SENIOR SIX TERM 2

TOPIC 2/2: Periodicity II

Topic competency: The learner analyses the trends in the physical and chemical properties of Group 14 elements, Group 17 elements and d-block elements and relates these trends to their applications in industrial and environmental contexts.

Group 14 Elements, carbon, Silicon, germanium, tin and lead

Members
Elements
symbol Carbon
C Silicon Si
Germanium Ge
Tin Sn
Lead Pb

Physical properties

- Carbon and silicon are nonmetals.
- Germanium is a metalloid
- Tin and lead are metal

Electron configuration

General electron configuration of group 14 elements is ns^2np^2

Oxidation states

The common oxidation state of group 14 elements is +2 and +4

Stability of oxidation states

Oxidation state +2 become more stable down the group
Oxidation state +4 become less stable down the group.

For instance carbon burns in oxygen to form carbon (IV) oxide (**CO_2**) whereas lead form Lead (II) oxide (PbO).

Secondly, **CCl_4** is stable whereas **$PbCl_4$** easily decomposes on heating giving lead (II)

chloride and chlorine
$PbCl_4$ (g) (heat) →$PbCl_2$ (s) + Cl_2 (g)

Reasons for Variation of Stability

(i) **Inert pair effect**: Down the group, the ns^2 electrons (valence s-electrons) are less likely to participate in bonding. This makes the +2 oxidation state more stable for heavier elements (Sn, Pb). Example: Pb^{2+} is more stable than Pb^{4+}.
(ii) **Atomic size**: Larger atoms (like Sn and Pb) have weaker effective nuclear charge on outer electrons.This reduces the ability to stabilize higher oxidation states.
(iii) **Shielding effect**: Poor shielding by d and f electrons in heavier elements reduces the effective nuclear attraction. This favors lower oxidation states.
(iv) Relativistic effects**:** In very heavy atoms (like Pb), relativistic contraction of the s-orbital makes the ns^2 pair even more inert. This strongly stabilizes the +2 oxidation state.

Relativistic Effects

Relativistic effects in chemistry refer to changes in the behavior of electrons in **heavy atoms** (especially those with high atomic numbers) due to the principles of Einstein's theory of relativity. When electrons move at speeds close to the speed of light, their **mass increases** and their orbitals contract or expand in unusual ways.

s-orbital contraction:

- Electrons in s-orbitals (closest to the nucleus) move fastest.
- Their relativistic mass increases, causing the orbital to contract and electrons to be held more tightly.
- Example: In gold (Z = 79), the 6s orbital contracts significantly.

Properties of compound with +2 and +4 oxidation states

(i) Compounds in oxidation state +4 are predominantly covalent because formation $\mathbf{M^{4+}}$ requires a lot energy whereas compound in oxidation state +2 are ionic

This explains the fact that $PbCl_4$ is soluble in organic solvents like ethanol whereas $PbCl_2$ does not.

Note that

a. covalent compounds are soluble in organic solvents whereas ionic compounds do not.
b. Covalent compound have low melting and boiling points whereas ionic compounds have high melting and boiling point.
c. Covalent compounds do not conduct electricity whereas ionic compounds do. On this basis compound in oxidation state +4 show properties of covalent compounds because they are predominately covalent.

Chemical properties

Reaction of group 14 elements with water

Carbon does not react with cold water but reacts with steam to form water gas

$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$

Silicon, germanium and Tin do not react with water up to 100^{0}C because they are protected by thin layer of oxide. But they react with steam at very high temperatures to form dioxides

$Ge(s) + 2H_2O(g) \rightarrow GeO_2(s) + 2H_2(g)$

Lead reacts with soft water (water that contains oxygen) to form lead II hydroxide.

$Pb(s) + 2H_2O(g) + O_2(g) \rightarrow Pb(OH)_2(s)$

Reaction of group 14 elements with acids

(i) Dilute non oxidizing acid like HCl.

C, Si, and Ge do not react

Sn liberates hydrogen

$Sn(s) + 2H^+(aq) \quad Sn^{2+}(aq) + H_2(g)$

Pb lead does not react with dilute hydrochloric acid and sulphuric acid due to formation of insoluble salts.

(ii) Nitric acid

With concentrated nitric acid.

C, Si, Ge and Sn react to form dioxide

$C(s) + 4HNO_3(aq) \rightarrow CO_2(g) + 4NO_2(g) + 2H_2O(l)$

Pb reacts to form lead II nitrate and nitrogen dioxide.

$Pb(s) + 4HNO_3(aq) \rightarrow Pb(NO_3)_2(aq) + 2NO_2(aq) + 2H_2O(l)$

With 50% nitric acid.

Pb reacts to form lead II nitrate and nitrogen monoxide.

$3Pb(s) + 8HNO_3(aq) \rightarrow 3Pb(NO_3)_2(aq) + 2NO(aq) + 4H_2O(l)$

(iii) With sulphuric acid

Dilute sulphuric acid

C, Si and Ge do not react.

Sn and Pb reacts dilute concentrated sulphuric acid liberating hydrogen.

$Pb(s) + H_2SO_4(aq) \rightarrow PbSO_4(s) + H_2(g)$

With hot concentrated sulphuric acid

C, Si and Ge react to form dioxides

$C(s) + 2H_2SO_4(aq) \rightarrow CO_2(g) + 2SO_2(g) + 2H_2O(l)$

Sn and Pb reacts hot concentrated sulphuric acid liberating sulphur dioxide.

$Pb(s) + 2H_2SO_4(aq) \rightarrow PbSO_4(s) + SO_2(g) + 2H_2O(l)$

$Sn(s) + 2H_2SO_4(aq) \rightarrow SnSO_4(s) + SO_2(g) + 2H_2O(l)$

(iv) With acetic or ethanoic acid

C, Si Ge and Sn do not react.

Pb reacts ethanoic acid in presence of air giving lead II ethanoate and water

$Pb(s) + 4CH_3COOH(aq) + O_2(g) \rightarrow Pb(CH_3COO-)_2(aq) + 2H_2O(l)$

Reaction with sodium hydroxide

C does not react.

Si Ge and Sn react liberating hydrogen and silicate (IV), germates (IV) and stannates (IV) respectively

$Si(s) + 2NaOH(aq) + H_2O(l) \rightarrow Na_2SiO_3(aq) + 2H_2(l)$

Lead reacts to form plumbates (II).

$Pb(s) + 2NaOH(aq) \rightarrow Na_2PbO_2(aq) + 2H_2(g)$

Unique characteristics of carbon

1. Forms gaseous oxides, the rest form solid oxides

Note that

a. Carbon dioxide is a gas because its molecules are bonded by weak van der Waal forces.

b. Silicon dioxide is a solid of high melting point because each silicon atom is bonded to four oxygen atom by strong covalent bonds.

2. **Catenation:** carbon forms chains, rings and branches with single, double and triple bonds while others do not

3. Forms compounds mainly with oxidation sate (IV); other elements form compounds with oxidation states +2 and +4.

4. Carbon tetrachloride and carbon tetrahydride do not hydrolyze in water. Chlorides of other elements hydrolyze in water.

5. Carbon form CF_4 and not CF_6^{-2}

Reason for uniqueness of carbon

- Has a very small atomic radius allows formation of strong C-C bonds.
- Has high electronegativity enables formation of stable covalent bonds with other elements like N, O and H
- Lacks easily accessible d-orbital in its valence shell stabilizes the double and triple bonds
- **Variety of hybridization:** Carbon undergoes sp^3 (tetrahedral), sp^2 (planar), and sp (linear) hybridization. This leads to diverse structures (alkanes, alkenes, alkynes, aromatic compounds). Heavier elements rarely show such versatility.

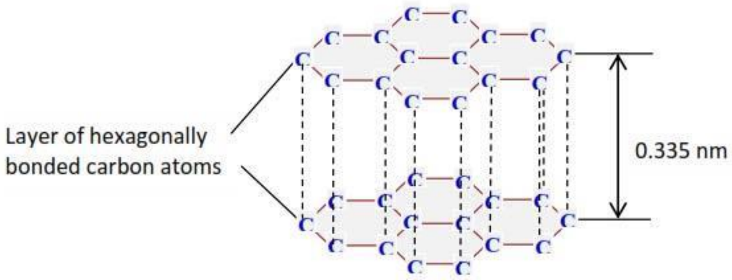
Allotropes of carbon

Allotropy is the existence of two or more different physical forms in the same state of a chemical element.

An **allotrope** is any of the different physical form in the same state into which a chemical element can exist.
Carbon exists in two main allotropes, i.e. graphite and diamond.

Graphite

In graphite, each carbon atom is covalently bonded to 3 carbon atoms to form a layer of hexagons. Each layer is bonded to another by weak van der Waal forces.

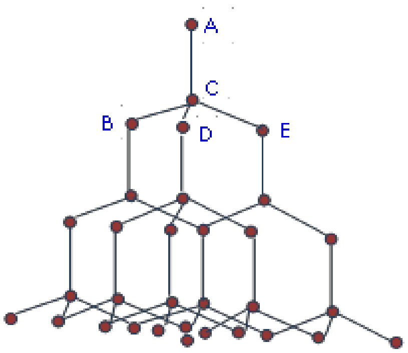


Properties of graphite as a result of its structure

1. Has open structure and low density.
2. It is slippery and used as a lubricant.
3. Has unbonded π-electron that is free to move about making graphite a good conductor of electricity and heat

b. Diamond

Structure of diamond



Each carbon atom is bonded tetrahedrally to four carbon atoms to form a 3D compact structure by strong covalent bonds. As a result diamond has a high density, melting and boiling point. It is the hardest substance known.

Diamond is used as an ornament, and to drill and cut other substances.

Differences between diamond and graphite

1. The density of graphite (2.3 gcm^{-3}) that of diamond (3.5 g cm^{-3})
2. Diamond is very hard while graphite is soft
3. Graphite is slippery while diamond is not
4. Graphite conducts electricity while diamond does not.

Experiment to show that graphite and diamond are allotropes of carbon

When equal masses of graphite and diamond are burn in air, they give equal volume of carbon dioxide.

Compounds of carbon

1. Hydrides: they include alkanes, alkenes, alkyne and aromatic compounds studied in organic chemistry
2. **Halides of carbon**

   Carbon forms all the four tetrahalides: CF_4, CCl_4, CBr_4 and CI_4

   Comments

   a. The melting points of halides increase with molecular masses. All tetrahalides are volatile liquids .
   b. The stability of the halides decrease from $CF_4 > CCl_4 > CBr_4 > CI_4$ due to decrease in the bond strengths as electronegativity of the halogen decrease.
   c. CCl_4 is a good solvent, being very stable and heavier than air; is used in fire extinguisher to protect the burning substance from oxygen.
   d. CCl_4 is not hydrolyzed by water due to lack of accessible d-orbital to accommodate the lone pair of electron from water and weaken the C-X bond.

3. Oxides f carbon

(a) **Carbon monoxide (CO)**

Preparation

By dehydration of methanoic acid with concentrated sulphuric acid.

$HCO_2H(l) + \text{Conc. } H_2SO_4(l) \rightarrow CO(g) + H_2O(l)$

Uses of carbon monoxide

(i) It reduces most metal oxides to metals.

$Fe_2O_3\ (s) + 3CO\ (g) \rightarrow 2Fe\ (s) + 3CO_2\ (g)$

$NiO\ (s) + CO\ (g) \rightarrow Ni\ (s) + CO_2\ (g)$

This property is employed industrially in the extraction of iron and nickel.

It is used to purify nickel: it forms a volatile carbonyl that decompose to give a pure Metal

$Ni\ (s) + 4CO(g) \xrightarrow{90^0} Ni(CO)_4(g)$

$Ni(CO)_4(g) \xrightarrow{180^0 C} Ni\ (s) + 4CO\ (g)$

(ii) It is used preparation of carbonyl chloride that is used in the production of polyurethane form of plastics and pesticides.

$CO\ (g) + Cl_2\ (g) \rightarrow COCl_2\ (g)$

[carbonyl chloride]

(iii) *CO reacts with fused NaOH under pressure to give sodium methanoate. Methanoic* acid is produced from this salt by the addition of dilute HCl.

$NaOH\ (l) + CO\ (g) \rightarrow HCOONa\ (s)$

then $HCOO^-\ (aq) + H^+\ (aq) \rightarrow HCOOH\ (l)$

Methanoic acid is **used** to produce insecticides and for dyeing, tanning, and electroplating.

