRINCIPAL PARTS OF BUNSEN FLAME

1. The Inner Dark Cone, A E C

This is innermost dark cone, which is just above the burner tube. It consists of unburnt gases. This zone is the coldest zone of the flame and no combustion takes place here.

2. The Middle Blue Cone, A D C E A

This is middle part of the flame. This becomes luminous when the air vent is slightly closed. Luminosity of this part is due to the presence of unburnt carbon particles produced by decomposition of some gas. These particles get heated up to incandescence and glow but do not burn. Since the combustion is not complete in this part, the temperature is not very high.

3. The Outer Non-luminous Mantle, A B C D A

This is purplish outer cone. It is the hottest part of the flame. It is in direct contact with the atmosphere and combustion is quite complete in this zone.

Bunsen identified six different regions in these three principal parts of the flame:

(i) The upper oxidising zone (f)

Its location is in the non-luminous tip of the flame which is in the air. In comparison to inner portions of the flame large excess of oxygen is present here. The temperature is not as high as in region (c) described below. It may be used for all oxidation processes in which highest temperature of the flame is not required.

(ii) Upper reducing zone (e)

This zone is at the tip of the inner blue cone and is rich in incandescent carbon. It is especially useful for reducing oxide incrustations to the metals.

(iii) Hottest portion of flame (d)

It is the fusion zone. It lies at about one-third of the height of the flame and is approximately equidistant from inside and outside of the mantle i.e. the outermost cone of the flame. Fusibility of the substance can be tested in this region. It can also be employed for testing relative volatility of substances or a mixture of substances.

(iv) Lower oxidising zone (c)

It is located on the outer border of the mantle near the lower part of the flame and may be used for the oxidation of substances dissolved in beads of borax or sodium carbonate etc.

(v) Lower reducing zone (b)

It is situated in the inner edge of the outer mantle near to the blue cone and here reducing gases mix with the oxygen of the air. It is a less powerful reducing zone than (e) and may be employed for the reduction of fused borax and similar beads.

(vi) Lowest temperature zone (a)

Zone (a) of the flame has lowest temperature. It is used for testing volatile substances to determine whether they impart colour to the flame.

(C) STRIKING BACK OF THE BUNSEN BURNER

Striking back is the phenomenon in which flame travels down the burner tube and begins to burn at the nozzle near the base. This happens when vents are fully open.The flow of much air and less gas makes the flame become irregular and it strikes back.

The tube becomes very hot and it may produce burns on touching. This may melt attached rubber tube also. If it happens, put off the burner and cool it under the tap and light it again by keeping the air vent partially opened.

SPIRIT LAMP

If Bunsen burner is not available in the laboratory then spirit lamp can be used for heating. It is a devise in which one end of a wick of cotton thread is dipped in a spirit container and the other end of the wick protrudes out of the nozzle at upper end of the container. Spirit rises upto the upper end of the wick due to the capillary action and can be burnt. The flame is non luminous hence can be used for all heating purposes in the laboratory. To put off the lamp, burning wick is covered with the cover. **Never try to put off the lighted burner by blowing at the flame.**

Fig. 1.14 : *The spirit lamp*

KEROSENE HEATING LAMP

A kerosene lamp has been developed by National Council of Educational Research and Training (NCERT), which is a versatile and cheaper substitute of spirit lamp. It may be used in laboratories as a source of heat whereever spirit and gas burner are not available. Parts of kerosene lamp are shown in Fig.

Working of the Kerosene Lamp

More than half of the container is filled with kerosene. Outer sleeve is removed for lighting the wicks. As the outer sleeve is placed back in position, the flames of four wicks combine to form a big soot-free blue flame.

The lighted heating lamp can be put off only by covering the top of the outer sleeve with a metal or asbestos sheet.

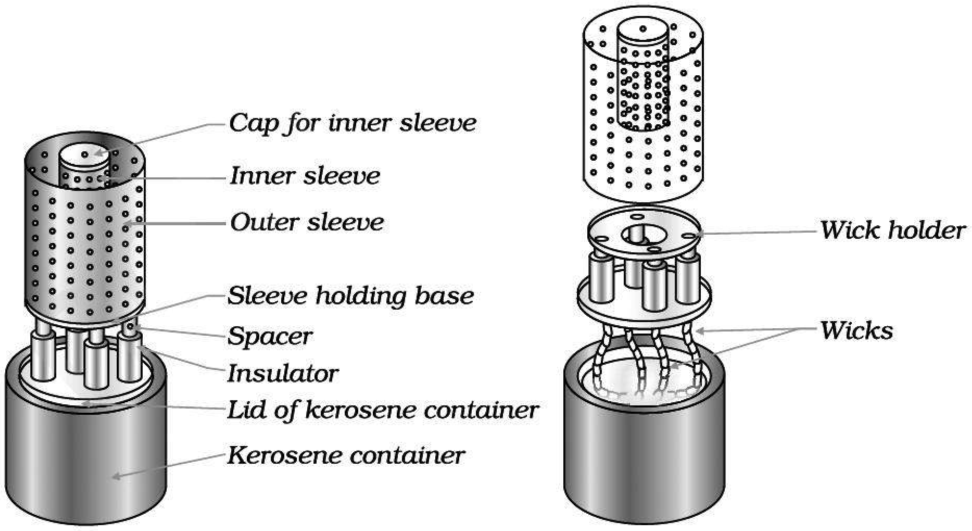


Fig. 1.15 : *Parts of Kerosene Heating Lamp*

SYSTEMATIC ANALYSIS OF CATIONS

The tests for cations may be carried out according to the following scheme.

Step - I : Preliminary Examination of the Salt for Identification of Cation

1. Colour Test

Observe the colour of the salt carefully, which may provide useful information about the cations. Table 6 gives the characteristic colours of the salts of some cations.

Table 6 Characteristic colours of the some metal ions

Ion	Confirmatory Test
Light green	Fe^{2+}
Yellowis Brown	Fe^{3+}
Blue	Cu^{2+}
Bright green	Ni^{2+}
Blue, Red Violet, Pink	Co^{2+}
Light pink	Mn^{2+}

2. Dry Heating Test

(i) Take about 0.1 g of the dry salt in a clean and dry test tube.

(ii) Heat the above test tube for about one minute and observe the colour of the residue when it is hot and also when it becomes cold. Observation of changes gives indications about the presence of cations, which may not be taken as conclusive evidence (see Table 7).

Table 7 : Inferences from the colour of the salt in cold and on heating

Colour when cold	Colour when hot	Inference
Blue	White	Cu^{2+}
Green	Dirty white or yellow	Fe^{2+}
White	Yellow	Zn^{2+}
Pink	Blue	Co^{2+}

3. Flame Test

The chlorides of several metals impart characteristic colour to the flame because they are volatile in non-luminous flame. This test is performed with the help of a platinum wire as follows :

(i) Make a tiny loop at one end of a platinum wire.

(ii) To clean the loop dip it into concentrated hydrochloric acid and hold it in a non-luminous flame (Fig. 1.3).

(iii) Repeat step (ii) until the wire imparts no colour to the flame.

(iv) Put 2-3 drops of concentrated hydrochloric acid on a clean watch glass and make a paste of a small quantity of the salt in it.

(v) Dip the clean loop of the platinum wire in this paste and introduce the loop in the non-luminous (oxidising) flame (Fig. 1.3).

(vi) Observe the colour of the flame first with the naked eye and then through a blue glass and identify the metal ion with the help of Table 8.

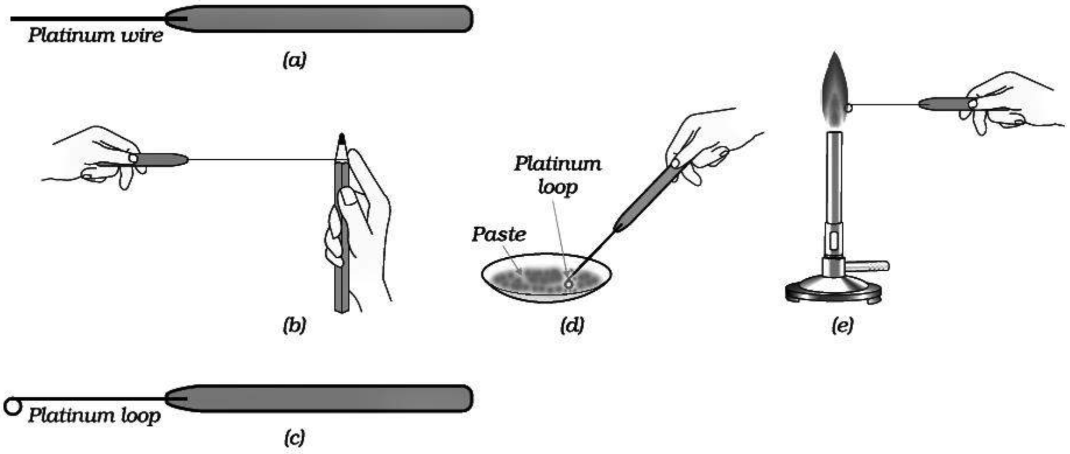


Fig. 1.3 : Performing flame test

Table 8 : Inference from the flame test

Colour fo the flame observed by naked eye	Colour of the flame observed through blue glass	Inference
Green flame with blue centre	Same colour as observed without glass	Cu^{2+}
Crimson red	Purple	Sr^{2+}
Apple green	Bluish green	Ba^{2+}
Brick red	Green	Ca^{2+}

4. Borax Bead Test

This test is employed only for coloured salts because borax reacts with metal salts to form metal borates or metals, which have characteristic colours.

(i) To perform this test make a loop at the end of the platinum wire and heat it in a flame till it is red hot.

(ii) Dip the hot loop into borax powder and heat it again until borax forms a colourless transparent bead on the loop. Before dipping the borax bead in the test salt or mixture, confirm that the bead is transparent and colourless. If it is coloured this means that, the platinum wire is not clean. Then make a fresh bead after cleaning the wire.

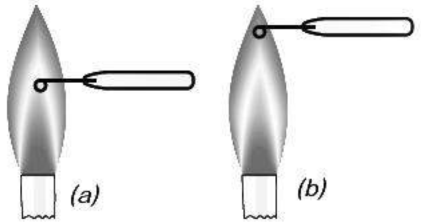


Fig. 1.4 : Borax bead test (a) Heating in reducing flame (b) Heating in oxidising flame

(iii) Dip the bead in a small quantity of the dry salt and again hold it in the flame.

(iv) Observe the colour imparted to the bead in the non - luminous flame as well as in the luminous flame while it is hot and when it is cold (Fig. 1.4).

(v) To remove the bead from the platinum wire, heat it to redness and tap the platinum wire with your finger. (Fig.1.5).

On heating, borax loses its water of crystallisation and decomposes to give sodium metaborate and boric anhydride.

$$\underset{\text{Borax}}{Na_2B_4O_7 \cdot 10H_2O} \longrightarrow Na_2B_4O_7 + 10H_2O$$

$$Na_2B_4O_7 \longrightarrow \underset{\text{Sodium metaborate}}{2NaBO_2} + \underset{\text{Boric anhydride}}{B_2O_3}$$

On treatment with metal salt, boric anhydride forms metaborate of the metal which gives different colours in oxidising and reducing flame. For example, in the case of copper sulphate, following reactions occur.

$$CuSO_4 + B_2O_3 \xrightarrow{\text{Non-luminous flame}} \underset{\substack{\text{Cupric metaborate}\\ \text{Blue-green}}}{Cu(BO_2)_2} + SO_3$$

Two reactions may take place in the reducing flame:

(i) The blue $Cu(BO_2)_2$ is reduced to colourless cuprous metaborate as follows:

$$2Cu(BO_2)_2 + 2NaBO_2 + C \xrightarrow{\text{Luminous flame}} 2CuBO_2 + Na_2B_4O_7 + CO$$

or (ii) Cupric metaborate may be reduced to metallic copper and the bead appears red and opaque.

$$2Cu(BO_2)_2 + 4NaBO_2 + 2C \xrightarrow{\text{Luminous flame}} 2Cu + 2Na_2B_4O_7 + 2CO$$

The preliminary identification of metal ion can be made from Table 9.

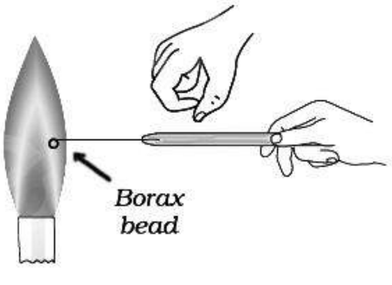


Fig. 1.5 : Removing borax bead

Table 9 : Inference from the borax bead test

Heating in oxidising (non-luminous) flame		Heating in reducing (luminous) flame		Inference
Colour of the salt bead		Colour of the salt bead		
In cold	In hot	In cold	In hot	
Blue	Gren	Red opaque	Colourless	Cu^{2+}
Reddish brown	Violet	Grey	Grey	Ni^{2+}
Light violet	Light violet	Colourless	Colourless	Mn^{2+}
Yellow	Yellowish brown	Green	Green	Fe^{3+}

5. Charcoal Cavity Test

Metallic carbonate when heated in a charcoal cavity decomposes to give corresponding oxide. The oxide appears as a coloured residue in the cavity. Sometimes oxide may be reduced to metal by the carbon of the charcoal cavity.

The test may be performed as follows:

(i) Make a small cavity in a charcoal block with the help of a charcoal borer [Fig.1.6 (a)].

(ii) Fill the cavity with about 0.2 g of the salt and about 0.5 g of anhydrous sodium carbonate.

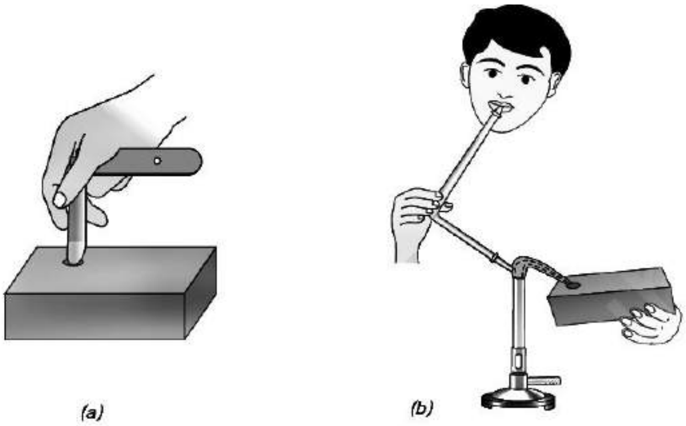


Fig. 1.6 : (a) Making charcoal cavity (b) Heating salt in the cavity

(iii) Moisten the salt in the cavity with one or two drops of water, otherwise salt/mixture will blow away.

(iv) Use a blowpipe to heat the salt in a luminous (reducing) flame and observe the colour of oxide/ metallic bead formed in the cavity both when hot and cold [Fig. (1.6 b)]. Obtain oxidising and reducing flame as shown in Fig. 1.7 a and b.

(v) Always bore a fresh cavity for testing the new salt.

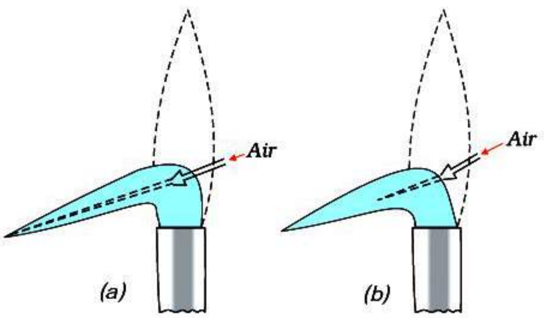


Fig. 1.7 : Obtaining oxidising and reducing flame (a) Oxidising flame; and (b) Reducing flame

When test is performed with $CuSO_4$, the following change occurs.

$$CuSO_4 + Na_2CO_3 \xrightarrow{\text{Heat}} CuCO_3 + Na_2SO_4$$

$$CuCO_3 \xrightarrow{\text{Heat}} CuO + CO_2$$

$$CuO + C \xrightarrow{\text{Heat}} Cu + CO$$

Red colour

In case of $ZnSO_4$:

$$ZnSO_4 + Na_2CO_3 \xrightarrow{\text{Heat}} ZnCO_3 + Na_2SO_4$$

$$ZnCO_3 \xrightarrow{\text{Heat}} ZnO + CO_2$$

Yellow when hot,
White when cold

The metal ion can be inferred from Table 10.

Table 10 : Inference from the charcoal cavity test

Observations	Inference
Yellow residue when hot and grey metal when cold	Pb^{2+}
White residue with the odour of garlic	As^{3+}
Brown residue	Cd^{2+}
Yellow residue when hot and white when cold	Zn^{2+}

6. Cobalt Nitrate Test

If the residue in the charcoal cavity is white, cobalt nitrate test is performed.

(i) Treat the residue with two or three drops of cobalt nitrate solution.

(ii) Heat it strongly in non-luminous flame with the help of a blow pipe and observe the colour of the residue.

On heating, cobalt nitrate decomposes into cobalt (II) oxide, which gives a characteristic colour with metal oxide present in the cavity.

Thus, with ZnO, Al_2O_3 and MgO, the following reactions occur.

$$2Co(NO_3)_2 \xrightarrow{\text{Heat}} 2CoO + 4NO_2 + O_2$$

$$CoO + ZnO \longrightarrow CoO.ZnO$$

Green

$$CoO + MgO \longrightarrow CoO.\ MgO$$

Pink

$$CoO + Al_2O_3 \longrightarrow CoO.\ Al_2O_3$$

Blue

Step-II : Wet Tests for Identification of Cations

The cations indicated by the preliminary tests given above are confirmed by systematic analysis given below. The first essential step is to prepare a clear and transparent solution of the salt. This is called original solution. It is prepared as follows:

Preparation of Original Solution (O.S.)

To prepare the original solution, following steps are followed one after the other in a systematic order. In case the salt does not dissolve in a particular solvent even on heating, try the next solvent.

The following solvents are tried:

1. Take a little amount of the salt in a clean boiling tube and add a few mL of distilled water and shake it. If the salt does not dissolved, heat the content of the boiling tube till the salt completely dissolves.
2. If the salt is insoluble in water as detailed above, take fresh salt in a clean boiling tube and add a few mL of dil.HCl to it. If the salt is insoluble in cold, heat the boiling tube till the salt is completely dissolved.
3. If the salt does not dissolve either in water or in dilute HCl even on heating, try to dissolve it in a few mL of conc. HCl by heating.
4. If salt does not dissolve in conc. HCl, then dissolve it in dilute nitric acid.
5. If salt does not dissolve even in nitric acid then a mixture of conc. HCl and conc. HNO_3 in the ratio 3 : 1 is tried. This mixture is called aqua regia. A salt not soluble in aqua regia is considered to be an insoluble salt.

Group Analysis

(I) Analysis of Zero group cation (NH_4^+ ion)

(a) Take 0.1 g of salt in a test tube and add 1-2 mL of NaOH solution to it and heat. If there is a smell of ammonia, this indicates the presence of ammonium ions. Bring a glass rod dipped in hydrochloric acid near the mouth of the test tube. White fumes are observed.

(b) Pass the gas through Nessler's reagent. Brown precipitate is obtained.

Chemistry of Confirmatory Tests for NH_4^+ ion

(a) Ammonia gas evolved by the action of sodium hydroxide on ammonium salts reacts with hydrochloric acid to give ammonium chloride, which is visible as dense white fume.

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2NH_3 + 2H_2O$$

$$NH_3 + HCl \longrightarrow NH_4Cl$$

On passing the gas through Nessler's reagent, a brown colouration or a precipitate of basic mercury(II) amido-iodine is formed.

$$2K_2[HgI_4] + NH_3 + 3KOH \longrightarrow \underset{\substack{\text{Basic mercury (II)}\\ \text{amido-iodine}\\ \text{(Brown precipitate)}}}{HgO.Hg(NH_2)I} + 7\,KI + 2H_2O$$

For the analysis of cations belonging to groups I-VI, the cations are precipitated from the original solution by using the group reagents (see Table 1.11) according to the scheme shown in the flow chart given below: The separation of all the six groups is represented as below :

Flow Chart*

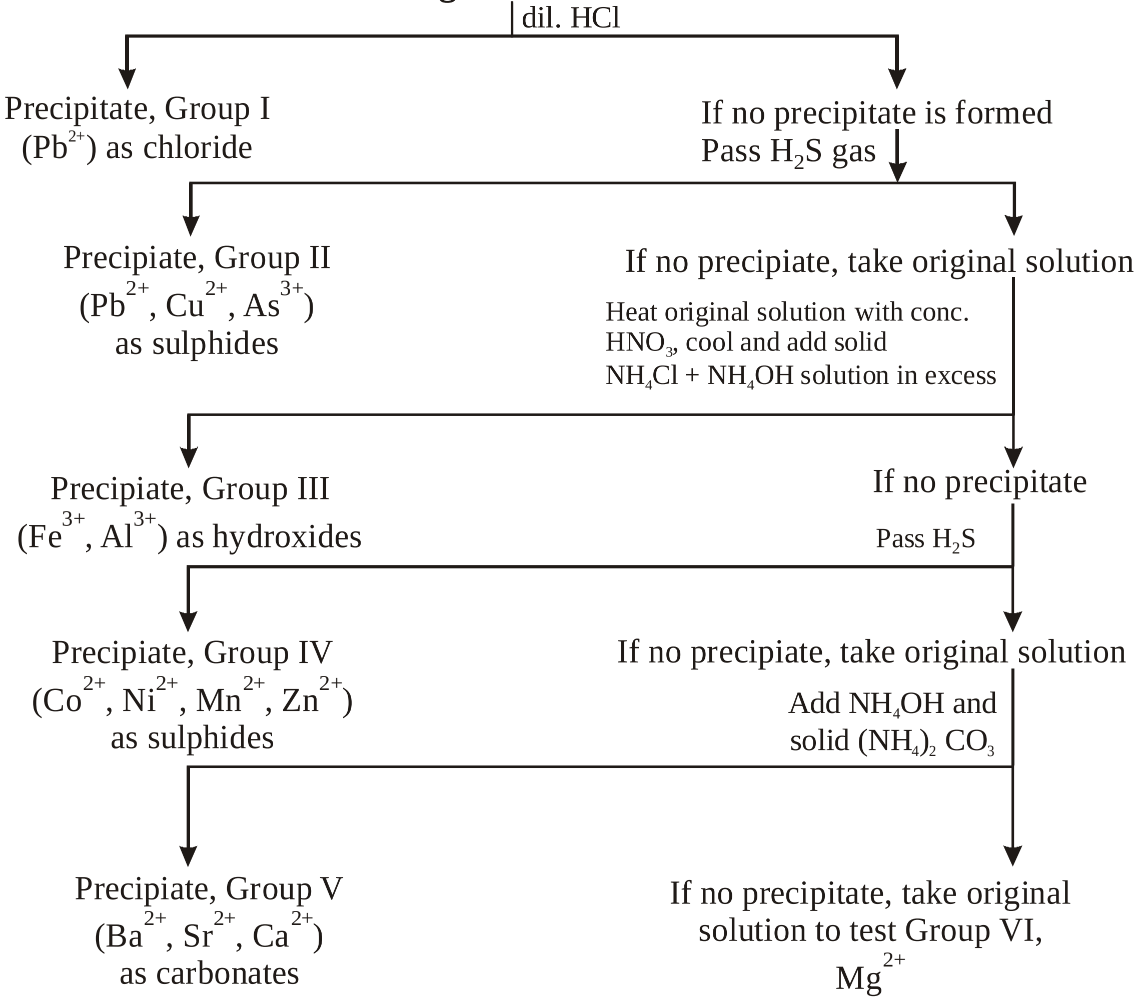


Table 11 : Group reagents for precipitating ions

Group	Cations*	Group Reagent
Group zero	NH_4^+	**None**
Group - I	Pb^{2+}	**Dilute HCl**
Group - II	Pb^{2+}, Cu^{2+}, As^{3+}	**H_2S gas in presence of dil. HCl**
Group - III	Al^{3+}, Fe^{3+}	**NH_4OH in presence of NH_4Cl**
Group - IV	Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}	**H_2S in presence of NH_4OH**
Group - V	Ba^{2+}, Sr^{2+}, Ca^{2+}	**$(NH_4)_2CO_3$ in presence of NH_4OH**
Group - VI	Mg^{2+}	**None**

(II) Analysis of Group-I cations

Take a small amount of original solution (if prepared in hot conc. HCl) in a test tube and add cold water to it and cool the test tube under tap water. If a white precipitate appears, this indicates the presence of Pb^{2+} ions in group –I. On the other hand, if the original solution is prepared in water and on addition of dil. HCl, a white precipitate appears, this may also be Pb^{2+}. Confirmatory tests are described below in Table 12.

Table 12 : Confirmatory tests for Group-I cation (Pb^{2+})

Experiment	Observation
Dissolve the precipiate in hot water and divide the hot solution into three parts,	
1. Add potassium idoide solution to the first part.	A yellow precipitate is obtained.
2. To the second part add potassium chromate solution.	A yellow precipitate is obtained which is soluble, in NaOH and insoluble in ammonium acetate solution.
3. To the thrid part of the hot solution add few drops of alcohol and dilute sulphuric acid.	A white precipitate is obtained which is soluble in ammonium acetate solution.

Chemistry of the Confirmatory Tests of Pb^{2+} ions

Lead is precipitated as lead chloride in the first group. The precipitate is soluble in hot water.

1. On adding potassium iodide (KI) solution, a yellow precipitate of lead iodide is obtained which confirms the presence of Pb^{2+} ions.

$$PbCl_2 + 2KI \longrightarrow PbI_2 + 2KCl$$

(Hot solution) Yellow precipitate

This yellow precipitate (PbI_2) is soluble in boiling water and reappears on cooling as shining crystals.

2. On addition of potassium chromate (K_2CrO_4) solution a yellow precipitate of lead chromate is obtained. This confirms the presence of Pb^{2+} ions.

$$PbCl_2 + K_2CrO_4 \longrightarrow PbCrO_4 + 2KCl$$

(Hot solution) Lead chromate

(Yellow precipitate)

The yellow precipitate ($PbCrO_4$) is soluble in hot NaOH solution.

$$PbCrO_4 + 4NaOH \longrightarrow Na_2[Pb(OH)_4] + Na_2CrO_4$$

Sodium tetra

hydroxoplumbate (II)

3. A white precipitate of lead sulphate ($PbSO_4$) is formed on addition of alcohol followed by dil. H_2SO_4.

$$PbCl_2 + H_2SO_4 \longrightarrow PbSO_4 + 2HCl$$

Lead sulphate

(White precipitate)

Lead sulphate is soluble in ammonium acetate solution due to the formation of tetraacetatoplumbate(II) ions. This reaction may be promoted by addition of few drops of acetic acid.

$$PbSO_4 + 4CH_3COONH_4 \longrightarrow (NH_4)_2[Pb(CH_3COO)_4] + (NH_4)_2SO_4$$

Ammonium

tetraacetatoplumbate(II)

(III) Analysis of Group–II cations

If group-I is absent, add excess of water to the same test tube. Warm the solution and pass H_2S gas for 1-2 minutes (Fig. 1.6). Shake the test tube. If a precipitate appears, this indicates the presence of group-II cations. Pass more H_2S gas through the solution to ensure complete precipitation and separate the precipitate. If the colour of the precipitate is black, itindicates the presence of Cu^{2+} or Pb^{2+} ions.

If it is yellow in colour, then presence of As^{3+} ions is indicated.

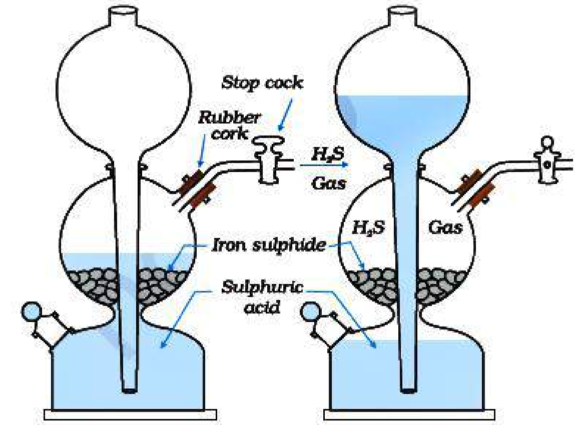


Fig. 1.8 : Kipp's apparatus for preparation of H_2S gas

Take the precipitate of group-II in a test tube and add excess of yellow ammonium sulphide solution to it. Shake the test tube. If the precipitate is insoluble, group II-A (copper group) is present. If the precipitate is soluble, this indicates the presence of group-II B (arsenic group).

Confirmatory tests for the groups II A and II B are given in Table 13.

Table 13 : Confirmatory tests for the groups II A and II B cations

Black precipitate of Group II A ions Pb^{2+}, Cu^{2+} (insoluble in yellow ammonium sulphide) is formed.		If a yellow precipitate soluble in yellow ammonium sulphide is formed then As^{3+} ion is present.
Boil the precipitate of Group II A with dilute nitric acid and add a few drops of alcohol and dil. H_2SO_4.		Acidify this solution with dilute HCl. A yellow precipitate is formed. Heat the precipitate with concentrated nitric acid and add ammonium molybdate solution. A canary yellow precipitate is formed.
White precipitate confirms the presence of Pb^{2+} ions. Dissolve the precipitate in ammonium acetate solution. Acidify with acetic acid and divide the solution into two parts. (i) To the first part add potassium chromate solution, a yellow precipitate is formed. (ii) To the second part, add potassium iodide solution, a yellow precipitate is formed.	If no precipitate is formed, add excess of ammonium hydroxide solution. A blue solution is obtained, acidify it with acetic acid and add potassium ferrocyanide solution. A chocolate brown precipitate is formed.	

Group-II A (Copper Group)

Chemistry of confirmatory tests of Group-II A cations

1. Test for Lead ion (Pb^{2+})

Lead sulphide precipitate dissolves in dilute HNO_3. On adding dil. H_2SO_4 and a few drops of alcohol to this solution a white precipitate of lead sulphate appears. This indicates the presence of lead ions.

$$3PbS + 8HNO_3 \longrightarrow 3Pb(NO_3)_2 + 2NO + 4H_2O + 3S$$

$$Pb(NO_3)_2 + H_2SO_4 \longrightarrow PbSO_4 + 2HNO_3$$

The white precipitate dissolves in ammonium acetate solution on boiling. When this solution is acidified with acetic acid and potassium chromate solution is added, a yellow precipitate of $PbCrO_4$ is formed. On adding potassium iodide solution, a yellow precipitate of lead iodide is formed.

$$PbSO_4 + 4CH_3COONH_4 \longrightarrow \underset{\text{Ammonium tetraacetatoplumbate(II)}}{(NH_4)_2[Pb(CH_3COO)_4]} + (NH_4)_2SO_4$$

$$Pb^{2+} + CrO_4^{2-} \longrightarrow \underset{\substack{\text{Lead chromate}\\\text{(Yellow precipitate)}}}{PbCrO_4} \;; \qquad Pb^{2+} + 2I^- \rightarrow \underset{\substack{\text{Lead iodide}\\\text{(Yellow precipitate)}}}{PbI_2}$$

2. Test for Copper ion (Cu^{2+})

(a) Copper sulphide dissolves in nitric acid due to the formation of copper nitrate.

$$3CuS + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 3S + 4H_2O$$

On heating the reaction mixture for long time, sulphur is oxidised to sulphate and copper sulphate is formed and the solution turns blue. A small amount of NH_4OH precipitates basic copper sulphate which is soluble in excess of ammonium hydroxide due to the formation of tetraamminecopper (II) complex.

$$S + 2HNO_3 \longrightarrow H_2SO_4 + 2NO$$

$$2Cu^{2+} + SO_4^{2-} + 2NH_3 + 2H_2O \longrightarrow Cu(OH)_2.CuSO_4 + 2NH_4^+$$

$$Cu(OH)_2.CuSO_4 + 8NH_3 \longrightarrow \underset{\substack{\text{Tetraamminecopper (II)}\\\text{sulphate (Deep blue)}}}{2[Cu(NH_3)_4]SO_4} + 2OH^- + SO_4^{2-}$$

(b) The blue solution on acidification with acetic acid and then adding potassium ferrocyanide $K_4[Fe(CN)_6]$ solution gives a chocolate colouration due to the formation of copper ferrocyanide

i.e. $Cu_2[Fe(CN)_6]$.

$$[Cu(NH_3)_4]SO_4 + 4CH_3COOH \longrightarrow CuSO_4 + 4CH_3COONH_4$$

$$2CuSO_4 + \underset{\substack{\text{Potassium}\\\text{hexacyanoferrate (II)}}}{K_4[Fe(CN)_6]} \longrightarrow \underset{\substack{\text{Copper}\\\text{hexacyanoferrate (II)}\\\text{(Chocolate brown precipitate)}}}{Cu_2[Fe(CN)_6]} + 2K_2SO_4$$

Group-II B (Arsenic Group)

If group- II precipitate dissolves in yellow ammonium sulphide and the colour of the solution is yellow, this indicates the presence of As^{3+} ions. Ammonium thioarsenide formed on dissolution of As_2S_3, decomposes with dil. HCl, and a yellow precipitate of arsenic (V) sulphide is formed which dissolves in concentrated nitric acid on heating due to the formation of arsenic acid. On adding ammonium molybdate solution to the reaction mixture and heating, a canary yellow precipitate is formed. This confirms the presence of As^{3+} ions.

$$As_2S_3 + \underset{\text{Yellow ammonium sulphide}}{3(NH_4)_2S} \longrightarrow 2(NH_4)_3AsS_4 + S$$

$$2(NH_4)_3AsS_4 + 6HCl \rightarrow As_2S_5 + 3H_2S + 6NH_4Cl$$

$$3As_2S_5 + 10HNO_3 + 4H_2O \rightarrow \underset{\text{Arsenic acid}}{6H_3AsO_4} + 10NO + 15S$$

$$\underset{\text{Arsenic acid}}{H_3AsO_4} + \underset{\text{Ammonium molybdate}}{12(NH_4)_2MoO_4} + 21HNO_3 \rightarrow \underset{\substack{\text{Ammonium arsenomolybdate}\\ \text{(yellow precipitate)}}}{(NH_4)_3[As\ (Mo_3O_{10})_4]} + 21NH_4NO_3 + 12H_2O$$

(IV) Analysis of Group–III cations

If group-II is absent, take original solution and add 2-3 drops of conc. HNO_3 to oxidise Fe^{2+} ions to Fe^{3+} ions. Heat the solution for a few minutes. After cooling add a small amount of solid ammonium chloride (NH_4Cl) and an excess of ammonium hydroxide (NH_4OH) solution till it smells of ammonia. Shake the test tube. If a brown or white precipitate is formed, this indicates the presence of group-III cations. Confirmatory tests of group-III cations are summarised in Table 14.

Observe the colour and the nature of the precipitate. A gelatinous white precipitate indicates the presence of aluminium ion ($A1^{3+}$). If the precipitate is brown in colour, this indicates the presence of ferric ions (Fe^{3+}).

Table 14 : Confirmatory test for Group-III cations

	Brown precipitate **Fe^{3+}**		**White precipitate** **Al^{3+}**
	Dissolve the precipitate in dilute HCl and divide the solution into two parts.		Dissolve the white precipitate in dilute HCl and divide into two parts. .
(a)	To the first part add potassium ferrocyanide solution [Potasium hexacyanoferrate (II)]. A blue precipitate/colouration appears.	(a)	To the first part add sodium hydroxide solution and warm. A white gelatinous precipitate soluble in excess of sodium hydroxide solution is obtained
(b)	To the second part add potassium thiocyanate solution. A blood red colouration appears.	(b)	To the second part first add blue litmus solution and then ammonium hydroxide solution drop by drop along the sides of the test tube. A blue floating mass in the colourless solution is obtained.

Chemistry of confirmatory tests of Group - III cations

When original solution is heated with concentrated nitric acid, ferrous ion are oxidised to ferric ions.

$$2FeCl_2 + 2HCl + [O] \longrightarrow 2FeCl_3 + H_2O$$

Their group cations are precipitated as their hydroxides, which dissolve in dilute hydrochloric acid due to the formation of corresponding chlorides.

1. Test for Aluminium ions (Al^{3+})

(a) When the solution containing aluminium chloride is treated with sodium hydroxide a white gelationus precipitate of aluminium hydroxide is formed which is soluble in excess of sodium hydroxide solution due to the formation of sodium meta aluminate.

$$AlCl_3 + 3NaOH \longrightarrow Al(OH)_3 + 3NaCl$$

$$\underset{\substack{\text{White gelatinous}\\ \text{precipitate}}}{Al(OH)_3} + NaOH \longrightarrow \underset{\substack{\text{Sodium}\\ \text{meta aluminate}}}{NaAlO_2} + 2H_2O$$

(b) In the second test when blue litmus is added to the solution, a red colouration is obtained due to the acidic nature of the solution. On addition of NH_4OH solution drop by drop, the solution becomes alkaline and aluminium hydroxide is precipitated. Aluminium hydroxide adsorbs blue colour from the solution and forms insoluble adsorption complex named 'lake'. Thus a blue mass floating in the colourless solution is obtained. The test is therefore called **lake test.**

2. Test for ferric ions (Fe^{3+})

Reddish brown precipitate of ferric hydroxide dissolves in hydrochloric acid and ferric chloride is formed.

$$Fe(OH)_3 + 3HCl \longrightarrow FeCl_3 + 3H_2O$$

(a) When the solution containing ferric chloride is treated with potassium ferrocyanide solution a blue precipitate/colouration is obtained. The colour of the precipitate is Prussian blue. It is ferric ferro-cyanide. The reaction takes place as follows:

$$4FeCl_3 + \underset{\substack{\text{Potassium}\\ \text{ferrocyanide}}}{3K_4[Fe(CN)_6]} \longrightarrow \underset{\substack{\text{Prussian blue}\\ \text{precipitate}}}{Fe_4[Fe(CN)_6]_3} + 12KCl$$

If potassium hexacyanoferrate (II) (i.e. potassium ferrocyanide) is added in excess then a product of composition $KFe[Fe(CN)_6]$ is formed. This tends to form a colloidal solution ('soluble Prussian blue') and cannot be filtered.

$$FeCl_3 + K_4[Fe(CN)_6] \longrightarrow \underset{\text{(Soluble prussian blue)}}{KFe[Fe(CN)_6]} + 3KCl$$

(b) To the second part of the solution, add potassium thiocyanate (potassium sulphocyanide) solution. The appearance of a blood red colouration confirms the presence of Fe^{3+} ions.

$$Fe^{3+} + SCN^{-} \longrightarrow \underset{\text{Blood red colour}}{[Fe(SCN)]^{3+}}$$

(V) Analysis of group-IV cations

If group-III is absent, pass H_2S gas in the solution of group-III for a few minutes. If a precipitate appears (white, black or flesh coloured), this indicates the presence of group-IV cations. Table 15 gives a summary of confirmatory tests of group-IV cations.

Table 15 : Confirmatory test for Group - IV cations

White precipitate (Zn^{2+})	**Flesh coloured precipitate (Mn^{2+})**	**Black precipitate (Ni^{2+}, Co^{2+})**
Dissolve the precipitate in dilute HCl by boiling. Divide the solution into two parts. (a) To the first part add sodium hydroxide solution. A white precipitate soluble in excess of sodium hydroxide solution confirms the presence of Zn^{2+} ions. (b) Neutralise the second part with a mmonium hydroxide solution and add potassium ferrocyanide solution. A bluish white precipitate appears	Dissolve the precipitate in dilute HCl by boiling, then add sodium hydroxide solution in excess. A white precipitate is formed which turns brown on keeping.	Dissolve the precipitate in aqua regia. Heat the solution to dryness and cool. Dissolve the residue in water and divide the solution into two parts. (a) To the first part of the solution add ammonium hydroxide solution till it becomes alkaline. Add a few drops of dimethyl glyoxime and shake the test tube. Formation of a bright red precipitate confirms the presence of Ni^{2+} ions. (b) Neutralise the second part with ammonium hydroxide solution. Acidify it with dilute acetic acid and add solid potassium nitrite. A yellow precipitate confirms the presence of Co^{2+} ions.

Chemistry of confirmatory tests of Group–IV cations

Fourth group cations are precipitated as their sulphides. Observe the colour of the precipitate. A white colour of the precipitate indicates the presence of zinc ions, a flesh colour indicates the presence of manganese ions and a black colour indicates the presence of Ni^{2+} or Co^{2+} ions.

1. Test for Zinc ion (Zn^{2+})

Zinc sulphide dissolves in hydrochloric acid to form zinc chloride.

$$ZnS + 2HCl \longrightarrow ZnCl_2 + H_2S$$

(a) On addition of sodium hydroxide solution it gives a white precipitate of zinc hydroxide, which is soluble in excess of NaOH solution on heating. This confirms the presence of Zn^{2+} ions.

$$ZnCl_2 + 2NaOH \longrightarrow Zn(OH)_2 + 2NaCl$$

$$Zn(OH)_2 + 2NaOH \longrightarrow \underset{\text{Sodium zincate}}{Na_2ZnO_2} + 2H_2O$$

(b) When potassium ferrocyanide $K_4[Fe(CN)_6]$ solution is added to the solution after neutralisation by NH_4OH solution, a white or a bluish white precipitate of zinc ferrocyanide appears.

$$2ZnCl_2 + K_4[Fe(CN)_6] \longrightarrow \underset{\substack{\text{Zinc}\\ \text{ferrocyanide}}}{Zn_2[Fe(CN)_6]} + 4KCl$$

2. Test for Manganese ion (Mn^{2+})

Manganese sulphide precipitate dissolves in dil. HCl on boiling. On addition of NaOH solution in excess, a white precipitate of manganese hydroxide is formed which turns brown due to atmospheric oxidation into hydrated manganese dioxide.

$$MnS + 2HCl \longrightarrow MnCl_2 + H_2S$$

$$MnCl_2 + 2NaOH \longrightarrow \underset{\text{(White precipitate)}}{Mn(OH)_2} + 2NaCl$$

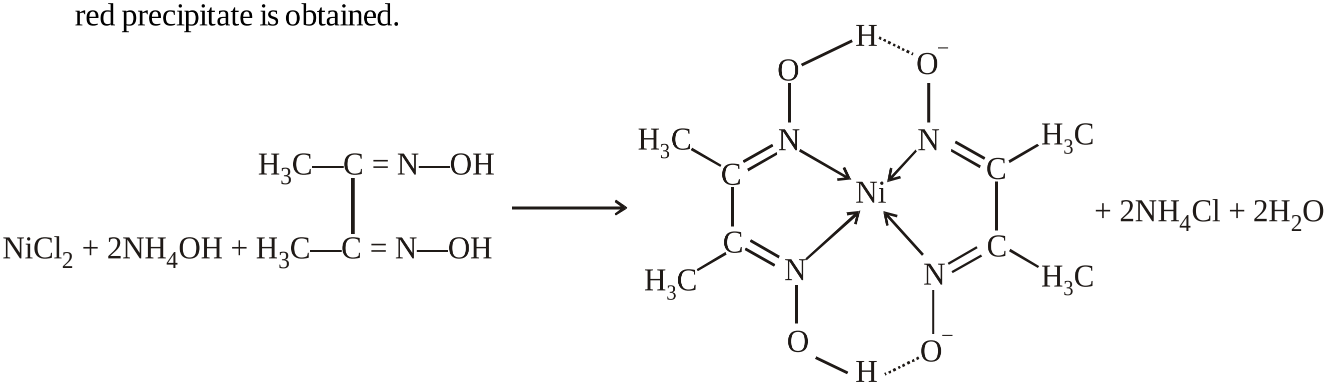
$$Mn(OH)_2 + [O] \longrightarrow \underset{\substack{\text{Hydrated manganese dioxide}\\ \text{(Brown colour)}}}{MnO(OH)_2}$$

3. Test for Nickel ion (Ni^{2+})

The black precipitate of nickel sulphide dissolves in aqua regia and the reaction takes place as follows:

$$3NiS + 2HNO_3 + 6HCl \longrightarrow 3NiCl_2 + 2NO + 3S + 4H_2O$$

After treatment with aqua regia nickel-chloride is obtained which is soluble in water. When dimethyl glyoxime is added to the aqueous solution of nickel chloride, made alkaline, by adding NH_4OH solution, a brilliant red precipitate is obtained.