(b) Carbon dioxide (CO2)

Preparation

By decomposition of calcium carbonate

$CaCO_3(s)\ (\text{heat}) \rightarrow CaO(s) + CO_2(g)$

Limestone quick lime

Uses of carbon dioxide

a. Flavors fizzy drinks.
b. It is heavy and stable so is used in fire extinguishers to displace oxygen from burning objects.

Carbonic acid

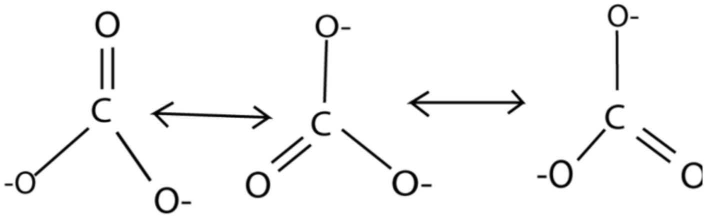
Preparation

By reacting carbon dioxide and water. There is however, equilibrium in solution of carbonic acid, hydrogen ions, hydrogen carbonate and carbonate ions.

CO_2 (g) + H_2O (l) ↔ H_2CO_3 (aq)
H^+(aq) + HCO_3^- (aq) ↔ $2H^+$ (aq) + CO_3^{2-} (aq)

Structure of carbonic acid

Has 3 resonance hybrid whose bond lengths are intermediate between a C=O and C-O bonds



Carbonates and hydrocarbonate

- ✓ Both react with acids to liberate carbon dioxide
  CO_3^{2-} (aq)+ $2H^+$ (aq) → H_2O (l) + CO_2 (g)
  HCO_3^- (aq)+ H^+ (aq) → H_2O (l) + CO_2 (g)
- ✓ CO_3^{2-} forms white ppt with Mg^{2+} whereas HCO_3^- does not.

Silicon

Existence

Exists as silica, SiO_2 or sand used for building or making glass.

Chemical properties of SiO_2

(a) **Reaction with NaOH**

SiO_2(s) + 2NaOH(aq) → Na_2SiO_3(aq) + H_2O(l)

SiO_2(s) + 2^-OH (aq) → SiO_3^{2-} (aq) + H_2O (l).

(b) **Reaction with HF**

SiO_2(s) + 4HF(g) → SiF_4(aq) + H_2O(l)

SiF_4(aq) + 2HF(aq) → H_2SiF_6(aq)

(c) **Reaction of silicon with acids**

Silicon does not react with most acids under normal conditions but is dissolved by hydrofluoric acid, **HF**, to form fluorosilicic acid, a reaction apparently driven by the stability of the Si(IV) fluoride complex $[SiF_6]^{2-}$.

Si(s) + 6HF(aq) → $2H_2$(g) +H_2SiF_6 (aq) (fluorosilicic acid)

Germanium, tin and lead

Points to note

a. They form compounds with oxidation states +2 and + 4. The stability of compounds with oxidation states +2 increases down the group due to 'inert pair effect' while those of oxidation states +4 decreases down the group.

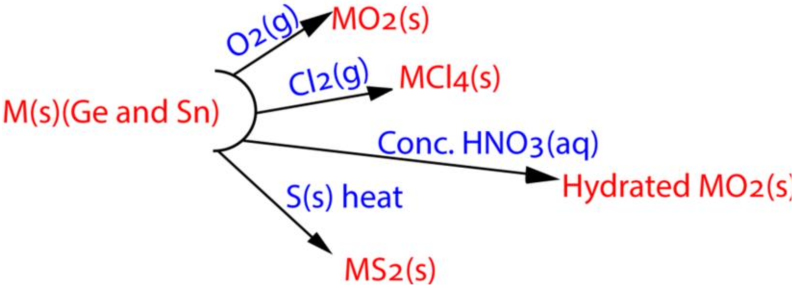
b. Compounds with oxidation state +2 are reducing. For instance tin II ions reduce iron III ions to iron II ions.
$Sn^{2+}(aq) + Fe^{3+}(aq) \rightarrow Sn^{4+}(aq) + Fe^{2+}(aq)$

c. Compounds with oxidation state +4 are oxidizing. For instance lead IV oxide ions oxidizes HCl ions to chlorine
$PbO_2 (s) + 4HCl (aq) \rightarrow PbCl_2(s) + 2H_2O (l) + Cl_2 (g)$

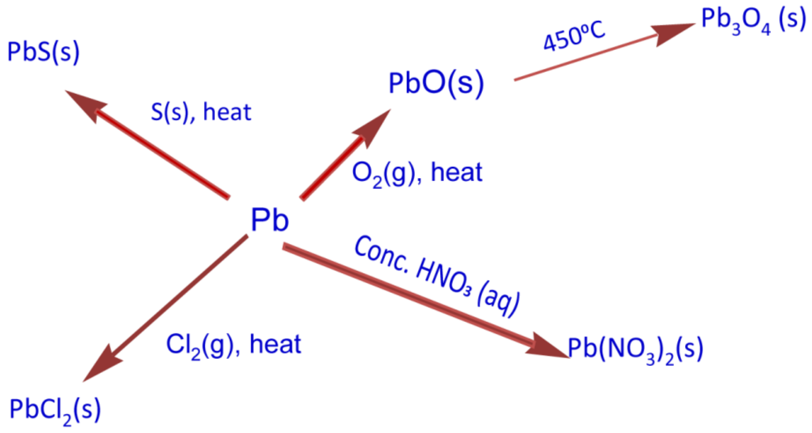
d. Compounds with oxidation state +4 are predominantly ionic whereas those in oxidation state +4 are predominantly covalent. This explains the fact that $PbCl_2$ is soluble in water but insoluble in ethanol whereas $PbCl_4$ is soluble in ethanol

Chemical properties

The principal reactions of germanium and tin are similar, both elements exhibiting oxidation state of 4



The principal reactions of lead are summarized below



Lead IV halide

Lead forms ionic $Pb^{4+}(F^-)_4$, and covalent liquid $PbCl_4$.
The tetra-bromide and tetra-iodide do not exist, presumably because bromine and iodine are not sufficiently strong oxidizing agents to convert Pb^{2+} to Pb^{4+}.

Lead IV chloride

Preparation

By reacting lead IV oxide with cold concentrated hydrochloric acid. PbO_2 (s) + 4 HCl (aq) (conc. and cold) → $PbCl_4$(aq) +2H_2O(l)

Effect of Heat on Lead (IV) chloride

Decomposes on heating liberating chlorine $PbCl_4$ (g) (heat) → $PbCl_2$ (s) + Cl_2 (g)

Hydrolysis of lead (IV) chloride

Lead tetrachloride is readily hydrolyzed by water (white fumes of HCl and brown precipitate of PbO_2 are observed)

$PbCl_4$ (s) + 2H_2O (l) → PbO_2 (s) + 4HCl (aq)

Reaction of lead (IV) chloride with sodium hydroxide solution

Lead(IV) chloride react with sodium hydroxide to produce lead(IV) oxide, sodium chloride and water. Sodium hydroxide - diluted solution.

$PbCl_4 + 4NaOH \rightarrow PbO_2 + 4NaCl + 2H_2O$

The compound PbO_2 reacts with the sodium hydroxide to produce the hexahydroxoplumbate(IV) ion $[Pb(OH)_6]^{2-}$, soluble with the water.

$PbO_2 + 2NaOH + 2H_2O \rightarrow Na_2[Pb(OH)_6]$

Reaction of lead (IV) chloride with ammonium chloride

Lead(IV) chloride react with ammonium chloride to form a yellow solid of ammonium hexachloridoplumbate(IV).

$PbCl_4 + 2NH_4Cl \rightarrow (NH_4)_2[PbCl_6]$

Lead II halide

Preparation

By reacting soluble salt like lead nitrate with soluble halide

Pb^{2+}(aq) + $2X^-$(aq) → PbX_2(s) (X = F, Cl, Br, I).

E.g. Pb^{2+}(aq) + $2Cl^-$(aq) → $PbCl_2$(s)

Properties of lead II chloride

Except the iodide, which is yellow, they are white solids. Lead (II) chloride forms chloro-complexes, e.g., $[PbCl_4]^{2-}$, with Cl^- ions and because of this, it is soluble in concentrated hydrochloric acid.

Reaction of lead (II) chloride with sodium hydroxide solution

Lead II chloride reacts with sodium hydroxide solution to form lead (II) hydroxide which dissolves inexcess sodium hydroxide to form sodium plumbate (II)

$PbCl_2$ (s) + $2OH^-$(aq) → $Pb(OH)_2$(s) + $2Cl^-$(aq)
Then
$Pb(OH)_2$(s) + $2OH^-$ (aq) → $Pb(OH)_4^{2-}$(aq)

Lead IV oxide

Preparation of lead (IV) oxide

(i) Lead (IV) oxide, PbO_2, is a brown solid obtained by oxidation of a soluble lead (II) salt with hot sodium chlorate (I).

Pb^{2+}(aq) + H_2O(l) + ClO^- (aq) → PbO_2(s) + Cl^-(aq) +$2H^+$(aq)

(ii) By action of nitric acid on trilead tetra oxide, Pb_3O_4.

Pb_3O_4 (s) + $4HNO_3$ (aq) → $2Pb(NO_3)_2$(aq) + PbO_2(s) + $2H_2O$(l)

Chemical properties of lead (IV) oxide

(i) Decomposes on heating

$2PbO_2$ (s) + heat → $2PbO$ (s) + O_2 (g)

(ii) Reacts with cold concentrated hydrochloric acid to form a yellow liquid lead (IV) chloride and water

PbO_2(s) + $4HCl$ (aq) → $PbCl_4$(l) + $2H_2O$(l)

(iii) Oxidize hot concentrated hydrochloric acid to chlorine

PbO_2(s) + $4HCl$(aq) → $PbCl_2$ (s) + $2H_2O$(l) + Cl_2(g)

(iv) React with the sodium hydroxide to produce the hexahydroxoplumbate (IV) ion $[Pb(OH)_6]^{2-}$, soluble with the water.

PbO_2 + $2NaOH$ + 2 H_2O → $Na_2[Pb(OH)_6]$

Qualitative analysis of Pb^{2+}

1. Forms a white precipitate with sodium hydroxide soluble in excess

Pb^{2+}(aq) + $2OH^-$(aq) → $Pb(OH)2$ (s) + 2OH-(aq) →$Pb(OH)4^{2-}$ (aq)

2. Forms white precipitate with ammonia solution insoluble in excess

Pb^{2+}(aq) + $2OH^-$(aq) → $Pb(OH)2$ (s)

3. Forms yellow precipitate with potassium iodide

Pb^{2+}(aq) + $2I^-$(aq) → $PbI2$ (s)

4. Forms white precipitate hydrochloric acid soluble on warming

$Pb^{2+}(aq) + 2Cl^{-}(aq) \rightarrow PbCl_2\ (s)$

5. Forms white precipitate with sulphate ions

   $Pb^{2+}(aq) + SO_4^{2+}(aq) \rightarrow PbSO_4\ (s)$

Trial 1

1. Explain the following observation:
   (i) Graphite and copper are both good conductors of electricity. (4 marks)
   (ii) Lead (II) chloride is insoluble in water whereas lead (IV) chlorides readily dissolve in the same solvent. (2marks)
   (iii) Carbon which is in the same group as lead in the periodic table shows one valence of 4 in its compounds but lead shows two valences of 2 and 4.
   (iv) Lead IV chloride readily decomposes to lead (II) chloride when heated but lead II chloride is not affected by heat. (2marks)

   (v) The solubility of lead (II) halides increase in order $PbI_2<PbBr_2<PbCl_2$.

   (vi) When dilute hydrochloric acid is added to a solution of lead ethanoate, a white precipitate is formed. The precipitate is soluble in excess concentrated hydrochloric acid. (4marks)

   (vii) Crystals of lead (II) chloride can be prepared in the laboratory by heating lead (II) oxide with dilute hydrochloric acid and cooling. When lead (II) oxide is treated with concentrated hydrochloric acid under the same conditions, no crystals form. Give a reason for this observation and illustrate your answer with equations.