Complex of red colour
(Stable form of complex)

4. Test for Cobalt ion (Co^{2+})

Cobalt sulphide dissolves in aqua regia in the same manner as nickel sulphide. When the aqueous solution of the residue obtained after treatment with aqua regia is treated with a strong solution of potassium nitrite after neutralisation with ammonium hydroxide and the solution is acidified with dil. acetic acid, a yellow precipitate of the complex of cobalt named potassium hexanitritocobaltate (III) is formed.

$$CoS + HNO_3 + 3HCl \longrightarrow CoCl_2 + NOCl + S + 2H_2O$$

$$CoCl_2 + 7KNO_2 + 2CH_3COOH \longrightarrow \underset{\substack{\text{Potassium}\\ \text{hexanitritocobaltate(III)}\\ \text{(Yellow precipitate)}}}{K_3[Co(NO_2)_6]} + 2KCl + 2CH_3COOK + NO + H_2O$$

(VI) Analysis of Group–V cations

If group-IV is absent then take original solution and add a small amount of solid NH_4Cl and an excess of NH_4OH solution followed by solid ammonium carbonate $(NH_4)_2CO_3$. If a white precipitate appears, this indicates the presence of group–V cations.

Dissolve the white precipitate by boiling with dilute acetic acid and divide the solution into three parts one each for Ba^{2+}, Sr^{2+} and Ca^{2+} ions. Preserve a small amount of the precipitate for flame test. Summary of confirmatory tests is given in Table 16.

16 : Confirmatory test for Group - V cations

Dissolve the precipitate by boiling with dilute acetic acid and divide the solution into three parts one each for Ba^{2+}, Sr^{2+} and Ca^{2+} ions		
Ba^{2+} ions	**Sr^{2+} ions**	**Ca^{2+} ions**
(a) To the first part add potassium chromate solution. A yellow precipitate appears. **(b) Perform the flame test with the preserved precipitate. A grassy green flame is obtained.**	**(a) If barium is absent, take second part of the solution and add ammonium sulphate solution. Heat and scratch the sides of the test tube with a glass rod and cool. A white precipitate is formed.** **(b) Perform the flame test with the preserved precipitate. A crimson-red flame confirms the presence of Sr^{2+} ions.**	**(a) If both barium and strontium are absent, take the third part of the solution. Add ammonium oxalate solution and shake well. A white precipitate of calcium oxalate is obtained.** **(b) Perform the flame test with the preserved precipitate. A brick red flame, which looks greenish-yellow through blue glass, confirms the presence of Ca^{2+} ions.**

Chemistry of Confirmatory Tests of Group–V cations

The Group–V cations are precipitated as their carbonates which dissolve in acetic acid due to the formation of corresponding acetates.

1. Test for Barium ion (Ba^{2+})

(a) Potassium chromate (K_2CrO_4) solution gives a yellow precipitate of barium chromate when the solution of fifth group precipitate in acetic acid is treated with it.

$$BaCO_3 + 2CH_3COOH \longrightarrow (CH_3COO)_2\,Ba + H_2O + CO_2$$

$$(CH_3COO)_2Ba + K_2CrO_4 \longrightarrow \underset{\substack{\text{Barium chromate} \\ \text{(yellow precipitate)}}}{BaCrO_4} + 2CH_3COOK$$

(b) **Flame test :** Take a platinum wire and dip it in conc. HCl. Heat it strongly until the wire does not impart any colour to the non-luminous flame. Now dip the wire in the paste of the (Group–V) precipitate in conc. HCl. Heat it in the flame. A grassy green colour of the flame confirms the presence of Ba^{2+} ions.

2. Test for Strontium ion (Sr^{2+})

(a) Solution of V group precipitate in acetic acid gives a white precipitate of strontium sulphate with ammonium sulphate solution on heating and scratching the sides of the test tube with a glass rod.

$$SrCO_3 + 2CH_3COOH \longrightarrow (CH_3COO)_2Sr + H_2O + CO_2$$

$$(CH_3COO)_2\,Sr + (NH_4)_2SO_4 \longrightarrow \underset{\substack{\text{Strontium} \\ \text{sulphate} \\ \text{(White precipitate)}}}{SrSO_4} + 2CH_3COONH_4$$

(b) **Flame test :** Perform the flame test as given in the case of Ba^{2+}. A crimson red flame confirms the presence of Sr^{2+} ions.

3. Test for Calcium ion (Ca^{2+})

(a) Solution of the fifth group precipitate in acetic acid gives a white precipitate with ammonium oxalate solution.

$$CaCO_3 + 2CH_3COOH \longrightarrow (CH_3COO)_2Ca + H_2O + CO_2$$

$$(CH_3COO)_2Ca + \underset{\substack{\text{Ammonium} \\ \text{oxalate}}}{(NH_4)_2C_2O_4} \longrightarrow \underset{\substack{\text{Calcium oxalate} \\ \text{(White precipitate)}}}{(COO)_2Ca} + 2CH_3COONH_4$$

(b) **Flame test :** Perform the flame test as mentioned above. Calcium imparts brick red colour to the flame which looks greenish-yellow through blue glass.

(VII) Analysis of Group–VI cations

If group–V is absent then perform the test for Mg^{2+} ions as given below.

Chemistry of Confirmatory Tests of Group–VI cations

Test for Magnesium ion (Mg^{2+})

(a) If group–V is absent then the solution may contain magnesium carbonate, which is soluble in water in the presence of ammonium salts because the equilibrium is shifted towards the right hand side.

$$NH_4^+ + CO_3^{2-} \longrightarrow NH_3 + HCO_3^-$$

The concentration of carbonate ions required to produce a precipitate is not attained. When disodium hydrogenphosphate solution is added and the inner walls of the test tube are scratched with a glass rod, a white crystalline precipitate of magnesium ammonium phosphate is formed which indicates the presence of Mg^{2+} ions.

$$Mg^{2+} + Na_2HPO_4 \longrightarrow \underset{\text{phosphate (White precipitate)}}{\underset{\text{Magnesium ammonium}}{Mg(NH_4)PO_4}} + NH_4OH + 2Na^+ + H_2O$$

Note down the observations and the inferences of the qualitative analysis in tabular form as given in the specimen record

Precautions

***Fig. 1.9** : How to smell a gas*

(a) Always use an apron, an eye protector and hand gloves while working in the chemistry laboratory.

(b) Before using any reagent or a chemical, read the label on the bottle carefully. Never use unlabelled reagent.

(c) Do not mix chemicals and reagents unnecessarily. Never taste any chemical.

(d) Be careful in smelling chemicals or vapours.

Always fan the vapours gently towards your nose (Fig. 1.9).

(e) Never add sodium metal to water or throw it in the sink or dustbin.

(f) Always pour acid into water for dilution. Never add water to acid.

(g) Be careful while heating the test tube. The test tube should never point towards yourself or towards your neighbours while heating or adding a reagent. Fig. 1.9 : How to smell a gas

(h) Be careful while dealing with the explosive compounds, inflammable substances, poisonous gases, electric appliances, glass wares, flame and the hot substances.

(i) Keep your working surroundings clean. Never throw papers and glass in the sink. Always use dustbin for this purpose.

(j) Always wash your hands after the completion of the laboratory work.

(k) Always use the reagents in minimum quantity. Use of reagents in excess, not only leads to wastage of chemicals but also causes damage to the environment.

Discussion Questions

(i) What is the difference between a qualitative and a quantitative analysis?

(ii) Can we use glass rod instead of platinum wire for performing the flame test? Explain your answer.

(iii) Why is platinum metal preferred to other metals for the flame test?

(iv) Name the anions detected with the help of dilute H_2SO_4?

(v) Why is dilute H_2SO_4 preferred over dilute HCl while testing anions?

(vi) Name the anions detected by conc. H_2SO_4.

(vii) How is sodium carbonate extract prepared ?

(viii) What is lime water and what happens on passing carbon dioxide gas through it?

(ix) Carbon dioxide gas and sulphur dioxide gas both turn lime water milky. How will you distinguish these two?

(x) How will you test the presence of carbonate ion?

(xi) What is the composition of dark brown ring which is formed at the junction of two layers in the ring test for nitrates?

(xii) Name the radical confirmed by sodium nitroprusside test.

(xiii) What is chromyl chloride test ? How do you justify that CrO_2Cl_2 is acidic in nature?

(xiv) Why do bromides and iodides not give tests similar to chromyl chloride test?

(xv) Describe the layer test for bromide and iodide ions.

(xvi) Why is silver nitrate solution stored in dark coloured bottles?

(xvii) How do you test the presence of sulphide ion?

(xviii) Why does iodine give a blue colour with starch solution?

(xix) What is Nessler's reagent?

(xx) Why is original solution for cations not prepared in conc. HNO_3 or H_2SO_4?

(xxi) Why cannot conc. HCl be used as a group reagent in place of dil. HCl for the precipitation of Ist group cations?

(xxii) How can one prevent the precipitation of Group–IV radicals, with the second group radicals?

(xxiii) Why is it essential to boil off H_2S gas before precipitation of radicals of group–III?

(xxiv) Why is heating with conc. nitric acid done before precipitation of group–III?

(xxv) Can we use ammonium sulphate instead of ammonium chloride in group–III?

(xxvi) Why is NH_4OH added before $(NH_4)_2CO_3$ solution while precipitating group–V cations?

(xxvii) Why do we sometimes get a white precipitate in group–VI even if the salt does not contain Mg^{2+} radical?

(xxviii) What is aqua regia?

(xxix) Name a cation, which is not obtained from a metal.

(xxx) How can you test the presence of ammonium ion?

(xxxi) Why are the group–V radicals tested in the order Ba^{2+}, Sr^{2+} and Ca^{2+} ?

(xxxii) Why does conc. HNO_3 kept in a bottle turn yellow in colour?

(xxxiii) Why should the solution be concentrated before proceeding to group–V?

(xxxiv) Why is the reagent bottle containing sodium hydroxide solution never stoppered?

(xxxv) What do you understand by the term common ion effect?

(xxxvi) Why is zinc sulphide not precipitated in group–II?

SPECIMEN RECORD OF SALT ANALYSIS

Aim

To analyse the given salt for one anion and one cation present in it.

S. No.	Experiment	Observation	Inference
1.	**Noted the colour of the given salt.**	**White**	**Cu^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+} are absent.**
2.	**Noted the smell of the salt.**	**No specific smell.**	**S^{2-}, SO_3^{2-}, CH_3COO^- may be absent.**
3.	**Heated 0.5 g of the salt in a dry test tube and noted the colour of the gas evolved and change in the colour of the residue on heating and cooling.**	**(i) No gas was evolved. (ii) No particular change in colour of the residue is observed when heated and when cooled.**	**(i) CO_3^{2-} may be present, NO_3^-, NO_2^-, Br^- may be absent. (ii) Zn^{2+} may be absent.**
4.	**Prepared a paste of the salt with conc. HCl and performed the flame test.**	**No distinct colour of the flame seen.**	**Ca^{2+}, Sr^{2+}, Ba^{2+} Cu^{2+} may be absent.**
5.	**Borax bead test was not performed as the salt was white in colour.**	—	—
6.	**Treated 0.1 g of salt with 1 mL dil.H_2SO_4 and warmed.**	**No effervescence and evolution of vapours.**	**CO_3^{2-}, SO_3^{2-}, S^{2-}, NO_2^-, CH_3COO^- absent.**
7.	**Heated 0.1 g of salt with 1 mL conc. H_2SO_4.**	**No gas evolved.**	**Cl^-, Br^-, I^-, NO_3^-, $C_2O_4^{2-}$ are absent.**
8.	**Acidified 1mL of aqueous salt solution with conc. HNO_3. Warmed the contents and then added 4-5 drops of ammonium molybdate solution.**	**No yellow precipitate**	**PO_4^{3-} absent.**

Sl. No.	Experiment	Observation	Inference
9.	Acidified water extract of the salt with dil. HCl and then added 2mL of $BaCl_2$ solution.	A white ppt. is obtained which is insoluble in conc. HNO_3 and conc. HCl.	SO_4^{2-} present.
10.	Heated 0.1 g of salt with 2 mL NaOH solution.	Ammonia gas is not evolved.	NH_4^+ absent.
11.	Attempted to prepare original solution of the salt by dissolving 1g of it in 20 mL water.	Clear solution formed	Water soluble salt is present.
12.	To a small part of the above salt solution added 2 mL of dil. HCl.	No white precipitate formed.	Group–I absent.
13.	Passed H_2S gas through one portion of the solution of step 12.	No precipitate formed.	Group–II absent.
14.	Since salt is white, heating with conc. HNO_3 is not required. Added about 0.2 g of solid ammonium chloride and then added excess of ammonium hydroxide to the solution of step 12.	No precipitate formed.	Group–III absent.
15.	Passed H_2S gas through the above solution.	No precipitate formed.	Group–IV absent.
16.	Added excess of ammonium hydroxide solution to the original solution and then added 0.5 g of ammonium carbonate.	No precipitate formed.	Group–V absent.
17.	To the original solution of salt added ammonium hydroxide solution, followed by disodium hydrogen phosphate solution. Heated and scratched the sides of the test tube.	White precipitate	Mg^{2+} confirmed.

Result

the given salt contains

Anion : SO_4^{2-}

Cation : Mg^{2+}

EXERCISE # I

ANIONS : Class A (Subgroup - I)

1. The colour developed, when sodium sulphide is added to sodium nitroprusside is:

(A) Purple (B) yellow (C) red (D) black

2. When a neutral or slightly alkaline solution of thiosulphate is treated with the $[Ni(en)_3](NO_3)_2$ complex, then

(A) Green precipitate is obtained (B) Brown precipitate is obtained
(C) Violet precipitate is obtained (D) Yellow precipitate is obtained

3. When CH_3COONa heated with solid As_2O_3 then compound X is formed. The smell of compound X is -

(A) Pungent smell (B) Rotten Fish smell (C) Nauseating smell (D) Rotten egg smell

4. NO_2^- ion can be destroyed by -

(A) Sulphamic acid (B) Thiourea (C) Urea (D) All of these

5. Solutions of sodium azide(NaN_3) and iodine (as KI_3) do not react but on addition of a trace of 'X' ion, which acts as a catalyst there is an immediate vigorous evolution of nitrogen. Then 'X' may be:

(A) $S_2O_3^{2-}$ (B) S^{2-} (C) $\overset{\ominus}{S}CN$ (D) All are correct.

6. When $AgNO_3$ react with 'X' ion then initially no visible change occurs due to formation of water soluble complex.Then ion 'X' may be:

(A) SO_3^{2-} (B) $S_2O_3^{2-}$ (C) S^{2-} (D) CO_3^{2-}

7. Match the column

Column-I	**Column-II**
(A) S^{2-}	(P) Produces white ppt. with excess $AgNO_3$
(B) HSO_3^-	(Q) Evolves gas with dil. HCl which turns lime water milky
(C) SO_3^{2-}	(R) Evolves gas with dil.H_2SO_4 which does **not** turn Baryta water milky
(D) $S_2O_3^{2-}$	(S) Produces ppt. with $Pb(OAc)_2$ solution.
	(T) Produces white ppt with $BaCl_2$ solution.

8. Find the number of acidic radical(s) which can form coloured gas when treated with **dil.** H_2SO_4.
CO_3^{2-}, NO_2^-, Br^-, I^-, SO_3^{2-}

Class A (Subgroup - II)

9. Chromyl chloride test is given by -

(A) CH_3Cl (B) AgCl (C) Hg_2Cl_2 (D) NH_4Cl

10. $BO_3^{3-} + \underset{\text{Conc.}}{H_2SO_4} \xrightarrow{\Delta} \underset{\text{White fumes}}{(P)}$

$BO_3^{3-} + \underset{\text{Conc.}}{H_2SO_4} + C_2H_5OH \xrightarrow{\Delta} \underset{\text{Vapours}}{(Q)}$

P & Q are respectively -

(A) H_3BO_3 , H_3BO_3 (B) $(C_2H_5)_3BO_3$, H_3BO_3
(C) $(C_2H_5)_3BO_3$, $(C_2H_5)_3BO_3$ (D) H_3BO_3, $(C_2H_5)_3BO_3$

11. In layer test of I^- and Br^-. If reddish -brown layer comes first then -

(A) Br^- present (B) I^- absent (C) Both (A) and (B) (D) None of these

All Anions Of Class A

12. **Statement-1** : When H_2S gas is passed through Na-nitroprusside soluton it gives purple colouration

Statement-2 : H_2S is an weak acid

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

13. When the soda extract containing thiosulphate ion treated with excess of $AgNO_3$ solution followed by boiling, then.

(A) White precipitate is formed (B) Black precipitate is formed

(C) brown precipitate is formed (D) No ppt precipitate is formed

14. "Cacodyl oxide" is formed in the specific test of -

(A) Formate (B) Oxalate (C) Acetate (D) Nitrate

15. An aqueous solution of gas (X) gives the white turbidity on passing H_2S in the solution. Identify (X)

(A) NH_3 (B) SO_2 (C) CO_2 (D) None of these

16. NO_2^- and NO_3^- can be distinguished by which of the following reagent.

(A) dil. H_2SO_4 (B) conc. H_2SO_4

(C) Devarda's alloy + conc.NaOH (D) None of these

17. $[Fe(H_2O)_5NO]^{2+}$ is unstable because -

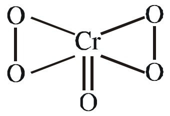
(A) It liberates NO gas on warming

(B) It liberates NO gas on shaking

(C) The charge of central atom is +1 (relatively low enough)

(D) None of these

Class B

18. $Cr_2O_7^{2-} + 4H_2O_2 + 2H^+ \xrightarrow[\text{Solvent}]{\text{Organic}} 2$  $+ 5H_2O$

In above reaction amyl alcohol is recommended.

Dimethyl ether is not recommended for general use owing to its -

(A) Highly non-flammable character (B) Highly inflammable character

(C) Highly poisonious character (D) None of these

19. If barium sulphate is precipitated in a solution containing potassium permanganate it is coloured pink (violet) by -

(A) Absorption of some of the permanganate (B) Adsorption of some of the permanganate

(C) Both (A) and (B) (D) None of these

All Anions Of Class A & Class B

20.

List–I (Reaction)	**List–II (Product)**
(P) $KI + NO_2^- \longrightarrow$	(1) NH_3
(Q) $NH_4NO_3 \xrightarrow{\Delta}$	(2) NO
(R) $NO_2^- \xrightarrow{Zn+NaOH}$	(3) N_2
(S) $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta}$	(4) N_2O

Code :

	P	Q	R	S		P	Q	R	S
(A)	3	4	1	2	(B)	4	2	1	3
(C)	4	2	3	1	(D)	2	4	1	3

21.

List–I (Reaction)	**List–II (Product)**
(P) $CO_3^{2-} \xrightarrow{dil.H_2SO_4}$	(1) H_2S
(Q) $S^{2-} \xrightarrow{dil.H_2SO_4}$	(2) SO_2
(R) $SO_3^{2-} \xrightarrow{dil.H_2SO_4}$	(3) CO_2
(S) $S_2O_3^{2-} \xrightarrow{dil.H_2SO_4}$	(4) $S + SO_2$

Code :

	P	Q	R	S		P	Q	R	S
(A)	3	4	1	2	(B)	2	1	4	3
(C)	3	1	2	4	(D)	2	4	1	3

22.

List–I (Molecule)	**List–II (Characteristic Odour)**
(P) CO_2	(1) Rotten egg smell
(Q) SO_2	(2) Suffocating smell of burning sulphur
(R) H_2S	(3) Vineger like smell
(S) CH_3COOH	(4) Odour less

Code :

	P	Q	R	S		P	Q	R	S
(A)	4	2	1	3	(B)	2	4	1	3
(C)	3	1	2	4	(D)	2	4	1	3

23.

List–I (Acidic radicals)	**List–II (Test)**
(P) NO_2^-	(1) Green flame test
(Q) BO_3^{3-}	(2) Cacodyl oxide reaction
(R) Br^-	(3) Griess Ilosvay test
(S) CH_3COO^-	(4) Layer test

Code :

	P	Q	R	S		P	Q	R	S
(A)	4	2	1	3	(B)	3	1	4	2
(C)	3	4	2	1	(D)	4	3	2	1

CATIONS : DRY TEST

24. Find the number of water of crystallization in microcosmic salt -

(A) 5 (B) 4 (C) 6 (D) 10

25. What is the colour of K^+ through cobalt/double blue glass -

(A) Lilac, (B) Violet (C) Brick red (D) Crimson red

26. What is the colour of $CoO.Al_2O_3$ is -

(A) pink (B) Thenard blue (C) Bluish white (D) None of these

27. The correct formula of Canary yellow ppt and it is the test of ------------ acid radical-

(A) $(NH_4)_2\ [PMo_{12}O_{40}]$ and phosphate (B) $(NH_4)\ H\ [P(Mo_3O_{10})_4]$ and sulphate

(C) $(NH_4)_3\ [P(Mo_3O_{10})_4]$ and phosphate (D) $Na_3\ [P(Mo_3O_{10})_4]$ and phosphate

28. Sodium carbonate bead test generally used for ....compounds.

(A) Mn (B) Cr (C) Zn (D) Cu

WET TEST : GROUP ZERO

29. **Statement-1 :** Test of NH_4^+ can not be done within group analysis

Statement-2 : During group analysis several times NH_4^+ - compound is added at the different steps.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1

(C) Statement-1 is false, statement-2 is true.

(D) Statement-1 is true, statement-2 is false.

GROUP - I

30. Which of the following is not group-I cation though the chlorides of all cations are sparingly soluble in water.

(A) Ag^+ (B) Hg_2^{2+} (C) Cu^+ (D) Pb^{2+}

GROUP - II A

31. Cu^{2+} + KCN (in excess) $\rightarrow$ soluble complex (X). How many statements are correct regarding complex (X) -

(i) the central atom has the co-ordination number of 6

(ii) the central atom has the co-ordination number of 4

(iii) the complex is sq.planar

(iv) the complex is diamagnetic

(v) the complex is paramagnetic

32. $BiCl_3 \xrightarrow{KI}$ black ppt (M) $\xrightarrow{\text{excess KI}}$ soluble complex (N)

Find the number of moles of I^- ions involved for the formation of per mole of (N).

GROUP - II B

33. Sn^{2+} and Sn^{4+} can be distinguished by how many of the following methods -

(i) by passing H_2S in their solution (in acidic medium)

(ii) by addition of NaOH in their solution

(iii) by addition of excess NaOH in their solution

(iv) by addition of dil. HCl in their solution

(v) by addition of $HgCl_2$ solution in their solution

GROUP - III

34. What is the group-III reagent is generally used for group analysis.

(A) $NH_4OH + NH_4NO_3$ (B) $NH_4Cl + (NH_4)_2CO_3$

(C) $NH_4OH + (NH_4)_2SO_4$ (D) $NH_4OH + NH_4Cl$

35. $CrCl_3$ solution + Na_2S solution $\longrightarrow$ ppt(A)

The correct formula and colour of A are

(A) Cr_2S_3, Black (B) $Cr(OH)_3$, Green

(C) $Na[Cr(OH)_4]$, Green (D) None of these

GROUP - IV

36. The auxiliary reagent in group-IV reagent is

(A) H_2S (B) dil.HCl (C) NaOH (D) NH_4OH

All Group Cations

37. Which of the following cation gives ppt in two groups during group analysis.

(A) Hg^{2+} (B) Hg_2^{2+} (C) Pb^{2+} (D) Cu^{2+}

38. Which of the following cation produces coloured ppt with Na_2SO_4 solution -

(A) Pb^{2+} solution (B) Ba^{2+} solution (C) Hg^{2+} solution (D) Ca^{2+} solution

39. NH_4^+ and K^+ ions can be distinguished by the use of following reagent

(A) $Na_3[Co(NO_2)_6]$ (B) $Na_2[PtCl_6]$

(C) $HClO_4$ or $NaClO_4$ (D) Boiling with NaOH

40. Which of the following sulphides is yellow in colour?

(A) CuS (B) CdS (C) ZnS (D) CoS

MISCELLANEOUS

41.

List–I (Compound)	**List–II (Colour)**
(P) HgO	(1) Purple solution
(Q) $BaCO_3$	(2) Yellow ppt
(R) $Na_4[Fe(CN)_5NOS]$	(3) Dark brown
(S) KI_3	(4) White ppt

Code :	**P**	**Q**	**R**	**S**
(A)	3	4	1	2
(B)	2	4	1	3
(C)	2	4	3	1
(D)	2	4	3	1

42.

List–I (Basic Radical)	**List–II (Group)**
(P) Al^{+3}	(1) II group
(Q) Zn^{+2}	(2) V group
(R) Ba^{+2}	(3) IV group
(S) Pb^{+2}	(4) III group

Code :	**P**	**Q**	**R**	**S**
(A)	4	2	1	3
(B)	2	4	1	3
(C)	3	1	2	4
(D)	4	3	2	1

43.

List–I (Cations)	**List–II (Group reagent)**
(P) Co^{+2}	(1) $(NH_4)_2CO_3$ in presence of NH_4Cl
(Q) Fe^{+3}	(2) H_2S gas in acidic medium
(R) Cu^{+2}	(3) H_2S in presence of NH_4OH
(S) Ca^{+2}	(4) NH_4OH in presence of NH_4Cl

Code :	**P**	**Q**	**R**	**S**
(A)	4	2	1	3
(B)	3	1	4	2
(C)	1	2	3	4
(D)	3	4	2	1

EXERCISE # II

ANIONS : Class A (Subgroup - I)

1. **Statement-1:** On passing CO_2 gas through lime water, the solution turns milky.

because

Statement-2: Acid-Base (neutralisation) reaction takes place.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
(C) Statement-1 is true, statement-2 is false.
(D) Statement-1 is false, statement-2 is true.

2. A substance on treatment with dil. H_2SO_4 liberates a colourless gas which produces (i) turbidity with baryta water and (ii) turns acidified dichromate solution green. The reaction indicates the presence of

(A) CO_3^{2-} (B) S^{2-} (C) SO_3^{2-} (D) NO_2^-

3. When $S_2O_3^{2-}$ react with solution of 'X' reagent then reaction is redox followed by precipitation then 'X' is:

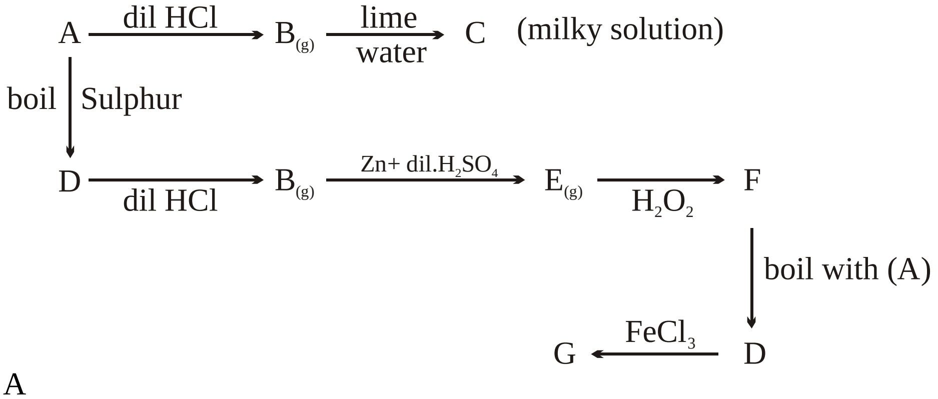
(A) $FeCl_3$ solution (B) $AgNO_3$ solution
(C) $CuSO_4$ solution (D) None of these

4. In the test for iodine, when I_2 is treated with sodium thiosulphate, $Na_2S_2O_3$

$$Na_2S_2O_3 + I_2 \longrightarrow NaI + ...$$

(A) $Na_2S_4O_6$ (B) Na_2SO_4 (C) Na_2S (D) Na_3ISO_4

Paragraph for Q. 5 to Q. 7



5. Identify A

(A) CO_3^{2-} (B) SO_3^{2-} (C) $S_2O_3^{2-}$ (D) none of these

6. When A react with $Pb(NO_3)_2$ then compound X is formed. Compound X is oxidized by atmospheric oxygen on boiling, then Y is formed what is the colour of Y

(A) yellow (B) White (C) Black (D) Green

7. When gas E react with sodium nitroprusside in basic medium then compound Z is formed. The colour of compound Z is:

(A) Green (B) purple (C) Reddish brown (D) Black

Class A (Subgroup - II)

8. When a mixture of solid NaCl, solid $K_2Cr_2O_7$ is heated with conc. H_2SO_4, orange red vapours are obtained. These are of the compound

(A) chromous chloride (B) chromyl chloride

(C) chromic chloride (D) chromic sulphate

9. Which of the following will not give positive chromyl chloride test?

(A) Copper chloride, $CuCl_2$ (B) Mercuric chloride, $HgCl_2$

(C) Zinc chloride, $ZnCl_2$ (D) Aniline chloride, $C_6H_5NH_3Cl$

10. Sodium borate on reaction with conc. H_2SO_4 and C_2H_5OH gives a compound A which burns with a green edged flame. The compound A is

(A) $H_2B_4O_7$ (B) $(C_2H_5)_2B_4O_7$ (C) H_3BO_3 (D) $(C_2H_5)_3BO_3$

11. Nitrate is confirmed by ring test. The brown colour of the ring is due to formation of

(A) ferrous nitrite (B) nitroso ferrous sulphate

(C) ferrous nitrate (D) $FeSO_4NO_2$

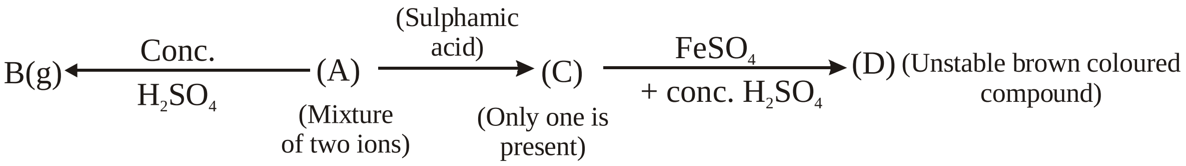
12. A salt gives violet vapours when treated with conc. H_2SO_4, it contains

(A) Cl^- (B) I^- (C) Br^- (D) NO_3^-

13. Unknown salt + Al-powder + NaOH (conc.) → gas comes out which turns Nesslar's reagent brown. The salt may be -

(A) $NaNO_2$ (B) $NaNO_3$ (C) NH_4Cl (D) NH_4HCO_3

Paragraph for Q. 14 to Q. 17



14. Identify mixture of ions (A) -

(A) NO_2^- and Br^- (B) NO_2^- and I^- (C) NO_2^- and NO_3^- (D) None of these

15. What is oxidation state of central atom of (D)

(A) +3 (B) +2 (C) +1 (D) Zero

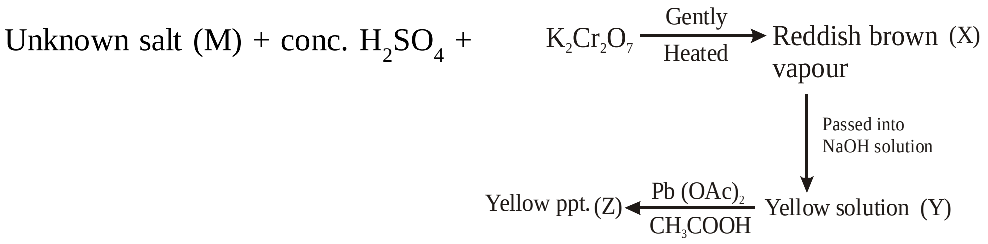
16. Identify gas B-

(A) Br_2 (B) $Br_2 + NO_2$ (C) NO_2 (D) None of these

17. What is the hybridisation of central atom of D-

(A) d^2sp^3 (B) sp^3d^2 (C) sp^3d (D) sp^3

Paragraph for Q. 18 to Q. 20



18. The salt (M) is/are-

(A) AgCl (B) $NH_4Cl + NaBr$ (C) NaBr (D) $Ca(ClO_4)_2$

19. How many non axial d-orbitals are involved in hybridisation of central atom of compound (X)-

(A) 2 (B) 3 (C) 4 (D) None of these

20. What is the formula of yellow ppt (Z)-

(A) $BaCrO_4$ (B) Na_2CrO_4 (C) Ag_2CrO_4 (D) $PbCrO_4$

CATIONS : DRY TEST

21. In the borax bead test of Co^{2+}, the blue colour of bead is due to the formation of:

(A) B_2O_3 (B) Co_3B_2 (C) $Co(BO_2)_2$ (D) CoO

22. Which of the following leaves no residue on heating?

(A) $Pb(NO_3)_2$ (B) NH_4NO_3 (C) $Cu(NO_3)_2$ (D) $NaNO_3$

23. Which of the following cations is detected by the flame test?

(A) NH_4^+ (B) K^+ (C) Mg^{2+} (D) Al^{3+}

24. Which metal salt gives a violet coloured bead in the borax bead test (oxidising flame, cold)?

(A) Fe^{2+} (B) Ni^{2+} (C) Co^{2+} (D) Mn^{2+}

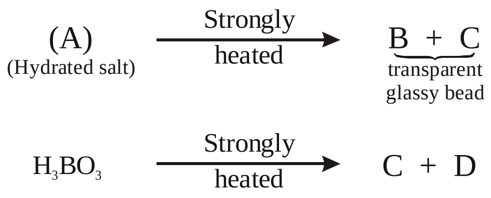
25. The compound formed in the borax bead test of Cu^{2+} ion in oxidising flame is:

(A) Cu (B) $CuBO_2$ (C) $Cu(BO_2)_2$ (D) None of these

26. In microcosmic salt bead test Co^{2+} produce blue bead due to the formation of -

(A) $Cu(BO_2)_2$ (B) $NaCoPO_4$ (C) $Co_2(PO_4)(BO_2)$ (D) $NaPO_3$

Paragraph for Q. 27 to Q. 30



27. Identify C-

(A) $(BN)_X$ (B) $NaPO_3$ (C) B_2O_3 (D) $Mg(NH_4)PO_4$

28. Find the number of water of crystallizations in (A)-

(A) 4 (B) 5 (C) 10 (D) 24

29. How many X–O–X linkages are present in structure of A (X = central atom)-

(A) 4 (B) 3 (C) 5 (D) 2

30. Find the number of tetrahedral and trigonal planar units in structure of A -

(A) 2,1 (B) 2,2 (C) 2,4 (D) 5,2

WET TEST : GROUP - I

31. Mercurous ion is represented as:

(A) Hg_2^{2+} (B) Hg^{2+} (C) $Hg + Hg^{2+}$ (D) Hg_2^{+}

32. 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 solution, a white precipitate is obtained which does not dissolve in dil. HNO_3. The anion could be:

(A) CO_3^{2-} (B) Cl^- (C) SO_4^{2-} (D) S^{2-}

33. An aqueous solution of a substance gives a white ppt. on treatment with dil. HCl, which dissolves on heating. When hydrogen sulphide is passed through the hot acidic solution, a black ppt. is obtained. The substance is a

(A) Hg^{2+} salt (B) Cu^{2+} salt (C) Ag^+ salt (D) Pb^{2+} salt

34. A white ppt obtained in a analysis of a mixture becomes black on treatment with NH_4OH. It may be

(A) $PbCl_2$ (B) $AgCl$ (C) $HgCl_2$ (D) Hg_2Cl_2

GROUP - II

35. When bismuth chloride is poured into a large volume of water the white precipitate produced is

(A) $Bi(OH)_3$ (B) Bi_2O_3 (C) $BiOCl$ (D) Bi_2OCl_3

36. $CuSO_4$ decolourises on addition of excess KCN, the product is

(A) $[Cu(CN)_4]^{2-}$. (B) Cu^{2+} get reduced to form $[Cu(CN)_4]^{3-}$

(C) $Cu(CN)_2$ (D) $CuCN$

37. When H_2S gas is passed through the HCl containing aqueous solution of $CuCl_2$, $HgCl_2$, $BiCl_3$ and $CoCl_2$, it does not precipitate out:

(A) CuS (B) HgS (C) Bi_2S_3 (D) CoS

38. Which of the following is soluble in yellow ammonium sulphide?

(A) CuS (B) CdS (C) SnS (D) PbS

39. When excess of $SnCl_2$ is added to a solution of $HgCl_2$, a white ppt turning grey is obtained. The grey colour is due to the formation of

(A) Hg_2Cl_2 (B) $SnCl_4$ (C) Sn (D) Hg

40. On passing H_2S gas in II group sometimes the solution turns milky. It indicates the presence of

(A) oxidising agent (B) acidic salt (C) s-block cation (D) reducing agent.

41. Which fo the following yellow coloured sulphide is insouble in yellow ammonium sulphide.

(A) SnS_2 (B) As_2S_5 (C) CdS (D) Bi_2S_3

42. Type of sulphide ppt may be obtained in the group-II ppt during group analysis.

(A) M_2S_3 (B) M_2S (C) MS (D) MS_2

43. The metal ion which is precipitated when H_2S is passed with HCl:

(A) Zn^{2+} (B) Ni^{2+} (C) Cd^{2+} (D) Mn^{2+}

GROUP - III

44. In the precipitation of the iron group in qualitative analysis, ammonium chloride is added before adding ammonium hydroxide to

(A) decrease concentration of OH^- ions. (B) prevent interference by phosphate ions.

(C) increase concentration of Cl^- ions. (D) increase concentration of NH_4^+ ions.

45. If reddish brown ppt (only) is obtained in group-III during group analysis, then oxidation state of Fe in the original sample may be

(A) +2 (B) +3 (C) +2 and +3 both (D) Neither +2 nor +3

46. If NH_4Cl is not added to the group-III reagent which of the following ppt could be obtained

(A) $Cr(OH)_2$ (B) $Fe(OH)_3$ (C) $Mn(OH)_2$ (D) $Mg(OH)_2$

47. In which of the following cases blue ppt is obtained

(A) $Fe^{2+} + [Fe(CN)_6]^{3-} \longrightarrow$ (B) $Fe^{2+} + [Fe(CN)_6]^{4-} \longrightarrow$

(C) $Fe^{3+} + [Fe(CN)_6]^{4-} \longrightarrow$ (D) $Fe^{3+} + [Fe(CN)_6]^{3-} \xrightarrow{SnCl_2}$

48. What are the following steps are to be done before adding group-III reagent into the group-II filtrate.

(A) Group-II filtrate is to be evapourated to dryness

(B) Group-II filtrate is to be boiled of first

(C) After boiling 2-3 drops of dil.H_2SO_4 is added and boiled again.

(D) After boiling 2-3 drops of HNO_3 is added and boiled again.

49. A pale green crystalline metal salt of M dissolves freely in water. On standing it gives a brown ppt on addition of aqueous NaOH. The metal salt solution also gives a black ppt on bubbling H_2S in basic medium. An aqueous solution of the metal salt decolourizes the pink colour of the permanganate solution. The metal in the metal salt solution is

(A) copper (B) aluminium (C) lead (D) iron

50. Which of the following compound on reaction with NaOH and Na_2O_2 gives yellow colour?

(A) $Cr(OH)_3$ (B) $Zn(OH)_2$ (C) $Al(OH)_3$ (D) None of these

GROUP - IV

51. Colour of nickel chloride solution is

(A) pink (B) black (C) colourless (D) green

52. Dimethyl glyoxime in a suitable solvent was refluxed for 10 minutes with pure pieces of nickel sheet, it will result in

(A) Red ppt (B) Blue ppt. (C) Yellow ppt. (D) No ppt.

53. Which one of the following does not produce metallic sulphide with H_2S?

(A) $ZnCl_2$(Neutral sol^n) (B) $CdCl_{2(aq)}$ (C) $CoCl_{2(aq)}$ (D) $CuCl_{2(aq)}$

54. Which is not dissolved by dil HCl?

(A) ZnS (B) MnS (C) $BaSO_3$ (D) $BaSO_4$

GROUP - V

55. In III group, NH_4Cl is added to decrease concentation of hydroxide ion by NH_4OH. We do not add $(NH_4)_2SO_4$ along with NH_4OH because -

(A) $(NH_4)_2SO_4$ is insoluble in water (B) It precipitate other insoluble sulphates

(C) It is weak electrolyte (D) None of these

GROUP - VI

56. A metal is burnt in air and the ash on moistening smells of ammonia. The metal is

(A) Na (B) Fe (C) Mg (D) Al

57. A metal 'X' on heating in nitrogen gas gives 'Y' . 'Y' on treatment with H_2O gives a colourless gas which when passed through $CuSO_4$ solution gives a blue colour Y is:

(A) $Mg(NO_3)_2$ (B) Mg_3N_2 (C) NH_3 (D) MgO

MISCELLANEOUS

58. Na_2HPO_4 + Reagent 'M' → white ppt. The reagent 'M' is -

(A) $BaCl_2$ solution (B) $AlCl_3$ solution (C) $MnSO_4$ solution (D) $FeCl_3$ solution

59. A white solid is first heated with dil H_2SO_4 and then with conc. H_2SO_4. No action was observed in either case. The solid salt contains

(A) sulphide (B) sulphite (C) thiosulphate (D) sulphate

60. A mixture of chlorides of copper, cadmium, chromium, iron and aluminium was dissolved in water acidified with HCl and hydrogen sulphide gas was passed for sufficient time. It was filtered, boiled and a few drops of nitric acid were added while boiling. To this solution ammonium chloride and sodium hydroxide were added in excess and filtered. The filtrate shall give test for

(A) sodium and iron ion (B) sodium, chromium and aluminium ion

(C) aluminium and iron ion (D) sodium, iron, cadmium and aluminium ion

61. In Nessler's reagent, the ion present is:

(A) HgI^{2-} (B) HgI_4^{2-} (C) Hg^+ (D) Hg^{2+}

62. The cations present in slightly acidic solution are Fe^{3+}, Zn^{2+} and Cu^{2+}. The reagent which when added in excess to this solution would identify and separte Fe^{3+} in one step is:

(A) 2 M HCl (B) 6 M NH_3 (C) 6 M NaOH (D) H_2S gas

63. In the separation of Cu^{2+} and Cd^{2+} in 2nd group qualitative analysis of cation, tetrammine copper (II) sulphate and tetrammine cadmium (II) sulphate react with KCN to form the corresponding cyano complexes. Which one of the following pairs of the complexes and their relative stability enables the separation of Cu^{2+} and Cd^{2+}?

(A) $K_3[Cu(CN)_4]$ more stable and $K_2[Cd(CN)_4]$ less stable.

(B) $K_2[Cu(CN)_4]$ less stable and $K_2[Cd(CN)_4]$ more stable.

(C) $K_2[Cu(CN)_4]$ more stable and $K_2[Cd(CN)_4]$ less stable.

(D) $K_3[Cu(CN)_4]$ less stable and $K_2[Cd(CN)_4]$ more stable.

64. Which one has the minimum solubility product?

(A) AgCl (B) $AlCl_3$ (C) $BaCl_2$ (D) NH_4Cl

65. Which of the following sulphate is insoluble in water?

(A) $CuSO_4$ (B) $CdSO_4$ (C) $PbSO_4$ (D) $Bi_2(SO_4)_3$

66. Which of the following gives blood red colour with KSCN?

(A) Cu^{2+} (B) Fe^{3+} (C) Al^{3+} (D) Zn^{2+}

67. Which one of the following metal sulphide has maximum solubility in water?

(A) HgS, $K_{sp} = 10^{-54}$ (B) CdS, $K_{sp} = 10^{-30}$

(C) FeS, $K_{sp} = 10^{-20}$ (D) ZnS, $K_{sp} = 10^{-22}$

68. Identify the correct order of solubility of Na_2S, CuS and ZnS in aqueous medium is:

(A) CuS > ZnS > Na_2S (B) ZnS > Na_2S > CuS

(C) Na_2S > CuS > ZnS (D) Na_2S > ZnS > CuS

69. Match the column -

Column-I **(Element)**	**Column-II** **(Correct characteristics)**
(A) Ba	(P) cation in solution produces brick red ppt. with CrO_4^{2-}
(B) Pb	(Q) cation in solution produces yellow ppt .with CrO_4^{2-}
(C) Ag	(R) corresponding salt produces apple green colour in the flame test
(D) Ca	(S) corresponding salt produces brick red colour in the flame test
	(T) cation in solution produces no ppt. with CrO_4^{2-} ion

70.

Column-I **Cation in solution**	**Column-I** **Correct characteristics when no where excess reagent is used**
(A) Ag^+ and Pb^{2+}	(P) can be distinguished by Na_2HPO_4 solution
(B) Zn^{2+} and Mg^{2+}	(Q) can be distinguished by dil.HCl
(C) Pb^{2+} and Hg_2^{2+}	(R) can be distinguished by KI solution
(D) Ag^+ and Fe^{3+}	(S) can not be distinguished by NH_4OH solution

The following column 1, 2, 3 represent the various tests carried out for identification of various group basic radicals, using various reagents and nature of reaction/properties of products observed. Answer the questions that follow

Column-1 - Cations/Basic Radical

Column-2 - Excess Reagent used with cation

Column-3 - Nature of Reaction/Properties of product formed

Column - 1 Cations	**Column - 2 Excess Reagent used with cation**	**Column - 3 Nature of Reaction/ Properties of product formed**
(I) Cu^{2+}	(i) KI (< 6M)	(P) Reduction of cation occurs
(II) Fe^{3+}	(ii) $K_4[Fe(CN)_6]$	(Q) Coloured complex formation
(III) Pb^{2+}	(iii) KCN	(R) Precipitation occurs
(IV) Ni^{2+}	(iv) NH_4OH	(S) Diamagnetic & square planar complex formation

71. For a **group-II** basic radical, which is the only **INCORRECT** combination?
(A) (I), (i), (P) (B) (IV), (iii), (S) (C) (III), (iv), (R) (D) (III), (iii), (R)

72. For a **group-IV** basic radical, which is the only **CORRECT** combination?
(A) (I), (iv), (S) (B) (IV), (iii), (P) (C) (II), (iv), (Q) (D) (IV), (iv), (Q)

73. Which combination has a entirely different colour from others?
(A) (IV), (iv), (Q) (B) (I), (iv), (Q) (C) (II), (iii), (Q) (D) (II), (ii), (Q)

74. How many of the following gives green ppt.
(i) $CrCl_3 + NaOH \rightarrow$ (ii) $CrCl_3$ + excess $NaOH \rightarrow$
(iii) $NiCl_2$ + excess $NaOH \rightarrow$ (iv) $NiCl_2$ + excess $NH_4OH \rightarrow$
(v) $Hg_2^{2+} + KI \rightarrow$

75. Find the no. of cation which gives white ppt with $K_4[Fe(CN)_6]$
Sr^{2+} Ca^{2+}, Zn^{2+}, Fe^{3+} , Cu^{2+}

EXERCISE # JEE MAINS

1. Which products are expected from the disproportionation of hypochlorous acid : **[AIEEE-2002]**

(1) $HClO_3$ and Cl_2O (2) $HClO_2$ and $HClO$ (3) HCl and Cl_2O (4) HCl and $HClO_3$

2. A metal M readily forms its sulphate MSO_4 which is water soluble. It forms oxide MO which becomes inert on heating. It forms insoluble hydroxide which is soluble in NaOH. The metal M is:- **[AIEEE-2002]**

(1) Mg (2) Ba (3) Ca (4) Be

3. Which statement is correct :- **[AIEEE-2003]**

(1) Fe^{3+} ions give deep green precipitate with $K_4[Fe(CN)_6]$

(2) On heating K^+, Ca^{2+} and HCO_3^- ions, we get a precipitate of $K_2[Ca(CO_3)_2]$

(3) Manganese salts give a violet borax bead test in reducing flame

(4) From a mixed precipitate of AgCl and AgI ammonia solution dissolves only AgCl

4. What would happen when a solution of potassium chromate is treated with an excess of dilute nitric acid - **[AIEEE-2003]**

(1) Cr^{3+} and $Cr_2O_7^{2-}$ are formed (2) $Cr_2O_7^{2-}$ and H_2O are formed

(3) $Cr_2O_7^{2-}$ is reduced to +3 state of Cr (4) $Cr_2O_7^{2-}$ is oxidised to +7 state of Cr

5. Ammonia forms the complex ion $[Cu(NH_3)_4]^{2+}$ with copper ions in alkaline solutions but not in acidic solution. What is the reason for it :- **[AIEEE-2003]**

(1) In acidic solutions hydration protects copper ions

(2) In acidic solutions protons coordinate with ammonia molecules forming NH_4^+ ions and NH_3 molecules are not available

(3) In alkaline solutions insoluble $Cu(OH)_2$ is precipitated which is soluble in excess of any alkali

(4) Copper hydroxide is an amphoteric substance

6. Excess of KI reacts with $CuSO_4$ solution and then $Na_2S_2O_3$ solution is added to it. Which of the statements is incorrect for this reaction : **[AIEEE-2004]**

(1) Evolved I_2 is reduced (2) CuI_2 is formed

(3) $Na_2S_2O_3$ is oxidised (4) Cu_2I_2 is formed

7. Calomel on reaction with NH_4OH gives **[AIEEE-2004]**

(1) $HgNH_2Cl$ (2) $NH_2–Hg–Hg–Cl$ (3) Hg_2O (4) HgO

8. One mole of magnesium nitride on reaction with excess of water gives :- **[AIEEE-2004]**

(1) Two mole of HNO_3 (2) Two mole of NH_3

(3) 1 mole of NH_3 (4) 1 mole of HNO_3

9. The products obtained on heating $LiNO_3$ will be :- **[AIEEE-2011]**

(1) $LiNO_2 + O_2$ (2) $Li_2O + NO_2 + O_2$

(3) $Li_3N + O_2$ (4) $Li_2O + NO + O_2$

10. What is the best description of the change that occurs when $Na_2O(s)$ is dissolved in water ? **[AIEEE-2011]**

(1) Oxidation number of sodium decreases

(2) Oxide ion accepts sharing in a pair of electrons

(3) Oxide ion donates a pair of electrons

(4) Oxidation number of oxygen increases

11. Which of the following on thermal-decomposition yields a basic as well as an acidic oxide ? **[AIEEE-2012]**

(1) NH_4NO_3 (2) $NaNO_3$ (3) $KClO_3$ (4) $CaCO_3$

12. The correct statement for the molecule, CsI_3, is: **[JEE(Main)-2014]**

(1) it contains Cs^{3+} and I^- ions (2) it contains Cs^+, I^- and lattice I_2 molecule

(3) it is a covalent molecule (4) it contains Cs^+ and I_3^- ions

13. A metal M on heating in nitrogen gas gives Y. Y on treatment with H_2O gives a colourless gas which when passed through $CuSO_4$ solution gives a blue colour, Y is :-

[JEE(Main)-2012 online_P-4]

(1) NH_3 (2) MgO (3) Mg_3N_2 (4) $Mg(NO_3)_2$

14. Potassium dichromate when heated with concentrated sulphuric acid and a soluble chloride, gives brown - red vapours of: **[JEE(Main)-2013 online_P-1]**

(1) CrO_3 (2) Cr_2O_3 (3) $CrCl_3$ (4) CrO_2Cl_2

15. Sodium Carbonate cannot be used in place of $(NH_4)_2CO_3$ for the identification of Ca^{2+} , Ba^{2+} and Sr^{2+} ions (in group V) during mixture analysis because : **[JEE(Main)-2013 online_P-1]**

(1) Sodium ions will react with acid radicals (2) Concentration of CO_3^{2-} ions is very low

(3) Mg^{2+} ions will also be precipitated

(4) Na^+ ions will interfere with the detection of Ca^{2+}, Ba^{2+}, Sr^{2+} ions

16. Which of the following statements is incorrect? **[JEE(Main)-2013 online_P-2]**

(1) Fe^{2+} ion also gives blood red colour with SCN^- ion

(2) Cupric ion reacts with excess of ammonia solution to give deep blue colour of $[Cu(NH_3)_4]^{2+}$ ion.

(3) Fe^{3+} ion gives blood red colour with SCN^- ion.

(4) On passing H_2S into Na_2ZnO_2 solution, a white ppt of ZnS is formed.

17. Identify incorrect statement **[JEE(Main)-2013 online_P-3]**

(1) Copper (I) compounds are colourless except where colour results from charge transfer

(2) Copper (I) compounds are diamagnetic

(3) Cu_2S is black (4) Cu_2O is colourless

18. Which one of the following cannot function as an oxidising agent ?

[JEE(Main)-2013 online_P-4]

(1) $NO_3^-(aq)$ (2) I^- (3) $Cr_2O_7^{2-}$ (4) $S_{(S)}$

19. Which of the following statements about Na_2O_2 is **not** correct ? **[JEE(Main)-2014 online_P-2]**

(1) Na_2O_2 oxidises Cr^{3+} to CrO_4^{2-} in acid medium (2) It is diamagnetic in nature

(3) It is the super oxide of sodium (4) It is a derivative of H_2O_2

20. Consider the following equilibrium **[JEE(Main)-2014 online_P-2]**

$$AgCl\downarrow + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ + Cl^-$$

White precipitate of AgCl appears on adding which of the following?

(1) NH_3 (2) Aqueous NaCl (3) Aqueous NH_4Cl (4) Aqueous HNO_3

21. Consider the reaction **[JEE(Main)-2014 online_P-4]**

$$H_2SO_{3(aq)} + Sn^{4+}_{(aq)} + H_2O_{(l)} \rightarrow Sn^{2+}_{(aq)} + HSO^-_{4(aq)} + 3H^+_{(aq)}$$

Which of the following statements is correct?

(1) H_2SO_3 is the reducing agent because it undergoes oxidation

(2) H_2SO_3 is the reducing agent because it undergoes reduction

(3) Sn^{4+} is the reducing agent because it undergoes oxidation

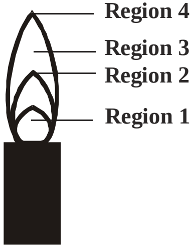
(4) Sn^{4+} is the oxidizing agent because it undergoes oxidation

22. Amongst the following, identify the species with an atom in +6 oxidation state :

[JEE(Main)-2014 online_P-4]

(1) $[MnO_4]^-$ (2) $[Cr(CN)_6]^{3-}$ (3) Cr_2O_3 (4) CrO_2Cl_2

23. The hottest region of Bunsen flame shown in the figure below is : **[JEE(Main)-2016]**



(1) region 4

(2) region 1

(3) region 2

(4) region 3

24. Sodium extract is heated with concentrated HNO_3 before testing for halogens because :
(1) S^{2-} and CN^-, if present are decomposed by conc. HNO_3 and hence do not interfere in the test.
(2) Ag reacts faster with halides in acidic medium **[JEE(Main)-2016 online]**
(3) Ag_2S and AgCN are soluble in acidic medium.
(4) Silver halides are totally insoluble in nitric acid.

25. In the following reactions, ZnO is respectively acting as a/an :
(a) $ZnO + Na_2O \rightarrow Na_2ZnO_2$ (b) $ZnO + CO_2 \rightarrow ZnCO_3$ **[JEE(Main)-2017 off line]**
(1) base and acid (2) base and base (3) acid and acid (4) acid and base

26. The products obtained when chlorine gas reacts with cold and dilute aqueous NaOH are :-
(1) ClO^- and ClO_3^- (2) ClO_2^- and ClO_3^- **[JEE(Main)-2017 off line]**
(3) Cl^- and ClO^- (4) Cl^- and ClO_2^-

27. Sodium salt of an organic acid 'X' produces effervescence with conc. H_2SO_4. 'X' reacts with the acidified aqueous $CaCl_2$ solution to give a white precipitate which decolourises acidic solution of $KMnO_4$. 'X' is :- **[JEE(Main)-2017 off line]**
(1) C_6H_5COONa (2) HCOONa (3) CH3COONa (4) $Na_2C_2O_4$

28. 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 : **[JEE(Main)-2017 on line]**
(1) Mn^{2+} (2) Zn^{2+} (3) Ni^{2+} (4) Co^{2+}

29. Which of the following ions does **not** liberate hydrogen gas on reaction with dilute acids?
(1) Ti^{2+} (2) Cr^{2+} **[JEE(Main)-2017 on line]**
(3) Mn^{2+} (4) V^{2+}

30. When metal 'M' is treated with NaOH, a white gelatinous precipitate 'X' is obtained, which is soluble in excess of NaOH. Compound 'X' when heated strongly gives an oxide which is used in chromatography as an adsorbent. The metal 'M' is **[JEE(Main)-2018 off line]**
(1) Ca (2) Al (3) Fe (4) Zn

31. 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 : **[JEE(Main)-2018 on line]**
(1) S^{2-} (2) SO_4^{2-} (3) CO_3^{2-} (4) Cl^-

32. The incorrect statement is :- **[JEE(Main)-2018 on line]**
(1) Ferric ion gives blood red colour with potassium thiocyanate.
(2) Cu^{2+} and Ni^{2+} ions give black precipitate with H_2S in presence of HCl solution.
(3) Cu^{2+} salts give red coloured borax bead test in reducing flame.
(4) Cu^{2+} ion gives chocolate coloured precipitate with potassium ferrocyanide solution.

33. When XO_2 is fused with an alkali metal hydroxide in presence of an oxidizing agent such as KNO_3; a dark green product is formed which disproportionates in acidic solution to afford a dark purple solution. X is : **[JEE(Main)-2018 on line]**
(1) Ti (2) Cr (3) V (4) Mn

EXERCISE # J-ADVANCED

1. Which of the following statement(s) is (are) correct with reference to the ferrous and ferric ions:

(A) Fe^{3+} gives brown colour with potassium ferricyanide **[JEE 1998]**

(B) Fe^{2+} gives blue precipitate with potassium ferricyanide

(C) Fe^{3+} give red colour with potassium thiocyanate

(D) Fe^{2+} gives brown colour with ammonium thiocyanate

2. Which of the following statement(s) is /are correct. When a mixture of NaCl and $K_2Cr_2O_7$ is gently warmed with conc. H_2SO_4? **[JEE 1998]**

(A) A deep red vapours is evolved.

(B) The vapours when passed into NaOH solution gives a yellow solution of Na_2CrO_4

(C) Chlorine gas is evolved

(D) Chromyl chloride is formed.

3. An aqueous solution of a substance gives a white precipitate on treatment with dilute hydrochloric acid, which dissolves on heating. When hydrogen sulphide is passed through the hot acidic solution, a black precipitate is obtained. The substance is a : **[JEE 2000]**

(A) Hg_2^{+} salt (B) Cr^{2+} salt (C) Ag^{+} salt (D) Pb^{2+} salt

4. A gas 'X' is passed through water to form a saturated solution. The aqueous solution on treatment with silver nitrate gives a white precipitate. The saturated aqueous solution also dissolves magnesium ribbon with evolution of a colourless gas 'Y'. Identify 'X' and 'Y': **[JEE 2002(Mains)]**

(A) $X = CO_2$, $Y = Cl_2$ (B) $X = Cl_2$, $Y = CO_2$

(C) $X = Cl_2$, $Y = H_2$ (D) $X = H_2$, $Y = Cl_2$

5. $[X] + H_2SO_4 \rightarrow [Y]$ a colourless gas with irritating smell **[JEE 2003]**

$[Y] + K_2Cr_2O_7 + H_2SO_4 \longrightarrow$ green solution

[X] and [Y] are:

(A) SO_3^{2-}, SO_2 (B) Cl^-, HCl (C) S^{2-}, H_2S (D) CO_3^{2-}, CO_2

6. A sodium salt of an unknown anion when treated with $MgCl_2$ give white precipitate only on boiling. The anion is: **[JEE 2004]**

(A) SO_4^{2-} (B) HCO_3^- (C) CO_3^{2-} (D) NO_3^-

7. $(NH_4)_2Cr_2O_7$ on heating gives a gas which is also given by: **[JEE 2004]**

(A) heating NH_4NO_2 (B) heating NH_4NO_3

(C) $Mg_3N_2 + H_2O$ (D) $NaNO_2 + H_2O_2$

8. A metal nitrate reacts with KI to give a black precipitate which on addition of excess of KI convert into orange colour solution. The cation of metal nitrate is: **[JEE 2005]**

(A) Hg^{2+} (B) Bi^{3+} (C) Pb^{2+} (D) Cu^{+}

9. A solution when diluted with H_2O and boiled, it gives a white precipitate. On addition of excess NH_4Cl / NH_4OH, the volume of precipitate decreases leaving behind a white gelatinous precipitate. Identify the precipitate which dissolves in NH_4OH / NH_4Cl. **[JEE 2006]**

(A) $Zn(OH)_2$ (B) $Al(OH)_3$ (C) $Mg(OH)_2$ (D) $Ca(OH)_2$

10. $CuSO_4$ decolourises on addition of excess KCN, the product is: **[JEE 2006]**

(A) $[Cu(CN)_4]^{2-}$ (B) Cu^{2+} get reduced to form $[Cu(CN)_4]^{3-}$

(C) $Cu(CN)_2$ (D) CuCN

11. Consider a titration of potassium dichromate solution with acidified Mohr's salt solution using diphenylamine as indicator. The number of moles of Mohr's salt required per mole of dichromate is: **[JEE 2007]**

(A) 3 (B) 4 (C) 5 (D) 6

12. The species present in solution when CO_2 is dissolved in water are **[JEE 2007]**

(A) $CO_2, H_2CO_3, HCO_3^-, CO_3^{2-}$ (B) H_2CO_3, CO_3^{2-}

(C) CO_3^{2-}, HCO_3^- (D) CO_2, H_2CO_3

13. Sodium fusion extract, obtained from aniline, on treatment with iron (II) sulphate and H_2SO_4 in presence of air gives a Prussian blue precipitate. The blue colour is due to the formation of : **[JEE 2007]**

(A) $Fe_4[Fe(CN)_6]_3$ (B) $Fe_3[Fe(CN)_6]_2$

(C) $Fe_4[Fe(CN)_6]_2$ (D) $Fe_3[Fe(CN)_6]_3$

14. **[JEE 2007]**

Column I	**Column II**
(A) $O_2^- \rightarrow O_2 + O_2^{2-}$	(P) Redox reaction
(B) $CrO_4^{2-} + H^+ \rightarrow$	(Q) One of the products has trigonal planar structure
(C) $MnO_4^- + NO_2^- + H^+ \rightarrow$	(R) Dimeric bridged tetrahedral metal ion
(D) $NO_3^- + H_2SO_4 + Fe^{2+} \rightarrow$	(S) Disproportionation

15. A solution of a metal ion when treated with KI gives a red precipitate which dissolves in excess KI to give a colourless solution. Moreover, the solution of metal ion on treatment with a solution of cobalt (II) thiocyanate gives rise to a deep blue crystalline precipitate. The metal ion is **[JEE 2007]**

(A) Pb^{2+} (B) Hg^{2+} (C) Cu^{2+} (D) Co^{2+}

16. A solution of colourless salt H on boiling with excess NaOH produces a non-flammable gas. The gas evolution ceases after sometime. Upon addition of Zn dust to the same solution, the gas evolution restarts. The colourless salt(s) H is (are) **[JEE 2008]**

(A) NH_4NO_3 (B) NH_4NO_2 (C) NH_4Cl (D) $(NH_4)_2SO_4$

Paragraph for Question Nos. 17 to 19

p-Amino-N, N-dimethylaniline is added to a strongly acidic solution of **X**. The resulting solution is treated with a few drops of aqueous solution of **Y** to yield blue coloration due to the formation of methylene blue. Treatment of the aqueous solution of **Y** with the reagent potassium hexacyanoferrate(II) leads to the formation of an intense blue precipitate. The precipitate dissolves on excess addition of the reagent. Similarly, treatment of the solution of **Y** with the solution of potassium hexacyanoferrate(III) leads to a brown coloration due to the formation of **Z**. **[JEE 2009]**

17. The compound **X** is

(A) $NaNO_3$ (B) NaCl (C) Na_2SO_4 (D) Na_2S

18. The compound **Y** is

(A) $MgCl_2$ (B) $FeCl_2$ (C) $FeCl_3$ (D) $ZnCl_2$

19. The compound Z is

(A) $Mg_2[Fe(CN)_6]$ (B) $Fe[Fe(CN)_6]$ (C) $Fe_4[Fe(CN)_6]_3$ (D) $K_2Zn_3[Fe(CN)_6]_2$

20. Match each of the reactions given in Column I with the corresponding product(s) given in Column II.

[JEE 2009]

Column I	**Column II**
(A) Cu + dil. HNO_3	(P) NO
(B) Cu + conc. HNO_3	(Q) NO_2
(C) Zn + dil. HNO_3	(R) N_2O
(D) Zn + conc. HNO_3	(S) $Cu(NO_3)_2$
	(T) $Zn(NO_3)_2$

21. Passing H_2S gas into a mixture of Mn^{2+}, Ni^{2+}, Cu^{2+} and Hg^{2+} ions in an acidified aqueous solution precipitates **[JEE 2011]**

(A) CuS and HgS (B) MnS and CuS (C) MnS and NiS (D) NiS and HgS

22. Reduction of the metal centre in aqueous permanganate ion involves - **[JEE 2011]**

(A) 3 electrons in neutral medium (B) 5 electrons in neutral medium

(C) 3 electrons in weak alkaline medium (D) 5 electrons in acidic medium

23. The equilibrium **[JEE 2011]**

$$2Cu^{I} \rightleftharpoons Cu^{o} + Cu^{II}$$

in aqueous medium at 25°C shifts towards the left in the presence of

(A) NO_3^- (B) Cl^- (C) SCN^- (D) CN^-

Paragraph for Questions Nos. 24 to 26

When a metal rod M is dipped into an aqueous colourless concentrated solution of compound N, the solution turns light blue. Addition of aqueous NaCl to the blue solution gives a white precipitate O. Addition of aqueous NH_3 dissolves O and gives are intense blue solution. **[JEE 2011]**

24. The metal rod M is -

(A) Fe (B) Cu (C) Ni (D) Co

25. The compound N is -

(A) $AgNO_3$ (B) $Zn(NO_3)_2$ (C) $Al(NO_3)_3$ (D) $Pb(NO_3)_2$

26. The final solution contains -

(A) $[Pb(NH_3)_4]^{2+}$ and $[CoCl_4]^{2-}$ (B) $[Al(NH_3)_4]^{3+}$ and $[Cu(NH_3)_4]^{2+}$

(C) $[Ag(NH_3)_2]^{+}$ and $[Cu(NH_3)_4]^{2+}$ (D) $[Ag(NH_3)_2]^{+}$ and $[Ni(NH_3)_6]^{2+}$

27. Which of the following hydrogen halides react(s) with $AgNO_3$(aq) to give a precipitate that dissolves in $Na_2S_2O_3$(aq): **[JEE 2012]**

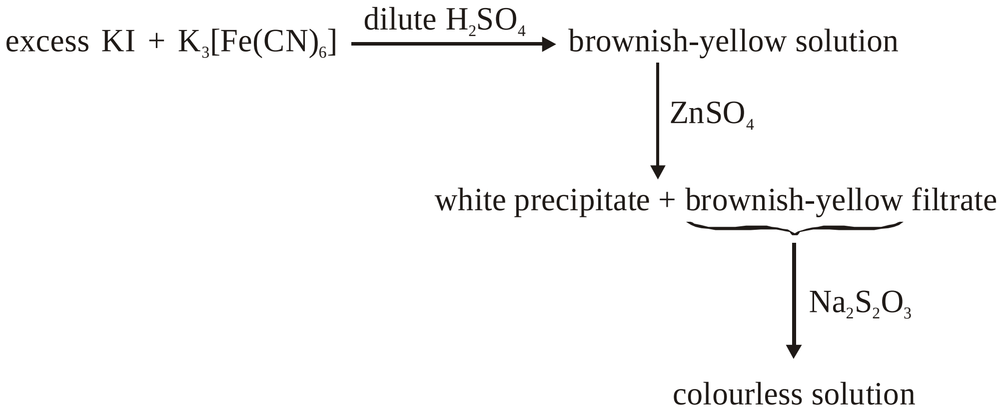
(A) HCl (B) HF (C) HBr (D) HI

28. The reaction of white phosphorus with aqueous NaOH gives phosphine along with another phosphorus containing compound. The reaction type ; the oxidation states of phosphorus in phosphine and the other product are respectively **[JEE 2012]**

(A) redox reaction ; –3 and –5 (B) redox reaction ; +3 and +5

(C) disproportionation reaction ; –3 and +1 (D) disproportionation reaction ; –3 and +3

29. For the given aqueous reactions, which of the statement(s) is (are) true ? **[JEE 2012]**



(A) The first reaction is a redox reaction.

(B) White precipitate is $Zn_3[Fe(CN)_6]_2$.

(C) Addition of filtrate to starch solution gives blue colour.

(D) White precipitate is soluble in NaOH solution.

30. Upon treatment with ammonical H_2S , the metal ion that precipitates as a sulfide is -

(A) Fe(III) (B) Al(III) (C) Mg(II) (D) Zn (II) **[JEE 2013]**

Paragraph for Question 31 and 32

An aqueous solution of a mixture of two inorganic salts, when treated with dilute HCl, gave a precipitate **(P)** and a filtrate **(Q)**. The precipitate **(P)** was found to dissolve in hot water. The filtrate **(Q)** remained unchanged, when treated with H_2S in a dilute mineral acid medium. However, it gave a precipitate **(R)** with H_2S in an ammoniacal medium. The precipitate R gave a coloured solution **(S)**, when treated with H_2O_2 in an aqueous NaOH medium. **[JEE 2013]**

31. The coloured solution **(S)** contains

(A) $Fe_2(SO_4)_3$ (B) $CuSO_4$ (C) $ZnSO_4$ (D) Na_2CrO_4

32. The precipitate **(P)** contains

(A) Pb^{2+} (B) Hg_2^{2+} (C) Ag^+ (D) Hg^{2+}

33. Consider the following list of reagents : **[JEE Adv. 2014]**

Acidified $K_2Cr_2O_7$, alkaline $KMnO_4$, $CuSO_4$, H_2O_2 , Cl_2, O_3, $FeCl_3$, HNO_3 and $Na_2S_2O_3$.

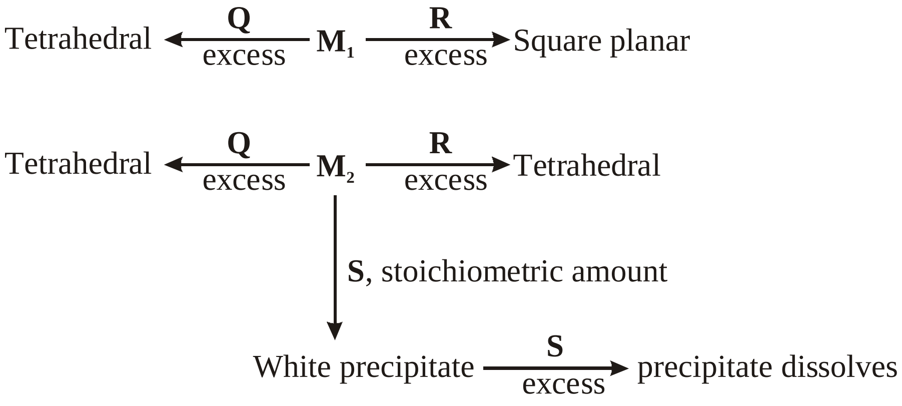
The total number of reagents that can oxidise aqueous iodide to iodine is

34. Among PbS, CuS, HgS, MnS, Ag_2S, NiS, CoS, Bi_2S_3 , and SnS_2 the total number of **BLACK** coloured sulphides is **[JEE Adv. 2014]**

Paragraph for Q.No. 35 to 36

An aqueous solution of metal ion $\mathbf{M_1}$ reacts separately with reagents **Q** and **R** in excess to give tetrahedral and square planar complexes, respectively. An aqueous solution of another metal ion $\mathbf{M_2}$ always forms tetrahedral complexes with these reagents. Aqueous solution of $\mathbf{M_2}$ on reaction with reagent **S** gives white precipitate which dissolves in excess of **S**. The reactions are summarized in the scheme given below. **[JEE Adv. 2014]**

SCHEME:



35. $\mathbf{M_1}$, **Q** and **R**, respectively are

(A) Zn^{2+}, KCN and HCl (B) Ni^{2+}, HCl and KCN

(C) Cd^{2+} , KCN and HCl (D) Co^{2+}, HCl and KCN

36. Reagent **S** is

(A) $K_4[Fe(CN)_6]$ (B) Na_2HPO_4 (C) K_2CrO_4 (D) KOH

37. Fe^{3+} is reduced to Fe^{2+} by using - **[JEE Adv. 2015]**

(A) H_2O_2 in presence of NaOH (B) Na_2O_2 in water

(C) H_2O_2 in presence of H_2SO_4 (D) Na_2O_2 in presence of H_2SO_4

38. The pair(s) of ions where BOTH the ions are precipitated upon passing H_2S gas in presence of dilute HCl, is(are) **[JEE Adv. 2015]**

(A) Ba^{2+}, Zn^{2+} (B) Bi^{3+}, Fe^{3+} (C) Cu^{2+}, Pb^{2+} (D) Hg^{2+}, Bi^{3+}

39. The reagent(s) that can selectively precipitate S^{2-} from a mixture of S^{2-} and SO_4^{2-} in aqueous soltuion is(are) : **[JEE(Adv.)-2016]**

(A) $CuCl_2$ (B) $BaCl_2$ (C) $Pb(OOCCH_3)_2$ (D) $Na_2[Fe(CN)_5NO]$

40. In the following reaction sequence in aqueous soluiton, the species **X**, **Y** and **Z** respectively, are - **[JEE(Adv.)-2016]**

$$S_2O_3^{2-} \xrightarrow{Ag^+} \underset{\substack{\text{clear}\\\text{solution}}}{X} \xrightarrow{Ag^+} \underset{\substack{\text{white}\\\text{precipitate}}}{Y} \xrightarrow{\text{With time}} \underset{\substack{\text{black}\\\text{precipitate}}}{Z}$$

(A) $[Ag(S_2O_3)_2]^{3-}$, $Ag_2S_2O_3$, Ag_2S (B) $[Ag(S_2O_3)_3]^{5-}$, Ag_2SO_3, Ag_2S

(C) $[Ag(SO_3)_2]^{3-}$, $Ag_2S_2O_3$, Ag (D) $[Ag(SO_3)_3]^{3-}$, Ag_2SO_4, Ag

41. Which of the following combination will produce H_2 gas ? **[JEE(Adv.)-2017]**

(A) Zn metal and NaOH(aq) (B) Au metal and NaCN(aq) in the presence of air

(C) Cu metal and conc. HNO_3 (D) Fe metal and conc. HNO_3

42. Addition of excess aqueous ammonia to a pink coloured aqueous solution of $MCl_2 . 6H_2O$ (X) and NH_4Cl gives an octahedral complex Y in the presence of air. In aqueous solution, complex Y behaves as 1 : 3 electrolyte. The reaction of X with excess HCl at room temperature results in the formation of a blue coloured complex Z. The calculated spin only magnetic moment of X and Z is 3.87 B.M., whereas it is zero for complex Y. **JEE(Adv.)-2017]**

Among the following options, which statements is(are) correct ?

(A) The hybridization of the central metal ion in Y is d^2sp^3

(B) Z is tetrahedral complex

(C) Addition of silver nitrate to Y gives only two equivalents of silver chloride

(D) When X and Z are in equilibrium at 0°C, the colour of the solution is pink

43. The correct option(s) to distinguish nitrate salts of Mn^{2+} and Cu^{2+} taken separately is (are) :-

(A) Mn^{2+} shows the characteristic green colour in the flame test **JEE(Adv.)-2018]**

(B) Only Cu^{2+} shows the formation of precipitate by passing H_2S in acidic medium

(C) Only Mn^{2+} shows the formation of precipitate by passing H_2S in faintly basic medium

(D) Cu^{2+}/Cu has higher reduction potential than Mn^{2+}/Mn (measured under similar conditions)

44. The green colour produced in the borax bead test of a chromium(III) salt is due to-

JEE(Adv.)-2019]

(A) $Cr(BO_2)_3$ (B) CrB (C) $Cr_2(B_4O_7)_3$ (D) Cr_2O_3

ANSWER-KEY

EXERCISE # I

1. (A) 2. (C) 3. (C) 4. (D) 5. (D) 6. (A,B)

7. (A) → R,S; (B) → Q; (C) → P,Q,S,T; (D) → P,Q,S,T 8. (1)

9. (D) 10. (D) 11. (C) 12. (D) 13. (B) 14. (C) 15. (B)

16. (A) 17. (C) 18. (B) 19. (B) 20. (D) 21. (C) 22. (A)

23. (B) 24. (B) 25. (D) 26. (B) 27. (C) 28. (A,B) 29. (A)

30. (C) 31. (2) 32. (4) 33. (2) 34. (D) 35. (B) 36. (D)

37. (C) 38. (C) 39. (C,D) 40. (B) 41. (B) 42. (D) 43. (D)

EXERCISE # II

1. (B) 2. (C) 3. (C) 4. (A) 5. (B) 6. (B) 7. (B)

8. (B) 9. (B) 10. (D) 11. (B) 12. (B) 13. (A,B,C,D) 14. (C)

15. (C) 16. (C) 17. (B) 18. (B) 19. (B) 20. (D) 21. (C)

22. (B) 23. (B) 24. (D) 25. (C) 26. (B) 27. (C) 28. (C)

29. (C) 30. (B) 31. (A) 32. (B) 33. (D) 34. (D) 35. (C)

36. (B) 37. (D) 38. (C) 39. (D) 40. (A) 41. (C) 42. (A,C,D)

43. (C) 44. (A) 45. (A,B,C) 46. (B,C,D) 47. (A,C,D) 48. (B,D) 49. (D)

50. (A) 51. (D) 52. (D) 53. (A,C) 54. (D) 55. (B) 56. (C)

57. (B) 58. (A,B) 59. (D) 60. (B) 61. (B) 62. (B) 63. (A)

64. (A) 65. (C) 66. (B) 67. (C) 68. (D)

69. (A) → Q , R; (B) → Q ; (C) → P ; (D) → S , T 70. (A) → P ; (B) → S ; (C) → R ; (D) → Q, R

71. (B) 72. (D) 73. (C) 74. (3) 75. (2)

EXERCISE # JEE MAINS

1. (4) 2. (4) 3. (4) 4. (2) 5. (2) 6. (2) 7. (1)

8. (2) 9. (2) 10. (3) 11. (4) 12. (4) 13. (3) 14. (4)

15. (3) 16. (1) 17. (4) 18. (2) 19. (3) 20. (4) 21. (1)

22. (4) 23. (3) 24. (1) 25. (4) 26. (3) 27. (4) 28. (2)

29. (3) 30. (2) 31. (4) 32. (2) 33. (4)

EXERCISE # J-ADVANCED

1. (A, B, C) 2. (A, B, D) 3. (D) 4. (C) 5. (A) 6. (B) 7. (A)

8. (B) 9. (A) 10. (B) 11. (D) 12. (A) 13. (A)

14. (A) → P , S ; (B) → R ; (C) → P , Q ; (D) → P 15. (B) 16. (A),(B) 17. (D)

18. (C) 19. (B) 20. (A) → P,S; (B) → Q,S; (C) → R,T; (D) → Q, T 21. (A)

22. (A,C,D) 23. (B,C,D) 24. (B) 25. (A) 26. (C) 27. (A,C,D) 28. (C)

29. (A,C,D) 30. (D) 31. (D) 32. (A) 33. (7) 34. (6) / (7) 35. (B)

36. (D) 37. (A, B) 38. (C,D) 39. (A OR A, C) 40. (A) 41. (A)

42. (A,B,D) 43. (B,D) 44. (A)

HEATING EFFECTS

1. HEATING EFFECT OF CARBONATE & BICARBONATE SALTS :

(a) Heating effect of carbonate salts :

Metal carbonate $\xrightarrow{\Delta}$ metal oxide + $CO_2\uparrow$

(i) $MCO_3 \xrightarrow{\Delta} MO + CO_2$ [M = Be, Mg, Ca, Sr, Ba]

(ii) $MgCO_3 \xrightarrow{\Delta} MgO + CO_2$

(iii)
$$\begin{tikzcd}
\underbrace{Cu(OH)_2.CuCO_3}_{\text{Basic Cu(II) carbonate}} \arrow[r, "\Delta"] & \underset{\text{(black)}}{2CuO} + CO_2 + H_2O \arrow[d, "\text{high temperature}"] \\
 & \underset{\text{(red)}}{Cu_2O} + O_2
\end{tikzcd}$$

(iv) $\underset{\text{white}}{ZnCO_3} \xrightarrow{\Delta} \underset{\substack{\text{Yellow(hot)} \\ \text{white(cold)}}}{ZnO} + CO_2$

(v) $PbCO_3 \xrightarrow{\Delta} \underset{\text{Yellow}}{PbO} + CO_2$

(vi) $Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$

(vii) $\boxed{(NH_4)_2CO_3 \xrightarrow{\Delta} 2NH_3 + H_2O + CO_2 \quad \textbf{Very Important}}$

(viii)
$$\begin{tikzcd}
 & Pb_3O_4 + CO\uparrow + CO_2\uparrow + H_2O\uparrow \\
\underset{\text{White lead}}{Pb(OH)_2.2PbCO_3} \arrow[ru, "350^\circ C"] \arrow[rd, "700\text{–}800^\circ C"', "\text{Bunsen burner temperature}"] & \\
 & 3PbO + 2CO_2\uparrow + H_2O\uparrow
\end{tikzcd}$$

(ix) All carbonates **except** (Na, K, Rb, Cs) decompose on heating giving CO_2

(x) Carbonates salts of (Na, K, Rb, Cs) do not decompose on heating, they are melt on high temperature.

(xi) Oxides of heavier metals are less stable so further decompose into metal & oxygen

(xii) $\underset{\substack{\text{white} \\ \text{(yellowish white)}}}{Ag_2CO_3} \xrightarrow{\Delta} \underset{\text{Black}}{2Ag} + CO_2 + \frac{1}{2}O_2$

(xi) $HgCO_3 \xrightarrow{\Delta} Hg + \frac{1}{2}O_2\uparrow + CO_2$

(b) Heating effect of bicarbonate :

(i) $$\begin{tikzcd} \text{Metal bicarbonate} \arrow[r, "\Delta"] & \underset{\text{except (Na, K, Rb, Cs)}}{\text{metal carbonate} + CO_2\uparrow} \arrow[d] \\ & \text{metal oxide} + CO_2 \end{tikzcd}$$

(ii) [General reaction $2HCO_3^- \xrightarrow{\Delta} CO_3^{2-} + H_2O + CO_2$]

(iii) All bicarbonates decompose to give carbonates and CO_2. eg.

(iv) $2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + CO_2 + H_2O$

(v) $Mg(HCO_3)_2 \xrightarrow{\Delta} MgO + 2CO_2 + H_2O$

2. HEATING EFFECT OF HYDRATED SULPHATE SALTS :

(i) $$\begin{tikzcd} \underset{\text{(M=Be,Zn,Mg,Ca,Cu,Pb)}}{\text{Metal Sulphate}} \arrow[r, "\Delta"] & \text{Metal Oxide} + SO_3 \arrow[d, "T > 800^\circ C"] \\ & SO_2 + \frac{1}{2}O_2 \end{tikzcd}$$

$$\xrightarrow{1100^\circ C} \tfrac{1}{2}Cu_2O + \tfrac{1}{2}O_2$$

(ii) $$\begin{tikzcd} \underset{\text{Blue vitriol}}{CuSO_4.5H_2O} \arrow[r, "100^\circ C", "-4H_2O"'] & \underset{\text{Bluish White}}{CuSO_4.H_2O} \arrow[r, "220^\circ C", "-H_2O"'] & \underset{\text{White}}{CuSO_4} \arrow[r, ">800^\circ C"] \arrow[d, "750^\circ C"] & CuO + SO_2 + \frac{1}{2}O_2 \\ & & \underset{\text{Black}}{CuO} + SO_3 & \end{tikzcd}$$

(iii) $$\boxed{\underset{\text{Green vitriol}}{FeSO_4.7H_2O} \xrightarrow[-7H_2O]{300^\circ C} FeSO_4 \xrightarrow[\text{Strongly}]{\Delta} Fe_2O_3 + SO_2 + SO_3 \text{ (very important)}}$$

(iv) $Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 + 3SO_3$

(v) $$\begin{tikzcd} \underset{\text{gypsum}}{CaSO_4.2H_2O} \arrow[r, "120^\circ C-150^\circ C"] & \underset{\text{(Plaster of paris) or calcium sulphate hemihydrate}}{(CaSO_4.\frac{1}{2}H_2O) + 1\frac{1}{2}H_2O} \arrow[dl, "1\frac{1}{2}H_2O"'] \arrow[dr, "\Delta"] & \\ \underset{\text{another crystallographic form of gypsum hard \& porous}}{CaSO_4.2H_2O} & & \underset{\text{Dead burnt}}{CaSO_4 + \frac{1}{2}H_2O} \arrow[d, "1100^\circ C"] \\ & & CaO + SO_3 \end{tikzcd}$$

(vi) $ZnSO_4.7H_2O \xrightarrow[-H_2O]{70^\circ C} ZnSO_4.6H_2O \xrightarrow[-5H_2O]{70^\circ-200^\circ C} ZnSO_4.H_2O \xrightarrow[-H_2O]{>200^\circ C} ZnSO_4 \xrightarrow{\Delta > 800^\circ C} ZnO + SO_2 + \frac{1}{2}O_2$

(vii) $\underset{\text{epsom salt}}{MgSO_4.7H_2O} \xrightarrow[-7H_2O]{\Delta} MgSO_4 \downarrow$ [Same as $ZnSO_4$]

(viii) $$\begin{tikzcd} 2NaHSO_3 \arrow[r, "\Delta"] & Na_2S_2O_5 + H_2O \arrow[r, "\Delta"] & Na_2SO_3 + SO_2 \arrow[dr] & \\ & & & Na_2S + Na_2SO_4 \end{tikzcd}$$

(ix) $2NaHSO_4 \xrightarrow{\Delta} Na_2SO_4 + H_2O + SO_3$

(x) $$\begin{tikzcd} Na_2S_2O_3.5H_2O \arrow[r, "220^\circ C"] & Na_2S_2O_3 + 5H_2O \arrow[d, "\Delta", "\text{(From 4 moles)}"'] \\ & 3Na_2SO_4 + Na_2S_5. \end{tikzcd}$$

3. HEATING EFFECT OF NITRATE SALTS

(i) Metal nitrate $\xrightarrow{\Delta}$ metal oxide + $NO_2 + O_2$

(ii) $2M(NO_3)_2 \xrightarrow{\Delta} 2MO + 4NO_2 + O_2$
[M = all bivalent metals eg. Zn^{+2}, Mg^{+2}, Sr^{+2}, Ca^{+2}, Ba^{+2}, Cu^{+2}, Pb^{+2}]

(iii) $2LiNO_3 \xrightarrow{\Delta} Li_2O + 2NO_2 + \frac{1}{2}O_2$

(iv)
$$\begin{tikzcd} MNO_3 \arrow[r, "\Delta"] & MNO_2 + \frac{1}{2}O_2 \arrow[d, "\text{high temperature}"] \\ & M_2O + N_2 + \frac{3}{2}O_2 \end{tikzcd}$$
[M=Na,K,Rb,Cs]

$$\boxed{\begin{array}{ll} \text{(v)} & NaNO_3 \xrightarrow{500^\circ C} NaNO_2 + \frac{1}{2}O_2 \\ \text{(vi)} & NaNO_2 \xrightarrow{800^\circ C} Na_2O + N_2 + \frac{3}{2}O_2 \end{array}}$$

(vii)
$$\begin{tikzcd} & & & BeO + 2NO_2 + 1/2\ O_2 \\ BeCl_2 \arrow[r, "N_2O_4"] & Be(NO_3)_2.2N_2O_4 \arrow[r, "\text{Warm to 50ºC}", "\text{under vaccum}"'] & Be(NO_3)_2 \arrow[ur, "700\text{–}800^\circ C"] \arrow[r, "125^\circ C"] & [Be_4O(NO_3)_6] \end{tikzcd}$$
basic beryllium nitrate

Exception : If formed oxide is of heavier metal then it being less stable and further decomposed in to metal and oxygen.