Solutions

(i) Both copper and graphite conduct electricity because they both possess mobile electrons. The mobile electrons of copper are the delocalized valence electrons whereas those of graphite are those of unbounded p-electrons.

(ii) Lead (II) chloride is ionic whereas lead (IV) chloride is covalent. Lead (IV) chloride is formed by sharing electrons because the amount of energy required to form Pb^{4+} is too much. Lead (IV) chloride is easily hydrolysed rather than dissolving

(iii)Carbon form compound with oxidation state +4 because it experiences no inert pair effect while lead does. Thus, lead for compounds predominantly of oxidation of II due to inert pair effect; i.e. the $6s^2$ electrons are reluctant to participate in reactions.

(iv)Lead (II) oxidation state is more stable due to inert pair effect.

(v) Because the lattice energy decrease in order $PbI_2>PbBr_2>PbCl_2$ and the ionic charater increase in order $PbI_2<PbBr_2< PbCl_2$ because electronegativity of chloride is in order Cl> Br> I

(vi) A white precipitate of $PbCl_2$ is formed with dilute HCl which dissolves in concentrated HCl due to formation of a soluble complex.

$Pb^{2+}(aq) + 2Cl^{-}(aq) \rightarrow PbCl_2(s)$ (aq)

(vii) (g) Lead (II) oxide forms insoluble lead (II) chloride with dilute hydrochloric acid which dissolves in concentrated hydrochloric acid to form a soluble complex.

$Pb^{2+}(aq) + 2Cl^{-}(aq) \rightarrow PbCl_2(s)$
$PbCl_2(s) + 2Cl^{-}(aq) \rightarrow [PbCl_4]^{2-(}aq)$

Trial 2

(a) (i) Define the term allotrope.
 (ii) Give evidence that shows that graphite and diamond are allotropes of carbon.
(b) Explain the following:
 (i) Graphite conducts heat and electricity yet it is a non-metal.
 (ii) Diamond is a very hard element.
(c) Some properties of graphite and diamond are shown in the table below:

Allotrope	Density g/cm^3	Heat of combustion at 298K (KJ/mol.)
Graphite	2.25	-393.5
Diamond	3.51	-395.4

(i) Calculate the heat of conversion of graphite to diamond and state the allotrope that is more stable at room temperature (298 K). Give your reasoning.
(ii) State what would happen to the total volume of the system if a given mass of diamond is converted completely into graphite. Explain your answer.
(iii) Suggest, with a reason, one condition required for the converting of graphite to diamond.
(iv) Calculate the change in volume when one gram of graphite is converted completely into diamond.
(iv) Give one use of diamond and graphite.

Solution

(a)(i) An allotrope is one of the structural forms of the same element
 (ii) When equal masses of graphite and diamond are burnt in oxygen they produce equal columes of carbon dioxide only.

(b)(i) Graphite has mobile unbounded p-electrons that conduct heat and electricity

 (ii) Each carbon atom is bonded to four carbon atoms by strong covalent bonds to form a compact solid

(c)(i) +1.9kJmol^{-1}

 (ii) graphite is more stable because it contains less energy.

(iii) heat or high pressure

(iv) volume decrease by 0.16cm^3

Trial 3

State four properties in which carbon differs from the rest of members in group (IV). (4 marks)

Trial 4

Carbonates are salts of carbonic acid which its self is obtained when carbon dioxide dissolves in water.

(a) Write the structural formulae of carbon dioxide and carbonate ions. On the structure you have written, indicate the type of bonding.

(b) The bond length of carbon-oxygen single bond and carbon-oxygen double bond are 0.143 nm and 0.122 nm respectively.

(i) Estimate the bond lengths in carbonate ions and carbon dioxide. Give reason for your answers. (4 marks)

(ii) Write the structural formula of carbonic acid and estimate the oxygen-carbon bond length. (2 marks)

(iii) Give approximate value of the OCO bond angle in the structure you gave in (ii) and explain your answer.

(c) Write the formulae of two ions which are isoelectric (contain equal number of electrons) with carbonate ions (2 marks)

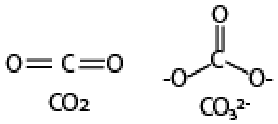
(d) The solubility of carbon dioxide in water is 0.51 cm^3/g at s.t.p. Assuming the density of water is 1 g cm^{-3}, calculate the solubility of carbon dioxide in moldm^{-3} at s.t.p (1mole of a gas occupies 22.4 l at s.t.p). (3 marks)

(e) A sample of potassium carbonate was dissolved in water and the pH of solution determined. Was the pH of solution greater or less than 7? Explain your answer. (2 marks)

(f) Explain why it's possible to get two end-points when carbonate ions are titrated against an acid. (2 marks)

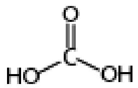
Solution

(a)



(b) (i) Bond length in CO_2 = 0.122nm

Bond length in CO_3^{2-} = 0.136 and average between two single bond and 1 double bond

(ii) 

H_2CO_3

(iii) Bond angle = 120^0 due to uniform repulsion between the bonds

(c) SO_3^{2-}

(d) 0.0446moldm^{-3}

(e) pH will be more than 7 due to hydrolysis of carbonate ions to form hydroxide ions

$CO_3^{2-}(a) + H_2O(l) \leftrightarrow HCO_3^-\,(aq) + OH^-(aq)$

(f) The first end point occurs due to formation of hydrogen carbonate ions (HCO_3^-) and the second one due to formation of carbon dioxide and water.

Trial 5

Write an ionic equation for the reaction between sodium hydroxide and silicon (IV) oxide.

Trial 6

Carbon, silicon, tin and lead are elements of group (IV) of the periodic table.

(i) How do these elements react with sodium hydroxide?

Trial 7

Carbon, silicon, tin and lead are elements of in group IV of the periodic table.

(a) State:

(i) the common oxidation states shown by elements in group IV of the P.T. (1 marks)

(ii) how the stability of the oxidation states of group (IV) elements varies down the group.
(Illustrate your answer with the chlorides of carbon and lead). (03 marks)

(b) Give a reason for your answer in (a) (ii). (01 mark)

Trial 8

(a) When red lead Pb3O4 was reacted with nitric acid, a solid was formed.

Write the equation for the reaction. (2 marks)

(b) The mixture from (a) was filtered and the residue warmed with concentrated hydrochloric acid,

(i) What was observed? Explain your answer. (1 marks)

(ii) Write the equation for the reaction. (1½ mark)

(c) The filtrate from (a) was divided into two parts.

(i) To the first part was added aqueous potassium iodide. State what was observed and write the equation for the reaction. (2 marks)

(ii) The second part was evaporated to dryness and heated strongly. Explain what was observed and write the equation for the reaction that took place. (2½ marks)

Solution

(a) $Pb_3O_4(s) + 4HNO_3(aq) \rightarrow PbO_2(s) + 2Pb(NO_3)_2(aq) + 2H_2O(l)$

(b) Green gas and white solid that dissolved in excess acid to form colorless solution

$PbO_2(s) + 4HCl(aq) \rightarrow PbCl_2(s) + Cl_2(g) + 2H_2O(l)$

Then $PbCl_2(s) + 2Cl^-(aq) \rightarrow PbCl_4(aq)$

(c) (i) yellow ppt

$Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)$

(ii) orange residue and brown fumes

$2Pb(NO_3)_2(s) \rightarrow 2PbO(s) + 4NO_2(g) + O_2(g)$

Trial 9

A sample of lead (IV) oxide was treated with warm concentrated hydrochloric acid.

(i) State what was observed. (1½ marks) (ii) Write the equation for the reaction. (02 marks)

Trial 10

Write down the equations for the reactions between:

i. The oxides of group (IV) elements and sodium hydroxide. (06 marks)

ii. Lead IV oxide and concentrated hydrochloric acid. (1½ marks)

(b) Write the ionic equation for the reaction between sodium hydroxide and lead (II) oxide. (1 ½ marks)

Trial 11

(a) State two industrial uses of tin.

(b) Tin is said to be enantiotropic, explain what this means.

(c) How would you convert a solution containing tin (II) ions into a solution containing tin (IV) ions?

(d) Pure tin was reacted with chlorine to give a colorless liquid that fumed in moist air. A solution of 0.162 g of the liquid in water was equivalent to 24.00 cm^3 of exactly 0.1 M sodium hydroxide solution using methyl orange as the indicator. Calculate the percentage purity of the liquid in tin compound.

Solution

(a) Tin is widely used in industry for **soldering, protective coatings (tin plating), alloy formation (bronze, pewter), glass production, and electronics**. Its corrosion resistance and non-toxic nature make it valuable in food packaging and specialized manufacturing.

(b) Tin is enantiotropic because it exists in two different interconvertible crystalline forms (allotropes) that are stable under different temperature conditions. i.e. Grey tin (α-tin): Stable below 13.2 °C. It has a diamond-like structure and is brittle, non-metallic. And white tin (β-tin): Stable above 13.2 °C. It has a metallic structure, is malleable, and conducts electricity.

(c) By oxidation with acidified potassium permanganate or dichromate solution or iron (III) salt.

(d) $SnCl_4(aq) + 2H_2O(l) \rightarrow SnO_2(s) + 4HCl(aq)$

Moles of HCl produced = moles of NaOH $= \frac{24 \, x \, 0.1}{1000} = 0.0024$moles

Moles of $SnCl_4$ $= \frac{0.0024}{4} = 0.0006 moles$

Mass of pure $SnCl_4$ = 0.0006 x(119 + 35.4 x 4) = 0.15636

% of $SnCl_4$ $= \frac{0.15636}{0.16} x100 = 96.5\%$

Trial 12

Give a comparative account of the Chemistry of the oxides and chlorides of silicon, germanium, tin and lead, paying particular attention to: -

(a) the formation, composition and stability of oxides.

(b) the formation, hydrolytic behavior and stability of chlorides.

Trial 13

Give a concise account of the Chemistry of elements of group 4 of the periodic table (carbon, silicon, germanium, tin and lead) referring your answer to all the following aspects:

(a) The variation in the first ionization energy.
(b) The hydrolysis of the tetrachloride.
(c) The acid-base character of the oxides of the elements in the oxidation states II and IV.
(d) The relative stabilities of II and IV oxidation states of elements in oxides and chlorides.
(e) Show how the electron pair repulsion theory can be used to predict the shape of the silicon tetrachloride molecule.

Trial 14

(a) Carbon, silicon, germanium, tin and lead are elements of group IV in the periodic table. (i) Describe the types of chlorides formed by these elements.
(ii) Show how the chlorides of these elements react with water.
(b) Describe the trends in the basicity of the oxides of group IV elements and write equations to show how the oxides of carbon, silicon and germanium react with sodium hydroxide.
(c)When a mixture of carbon and an oxide of a group II element was heated to a very high temperature, a compound X was formed. X reacted with cold water to give a gas Y that decolourised chlorine water.
(i) Identify the element in group (II) and substances Xand Y.
(ii) Write equations leading to the formation of Y.

Solution

(c)(i) Element is calcium, X is CaC_2 and Y is $HC\equiv CH$.
(ii) $Ca(s) + 2C(s) \rightarrow CaC_2(s)$
then $CaC_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + Y\ (HC\equiv CH)(g)$

Trial 15

(a) Illustrate the transition from nonmetallic to metallic character of carbon, silicon and tin by describing the structure of and giving one chemical property of, any one type of these elements.
(b) One of the products of the reaction between magnesium silicide (Mg_2Si) and sulphuric acid is a gas X. A 0.620 g sample of X occupied 224 cm^3. When hydrolysed, this sample yielded1568 cm^3 of hydrogen and a residue (SiO_2) which, after it had been strongly heated, weighed1.200 g. (All gas volumes corrected to S.T.P.)

(i) What is the molecular formula of X? [SiH_4]

(ii) Write an equation for the hydrolysis of X.

[$SiH_4(g) + 2H_2O(l) \rightarrow SiO_2(s) + 4H_2(g)$]

Trial 16

(a) (i) State two important oxidation states exhibited by carbon, silicon, tin and lead.
(ii) Describe how the stability of the two states varies from carbon to lead. Use the oxides of the elements to illustrate your answer.

(iii) Explain the inert pair effect in group (IV) elements.

(b) State what would happen if tetrachloromethane, silicon (IV) chloride, tin(IV) chloride and lead (IV) chloride are separately shaken with water. Write equations to illustrate your answer where necessary.