(viii) $Hg(NO_3)_2 \xrightarrow{\Delta} Hg + 2NO_2 + O_2$

(ix) $2AgNO_3 \xrightarrow{\Delta} 2Ag + 2NO_2 + O_2$

4. HEATING EFFECT OF AMMONIUM SALTS :

If anionic part is oxdising in nature, then N_2 will be the product (some times N_2O).

(i) $\underset{\text{(orange solid)}}{(NH_4)_2Cr_2O_7} \xrightarrow{\Delta} N_2 + \underset{\text{(green)}}{Cr_2O_3} + 4H_2O$ {This reaction is used for making artificial volcano}

(ii) $NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$

(iii) $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$

(iv) $2NH_4ClO_4 \xrightarrow{\Delta} N_2 + Cl_2 + 2O_2 + 4H_2O$

(v) $2NH_4IO_3 \xrightarrow{\Delta} N_2 + I_2 + O_2 + 4H_2O$

If anionic part weakly oxidising or non oxidising in nature then NH_3 will be the product.

(i) $(NH_4)_2HPO_4 \xrightarrow{\Delta} HPO_3 + H_2O + 2NH_3$

(ii) $(NH_4)_2SO_4 \xrightarrow{\Delta} NH_3 + H_2SO_4$

(iii) $2(NH_4)_3PO_4 \xrightarrow{\Delta} 2NH_3 + P_2O_5 + 3H_2O$

(iv) $(NH_4)_2CO_3 \xrightarrow{\Delta} 2NH_3 + H_2O + CO_2$

(v) $NH_4Cl \xrightarrow{\Delta} NH_3\uparrow + HCl\uparrow$

(vi) $(NH_4)_2S \xrightarrow{\Delta} NH_3\uparrow + H_2S\uparrow$

(vii) $NH_4F \xrightarrow{\Delta} NH_3 + HF$

(viii) $(NH_4)_2MoO_4 \xrightarrow{\Delta} NH_3\uparrow + MoO_3 + H_2O$

5. HEATING EFFECT OF PHOSPHATE SALTS :

(i) 1° Phosphate salts gives metaphosphate salt on heating.

$NaH_2PO_4 \xrightarrow{\Delta} H_2O + NaPO_3$

(ii) 2° Phosphate salts gives pyrophosphate

$Na_2HPO_4 \xrightarrow{\Delta} H_2O + Na_4P_2O_7$

(iii) 3° Phosphate salt have no heating effect

$Na_3PO_4 \xrightarrow{\Delta}$ No effect

(iv) $\underset{\text{microcosmic salt}}{Na(NH_4)HPO_4.4H_2O} \xrightarrow[-4H_2O]{\Delta} NaNH_4HPO_4 \xrightarrow{\text{High temp.}} NaPO_3 + NH_3 + H_2O$

(v) $2Mg(NH_4)PO_4 \xrightarrow{\Delta} Mg_2P_2O_7 + 2NH_3 + H_2O$

6. HEATING EFFECT OF HALIDES SALTS :

(i) $2FeCl_3 \xrightarrow{\Delta} 2FeCl_2 + Cl_2$

(ii) $AuCl_3 \xrightarrow{\Delta} AuCl + Cl_2$

(iii) $Hg_2Cl_2 \xrightarrow{\Delta} HgCl_2 + Hg$

(iv) $NH_4Cl \xrightarrow{\Delta} NH_3 + HCl$

(v) $Pb(SCN)_4 \xrightarrow{\Delta} Pb(SCN)_2 + (SCN)_2$

(vi) $PbCl_4 \xrightarrow{\Delta} PbCl_2 + Cl_2$

(vii) $PbBr_4 \xrightarrow{\Delta} PbBr_2 + Br_2$ **[PbI_4 does not exists]**

(viii) $\underset{\text{scarlet red}}{HgI_2} \underset{\text{On Rubbing}}{\overset{127°C}{\rightleftarrows}} \underset{\text{yellow}}{HgI_2}$

7. HEATING EFFECT OF HYDRATED CHLORIDE SALTS

(i) $MgCl_2 . 6H_2O \xrightarrow{\Delta} MgO + 2HCl + 5H_2O$

(ii) $2FeCl_3 . 6H_2O \xrightarrow{\Delta} Fe_2O_3 + 6HCl + 9H_2O$

(iii) $2AlCl_3 . 6H_2O \xrightarrow{\Delta} Al_2O_3 + 6HCl + 9H_2O$

(iv) $\underset{\text{Pink}}{CoCl_2.6H_2O} \xrightarrow[-2H_2O]{50°C} \underset{\text{blue}}{CoCl_2.4H_2O} \xrightarrow[-2H_2O]{58°C} \underset{\text{Red violet}}{CoCl_2.2H_2O} \xrightarrow[-2H_2O]{140°C} \underset{\text{Blue}}{CoCl_2}$

Hydrated Co^{2+} salt - Pink Anhydrous Co^{2+} salt - Blue

8. HEATING EFFECT OF OXIDE :

(i) $2Ag_2O \xrightarrow[300°C]{\Delta} 4Ag + O_2$

(ii) $\underset{\text{white}}{ZnO} \underset{\text{Cold}}{\overset{\text{Hot}}{\rightleftharpoons}} \underset{\text{yellow}}{ZnO}$

(iii) $PbO_2 \xrightarrow{\Delta} PbO + \frac{1}{2}O_2$

(iv) $\underset{\text{yellow}}{PbO}$ (Massicot) $\xrightarrow[\text{Cooled \& powdered}]{\text{Fused}} \underset{\text{Litharge (red)}}{PbO}$

(v) $3MnO_2 \xrightarrow{900°C} Mn_3O_4 + O_2$

(vi) $\underset{\text{Red lead}}{Pb_3O_4} \underset{350°C}{\overset{500°C}{\rightleftharpoons}} \underset{\text{Litharge}}{6PbO} + O_2$

(vii) $2CrO_5 \xrightarrow{\Delta} Cr_2O_3 + \frac{7}{2}O_2$

(viii) $\underset{\text{(White)}}{K_2O} \underset{\text{cold}}{\overset{\Delta}{\rightleftharpoons}} \underset{\text{(yellow)}}{K_2O}$

(ix) $I_2O_5 \xrightarrow{\Delta} I_2 + \frac{5}{2}O_2$

(x) $\underset{\text{yellow}}{HgO} \xrightarrow{\Delta} \underset{\text{red}}{HgO} \xrightarrow[\text{strong heating}]{400°C} Hg + \frac{1}{2}O_2$

(xi) $2CrO_3 \xrightarrow{420°C} Cr_2O_3 + \frac{3}{2}O_2$

9. HEATING EFFECT OF PERMANGANATE :

$$\underset{\substack{\text{dark puple}\\\text{(almost black)}}}{2KMnO_4} \xrightarrow{513K} \underset{\text{(green)}}{K_2MnO_4} + \underset{\text{(black)}}{MnO_2} + O_2$$

10. HEATING EFFECT OF DICHROMATE & CHROMATE SALTS :

$$\underset{\text{orange}}{2K_2Cr_2O_7} \xrightarrow{\Delta} \underset{\text{yellow}}{2K_2CrO_4} + \underset{\text{green}}{Cr_2O_3} + \frac{3}{2}O_2\uparrow$$

11. HEATING EFFECT OF ACIDS :

(i) $\underset{\text{conc.}}{2HNO_3} \xrightarrow{\Delta} H_2O + 2NO_2 + \frac{1}{2}O_2$

(ii) $H_2SO_4 \xrightarrow{444°C} H_2O + SO_3$

(iii) $H_2SO_4 \xrightarrow{>800°C} H_2O + SO_2 + \frac{1}{2}O_2$

$$\left.\begin{array}{l}
\text{(iv) } 3H_2SO_3 \longrightarrow 2H_2SO_4 + S\downarrow + H_2O \\
\text{(v) } 3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O \\
\text{(vi) } HClO_3 \longrightarrow HClO_4 + ClO_2 + H_2O \\
\text{(vii) } 3HOCl \longrightarrow 2HCl + HClO_3 \\
\text{(viii) } 4H_3PO_3 \xrightarrow[200°C]{\Delta} 3H_3PO_4 + PH_3 \\
\text{(ix) } 2H_3PO_2 \longrightarrow H_3PO_4 + PH_3 \\
\text{(x) } 2NaH_2PO_2 \longrightarrow Na_2HPO_4 + PH_3
\end{array}\right\} \begin{array}{l}\text{Undergoes}\\\text{dispropor-}\\\text{-tionation}\\\text{reaction}\end{array}$$

(xi) $H_2C_2O_4 \xrightarrow{\Delta} H_2O + CO + CO_2$

(xii) $H_3PO_4 \xrightarrow{220°C} H_4P_2O_7 \xrightarrow{320°C} 4HPO_3 \xrightarrow{>320°C} 2P_2O_5 + 2H_2O$

(xiii) $H_3BO_3 \xrightarrow{100°C} 4HBO_2 \xrightarrow{140°C} H_2B_4O_7 \xrightarrow[\text{hot}]{\text{Red}} 2B_2O_3 + H_2O$

12. HEATING EFFECTS OF ACETATE SALTS

$$\begin{tikzcd}
\text{Metal acetate} \arrow[r, "\Delta"] & \begin{array}{l}\text{Metal}\\ \text{Carbonate}\\ \scriptstyle (M = LiBe\ Mg)\end{array} \arrow[d, "\Delta"] & + \ CH_3COCH_3 \\
 & \text{Metal oxide} + CO_2 &
\end{tikzcd}$$

(i) $Pb(OAc)_2 \xrightarrow{\Delta} PbO + CO_2 + CH_3COCH_3$

(ii) $Mg(OAc)_2 \xrightarrow{\Delta} MgO + CO_2 + CH_3COCH_3$

(iii) $Be(OAc)_2 \xrightarrow{\Delta} BeO + CO_2 + CH_3COCH_3$

(iv) $Ca(OAc)_2 \xrightarrow{\Delta} CaCO_3 + CH_3COCH_3$

(v) $Ba(OAc)_2 \xrightarrow{\Delta} BaCO_3 + CH_3COCH_3$

(vi) $CH_3CO_2K \xrightarrow{\Delta} K_2CO_3 + CH_3COCH_3$

13. HEATING EFFECTS OF OXALATE SALTS

$$\begin{tikzcd}
\text{Metal oxalate} \arrow[r, "\Delta"] & \begin{array}{l}\text{Metal}\\ \text{Carbonate}\\ \scriptstyle (M = LiBe\ Mg)\end{array} \arrow[d, "\Delta"] & + \ CO + CO_2 \\
 & \text{Metal oxide} + CO_2 &
\end{tikzcd}$$

(i) $\boxed{7Na_2C_2O_4 \xrightarrow{\Delta} 7Na_2CO_3 + 2CO_2 + 3CO + 2C}$

(ii) $SnC_2O_4 \xrightarrow{\Delta} SnO + CO_2 + CO$

(iii) $FeC_2O_4 \xrightarrow{\Delta} FeO + CO + CO_2$

(iv) $Ag_2C_2O_4 \xrightarrow{\Delta} 2Ag + 2CO_2$

(v) $HgC_2O_4 \xrightarrow{\Delta} Hg + 2CO_2$

14. HEATING EFFECTS OF FORMATE SALTS

(i) $HCO_2Na \xrightarrow{350°C} Na_2C_2O_4 + H_2\uparrow$

(ii) $HCOOAg \xrightarrow{\Delta} HCOOH + 2Ag + \frac{1}{2}\underbrace{O_2 + CO}_{\substack{\downarrow \\ CO_2}}$

(iii) $(HCOO)_2Hg \longrightarrow HCOOH + Hg + \frac{1}{2}\underbrace{O_2 + CO}_{\substack{\downarrow \\ CO_2}}$

EXERCISE

Single correct

1. Which of the following does not give metal oxide on heating

(A) $NaCO_3$ (B) K_2CO_3 (C) Rb_2CO_3 (D) All of these

2. Which of the following metal bicarbonate will give metal oxide and CO_2 on heating

(A) $NaHCO_3$ (B) $Mg(HCO_3)_2$ (C) $KHCO_3$ (D) Rb_2CO_3

3. Which of the following metal nitrate will give metal and oxygen on heating :

(A) KNO_3 (B) $NaNO_3$ (C) $AgNO_3$ (D) $RbNO_3$

4. Which of the following nitrate will give N_2O on heating :

(A) NH_4NO_3 (B) NH_4NO_2 (C) $NaNO_3$ (D) $AgNO_3$

5. Which of the following ammonium salt will not give acid on heating :

(A) $(NH_4)_2HPO_4$ (B) $(NH_4)_2MoO_4$ (C) $(NH_4)_2SO_4$ (D) NH_4Cl

6. Which of the following halide will not give halogen gas on heating :

(A) $PbCl_4$ (B) $PbBr_4$ (C) Hg_2Cl_2 (D) All of these

7. Select the correct statements

(A) Hydrated Co^{+2} salt is pink (B) Anhydrous Co^{+2} salt is of blue colour

(C) Hybridisation of $CoCl_2.6H_2O$ is sp^3d^2 (D) All of these

8. Which of the following metal sulphate will give SO_2 and SO_3 both gaseous product on heating :

(A) $CuSO_4$ (B) $FeSO_4$ (C) $Fe_2(SO_4)_3$ (D) $CaSO_4$

9. Which of the following compound is called dead burnt plaster :

(A) $CaSO_4.\frac{1}{2}H_2O$ (B) $CaSO_4.2H_2O$ (C) $CaSO_4$ (anhy.) (D) None of these

10. When NaH_2PO_4 is heated then which of the following compound is formed :

(A) $Na_4P_2O_7$ (B) Na_3PO_4 (C) HPO_3 (D) $NaPO_3$

11. When $KMnO_4$ is heated then which of the following compound is formed :

(A) $K_2MnO_4 + MnO_2$ (B) $K_2MnO_4 + MnO$ (C) $MnO_2 + MnO$ (D) No change

12. When CrO_3 is heated then .... + ... are formed :

(A) Cr_2O_3, O_2 (B) CrO_2, O_2 (C) $Cr_2O_7^{-2}$, O_2 (D) None of these

More than one may be correct

13. Which of the following metal carbonate will give of metal and oxyen on heating-

(A) Ag_2CO_3 (B) $HgCO_3$ (C) $(NH_4)_2CO_3$ (D) $PbCO_3$

14.
$$\begin{tikzcd} \underset{\substack{\text{(Carbonate salt)}\\ \text{(Green colour)}}}{A} \arrow[r, "\Delta"] & \underset{\text{(Black)}}{B} + CO_2 + H_2O \arrow[d, "920^{\circ}C"', "\substack{\text{High}\\ \text{temperature}}"] \\ & (C) + (D) \end{tikzcd}$$

Select the correct statements -

(A) Compound (A) is basic copper carbonate

(B) Compound (B) CuO

(C) Compound (C) is Cu_2O

(D) Compound (D) is paramagnetic in naturue

15. When Ag_2CO_3 is heated then product will be -

(A) Ag_2O (B) Ag (C) O_2 (D) CO_2

16. When compound A (orange red) is heated then green colour oxide of (B) is formed and inert gas (C) is formed then select the correct statements :

(A) Compound (A) is $(NH_4)_2 Cr_2O_7$

(B) Compound (B) is used in fire works

(C) Gas C is N_2

(D) Heating effect of (A) is a type of intra molecular redox reaction

17. Which of the following hydrated salts will not become anhydrous on heating :

(A) $MgCl_2.6H_2O$ (B) $FeCl_3.6H_2O$ (C) $AlCl_3.6H_2O$ (D) $CoCl_2.6H_2O$

18. Which of the following metal nitrate produce NO_2 on heating

(A) $Hg(NO_3)_2$ (B) $RbNO_3$ (C) $Pb(NO_3)_2$ (D) $Cu(NO_3)_2$

19. Which of the following oxides turns yellow on heating and becomes white on cooling :

(A) ZnO (B) K_2O (C) PbO (D) Ag_2O

Paragraph for Q. No. 20 to Q. No. 21

$$\underset{\text{(Orange solid)}}{(A)} \xrightarrow{\Delta} \underset{\text{(yellow)}}{(B)} + \underset{\text{(green)}}{(C)} + \underset{\text{(Paramagnetic)}}{(D)}$$

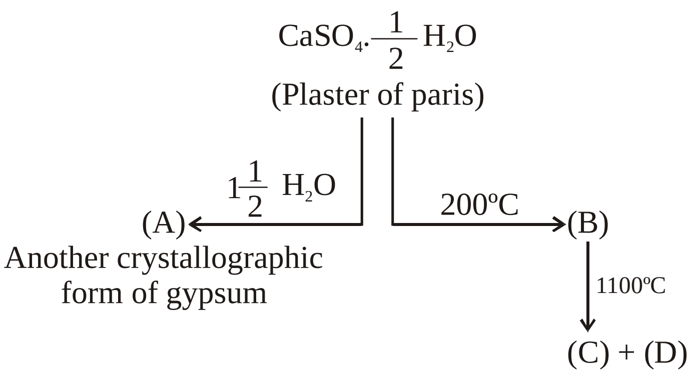
20. Compound (A) is :

(A) $K_2Cr_2O_7$ (B) K_2CrO_4 (C) Cr_2O_3 (D) O_2

21. Compound (C) is also obtained on heating of :

(A) $(NH_4)_2Cr_2O_7$ (B) NH_4ClO_4 (C) NH_4NO_3 (D) None of these

Paragarph for Q. No. 22 & 23



22. Compound "A" is :

(A) $CaSO_4.2H_2O$ (B) $2CaSO_4.H_2O$ (C) $CaSO_4.3H_2O$ (D) $CaSO_4.5H_2O$

23. Compound "C" and "D" are respectivelly :

(A) CaO + $CaSO_4$ (B) $CaSO_4$ + SO_2 (C) $CaSO_4$ + SO_3 (D) CaO + SO_3

Matrix match

24. Match the column

Column-I	**Column-II**
(A) $Be(NO_3)_2 \xrightarrow{\Delta}$	(P) Gives H_2O
(B) $HNO_2 \xrightarrow{\Delta}$	(Q) Oxyacid is obtained
(C) $NaH_2PO_4 \xrightarrow{\Delta}$	(R) Gives disproportionation reaction
(D) $H_3PO_3 \xrightarrow{\Delta}$	(S) Oxygen gas is evolved

25.

Column-I (Compound)	**Column-II (Products on heating)**
(A) NH_4ClO_4	(P) CO_2 gas is evolved
(B) $Mg(OAc)_2$	(Q) H_2 gas is evolved
(C) HCOONa (above 350ºC)	(R) N_2 gas is evolved
(D) $(NH_4)_2CO_3$	(S) Same gas is evolved which is obtained by heating $(NH_4)_2SO_4$
	(T) Intra molecular redox reaction

Integer

26. When calamine is heated then a product (A) is formed then find the total number of following options are correct for compound (A) -

(i) Compound (A) is white in cold conditions

(ii) Compound (A) is yellow in hot conditions

(iii) Compound (A) is called phillosopher's wool

(iv) Compound (A) when combined with CoO, then compound (B) is formed & colour of new compound (B) is green

(v) Compound (B) is called Rinmann's green

27. $NaNO_3 \xrightarrow{500°C} (A) + (B)$

$(A) \xrightarrow{800°C} (C) + (D) + (E)$

Find the number of correct statements

(1) Compound (B) is paramagnetic in nature

(2) Compound (B) when undergoes dimerisation then dimer product is diamagnetic in nature

(3) Bond order of compound (B) is two

(4) D is N_2 gas

(5) Compound B and E are same gas

28. $$\underset{\text{(dark purple almost black)}}{(A)} \xrightarrow{\Delta} \underset{\text{(green)}}{(B)} + \underset{\text{(black)}}{(C)} + (D)$$

Find the number of correct statements

(1) Compound B is K_2MnO_4

(2) Compound C is MnO_2

(3) Compound D is O_2

(4) Compound B is paramagnetic in nature

(5) Compound D has two unpaired electron in bonding molecular orbital

29. Total number of compounds undergoes disproportionation redox reaction on heating

MnO_2, HOCl, H_3PO_3, HNO_2, CrO_5, $HClO_3$

30. On strong heating of H_3PO_4 and H_3BO_3, sum of oxidation number of P & B in the final product obtained is

EXERCISE

Que.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Ans.	D	B	C	A	B	C	D	B	C	D
Que.	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
Ans.	A	A	A, B	A,B,C,D	B,C,D	A,B,C,D	A, B, C	A,C,D	A, B	A
Que.	**21**	**22**	**23**	**24**						
Ans.	A	A	D	(A)→(S);(B)→(P,Q,R);(C)→(P);(D)→(Q,R)						
Que.	**25**					**26**	**27**	**28**	**29**	**30**
Ans.	(A)→(R,T);(B)→(P);(C)→(P,Q,T);(D)→(P,S)					5	4	4	4	8

s-Block Element

OBJECTIVES

After studying this unit you will be able to :

- Describe the general characteristics of the alkali metals and their compounds;
- Explain the general characteristics of the alkaline earth metals and their compounds;
- Describe the manufacture, properties and uses of industrially important sodium and calcium compounds including Portland cement :
- Appreciate the biological significance of sodium, potassium, magnesium and calcium.

The *s*-block elements of the Periodic Table are those in which the last electron enters the outermost *s*-orbital. As the *s*-orbital can accommodate only two electrons, two groups (1 & 2) belong to the s-block of the Periodic Table. Group 1 of the Periodic Table consists of the elements: lithium, sodium, potassium, rubidium, caesium and francium. They are collectively known as the *alkali metals*. These are so called because they form hydroxides on reaction with water which are strongly alkaline in nature. The elements of Group 2 include beryllium, magnesium, calcium, strontium, barium and radium. These elements with the exception of beryllium are commonly known as the *alkaline earth metals*. These are so called because their oxides and hydroxides are alkaline in nature and these metal oxides are found in the earth's crust*****.

Among the alkali metals sodium and potassium are abundant and lithium, rubidium and caesium have much lower abundances. Francium is highly radioactive; its longest-lived isotope 223Fr has a half-life of only 21 minutes. Of the alkaline earth metals calcium and magnesium rank fifth and sixth in abundance respectively in the earth's crust. Strontium and barium have much lower abundances. Beryllium is rare and radium is the rarest of all comprising only 10–10 per cent of igneous rocks .

The general electronic configuration of *s*-block elements is [noble gas]*ns*1 for alkali metals and [noble gas] ns^2 for alkaline earth metals.

* *The thin, rocky outer layer of the Earth is crust.* † *A type of rock formed from magma (molten rock) that has cooled and hardened.*

Lithium and beryllium, the first elements of Group 1 and Group 2 respectively exhibit some properties which are different from those of the other members of the respective group. In these anomalous properties they resemble the second element of the following group. Thus, lithium shows similarities to magnesium and beryllium to aluminium in many of their properties. This type of diagonal similarity is commonly referred to as *diagonal relationship* in the periodic table. The diagonal relationship is due to the similarity in ionic sizes and /or charge/radius ratio of the elements. Monovalent sodium and potassium ions and divalent magnesium and calcium ions are found in large proportions in biological fluids. These ions perform important biological functions such as maintenance of ion balance and nerve impulse conduction.

10.1 GROUP 1 ELEMENTS : ALKALI METALS

The alkali metals show regular trends in their physical and chemical properties with the increasing atomic number. The atomic, physical and chemical properties of alkali metals are discussed below.

10.1.1 Electronic Configuration

All the alkali metals have one valence electron, ns^1 outside the noble gas core. The loosely held *s*-electron in the outermost valence shell of these elements makes them the most electropositive metals. They readily lose electron to give monovalent M^+ ions. Hence they are never found in free state in nature.

Element	**Symbol**	**Electronic configuration**
Lithium	Li	$1s^2s^1$
Sodium	Na	$1s^2\,2s^22p^63s^1$
Potassium	K	$1s^22s^22p^63s^23p^64s^1$
Rubidium	Rb	$1s^22s^22p^63s^23p^63d^{10}4s^24p^65s^1$
Caesium	Cs	$1s^22s^22p^63s^23p^63d^{10}4s^24p^6\,4d^{10}5s^65p^66s^1$ or $[Xe]\,6s^1$
Francium	Fr	$[Rn]7s^1$

10.1.2 Atomic and Ionic Radii

Li < Na < K < Rb < Cs

Increase down the group, because value of n (principal quantum number) increases.

10.1.3 Ionization Enthalpy

Li > Na > K > Rb > Cs.

This is because the effect of increasing size outweighs the increasing nuclear charge, and the outermost electron is very well screened from the nuclear charge.

10.1.4 Hydration Enthalpy

The hydration enthalpies of alkali metal ions decrease with increase in ionic sizes.

$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

Li^+ has maximum degree of hydration and for this reason lithium salts are mostly hydrated,

e.g., $LiCl\cdot 2H_2O$

10.1.5 Physical Properties

(i) All the alkali metals are silvery white, soft and light metals.

(ii) Because of the large size, these elements have low density which increases down the group from Li to Cs. However, potassium is lighter than sodium.

Li < **K** < Na < Rb < Cs.

(iii) The melting and boiling points of the alkali metals are low indicating weak metallic bonding due to the presence of only a single valence electron in them.

(iv) The alkali metals and their salts impart characteristic colour to an oxidizing flame. This is because the heat from the flame excites the outermost orbital electron to a higher energy level. When the excited electron comes back to the ground state, there is emission of radiation in the visible region as given below :

Metal	**Li**	**Na**	**K**	**Rb**	**Cs**
Colour	Crimson red	Yellow	Violet	Red violet	Blue
λ/nm	670.8	589.2	766.5	780.0	455.5

(v) Alkali metals can therefore, be detected by the respective flame tests and can be determined by flame photometry or atomic absorption spectroscopy.

(vi) These elements when irradiated with light, the light energy absorbed may be sufficient to make an atom lose electron.

Table : Atomic and Physical Properties of the Alkali Metals

Property	**Lithium Li**	**Sodium Na**	**Potassium K**	**Rubidium Rb**	**Caesium Cs**	**Francium Fr**
Atomic number	3	11	19	37	55	87
Atomic mass (g mol^{-1})	6.94	22.99	39.10	85.47	132.91	(223)
Electronic configuration	[He]2s^1	[Ne] 3s^1	[Ar] 4s^1	[Kr] 5s^1	[Xe] 6s^1	[Rn] 7s^1
Ionization enthalpy/kJ mol^{-1}	520	496	419	403	376	~375
Hydration enthalpy/kJ mol^{-1}	–506	–406	–330	–310	–276	-
Metallic radius/pm	152	186	227	248	265	-
Ionic radius M$^+$/pm	76	102	138	152	167	(180)
m.p./K	454	371	336	312	302	-
b.p/K	1615	1156	1032	961	944	-
Density / g cm^{-3}	0.53	0.97	0.86	1.53	1.90	-
Standard Potentials E$^-$ /V for (M$^+$/M)	–3.04	–2.714	–2.925	–2.930	–2.927	-
Occurrence in lithosphere	18*	2.27**	1.84**	78-12*	2-6*	~10^{-18}*

**ppm (part per million), ** percentage by weight; † Lithosphere: The Earth's outer layer: its crust and part of the upper mantle.*

This property makes caesium and potassium useful as electrodes in photoelectric cells.

10.1.6 Chemical Properties

The alkali metals are highly reactive due to their large size and low ionization enthalpy. The reactivity of these metals increases down the group.

(i) ***Reactivity towards air :*** The alkali metals tarnish in dry air due to the formation of their oxides which in turn react with moisture to form hydroxides. They burn vigorously in oxygen forming oxides. Lithium forms monoxide, sodium forms peroxide, the other metals form superoxides. The superoxide O_2^- ion is stable only in the presence of large cations such as K, Rb, Cs.

$4Li + O_2 \rightarrow 2Li_2O$ (oxide)

$2Na + O_2 \rightarrow Na_2O_2$ (peroxide)

$M + O_2 \rightarrow MO_2$ (superoxide)

(M = K, Rb, Cs)

In all these oxides the oxidation state of the alkali metal is +1. Lithium shows exceptional behaviour in reacting directly with nitrogen of air to form the nitride, Li_3N as well. Because of their high reactivity towards air and water, **alkali metals are normally kept in kerosene oil.**

Problem 10.1

What is the oxidation state of K in KO_2?

Solution

The superoxide species is represented as O_2^-; since the compound is neutral, therefore, the oxidation state of potassium is +1.

(ii) ***Reactivity towards water :*** The alkali metals react with water to form hydroxide and dihydrogen.

$$2M + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2$$

(M = an alkali metal)

It may be noted that although lithium has most negative $E^\ominus$ value , its reaction with water is less vigorous than that of sodium which has the least negative $E^\ominus$ value among the alkali metals. This behaviour of lithium is attributed to its small size and very high hydration energy. Other metals of the group react explosively with water.

They also react with proton donors such as alcohol, gaseous ammonia and alkynes.

(iii) ***Reactivity towards dihydrogen:*** The alkali metals react with dihydrogen at about 673K (lithium at 1073K) to form hydrides. All the alkali metal hydrides are ionic solids with high melting points.

$$2M + H_2 \rightarrow 2M^+H^-$$

(iv) ***Reactivity towards halogens :*** The alkali metals readily react vigorously with halogens to form ionic halides, M+X–. However, lithium halides are somewhat covalent. It is because of the high polarisation capability of lithium ion (The distortion of electron cloud of the anion by the cation is called polarisation). The Li+ ion is very small in size and has high tendency to distort electron cloud around the negative halide ion. Since anion with large size can be easily distorted, among halides, lithium iodide is the most covalent in nature.

(v) ***Reducing nature :*** The alkali metals are strong reducing agents, lithium being the most and sodium the least powerful. The standard electrode potential ($E^\ominus$) which measures the reducing power represents the overall change :

$M(s) \rightarrow M(g)$ sublimationenthalpy

$M(g) \rightarrow M^+(g) + e^-$ ionizationenthalpy

$M^+ (g) + H_2O \rightarrow M^+ (aq)$ hydrationenthalpy

With the small size of its ion, lithium has the highest hydration enthalpy which accounts for its high negative $E^\ominus$ value and its high reducing power.

Problem 10.2

The $E^\ominus$ for Cl_2/Cl^- is +1.36, for I_2/I^- is + 0.53, for Ag^+/Ag is +0.79, Na^+/Na is –2.71 and for Li+ /Li is – 3.04. Arrange the following ionic species in decreasing order of reducing strength :

I^-, Ag, Cl^-, Li, Na

Solution

The order is Li > Na > I– > Ag > Cl–

(vi) ***Solutions in liquid ammonia :*** The alkali metals dissolve in liquid ammonia giving deep blue solutions which are conducting in nature.

$$M+(x + y)NH_3 \rightarrow [M(NH_3)_x]^+ + [e(NH_3)y]^-$$

The blue colour of the solution is due to the ammoniated electron which absorbs energy in the visible region of light and thus imparts blue colour to the solution. The solutions are paramagnetic and on standing slowly liberate hydrogen resulting in the formation of amide.

$M^+_{(am)} + e^- + NH_3(1) \rightarrow MNH_{2(am)} + \frac{1}{2}H_2(g)$ (where 'am' denotes solution in ammonia.) In concentrated solution, the blue colour changes to bronze colour and becomes diamagnetic.

(vii) Reaction with H_2

They react with H_2 forming metal hydride with formula MH which are of ionic nature. Stability of hydride decreases down the group.

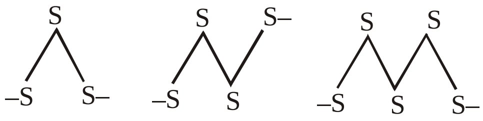
(viii) Reaction with N_2

Only Lithium reacts with N_2 to form ionic lithium nitride Li_3N.

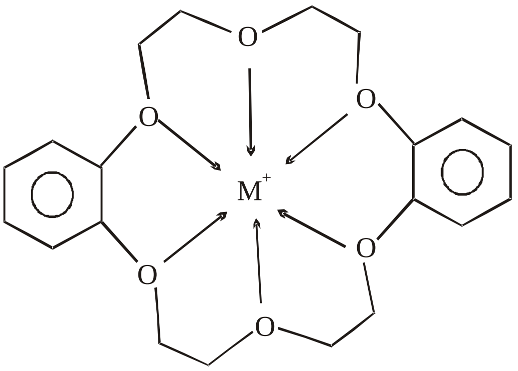
$$3Li + \frac{3}{2}N_2 \rightarrow Li_3N$$

(ix) Sulphides

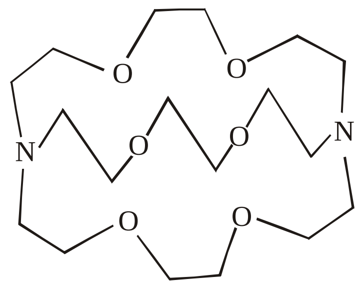
All metals react with S forming sulphides such as Na_2S and Na_2S_n (n = 2, 3, 4, 5 or 6). The polysulphide ions are made from zig-zag chains of sulphur atoms.



(x) Crown Ethers and Cryptands :



Dibenzo-18-Crown-6



Cryptand - 222

[Na (Cryptand 222)]$^+$ Na$^-$ [Contains Na$^-$ (sodide ion)]

[Cs$^+$(Cryptand - 222)] [(Cyrptand-222)e$^-$] [electride]

10.1.7 Uses :

Lithium metal is used to make useful alloys, for example with lead to make 'white metal' bearings for motor engines, with aluminium to make aircraft parts, and with magnesium to make armour plates. It is used in thermonuclear reactions.

Lithium is also used to make electrochemical cells. Sodium is used to make a Na/Pb alloy needed to make $PbEt_4$ and $PbMe_4$. These organolead compounds were earlier used as anti-knock additives to petrol, but nowadays vehicles use lead-free petrol. Liquid sodium metal is used as a coolant in fast breeder nuclear reactors. Potassium has a vital role in biological systems. Potassium chloride is used as a fertilizer. Potassium hydroxide is used in the manufacture of soft soap. It is also used as an excellent absorbent of carbon dioxide. Caesium is used in devising photoelectric cells.

10.2 GENERAL CHARACTERISTICS OF THE COMPOUNDS OF THE ALKALI METALS

All the common compounds of the alkali metals are generally ionic in nature. General characteristics of some of their compounds are discussed here.

10.2.1 Oxides and Hydroxides

On combustion in excess of air, lithium forms mainly the oxide, Li_2O (plus some peroxide Li_2O_2), sodium forms the peroxide, Na_2O_2 (and some oxide Na_2O) whilst potassium, rubidium and caesium form the superoxides, MO_2. Under appropriate conditions pure compounds M_2O, M_2O_2 and MO_2 may be prepared. The increasing stability of the peroxide or superoxide, as the size of the metal ion increases, is due to the stabilisation of large anions by larger cations through lattice energy effects. These oxides are easily hydrolysed by water to form the hydroxides according to the following reactions :

$$M_2O + H_2O \rightarrow 2M^+ + 2OH^-$$

$$M_2O_2 + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2O_2$$

$$2MO_2 + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2O_2 + O_2$$

The oxides and the peroxides are colourless when pure, but the superoxides are yellow or orange in colour. The superoxides are also paramagnetic. Sodium peroxide is widely used as an oxidising agent in inorganic chemistry.

Problem 10.3

Why is KO_2 paramagnetic ?

Solution

The superoxide O_2^- is paramagnetic because of one upaired electron in π*2p molecular orbital. The hydroxides which are obtained by the reaction of the oxides with water are all white crystalline solids. The alkali metal hydroxides are the strongest of all bases and dissolve freely in water with evolution of much heat on account of intense hydration.

Sodium Oxide (Na_2O) :

Preparation :

(i) It is obtained by burning sodium at 180°C in a limited supply of air or oxygen and distilling off the excess of sodium in vacuum.

$$2Na + \frac{1}{2}O_2 \xrightarrow{180^\circ} Na_2O$$

(ii) By heating sodium peroxide, nitrate or nitrite with sodium.

$$Na_2O_2 + 2Na \xrightarrow{\Delta} 2Na_2O$$

$$2NaNO_3 + 10Na \xrightarrow{\Delta} 6Na_2O + N_2$$

$$2NaNO_2 + 6Na \xrightarrow{\Delta} 4Na_2O + N_2$$

Properties :

(i) It is white amorphous mass.

(ii) It decomposes at 400°C into sodium peroxide and sodium

$$2Na_2O \xrightarrow{400°C} Na_2O_2 + 2Na$$

(iii) It dissolve violently in water, yielding caustic soda.

$$Na_2O + H_2O \longrightarrow 2NaOH$$

Sodium Peroxides (Na_2O_2) :

Preparation: It is formed by heating the metal in excess of air or oxygen at 300°, which is free from moisture and CO_2.

$$2Na + O_2 \longrightarrow Na_2O_2$$

Properties:

(i) It is a pale yellow solid, becoming white in air from the formation of a film of NaOH and Na_2CO_3.

(ii) In cold water (~0°C) produces H_2O_2 but at room temperature produces O_2. In ice-cold mineral acids also produces H_2O_2.

$$Na_2O_2 + 2H_2O \xrightarrow{\sim 0°C} 2NaOH + H_2O_2$$

$$2Na_2O_2 + 2H_2O \xrightarrow{25°C} 4NaOH + O_2$$

$$Na_2O_2 + H_2SO_4 \xrightarrow{\sim 0°C} Na_2SO_4 + H_2O_2$$

(iii) It reacts with CO_2, giving sodium carbonate and oxygen and hence its use for purifying air in a confined space e.g. submarine, ill-ventilated room,

$$2Na_2O_2 + 2CO_2 \longrightarrow 2Na_2CO_3 + O_2$$

(iv) It is an oxidising agent and oxidises charcoal, CO, NH_3, SO_2.

$3Na_2O_2 + 2C \longrightarrow 2Na_2CO_3 + 2Na$ [deposition of metallic Na]

$$CO + Na_2O_2 \longrightarrow Na_2CO_3$$

$$SO_2 + Na_2O_2 \longrightarrow Na_2SO_4$$

$$2NH_3 + 3Na_2O_2 \longrightarrow 6NaOH + N_2$$

(v) It contains peroxide ion $[–O–O–]^{-2}$

Uses:

(i) For preparing H_2O_2, O_2

(ii) Oxygenating the air in submarines

(iii) Oxidising agent in the laboratory.

Oxides of Potassium :

	K_2O,	K_2O_2,	K_2O_3,	KO_2 and	KO_3
Colours :	White	White	Red	Bright Yellow	Orange Solid

Preparation :

(i) $2KNO_3 + 10K \xrightarrow{\text{heating}} 6K_2O + N_2$

** $\underset{\text{(White)}}{K_2O} \xrightarrow{\text{heating}} \underset{\text{(Yellow)}}{K_2O}$

** $K_2O + H_2O \longrightarrow 2KOH$

(ii) $2K + O_2 \xrightarrow[\text{air at 300°C}]{\text{Controlled}} K_2O_2$ [Props: Similar with Na_2O_2]

(iii) Passage of O_2 through a blue solution of K in liquid NH_3 yields oxides K_2O_2 (white), K_2O_3 (red) and KO_2 (deep yellow) i.e

$$\text{K in liq. } NH_3 \xrightarrow{O_2} \underset{\text{white}}{K_2O_2} \longrightarrow \underset{\text{red}}{K_2O_3} \longrightarrow \underset{\text{yellow}}{KO_2}$$

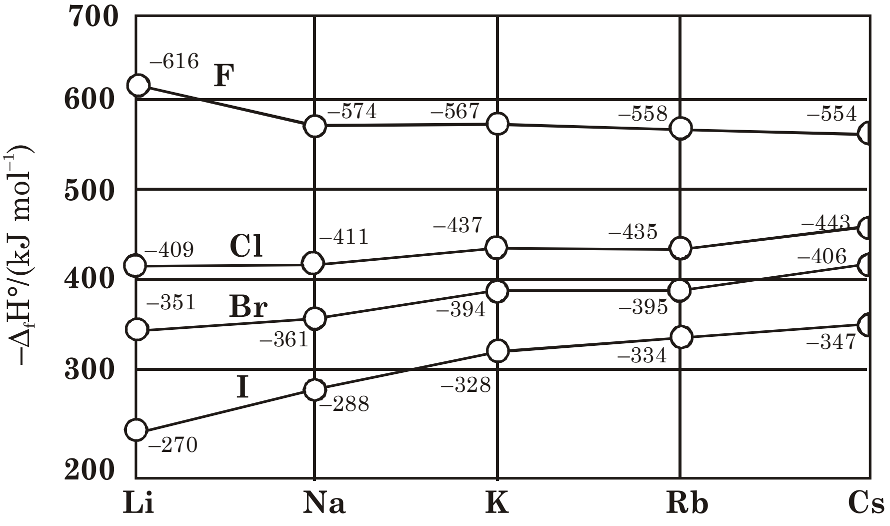
** KO_2 reacts with H_2O and produces H_2O_2 and O_2 both

$$2KO_2 + 2H_2O \xrightarrow{\sim 0°C} 2KOH + H_2O_2 + O_2$$

KO_3 : $\underset{\text{(Dry powdered)}}{KOH} + O_3 \text{ (ozonised oxygen)} \xrightarrow{-10°\text{to}-15°C} \underset{\text{(orange solid)}}{KO_3}$

10.2.2 Halides

The alkali metal halides, MX, (X=F,Cl,Br,I) are all high melting, colourless crystalline solids. They can be prepared by the reaction of the appropriate oxide, hydroxide or carbonate with aqueous hydrohalic acid (HX). All of these halides have high negative enthalpies of formation; the $\Delta_f H^\ominus$ values for fluorides become less negative as we go down the group, whilst the reverse is true for $\Delta_f H^\ominus$ for chlorides, bromides and iodides. For a given metal $\Delta_f H^\ominus$ always becomes less negative from fluoride to iodide.



The standard enthalpies of formation of the halides of Group 1 elements at 298 K

10.2.3 Salts of Oxo-Acids

Oxo-acids are those in which the acidic proton is on a hydroxyl group with an oxo group attached to the same atom e.g., carbonic acid, H_2CO_3 ($OC(OH)_2$; sulphuric acid, H_2SO_4 ($O_2S(OH)_2$). The alkali metals form salts with all the oxo-acids. They are generally soluble in water and thermally stable.

Their carbonates (M_2CO_3) and in most cases the hydrogencarbonates ($MHCO_3$) also are highly stable to heat. As the electropositive character increases down the group, the stability of the carbonates and hydorgencarbonates increases. Lithium carbonate is not so stable to heat; lithium being very small in size polarises a large CO_3^{2-} ion leading to the formation of more stable Li_2O and CO_2. Its hydrogencarbonate does not exist as a solid.

10.3 ANOMALOUS PROPERTIES OF LITHIUM

The anomalous behaviour of lithium is due to the : (i) exceptionally small size of its atom and ion, and (ii) high polarising power (i.e., charge/ radius ratio). As a result, there is increased covalent character of lithium compounds which is responsible for their solubility in organic solvents. Further, lithium shows diagonal relationship to magnesium which has been discussed subsequently.

10.3.1 Points of Difference between Lithium and other Alkali Metals

(i) Lithium is much harder. Its m.p. and b.p. are higher than the other alkali metals.

(ii) Lithium is least reactive but the strongest reducing agent among all the alkali metals. On combustion in air it forms mainly monoxide, Li_2O and the nitride, Li_3N unlike other alkali metals.

(iii) LiCl is deliquescent and crystallises as a hydrate, $LiCl.2H_2O$ whereas other alkali metal chlorides do not form hydrates.

(iv) Lithium hydrogencarbonate is not obtained in the solid form while all other elements form solid hydrogencarbonates.

(v) Lithium unlike other alkali metals forms no ethynide on reaction with ethyne.

(vi) Lithium nitrate when heated gives lithium oxide, Li_2O, whereas other alkali metal nitrates decompose to give the corresponding nitrite.

$$4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$$

$$2NaNO_3 \rightarrow 2NaNO_2 + O_2$$

(vii) LiF and Li_2O are comparatively much less soluble in water than the corresponding compounds of other alkali metals.

10.3.2 Points of Similarities between Lithium and Magnesium

The similarity between lithium and magnesium is particularly striking and arises because of their similar sizes : atomic radii, Li = 152 pm, Mg = 160 pm; ionic radii : $Li^+ = 76$ pm, $Mg^{2+} = 72$ pm. The main points of similarity are :

(i) Both lithium and magnesium are harder and lighter than other elements in the respective groups.

(ii) Lithium and magnesium react slowly with water. Their oxides and hydroxides are much less soluble and their hydroxides decompose on heating. Both form a nitride, Li_3N and Mg_3N_2, by direct combination with nitrogen.

(iii) The oxides, Li_2O and MgO do not combine with excess oxygen to give any superoxide.

(iv) The carbonates of lithium and magnesium decompose easily on heating to form the oxides and CO_2. Solid hydrogencarbonates are not formed by lithium and magnesium.

(v) Both LiCl and $MgCl_2$ are soluble in ethanol.

(vi) Both LiCl and $MgCl_2$ are deliquescent and crystallise from aqueous solution as hydrates, $LiCl{\cdot}2H_2O$ and $MgCl_2{\cdot}8H_2O$.

10.4 SOME IMPORTANT COMPOUNDS OF SODIUM

Industrially important compounds of sodium include sodium carbonate, sodium hydroxide, sodium chloride and sodium bicarbonate. The large scale production of these compounds and their uses are described below :

Sodium Carbonate (Washing Soda), $Na_2CO_3{\cdot}10H_2O$

Sodium carbonate is generally prepared by **Solvay Process**. In this process, advantage is taken of the low solubility of sodium hydrogencarbonate whereby it gets precipitated in the reaction of sodium chloride with ammonium hydrogencarbonate. The latter is prepared by passing CO_2 to a concentrated solution of sodium chloride saturated with ammonia, where ammonium carbonate followed by ammonium hydrogencarbonate are formed.

The equations for the complete process may be written as:

$$2NH_3 + H_2O + CO_2 \rightarrow (NH_4)_2\,CO_3$$

$$(NH_4)_2\,CO_3 + H_2O + CO_2 \rightarrow 2NH_4HCO_3$$

$$NH_4HCO_3 + NaCl \rightarrow NH_4Cl + NaHCO_3$$

Sodium hydrogencarbonate crystal separates. These are heated to give sodium carbonate.

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$

In this process NH_3 is recovered when the solution containing NH_4Cl is treated with $Ca(OH)_2$. Calcium chloride is obtained as a by-product.

$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + CaCl_2 + H_2O$$

It may be mentioned here that Solvay process cannot be extended to the manufacture of potassium carbonate because potassium hydrogencarbonate is too soluble to be precipitated by the addition of ammonium hydrogencarbonate to a saturated solution of potassium chloride.

Properties : Sodium carbonate is a white crystalline solid which exists as a decahydrate, $Na_2CO_3{\cdot}10H_2O$. This is also called washing soda. It is readily soluble in water. On heating, the decahydrate loses its water of crystallisation to form monohydrate. Above 373K, the monohydrate becomes completely anhydrous and changes to a white powder called soda ash.

$$Na_2CO_2.10H_2O \xrightarrow{375K} Na_2CO_3.H_2O + 9H_2O$$

$$Na_2CO_3.H_2O \xrightarrow{>373K} Na_2CO_3 + H_2O$$

Carbonate part of sodium carbonate gets hydrolysed by water to form an alkaline solution.

$$CO_3^{2-} + H_2O \rightarrow HCO_3^{-} + OH^{-}$$

Uses:
- **(i)** It is used in water softening, laundering and cleaning.
- **(ii)** It is used in the manufacture of glass, soap, borax and caustic soda.
- **(iii)** It is used in paper, paints and textile industries.
- **(iv)** It is an important laboratory reagent both in qualitative and quantitative analysis.

Note: K_2CO_3 cannot be prepared by **Solvey process** because $KHCO_3$ is soluble in water and cannot be separated form NH_4Cl.

Sodium Chloride, NaCl

The most abundant source of sodium chloride is sea water which contains 2.7 to 2.9% by mass of the salt. In tropical countries like India, common salt is generally obtained by evaporation of sea water. Approximately 50 lakh tons of salt are produced annually in India by solar evaporation. Crude sodium chloride, generally obtained by crystallisation of brine solution, contains sodium sulphate, calcium sulphate, calcium chloride and magnesium chloride as impurities. Calcium chloride, $CaCl_2$, and magnesium chloride, $MgCl_2$ are impurities because they are deliquescent (absorb moisture easily from the atmosphere).

To obtain pure sodium chloride, the crude salt is dissolved in minimum amount of water and filtered to remove insoluble impurities. The solution is then saturated with hydrogen chloride gas. Crystals of pure sodium chloride separate out. Calcium and magnesium chloride, being more soluble than sodium chloride, remain in solution.

Sodium chloride melts at 1081K. It has a solubility of 36.0 g in 100 g of water at 273 K. The solubility does not increase appreciably with increase in temperature.

Uses :

(i) It is used as a common salt or table salt for domestic purpose.

(ii) It is used for the preparation of Na_2O_2, NaOH and Na_2CO_3.

(iii) It is used to prepare freezing mixture in laboratory [Ice-common salt mixture is called freezing mixture and temperature goes down to –23°C.]

(iv) For melting ice and snow on road.

Sodium Hydroxide (Caustic Soda), NaOH

Sodium hydroxide is generally prepared commercially by the electrolysis of sodium chloride in Castner-Kellner cell. A brine solution is electrolysed using a mercury cathode and a carbon anode. Sodium metal discharged at the cathode combines with mercury to form sodium amalgam. Chlorine gas is evolved at the anode. **Cathode :** $Na^+ + e^- \xrightarrow{Hg} Na-\text{ amalgam}$

$$\textbf{Anode :}\ Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$$

The amalgam is treated with water to give sodium hydroxide and hydrogen gas.

$$2Na\text{-amalgam} + 2H_2O \rightarrow 2NaOH + 2Hg + H_2$$

Sodium hydroxide is a white, translucent solid. It melts at 591 K. It is readily soluble in water to give a strong alkaline solution. Crystals of sodium hydroxide are deliquescent. The sodium hydroxide solution at the surface reacts with the CO_2 in the atmosphere to form Na_2CO_3.

Uses : It is used in

(i) The manufacture of soap, paper, artificial silk and a number of chemicals,

(ii) In petroleum refining,

(iii) In the purification of bauxite,

(iv) In the textile industries for mercerising cotton fabrics, (v) for the preparation of pure fats and oils, and

(vi) As a laboratory reagent.

***Sodium Hydrogencarbonate (Baking Soda),* $NaHCO_3$**

Sodium hydrogencarbonate is known as baking soda because it decomposes on heating to generate bubbles of carbon dioxide (leaving holes in cakes or pastries and making them light and fluffy).

Sodium hydrogencarbonate is made by saturating a solution of sodium carbonate with carbon dioxide. The white crystalline powder of sodium hydrogencarbonate, being less soluble, gets separated out.

$$Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3$$

Sodium hydrogencarbonate is a mild antiseptic for skin infections. **It is used in fire extinguishers.**

***Potassium carbonate,* K_2CO_3**

It is also called potash or pearl ash. It cannot be made by the use of solvay process as potassium bicarbonate is more soluble than sodium bicarbonate. However, it can be prepared by **Le-Blanc process**. KCl is first converted into K_2SO_4. Potassium sulphate (K_2SO_4) is then heated with $CaCo_3$ and carbon.

$$KCl + H_2SO_4 \longrightarrow KHSO_4 + HCl$$

$$KHSO_4 + KCl \longrightarrow K_2SO_4 + HCl$$

$$K_2SO_4 + CaCO_3 + 2C \longrightarrow K_2CO_3 + CaS + 2CO_2$$

It is a white powder , deliquescent in nature. It is highly soluble in water.

Uses : It is used in the manufacture of hard glass. The mixture of K_2CO_3 and Na_2CO_3 is used a **fusion mixture** in laboratory.

10.5 BIOLOGICAL IMPORTANCE OF SODIUM AND POTASSIUM

A typical 70 kg man contains about 90 g of Na and 170 g of K compared with only 5 g of iron and 0.06 g of copper. Sodium ions are found primarily on the outside of cells, being located in blood plasma and in the interstitial fluid which surrounds the cells. These ions participate in the transmission of nerve signals, in regulating the flow of water across cell membranes and in the transport of sugars and amino acids into cells. Sodium and potassium, although so similar chemically, differ quantitatively in their ability to penetrate cell membranes, in their transport mechanisms and in their efficiency to activate enzymes.

Thus, potassium ions are the most abundant cations within cell fluids, where they activate many enzymes, participate in the oxidation of glucose to produce ATP and, with sodium, are responsible for the transmission of nerve signals.

There is a very considerable variation in the concentration of sodium and potassium ions found on the opposite sides of cell membranes. As a typical example, in blood plasma, sodium is present to the extent of 143 mmolL^{-1}, whereas the potassium level is only 5 mmolL^{-1} within the red blood cells. These concentrations change to 10 mmolL^{-1} (Na^+) and 105 mmolL^{-1} (K^+). These ionic gradients demonstrate that a discriminatory mechanism, called the sodium-potassium pump, operates across the cell membranes which consumes more than one-third of the ATP used by a resting animal and about 15 kg per 24 h in a resting human.

10.6 GROUP 2 ELEMENTS : ALKALINE EARTH METALS

The group 2 elements comprise beryllium, magnesium, calcium, strontium, barium and radium. They follow alkali metals in the periodic table. These (except beryllium) are known as alkaline earth metals. The first element beryllium differs from the rest of the members and shows diagonal relationship to aluminium. The atomic and physical properties of the alkaline earth metals are shown in Table.

10.6.1 Electronic Configuration

These elements have two electrons in the *s*-orbital of the valence shell. Their general electronic configuration may be represented as [noble gas] ns^2. Like alkali metals, the compounds of these elements are also predominantly ionic.

Element	Symbol	Electronic configuration
Beryllium	Be	$1s^2 2s^2$
Magnesium	Mg	$1s^2 2s^2 2p^6 3s^2$
Calcium	Ca	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
Strontium	Sr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$
Barium	Ba	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2$ or $[Xe]\, 6s^2$
Radium	Ra	$[Rn] 7s^2$

10.6.2 Atomic and Ionic Radii

The atomic and ionic radii of the alkaline earth metals are smaller than those of the Corresponding alkali metals in the same periods. This is due to the increased nuclear charge in these elements. Within the group, the atomic and ionic radii increase with increase in atomic number.

Table : Atomic and Physical Properties of the Alkaline Earth Metals

Property	**Beryllium** **Be**	**Magnesium** **mg**	**Calcium** **Ca**	**Strontium** **Sr**	**Barium** **Ba**	**Radium** **Ra**
Atomic number	4	12	20	38	56	88
Atomic mass (g mol^{-1})	9.01	24.31	40.08	87.62	137.33	226.03
Electronic configuration	$[He]2s^2$	$[Ne]\ 3s^2$	$[Ar]\ 4s^2$	$[Kr]\ 5s^2$	$[Xe]\ 6s^2$	$[Rn]\ 7s^2$
Ionization enthalpy (I)/kJ mol^{-1}	899	737	590	549	503	509
Ionization enthyalpy(II) kJ mol^{-1}	1757	1450	1145	1064	965	979
Hydration enthalpy/kJ mol^{-1}	–2494	–1921	–1577	–1443	–1305	-
Metallic radius/pm	111	160	197	215	222	-
Ionic radius M^+/pm	31	72	100	118	135	148
m.p./K	1560	924	1124	1062	1002	973
b.p/K	2745	1363	1767	.1655	2078	(1973)
Density / g cm^{-3}	1.84	1.74	1.55	2.63	3.59	(5.5)
Standard Potentials E^{-} /V for (M^{+2}/M)	–1.97	–2.36	–2.84	–2.89	–2.92	–2.92
Occurrence in lithosphere	2*	2.76**	4.6**	384*	390*	10^{-6}*

**ppm (part per million); ** percentage by weight :*

10.6.3 Ionization Enthalpies

Ionization Enthalpy

Be > Mg > Ca > Sr > Ba

Down the group IE decreases due to increase in size

Q. IE_1 of AM < IE_1 of AEM

IE_2 of AM > IE_2 of AEM

[where AM = Alkali metal, AEM = Alkaline earth metal]

Reason : IE_1 of AEM is large due to increased nuclear charge in AEM as compared to AM but IE_2 of AM is large because second electron in AM is to be removed from cation which has already acquired noble gas configuration.

10.6.4 Hydration Enthalpies

Like alkali metal ions, the hydration enthalpies of alkaline earth metal ions decrease with increase in ionic size down the group.

$Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$

The hydration enthalpies of alkaline earth metal ions are larger than those of alkali metal ions. Thus, compounds of alkaline earth metals are more extensively hydrated than those of alkali metals, e.g., $MgCl_2$ and $CaCl_2$ exist as $MgCl_2.6H_2O$ and $CaCl_2 \cdot 6H_2O$ while NaCl and KCl do not form such hydrates.

10.6.5 Physical Properties

(i) The alkaline earth metals, in general, are silvery white, lustrous and relatively soft but harder than the alkali metals. Beryllium and magnesium appear to be somewhat greyish.

(ii) The melting and boiling points of these metals are higher than the corresponding alkali metals due to smaller sizes. The trend is, however, not systematic.

(iii) Because of the low ionisation enthalpies, they are strongly electropositive in nature. The electropositive character increases down the group from Be to Ba.

(iv) Calcium, strontium and barium impart characteristic brick red, crimson and apple green colours respectively to the flame. In flame the electrons are excited to higher energy levels and when they drop back to the ground state, energy is emitted in the form of visible light. The electrons in beryllium and magnesium are too strongly bound to get excited by flame. Hence, these elements do not impart any colour to the flame. The flame test for Ca, Sr and Ba is helpful in their detection in qualitative analysis and estimation by flame photometry.

(v) The alkaline earth metals like those of alkali metals have high electrical and thermal conductivities which are typical characteristics of metals.

10.6.6 Chemical Properties

The alkaline earth metals are less reactive than the alkali metals. The reactivity of these elements increases on going down the group.

(i) ***Reactivity towards air :*** Beryllium and magnesium are kinetically inert to oxygen and water because of the formation of an oxide film on their surface. However, powdered beryllium burns brilliantly on ignition in air to give BeO and Be_3N_2. Magnesium is more electropositive and burns with dazzling brilliance in air to give MgO and Mg_3N_2. Calcium, strontium and barium are readily attacked by air to form the oxide and nitride.

(ii) ***Reactivity towards water.***

Reaction with H_2***O :*** AEM have lesser tendency to react with water as compared to AM. They form hydroxides and liberate H_2 on reaction with H_2O

$$M + 2H_2O \xrightarrow{\Delta} M(OH)_2 + H_2$$

* Be is inert towards water.

* Magnesium react as

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$$

or $$Mg + H_2O \rightarrow MgO + H_2O$$

MgO forms protective layer, that is why it does not react readily unless layer is removed amalgamating with Hg. Other metals react quite readily (Ca, Sr, Ba).

Note: $Be(OH)_2$ is amphoteric but other hydroxides are basic in nature.

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(iii) ***Reactivity towards the halogens :*** All the alkaline earth metals combine with halogen at elevated temperatures forming their halides.

$$M + X_2 \rightarrow MX_2 \ (X = F, Cl, Br, I)$$

Thermal decomposition of $(NH_4)_2BeF_4$ is the best route for the preparation of BeF_2, and $BeCl_2$ is conveniently made from the oxide.

$$BeO + C + Cl_2 \xrightleftharpoons{600-800K} BeCl_2 + CO$$

(iv) ***Reactivity towards hydrogen :*** All the elements except beryllium combine with hydrogen upon heating to form their hydrides, MH_2. BeH_2, however, can be prepared by the reaction of $BeCl_2$ with $LiAlH_4$.

$$2BeCl_2 + LiAlH_4 \rightarrow 2BeH_2 + LiCl + AlCl_3$$

(v) ***Reactivity towards acids :*** AEM react with acids & liberate H_2

$$Mg + 2HCl \rightarrow MgCl_2 + H_2$$

Be is amphoteric as it also react with NaOH, other metals do not react as they are purely basic.

$$Be + 2NaOH \rightarrow Be(OH)_2 \xrightarrow{\text{excess NaOH}} [Be(OH)_4]^{2-}$$

(vi) ***Reducing nature :*** Like alkali metals, the alkaline earth metals are strong reducing agents. This is indicated by large negative values of their reduction potentials. However their reducing power is less than those of their corresponding alkali metals. Beryllium has less negative value compared to other alkaline earth metals. However, its reducing nature is due to large hydration energy associated with the small size of Be^{2+} ion and relatively large value of the atomization enthalpy of the metal.

(vii) ***Solutions in liquid ammonia :*** Like alkali metals, the alkaline earth metals dissolve in liquid ammonia to give deep blue black solutions forming ammoniated ions.

$$M + (x + y)\ NH_3 \rightarrow [M(NH_3)_x]^{2+} + 2[e(NH_3)_y]^- \text{ (except : Be and Mg)}$$

From these solutions, the ammoniates, $[M(NH_3)_6]^{2+}$ can be recovered.

10.6.7 Uses :

Be : Beryllium is used in the manufacture of alloys. Copper-beryllium alloys are used in the preparation of high strength springs. Metallic beryllium is used for making windows of X-ray tubes.

Mg : Magnesium forms alloys with aluminium, zinc, manganese and tin. Magnesium-aluminium alloys being light in mass are used in air-craft construction. Magnesium (powder and ribbon) is used in flash powders and bulbs, incendiary bombs and signals. A suspension of magnesium hydroxide in water (called *milk of magnesia*) is used as antacid in medicine. Magnesium carbonate is an ingredient of toothpaste.

Ca : Calcium is used in the extraction of metals from oxides which are difficult to reduce with carbon. Calcium and barium metals, owing to their reactivity with oxygen and nitrogen at elevated temperatures, have often been used to remove air from vacuum tubes.

Ra : Radium salts are used in radiotherapy, for example, in the treatment of cancer.

10.7 GENERAL CHARACTERISTICS OF COMPOUNDS OF THE ALKALINE EARTH METALS

The dipositive oxidation state (M^{2+}) is the predominant valence of Group 2 elements. The alkaline earth metals form compounds which are predominantly ionic but less ionic than the corresponding compounds of alkali metals. This is due to increased nuclear charge and smaller size. The oxides and other compounds of beryllium and magnesium are more covalent than those formed by the heavier and large sized members (Ca, Sr, Ba). The general characteristics of some of the compounds of alkali earth metals are described below.

(i) Oxides and Hydroxides :

The alkaline earth metals burn in oxygen to form the monoxide, MO which, except for BeO, have rock-salt structure. The BeO is essentially covalent in nature. The enthalpies of formation of these oxides are quite high and consequently they are very stable to heat. BeO is amphoteric while oxides of other elements are ionic in nature. All these oxides except BeO are basic in nature and react with water to form sparingly soluble hydroxides.

$$MO + H_2O \rightarrow M(OH)_2$$

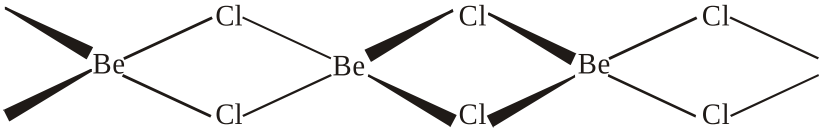
The solubility, thermal stability and the basic character of these hydroxides increase with increasing atomic number from $Mg(OH)_2$ to $Ba(OH)_2$. The alkaline earth metal hydroxides are, however, less basic and less stable than alkali metal hydroxides. Beryllium hydroxide is amphoteric in nature as it reacts with acid and alkali both.

$$Be(OH)_2 + 2OH^- \rightarrow \underset{\text{Beryllate ion}}{[Be(OH)_4]^{2-}}$$

$$Be(OH)_2 + 2HCl \rightarrow 2H_2O + BeCl_2$$

(ii) Halides :

Except for beryllium halides, all other halides of alkaline earth metals are ionic in nature. Beryllium halides are essentially covalent and soluble in organic solvents. Beryllium chloride has a chain structure in the solid state as shown below:



In the vapour phase $BeCl_2$ tends to form a chloro-bridged dimer which dissociates into the linear monomer at high temperatures of the order of 1200 K. The tendency to form halide hydrates gradually decreases (for example, $MgCl_2 \cdot 8H_2O$, $CaCl_2 \cdot 6H_2O$, $SrCl_2 \cdot 6H_2O$ and $BaCl_2 \cdot 2H_2O$) down the group. The dehydration of hydrated chlorides, bromides and iodides of Ca, Sr and Ba can be achieved on heating; however, the corresponding hydrated halides of Be and Mg on heating suffer hydrolysis. The fluorides are relatively less soluble than the chlorides owing to their high lattice energies.

(iii) ***Salts of Oxoacids :*** The alkaline earth metals also form salts of oxoacids. Some of these are :

Carbonates : Carbonates of alkaline earth metals are insoluble in water and can be precipitated by addition of a sodium or ammonium carbonate solution to a solution of a soluble salt of these metals. The solubility of carbonates in water decreases as the atomic number of the metal ion increases. All the carbonates decompose on heating to give carbon dioxide and the oxide. Beryllium carbonate is unstable and can be kept only in the atmosphere of CO_2. The thermal stability increases with increasing cationic size.

Sulphates : The sulphates of the alkaline earth metals are all white solids and stable to heat. $BeSO_4$, and $MgSO_4$ are readily soluble in water; the solubility decreases from $CaSO_4$ to $BaSO_4$. The greater hydration enthalpies of Be^{2+} and Mg^{2+} ions overcome the lattice enthalpy factor and therefore their sulphates are soluble in water.

Nitrates : The nitrates are made by dissolution of the carbonates in dilute nitric acid. Magnesium nitrate crystallises with six molecules of water, whereas barium nitrate crystallises as the anhydrous salt. This again shows a decreasing tendency to form hydrates with increasing size and decreasing hydration enthalpy. All of them decompose on heating to give the oxide like lithium nitrate.

$$2M\,(NO_3)_2 \rightarrow 2MO + 4NO_2 + O_2$$

(M + Be, Mg, Ca, Sr, Ba)

Problem 10.4

Why does the solubility of alkaline earth metal hydroxides in water increase down the group?

Solution

Among alkaline earth metal hydroxides, the anion being common the cationic radius will influence the lattice enthalpy. Since lattice enthalpy decreases much more than the hydration enthalpy with increasing ionic size, the solubility increases as we go down the group.

Problem 10.5

Why does the solubility of alkaline earth metal carbonates and sulphates in water decrease down the group?

Solution

The size of anions being much larger compared to cations, the lattice enthalpy will remain almost constant within a particular group. Since the hydration enthalpies decrease down the group, solubility will decrease as found for alkaline earth metal carbonates and sulphates.

10.8 ANOMALOUS BEHAVIOUR OF BERYLLIUM

Beryllium, the first member of the Group 2 metals, shows anomalous behaviour as compared to magnesium and rest of the members. Further, it shows diagonal relationship to aluminium which is discussed subsequently.

(i) Beryllium has exceptionally small atomic and ionic sizes and thus does not compare well with other members of the group. Because of high ionisation enthalpy and small size it forms compounds which are largely covalent and get easily hydrolysed.

(ii) Beryllium does not exhibit coordination number more than four as in its valence shell there are only four orbitals. The remaining members of the group can have a coordination number of six by making use of *d*-orbitals.

(iii) The oxide and hydroxide of beryllium, unlike the hydroxides of other elements in the group, are amphoteric in nature.

10.8.1 Diagonal Relationship between Beryllium and Aluminium

The ionic radius of Be^{2+} is estimated to be 31 pm; the charge/radius ratio is nearly the same as that of the Al^{3+} ion. Hence beryllium resembles aluminium in some ways. Some of the similarities are:

(i) Like aluminium, beryllium is not readily attacked by acids because of the presence of an oxide film on the surface of the metal.

(ii) Beryllium hydroxide dissolves in excess of alkali to give a beryllate ion, $[Be(OH)_4]^{2-}$ just as aluminium hydroxide gives aluminate ion, $[Al(OH)_4]^-$.

(iii) The chlorides of both beryllium and aluminium have Cl^- bridged chloride structure in vapour phase. Both the chlorides are soluble in organic solvents and are strong Lewis acids. They are used as Friedel Craft catalysts.

(iv) Beryllium and aluminium ions have strong tendency to form complexes, BeF_4^{2-}, AlF_6^{3-}

10.9 SOME IMPORTANT COMPOUNDS OF CALCIUM

Important compounds of calcium are calcium oxide, calcium hydroxide, calcium sulphate, calcium carbonate and cement. These are industrially important compounds. The large scale preparation of these compounds and their uses are described below.

***Calcium Oxide or Quick Lime,* CaO**

It is prepared on a commercial scale by heating limestone ($CaCO_3$) in a rotary kiln at 1070-1270 K.

$$CaCO_3 \xrightleftharpoons{\text{heat}} CaO + CO_2$$

The carbon dioxide is removed as soon as it is produced to enable the reaction to proceed to completion. Calcium oxide is a white amorphous solid. It has a melting point of 2870 K. On exposure to atmosphere, it absorbs moisture and carbon dioxide.

$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$CaO + CO_2 \rightarrow CaCO_3$$

The addition of limited amount of water breaks the lump of lime. This process is called *slaking of lime*. Quick lime slaked with soda gives solid sodalime. Being a basic oxide, it combines with acidic oxides at high temperature.

$$CaO + SiO_2 \rightarrow CaSiO_3$$

$$6CaO + P_4O_{10} \rightarrow 2Ca_3(PO_4)_2$$

Uses : **(i)** It is an important primary material for manufacturing cement and is the cheapest form of alkali.

(ii) It is used in the manufacture of sodium carbonate from caustic soda.

(iii) It is employed in the purification of sugar and in the manufacture of dye stuffs.

Calcium Hydroxide (Slaked lime), $Ca(OH)_2$

Calcium hydroxide is prepared by adding water to quick lime, CaO.

It is a white amorphous powder. It is sparingly soluble in water. The aqueous solution is known as *lime water* and a suspension of slaked lime in water is known as *milk of lime*.

When carbon dioxide is passed through lime water it turns milky due to the formation of calcium carbonate.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

On passing excess of carbon dioxide, the precipitate dissolves to form calcium hydrogencarbonate.

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca\ (HCO_3)_2$$

Milk of lime reacts with chlorine to form hypochlorite, a constituent of bleaching powder.

$$2Ca(OH)_2 + 2Cl_2 \rightarrow CaCl_2 + Ca(OCl)_2 + 2H_2O$$

Uses: **(i)** It is used in the preparation of mortar, a building material.

(ii) It is used in white wash due to its disinfectant nature.

(iii) It is used in glass making, in tanning industry, for the preparation of bleaching powder and for purification of sugar.

Calcium Carbonate, $CaCO_3$

Calcium carbonate occurs in nature in several forms like limestone, chalk, marble etc. It can be prepared by passing carbon dioxide through slaked lime or by the addition of sodium carbonate to calcium chloride.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$$

Excess of carbon dioxide should be avoided since this leads to the formation of water soluble calcium hydrogencarbonate.

Calcium carbonate is a white fluffy powder. It is almost insoluble in water. When heated to 1200 K, it decomposes to evolve carbon dioxide.

$$CaCO_3 \xrightarrow{1200K} CaO + CO_2$$

It reacts with dilute acid to liberate carbon dioxide.

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$$

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$$

Uses: It is used as a building material in the form of marble and in the manufacture of quick lime. Calcium carbonate along with magnesium carbonate is used as a flux in the extraction of metals such as iron.

Specially precipitated $CaCO_3$ is extensively used in the manufacture of high quality paper. It is also used as an antacid, mild abrasive in tooth paste, a constituent of chewing gum, and a filler in cosmetics.

***Calcium Sulphate (Plaster of Paris),* $CaSO_4 \cdot \frac{1}{2} H_2O$**

It is a hemihydrate of calcium sulphate. It is obtained when gypsum, $CaSO_4 \cdot 2H_2O$, is heated to 393 K.

$$2(CaSO_4.2H_2O) \rightarrow 2(CaSO_4).H_2O + 3H_2O$$

Above 393 K, no water of crystallisation is left and anhydrous calcium sulphate, $CaSO_4$ is formed. This is known as 'dead burnt plaster'.

It has a remarkable property of setting with water. On mixing with an adequate quantity of water it forms a plastic mass that gets into a hard solid in 5 to 15 minutes.

Uses: The largest use of Plaster of Paris is in the building industry as well as plasters. It is used for immoblising the affected part of organ where there is a bone fracture or sprain. It is also employed in dentistry, in ornamental work and for making casts of statues and busts.

Cement: Cement is an important building material. It was first introduced in England in 1824 by Joseph Aspdin. It is also called **'Portland cement'** because it resembles with the natural limestone quarried in the Isle of Portland, England.

Cement is a product obtained by combining a material rich in lime, CaO with other material such as clay which contains silica, SiO_2 along with the oxides of aluminium, iron and magnesium. The average composition of Portland cement is :

CaO, 50-60%; SiO_2, 20-25%; Al_2O_3, 5-10%; MgO, 2-3%; Fe_2O_3, 1-2% and SO_3, 1-2%. For a good quality cement, the ratio of silica (SiO_2) to alumina (Al_2O_3) should be between 2.5 and 4 and the ratio of lime (CaO) to the total of the oxides of silicon (SiO_2) aluminium (Al_2O_3) and iron (Fe_2O_3) should be as close as possible to 2.

The raw materials for the manufacture of cement are limestone and clay. When clay and lime are strongly heated together they fuse and react to form 'cement clinker'. This clinker is mixed with 2-3% by weight of gypsum ($CaSO_4 \cdot 2H_2O$) to form cement. Thus important ingredients present in Portland cement are dicalcium silicate (Ca_2SiO_4) 26%, tricalcium silicate (Ca_3SiO_5) 51% and tricalcium aluminate ($Ca_3Al_2O_6$) 11%.

Setting of Cement : When mixed with water, the setting of cement takes place to give a hard mass. This is due to the hydration of the molecules of the constituents and their rearrangement. The purpose of adding gypsum is only to slow down the process of setting of the cement so that it gets sufficiently hardened.

Uses: Cement has become a commodity of national necessity for any country next to iron and steel. It is used in concrete and reinforced concrete, in plastering and in the construction of bridges, dams and buildings.

10.10 BIOLOGICAL IMPORTANCE OF MAGNESIUM AND CALCIUM

An adult body contains about 25 g of Mg and 1200 g of Ca compared with only 5 g of iron and 0.06 g of copper. The daily requirement in the human body has been estimated to be 200 – 300 mg. All enzymes that utilise ATP in phosphate transfer require magnesium as the cofactor. The main pigment for the absorption of light in plants is chlorophyll which contains magnesium. About 99 % of body calcium is present in bones and teeth. It also plays important roles in neuromuscular function, interneuronal transmission, cell membrane integrity and blood coagulation. The calcium concentration in plasma is regulated at about 100 mgL^{-1}. It is maintained by two hormones: calcitonin and parathyroid hormone. Do you know that bone is not an inert and unchanging substance but is continuously being solubilised and redeposited to the extent of 400 mg per day in man? All this calcium passes through the plasma.

Summary : The ***s*-Block** of the periodic table constitutes **Group1** (alkali metals) and **Group 2** (alkaline earth metals). They are so called because their oxides and hydroxides are alkaline in nature. The alkali metals are characterised by one *s*-electron and the alkaline earth metals by two *s*-electrons in the valence shell of their atoms. These are highly reactive metals forming monopositive **(M^+)** and dipositve **(M^{2+})** ions respectively.

There is a regular trend in the physical and chemical properties of the alkali metal with increasing atomic numbers. The **atomic** and **ionic** sizes increase and the **ionization enthalpies** decrease systematically down the group.

Somewhat similar trends are observed among the properties of the alkaline earth metals. The first element in each of these groups, lithium in Group 1 and beryllium in Group 2 shows similarities in properties to the second member of the next group. Such similarities are termed as the **'diagonal relationship'** in the periodic table.

As such these elements are anomalous as far as their group characteristics are concerned.

The alkali metals are silvery white, soft and low melting. They are highly reactive. The compounds of alkali metals are predominantly ionic. Their oxides and hydroxides are soluble in water forming strong alkalies. Important compounds of sodium includes sodium carbonate, sodium chloride, sodium hydroxide and sodium hydrogencarbonate. Sodium hydroxide is manufactured by **Castner-Kellner** process and sodium carbonate by **Solvay** process.

The chemistry of alkaline earth metals is very much like that of the alkali metals. However, some differences arise because of reduced atomic and ionic sizes and increased cationic charges in case of alkaline earth metals. Their oxides and hydroxides are less basic than the alkali metal oxides and hydroxides. Industrially important compounds of calcium include calcium oxide (lime), calcium hydroxide (slaked lime), calcium sulphate **(Plaster of Paris),** calcium carbonate (limestone) and cement. **Portland cement** is an important constructional material.

It is manufactured by heating a pulverised mixture of limestone and clay in a rotary kiln. The clinker thus obtained is mixed with some gypsum (2-3%) to give a fine powder of cement. All these substances find variety of uses in different areas.

Monovalent sodium and potassium ions and divalent magnesium and calcium ions are found in large proportions in **biological fluids**. These ions perform important **biological functions** such as maintenance of ion balance and nerve impulse conduction.

FEW IMPORTANT POINTS

(i) Magnesium Peroxide (MgO_2) and Calcium Peroxide (CaO_2) are obtained by passing H_2O_2 in a suspension of $Mg(OH)_2$ and $Ca(OH)_2$.

(ii) MgO_2 is used as an antiseptic in tooth paste and as a bleaching agent.

(iii) Preperation of NaOH : Caustication of Na_2CO_3 (Gossage's method):

$$Na_2CO_3 + \underset{\text{(suspension)}}{Ca(OH)_2} \rightarrow 2NaOH + CaCO_3\downarrow$$

Since the K_{sp} $(CaCO_3) < K_{sp}$ $(Ca(OH)_2)$, the reaction shifts towards right.

(iv) As a reagent KOH is less frequently used but in absorption of CO_2, KOH is preferably used compared to NaOH. Because $KHCO_3$ formed is soluble whereas $NaHCO_3$ is sparingly soluble and may therefore choke the tubes of apparatus used.

(v) Calcium hydroxide is used as a mortar.

[Mortar is a mixture of slaked lime (1 Part) and sand (3 Parts) made into paste with water.]

(vi) NaCl is used to prepare freezing mixture in laboratory [Ice-common salt mixture is called freezing mixture and temperature goes down to –23°C.]

(vii) On heating $MgCl_2{\cdot}6H_2O$ undergoes hydrolysis as follows:

$$MgCl_2{\cdot}6H_2O \xrightarrow{\Delta} Mg(OH)Cl + HCl + 5H_2O$$

$$Mg(OH)Cl \longrightarrow MgO + HCl$$

** Hence, Anh. $MgCl_2$ cannot be prepared by heating this hydrate.

** Because of the formation of HCl , sea water cannot be used in marine boilers which corrodes the iron body.

(viii) Anhydrous $MgCl_2$ can be prepared by heating a double salt like $MgCl_2 \,.\, NH_4Cl \,.\, 6H_2O$ as follows:

$$MgCl_2 \,.\, NH_4Cl \,.\, 6H_2O \xrightarrow[\Delta]{-H_2O} MgCl_2 \,.\, NH_4Cl \xrightarrow[\Delta]{\text{strong}} MgCl_2 + NH_3 + HCl$$

(ix) Sorel Cement is a mixture of MgO and $MgCl_2$ (paste like) which set to hard mass on standing, this is used in dental filling, flooring etc.

(x) Anh. $CaCl_2$ is used in drying gases and organic compounds but not NH_3 or alcohol due to the formation of $CaCl_2 \,.\, 8NH_3$ and $CaCl_2 \,.\, 4C_2H_5OH$.

(xi) One interesting feature of the solubility of glauber's salt is; when crystallised at below 32.4°C, then $Na_2SO_4.\ 10H_2O$ is obtained but above 32.4°C, Na_2SO_4 (anh.) comes out.