(c) (i) Write equations to show how lead (II) chloride can be prepared in the laboratory. State the conditions for the reaction.

(ii) What type of bonding exists in lead (II) chloride?

(iii) State two physical properties that show that lead (II) chloride exhibits the type of bonding you have stated in (ii) above.

Trial 17

(a) Write the outermost electronic configuration of group (IV) elements. (01 marks)

ns^2np^2

(b) Describe the reaction of:

(i) Carbon, silicon, tin and lead with water (6½ marks)

Carbon does not react with cold water but reacts with steam to form water gas

$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$

Silicon, germanium and Tin do not react with water up to 100^{0}C because they are protected by thin layer of oxide. But they react with steam at very high temperatures to form dioxides

$Ge(s) + 2H_2O(g) \rightarrow GeO_2(s) + 2H_2(g)$

Lead reacts with soft water (water that contains oxygen) to form lead II hydroxide.

$Pb(s) + 2H_2O(g) + O_2(g) \rightarrow Pb(OH)_2(s)$

(ii) Lead with ethanoic acid (2½ marks)

Pb reacts ethanoic acid in presence of air giving lead II ethanoate and water

$Pb(s) + 4CH_3COOH(aq) + O_2(g) \rightarrow Pb(CH_3COO-)_2(aq) + 2H_2O(l)$

(iii) Chlorides of lead with sodium hydroxide solution (04marks)

Lead II chloride reacts with sodium hydroxide solution to form lead (II) hydroxide which dissolves in excess sodium hydroxide to form sodium plumbate (II)

$PbCl_2(s) + 2OH^-(aq) \rightarrow Pb(OH)_2(s) + 2Cl^-(aq)$

Then

$Pb(OH)_2(s) + 2OH^-(aq) \rightarrow [Pb(OH)_4]^{2-}(aq)$

Lead(IV) chloride react with sodium hydroxide to produce lead(IV) oxide, sodium chloride and water. Sodium hydroxide - diluted solution.
$PbCl_4 + 4NaOH \rightarrow PbO_2 + 4NaCl + 2H_2O$

The compound PbO_2 reacts with the sodium hydroxide to produce the hexahydroxoplumbate (IV) ion $[Pb(OH)_6]^{2-}$, soluble with the water.

$PbO_2 + 2NaOH + 2H_2O \rightarrow Na_2[Pb(OH)_6](aq)$

(iv) Silicon with acids (03 marks)

Silicon does not react with most acids under normal conditions but is dissolved by hydrofluoric acid, HF, to form fluorosilicic acid, a reaction apparently driven by the stability of the Si(IV) fluoride complex $[SiF_6]^{2-}$.

$Si(s) + 6HF(aq) \rightarrow 2H_2(g) + H_2SiF_6 (aq)$ (fluorosilicic acid)

(c) Carbon does not react with chlorine but reacts readily with fluorine.
Explain this observation. (03 marks)

Fluorine is a stronger oxidizing agent than chlorine, has very low F-F bond energy and form stronger
C-F bond the C-Cl bond, these factors promote reaction of fluorine with carbon.

Trial 17

C, Si, Ge, Sn and Pb are elements of group (IV) of the periodic table. (a)
Explain the following trends among the group (IV) elements:
(i) electropositivity. (4marks)
(ii) stability of +2 oxidation state. (2 ½ marks)
(b) State four properties in which carbon differs from the rest of the members of group (IV). (4 marks)
(c) Explain why carbon tetrachloride molecule is nonpolar yet the bonds in carbon tetrachloride are polar. (3 marks)
(d) A sample of lead (IV) oxide was treated with warm concentrated hydrochloric acid
(i) State what was observed. (½ marks)
(ii) Write an equation for the reaction. (2 marks)

Trial 18

Carbon, silicon, tin and lead are elements of in group (IV) of the periodic table

(a) State

  (i) The common oxidation state shown by the elements of group (IV). (1 mark)

  (ii) How the stability of the oxidation states of group (IV) elements varies down the group. (Illustrate your answer with the chlorides of carbon and lead). (03 marks)

(b) Give a reason for your answer in (a)(i) . (01 mark)

(c) Discuss the reactions of the chlorides of each element with water (06marks)

(d) Write down equations for the reactions between:

  i. The oxide of each element and sodium hydroxide. (06 marks)

  ii. Lead (IV) oxide and concentrated hydrochloric acid. (1½ marks)

Group 17: Fluorine, chlorine, bromine, iodine

Members

Elements	Symbols
Fluorine	F
Chlorine	Cl
Bromine	Br
Iodine	I

General comment

(a) The halogens are one electron short of the noble gas configurations, and the elements form the anion X^- or a single covalent bond.

(b) They are all non-metals

(c) The changes in behavior with increasing size are gradual. i.e., fluorine and chlorine are gases, bromine is a volatile liquid and iodine is a dark shiny dark solid.

Generally the properties of fluorine are different from those of other halogens because it

(i) Has small atomic radius

(ii) Has high electronegativity

(iii) Has abnormally low F-F bond energy (158kJ/mol) due to high electron repulsion of non bonding electron pairs.

NB: Generally bond energy decreases down the group from chlorine to iodine due to decrease in electronegativity as the size of the atoms increase, i.e,

Cl-Cl = 242
Br-Br = 193
I-I = 151

Properties

Fluorine is the most chemically reactive of all the elements and combines directly (often with extreme vigor), at ordinary or elevated temperatures, with all elements other than O_2, He, Ne, and Kr.

(i) Fluorine is the most electronegative element and displaces all other halogens from their ionic halides.

$$2Cl^- + F_2\ (g) \rightarrow 2F^- + Cl_2\ (g)$$

(ii) Fluorine substitutes oxygen from silicon dioxide and water.

$$SiO_2(s) + 2F_2(g) \rightarrow SiF_4(g) + O_2(g)$$
$$2H_2O(l) + 2F_2(g) \rightarrow 4HF(aq) + O_2\ (g)$$

(iii) Fluorine reacts with cold dilute solutions of alkalis to give oxygen difluoride; F_2O, and with warm concentrated alkalis to give oxygen.

(Cold dilute) $2OH^-\ (aq) + 2F_2\ (g) \rightarrow F_2O\ (g) + 2F^-\ (aq) + H_2O\ (l)$

(Warm conc.) $4OH^-\ (aq) + 2F_2\ (g) \rightarrow O_2\ (g) + 4F^-\ (aq) + 2H_2O\ (l)$

Reason for high reactivity of fluorine

(i) It has abnormally low (F-F) bond energy by comparison with other halogens (i.e., F_2, 158; Cl_2, 247; Br_2, 193; I_2, 151 kJ mol^{-1}).

The low (F-F) bond energy is probably due to greater repulsion between nonbonding electrons.

(ii) Fluorine forms strong covalent bonds with other elements, e.g., C-F, 484; C-Cl, 338; C-Br, 276; C-I, 238 kJ mol^{-1}.

(iii) Fluorine has the highest electronegativity of all elements.

Trial 19

(a) Explain why fluorine shows some differences in its properties from the rest of the group 7 elements (chlorine, bromine, and iodine) of the periodic table: (3marks)

(b) State the difference between the chemistry of fluorine and the rest of the elements of group VII of PT. (8 marks)

Preparation of hydrogen fluoride

(i) By the action of concentrated sulphuric acid on calcium fluoride.

$CaF_2\ (s) + H_2SO_4\ (l) \rightarrow CaSO_4\ (s) + 2HF\ (g)$

(ii) By heating acid fluoride in a copper or platinum tube,

e.g., $KHF_2\ (s) \rightarrow HF\ (g) + KF\ (s)$

Chemical properties of hydrogen floride

(i) In dilute solution it partially ionizes to form a weak acid

$HF\ (g) + H_2O(l) \rightarrow H_3O^+(aq) + F^-(aq)$

(ii) In concentrated solution, partially ionizes as in dilute solution but excess HF molecules complex with F^- ions leading to further ionization of the acid producing more H^+.

$F^-\ (aq) + HF\ (g) \rightarrow HF_2^-\ (aq)$

This makes concentrated HF stronger acid than dilute acid solution

Trial 20

(a) Write the equations for the ionization of aqueous hydrogen fluoride in.

(i) Dilute solution. (1marks)

(ii) Concentrated solution. (1mark)

In which of the solutions in (a) above would you expect hydrogen fluoride to be relatively more acidic? Explain your answer.

(iii) Moist hydrogen fluoride and aqueous solutions of the acid attack silica and glass, so the solution is stored in polythene containers.

SiO_2 (s) + 4HF (aq) → SiF_4 (aq) + $2H_2O$ (l)

SiF_4 (aq) + 2HF (aq) → H_2SiF_6 (aq) (fluorosilicic acid)

Trial 21

Write an equation for the reaction between hydrofluoric acid and silicon dioxide (1½ marks)

Uses fluorine and its compounds

(i) Calcium fluoride is used in toothpastes to prevent tooth decay.

(ii) Caryolite, Na_3AlF_6, is added to aluminium oxide to lowers its melting point to about 900^{0}C and improves conduction during extraction of aluminium metal by electrolysis of bauxite.

Chlorine, bromine and iodine

Industrial preparation

(i) Chlorine is prepared by electrolysis of brine (concentrated sodium chloride solution)
(ii) Bromine and iodine are prepared by displacement with chlorine from sea water.

Laboratory preparation

By oxidation of acidified solutions of the halides with manganese dioxide or potassium permanganate (VII).

MnO_2 (s) + $4H^+$ (aq) + $2X^-$ (aq) → Mn^{2+} (aq) + $2H_2O$ (l) + X_2 (s)

$2MnO_4^-$ (as) + $16H^+$ (aq) + $10X^-$ (aq) → $2Mn^{2+}$ (aq) + $8H_2O$ (l) + $5X_2$ (s)

Trial 22

(a) Describe one general method for preparing the halogens (excluding fluorine) in the laboratory and write equations for the reactions. (4½ marks)

(b) How can you distinguish between sodium bromide and sodium iodide, given chlorine water and tetrachloromethane. (3½ marks)

Physical properties of chlorine, bromine and iodine

Chlorine is a greenish - yellow poisonous gas with an extremely irritant smell. Chlorine is easily liquefied at room temperature under a pressure of about 7 atmospheres to a yellow liquid.

Bromine is a dark red liquid with an unpleasant and poisonous vapour, and iodine is a dark shiny solid which produces purple vapors on heating.

Chemical properties of chlorine, bromine and iodine

(a) **Reactions Cl, Br, I with other elements.**

Chlorine, bromine and iodine combine with many metals and non-metals. Usually, the combination with chlorine is most vigorous and with iodine is least vigorous.

Metals that form more than one chloride form the higher one in combination with chlorine, e.g., iron forms iron (III) chloride and not iron (II) chloride because chlorine is a strong oxidizing agent.

Trial 23

(a) Explain why chlorine reacts with iron to form $FeCl_3$ but not $FeCl_2$.
(b) Describe the process for the formation of $FeCl_3(s)$.

b) **Reaction Cl, Brand I with water.**

Chlorine and bromine are moderately soluble in water (bromine more so than chlorine); while iodine is only sparingly soluble. Chlorine is hydrolyzed in water to some extent.

$$Cl_2(g) + H_2O(l) \rightarrow HCl\ (aq) + HOCl\ (aq)$$

Iodine is more soluble in KI than in water due to formation of complexes.

$$KI + nI_2 \rightarrow KI_{(2n+1)}$$

Trial 24

Explain the following observation.
Iodine is more soluble in potassium iodide than in water. (3 marks)

c) **Reaction Cl, Brand I with alkalis.**

Chlorine reacts with cold dilute sodium hydroxide solution to give sodium chloride and sodium chlorate (I).

$$2OH^-\ (aq) + Cl_2\ (g) \rightarrow Cl^-\ (aq) + ClO^-\ (aq) + H_2O\ (l)$$

Chlorine reacts with warm concentrated sodium hydroxide solution to give sodium chloride and sodium chlorate (V):

$$6OH^-\ (aq) + 3Cl_2\ (g) \rightarrow 5Cl^-\ (aq) + \underset{\text{Chlorate (V)}}{ClO_3^-}\ (aq) + 3H_2O\ (l)$$

Bromine and iodine react with sodium hydroxide solution to give the halide and halate (V):

$$6OH^-\ (aq) + 3Br_2\ (g) \rightarrow 5Br^-\ (aq) + BrO_3^-\ (aq) + 3H_2O\ (l)$$
$$6OH^-\ (aq) + 3I_2\ (g) \rightarrow 5I^-\ (aq) + IO_3^-\ (aq) + 3H_2O\ (l)$$

Trial 25

Discuss the reactions between the elements of group (VII) of the periodic table (fluorine, chlorine bromine and iodine) with

(i) water. (5 marks)
(ii) sodium hydroxide. (7 marks)

Trial 26

Write equations to show how fluorine and chlorine react with:

(a) water. (3 marks)
(b) cold dilute sodium hydroxide solution. (3 marks)
(c) hot concentrated sodium hydroxide solution. (3 marks)

Trial 27

Describe briefly how chlorine can be converted to potassium chlorate (V) crystals in the laboratory. (5 marks)

The hydrides of chlorine, bromine and iodide

(a) Ease of oxidation of HX:

Hydrogen iodide is very easily oxidized even by atmospheric oxygen, it is therefore, a strong reducing agent, and is used as a test for oxidizing agents.