(xii) Leblanc Process (Preparation of Na_2CO_3) :

$$NaCl + H_2SO_4\,(\text{conc.}) \xrightarrow{\text{mild heating}} NaHSO_4 + HCl$$

$$NaCl + NaHSO_4 \xrightarrow[\text{heated}]{\text{Strongly}} \underset{\text{(Salt Cake)}}{Na_2SO_4} + HCl$$

$$Na_2SO_4 + 4C \longrightarrow Na_2S + 4CO\uparrow$$

$$Na_2S + CaCO_3 \longrightarrow Na_2CO_3 + CaS$$

EXERCISE # O-1

SELECT THE CORRECT ALTERNATIVE (ONLY ONE CORRECT ANSWER)

Alkali metals

1. Cs^+ ions impart violet colour to Bunsen flame. This is due to the fact that the emitted radiations are of -

(A) high energy (B) lower frequencies

(C) longer wave-lengths (D) zero wave number

2. The reaction of an element A with water produces combustible gas B and an aqueous solution of C. When another substance D reacts with this solution C also produces the same gas B. D also produces the same gas even on reaction with dilute H_2SO_4 at room temperature. Element A imparts golden yellow colour to Bunsen flame. Then, A, B, C and D may be identified as

(A) Na, H_2, NaOH and Zn (B) K, H_2, KOH and Zn

(C) K, H_2, NaOH and Zn (D) Ca, H_2, $CaCOH_2$ and Zn

3. Which of the following carbonate of alkali metals has the least thermal stability?

(A) Li_2CO_3 (B) K_2CO_3 (C) Cs_2CO_3 (D) Na_2CO_3

4. The alkali metals which form normal oxide, peroxide as well as super oxides are

(A) Na, Li (B) K, Li (C) Li, Cs (D) K, Rb

5. The pair of compounds, which cannot exist together in a solution is

(A) $NaHCO_3$ and NaOH (B) Na_2CO_3 and NaOH

(C) $NaHCO_3$ and Na_2CO_3 (D) $NaHCO_3$ and H_2O

6. Solution of sodium metal in liquid ammonia is a strong reducing agent due to presence of

(A) solvated sodium ions (B) solvated hydrogen ions

(C) sodium atoms or sodium hydroxide (D) solvated electrons

7. The order of solubility of lithium halides in non-polar solvents follows the order

(A) LiI > LiBr > LiCl > LiF (B) LiF > LiI > LiBr > LiCl

(C) LiCl > LiF > LiI > LiBr (D) LiBr > LiCl > LiF > LiI

8. The salt which finds uses in qualitative inorganic analysis is

(A) $CuSO_4 \cdot 5H_2O$ or $ZnSO_4 \cdot 5H_2O$ (B) $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$

(C) $Na(NH_4)HPO_4 \cdot 4H_2O$ (D) $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$

9. Fire extinguishers contain

(A) conc. H_2SO_4 solution (B) H_2SO_4 and $NaHCO_3$ solutions

(C) $NaHCO_3$ solution (D) $CaCO_3$ solution

10. $CsBr_3$ contains

(A) Cs–Br covalent bonds (B) Cs^{3+} and Br^- ions

(C) Cs^+ and Br_3^- ions (D) Cs^{3+} and Br_3^{3-} ions

11. $Na + Al_2O_3 \xrightarrow{\text{High temperature}} X \xrightarrow[\text{water}]{CO_2 \text{ in}} Y$; compound Y is

(A) $NaAlO_2$ (B) $NaHCO_3$ (C) Na_2CO_3 (D) Na_2O_2

12. aq. NaOH + P_4 (white) $\longrightarrow$ PH_3 + X; compound X is

(A) NaH_2PO_2 (B) $NaHPO_4$ (C) Na_2CO_3 (D) $NaHCO_3$

13. When K_2O is added to water, the solution becomes basic in nature because it contains a significant concentration of

(A) K^+ (B) O^{2-} (C) OH^- (D) O_2^{2-}

14. The order of melting point of chlorides of alkali metals is

(A) LiCl > NaCl > KCl < CsCl (B) LiCl > NaCl > KCl > CsCl

(C) NaCl > KCl > CsCl > LiCl (D) LiCl > NaCl > CsCl > KCl

15. NaOH(Solid) + CO $\xrightarrow{200°C}$ X; product X is

(A) $NaHCO_3$ (B) Na_2CO_3 (C) HCOONa (D) H_2CO_3

16. The aqueous solutions of lithium salts are poor conductor of electricity rather than other alkali metals because of

(A) high ionisation energy

(B) high electronegativity

(C) lower ability of Li^+ ions to polarize water molecules

(D) higher degree of hydration of Li^+ ions

17. In $LiAlH_4$, metal Al is present in

(A) anionic part (B) cationic part

(C) in both anionic and cationic part (D) neither in cationic nor in anionic part

18. Which one of the following fluoride of alkali metals has the highest lattice energy?

(A) LiF (B) CsF (C) NaF (D) KF

19. Crown ethers and cryptands form

(A) complexes with alkali metals

(B) salts of alkali metals

(C) hydroxides of alkali metals used for inorganic quantitative analysis

(D) organic salts of alkali metals

20. The correct order of degree of hydration of M^+ ions of alkali metals is

(A) $Li^+ < K^+ < Na^+ < Rb^+ < Cs^+$ (B) $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$

(C) $Cs^+ < Rb^+ < K^+ < Na^+ < Li^+$ (D) $Cs^+ < Rb^+ < Na^+ < K^+ < Li^+$

21. The commercial method of preparation of potassium by reduction of molten KCl with metallic sodium at 850°C is based on the fact that

(A) potassium is solid and sodium distils off at 850 °C

(B) potassium being more volatile and distils off thus shifting the reaction forward

(C) sodium is less reactive than potassium at 850 °C with respect to Cl_2

(D) sodium has less affinity to chloride ions in the presence of potassium ion

Alkaline earth metals

22. The 'milk of magnesia' used as an antacid is chemically

(A) $Mg(OH)_2$ (B) MgO (C) $MgCl_2$ (D) MgO + $MgCl_2$

23. An alkaline earth metal (M) gives a salt with chlorine, which is soluble in water at room temperature. It also forms an insoluble sulphate whose mixture with a sulphide of a transition metal is called 'lithopone' - a white pigment. Metal M is

(A) Ca (B) Mg (C) Ba (D) Sr

24. The hydroxide of IInd A metal, which has the lowest value of solubility product (K_{sp}) at normal temperature (25°C) is

(A) $Ca(OH)_2$ (B) $Mg(OH)_2$ (C) $Sr(OH)_2$ (D) $Be(OH)_2$

25. $$(\text{Yellow ppt})\,T \xleftarrow{K_2CrO_4/H^+} X \xrightarrow{\text{dil.HCl}} Y(\text{Yellow ppt}) + Z\uparrow (\text{pungent smelling gas})$$

If X gives green flame test. Then, X is

(A) $MgSO_4$ (B) BaS_2O_3 (C) $CuSO_4$ (D) PbS_2O_3

26. $Mg_2C_3 + H_2O \longrightarrow X$ (organic compound). Compound X is

(A) C_2H_2 (B) CH_4 (C) propyne (D) ethene

27. The hydration energy of Mg^{2+} is

(A) more than that of Mg^{3+} ion (B) more than that of Na^+ ion

(C) more than that of Al^{3+} ion (D) more than that of Be^{2+} ion

28. The correct order of second ionisation potentials (IP) of Ca, Ba and K is

(A) K > Ca > Ba (B) Ba > Ca > K (C) K > Ba > Ca (D) K = Ba = Ca

29. EDTA is used in the estimation of

(A) Mg^{2+} ions (B) Ca^{2+} ions

(C) both Ca^{2+} and Mg^{2+} ions (D) Mg^{2+} ions but not Ca^{2+} ions

30. The correct order of solubility is

(A) $CaCO_3 < KHCO_3 < NaHCO_3$ (B) $KHCO_3 < CaCO_3 < NaHCO_3$

(C) $NaHCO_3 < CaCO_3 < KHCO_3$ (D) $CaCO_3 < NaHCO_3 < KHCO_3$

31. The complex formation tendency of alkaline earth metals decreases down the group because

(A) atomic size increases

(B) availability of empty d and f-orbitals increases

(C) nuclear charge to volume ratio increases (D) all the above

32. The alkaline earth metals, which do not impart any colour to Bunsen flame are

(A) Be and Mg (B) Mg and Ca (C) Be and Ca (D) Be and Ba

33. $Y \xleftarrow{\Delta,205^\circ C} CaSO_4{\cdot}2H_2O \xrightarrow{\Delta,120^\circ C} X$. X and Y are respectively

(A) plaster of paris, dead burnt plaster

(B) dead burnt plaster, plaster of paris

(C) CaO and plaster of paris

(D) plaster of paris, mixture of gases

34. A metal M readily forms water soluble sulphate, and water insoluble hydroxide $M(OH)_2$. Its oxide MO is amphoteric, hard and having high melting point. The alkaline earth metal M must be

(A) Mg (B) Be (C) Ca (D) Sr

35.

$$\begin{tikzcd}
\text{(White ppt) D} & \text{A} \arrow[l, "Na_2CO_3"'] \arrow[r, "K_2CrO_4", "\text{(in acetic acid)}"'] \arrow[d, "\text{dil.}H_2SO_4"'] & \text{B(Yellow ppt)} \\
 & \text{C(White ppt)} &
\end{tikzcd}$$

If A is the metallic salt, then the white ppt. of D must be of

(A) stronsium carbonate (B) red lead

(C) barium carbonate (D) calcium carbonate

36. (Milky Cloud) C $\xleftarrow{CO_2}$ A + $Na_2CO_3 \longrightarrow$ B + C

The chemical formulae of A and B are

(A) NaOH and $Ca(OH)_2$ (B) $Ca(OH)_2$ and NaOH

(C) NaOH and CaO (D) CaO and $Ca(OH)_2$

37. The correct order of basic-strength of oxides of alkaline earth metals is

(A) BeO > MgO > CaO > SrO

(B) SrO > CaO > MgO > BeO

(C) BeO > CaO > MgO > SrO

(D) SrO > MgO > CaO > BeO

38. $X \xrightarrow{N_2,\Delta} Y \xrightarrow{H_2O} \text{Z(colourless gas)} \xrightarrow[CuSO_4]{} \text{T(blue colour)}$

Then, substances Y and T are

(A) Y = Mg_3N_2 and T = $CuSO_4{\cdot}5H_2O$ (B) Y = Mg_3N_2 and T = $CuSO_4{\cdot}4NH_3$

(C) Y = $Mg(NO_3)_2$ and T = CuO (D) Y = MgO and T = $CuSO_4{\cdot}4NH_3$

39. Weakest base among KOH, NaOH, $Ca(OH)_2$ and $Zn(OH)_2$ is

(A) $Ca(OH)_2$ (B) KOH

(C) NaOH (D) $Zn(OH)_2$

40. If X and Y are the second ionisation potentials of alkali and alkaline earth metals of same period, then -

(A) X > Y (B) X < Y (C) X = Y (D) X << Y

41. $X \xrightarrow{CoCl_2} CaCl_2 + Y\uparrow$; the effective ingredient of X is

(A) OCl^- (B) Cl^- (C) OCl^+ (D) OCl_2^-

42. White heavy precipitate is formed when $BaCl_2$ is added to a clear solution of compound **A**. Precipitate is insoluble in dilute HCl. Then, the compound **A** is

(A) a bicarbonate (B) a carbonate

(C) a sulphate (D) a chloride

43. $X + C + Cl_2 \xrightarrow[\text{of about } 1000\,K]{\text{High temperature}} Y + CO$; $Y + 2H_2O \rightarrow Z + 2HCl$

Compound Y is found in polymeric chain structure and is an electron deficient molecule. Y must be

(A) BeO (B) $BeCl_2$ (C) BeH_2 (D) $AlCl_3$

44. $BeCl_2 + LiAlH_4 \longrightarrow X + LiCl + AlCl_3$

(A) X is LiH (B) X is BeH_2

(C) X is $BeCl_2 \cdot 2H_2O$ (D) None

45. The order of thermal stability of carbonates of IIA group is

(A) $BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3$

(B) $MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$

(C) $CaCO_3 > SrCO_3 > BaCO_3 > MgCO_3$

(D) $MgCO_3 = CaCO_3 > SrCO_3 = BaCO_3$

46. A pair of substances which gives all the same products on reaction with water is

(A) Mg and MgO (B) Sr and SrO (C) Ca and CaH_2 (D) Be and BeO

47. A metal which is soluble in both water and liquid NH_3 separately -

(A) Cr (B) Mn (C) Ba (D) Al

48. $Be_2C + H_2O \longrightarrow BeO + X$

$CaC_2 + H_2O \longrightarrow Ca(OH)_2 + Y$; then X and Y are respectively

(A) CH_4, CH_4 (B) CH_4, C_2H_6 (C) CH_4, C_2H_2 (D) C_2H_2, CH_4

49. Which of the following groups of elements have chemical properties that are most similar

(A) Na, K, Ca (B) Mg, Sr, Ba (C) Be, Al, Ca (D) Be, Ra, Cs

50. $MgBr_2$ and MgI_2 are soluble in acetone because of

(A) Their ionic nature (B) Their coordinate nature

(C) Their metallic nature (D) Their covalent nature

EXERCISE # O-2

SELECT THE CORRECT ALTERNATIVES (ONE OR MORE THEN ONE CORRECT ANSWERS)

Alkali metals

1. Nitrogen dioxide can be prepared by heating -

(A) KNO_3 (B) $AgNO_3$ (C) $Pb(NO_3)_2$ (D) $Cu(NO_3)_2$

2. Which of the following compounds are not paramagnetic in nature?

(A) KO_2 (B) K_2O_2 (C) Na_2O_2 (D) RbO_2

3. The golden yellow colour associated with NaCl to Bunsen flame can be explained on the basis of

(A) low ionisation potential of sodium

(B) emission spectrum

(C) photosensitivity of sodium

(D) sublimation of metallic sodium of yellow vapours

4. KO_2 finds use in oxygen cylinders used for space and submarines. The fact(s) related to such use of KO_2 is/are

(A) it produces O_2 (B) it produces O_3

(C) it absorbs CO_2 (D) it absorbs both CO and CO_2

5. The compound(s) which have –O–O– bond(s) is/are

(A) BaO_2 (B) Na_2O_2 (C) CrO_5 (D) Fe_2O_3

6. Highly pure dilute solution of sodium in ammonia

(A) shows blue colouration due to solvated electrons

(B) shows electrical conductivity due to both solvated electrons as well as solvated sodium ions

(C) shows red colouration due to solvated electrons but a bad conductor of electricity

(D) produces hydrogen gas or carbonate

7. Sodium metal is highly reactive and can be stored under

(A) toluene (B) kerosene oil (C) alcohol (D) benzene

Alkaline earth metals

8. The compound(s) of IInd A metals, which are amphoteric in nature is/are

(A) BeO (B) MgO (C) $Be(OH)_2$ (D) $Mg(OH)_2$

9. The correct statement is/are

(A) $BeCl_2$ is a covalent compound (B) $BeCl_2$ is an electron deficient molecule

(C) $BeCl_2$ can form dimer (D) the hybrid state of Be in $BeCl_2$ is sp^2

10. Which of the following substance(s) is/are used in laboratory for drying purposes?

(A) anhydrous P_2O_5 (B) graphite

(C) anhydrous $CaCl_2$ (D) Na_3PO_4

11. Na_2SO_4 is water soluble but $BaSO_4$ is insoluble because

(A) the hydration energy of Na_2SO_4 is higher than that of its lattice energy

(B) the hydration energy of Na_2SO_4 is less than that of its lattice energy

(C) the hydration energy of $BaSO_4$ is less than that of its lattice energy

(D) the hydration energy of $BaSO_4$ is higher than that of its lattice energy

12. Which of the following statements are false?

(A) $BeCl_2$ is a linear molecule in the vapour state but it is polymeric form in the solid state

(B) Calcium hydride is called hydrolith.

(C) Carbides of both Be and Ca react with water to form acetylene

(D) Oxides of both Be and Ca are amphoteric.

13. Which of the following are ionic carbides?

(A) CaC_2 (B) Al_4C_3 (C) SiC (D) Be_2C

14. Which of the following orders are **CORRECT** :

(A) AgCl > AgF : Covalent character order

(B) $BaO > BaF_2$: Melting point order

(C) $BeF_2 > BaF_2$: Solubility order

(D) $LiNO_3 < RbNO_3$: Thermal stability order

15. Which of the following statements are **CORRECT** :

(A) Mg is present in chlorophyll

(B) Alkaline earth metals does not form super oxide

(C) $NaHCO_3$ is known as baking soda

(D) Permanent hardness of water is removed by boiling

16. Which of the following carbides on hydrolysis does not form methane :

(A) Be_2C (B) CaC_2 (C) SrC_2 (D) Mg_2C_3

17. Select the incorrect order for given properties :

(A) Thermal stability : $BaSO_4 > SrSO_4 > CaSO_4$

(B) Solubility : $BaSO_4 > SrSO_4 > CaSO_4$

(C) Thermal stability : $Li_2CO_3 < Na_2CO_3 < K_2CO_3$

(D) Solubility : $Li_2CO_3 > Na_2CO_3 > K_2CO_3$

18. The correct statement(s) is/are

(A) Mg cannot form complexes

(B) Be can form complexes due to a very small atomic size

(C) the first ionisation potential of Be is higher than that of Mg

(D) Mg forms an alkaline hydroxide while Be forms amphoteric oxides

19. Which of the following is are the characteristic of barium?

(A) It produce water soluble sulphide, sulphite and sulphate

(B) It is a silvery white metal

(C) It forms $Ba(NO_3)_2$ which is used in preparation of green fire

(D) It produce blue-black solution in liquid ammonia

EXERCISE # S-1

NUMERIC GRID TYPE QUESTIONS :

1. Find the number of compounds from the following in which the element in the anionic part is in the minimum oxidation state of it

LiH, Mg_3Bi_2, Al_4C_3, Ca_3P_2, BaO_2

2. How many nitrate groups are present in 1 molecule of Basic beryllium nitrate?

3. Consider the following order :

(1) $CH_4 < CCl_4 < CF_4$: E.N. of central atom C

(2) $Mg^{+2} < K^{+} < S^{-2} < Se^{-2}$: Ionic radius

(3) $Be^{+2}_{(aq)} > Mg^{+2}_{(aq)} > Ca^{+2}_{(aq)}$: Ionic mobility

(4) $Be^{+2} > Li^{+} > Al^{+3}$: Hydrated size

(5) Be > Li > Cs : Reducing power

(6) $F^{\ominus}_{(aq)} > Cl^{\ominus}_{(aq)} > Br^{\ominus}_{(aq)}$: Electrical conductance in infinite dilute solution

Then calculate value of $|x - y|^2$, where x and y are correct and incorrect orders respectively.

4. Consider the following elements :

Li, Cs, Mg, Pb, Al, N

- x = number of elements which can form MO type of oxides.
- y = the highest oxidation state shown by any one of them.
- z = the number of elements which can form amphoteric oxide(s).

Find the sum of x, y and z.

Fill your answer as sum of digits till you get the single digit answer.

5. Find the number of s-block elements which can produce ammoniated cation and ammoniated electron with liquid ammonia.

Li, Na, K, Rb, Cs, Ca, Sr, Ba

6. How many of the following metal chlorides impart characteristic colour to the oxidising flame.

$LiCl$, $NaCl$, KCl, $BeCl_2$, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$

EXERCISE # S-2

COMPREHENSION BASED QUESTIONS

Comprehension # 1

$$A \xrightarrow{\Delta} B\ (\text{oxide}) + CO_2$$

$$B + H_2O \longrightarrow C$$

$$C + CO_2 \longrightarrow A\ (\text{milky})$$

$$C + NH_4Cl \xrightarrow{\Delta} D\ (\text{gas})$$

$$D + H_2O + CO_2 \longrightarrow E$$

$$E + NaCl \longrightarrow F$$

$$F \xrightarrow{\Delta} Na_2CO_3 + CO_2 + H_2O$$

1. A is :

(A) $Ca(HCO_3)_2$ (B) $CaCO_3$ (C) CaO (D) Na_2CO_3

2. B and C are :

(A) CaO, $Ca(OH)_2$ (B) $Ca(OH)_2$, $CaCO_3$

(C) $CaCO_3$, $Ca(OH)_2$ (D) $Ca(OH)_2$, CaO

3. D, E and F are :

(A) NH_3, NH_4Cl, NH_4HCO_3 (B) NH_3, NH_4HCO_3, $NaHCO_3$

(C) NH_4HCO_3, Na_2CO_3, $NaHCO_3$ (D) None

Comprehension # 2

Alkali metals readily react with oxyacids forming corresponding salts like M_2CO_3, $MHCO_3$, MNO_3, M_2SO_4 etc. with evolution of hydrogen. They also dissolve in liquid NH_3 but without the evolution of hydrogen. The colour of its dilute solution is blue but when it is heated and concentrated then its colour becomes bronze.

4. Among the nitrate of alkali metals which one can be decomposed to its oxide easily?

(A) $NaNO_3$ (B) KNO_3 (C) $LiNO_3$ (D) $RbNO_3$

5. Among the carbonates of alkali metals which one has highest stability?

(A) Cs_2CO_3 (B) Rb_2CO_3 (C) K_2CO_3 (D) Na_2CO_3

6. Which of the following statement about the sulphate of alkali metal is correct?

(A) Except Li_2SO_4 all sulphate of other alkali metals are soluble in water

(B) All sulphates of alkali metals except lithium sulphate forms alum.

(C) The sulphates of alkali metals cannot be hydrolysed.

(D) All of these

7. Which of the following statement about solution of alkali metals in liquid ammonia is correct?

(A) The solution have strong oxidizing properties.

(B) Both the dilute solution as well as concentrated solution are paramagnetic in nature

(C) Charge transfer is the responsible for the colour of the solution

(D) None of these

8. Which metal bicarbonates does not exist in solid state?

(i) $LiHCO_3$ (ii) $Ca(HCO_3)_2$ (iii) $Zn\ (HCO_3)_2$

(iv) $NaHCO_3$ (v) $AgHCO_3$

(A) (i), (ii), (iii), (v) (B) (i), (ii), (iii) (C) (i), (ii), (v) (D) (ii), (iii), (iv)

MATCH THE COLUMN :

9.

Column-I	**Column-II**
(A) Hydrolith	(P) Contain Ca
(B) Nitrolim	(Q) Used as a fertilizer
(C) Dolomite	(R) Used to prepare H_2
(D) Pearl's ash	(S) Contain potassium

10.

Column-I	**Column-II**
(A) Metal sulphate $\xrightarrow{\Delta}$ metal oxide + SO_2 + O_2	(P) Ba
(B) Metal cation + $K_2CrO_4 \longrightarrow$ yellow ppt	(Q) Sr
(C) Metal + $NH_3 \xrightarrow{\text{(liquid)}}$ blue solution	(R) Na
(D) MCl_2 + conc. $H_2SO_4 \longrightarrow$ white ppt.	(S) Mg

MATCH THE CODE :

11.

List–I	**List–II**
(P) CaH_2	(1) Paramagnetic anion
(Q) K_2O_2	(2) Homodiatomic, diamagnetic anion
(R) KO_2	(3) Neutral aqueous solution
(S) NaCl	(4) Gives hydrogen on hydrolysis

Codes :

	P	**Q**	**R**	**S**
(A)	3	2	1	4
(B)	4	2	3	1
(C)	4	3	2	1
(D)	4	2	1	3

12.

Column-I	**Column-II**
(P) Solvay process used for	(1) NaCl
(Q) Evolve $CO_2\uparrow$ on heating	(2) Na_2O_2
(R) aq. soln. is neutral towards litmus	(3) $NaHCO_3$
(S) Oxone	(4) Na_2CO_3

Codes :

	P	**Q**	**R**	**S**
(A)	3,4	3	1	2
(B)	4,1	1	3	2
(C)	2,3	4	1	3
(D)	2,4	1	3	4

ASSERATION & REASONING :

Questions given below consist of two statements each printed as Assertion (A) and Reason (R); while answering these questions you are required to choose any one of the following four responses:

(A) if both (A) and (R) are true and (R) is the correct explanation of (A)

(B) if both (A) and (R) are true but (R) is not correct explanation of (A)

(C) if (A) is true but (R) is false

(D) if (A) is false and (R) is true

13. **Assertion** : Beryllium does not impart any characteristic colour to the bunsen flame.

Reason : Due to its very high ionization energy, beryllium requires a large amount of energy for exciation of the electrons.

14. **Assertion** : In fused state, calcium chloride cannot be used to dry alcohol or NH_3.

Reason : Anhy. $CaCl_2$ is not a good desiccant.

15. **Assertion** : Diagonal relationship is shown between Be and Al.

Reason : Ionic potential of Be is almost the same as that of Al.

16. **Assertion** : Beryllium halides dissolve in organic solvents.

Reason : Beryllium halides are ionic in character.

17. **Assertion** : $BeCl_2$ fumes in moist air.

Reason : $BeCl_2$ reacts with moisture to form HCl gas.

18. **Assertion** : Calcium carbide on hydrolysis gives methane.

Reason : Calcium carbide contains C_2^{2-} anion.

19. **Assertion** : When CO_2 is passed through lime water, it first turns milky and then the solution becomes clear when the passage of CO_2 is continued.

Reason : The milkiness is due to the formation of insoluble $CaCO_3$ which then changes to soluble $Ca(HCO_3)_2$ when excess of CO_2 is present.

20. **Assertion** : $MgCO_3$ is soluble in water when a current of CO_2 is passed.

Reason : The solubility of $MgCO_3$ is due to the formation of $Mg(HCO_3)_2$.

MATCHING LIST TYPE 1 × 3 Q. (THREE LIST TYPE Q.)

The following column 1, 2, 3 represent elements of s block and their different oxide formation abilities. Answer the questions that follow

Column-1 - Elements of s-Block

Column-2 - Product formed on reaction with excess oxygen

Column-3 - Characteristics of species form on reaction with excess oxygen

Column - 1 Elements	**Column - 2 Product formed on reaction with excess oxygen**	**Column - 3 Characteristics of species form on reaction with excess oxygen**
(I) Na	(A) Superoxide	(P) Paramagnetic
(II) Ba	(B) Peroxide	(Q) Diamagnetic
(III) K	(C) Monooxide	(R) Bond order = 1.5
(IV) Ca	(D) Dioxide	(S) Bond order = 1

21. Which of the following is an **INCORRECT** match.

(A) (I), (B), (QS) (B) (II), (B), (QS) (C) (II), (A), (PR) (D) (IV), (C), (Q)

22. Which of the following matches will result in species having magnetic moment equal to that of Mn^{+6}

(A) I, (B), QS (B) IV, B, (QS) (C) IV, (A), (PR) (D) III, (A), (PR)

23. On reaction with oxygen, which of the following combination is possible

(A) I, (A, C), (P, Q) (B) I, (B), (Q)

(C) II, (A, B), (P, Q, S) (D) IV, (B, C), Q

EXERCISE # JEE-MAIN

1. A metal M readily forms its sulphate MSO_4 which is water soluble. It forms oxide MO which becomes inert on heating. It forms insoluble hydroxide which is soluble in NaOH. The metal M is:- **[AIEEE-2002]**

(1) Mg (2) Ba (3) Ca (4) Be

2. KO_2 is used in space and submarines because it **[AIEEE-2002]**

(1) Absorbs CO_2 and increase O_2 concentration

(2) Absorbs moisture

(3) Absorbs CO_2

(4) Produces ozone

3. In curing cement plasters, water is sprinkled from time to time. This helps in :- **[AIEEE-2003]**

(1) Hydrating sand and gravel mixed with cement

(2) Converting sand into silicate

(3) Developing interlocking needle like crystals of hydrated silicates

(4) Keeping it cool

4. The solubilities of carbonates decreases down the magnesium group due to decrease in- **[AIEEE-2003]**

(1) Inter-ionic attraction

(2) Entropy of solution formation

(3) Lattice energy of solids

(4) Hydration energy of cations

5. The substance not likely to contain $CaCO_3$ is :- **[AIEEE-2003]**

(1) Sea shells (2) Dolomite

(3) A marble statue (4) Calcined gypsum

6. One mole of magnesium nitride on reaction with excess of water gives :- **[AIEEE-2004]**

(1) Two mole of HNO_3 (2) Two mole of NH_3

(3) 1 mole of NH_3 (4) 1 mole of HNO_3

7. Berylium and aluminium exhibit many properties which are similar. But the two elements differ in - **[AIEEE-2004]**

(1) Exhibiting maximum covalency in compounds

(2) Forming polymeric hydrides

(3) Forming covalent halides

(4) Exhibiting amphoteric nature in their oxides.

8. The ionic mobility of alkali metal ioins in aqueous solution is maximum for :- **[AIEEE-2006]**

(1) Rb^+ (2) Li^+ (3) Na^+ (4) K^+

9. The products obtained on heating $LiNO_3$ will be :- **[AIEEE-2011]**

(1) $LiNO_2 + O_2$ (2) $Li_2O + NO_2 + O_2$

(3) $Li_3N + O_2$ (4) $Li_2O + NO + O_2$

10. What is the best description of the change that occurs when $Na_2O(s)$ is dissolved in water ? **[AIEEE-2011]**

(1) Oxidation number of sodium decreases

(2) Oxide ion accepts sharing in a pair of electrons

(3) Oxide ion donates a pair of electrons

(4) Oxidation number of oxygen increases

11. Which of the following on thermal-decomposition yields a basic as well as an acidic oxide ? **[AIEEE-2012]**

(1) NH_4NO_3 (2) $NaNO_3$ (3) $KClO_3$ (4) $CaCO_3$

12. Fire extinguishers contain H_2SO_4 and which one of the following :-**[JEE MAIN-2012, Online]**

(1) $CaCO_3$ (2) $NaHCO_3$ and Na_2CO_3

(3) Na_2CO_3 (4) $NaHCO_3$

13. Based on lattice energy and other considerations, which one of the following alkali metal chloride is expected to have the highest melting point ? **[JEE MAIN-2012, Online]**

(1) RbCl (2) LiCl (3) KCl (4) NaCl

14. Which one of the following will react most vigorously with water ? **[JEE MAIN-2012, Online]**

(1) Li (2) K (3) Rb (4) Na

15. A metal M on heating in nitrogen gas gives Y. Y on treatment with H_2O gives a colourless gas which when passed through $CuSO_4$ solution gives a blue colour, Y is :- **JEE MAIN-2012, Online]**

(1) NH_3 (2) MgO (3) Mg_3N_2 (4) $Mg(NO_3)_2$

16. The correct statement for the molecule, CsI_3, is : **[JEE(Main)-2014]**

(1) it contains Cs^{3+} and I^- ions

(2) it contains Cs^+, I^- and lattice I_2 molecule

(3) it is a covalent molecule

(4) it contains Cs^+ and I_3^- ions

17. Which of the following statements about Na_2O_2 is **not** correct ? **[JEE MAIN-2014, Online]**

(1) Na_2O_2 oxidises Cr^{3+} to CrO_4^{2-} in acid medium

(2) It is diamagnetic in nature

(3) It is the super oxide of sodium

(4) It is a derivative of H_2O_2

18. Amongst LiCl, RbCl, $BeCl_2$ and $MgCl_2$ the compounds with the greatest and the least ionic character, respectively are : **[JEE MAIN-2014, Online]**

(1) RbCl and $MgCl_2$ (2) LiCl and RbCl

(3) $MgCl_2$ and $BeCl_2$ (4) RbCl and $BeCl_2$

19. The correct order of thermal stability of hydroxides is : **JEE(Main)Online-2015]**

(1) $Ba(OH)_2 < Sr(OH)_2 < Ca(OH)_2 < Mg(OH)_2$ (2) $Mg(OH)_2 < Sr(OH)_2 < Ca(OH)_2 < Ba(OH)_2$

(3) $Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$ (4) $Ba(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Mg(OH)_2$

20. Which of the alkaline earth metal halides given below is essentially covalent in nature :-

(1) $SrCl_2$ (2) $CaCl_2$ (3) $BeCl_2$ (4) $MgCl_2$

JEE(Main)Online-2015]

21. Which one of the following alkaline earth metal sulphates has its hydration enthalpy greater than its lattice enthalpy ? **[JEE(Main)-2015]**

(1) $BaSO_4$ (2) $SrSO_4$ (3) $CaSO_4$ (4) $BeSO_4$

22. The commercial name for calcium oxide is : **[JEE(Main)-2016]**

(1) Quick lime (2) Milk of lime (3) Limestone (4) Slaked lime

23. The correct order of the solubility of alkaline-earth metal sulphates in water is : **[JEE(Main)-2016]**

(1) Mg < Sr < Ca < Ba (2) Mg < Ca < Sr < Ba

(3) Mg > Ca > Sr > Ba (4) Mg > Sr > Ca > Ba

24. The main oxides formed on combustion of Li, Na and K in excess of air are respectively :

(1) Li_2O, Na_2O_2 and KO_2 (2) Li_2O, Na_2O and KO_2 **[JEE(Main)-2016]**

(3) LiO_2, Na_2O_2 and K_2O (4) Li_2O_2, Na_2O_2 and KO_2

25. Both lithium and magnesium display several similar properties due to the diagonal relationship ; however, the one which is incorrect is : **[JEE(Main)-2017]**

(1) Both form basic carbonates

(2) Both form soluble bicarbonates

(3) Both form nitrides

(4) Nitrates of both Li and Mg yield NO2 and O2 on heating

26. Which of the following ions does **not** liberate hydrogen gas on reaction with dilute acids?

(1) Ti^{2+} (2) Cr^{2+} **[JEE(Main)-2017 on line]**

(3) Mn^{2+} (4) V^{2+}

27. In KO_2, the nature of oxygen species and the oxidation state of oxygen atom are, respectively **[JEE(Main)ONLINE-2018]**

(1) Superoxide and –1/2

(2) Oxide and -–2

(3) Peroxide and –1/2

(4) Superoxide and –1

EXERCISE # JEE-ADVANCED

1. The species that do not contain peroxide linkage are - **[JEE 1992]**

(A) PbO_2 (B) H_2O_2 (C) SrO_2 (D) BaO_2

2. Read the following statement and explanation and answer as per the options given below :

Statement-1 : The alkali metals can form ionic hydrides which contain the hydride ion H^-.

Statement-2 : The alkali metals have low electronegativity ; their hydrides conduct electricity when fused and liberate hydrogen at the anode. **[JEE 1994]**

(A) Both 1 and 2 are true and 2 is the correct explanation of 1.

(B) Both 1 and 2 are true but 2 is not the correct explanation of 1.

(C) 1 is true but 2 is false.

(D) 1 is false but 2 is true.

3. The following compounds have been arranged in order of their increasing thermal stabilities. Identify the correct order. **[JEE 1996]**

K_2CO_3(I) $MgCO_3$(II) $CaCO_3$(III) $BeCO_3$(IV)

(A) I < II < III < IV (B) IV < II < III < I

(C) IV < II < I < III (D) II < IV < III < I

4. Property of all the alkaline earth metals that increase with their atomic number is - **[JEE 1997]**

(A) ionisation energy (B) solubility of their hydroxides

(C) solubility of their sulphate (D) electronegativity

5. Highly pure dilute solution of sodium in liquid ammonia - **[JEE 1998]**

(A) shows blue colour (B) exhibits electrical conductivity

(C) produces sodium amide (D) produces hydrogen gas

6. The set representing the correct order of first ionization potential is - **[JEE 2001S]**

(A) K > Na > Li (B) Be > Mg > Ca (C) B > C > N (D) Ge > Si > C

Asseration and Reason

7. This questions contains statement-1 (asseration) and statement-2 (reason) and has 4 choices (a), (b), (c) and (d) out of which only one is correct.

Statement-1 : Alkali metals dissolve in liquid ammonia to give blue solutions. because.

Statement-1 : Alkali metals is liquid ammonia give solvated species of the type $[M(NH_3)_n]^+$ (M = alkali metals). **[JEE 2007]**

(A) Both 1 and 2 are true and 2 is the correct explanation of 1.

(B) Both 1 and 2 are true but 2 is not the correct explanation of 1.

(C) 1 is true but 2 is false.

(D) 1 is false but 2 is true.

8. The compound(s) formed upon combustion of sodium metal in excess air is (are) **[JEE 2009]**

(A) Na_2O_2 (B) Na_2O (C) NaO_2 (D) NaOH

ANSWER KEY

EXERCISE # O-1

1. (A)
2. (A)
3. (A)
4. (D)
5. (A)
6. (D)
7. (A)
8. (C)
9. (B)
10. (C)
11. (C)
12. (A)
13. (C)
14. (C)
15. (C)
16. (D)
17. (A)
18. (A)
19. (A)
20. (C)
21. (B)
22. (A)
23. (C)
24. (D)
25. (B)
26. (C)
27. (B)
28. (A)
29. (C)
30. (D)
31. (A)
32. (A)
33. (A)
34. (B)
35. (C)
36. (B)
37. (B)
38. (B)
39. (D)
40. (A)
41. (A)
42. (C)
43. (B)
44. (B)
45. (A)
46. (C)
47. (C)
48. (C)
49. (B)
50. (D)

EXERCISE # O-2

1. (B),(C), (D)
2. (B),(C)
3. (A),(B)
4. (A),(C)
5. (A),(B),(C)
6. (A), (B)
7. (A), (B),(D)
8. (A),(C)
9. (A),(B),(C)
10. (A),(C)
11. (A), (C)
12. (C),(D)
13. (A),(B),(D)
14. (A),(B),(C),(D)
15. (A),(B),(C)
16. (B),(C),(D)
17. (B), (D)
18. (B),(C),(D)
19. (B),(C),(D)

EXERCISE # S-1

1. (4)
2. (6)
3. (4)
4. (10), OMR - (1)
5. (8)
6. (6)

Except Be & Mg other s-block metals impart characteristic colour to oxidising flame.

EXERCISE # S-2

- **Comprehension Based Questions**

Comprehension # 1

1. (B) **2.** (A) **3.** (B)

Comprehension # 2

4. (C) **5.** (A) **6.** (D) **7.** (D) **8.** (A)

- **Match the column**

9. (A) → P,R ; (B) → P,Q ; (C) → P ; (D) → S

10. (A) → P,Q,S ; (B) → P,Q; (C) → P,Q,R ; (D) → P,Q

- **Match the code**

11. (D) **12.** (A)

- **Asseration & Reasoning**

13. A **14. C** **15. A** **16. C**

17. A **18. D** **19. A** **20. A**

21. C **22. D** **23. B**

EXERCISE # JEE-MAIN

1. (4) **2.** (1) **3.** (3) **4.** (4)

5. (4) **6.** (2) **7.** (1) **8.** (1)

9. (2) **10.** (3) **11.** (4) **12.** (4)

13. (4) **14.** (3) **15.** (3) **16.** (4)

17. (3) **18.** (4) **19.** (3) **20.** (3)

21. (4) **22.** (1) **23.** (3) **24.** (1)

25. (1) **26.** (3) **27.** (1)

EXERCISE # JEE-ADVANCED

1. A **2. A** **3. B** **4. B**

5. A,B **6. B** **7. B** **8. A,B**

d-BLOCK COMPOUNDS

TRANSITION ELEMENTS

Definition : They one often called 'transition elements' because their position in the periodic table is between s-block and p-block elements

Typically, the transition elements have incompletely filled d-level. Since Zn group has d^{10} configuration in their ground state as well as in stable oxidation state, they are not considered as transition elements but they ared-block elements.

1st Series										
	Sc	Ti	V	**Cr**	Mn	Fe	Co	Ni	**Cu**	Zn
Z	21	22	23	24	25	26	27	28	29	30
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10

2nd Series										
	Y	Zr	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	Cd
Z	39	40	41	42	43	44	45	46	47	48
5s	2	2	1	1	2	1	1	0	1	2
4d	1	2	4	5	5	7	8	10	10	10

3rd Series										
	La	Hf	Ta	W	Re	Os	Ir	**Pt**	**Au**	Hg
Z	57	72	73	74	75	76	77	78	79	80
6s	2	2	2	2	2	2	2	1	1	2
5d	1	2	3	4	5	6	7	9	10	10

4th Series										
	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	**Rg**	Uub
Z	89	104	105	106	107	108	109	110	111	112
7s	2	2	2	2	2	2	2	2	1	2
6d	1	2	3	4	5	6	7	8	10	10

General Characteristics :

(i) **Metallic character :** They are all metal and good conductor of heat & electricity

(ii) **Electronic configuration :** $(n-1)d^{1-10}ns^{1-2}$

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
others are				$4s^1$					$4s^1$	
as usual				$3d^5$					$3d^{10}$	

(iii) **M.P.**

Cr
Mo
W

$\longrightarrow$ Maximum
6 no. of unpaired e^-s
are involved in metallic bonding

Zn
Cd
Hg

lowest m.p.
due to no unpaired e^-
for metallic bonding

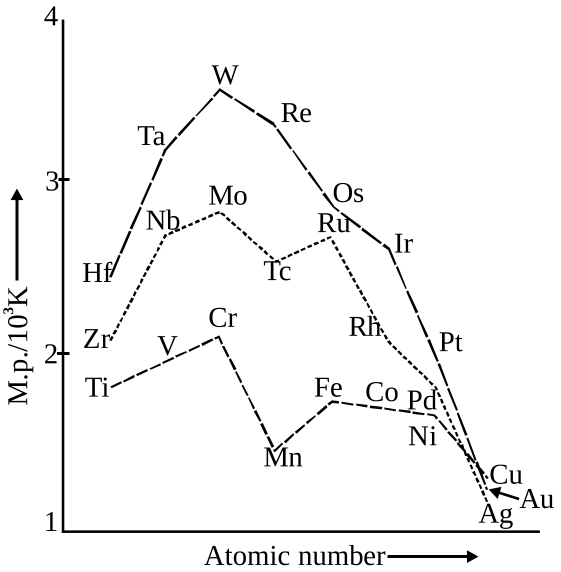


Fig. : Trends in melting points of transition elements

(iv) Variation in atomic radius :

$$\underset{\text{decreases}}{Sc \longrightarrow Mn}\ \underbrace{Fe\ Co\ Ni}_{\text{remains same}}\ \underset{\text{increases again}}{Cu\ Zn}$$

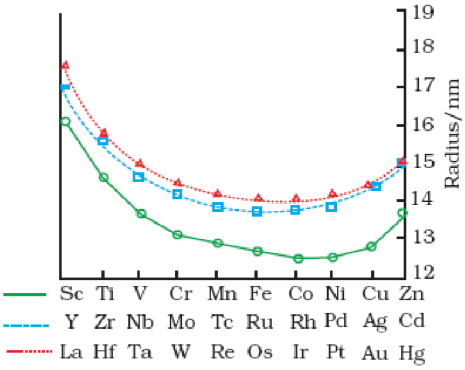


Fig. 8.3: Trends in atomic radii of transition elements

(v) Ionisation energy :

1st, 2nd, 3rd IE's are increasing from left to right for 1st Transition series, but not regularly.

For 2nd IE Cr > Fe > Mn and Cu > Zn

For 3rd IE Mn > Cr > Fe and Zn has highest.

(vi) DENSITY

(a) The atomic volume of the transition elements are low, compared with s-block, so their density is comparatively high (D = M/V)

(b) Os (22.57 gm cm^{-3}) and Ir (22.61 gm cm^{-3}) have highest density.

(c) In all the groups (except IIIB) there is normal increase in density from 3d to 4d series, and from 4d to 5d, it increases just double. Due to lanthanide contraction **Ex. :** Ti < Zr << Hf

(d) **In 3d series**

	Sc	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
Density/g cm^{-3}	3.43	4.1	6.07	7.19	7.21	7.8	8.7	8.9	8.9	7.1

(e) In 3d series highest density – Cu lowest density – Sc

(f) Some important orders of density

Fe < Ni < Cu Fe < Cu < Au Fe < Hg < Au

Electronic configurations and some other properties of the first series of transition elements

Element		Sc	Ti	v	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number		21	22	23	24	25	26	27	28	29	30
Electronic configuration											
	M	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^2$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^{10} 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$
	M^+	$3d^1 4s^1$	$3d^2 4s^1$	$3d^3 4s^1$	$3d^5$	$3d^5 4s^1$	$3d^6 4s^1$	$3d^7 4s^1$	$3d^8 4s^1$	$3d^{10}$	$3d^{10} 4s^1$
	M^{2+}	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$	$3d^{10}$
	M^{3+}	[Ar]	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	–	–
Enthalpy of atomisation, $\Delta_a H^\ominus$/kJ mol^{-1}											
		326	473	515	397	281	416	425	430	339	126
Ionisation Enthalpy, $\Delta_1 H^\ominus$/kJ mol^{-1}											
$\Delta_1 H^\ominus$	I	631	656	650	653	717	762	758	736	745	906
	II	1235	1309	1414	1592	1509	1561	1644	1752	1958	1734
	III	2393	2657	2833	2990	3260	2962	3243	3402	3556	3829
Metallic/Ionic radii/pm	M	164	147	135	129	137	126	125	125	128	137
	M^{2+}	–	–	79	82	82	77	74	70	73	75
	M^{3+}	73	67	64	62	65	65	61	60	–	–
Standard electrode potential $E^\ominus$/V	M^{2+}/M	–	–1.63	–1.18	–0.90	–1.18	–0.44	–0.28	–0.25	+0.34	–0.76
	M^{3+}/M^{2+}	–	–0.37	–0.26	–0.41	+1.57	+0.77	+1.97	–	–	–
Density/g cm^{-3}		3.43	4.1	6.07	7.19	7.21	7.8	8.7	8.9	8.9	7.1

VARIABLE OXIDATION STATES POSSIBLE :

(1) The elements which give the greatest number of oxidation states occur in or near the middle of the series. Manganese, for example, exhibits all the oxidation states from +2 to +7.

(2) The lesser number of oxidation states at the extreme ends stems from either too few electrons to lose or share (Sc, Ti) or too many d electrons (hence fewer orbitals available in which to share electrons with others) for higher valence (Cu, Zn).

(3) Thus, early in the series scandium(II) is virtually unknown and titanium (IV) is more stable than Ti(III) or Ti(II).

(4) At the other end, the only oxidation state of zinc is +2 (no d electrons are involved).

(5) The maximum oxidation states of reasonable stability correspond in value to the sum of the s and d electrons upto manganese ($Ti^{IV}O_2$, $V^VO_2^{\ +}$, $Cr^{V1}O_4^{2-}$, $Mn^{VII}O_4^-$) followed by a rather abrupt decrease in stability of higher oxidation states, so that the typical species to follow are $Fe^{II,III}$, $Co^{II,III}$, Ni^{II}, $Cu^{I,II}$, Zn^{II}.

(6) The variability of oxidation states, a characteristic of transition elements, arises out of incomplete filling of d orbitals in such a way that their oxidation states differ from each other by unity, e.g., V^{II}, V^{III}, V^{IV}, V^{V}.

(7) This is in contrast with the variability of oxidation states of non transition elements where oxidation states normally differ by a unit of two.

(8) An interesting feature in the variability of oxidation states of the d–block elements is noticed among the groups (groups 4 through 10).

(9) In group 6, Mo(VI) and W(VI) are found to be more stable than Cr(VI). Thus Cr(VI) in the form of dichromate in acidic medium is a strong oxidising agent, whereas MoO_3 and WO_3 are not.

(10) Low oxidation states are found when a complex compound has ligands capable of π-acceptor character in addition to the σ-bonding. For example, in $Ni(CO)_4$ and $Fe(CO)_5$, the oxidation state of nickel and iron is zero.

(11) As the oxidation number of a metal increases, ionic character decreases. In the case of Mn, Mn_2O_7 is a covalent green oil. Even CrO_3 and V_2O_5 have low melting points. In these higher oxides, the acidic character is predominant. Thus, Mn_2O_7 gives $HMnO_4$ and CrO_3 gives H_2CrO_4 and $H_2Cr_2O_7$. V_2O_5 is, however, amphoteric though mainly acidic and it gives VO_4^{3-} as well as VO_2^+ salts. In vanadium there is gradual change from the basic V_2O_3 to less basic V_2O_4 and to amphoteric V_2O_5. V_2O_4 dissolves in acids to give VO^{2+} salts. Similarly, V_2O_5 reacts with alkalies as well as acids to give VO_4^{3-} and VO_2^+ respectively. The well characterised CrO is basic but Cr_2O_3 is amphoteric.

Oxidation states of the I^st transition series

most common ones are in bold types :

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
			+1					+1	
	+2	+2	+2	+**2**	+**2**	+**2**	+**2**	+**2**	+**2**
+**3**	+**3**	+**3**	+**3**	+3	+**3**	+**3**	+3		
	+**4**	+4	+4	+**4**	+4	+4	+4		
		+**5**	+5	+5					
			+**6**	+6	+6				
				+**7**					

Trends in stability of higher oxidation state :

(1) Table shows the stable halides of the 3*d* series of transition metals. The highest oxidation numbers are achieved in TiX_4 (tetrahalides), VF_5 and CrF_6. The +7 state for Mn is not represented in simple halides but MnO_3F is known, and beyond Mn no metal has a trihalide except FeX_3 and CoF_3.

(2) The ability of fluorine to stabilise the highest oxidation state is due to either higher lattice energy as in the case of CoF_3, or higher bond enthalpy terms for the higher covalent compounds, e.g., VF_5 and CrF_6.

(3) Although V^V is represented only by VF_5, the other halides, however, undergo hydrolysis to give oxohalides, VOX_3.

(4) Another feature of fluorides is their instability in the low oxidation states e.g., VX_2 (X = CI, Br or I)

Formulas of halides of 3d-metals

Oxidation Number									
+ 6			CrF_6						
+ 5		VF_5	CrF_5						
+ 4	TiX_4	VX^I_4	CrX_4	MnF_4					
+ 3	TiX_3	VX_3	CrX_3	MnF_3	FeX^I_3	CoF_3			
+ 2	TiX_2^{III}	VX_2	CrX_2	MnX_2	FeX_2	CoX_2	NiX_2	CuX^{II}_2	ZnX_2
+ 1								CuX^{III}	

Key : $X = F \rightarrow I$; $X^I = F \rightarrow Br$; $X^{II} = F \rightarrow Cl$; $X^{III} = Cl \rightarrow I$

and the same applies to CuX. On the other hand, all Cu(II) halides are known except the iodide. In this case, Cu^{2+} oxidises I^- to I_2:

$$2Cu^{2+} + 4I^- \rightarrow Cu_2I_2(s) + I_2$$

(5) However, many copper (I) compounds are unstable in aqueous solution and undergo disproportionation.

$$2Cu^+ \rightarrow Cu^{2+} + Cu$$

(6) The stability of $Cu^{2+}(aq)$ rather than $Cu^+(aq)$ is due to the much more negative $\Delta_{Hyd}H^\ominus$ of $Cu^{2+}(aq)$ than Cu^+, which more than compensates for the second ionisation enthalpy of Cu.

(7) The ability of oxygen to stabilise the highest oxidation state is demonstrated in the oxides.

(8) The highest oxidation number in the oxides coincides with the group number and is attained in Sc_2O_3 to Mn_2O_7.

(9) Beyond Group 7, no higher oxides of Fe above Fe_2O_3, are known, although ferrates (VI)$(FeO_4)^{2-}$, are formed in alkaline media but they readily decompose to Fe_2O_3 and O_2.

(10) Besides the oxides, oxocations stabilise V^v as VO_2^+, V^{IV} as VO^{2+} and Ti^{IV} as TiO^{2+}

(11) The ability of oxygen to stabilise these high oxidation states exceeds that of fluorine. Thus the highest Mn fluoride is MnF_4 whereas the highest oxide is Mn_2O_7. The ability of oxygen to form multiple bonds to metals explains its superiority.

(12) In the covalent oxide Mn_2O_7, each Mn is tetrahedrally surrounded by O's including a Mn–O–Mn bridge.

(13) The tetrahedral $[MO_4]^n$ ions are known for V^V, Cr^{VI}, Mn^V, Mn^{VI} and Mn^{VII}.

FORMATION OF COLOURED ION :

<u>Colour</u> : (aquated)

$Ti^{4+} \longrightarrow$ colourless

$V^{4+} \longrightarrow$ blue

$V^{2+} \longrightarrow$ violet

$Cr^{3+} \longrightarrow$ violet

$Mn^{2+} \longrightarrow$ light pink

$Fe^{3+} \longrightarrow$ yellow

$Ni^{2+} \longrightarrow$ green

$Zn^{2+} \longrightarrow$ colourless

$Sc^{3+} \longrightarrow$ colourless

$Ti^{3+} \longrightarrow$ purple

$V^{3+} \longrightarrow$ green

$Cr^{2+} \longrightarrow$ blue

$Mn^{3+} \longrightarrow$ violet

$Fe^{2+} \longrightarrow$ light green

$Co^{2+} \longrightarrow$ pink

$Cu^{2+} \longrightarrow$ blue

CATALYTIC PROPERTIES

(1) The transition metals and their compounds are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states and to form complexes. Vanadium(V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in Catalytic Hydrogenation) are some of the examples.

(2) Catalysts at a solid surface involve the formation of bonds between reactant molecules and atoms of the surface of the catalyst (first row transition metals utilise 3d and 4s electrons for bonding).

(3) This has the effect of increasing the concentration of the reactants at the catalyst surface and also weakening of the bonds in the reacting molecules (the activation energy is lowering).

(4) Also because the transition metal ions can change their oxidation states, they become more effective as catalysts. For example, iron(III) catalyses the reaction between iodide and persulphate ions.

$$2I^{-} + S_2O_8^{2-} \rightarrow I_2 + 2SO_4^{2-}$$

An explanation of this catalytic action can be given as:

$$2Fe^{3+} + 2I^{-} \rightarrow 2\,Fe^{2+} + I_2$$

$$2\,Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$$

Catalyst		Used
$TiCl_3$	⟶	Used as the Ziegler-Natta catalyst in the production of polythene.
V_2O_5	⟶	Convert SO_2 to SO_3 in the contact process for making H_2SO_4
MnO_2	⟶	Used as a catalyst to decompose $KClO_3$ to give O_2
Fe	⟶	Promoted iron is used in the Haber-Bosch process for making NH_3
$FeCl_3$	⟶	Used in the production of CCl_4 from CS_2 and Cl_2
$PdCl_2$	⟶	Wacker process for converting $C_2H_4 + H_2O + PdCl_2$ to $CH_3CHO + 2HCl + Pd$.
Pd	⟶	Used for hydrogenation (e.g. phenol to cyclohexanone).
Pt/PtO	⟶	Adams catalyst, used for reductions.
Pt	⟶	Formerly used for $SO_2 \longrightarrow SO_3$ in in the contace process for making H_2SO_4
Pt/Rh	⟶	Formerly used in the ostwald process for making HNO_3 to oxidize NH_3 to NO
Cu	⟶	Is used in the direct process for manufacture of $(CH_3)_2SiCl_2$ used to make silicones.
Cu/V	⟶	Oxidation of cyclohexanol/cyclohexanone mixture to adipic acid which is used to make nylon-66
$CuCl_2$	⟶	Deacon process of making Cl_2 from HCl
Ni	⟶	Raney nickel, numerous reduction processes (e.g. manufacture of hexamethylenediamine, productiomn of H_2 from NH_3, reducing anthraquinone to anthraquinol in the production of H_2O_2
$FeSO_4 + H_2O_2$	⟶	Used as Fenton's reagent for oxidizing alcohols to aldehydes.

Formation of Interstitial Compounds

Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals. The principal physical and chemical characteristics of these compounds are as follows:

(i) They have high melting points, higher than those of pure metals.

(ii) They are very hard, some borides approach diamond in hardness.

(iii) They retain metallic conductivity.

(iv) They are chemically inert.

Alloy Formation

An alloy is a blend of metals prepared by mixing the components. Alloys may be homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other. Such alloys are formed by atoms with metallic radii that are within about 15 percent of each other. Because of similar radii and other characteristics of transition metals, alloys are readily formed by these metals. The alloys so formed are hard and have often high melting points.

The best known are ferrous alloys: chromium, vanadium, tungsten, molybdenum and manganese are used for the production of a variety of steels and stainless steel. Alloys of transition metals with non transition metals such as brass (copper-zinc) and bronze (copper-tin), are also of considerable industrial importance.

CHROMATE -DICHROMATE

Residue(Fe_2O_3)

Filtrate(Na_2CrO_4)

Preparation : $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \xrightarrow[\text{red hot in presence of air}]{1000°–1300°C} \overbrace{8Na_2CrO_4 + 2Fe_2O_3}^{\text{Dissolve in water and filtered}} + 8CO_2\uparrow$

(chromite ore)

[Lime (CaO) added with Na_2CO_3 which keeps the mass porous so that air has access to all parts and prevents fusion]

Then, $\underset{\text{conc.}}{2Na_2CrO_4 + H_2SO_4} \longrightarrow Na_2SO_4\downarrow + Na_2Cr_2O_7 + H_2O$

It's solubility upto 32°C increases and then decreases } Hence, suitable temp. is to be employed to crystallise out Na_2SO_4 first.

Then $Na_2Cr_2O_7$ is crystallised out as $\underset{\text{(red crystal)}}{Na_2Cr_2O_7\cdot 2H_2O}$ on evaporation.

How to get $K_2Cr_2O_7$:

$$\underset{\text{hot conc.}}{Na_2Cr_2O_7} + 2KCl \xrightarrow[\text{decomposition}]{\text{double}} K_2Cr_2O_7 + 2NaCl$$

NaCl crystallises out first and filtered off. Then $K_2Cr_2O_7$ crystallised out on cooling

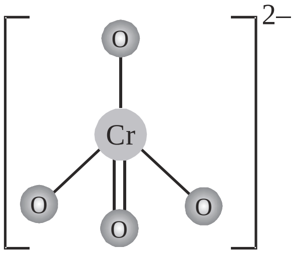
The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution. The oxidation state of chromium in chromate and dichromate is the same.

$$2\,CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$$

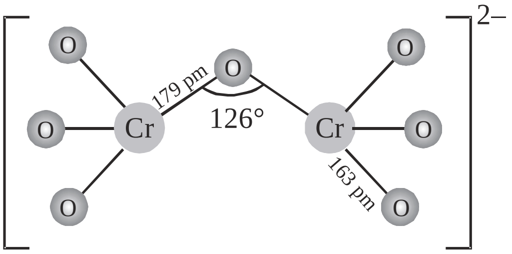
$$Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$$

The structures of chromate ion, CrO_4^{2-} and the dichromate ion, $Cr_2O_7^{2-}$ are shown below. The chromate ion is tetrahedral whereas the dichromate ion consists of two tetrahedra sharing one corner with Cr–O–Cr bond angle of 126°. Sodium and potassium dichromates are strong oxidising agents; the sodium salt has a greater solubility in water and is extensively used as an oxidising agent in organic chemistry. Potassium dichromate is used as a primary standard in volumetric analysis. In acidic solution, its oxidising action can be represented as follows:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O\ (E^{\ominus} = 1.33V)$$



Chromate ion



Dichromate ion

Thus, acidified potassium dichromate will oxidise iodides to iodine, sulphides to sulphur, tin(II) to tin(IV) and iron(II) salts to iron(III). The half-reactions are noted below:

$6\ I^- \rightarrow 3I_2 + 6e^-$; $\quad 3\ Sn^{2+} \rightarrow 3Sn^{4+} + 6e^-$

$3H_2S \rightarrow 6H^+ + 3S + 6e^-$; $\quad 6\ Fe^{2+} \rightarrow 6Fe^{3+} + 6e^-$

The full ionic equation may be obtained by adding the half-reaction for potassium dichromate to the half-reaction for the reducing agent, for e.g.,

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

* Similarities between hexavalent Cr & S-compounds :

(i) SO_3 & $CrO_3 \longrightarrow$ both acidic.

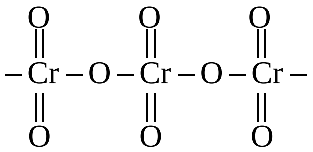
(ii) $S \longrightarrow SO_4^{2-}, S_2O_7^{2-}, Cr \longrightarrow CrO_4^{2-}, Cr_2O_7^{2-}$

(iii) CrO_4^{-2} & SO_4^{2-} are isomorphous

(iv) SO_2Cl_2 & $CrO_2Cl_2 \xrightarrow{OH^-} SO_4^{2-}$ & CrO_4^{2-} respectively.

(v) SO_3Cl^- & $CrO_3Cl^- \xrightarrow{OH^-} SO_4^{2-}$ & CrO_4^{2-}

(vi) CrO_3 & $\beta(SO_3)$ has same structure



$$-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{Cr}}-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{Cr}}-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{Cr}}-$$

Q. In laboratory $K_2Cr_2O_7$ is used mainly not $Na_2Cr_2O_7$. Why?

Sol. $Na_2Cr_2O_7$ is deliquescent enough and changes its concentration and can not be taken as primary standard solution whereas $K_2Cr_2O_7$ has no water of crystallisation and not deliquescent.

Q. How to standardise $Na_2S_2O_3$ solution in iodometry?

Sol. $K_2Cr_2O_7$ is primary standard ⇒ strength is known by weighing the salt in chemical balance and dissolving in measured amount of water.

Then in acidic solution add. KI

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

This I_2 is liberated can be estimated with $S_2O_3^{2-}$.

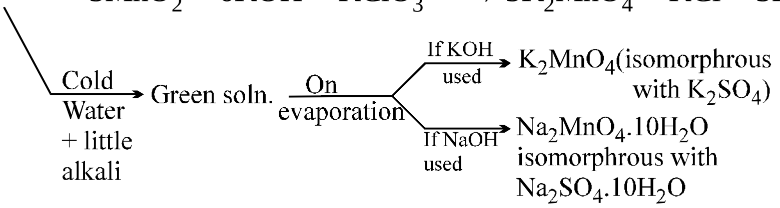
MANGANATE & PERMANGANATE

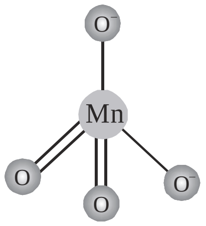
PREPARATION OF MANGANATE (MnO_4^{2-}) :-

$MnO_2 \xrightarrow[\text{or NaOH, } \Delta \text{ in presence of air}]{\text{KOH}} \underset{\text{green melt}}{MnO_4^{2-}}$ $[2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O]$

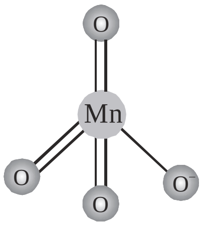
$MnO_2 + 2KOH + KNO_3 \longrightarrow K_2MnO_4 + KNO_2 + H_2O$

$3MnO_2 + 6KOH + KClO_3 \longrightarrow 3K_2MnO_4 + KCl + 3H_2O$





Tetrahedral
manganate
(green) ion



Tetrahedral
permanganate
(purple) ion

In presence of $KClO_3$ & KNO_3 the above reaction is more faster because these two on decomposition provides O_2 easily.

* Manganate is also obtained when $KMnO_4$ is boiled with KOH.

$4KMnO_4 + 4KOH \xrightarrow{\text{boiled}} 4K_2MnO_4 + 2H_2O + O_2$

Properties : The above green solution is quite stable in alkali, but in pure water and in presence of acids, depositing MnO_2 and giving a purple solution of permanganate.

$3K_2MnO_4 + 2H_2O \longrightarrow \underset{\text{purple}}{2KMnO_4} + \underset{\text{drak brown}}{MnO_2 \downarrow} + 4KOH$

Prob. : $E^o_{MnO_4^{2-}/MnO_2} = 2.26\ V$; $E^o_{MnO_4^{2-}/MnO_4^-} = -0.56\ V$

Prove that MnO_4^{2-} will disproportionate in acidic medium.

Conversion of MnO_4^{2-} to MnO_4^-

$3K_2MnO_4 + 2H_2SO_4 \longrightarrow 2KMnO_4 + MnO_2 \downarrow + 2K_2SO_4 + 2H_2O$

or $3K_2MnO_4 + 2H_2O + 4CO_2 \longrightarrow 2KMnO_4 + MnO_2 + 4KHCO_3$

But in the above method $\frac{1}{3}$ of Mn is lost as MnO_2 but when oxidised either by Cl_2 or by O_3

$2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$ [Unwanted MnO_2 does not form]

OR

$$2K_2MnO_4 + O_3 + H_2O \longrightarrow 2KMnO_4 + 2KOH + O_2$$

OR

$$\underset{\text{Manganate}}{MnO_4^{2-}} \xrightarrow[\text{alkaline solution}]{\text{Electrolytic oxidation in}} \underset{\text{permanganate ion}}{MnO_4^-}$$

Oxidising Prop. of $KMnO_4$: (in acidic medium)

(i) $MnO_4^- + Fe^{+2} + H^+ \longrightarrow Fe^{+3} + Mn^{+2} + H_2O$

(ii) $MnO_4^- + I^- + H^+ \longrightarrow Mn^{+2} + I_2 + H_2O$

(iii) $MnO_4^- + H_2O_2 + H^+ \longrightarrow Mn^{+2} + O_2 + H_2O$

(iv) $MnO_4^- + SO_2 \xrightarrow{H^\oplus} Mn^{+2} + H_2SO_4$

(v) $MnO_4^- + NO_2^- + H^+ \longrightarrow Mn^{+2} + NO_3^- + H_2O$

(vi) $MnO_4^- + H_2C_2O_4 + H^+ \longrightarrow Mn^{+2} + CO_2 + H_2O$

(vii) $MnO_4^- + H_2S \longrightarrow Mn^{2+} + S\downarrow + H_2O$

(viii) $MnO_4^- + S_2O_3^{2-} \longrightarrow Mn^{2+} + S\downarrow + SO_4^{2-}$

(1)* It is not a primary standard since it is difficult to get it in a high degree of purity and free from traces of MnO_2.

(2)* It is slowly reduced to MnO_2 especially in presence of light or acid

$$4MnO_4^- + 4H^+ \longrightarrow 4MnO_2 + 2H_2O + 3O_2$$

Hence it should be kept in dark bottles and standardise just before use.

(ix) $2KMnO_4 + 16HCl \longrightarrow 2KCl + 5Cl_2 + 8H_2O + 2MnCl_2$

***Note*: Permanganate titrations in presence of hydrochloric acid are unsatisfactory since hydrochloric acid is oxidised to chlorine.**

Oxidising Prop. of $KMnO_4$ in neutral or faintly alkaline solution.

$2MnO_4^- + 2OH^- \longrightarrow 2MnO_4^{2-} + H_2O + O$. Then $2MnO_4^{2-} + 2H_2O \longrightarrow 2MnO_2 + 4OH^- + 2O$

(i) $2KMnO_4 + H_2O + KI \longrightarrow 2MnO_2 + 2KOH + KIO_3$

(ii) $2KMnO_4 + 3HCO_2K \longrightarrow 2MnO_2 + KHCO_3 + 2K_2CO_3 + H_2O$

(iii) $2KMnO_4 + 3H_2O_2 \longrightarrow 2KOH + 2MnO_2 + 2H_2O + 3O_2$

(iv) Thiosulphate is oxidised almost quantitatively to sulphate:

$$8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$$

Oxidising Prop. in neutral or weakly acidic solution:

(i) $2KMnO_4 + 3MnSO_4 + 2H_2O \xrightarrow{\text{in presence } Zn^{+2} \text{ or } ZnO} 5MnO_2 + K_2SO_4 + 2H_2SO_4$

or $MnO_4^- + Mn^{+2} + 2H_2O \longrightarrow 5MnO_2 + 4H^+$

In absence of Zn^{+2} ions, some of the Mn^{+2} ion may escape, oxidation through the formation of insoluble $Mn^{II}[Mn^{IV}O_3]$ manganous permanganite.

Uses of $KMnO_4$:

Besides its use in analytical chemistry, potassium permanganate is used as a favourite oxidant in preparative organic chemistry. Its uses for the bleaching of wool, cotton, silk and other textile fibres and for the decolourisation of oils are also dependent on its strong oxidising power.

** In laboratory conversion of Mn^{+2} to MnO_4^- is done by :

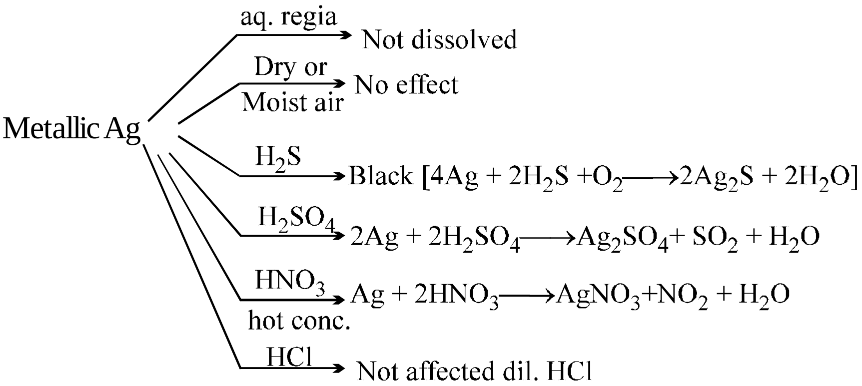
(i) PbO_2 (ii) $Pb_3O_4 + HNO_3$ (iii) $Pb_2O_3 + HNO_3$ (iv) $NaBiO_3 / H^+$

(v) $(NH_4)_2S_2O_8 / H^+$ (vi) KIO_4 / H^+

Heating effect : $2KMnO_4 \xrightarrow[200°C]{\Delta} \underset{\text{green}}{K_2MnO_4} + \underset{\text{Black}}{MnO_2} + O_2$

$$2K_2MnO_4 \xrightarrow[\text{hot}]{\text{at red}} 2K_2MnO_3 + O_2$$

SILVER AND ITS COMPOUND



(I) Metallic Ag

$\xrightarrow{\text{aq. regia}}$ Not dissolved

$\xrightarrow[\text{Moist air}]{\text{Dry or}}$ No effect

$\xrightarrow{H_2S}$ Black $[4Ag + 2H_2S + O_2 \longrightarrow 2Ag_2S + 2H_2O]$

$\xrightarrow{H_2SO_4}$ $2Ag + 2H_2SO_4 \longrightarrow Ag_2SO_4 + SO_2 + H_2O$

$\xrightarrow[\text{hot conc.}]{HNO_3}$ $Ag + 2HNO_3 \longrightarrow AgNO_3 + NO_2 + H_2O$

$\xrightarrow{HCl}$ Not affected dil. HCl

$E^o_{Ag/Ag^+} < E^o_{H_2/H^+}$

Hence in presence of O_2.

Ag reacts with dil.HCl

$4Ag + 4HCl + O_2 \longrightarrow 4AgCl\downarrow + 2H_2O$

In the same way in presence of O_2, Ag complexes with NaCN / KCN.

$4Ag + 8KCN + 2H_2O + O_2 \longrightarrow 4K[Ag(CN)_2] + 4KOH$

$AgNO_3$

Prepration : Reaction of Ag with dilute HNO_3 or conc. HNO_3.

Properties :

(i) It is called as lunar caustic because in contact with skin it produces burning sensation like that of caustic soda with the formation of finely devided silver (black colour)

(ii) Thermal decomposition : $2AgNO_3(s) \rightarrow 2Ag\,(s) + O_2\,(g) + 2NO_2\,(g)$

(iii) Props. of $AgNO_3$

$$\underset{\text{(excess)}}{6AgNO_3} + 3I_2 + 3H_2O \longrightarrow 5AgI + AgIO_3 + 6HNO_3$$

(iv) $Ag_2SO_4 \xrightarrow{\Delta} 2Ag + SO_2 + O_2$

(v)
$$\left.\begin{array}{l} A(AgNO_3) \xrightarrow[\text{added}]{B} \text{white ppt appears quickly} \\ B(Na_2S_2O_3) \xrightarrow[\text{added}]{A} \text{It takes time to give white ppt.} \end{array}\right\} \text{Explain}$$

(vi) $Ag_2S_2O_3 + H_2O \xrightarrow{\Delta} Ag_2S + H_2SO_4$

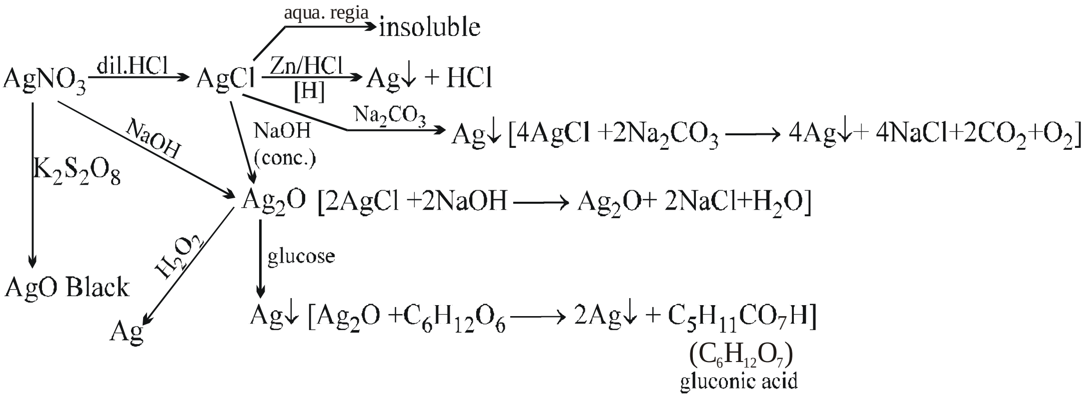
AgCl, AgBr, AgI (but not Ag_2S) are soluble in $Na_2S_2O_3$ forming $[Ag(S_2O_3)_2]^{-3}$ complexes

(vii) $AgBr + AgNO_3 \xrightarrow{KBr} \underset{\substack{\text{Pale yellow} \\ \text{ppt.}}}{AgBr\downarrow} + KNO_3$

Heating effect : $2AgNO_3 \xrightarrow{212°C} 2AgNO_2 + O_2$

$$2AgNO_2 \xrightarrow{500°C} 2Ag + 2NO + O_2$$

(viii)



$$Ag_2O + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$$

$$K_2S_2O_8 + 2AgNO_3 + 2H_2O \longrightarrow 2AgO + 2KHSO_4 + 2HNO_3$$

* AgO supposed to be paramagnetic due to d^9 configuration. But actually it is diamagnetic and exists as $Ag^I\,[Ag^{III}O_2]$

* Reaction involved in developer :

$$K_2Fe^{II}(C_2O_4)_2 + AgBr \longrightarrow KFe^{III}(C_2O_4)_2 + Ag\downarrow + KBr$$

ZINC COMPOUNDS

ZnO

It is called as phillospher's wool due to its wooly flock type appearance

Preparation: [1] $2Zn + O_2 \longrightarrow 2ZnO$

[2] Calcination of $ZnCO_3$ or $Zn(NO_3)_2$ or $Zn(OH)_2$

Purest ZnO : $4ZnSO_4 + 4Na_2CO_3 + 3H_2O \longrightarrow \underset{\text{white basic zinc carbonate}}{ZnCO_3 \cdot 3Zn(OH)_2} \downarrow + 4Na_2SO_4 + 3CO_2$

$$\big\downarrow \Delta$$

$$\underset{\text{pure}}{4ZnO} + 3H_2O \uparrow + CO_2 \uparrow$$

Properties: 1] $\underset{\text{white}}{ZnO(cold)} \overset{\Delta}{\rightleftharpoons} \underset{\text{yellow}}{ZnO(hot)}$

2] It is insoluble in water

3] It sublimes at 400°C

4] It is amphoteric oxide , react with acid & base both.

$ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$

$ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$

$ZnO + 2NaOH \longrightarrow Na_2ZnO_2 + H_2O$

5] $ZnO \longrightarrow Zn$ by H_2 & C

$ZnO + H_2 \xrightarrow{>400°C} Zn + H_2O$

$ZnO + C \longrightarrow Zn + CO$

6] It forms Rinmann's green with $Co(NO_3)_2$

$2Co(NO_3)_2 \longrightarrow 2CoO + 4NO_2 + O_2$

$CoO + ZnO \longrightarrow \underset{\text{Rinmann's green}}{CoZnO_2 \text{ or } CoO \cdot ZnO}$

Uses: (1) As white pigment, it is superior than white lead because it does not turn into black

(2) Rinmann's green is used as green pigment

(3) It is used as zinc ointment in medicine

$ZnCl_2$

Preparation : $ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$

$$\left.\begin{array}{l} ZnCO_3 + 2HCl \longrightarrow ZnCl_2 + H_2O + CO_2 \end{array}\right\} \text{It crystallises as } ZnCl_2 \cdot 2H_2O$$

$Zn(OH)_2 + 2HCl \longrightarrow ZnCl_2 + 2H_2O$

Anh. $ZnCl_2$ cannot be made by heating $ZnCl_2 \cdot 2H_2O$ because

$ZnCl_2 \cdot 2H_2O \xrightarrow{\Delta} Zn(OH)Cl + HCl + H_2O$

$Zn(OH)Cl \xrightarrow{\Delta} ZnO + HCl$

To get anh. $ZnCl_2$: $Zn + Cl_2 \longrightarrow ZnCl_2$

$Zn + 2HCl(dry) \longrightarrow ZnCl_2 + H_2$

or $Zn + HgCl_2 \longrightarrow ZnCl_2 + Hg$

Properties: (i) It is deliquescent white solid (when anhydrous)

(ii) $ZnCl_2 + H_2S \longrightarrow ZnS$

" $+ NaOH \longrightarrow Zn(OH)_2 \xrightarrow{\text{excess}} Na_2[Zn(OH)_4]$

" $+ NH_4OH \longrightarrow Zn(OH)_2 \xrightarrow{\text{excess}} [Zn(NH_3)_4]^{2+}$

Uses: 1] Used for impregnating timber to prevent destruction by insects

2] As dehydrating agent when anhydrous

3] $ZnO{\cdot}ZnCl_2$ used in dental filling

$ZnSO_4$

Preparation:→

$Zn + \text{dil } H_2SO_4 \longrightarrow ZnSO_4 + H_2$

$ZnO + \text{dil } H_2SO_4 \longrightarrow ZnSO_4 + H_2O$

$ZnCO_3 + \text{dil } H_2SO_4 \longrightarrow ZnSO_4 + H_2O + CO_2$

$$\left.\begin{array}{l} ZnS + 2O_2 \longrightarrow ZnSO_4 \\ ZnS + \frac{3}{2}O_2 \longrightarrow ZnO + SO_2 \end{array}\right\} \text{parallel reaction}$$

$ZnS + 4O_3 \longrightarrow ZnSO_4 + 4O_2$

Props.1] $ZnSO_4{\cdot}7H_2O \xrightarrow{39-70°C} ZnSO_4{\cdot}6H_2O \xrightarrow{>70°C} ZnSO_4{\cdot}H_2O \xrightarrow{>280°C} ZnSO_4$

$$\frac{1}{2}O_2 + SO_2 + ZnO \xleftarrow{>800°C} ZnSO_4$$

Uses: 1] in eye lotion

2] Lithophone ($ZnS + BaSO_4$) is used as white pigment

COPPER COMPOUNDS

CuO

Preparation : (i) $CuCO_3.Cu(OH)_2 \xrightarrow{\Delta} 2CuO + H_2O + CO_2$(Commercial process)

Malachite Green

(native Cu-carbonate)

(ii) $2Cu + O_2 \longrightarrow 2CuO$ & $Cu_2O + \frac{1}{2}O_2 \longrightarrow 2CuO$

(iii) $Cu(OH)_2 \xrightarrow{\Delta} CuO + H_2O$

(iv) $2Cu(NO_3)_2 \xrightarrow{250°C} 2CuO + 4NO_2 + O_2$

Properties : (i) CuO is insoluble in water

(ii) Readily dissolves in dil. acids

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

$$HCl \longrightarrow CuCl_2$$

$$HNO_3 \longrightarrow Cu(NO_3)_2$$

(iii) It decomposes when, heated above 1100°C

$$4CuO \longrightarrow 2Cu_2O + O_2$$

(iv) CuO is reduced to Cu by H_2 or C under hot condition

$$CuO + C \longrightarrow Cu + CO \uparrow$$

$$CuO + H_2 \longrightarrow Cu + H_2O \uparrow$$

$CuCl_2$

Preparation:→ $CuO + 2HCl(conc.) \longrightarrow CuCl_2 + H_2O$

$$Cu(OH)_2 \cdot CuCO_3 + 4HCl \longrightarrow 2CuCl_2 + 3H_2O + CO_2$$

Properties :→(i) It is crystallised as $CuCl_2 \cdot 2H_2O$ of Emerald green colour

(ii) dil. solution in water is blue in colour due to formation of $[Cu(H_2O)_4]^{2+}$complex.

(iii) When conc. HCl or KCl added to dil. solution of $CuCl_2$ the colour changes into yellow, owing to the formation of $[CuCl_4]^{2-}$

(iv) The conc. aq. solution is green in colour having the two complex ions in equilibrium $2[Cu(H_2O)_4]Cl_2 \rightleftharpoons [Cu(H_2O)_4]^{2+} + [CuCl_4]^{2-} + 4H_2O$

(v) $CuCl_2 \longrightarrow CuCl$ by no. of reagents

(a) $CuCl_2 + \text{Cu-turnings} \xrightarrow{\Delta} 2CuCl$

(b) $2CuCl_2 + H_2SO_3 + H_2O \longrightarrow 2CuCl + 2HCl + 2H_2SO_4$

(c) $2CuCl_2 + Zn/HCl \longrightarrow 2CuCl + ZnCl_2$

(d) $CuCl_2 + SnCl_2 \longrightarrow CuCl + SnCl_4$

** $CuF_2 \cdot 2H_2O \longrightarrow$ light blue

$CuCl_2 \cdot 2H_2O \longrightarrow$ green

$CuBr_2 \longrightarrow$ almost black

{Anh. $CuCl_2$ is dark brown mass obtained by heating $CuCl_2 \cdot 2H_2O$ at 150°C in presence of HCl vap.

CuI_2 does not exist $\quad CuCl_2 \cdot 2H_2O \xrightarrow[\text{HCl gas}]{150°C} CuCl_2 + 2H_2O$

$CuSO_4$

Preparation :→ $CuO + H_2SO_4(dil) \longrightarrow CuSO_4 + H_2O$

$$Cu(OH)_2 + H_2SO_4(dil) \longrightarrow CuSO_4 + 2H_2O$$

$$Cu(OH)_2 \cdot CuCO_3 + H_2SO_4\ (dil) \rightarrow CuSO_4 + 3H_2O + CO_2$$

$$Cu + H_2SO_4 + \frac{1}{2}O_2 \longrightarrow CuSO_4 + H_2O \quad \text{[Commercial scale]}$$

(Scrap)

$Cu + \text{dil. } H_2SO_4 \longrightarrow$ no reaction {Cu is a below H in electrochemical series}

Properties :→(i) It is crystallised as $CuSO_4\cdot5H_2O$

(ii) $$CuSO_4\cdot5H_2O \underset{\text{effloresence}}{\overset{\text{On exposure}}{\rightleftharpoons}} CuSO_4\cdot3H_2O \overset{100°C}{\rightleftharpoons} CuSO_4\cdot H_2O$$

Blue take places Pale blue Bluish white

$$\downarrow\uparrow\ 230°C$$

$CuSO_4$(anh.)

white

$$\overset{800°C}{\swarrow}\ CuO + SO_2 + \frac{1}{2}O_2 \quad \Big| \quad \overset{750°C}{\downarrow}\ CuO + SO_3$$

(iii) Revision with all others reagent

IRON COMPOUNDS

$FeSO_4\cdot7H_2O$

Preparation:→(i) Scrap Fe + $\underset{\text{(dil.)}}{H_2SO_4} \longrightarrow FeSO_4 + H_2\uparrow$

(ii) From Kipp's waste

$$FeS + H_2SO_4(dil) \longrightarrow FeSO_4 + H_2S\uparrow$$

(iii) $FeS_2 + 2H_2O + \frac{7}{2}O_2 \longrightarrow FeSO_4 + H_2SO_4$

Properties:→ (i) It undergoes aerial oxidation forming basic ferric sulphate

$$4FeSO_4 + H_2O + O_2 \longrightarrow 4Fe(OH)SO_4$$

(ii) $FeSO_4\cdot7H_2O \xrightarrow{300°C} \underset{\text{anh. white}}{FeSO_4} \xrightarrow[\text{temp.}]{\text{high}} Fe_2O_3+SO_2+SO_3$

(iii) Aq. solution is acidic due to hydrolysis

$$FeSO_4 + 2H_2O \rightleftharpoons \underset{\text{weak base}}{Fe(OH)_2} + H_2SO_4$$

(iv) It is a reducing agent

(a) $Fe^{2+} + MnO_4^- + H^+ \longrightarrow Fe^{3+} + Mn^{2+} + H_2O$

(b) $Fe^{2+} + Cr_2O_7^{2-} + H^+ \longrightarrow Fe^{3+} + Cr^{3+} + H_2O$

(c) $Au^{3+} + Fe^{2+} \longrightarrow Au + Fe^{3+}$

(d) $Fe^{2+} + HgCl_2 \longrightarrow \underset{\text{white ppt.}}{Hg_2Cl_2\downarrow} + Fe^{3+}$

(v) It forms double salt. Example $(NH_4)_2SO_4\cdot FeSO_4\cdot6H_2O$

FeO(Black)

Preparation : $FeC_2O_4 \xrightarrow[\text{in absence of air}]{\Delta} FeO + CO + CO_2$

Properties : It is stable at high temperature and on cooling slowly disproportionates into Fe_3O_4 and iron

$$4FeO \longrightarrow Fe_3O_4 + Fe$$

$FeCl_2$

Preparation: $Fe + 2HCl \xrightarrow[\text{a current of HCl}]{\text{heated in}} FeCl_2 + H_2$

OR

$$2FeCl_3 + H_2 \xrightarrow{\Delta} 2FeCl_2 + 2HCl$$

Properties:→ (i) It is deliquescent in air like $FeCl_3$

(ii) It is soluble in water, alcohol and ether also because it is sufficiently covalent in nature

(iii) It volatilises at about 1000°C and vapour density indicates the presence of Fe_2Cl_4. Above 1300°C density becomes normal

(iv) It oxidises on heating in air

$$12FeCl_2 + 3O_2 \longrightarrow 2Fe_2O_3 + 8FeCl_3$$

(v) H_2 evolves on heating in steam

$$3FeCl_2 + 4H_2O \longrightarrow Fe_3O_4 + 6HCl + H_2$$

(vi) It can exist as different hydrated form

$FeCl_2{\cdot}2H_2O \longrightarrow$ colourless

$FeCl_2{\cdot}4H_2O \longrightarrow$ pale green

$FeCl_2{\cdot}6H_2O \longrightarrow$ green

Ferric Chloride ($FeCl_3$)

This is the most important ferric salt. It is known in anhydrous and hydrated forms. The hydrated form consists of six water molecules, $FeCl_3.6H_2O$.

Preparation :

(i) Anhydrous ferric chloride is obtained by passing dry chlorine gas over heated iron fillings. The vapours are condensed in a bottle attached to the outlet of the tube.

$$2Fe + 3Cl_2 \rightarrow 2FeCl_3$$

(ii) $Fe_2(CO_3)_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O + 3CO_2$

$Fe(OH)_3 + 3HCl \rightarrow FeCl_3 + 3H_2O$

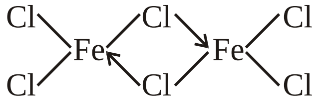
$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O$

The solution on evaporation and cooling deposits yellow crystals of hydrated ferric chloride. $FeCl_3.6H_2O$

Properties

(i) $Fe_2Cl_6 \underset{}{\overset{750°C}{\rightleftharpoons}} 2FeCl_3 \overset{Above\ 750°C}{\rightleftharpoons} 2FeCl_2 + Cl_2$

(ii)



(iii) It dissolves in water. The solution is acidic in nature due to its hydrolysis as shown below :

$FeCl_3 + 3HOH \rightleftharpoons Fe(OH)_3 + 3HCl$

(iv) $FeCl_3 + 6NH_3 \rightarrow FeCl_3.6NH_3$

(v) Ferric chloride acts as an oxidising agent.

(a) It oxidies stannous chloride to stannic chloride.

$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$

(b) It oxidises SO_2 to H_2SO_4

$2FeCl_3 + SO_2 + 2H_2O \rightarrow 2FeCl_2 + H_2SO_4 + 2HCl$

(c) It oxidises H_2S to S

$2FeCl_3 + H_2S \rightarrow 2FeCl_2 + 2HCl + S$

(d) It liberates iodine from KI.

$2FeCl_3 + 2KI \rightarrow 2FeCl_2 + 2KCl + I_2$

(e) Nascent hydrogen reduces $FeCl_3$ into $FeCl_2$

$FeCl_3 + [H] \rightarrow FeCl_2 + HCl$

(vi) $FeCl_3 + 3NH_4OH \rightarrow Fe(OH)_3 + 3NH_4Cl$

(vii) $FeCl_3 + NH_4SCN \rightarrow Fe(SCN)Cl_2 + NH_4Cl$

or $FeCl_3 + 3NH_4SCN \rightarrow Fe(SCN)_3 + 3NH_4Cl$

(viii) $4FeCl_3 + 3K_4Fe(CN)_6 \rightarrow Fe_4[Fe(CN)_6]_3 + 12KCl$

Prussian blue

(Ferri ferrocyanide)

(ix) On heating hydrated ferric chloride $FeCl_3.6H_2O$, anhydrous ferric chloride is not obtained. It is changed to Fe_2O_3 with evolution of H_2O and HCl.

$$2[FeCl_3.6H_2O] \xrightarrow{Heat} Fe_2O_3 + 6HCl + 9H_2O$$

Hydrated ferric chloride may be dehydrated by heating with thionyl chloride.

$$FeCl_3.6H_2O + 6SOCl_2 \longrightarrow FeCl_3 + 12HCl + 6SO_2$$

EXERCISE # O-1

SELECT ONLY ONE IS CORRECT OPTIONS :

General Properties of d-block

1. $N_2(g) + 3H_2(g) \xrightleftharpoons{Fe + Mo} 2NH_3(g)$; Haber's process, Mo is used as

(A) a catalyst (B) a catalytic promoter

(C) an oxidising agent (D) as a catalytic poison

2. An ornamental of gold having 75% of gold, it is of .... carat.

(A) 18 (B) 16 (C) 24 (D) 20

3. Transition elements having more tendency to form complex than representative elements (s and p-block elements) due to -

(A) availability of d-orbitals for bonding

(B) variable oxidation states are not shown by transition elements

(C) all electrons are paired in d-orbitals

(D) *f*-orbitals are available for bonding

4. A compound of mercury used in cosmetics, in Ayurvedic and Yunani medicines and known as Vermilion is -

(A) $HgCl_2$ (B) HgS (C) Hg_2Cl_2 (D) HgI

5. Transition elements are usually characterised by variable oxidation states but Zn does not show this property because of

(A) completion of np-orbitals (B) completion of (n–1)d orbitals

(C) completion of ns-orbitals (D) inert pair effect

6. The d-block element which is a liquid at room temperature, having high specific heat, less reactivity than hydrogen and its chloride (MX_2) is volatile on heating is

(A) Cu (B) Hg (C) Ce (D) Pm

7. Coinage metals show the properties of

(A) typical elements (B) normal elements

(C) inner-transition elements (D) transition element

8. The transition metal used in X-rays tube is

(A) Mo (B) Ta (C) Tc (D) Pm

9. The higher oxidation states of transition elements are found to be in the combination with A and B, which are

(A) F, O (B) O, N (C) O, Cl (D) F, Cl

10. The metals present in insulin and haemoglobin are respectively

(A) Zn, Hg (B) Zn, Fe (C) Co, Fe (D) Mg, Fe

11. A metal M which is not affected by strong acids like conc. HNO_3, conc. H_2SO_4 and conc. solution of alkalies like NaOH, KOH forms MCl_3 which finds use for toning in photography. The metal M is

(A) Ag (B) Hg (C) Au (D) Cu

12. Manganese steel is used for making railway tracks because

(A) it is hard with high percentage of Mn

(B) it is soft with high percentage of Mn

(C) it is hard with small concentration of manganese with impurities

(D) it is soft with small concentration of manganese with impurities

13. Transition elements in lower oxidation states act as Lewis acid because

(A) they form complexes (B) they are oxidising agents

(C) they donate electrons (D) they do not show catalytic properties

14. The electrons which take part in order to exhibit variable oxidation states by transition metals are

(A) ns only (B) (n–1)d only

(C) ns and (n–1)d only but not np (D) (n–1)d and np only but not ns

15. Solution of MnO_4^- is purple-coloured due to

(A) d-d-transition (B) charge transfer from O to Mn

(C) due to both d-d-transition and charge transfer (D) none of these

16. An element of 3d-transition series shows two oxidation states x and y, differ by two units then

(A) compounds in oxidation state x are ionic if x > y

(B) compounds in oxidation state x are ionic if x < y

(C) compounds in oxidation state y are covalent if x < y

(D) compounds in oxidation state y are covalent if y < x

Compounds of d-block

17.
$$(T) \xrightarrow{\text{compd. (U)} \ + \text{conc.} H_2SO_4} (V)_{\text{Red gas}} \xrightarrow{NaOH+AgNO_3} (W)_{\text{Red ppt.}} \xrightarrow{NH_3 \text{ soln.}} (X)$$

imparts violet
colour in the
flame test

$$(W)_{\text{Red ppt.}} \xrightarrow{\text{dil. HCl}} (Y)_{\text{white ppt.}}$$

$$(U) \xrightarrow[\Delta]{NaOH} (Z)_{\text{gas}} \text{ (gives white fumes with HCl)}$$

sublimes on
heating

Identify (T) to (Z).