Hydrogen bromide is a less strong reducing agent but is oxidized fairly easily, e.g., both hydrogen bromide and hydrogen iodide are oxidized by concentrated sulphuric acid to corresponding free halogens.

$2HBr (g) + H_2SO_4 (l) \rightarrow SO_2 (g) + 2H_2O (l) + Br_2 (aq)$
$2HI (g) + H_2SO_4 (l) \rightarrow SO_2 (g) + 2H_2O (l) + I_2 (aq)$

(b) Acidity of HX

Pure hydrogen halides are covalent, but polar; they ionize in water to give acidic solutions. The three acids - hydrochloric, hydrobromic and hydro iodic are all strong acids in water.

In other solvents, however, the strengths of these acids decrease in the order HI > HBr > HCl: due to the decrease in the H-X bond energy in the order HCl > HBr > HI.

Trial 28

Explain the following observation;

The acidity of halogens acids decrease in the order HI>HBr>HCl although their ionic characters increase in the reverse order. (4 marks)

Trial 29

The melting points of chlorine, bromine and iodine are in the order; iodine>bromine>chlorine but the temperatures at which the molecules of the halogens dissociate into atoms are in the reverse order.

Explain the trend in the melting points of the elements. (3 marks)

Transition elements

Transition elements are elements with partially filled d-orbital

Table of members of transition elements

Elements	Atomic number	Electronic configuration
Sc	21	$[Ar]\ 3d^1\ 4s^2$
Ti	22	$[Ar]\ 3d^2\ 4s^2$
V	23	$[Ar]\ 3d^3\ 4s^2$
Cr	24	$[Ar]\ 3d^5\ 4s^1$
Mn	25	$[Ar]\ 3d^5\ 4s^2$
Fe	26	$[Ar]\ 3d^6\ 4s^2$
Co	27	$[Ar]\ 3d^7 4s^2$
Ni	28	$[Ar]\ 3d^8\ 4s^2$
Cu	29	$[Ar]\ 3d^{10}\ 4s^1$
Zn	30	$[Ar]\ 3d^{10}\ 4s^2$

Properties of transition metals

(a) Physical properties

They are hard metals, with high melting and boiling points due to strong interatomic bonding that involves the participation of both the 4s- and 3d-electrons.

They are good conductors of heat and electricity due a big number of delocalized electrons in s- and d- orbitals.

They have high densities are due to small atomic radii and high atomic masses.

(b) Paramagnetism

Due to presence of unpaired electrons transition metals are weakly attracted by a magnet but they lose their magnetism in the absence of magnetic field.

Those that are strongly attracted by a magnet are said to be ferromagnetic, e.g., iron, cobalt and nickel.

(c) Formation of colored ions

Most compounds and complexes of transition metal ions are colored, with the actual color depending on the oxidation states of the central ions.

For example Fe^{2+} is green

Fe^{3+} is brown

Reason for formation of colored ions

Transition elements form colored ions because their **partially filled d-orbitals** allow electrons to absorb specific wavelengths of visible light when they transition between split energy levels. The remaining light is transmitted or reflected, giving the ion its characteristic color. E.g. Cu^{2+} ions appear blue because they absorb red/orange light while Ni^{2+} ions appear green because they absorb red light.

(d) Complex ions formation

Transition metals form many complex ions; e.g. $[Fe(CN)_6]^{3-}$

A **complex ion** is the one that contains a central ion linked to other atoms, ions or molecules called **ligands through dative bonds**.

A **dative bond** is a covalent bond in which the shared electron pair is contributed by a single atom.

Why transition element form complexes

(i) The ions of transition elements have a high charge density to attract electrons from ligands.

(ii) The ions of transition elements have vacant d-orbitals that can accommodate electron pairs to form dative bonds

(iii) **Variable oxidation states** enable transition elements to bond with different ligands under different conditions.

Coordination number

A coordination number is number of ligands that form dative bonds with the central ions. For example; $[Fe(CN)_6]^{3-}$ has a coordination number 6

Trial 30

Determine the oxidation states and co-ordination numbers of the central metal ions in each of the following complexes.

Complex	Oxidation state	Coordination number
$Cu(NH_3)_4(OH)_2$		
$[Cr(H_2O)_5Cl]Cl_2.H_2O$		
$[Co(CN)]^{3-}$		
$Cr_2O_7^{2-}$		

Trial 31

One of the properties of transition metals is complex ion formation

(a)(i) Define the term 'complex ion'. *(2 marks)*

(ii) Explain why transition metals form complexes *(2 marks)*

(b) $Fe(CN)_6^{3-}$ *and* $[CuCl_4]^{2-}$ *are complexes formed by iron and copper respectively.*

State;

(i) The oxidation states of;

Iron

Copper

(ii) *The co-ordination numbers of;*

Iron

Copper *(2marks)*

(e) Variable oxidation states

Most transition metals exhibit variable positive oxidation states. For example iron has Fe^{2+} and Fe^{3+}.

Transition metals form variable oxidation state because they have many electrons in outermost shell with almost the same energy.

f. Catalytic activity

Transition metals have high catalytic activity. The transition metals use their variable oxidation states to provide alternative mechanisms to the reactions that require low activation energies thus speeding up chemical reactions.

A catalyst is a substance that speeds up a chemical reaction without taking part in the reaction.

Example: V_2O_5, in Contact process

g. The formation of interstitial compounds

The sizes of transition metal atoms and their crystal structures are such that small atoms like hydrogen, boron, carbon and nitrogen can occupy the spaces within the crystal and form interstitial compounds. No definite chemical formula can be attached to these substances since they are non-stoichiometric.

Trial 32

With reference to transition metals, explain what is meant by the following:

(i) Complex-ion, (5 marks)

(ii) Catalytic activity, (3 marks)

(iii) Colored ion formation. (5 marks) iv.

Scandium

It is the first element in the first transition series. Apart from having partially filled d-orbital; it show no other property of transition elements. It has a fixed oxidation state of +3.

Titanium

Properties as a transition element

a) It has variable oxidation states i.e. +2, +3 and +4.

b) It is a catalyst as $TiCl_4$ in polymerization of ethene to polyethene.

Important compounds of titanium

a) Titanium IV oxide, TiO_2 is used as a white pigment in soaps and paints

b) Titanium IV chloride is used as a catalyst in the polymerization of ethene to polyethene.

Vanadium

Electron configuration $[Ar]3s^2 3d^3$

Characteristic as a transition element

a) Forms colored compounds; for instance V_2O_5 is yellow.

b) Has variable oxidation states; +2, +3, +4, +5.

c) Has catalytic properties; e.g. V_2O_5 is a catalyst in contact process for conversion of SO_2 to SO_3.

d) Forms complexes such as V_2O_3.

Chromium

Electron configuration of chromium.

$[Ar]4s^1 3d^5$

Characteristic of chromium as a transition element

(i) Forms colored compounds; for instance Cr^{3+} is green
(ii) Has variable oxidation states; +2, +3, +4, +5, +6.
(iii) Forms complexes, e.g. $Cr(NH_3)_6^{3+}$.
(iv) Has catalytic properties: for instance Cr_2O_3 + ZnO catalyzes formation of methanol from CO and hydrogen.

$$CO\,(g) + 2H_2(g) \rightarrow CH_3OH$$

Trial 33

(a) Write electron configuration of chromium.
(b) Giving examples state the properties that show that chromium is a transition metal.

Oxidation states of chromium

Chromium has oxidation states of +6 (oxidizing), +3 (the most stable) and +2 (reducing).

Reaction of chromium with Air

It is extremely stable and is not affected by moist air. The inertness is probably due to a protective oxide layer. It however burn at about 2000^{0}C with a brilliant flame to form chromium III oxide

$2Cr(s) + 3O_2(g) \rightarrow Cr_2O_3\ (s)$

Reaction of chromium with water

Chromium does not react with water but at red heat with steam is to form chromium III oxide

$2Cr(s) + 3H_2O(g) \rightarrow Cr_2O_3\ (s) + 2H_2(g)$

Reaction of chromium with Halogens

F_2 and Cl_2 combine with hot metal to give chromium III halides.

$2Cr(s) + 3X_2(g) \rightarrow 2CrX_3$ (X = Cl, F)

Chromium reacts directly with fluorine, F_2, at 400°C and 200-300 atmospheres to form chromium(VI) fluoride, CrF_6. $Cr(s) + 3F_2(g) \rightarrow CrF_6(s)$ [yellow]

Reaction of chromium with alkalis

Chromium does not react with alkalis at ordinary temperature.

Reaction chromium with ammonia or nitrogen

It forms nitrides

$2Cr\ (s) + 2NH_3(g) \rightarrow 2CrN(s) + 3H_2(g)$

$Cr\ (s) + N_2(g) \rightarrow CrN(s)$

Reaction of chromium with dilute acid

(a) In the absence of air, dil. HCl and dil. H_2SO_4, chromium react with air form chromium II chloride and chromium II sulphate.

$Cr\ (s) + 2HCl(aq) \rightarrow CrCl_2(s) + H_2(g)$

$Cr\ (s) + 2H_2SO_4(aq) \rightarrow CrSO_4\ (aq) + H_2(g)$

Reaction chromium with nitric acid

Chromium does not react with nitric acid due to the formation impervious oxide layer.

Important compounds in oxidation state 6

Chromates (VI) and dichromates (VI)

Sodium and potassium chromates (VI) are yellow solids that dissolve in water to form yellow solutions.

Silver chromate is red

Sodium and potassium dichromates (VI) are orange solids that dissolve in water to form orange solutions.

Uses Chromates (VI) and dichromates (VI)

(i) They are used as oxidizing agents in the laboratory

Half equations

$Cr_2O_7^{2-}(aq) + 6e + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

$CrO_4^{2-}(aq) + 3e + 8H^+(aq) \rightarrow Cr^{3+}(aq) + 4H_2O(l)$

In the process of oxidation dichromates are reduced to chromium (III) ions and the color changes from orange to green. Note that in acidic solution chromates are converted to dichromates while in alkaline solution dichromates are converted to chromates

$Cr_2O_7^{2-}(aq) + 2OH^-(aq) \rightarrow CrO_4^{2-}(aq)$

$CrO_4^{2-}(aq) + 2H^+(aq) \rightarrow Cr_2O_7^{2-}(aq) + H_2O(l)$

(ii) Pieces of filter paper impregnated with acidified solutions of sodium dichromate (VI) can be used to test for reducing gases, e.g., sulphur dioxide and hydrogen sulphide. E.g.

$Cr_2O_7^{2-}(aq) + 8H^+(aq) + 3H_2S(g) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3S(s)$

The orange spot turns green owing to the formation of chromium (III) ions.

(iii) Potassium dichromate (VI) is used in volumetric analysis to estimate reducing agents, e.g., Fe^{2+}

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6Fe^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 6Fe^{3+}(s) + 7H_2O(l)$

(iv) Dichromates are used in preparation of carbonyl compounds from alcohols and carboxylic acid from aldehydes and many oxidation processes. Dichromates are preferred to manganates (VII) because they are not very strong oxidizing agent to cleaves carbon-carbon bonds in organic chemistry

Advantage of potassium dichromate over potassium permangate in volumetric analysis

(i) Hydrochloric acid can be used to acidify titration involving potassium dichromate since are not strong oxidizing agents to oxidize chloride ions to chlorine like permangate (VII) would do.