(A) T = $KMnO_4$, U = HCl, V = Cl_2, W = HgI_2, X = $Hg(NH_2)NO_3$, Y = Hg_2Cl_2, Z = N_2

(B) T=$K_2Cr_2O_7$, U=NH_4Cl, V=CrO_2Cl_2, W=Ag_2CrO_4, X=$[Ag(NH_3)_2]^+$, Y=AgCl,Z = NH_3

(C) T = K_2CrO_4, U = KCl, V = CrO_2Cl_2, W = HgI_2, X = Na_2CrO_4, Y = $BaCO_3$, Z = NH_4Cl

(D) T = K_2MnO_4, U = NaCl, V = CrO_3, W = $AgNO_2$, X = $(NH_4)_2CrO_4$, Y = $CaCO_3$, Z = SO_2

18. The number of moles of acidified $KMnO_4$ required to convert one mole of sulphite ion into sulphate ion is

(A) 2/5 (B) 3/5 (C) 4/5 (D) 1

19. $Cr_2O_7^{2-} \underset{Y}{\overset{X}{\rightleftharpoons}} 2CrO_4^{2-}$, X and Y are respectively

(A) X = OH^-, Y = H^+ (B) X = H^+, Y = OH^-

(C) X = OH^-, Y = H_2O_2 (D) X = H_2O_2, Y = OH^-

20. CrO_3 dissolves in aqueous NaOH to give

(A) $Cr_2O_7^{2-}$ (B) CrO_4^{2-} (C) $Cr(OH)_3$ (D) $Cr(OH)_2$

21. During estimation of oxalic acid Vs $KMnO_4$, self indicator is

(A) $KMnO_4$ (B) oxalic acid (C) K_2SO_4 (D) $MnSO_4$

22. Acidified chromic acid + $H_2O_2 \xrightarrow{\text{Org.solvent}} \underset{\text{(blue colour)}}{X} + Y$, X and Y are

(A) CrO_5 and H_2O (B) Cr_2O_3 and H_2O (C) CrO_2 and H_2O (D) CrO and H_2O

23. $\underset{\text{(diatomic covalent molecule)}}{Y} \xleftarrow{KI} CuSO_4 \xrightarrow{\text{dil } H_2SO_4} X(\text{Blue colour})$, X and Y are

(A) X = I_2, Y = $[Cu(H_2O)_4]^{2+}$ (B) X = $[Cu(H_2O)_4]^{2+}$, Y = I_2

(C) X = $[Cu(H_2O)_4]^{+}$, Y = I_2 (D) X = $[Cu(H_2O)_5]^{2+}$, Y = I_2

24. $(NH_4)_2Cr_2O_7$ (Ammonium dichromate) is used in fire works. The green coloured powder blown in air is

(A) Cr_2O_3 (B) CrO_2 (C) Cr_2O_4 (D) CrO_3

25. Iron becomes passive by .... due to formation of ....

(A) dil. HCl, Fe_2O_3 (B) 80% conc. HNO_3, Fe_3O_4

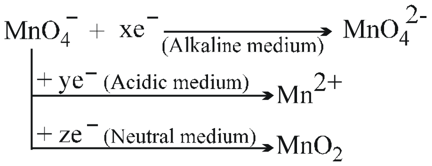
(C) conc. H_2SO_4, Fe_3O_4 (D) conc. HCl, Fe_3O_4

26. Bayer's reagent used to detect olifinic double bond is

(A) acidified $KMnO_4$ (B) aqueous $KMnO_4$

(C) 1% alkaline $KMnO_4$ solution (D) $KMnO_4$ in benzene

27.



x, y and z are respectively

(A) 1, 2, 3 (B) 1, 5, 3 (C) 1, 3, 5 (D) 5, 3, 1

28. $Cu + \underset{\text{(hot)}}{\text{conc. } HNO_3} \longrightarrow Cu(NO_3)_2 + X$ (oxide of nitrogen); then X is

(A) N_2O (B) NO_2 (C) NO (D) N_2O_3

29. $CuSO_4$ solution reacts with excess KCN to give

(A) $Cu(CN)_2$ (B) CuCN (C) $K_2[Cu(CN)_2]$ (D) $K_3[Cu(CN)_4]$

30. Pick out the incorrect statement:

(A) MnO_2 dissolves in conc. HCl, but does not form Mn^{4+} ions

(B) MnO_2 react with hot concentrated H_2SO_4 liberating oxygen

(C) K_2MnO_4 is formed when MnO_2 in fused KOH is oxidised by air, KNO_3 , PbO_2 or $NaBiO_3$

(D) Decomposition of acidic $KMnO_4$ is not catalysed by sunlight.

31. 1 mole of Fe^{2+} ions are oxidised to Fe^{3+} ions with the help of (in acidic medium)

(A) 1/5 moles of $KMnO_4$ (B) 5/3 moles of $KMnO_4$

(C) 2/5 moles of $KMnO_4$ (D) 5/2 moles of $KMnO_4$

32. To an acidified dichromate solution, a pinch of Na_2O_2 is added and shaken. What is observed:

(A) blue colour (B) Orange colour changing to green

(C) Copious evolution of oxygen (D) Bluish - green precipitate

33. The rusting of iron is formulated as $Fe_2O_3 \cdot xH_2O$ which involves the formation of

(A) Fe_2O_3 (B) $Fe(OH)_3$ (C) $Fe(OH)_2$ (D) $Fe_2O_3 + Fe(OH)_3$

34. Solid $CuSO_4 \cdot 5H_2O$ having covalent, ionic as well as co-ordinate bonds. Copper atom/ion forms .... co-ordinate bonds with water.

(A) 1 (B) 2 (C) 3 (D) 4

35. $\underset{\text{(acidified)}}{KMnO_4} + HCl \longrightarrow H_2O + X(g)$, X is a

(A) red liquid (B) violet gas

(C) greenish yellow gas (D) yellow-brown gas

36. Purple of cassius is:

(A) Pure gold (B) Colliodal solution of gold

(C) Gold (I) hydroxide (D) Gold (III) chloride

37. Amongst the following species, maximum covalent character is exhibited by

(A) $FeCl_2$ (B) $ZnCl_2$ (C) $HgCl_2$ (D) $CdCl_2$

38. Number of moles of $SnCl_2$ required for the reduction of 1 mole of $K_2Cr_2O_7$ into Cr_2O_3 is (in acidic medium)

(A) 3 (B) 2 (C) 1 (D) 1/3

39. Pick out the incorrect statement:

(A) MnO_4^{2-} is quite strongly oxidizing and stable only in very strong alkalies. In dilute alkali, neutral solutions, it disproportionates.

(B) In acidic solutions, MnO_4^- is reduced to Mn^{2+} and thus, $KMnO_4$ is widely used as oxidising agent

(C) $KMnO_4$ does not acts as oxidising agent in alkaline medium

(D) $KMnO_4$ is manufactured by the fusion of pyrolusite ore with KOH in presence of air or KNO_3, followed by electrolytic oxidation in strongly alkaline solution.

40. The aqueous solution of $CuCrO_4$ is green because it contains

(A) green Cu^{2+} ions (B) green CrO_4^{2-} ions

(C) blue Cu^{2+} ions and green CrO_4^{2-} ions
(D) blue Cu^{2+} ions and yellow CrO_4^{2-} ions

41. In nitroprusside ion, the iron exists as Fe^{2+} and NO as NO^+ rather than Fe^{3+} and NO respectively. These forms of ions are established with the help of

(A) magnetic moment in solid state
(B) thermal decomposition method
(C) by reaction with KCN
(D) by action with K_2SO_4

42. Which of the following reaction is possible at anode?

(A) $2Cr^{3+} + 7H_2O \longrightarrow Cr_2O_7^{2-} + 14\ H^+$
(B) $F_2 \longrightarrow 2\ F^-$
(C) $\frac{1}{2}O_2 + 2H^+ \longrightarrow H_2O$
(D) None of these

43. Colourless solutions of the following four salts are placed separately in four different test tubes and a strip of copper is dipped in each one of these. Which solution will turn blue?

(A) KNO_3
(B) $AgNO_3$
(C) $Zn(NO_3)_2$
(D) $ZnSO_4$

44. When acidified $KMnO_4$ is added to hot oxalic acid solution, the decolourization is slow in the beginning, but becomes very rapid after some time. This is because:

(A) Mn^{2+} acts as autocatalyst
(B) CO_2 is formed as the product
(C) Reaction is exothermic
(D) MnO_4^- catalyses the reaction

45. Metre scales are made-up of alloy

(A) invar
(B) stainless steel
(C) elektron
(D) magnalium

46. The Ziegler-Natta catalyst used for polymerisation of ethene and styrene is $TiCl_4 + (C_2H_5)_3Al$, the catalysing species (active species) involved in the polymerisation is

(A) $TiCl_4$
(B) $TiCl_3$
(C) $TiCl_2$
(D) TiCl

47. 'Bordeaux mixture' is used as a fungicide. It is a mixture of

(A) $CaSO_4 + Cu(OH)_2$
(B) $CuSO_4 + Ca(OH)_2$
(C) $CuSO_4 + CaO$
(D) $CuO + CaO$

48. Peacock ore is:

(A) FeS_2
(B) $CuFeS_2$
(C) $CuCO_3.Cu(OH)_2$
(D) Cu_5FeS_4

EXERCISE # O-2

SELECT MORE THAN ONE IS CORRECT OPTIONS

General Properties of d-block

1. Potash alum is a double salt, its aqueous solution shows the characteristics of

(A) Al^{3+} ions (B) K^+ ions (C) SO_4^{2-} ions (D) Al^{3+} ions but not K^+ ions

2. Addition of non-metals like B and C to the interstitial sites of a transition metal results the metal

(A) of more ductability (B) of less ductability

(C) less malleable (D) of more hardness

3. Mercury is a liquid at 0°C because of

(A) very high ionisation energy (B) weak metallic bonds

(C) high heat of hydration (D) high heat of sublimation

4. The correct statement(s) about transition elements is/are

(A) the most stable oxidation state is +3 and its stability decreases across the period

(B) transition elements of 3d-series have almost same atomic sizes from Cr to Cu

(C) the stability of +2 oxidation state increases across the period

(D) some transition elements like Ni, Fe, Cr may show zero oxidation state in some of their compounds

5. The ionisation energies of transition elements are

(A) less than p-block elements (B) more than s-block elements

(C) less than s-block elements (D) more than p-block elements

6. The metal(s) which does/do not form amalgam is/are

(A) Fe (B) Pt (C) Zn (D) Ag

7. Which of the following statements concern with d-block metals?

(A) compounds containing ions of transition elements are usually coloured

(B) Zinc has lowest melting point among 3d-series elements

(C) they show variable oxidation states, which differ by two units only

(D) they easily form complexes

8. The highest oxidation state among transition elements is

(A) + 7 by Mn (B) + 8 by Os (C) + 8 by Ru (D) + 7 by Fe

9. Amphoteric oxide(s) is/are

(A) Al_2O_3 (B) SnO (C) ZnO (D) Fe_2O_3

10. The catalytic activity of transition elements is related to their

(A) variable oxidation states (B) free suface valencies

(C) complex formation ability (D) magnetic moment

11. In the equation: $M + 8CN^- + 2H_2O + O_2 \longrightarrow 4[M(CN)_2]^- + 4OH^-$, metal M is

(A) Ag (B) Au (C) Cu (D) Hg

12. $CuSO_4(aq) + 4NH_3 \longrightarrow X$, then X is

(A) $[Cu(NH_3)_4]^{2+}$ (B) paramagnetic

(C) coloured (D) of a magnetic moment of 1.73 BM

13. Amphoteric oxide(s) of Mn is/are

(A) MnO_2 (B) Mn_3O_4 (C) Mn_2O_7 (D) MnO

14. The lanthanide contraction is responsible for the fact that

(A) Zr and H*f* have same atomic sizes (B) Zr and H*f* have same properties

(C) Zr and H*f* have different atomic sizes (D) Zr and H*f* have different properties

15. Ion(s) having non zero magnetic moment (spin only) is/are

(A) Sc^{3+} (B) Ti^{3+} (C) Cu^{2+} (D) Zn^{2+}

Compounds of d-block

16. Correct statement(s) is/are

(A) an acidified solution of $K_2Cr_2O_7$ liberates iodine from KI

(B) $K_2Cr_2O_7$ is used as a standard solution for estimation of Fe^{2+} ions

(C) in acidic medium, M = N/6 for $K_2Cr_2O_7$

(D) $(NH_4)_2Cr_2O_7$ on heating decomposes to yield Cr_2O_3 through an endothermic reaction

17. Interstitial compounds are formed by

(A) Co (B) Ni (C) Fe (D) Ca

18. Acidified $KMnO_4$ can be decolourised by

(A) SO_2 (B) H_2O_2 (C) $FeSO_4$ (D) $Fe_2(SO_4)_3$

EXERCISE # S-1

NUMERICAL GRID TYPE QUESTIONS :

1. When mixture of NaCl and $K_2Cr_2O_7$ is gently warmed with conc.H_2SO_4 then compound X is formed. What is the oxidation state of central atom of X.

2. Number of ions which gives blue colour in aqueous state :

V^{+4}, Ni^{+2}, Ti^{+3}, Co^{+2}, Fe^{+3}, Cu^{+2}

3. Define the oxidation states of Mn in product of the given reaction

$3K_2MnO_4+2H_2O+4CO_2 \rightarrow 2X+Y+4KHCO_3$

If the oxidation state of Mn in product X and Y are n_1 and n_2 respectively. Then find out the value of (n_1+n_2) -

4. Find number of metal ion which can produce high spin and low spin octahedral complex :

Sc^{+3}, Ti^{+3}, V^{+3}, Cr^{+3}, Mn^{+3}, Fe^{+3}, Co^{+3}, Ni^{+2}

5. How many non-axial d-orbitals are involved in hybridisation of CrO_2Cl_2.

6. Find the number of species from the following which has magnetic moment value of 1.73 B.M.

Fe^{2+}, Cu^{2+}, Ni^{2+}, NO_2, NO_2^-, Ti^{3+}

7. Total no. of moles of Mohr's salt are required for per mole of dichromate ions during volumetric analysis.

8. Find number of reaction(s) in which no redox change takes place -

(I) $BaCl_2 + Na_2CrO_4 \xrightarrow{CH_3COOH}$

(II) $K_2Cr_2O_7 + NaOH \longrightarrow$

(III) $Cr_2O_7^{2-} + NO_3^- \xrightarrow{H^+}$

(IV) $Cr_2O_7^{2-} + C_2H_5OH \xrightarrow{H^+}$

EXERCISE # S-2

COMPREHENSTION TYPE QUESTIONS :

Comprehension # 01 to 04

Transition metal and their compounds are used as catalysts in industry and in biological system. For example, in the Contact process, vanadium compounds in the +5 state (V_2O_5 or VO_3^-) are used to oxidise SO_2 to SO_3:

$$SO_2 + \frac{1}{2}O_2 \xrightarrow{V_2O_5} SO_3$$

It is thought that the actual oxidation process takes place in two stages. In the first step, V^{5+} in the presence of oxide ions converts SO_2 to SO_3. At the same time, V^{5+} is reduced to V^{4+}.

$$2V^{5+} + O^{2-} + SO_2 \longrightarrow 2V^{4+} + SO_3$$

In the second step, V^{5+} is regenerated from V^{4+} by oxygen :

$$2V^{4+} + \frac{1}{2}O_2 \longrightarrow 2V^{5+} + O^{2-}$$

The overall process is, of course, the sum of these two steps:

$$SO_2 + \frac{1}{2}O_2 \longrightarrow SO_3$$

1. Transition metals and their compounds catalyse reactions because **:**

(A) They have competely filled s-subshell

(B) They have a comparable size due to poor shielding of d-subshell

(C) They introduce an entirely new reaction mechanism with a lower activation energy

(D) They have variable oxidation states differ by two units

2. During the course of the reaction **:**

(A) Catalyst undergoes changes in oxidation state

(B) Catalyst increases the rate constant

(C) Catalyst is regenerated in its orginal form when the reactants form the products

(D) All are correct.

3. Catalytic activity of transition metals depends on **:**

(A) Their ability to exist in different oxidation states

(B) The size of the metal atoms

(C) The number of empty atomic orbitals available

(D) None of these

4. Which of the following ion involved in the above process will show paramagnetism?

(A) V^{5+} (B) V^{4+} (C) O^{2-} (D) VO_3^-

Comprehension # 05 & 06

(X) is very important laboratory reagent which is prepared by its naturally occuring ore which is called pyrolusite. Pyrolusite when fused with alkali in the presence of O_2, green compound **(Y)** is produced. **(Y)** is converted into **(X)** by electrolysis or by using ozone.

5. On small scale **(X)** is prepared by disproportion of **(Y)** in acidic solution. Which of the following is produced by disproportion of **(Y)** in slight alkaline solution.

(A) $KMnO_4$, Mn^{+2}
(B) $KMnO_4$, MnO_2
(C) MnO_2, Mn^{+2}
(D) K_2MnO_4, Mn^{+2}

6. Select the correct statements :

(A) **(X)** is tetrahedral & diamagnetic
(B) **(Y)** is tetrahedral & paramagnetic
(C) **(X)** produce dimangnese hepta oxide (oily liquid) with conc. H_2SO_4
(D) All are correct

Comprehension # 07 to 09

Due to availability of vacant orbitals of sufficiently low energy, d-block elements form complexes, d-block elements have different properties such as- catalytic, magnetic, alloy formation, interistitial compounds formation. Interistitial compounds are those compounds in which small atoms like carbon and boron fits into interistices of d-block elements crystal. In interistitial compounds, there is no chemical bond formation takes place so , chemical properties remain almost same but physical properties may change.

7. Which of the property of interistitial compounds has the same behaviour as that of the element -

(A) Malleability
(B) Ductility
(C) Electrical conductance
(D) Hardness

8. Which of the following property gets decreased in interistitial compounds compared to that of the element -

(A) Malleability
(B) Metallic lustre
(C) Hardness
(D) Density

9. Select correct statement -

(A) Highest oxidation state of 3d-series is +8.
(B) Ni, Cu and Zn are not transition element.
(C) Ziglar natta catalyst contain vanadium.
(D) Aq. solution of Cu^{2+}, Fe^{+3} and Cr^{3+} are blue, yellow and green respectively.

MATCH THE COLUMN : (Matrix Match)

10.

Column-I (Metals)	Column-II
(A) Zn	(P) Cyanide process involve in the comerical extration
(B) Cu	(Q) Extracted by hydrometallurgical process
(C) Ag	(R) Roasting involve in the comerical extration
(D) Au	(S) Present in Brass

11.

Column-I (catalyst)	Column-II (Used)
(A) $TiCl_4$	(P) Adams catalyst in reduction
(B) $PdCl_2$	(Q) In preparation of $(CH_3)_2 SiCl_2$
(C) Pt/PtO	(R) Used as the ziegler-natta catalyst in polythene production
(D) Cu	(S) Wacker process for converting C_2H_4 to CH_3CHO

SELECT CORRECT CODE :

12.

Column-I	Column-II
(P) Cr_2O_3	(1) Neutral oxide
(Q) CrO_3	(2) Amphoteric oxide
(R) Fe_3O_4	(3) Mix oxide
(S) N_2O	(4) Acidic oxide

Select correct code for matching -

Code :

	P	Q	R	S
(A)	2	4	3	1
(B)	2	3	4	1
(C)	4	2	3	1
(D)	4	3	1	2

13.

Column-I (Metal ion of 3d-series)	Column-II (Characterstic)
(P) Ni^{2+}	(1) produce blue aq. solution
(Q) Cr^{2+}	(2) half filled t_{2g} orbitals in octahedral complex
(R) V^{2+}	(3) diamagnetic ion
(S) Ti^{4+}	(4) calculated $\mu = 2.84$ B.M. (spin only)

Select correct code for matching -

Code :

	P	Q	R	S
(A)	4	2	1	3
(B)	3	1	2	4
(C)	4	1	2	3
(D)	1	2	4	3

ASSERATION & REASONING :

Questions given below consist of two statements each printed as Assertion (A) and Reason (R); while answering these questions you are required to choose any one of the following four responses:

(A) if both (A) and (R) are true and (R) is the correct explanation of (A)

(B) if both (A) and (R) are true but (R) is not correct explanation of (A)

(C) if (A) is true but (R) is false

(D) if (A) is false and (R) is true

14. **Assertion** : $KMnO_4$ is purple in colour due to charge transfer.

Reason : In MnO_4^-, there is no electron present in d-orbitals of manganese.

15. **Assertion** : K_2CrO_4 has yellow colour due to charge transfer.

Reason : CrO_4^{2-} ion is tetrahedral in shape.

16. **Assertion** : The highest oxidation state of chromium in its compounds is +6.

Reason : Chromium atom has only six electrons in ns and (n–1) d orbitals.

17. **Assertion** : CrO_3 reacts with HCl to form chromyl chloride gas.

Reason : Chromyl chloride (CrO_2Cl_2) has tetrahedral shape.

18. **Assertion** : Zinc does not show characteristic properties of transition metals.

Reason : In zinc outermost shell is completely filled.

19. **Assertion** : Tungsten has a very high melting point.

Reason : Tungsten is a covalent compound.

20. **Assertion** : Equivalent mass of $KMnO_4$ is equal to one-third of its molecular mass when it acts as an oxidising agent in an alkaline medium.

Reason : Oxidation number of Mn is +7 in $KMnO_4$.

21. **Assertion** : Cu^+ ion is colourless.

Reason : Four water molecules are coordinated to Cu^+ ion in water.

MATCHING LIST TYPE 1 × 3 Q. (THREE LIST TYPE Q.)

The following column 1, 2, 3 represent the different metals of 3d series and their properties Answer the questions that follow

Column-1 - Hexa aqua complex of dipositive ion of given metal
Column-2 - Magnetic moment (spin only)
Column-3 - Colour

Column - 1 **Hexa aqua complex of dipositive ion of given metal**	**Column - 2** **Magnetic moment (spin only)**	**Column - 3** **Colour**
(I) Co	(i) $\sqrt{8}$ B.M.	(P) Green
(II) Ni	(ii) $\sqrt{3}$ B.M.	(Q) Pink
(III) V	(iii) $\sqrt{15}$ B.M.	(R) Colourless
(IV) Zn	(iv) Zero	(S) Violet
		(T) Blue

22. Select **CORRECT** combination for metal which have same magnetism as in $[Ti(H_2O)_6]^{4+}$

(A) (II), (iv), (R) (B) (I), (iv), (R) (C) (IV), (iv), (R) (D) (IV), (iv), (T)

23. Which is **CORRECT** magnetic moment and colour combination of the product when $[Co(H_2O)_6]^{+2}$ is react with conc. HCl solution

(A) (ii), (Q) (B) (ii), (T) (C) (iii), (Q) (D) (iii), (T)

24. Select **CORRECT** combination for hexaaqua complex of metal ion M^{+2} which have half filled t_{2g} configuration (i.e. t_{2g}^3)

(A) (III), (iii), (S) (B) (III), (iii), (P) (C) (III), (ii), (S) (D) (III), (iv), (P)

25. $[M(H_2O)_6]^{+2}$ of a metal in **column-1** have combination (i), (P) in **column-2, 3**. Select **CORRECT** combination for hexaammine complex of same metal ion.

(A) (i), (T) (B) (i), (S) (C) (iv), (R) (D) (iv) (T)

EXERCISE # JEE-MAIN

1. What would happen when a solution of potassium chromate is treated with an excess of dilute nitric acid - **[AIEEE-2003]**

(1) Cr^{3+} and $Cr_2O_7^{2-}$ are formed (2) $Cr_2O_7^{2-}$ and H_2O are formed

(3) $Cr_2O_7^{2-}$ is reduced to +3 state of Cr (4) $Cr_2O_7^{2-}$ is oxidised to +7 state of Cr

2. Excess of KI reacts with $CuSO_4$ solution and then $Na_2S_2O_3$ solution is added to it. Which of the statements is incorrect for this reaction : **[AIEEE-2004]**

(1) Evolved I_2 is reduced (2) CuI_2 is formed

(3) $Na_2S_2O_3$ is oxidised (4) Cu_2I_2 is formed

3. Calomel on reaction with NH_4OH gives **[AIEEE-2004]**

(1) $HgNH_2Cl$ (2) $NH_2–Hg–Hg–Cl$ (3) Hg_2O (4) HgO

4. In context with the transition elements, which of the following statements is incorrect? **[AIEEE-2009]**

(1) In the highest oxidation states of the first five transition elements (Sc to Mn), all the 4s and 3d electrons are used for bonding.

(2) Once the d^5 configuration is exceeded, the tendency to involve all the 3d electrons in bonding decreases.

(3) In addition to the normal oxidation states, the zero oxidation state is also shown by these elements in complexes.

(4) In the highest oxidation states, the transition metal show basic character and form cationic complexes.

5. Iron exhibits +2 and +3 oxidation states. Which of the following statements about iron is **incorrect** ? **[AIEEE-2012]**

(1) Ferrous compounds are more easily hydrolysed than the corresponding ferric compounds.

(2) Ferrous oxide is more basic in nature than the ferric oxide.

(3) Ferrous compounds are relatively more ionic than the corresponding ferric compounds.

(4) Ferrous compounds are less volatile than the corresponding ferric compounds.

6. Consider the following reaction : **[JEE MAIN-2013]**

$$xMnO_4^- + yC_2O_4^{2-} + zH^+ \rightarrow xMn^{2+} + 2yCO_2 + \frac{z}{2} H_2O$$

The values of x, y and z in the reaction are respectively :-

(1) 5,2 and 16 (2) 2,5 and 8 (3) 2, 5 and 16 (4) 5,2 and 8

7. Which of the following arrangements does not represent the correct order of the property stated against it ? **[JEE MAIN-2013]**

(1) $V^{2+} < Cr^{2+} < Mn^{2+} < Fe^{2+}$: paramagnetic behaviour

(2) $Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+}$: ionic size

(3) $Co^{3+} < Fe^{3+} < Cr^{3+} < Sc^{3+}$: stability in aqueous solution

(4) Sc < Ti < Cr < Mn : number of oxidation states

8. Potassium dichromate when heated with concentrated sulphuric acid and a soluble chloride, gives brown - red vapours of: **[JEE MAIN-2013, Online]**

(1) CrO_3 (2) Cr_2O_3 (3) $CrCl_3$ (4) CrO_2Cl_2

9. The element with which of the following outer electron configuration may exhibit the largest number of oxidation states in its compounds : **[JEE MAIN-2013, Online]**

(1) $3d^74s^2$ (2) $3d^84s^2$ (3) $3d^54s^2$ (4) $3d^64S^2$

10. When a small amount of $KMnO_4$ is added to concentrated H_2SO_4, a green oily compound is obtained which is highly explosive in nature. Compound may be : **[JEE MAIN-2013, Online]**

(1)Mn_2O_3 (2) $MnSO_4$ (3) Mn_2O_7 (4) MnO_2

11. Which series of reactions correctly represents chemical relations related to iron and its compound?

(1) $Fe \xrightarrow{Cl_2,\ heat} FeCl_3 \xrightarrow{heat,\ air} FeCl_2 \xrightarrow{Zn} Fe$

(2) $Fe \xrightarrow{O_2,\ heat} Fe_3O_4 \xrightarrow{CO,\ 600^\circ C} FeO \xrightarrow{CO,700^\circ C} Fe$

(3) $Fe \xrightarrow{dil\ H_2SO_4} FeSO_4 \xrightarrow{H_2SO_4,\ O_2} Fe_2(SO_4)_3 \xrightarrow{Heat} Fe$

(4) $Fe \xrightarrow{O_2,\ heat} FeO \xrightarrow{dil\ H_2SO_4} FeSO_4 \xrightarrow{Heat} Fe$ **[JEE MAIN-2014]**

12. The equation which is balanced and represents the correct product (s) is : **[JEE MAIN-2014]**

(1) $[Mg(H_2O)_6]^{2+} + (EDTA)^{4-} \xrightarrow{excess\ NaOH} [Mg(EDTA)]^{2+} + 6H_2O$

(2) $CuSO_4 + 4KCN \rightarrow K_2[Cu(CN)_4] + K_2SO_4$

(3) $Li_2O + 2KCl \rightarrow 2LiCl + K_2O$

(4) $[CoCl(NH_3)_5]^+ + 5H^+ \rightarrow Co^{2+} + 5NH_4^+ + Cl^-$

13. Which of the following is **not** formed when H_2S reacts with acidic $K_2Cr_2O_7$ solution ?

(1) K_2SO_4 (2) $Cr_2(SO_4)_3$

(3) S (4) $CrSO_4$ **[JEE MAIN-2014, Online]**

14. Copper becomes green when exposed to moist air for a long period. This is due to :-

[JEE MAIN-2014, Online]

(1) the formation of a layer of cupric oxide on the surface of copper.

(2) the formation of basic copper sulphate layer on the surface of the metal

(3) the formation of a layer of cupric hydroxide on the surface of copper.

(4) the formation of a layer of basic carbonate of copper on the surface of copper.

15. Which one of the following exhibits the largest number of oxidation states ?

[JEE MAIN-2014, Online]

(1) Mn(25) (2) V(23) (3) Cr (24) (4) Ti (22)

16. How many electrons are involved in the following redox reaction ?**[JEE MAINS-2014,Online]**

$Cr_2O_7^{2-} + Fe^{2+} + C_2O_4^{2-} \rightarrow Cr^{3+} + Fe^{3+} + CO_2$ (Unbalanced)

(1) 3 (2) 4 (3) 5 (4) 6

17. Amongst the following, identify the species with an atom in +6 oxidation state:

[JEE MAIN-2014, Online]

(1) $[MnO_4]^-$ (2) $[Cr(CN)_6]^{3-}$ (3) Cr_2O_3 (4) CrO_2Cl_2

18. Match the catalysts to the correct processes :- **[JEE MAIN-2015]**

	Catalyst		Process
(A)	$TiCl_3$	(i)	Wacker process
(B)	$PdCl_2$	(ii)	Ziegler-Natta polymerization
(C)	$CuCl_2$	(iii)	Contact process
(D)	V_2O_5	(iv)	Deacon's process

(1) A-ii, B-iii, C-iv, D-i
(2) A-iii, B-i, C-ii, D-iv
(3) A-iii, B-ii, C-iv, D-i
(4) A-ii, B-i, C-iv, D-iii

19. Which of the following statements is false :- **[JEE MAIN-2015, Online]**

(1) $Cr_2O_7^{2-}$ has a Cr – O – Cr bond

(2) CrO_4^{2-} is tetrahedral in shape

(3) $Na_2Cr_2O_7$ is a primary standard in volumetry

(4) $K_2Cr_2O_7$ is less soluble than $Na_2Cr_2O_7$

20. The transition metal ions responsible for colour in ruby and emerald are, respectively : **[Jee Main 2016]**

(1) Cr^{3+} and Cr^{3+} (2) Cr^{3+} and Co^{3+} (3) Co^{3+} and Cr^{3+} (4) Co^{3+} and Co^{3+}

21. Galvanization is applying a coating of :- **[Jee Main 2016]**

(1) Zn (2) Pb (3) Cr (4) Cu

22. Which of the following compounds is metallic and ferromagnetic ? **[Jee Main 2016]**

(1) MnO_2 (2) TiO_2 (3) CrO_2 (4) VO_2

23. Which one of the following species is stable in aqueous solution? **[Jee Main 2016]**

(1) MnO_4^{3-} (2) MnO_4^{2-} (3) Cu^+ (4) Cr^{2+}

24. What will occur if a block of copper metal is dropped into a beaker containing a solution of 1M $ZnSO_4$? **[Jee Main 2016]**

(1) The copper metal will dissolve and zinc metal will be deposited
(2) No reaction will occur
(3) The copper metal will dissolve with evolution of oxygen gas
(4) The copper metal will dissolve with evolution of hydrogen gas

25. Which of the following ions does **not** liberate hydrogen gas on reaction with dilute acids? **[JEE MAIN-2017, Online]**

(1) Ti^{2+} (2) Cr^{2+} (3) Mn^{2+} (4) V^{2+}

26. In the following reactions, ZnO is respectively acting as a/an : **[JEE MAIN-2017]**

(a) $ZnO + Na_2O \rightarrow Na_2ZnO_2$
(b) $ZnO + CO_2 \rightarrow ZnCO_3$

(1) base and acid (2) base and base
(3) acid and acid (4) acid and base

EXERCISE # JEE-ADVANCED

TRUE/FALSE :

1. Cu^+ disproportionates to Cu^{2+} and elemental copper in solution. **[JEE 1991]**

FILL IN THE BLANKS :

2. When Fe(s) is dissolved in aqueous hydrochloric acid in a closed vessel, the work done is .... **[JEE 1997]**

3. Silver jewellery items tarnish slowly in the air due to their reaction with .... **[JEE 1997]**

MULTIPLE CHOICE QUESTIONS WITH ONE CORRECT ANSWER :

4. Which one is solder ? **[JEE 1995]**

(A) Cu and Pb (B) Zn and Cu (C) Pb and Sn (D) Fe and Zn

5. Which compound does not dissolve in hot, dilute HNO_3? **[JEE 1996]**

(A) HgS (B) PbS (C) CuS (D) CdS

6. Ammonium dichromate is used in some fireworks. The green coloured powder blown in the air is - **[JEE 1997]**

(A) CrO_3 (B) Cr_2O_3 (C) Cr (D) $CrO(O_2)$

7. The number of moles of $KMnO_4$ that will be needed to react with one mole of sulphite ion in acidic solution is - **[JEE 1997]**

(A) 2/5 (B) 3/5 (C) 4/5 (D) 1

8. Read the following statement and explanation and answer as per the options given below : **[JEE 1998]**

Assertion : Zn^{2+} is diamagnetic.

Reason : Two electrons are lost from 4s orbital to form Zn^{2+}.

(A) If both assertion and reason are correct, and reason is the correct explanation of the assertion.

(B) If both assertion and reason are correct, but reason is not the correct explanation of the assertion.

(C) If assertion is correct but reason is incorrect.

(D) If assertion is incorrect but reason is correct.

9. In the dichromatic anion, **[JEE 1999]**

(A) 4 Cr – O bonds are equivalent (B) 6 Cr – O bonds are equivalent

(C) all Cr – O bonds are equivalent (D) all Cr – O bonds are non-equivalent

10. Anhydrous ferric chloride is prepared by: **[JEE 2002]**

(A) heating hydrated ferric chloride at a high temperature in a stream of air

(B) heating metallic iron in a stream of dry chlorine gas

(C) reaction of ferric oxide with HCl

(D) reaction of metallic iron with HCl

11. When MnO_2 is fused with KOH, a coloured compound is formed, the product and its colour is:

(A) K_2MnO_4, green (B) $KMnO_4$, purple **[JEE 2003]**

(C) Mn_2O_3, brown (D) Mn_3O_4, black

12. The product of oxidation of I^- with MnO_4^- in alkaline medium is - **[JEE 2004]**

(A) IO_3^- (B) I_2 (C) IO^- (D) IO_4^-

13. $(NH_4)_2Cr_2O_7$ on heating liberates a gas. The same gas will be obtained by - **[JEE 2004]**

(A) heating NH_4NO_2 (B) heating NH_4NO_3

(C) treating H_2O_2 with $NaNO_2$ (D) treating Mg_3N_2 with H_2O

14. Which of the following combination will produce H_2 gas ? **[JEE Advance 2017]**

(A) Zn metal and NaOH(aq) (B) Au metal and NaCN(aq) in the presence of air

(C) Cu metal and conc. HNO_3 (D) Fe metal and conc. HNO_3

MULTIPLE CHOICE QUESTIONS WITH ONE OR MORE THAN ONE CORRECT ANSWER :

15. Which of the following alloys contains (s) Cu and Zn ? **[JEE 1993]**

(A) Bronze (B) Brass (C) Gun metal (D) Type metal

16. Addition of high proportions of magnanese makes steel useful in making rails of railroads, becuse manganese. **[JEE 1998]**

(A) gives hardness to steel

(B) helps the formation of oxides of iron

(C) can remove oxygen and sulphur

(D) can show highest oxidation state of +7.

17. The correct statement(s) about Cr^{2+} and Mn^{3+} is (are) **[JEE Advance 2015]**

[Atomic numbers of Cr = 24 and Mn = 25]

(A) Cr^{2+} is a reducing agent

(B) Mn^{3+} is an oxidizing agent

(C) Both Cr^{2+} and Mn^{3+} exhibit d^4 electronic configuration

(D) When Cr^{2+} is used as a reducing agent, the chromium ion attains d^5 electronic configuration

18. Fusion of MnO_2 with KOH in presence of O_2 produces a salt **W**. Alkaline solution of **W** upon eletrolytic oxidation yields another salt **X**. The manganese containing ions present in **W** and **X**, respectively, are **Y** and **Z**. Correct statement(s) is (are) **[JEE Advance 2019]**

(A) **Y** is diamagnetic in nature while **Z** is paramagnetic

(B) Both **Y** and **Z** are coloured and have tetrahedral shape

(C) In both **Y** and **Z** , π-bonding occurs between p-orbitals of oxygen and d-orbitals of manganese.

(D) In aqueous acidic solution, **Y** undergoes disproportionation reaction to give **Z** and MnO_2.

19. Consider the following reactions (unbalanced) **[JEE Advance 2019]**

$Zn + \text{hot conc. } H_2SO_4 \rightarrow G + R + X$

$Zn + \text{conc. } NaOH \rightarrow T + Q$

$G + H_2S + NH_4OH \rightarrow Z \text{ (a precipitate)} + X + Y$

Choose the correct option(s).

(A) The oxidation state of Zn in T is +1

(B) Bond order of Q is 1 in its ground state

(C) Z is dirty white in colour

(D) R is a V-shaped molecule

ANSWER KEY

EXERCISE # O-1

1. (B)	**2. (A)**	**3. (A)**	**4. (B)**
5. (B)	**6. (B)**	**7. (D)**	**8. (A)**
9. (A)	**10. (B)**	**11. (C)**	**12. (A)**
13. (A)	**14. (C)**	**15. (B)**	**16. (B,C)**
17. (B)	**18. (A)**	**19. (A)**	**20. (B)**
21. (A)	**22. (A)**	**23. (B)**	**24. (A)**
25. (B)	**26. (C)**	**27. (B)**	**28. (B)**
29. (D)	**30. (D)**	**31. (A)**	**32. (A,C)**
33. (D)	**34. (D)**	**35. (C)**	**36. (B)**
37. (C)	**38. (A)**	**39. (C)**	**40. (D)**
41. (A)	**42. (A)**	**43. (B)**	**44. (A)**
45. (A)	**46. (B)**	**47. (B)**	**48. (D)**

EXERCISE # O-2

1. (A, B, C)	**2. (B, C, D)**	**3. (A, B)**	**4. (A, C, D)**
5. (A, B)	**6. (A, B)**	**7. (A, B, D)**	**8. (B, C)**
9. (A, B, C)	**10. (A, B, C)**	**11. (A, B)**	**12. (A, B, C, D)**
13. (A, B)	**14. (A, B)**	**15. (B, C)**	**16. (A, B, C)**
17. (A, B, C)	**18. (A, B, C)**		

EXERCISE # S-1

1. **(6),** In this reaction CrO_2Cl_2 is formed in which Cr is +6.

2. **(2),** V^{+4}, Cu^{+2}

3. **(11),** +7, +4

4. **(3),** Mn^{+3}, Fe^{+3}, Co^{+3}

5. CrO_2Cl_2 has d^3S hybridisation and all 3d-orbitals are non-axial which are d_{xy} ; d_{yz} and d_{xz}.

6. **(003)**

7. **(6),** Mohr's salt

$FeSO_4 .(NH_4)_2SO_4.6H_2O$

$6\ Fe^{+2} + Cr_2O_7^{2-} + 14\ H^+ \rightarrow 2Cr^{+3} + 7H_2O + 6Fe^{+3}$

8. **3**

(I) $BaCl_2 + Na_2CrO_4 \xrightarrow{CH_3COOH} BaCrO_4 \downarrow + 2NaCl$

(II) $K_2Cr_2O_7 + NaOH \longrightarrow K_2CrO_4$

$CrO_4^{2-} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} Cr_2O_7^{2-}$

(III) $Cr_2O_7^{2-} + NO_3^- \xrightarrow{H^+}$ no reaction.

(IV) $Cr_2O_7^{2-} + C_2H_5OH \xrightarrow{H^+} CH_3 - COOH + Cr^{+3}$

EXERCISE # S-2

1. **(C)** **2. (D)** **3. (A)** **4. (B)**
5. **(B)** **6. (D)** **7. (C)** **8. (A)**
9. **(D)** **10. (A)-(R,S) ; (B)-(R,S) ; (C)-(P,Q) ; (D)-(P,Q)**
11. **(A)-(R) ; (B)-(S) ; (C)-(P) ; (D)-(Q)** **12. (A)** **13. (C)**
14. **(B)** **15. (B)** **16. (A)** **17.(B)**
18. **(C)** **19. (C)** **20. (B)** **21. (C)**
22. **(C)** **23. (D)** **24. (A)** **25. (A)**

EXERCISE # JEE-MAIN

1. **(2)** **2. (2)** **3. (1)** **4. (4)**
5. **(1)** **6. (3)** **7. (1)** **8. (4)**
9. **(3)** **10. (3)** **11. (2)** **12. (4)**
13. **(4)** **14. (4)** **15. (1)** **16. (4)**
17. **(4)** **18. (4)** **19. (3)** **20. (1)**
21. **(1)** **22. (3)** **23. (2)** **24. (2)** **25. (3)** **26. (4)**

EXERCISE # JEE-ADVANCED

TRUE/FALSE :

1. True

FILL IN THE BLANKS :

2. Zero **3.** H_2S

MULTIPLE CHOICE QUESTIONS WITH ONE CORRECT ANSWER :

4. (C) **5.** (A) **6.** (B) **7.** (A)
8. (B) **9.** (B) **10.** (B) **11.** (A)
12. (A) **13.** (A) **14. (A)**

MULTIPLE CHOICE QUESTIONS WITH ONE OR MORE THAN ONE CORRECT ANSWER :

15. (B, C) **16.** (A) **17.** (A), (B), (C)

18. **Ans.(2,3,4)**

$$MnO_2 + 2KOH + \frac{1}{2}O_2 \xrightarrow{\Delta} \underset{(W)}{K_2MnO_4} + H_2O$$

$$\left[(W) = K_2MnO_{4(aq)} \rightleftharpoons 2K^{\oplus}_{(aq)} + \underset{(Y)}{MnO^{2-}_{4(aq)}}\right]$$

$$K_2MnO_4 + H_2O \xrightarrow[\text{Redox}]{\text{Electolytic}} H_2 + KOH + \underset{(X)}{KMnO_4}$$

[anion of X = $\underset{(Z)}{MnO_4^-}$]

$$\left[\because\ \underset{(Y)}{MnO_4^{2-}} \xrightarrow[\text{Oxidation}]{\text{Electrolytic}} \underset{(Z)}{MnO_4^-} + e^-\right]$$

$\because$ In acidic solution; Y undergoes disproportionation reaction

$$\left[3MnO^{2-}_{4(aq)} + 4H^{\oplus} \longrightarrow \underset{(Z)}{2MnO_4^-} + MnO_2 + 2H_2O\right]$$

19. Ans.(2,3,4)

Sol. $Zn + 2H_2SO_4$ (Hot and conc.) $\rightarrow \underset{(G)}{ZnSO_4} + \underset{(R)}{SO_2\uparrow} + \underset{(X)}{2H_2O}$

$Zn + 2NaOH$ (conc.) $\rightarrow \underset{(T)}{Na_2ZnO_2} + \underset{(Q)}{H_2\uparrow}$

$ZnSO_4 + H_2S + 2NH_4OH \rightarrow \underset{(Z)}{ZnS\downarrow} + \underset{(X)}{2H_2O} + \underset{(Y)}{(NH_4)_2SO_4}$

Important Notes