(ii) Potassium dichromate can obtained in stable pure form.

Trial 34

A solution of potassium dichromate (VI) was added to an acidified solution of iron (II) sulphate.

(a) State what was observed. (1mark)

(b) Write an ionic equation for the reaction that took place. (1½ marks)

Trial 35

Potassium dichromate in the presence of sulphuric acid is widely used as an oxidizing agent. Write

(a) Half equation for the reaction between potassium dichromate and potassium iodide (2½ marks)

(b) Write an overall equation for the reaction between potassium dichromate and potassium iodide in acidic solution. (1 ½ mark)

(c) Name one practical application of potassium dichromate as an oxidizing agent.(1 mark)

Conversion dichromate to chromate

In presence of an alkali dichromate (orange) is converted into chromate (yellow) ions. And chromate ions in acid solution are converted into dichromate solution.

$Cr_2O_7^{2-}$(aq) + 2OH$^-$ (aq) → $2CrO_4^{2-}$(aq) + H_2O(l)

$2CrO_4^{2-}$(aq) + 2H$^+$ (aq) → $Cr_2O_7^{2-}$(aq) + H2O(l)

Trial 36

State what is observed and write equation for the reaction that took place when sodium hydroxide is added to potassium dichromate solution followed by excess dilute sulphuric acid

Use of chromate and dichromate to test for lead and barium ions

Potassium chromate and dichromate form yellow precipitates with Pb^{+2} and Ba^{2+} and are used

to test for these ions

M^{2+}(aq) + CrO_4^{2-}(aq) → MCrO4(s)$2M^{2+}$(aq) + $Cr_2O_7^{2-}$(aq) + H_2O(l) → MCr_2O_7(s)+ 2H$^+$(aq)**Lead chromate is soluble in sodium hydroxide whereas barium chromate is not.**

PbCrO4(s) + 4OH$^-$(aq) → PbO_2^{2-}(aq) +$2H_2O$(l)+ CrO_4^{2-}(as).

Reaction dichromate with hydrogen peroxide

In dilute acidified solutions, dichromate (VI) reacts with hydrogen peroxide solution to form a blue chromium peroxide $CrO(O_2)_2$:

$Cr_2O_7^{2-}$ (aq) + 2H$^+$ (aq) + $4H_2O_2$ (aq) → $2CrO(O_2)_2$ (aq) + 5H2O (l)

The reaction provides **a sensitive test. For chromium**

Chromium III chloride

It is particularly of interest in exams because it shows isomerism of inorganic compounds.

Isomerism is the existence of compounds with the same molecular formula but different structural formulae

Isomers of chromium III chloride are:

(a)	$[Cr(H_2O)_6]^{3+}(Cl^-)3$	Grey-green
(b)	$[Cr(H2O)5Cl]^{2+(}Cl^-)2.H2O$	Light green
(c)	$[Cr(H2O)4Cl]^{2+}(Cl^-)3.2H_2O$	

Method of distinguishing the isomers of chromium (III) chloride

(i) The structural isomers of chromium (III) chloride can be identified by titration with silver nitrate solution; the isomers precipitate different number of chloride ions per mole of the isomers

Moles of chloride ion precipitated per mole of the isomers

(a)	$[Cr(H_2O)_6]^{3+}(Cl^-)_3$	3 chloride ions per mole
(b)	$[Cr(H2O)5Cl]^{2+(}Cl^-)_2.H2O$	2 chloride ions per mole
(c)	$[Cr(H2O)4Cl]^{2+}(Cl^-)_3.2H_2O$	1 chloride ions per mole

2. By electrical conductivity.

(a)	$[Cr(H_2O)_6]^{3+}(Cl^-)_3$	4 conducting ions
(b)	$[Cr(H2O)5Cl]^{2+(}Cl^-)_2.H2O$	2 conducting ions
(c)	$[Cr(H2O)4Cl]^{2+}(Cl^-)_3.2H_2O$	1 conducting ions

Trial 37

(i) Write the structural formulae of the isomers of chromium (III) chloride, CrCl3.6H2O. (3 marks)

(ii) State one way of distinguishing the isomers. (½ mark)

Trial 38

Chromium (III) chrolide-6-water, CrCl3.6H2O, is an example of hydrate isomerism.

(a) Write the formulae of the three possible isomers of CrCl3.6H2O.

(b) The co-ordination number of chromium is the same in the isomers of CrCl3.6H2O.
   (i) Explain briefly what is meant by the term co-ordination number.
   (ii) What is the co-ordination number of chromium in CrCl3.6H2O.

Hydrolysis of chromium (III) salts

Chromium (III) salts hydrolyze in water to give acidic solutions, which turn blue litmus paper red and liberate carbon dioxide from carbonates

$Cr^{3+}(aq) + 3H_2O(l) \rightarrow Cr(OH)_3(s) + 3H^+(aq)$

Consequently, a solution of chromium (III) salt

(i) Has a pH less than 7

(ii) Change the color of blue litmus paper to pink

(iii) Liberates carbon dioxide (effervescence) from carbonate and hydrogen carbonates.

Trial 39

Chromium (III) sulphate was dissolved in water and a few drops of concentrated sodium carbonate solution added to the solution.

(i) State what was observed. (2marks)

(ii) Give a reason for your answer and equations for the reaction (2½ marks)

Solution

(i) Effervescence and green precipitate formed

(ii) Chromium three ions are hydrolyzed to produce acidic solution that liberates carbon dioxide from the carbonate. The green precipitate is chromium (III) hydroxide formed.

$2Cr^{3+}(aq) + 3CO_3^{2-}(aq) + 3H_2O\ (l) \rightarrow 2Cr(OH)_3(s) + 3CO_2(g)$

Qualitative analysis of chromium (III) salts

With sodium hydroxide solution:

It forms a green precipitate soluble in excess

$Cr^{3+}\ (aq) + 3OH^-(aq) \rightarrow Cr(OH)_3(s)$

$Cr(OH)_3(s) + OH^-(aq) \rightarrow Cr(OH)_4^-\ (aq)$

With dilute ammonia solution:

It forms a green precipitate insoluble in excess

$Cr^{3+}\ (aq) + 3OH^-\ (aq) \rightarrow Cr(OH)_3\ (s)$

Confirmatory test;

It forms a green precipitate with sodium hydroxide soluble in excess turns yellow with hydrogen peroxide solution and temporary blue when a few drops of concentrated sulphuric acid are added to the mixture..

Equations

$Cr^{3+}\ (aq) + 3OH^-(aq) \rightarrow Cr(OH)_3(s)$

$Cr(OH)_3(s) + OH^-(aq) \rightarrow Cr(OH)_4^-\ (aq)$

$Cr2O_7^{2-}(aq) + 2H^+\ (aq) + 4H_2O_2\ (aq) \rightarrow 2CrO(O_2)_2\ (aq) + 5H_2O\ (l)$

Trial 40

Dilute sodium hydroxide solution was added drop wise until in excess to aqueous chromium (III)chloride

(a) State what was observed. (1½ mark)

(b) Write an equation for the reaction. (2 marks)

(c) To the product in (a) was added a few drops of hydrogen peroxide and the mixture boiled
  (i) State what was observed. (1mark)
  (ii) Write an equation for the reaction. (1½ marks).

Trial 41

A dark purple crystalline solid Z dissolved in water to give violet solution. When aqueous sodium hydroxide was added to the solution of Z drop wise, a green precipitate was formed and it dissolved in excess sodium hydroxide to give a green solution.

(a) Identify the cation in Z. (1 mark)

(b) Write the formula of the species responsible for the formation of: The violet colour. (1 mark)

(c) Green solution (1 mark)

Trial 42

A dilute solution of chrome alum, $K_2Cr_2(SO_4)_4.2H_2O$ was prepared and divided into two portions.

(a) The first portion turned blue litmus red. Explain the observation and write an equation to illustrate your answer. (4 marks)

(b) To the second portion was added few drops of sodium carbonate solution. State what was observed and explain your answer. (3marks)

Trial 43

(a) When about $1cm^3$ of dilute sulphuric acid was added to about $1cm^3$ of potassium chromate, an orange solution was observed. Addition of an excess dilute sodium hydroxide solution to the mixture gave a yellow solution. Write an equation for the reaction that took place. (3 marks)

(b) Briefly describe a test that can be carried out in the laboratory to confirm that potassium chromate contains chromium ions. (3mark)

Trial 44

When hydrogen peroxide was added to the green solution, a yellow solution was formed, which on treatment with lead ethanoate solution formed a yellow solid. Write an equation for the reaction leading to the formation of:

(i) The Green solution.

(ii) The yellow solution.

Manganese and its compounds

Electron configuration of manganese

$[Ar]4s^2 3d^5$

Properties of manganese as a transition element

- (i) Forms colored compounds; for instance Mn^{7+} is purple
- (ii) Has variable oxidation states; +2, +3, +4, +5, +6, +7
- (iii) Forms complexes, e.g. MnO_4^-.
- (iv) Has catalytic properties, e.g., MnO_2 catalyze release of oxygen from hydrogen peroxide

Reaction of manganese with air

Manganese is not very reactive in regards to air. The surface of manganese lumps oxidizes a little. Finely divided manganese metal burns in air. In oxygen the oxide Mn_3O_4 is formed and in nitrogen the nitride Mn_3N_2 is formed.

$3\ Mn(s) + 2\ O_2(g) \rightarrow Mn_3O_4(s)$

$3\ Mn(s) + N_2(g) \rightarrow Mn_3N_2(s)$

Reaction of manganese with Halogens

Manganese reacts with the halogens, forming the corresponding manganese(II) halides. For fluoride, manganese(III)fluoride is also formed

$Mn(s) + F_2(g) \rightarrow MnF_2(s)$

$2\ Mn(s) + 3\ F_2(g) \rightarrow 2\ MnF_3(s)$

$Mn(s) + Cl_2(g) \rightarrow MnCl_2(s)$ [3]

$Mn(s) + Br_2(g) \rightarrow MnBr_2(s)$

$Mn(s) + I_2(g) \rightarrow MnI_2(s)$

Reaction of manganese with water

Manganese reacts slowly with water forming manganese dioxide

$Mn(s) + 2H_2O(l) \rightarrow MnO_2\ (s) + 2H_2(g)$

Reaction of manganese with acids

Manganese dissolves readily in dilute sulphuric acid, forming a colorless solution of Mn(II) ions and hydrogen gas, H_2.

$Mn(s) + H_2SO_4(aq) \rightarrow Mn^{2+}(aq) + SO_4^{2-}(aq) + H_2(g)$

Important compounds of manganese

Potassium Manganate (VII), $KMnO_4$

- It used as an oxidizing agent to oxidize alcohols and aldehydes to carbonyl compounds and carboxylic acids respectively.

- it is used to standardize iron (II), Hydrogen peroxide and oxalic acid

Half equation for manganate 7

MnO_4^- (aq) + 5e + $8H^+$(aq) → Mn^{2+}(aq) + $4H_2O$(l)

Trial 45

Complete and balance the following equations

Fe^{2+} (aq) + H^+ (aq) + MnO_4^-(aq) →

H_2O_2 (aq) + H^+ (aq) + MnO_4^-(aq) →

$C_2O_4^{2-}$ (aq) + H^+ (aq) + MnO_4^-(aq) →

Manganese (VII) oxidizes halides in the preparations of halogens

$2MnO_4^-$ (aq) + $10X^-$(aq) + $16H^+$(aq) → $2MnX_2$(aq) + $8H_2O$(l) + $5X_2$ (X= Cl, Br, I)

Solution

$5Fe^{2+}$ (aq) + $8H^+$ (aq) + MnO_4^-(aq) → $5Fe^{3+}$(aq) + Mn^{2+}(aq) + $4H_2O$(l)

$5H_2O_2$ (aq) + $6H^+$ (aq) + $2MnO_4^-$(aq) → $2Mn^{2+}$(aq) + $8H_2O$(l)

$5C_2O_4^{2-}$ (aq) + $16H^+$ (aq) + $2MnO_4^-$(aq) → $2Mn^{2+}$(aq) + $8H_2O$(l) + $10CO_2$(g)

Trial 46

Complete and balance the following equations

Cl^- (aq) + H^+ (aq) + MnO_4^-(aq) →

For this reason HCl is not used to acidify MnO_4^- in its oxidation reaction because Cl^- ion is oxidized as well.

Solution

$2MnO_4^-$ (aq) + $10Cl^-$(aq) + $16H^+$(aq) → $2MnCl_2$(aq) + $8H_2O$(l) + $5Cl_2$ (g)

Variation of oxidizing power of manganate (VII) ions with pH

The oxidizing power of potassium permanganate depends on the pH as shown below:

(a) Acidic solution

MnO_4^- (aq) + $8H^+$ (aq) + 5e → Mn^{2+} (aq) + $4H_2O$ (l)

(b) Neutral or alkaline solutions,

The manganate (VII) is reduced to manganese (IV) oxide.

MnO_4^- (aq) + $2H_2O$ (l) + 3e → MnO_2 (aq) + 4OH- (l)

(c) Strongly alkaline solution

Manganate (VII) is reduced to green manganate (VI).

MnO_4^- (aq) + e- → MnO_4^{2-} (aq)

Disadvantages of using potassium permanganate (VII) in volumetric analysis

(a) **Manganate (VII) cannot be used as a primary standard because**

- **(i) it cannot be obtained in pure form. The impurities are MnO_2.**
- **(ii)** Aqueous solutions of manganese (VII) is unstable and slowly deposit brown manganese (IV) oxide on standing.

(b) Hydrochloric acid cannot be used as an oxidizing agent of potassium permanganate VII

(c) Nitric acid cannot be used to oxidize potassium permanganate (VII) solution because it is an oxidizing agent

Trial 47

(a) *Potassium manganate (VII) is not used as a primary standard in volumetric analysis and has to be standardized*

- (i) *What is a primary standard? (2marks)*
- (ii) *State three characteristics of a primary standard.* *(3 marks)*
- (iii) *Explain why potassium manganate (VII) is not used as a primary standard.* *(2 marks)*
- (iv) *Name one substance, other than ethane dioc acid which can be used as a primary standard for potassium manganate. (VII)* *(1 mark*

(b) *Explain why hydrochloric acid is not used usually to acidify solutions of potassium manganate (VII)* *(2 marks)*

(c) *Acidified potassium manganate (VII) reacts with ethane dioc acid*

Write

(i) The half equations for the reaction. (2 marks)

(ii) The overall equation for the reaction. (2 marks)

(d) *20.00 cm^3 of 0.01 M manganate (VII) ions solution required exactly 16.65 cm^3 of a solution containing 5.1 g l^{-1} of an oxalate $(COO^-X^+)_2.2H_2O$. Calculate the atomic mass of X.*

Solution

(a) (i) A **primary standard** is a substance of known high purity which may be dissolved in a known volume of solvent to give a **primary standard** solution

(ii) Features of a primary standard include:

- High purity.
- Stability (low reactivity)
- Low hygroscopicity (to minimize weight changes due to humidity)
- High equivalent weight (to minimize weighing errors)
- Non-toxicity.
- Ready and cheap availability.

(b) Chloride ions react with manganate (VII) ions.

$2MnO_4^-(aq) + 10Cl^-(aq) + 16H^+(aq) \rightarrow Mn^{2+}(aq) + 5Cl_5(g) + 8H_2O(l)$

(c) (i) $MnO_4^-(aq) + 8H^+(aq) + 5e \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

$C_2O_4^{2-}(aq) - 2e \rightarrow 2CO_2(g)$

(ii) $5C_2O_4^{2-}(aq) + 16H^+(aq) + 2MnO_4^-(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$

(d) X =23

Trial 48

Iron (II) sulphate is normally used to standardize a solution of potassium manganate (VII) acidified with sulphuric acid

(a) Write an equation for the reaction between potassium manganate and iron (II) sulphate.(1 ½ marks)

(ii) State why hydrochloric acid is not used to acidify potassium manganate (VII). (2 ½ marks)

(b) 20.00 cm^3 of acidified solution of 0.02M potassium manganate (VII) reacted exactly with 25.10cm^3 of sodium nitrite. Potassium manganate (VII) reacts with sodium nitrite according to the following equation.

$2MnO_4^-(aq) + 5NO_2^-(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5NO_3^-(aq) + 3H_2O(l)$

Calculate the concentration of the sodium nitrite in moles per litre.[0.04M]

Manganese (VI) compounds:

The sodium and potassium manganates (VI) are the only pure compounds containing manganese in the +6 oxidation state. Both these compounds are dark green solids, the colour being due to the MnO_4^{2-} ion.

Manganese (VI) disproportionate in acidic medium to give purple manganate VII ions

$3MnO_4^{2-}$ (aq) + $2H_2O$ (l) → $2MnO_4^-$ (aq) + MnO_2 (s) + $4OH^-$ (aq)

Definition

Disproportionation reaction is a reaction where there is concurrent oxidation and reduction

Disproportion of manganese (VI) is speeded up by bubbling a stream of carbon dioxide through the solution, since this removes the hydroxyl ions as hydrogen carbonate ions

4^-OH (aq) + $4CO_2$ (g) → $4HCO_3^-$ (aq)

Manganese (IV) compounds

Manganese (IV) oxide, MnO_2, is the main manganese (IV) compound; it occurs naturally as the ore pyrolusite; and it can be made by the action of heat on manganese (II) nitrate.

$Mn(NO_3)_2$ (s) → MnO_2 (s) + $2NO_2$ (g)

Uses of manganese IV oxide

(i) preparation of chlorine

MnO_2 (s) + 4HCl (aq) → $MnCl_2$ (aq) + $2H_2O$ (l) + $2Cl_2$ (g)

(ii) it is a catalyst in the preparation of oxygen from hydrogen peroxide.

Reaction of Manganese (IV) compounds.

In presence of air or oxidizing agent (e.g. KNO_3, $KClO_3$) MnO_2 reacts with fused KOH to give potassium manganate, K_2MnO_4.

$2MnO_2$(s) + 4KOH(l) + O_2 (g)→ $2K_2MnO_4$(aq) + $2H_2O$(l)

Qualitative analysis of Manganese II

(a) Addition of dilute sodium hydroxide of ammonia solution drop wise until in excess.

A white ppt. insoluble in excess, rapidly turning brown.

Mn^{2+} (aq) + $2^{-}OH$ (aq) → $Mn(OH)_2$ (s)

Then

$4Mn(OH)_2$ (s) + O_2(g) → Mn_2O_3(s) + $2H_2O$(l)

Confirmatory test of Mn^{2+}

Mn^{2+} aqueous solution turn purple solution on addition concentrated nitric acid followed by sodium bismuthate or Lead (IV) oxide.

$2Mn^{2+}$ (aq) + $5BiO_3^-$ (s) + $14H^+$ (aq) → $2MnO_4^-$ (aq) + $5Bi^{3+}$ (aq) + $7H_2O$ (l)

$2Mn^{2+}$ (aq) + $5PbO_2$(s) + $4H^+$ (aq) → $2MnO_4^-$ (aq) + $5Pb^{2+}$ (aq) + $2H_2O$ (l)

Trial 49

A crystalline solid Y dissolved in water to give a pink solution. Addition of excess aqueous sodium hydroxide produced a dirty white precipitate which rapidly turned brown on standing.

When nitric acid was added to the solution Y followed by sodium bismuthate solution, the solution changed from pink to purple.

(a) *Identify the cation in Y. (1 mark)*

(b) Write:

(i) The equation for the reaction that took place when sodium hydroxide was added to the solution. (1½ marks)
(ii) The formula of the species responsible for the purple color. (1 mark)
(iii) Equation for the reaction leading to the formation of the brown solid. (1½ marks)

Trial 50

(a) Write the outer electronic configuration of manganese. (1 mark)

(iv) State the possible oxidation states of manganese. (2 ½ marks)
(v) How does the acidity of the oxides of manganese vary with increasing oxidation states? (½ marks)
(vi) What is the change in oxidation state of manganese when potassium manganate (VII) is reduced in alkaline medium? (1 mark)
(vii) State four applications of potassium manganate (VII) in the laboratory as oxidizing agent**?** (4 marks)

Iron and its compound

Electron configuration of Iron

$[Ar]3d^6 4s^2$

Properties of iron as a transition element

a) Forms colored compounds; for instance Fe^{2+} is green
b) Has variable oxidation states; +2, +3,
c) Forms complexes, e.g. $Fe(CN)_6^{3-}$.
d) Has catalytic properties, e.g., iron catalyze formation of ammonia from nitrogen and hydrogen.

Extraction of iron

Iron, which is the second most abundant metal occurring in the earth's crust, is extracted from its ores which are;

haematite,	Fe_2O_3
magnetite,	Fe_3O_4,
siderite,	$FeCO_3$.

Extraction of iron from hematite

Main Impurities

Silica, SiO_2

Reactions leading to reduction of iron oxide are

$C (s) + O_2 (g) \rightarrow CO_2 (g)$

$CO_2 (s) + C (s) \rightarrow 2CO (g)$

$Fe_2O_3 (s) + 3CO (g) \rightarrow 2Fe (s) + 3CO_2 (g)$

Reactions leading to removal of impurities

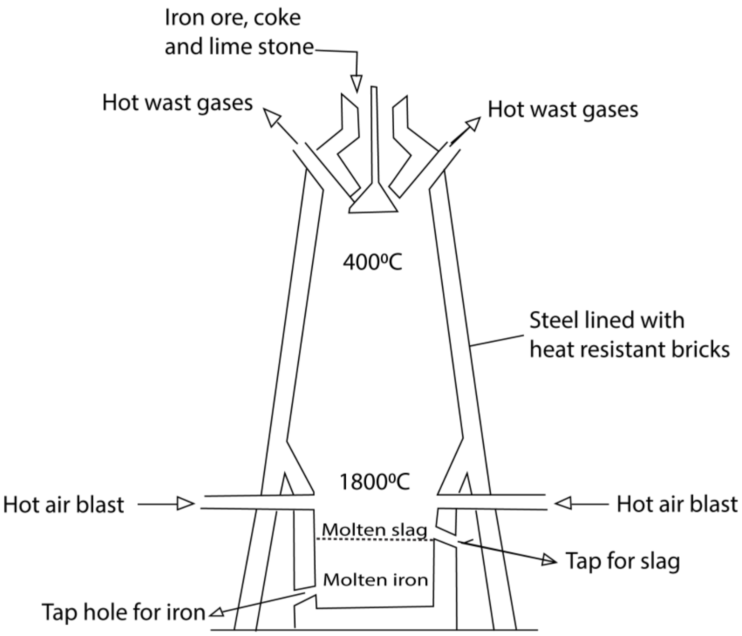
$CaCO_3 (s) \rightarrow CaO (s) + CO_2 (g)$

$CaO (s) + SiO_2 (s) \rightarrow CaSiO_3 (l)$

$CaO (s) + Al_2O_3 (s) \rightarrow CaSiO_3 (l)$ slag

Procedure

Iron ore, lime stone and coke in the correct proportions are reacted with preheated air in a blast furnace.



Blast Furnance

Molten iron and slag percolate to the bottom of the furnace and taped of through different taps.

Trial 1

In the production of iron metal, haematite, Fe_2O_3, is mixed with coke and lime stone and heated in a blast furnace.

(a) What is the purpose of adding

(i) lime stone (1 mark)

(i) coke? (1 mark)

(b) Write three different equations for the reaction in which haematite are converted into iron in the blast furnace. (3marks)

(c) Explain why it is possible to extract iron by the method described above. (2 marks)

(i) *Name one other method that can be used to extract iron from its ore. (1 marks)*

(ii) *Suggest a reason why the method you have named in d(i) is not used commonly in the production of iron.*

Oxidation states of Iron

Iron has oxidation states +2 and +3

Oxidation state Fe^{3+} ($[Ar]3d^5$) is more stable than F^{2+} ($[Ar]4s^13d^5$) because Fe^{3+} has stable half full electron configuration.

Trial 51

This explains why green iron II compounds rapidly turn into brown iron III compounds.

Properties of iron

Pure iron is a silvery colored metal with a melting point of 1535^0C and boiling point 3000^0C.

It is a soft, ductile and malleable metal, which is strongly ferromagnetic.

Rusting of iron

Iron in presence water and air form a brown coat called rust or hydrated iron (III) oxide, $Fe_2O_3.xH_2O$,

Disadvantage of rusting

(i) Weaken tools
(ii) Makes objects look ugly

Methods of preventing rusting

(a) Keeping objects in dry places.

(b) Painting

(c) Oiling

(d) Greasing

(e) Coating with another metal.

(f) Zinc plating

Reaction of iron with water

Iron does not react with cold water but with steam to form blue-black tri-iron trioxide oxide

$3Fe(s) + 4H_2O(g) \rightarrow Fe_3O_4(s) + 4H_2(g)$

Reaction of iron with acids

Iron displaces hydrogen readily from dilute hydrochloric acid and sulphuric acids, forming iron (II) salts. Dilute nitric acid forms iron (II) nitrate and oxides of nitrogen.

$Fe(s) + 2HCl(aq) \rightarrow FeCl_2\ (aq)\ 2H_2(g)$

$Fe(s) + H_2SO_4(aq) \rightarrow FeSO_4(aq) + H_2(g)$

Concentrated H_2SO_4 gives a mixture of ferrous and ferric sulphates.

$Fe(s) + 2H_2SO_4(aq) \rightarrow FeSO_4(aq) + SO_2(g) + 2H_2O(l)$

$2FeSO_4\ (aq) + 2H_2SO_4\ (aq) \rightarrow Fe_2(SO_4)_3\ (aq) + 2H_2O\ (l) + SO_2\ (g)$

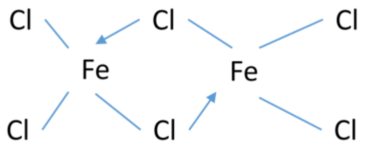
Action of alkalis, halogen and sulphur on iron

Iron does not react with alkalis.

Halogens and sulphur combine with the heated metal forming halides and sulphide respectively.

$2Fe(s) + 3Cl_2(g) \rightarrow 2FeCl_3\ (g)$

$Fe(s) + S(s) \rightarrow FeS\ (s)$



Displacement of less electropositive metals

Iron displaces copper from a solution of copper sulphate.

$Fe(s) + Cu^{2+}(aq) \rightarrow Fe^{2+}(aq) + Cu(s)$

Hydrolysis of Iron III slats in water

Iron III salts hydrolyze in water to form acidic solution

$Fe^{3+}(aq) + 3H_2O(l) \rightarrow Fe(OH)_3(s) + 3H^+(aq)$

Consequently, Iron III solution

- turns blue litmus paper red.

- Liberate carbon dioxide from carbonates with formation of brown precipitate
- Has pH less than 7

Reaction iron III solution with sodium carbonate solution

$2F^{3+}(aq) + 3CO_3^{2-}(aq) + 3H_2O(l) \rightarrow 2Fe(OH)_3(s) + 3CO_2(g)$

Observation

A brown ppt. formed with effervescence

Trial 52

State what would be observed and write an equation for the reaction that takes place when aqueous iron (III) chloride with sodium carbonate (3½ marks)

Reactions of iron (III) as an oxidizing agent

Iron (III) compounds are strong oxidizing agents, for instance, it oxidizes iodide ions (I^-) to iodine and tin (II) compounds to tin (IV) compounds and itself reduced to Fe^{2+} compounds.

$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2F^{2+}(aq) + I_2(aq)$

$2Fe^{3+}(aq) + Sn^{2+}(aq) \rightarrow 2F^{2+}(aq) + Sn^{2+}(aq)$

Trial 53

A solution of Iron (III) chloride was added to an aqueous solution of tin (II) chloride acidified with hydrochloric acid and the mixture shaken.

(a) State what was observed. (1 mark)

(b) Write an equation for the reaction that took place.

Qualitative analysis of Fe^{2+} salt

Common iron II salts include

- Ferrous sulphate: $FeSO_4.7H_2O$
- Ammonium ferrous sulphate $(NH_4)_2Fe(SO_4)_2.6H_2O$
- Ferrous oxalate. FeC_2O_4

Qualitative analysis of Fe^{2+} salt

(i) Addition of dilute sodium hydroxide or ammonia solution
Observation

A dirty green precipitate insoluble in excess turn brown on standing.

$Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s)$

(ii) Confirming presence of Iron II ions

Forms a deep blue solution with potassium hexacyanoferrate III.

Qualitative analysis of Fe^{3+} salt

(i) Addition of dilute sodium hydroxide or ammonia solution

Observation

A dirty brown precipitate insoluble in excess.

$Fe^{3+}(aq) + 3OH^{-}(aq) \rightarrow Fe(OH)_3(s)$

(ii) Confirming presence of Iron III ions

Forms a deep blue solution with potassium hexacyanoferrate II.

Forms a red solution with ammonium thiocyanate solution.

Cobalt and its compounds

Electron configuration of cobalt

$[Ar]4s^3d^7$

Properties as a transition element

a) Forms colored compounds; for instance Co^{2+} is pink

b) Has variable oxidation states; +2, +3,

c) Forms complexes, e.g. $CoCl_4^{2-}$.

Physical properties of cobalt

Cobalt is a silver-white lustrous metal, slightly harder than iron. It is malleable and ductile. It is more magnetic than all other metals except iron.

It has a density equal to 8.9. It melts at 1495^0C and boils at 2900^0C.

Action of air:

Dry air has no action on cobalt but the metal reacts with O_2 to form Co_3O_4 when red hot.

$3Co(s) + 2O_2(g) \rightarrow Co_3O_4(s)$

Action of water:

Cobalt does not react with cold water. However, it decomposes steam to hydrogen.

$Co(s) + H_2O(steam) \rightarrow CoO(s) + H_2(g)$

Action of acids

Dilute Hydrochloric acid and sulphuric acid form salts and hydrogen with cobalt.

$Co(s) + 2H^+(g) \rightarrow Co^{2+}(aq) + H_2(g)$

Dilute nitric acid dissolves the metal and renders it passive due to formation of a protecting thin layer of metal oxide on the surface of the metal.

Action of alkalis:

Even concentrated alkali has no action on the metal. The metal is dissolved in fused caustic potash at 550^0C.

Action of Carbon monoxide:

Finely divided Cobalt combines with carbon monoxide at 150^0C and under 30 atmospheres to form orange-red $Co_2(CO)_8$

Action of ammonia:

Co_4N_2 is formed.

$4Co(s) + 2NH_3(g) \rightarrow Co_4N_2(s) + 3H_2(g)$

Action with other elements:

Cobalt readily combines with H_2, S, P and B but N_2 has no action on it. $Co(s) + H_2(g) \rightarrow CoH_2(s)$

$Co(s) + S(s) \rightarrow CoS(s)$

$3Co(s) + 2P(s) \rightarrow Co_3P_2(s)$

Uses of cobalt

(i) Cobalt is used for electroplating.

(ii) For preparation of alloys; e.g. cobalt steel for making permanent magnets, stellite (Co, Cr and W (tungsten)) for making surgical instruments, and Co-chrome (Co, Cr and Fe) for making resistance wires.

(iii) Cobalt oxides and silicates are used for coloring glass, pottery and glazes.

Qualitative analysis of cobalt II salts

Common salt: Cobalt sulphate: $CoSO_4$

With dilute sodium hydroxide solution and ammonium solution

Observation

Blue precipitate insoluble in excess turns brown on standing

Confirmatory test

Forms deep blue solution with concentrated hydrochloric acid.

$Co(H_2O)_6^{2+}(aq) + 4Cl^-(aq) \rightarrow CoCl_4^{2-}(aq) + 6H_2O(l)$

(b) With Concentrated ammonia forms a blue precipitate soluble in excess to give pale yellow solution; the solution turns brown on standing.

$\underset{\text{pink}}{[Co(H_2O)_6]^{2+}}(aq) + 2OH^-(aq) \rightarrow \underset{\text{blue}}{Co(OH)_2}(s)$

ppt

$Co(OH)_2(s) + 6NH_3(aq)\ s \rightarrow \underset{\text{red-brown}}{*Co(NH_3)_6]^{2+}}(aq)$

$\underset{\text{red-brown}}{[Co(NH_3)_6]^{2+}}(aq) \rightarrow \underset{\text{yellow solution}}{Co(NH_3)_6]^{3+}}(aq)$

Trial 54

(a) Write equations for the reactions which take place and in each case, state what would be observed when;

(i) Concentrated ammonia is added drop wise to an aqueous solution of cobalt (II) sulphate and when the resultant solution is allowed to stand in air. (4 marks)

Nickel and its compounds

Electron configuration

$[Ar]4s^2 3d^8$

Properties as a transition element

a) Forms colored compounds; for instance Ni^{2+} is green
b) Has variable oxidation states; +2, +3,
c) Forms complexes, e.g. $Ni(NH_3)_6^{2+}$.
d) Catalytic property: it is a catalyst in hydrogenation of alkenes, alkyne

Physical Properties

Nickel is a hard metal that is quite lustrous. It melts at 1452^0C and has a density of 8.90 $g\ cm^{-3}$. Nickel is used in making of alloys, electroplating of materials; and as a catalyst in the hydrogenation of fats and in making synthesis gas.

Reaction of air with nickel:

It reacts slowly at ordinary temperature but vigorously at high temperature to form nickel oxide

$2Ni(s) + O_2(g) \rightarrow 2NiO(g)$

Action of water on nickel

Nickel decomposes steam at red heat to hydrogen

$Ni(s) + H_2O(g) \leftrightarrow NiO(s) + H_2(g)$

Action of acids on nickel

Dilute hydrochloric acid sulphuric acids have slow action on nickel.

But nitric acid readily dissolves the metal.

$3Ni(s) + 8HNO_3(aq) \rightarrow 3Ni(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$

Action of halogen on nickel

Chlorine reacts with nickel to form nickel (II) chloride.

$Ni(s) + Cl_2(g) \rightarrow NiCl_2(s)$

Action of sulphur on nickel

Sulpur reacts with nickel to form nickel sulphide

$Ni(s) + S(s) \rightarrow NiS(s)$

Qualitative analysis f nickel II ions

Common nickel II salts

Nickel (II) sulphate, $NiSO_4.7H_2O$

Nickel (II) carbonate, $NiCO_3$

$(NH_4)_2SO_4.NiSO_4.6H_2O$

Addition of dilute sodium hydroxide

Forms a green precipitate insoluble in excess

$Ni^{2+}(aq) + 2OH^-(aq) \rightarrow Ni(OH)_2(s)$

Addition of dilute ammonia solution

Forms a green precipitate soluble in excess

$Ni^{2+}(aq) + 2OH^-(aq) \rightarrow Ni(OH)_2(s)$

Then

$Ni(OH)_2(s) + 6NH3(aq) \rightarrow Ni(NH_3)_6^{2+}$

Confirming Ni^{2+} ions

Forms a pink ppt on addition of a few drops of ammonia followed by dimethylglyoxime.

Trial 55

When a pale green solid was heated, it decomposed to a green solid, Q, and a gas that turned lime water milky was evolved. Q dissolved in dilute nitric acid to give a green solution, R. On addition of dilute sodium hydroxide solution to R, a green precipitate, S, insoluble in excess alkali was obtained. S dissolved in aqueous ammonia to give a purplish blue solution.

(a) Identify compounds P, Q, S and solution R. (4 marks)

(b) Write equations for the reactions between;

(i) Q and nitric acid. (1½ marks)

(ii) R and sodium hydroxide.(1½ marks) (iii) S and ammonia. (2 marks)

Copper and its compounds

Electron configuration of copper

$[Ar]4s^1 3d^{10}$

Properties of copper as a transition element

a) Forms colored compounds; for instance Cu^{2+} is blue

b) Has variable oxidation states; +1, +2,

c) Forms complexes, e.g. $Cu(NH_3)_4^{2+}$.

d) $CuSO_4$ is a catalyst in preparation of hydrogen from dil. sulphuric acid

Trial 56

(i) Write the electron configuration of copper. (01mark)

(ii) State properties which show copper as a d-block element. (01mark)

Properties and uses of copper

Copper has a melting point of 1083^0C and a density of 8.94 $g\ cm^{-3}$. It is a tough, malleable and ductile metal with an attractive golden color. It has electrical and thermal conductivity, thus used for electric cables and calorimetres.

Extraction of copper

copper pyrites, $CuFeS_2$,

copper glance, CuS,

cuprite, Cu_2O.

Extraction of copper from pyrites

1. **Concentration of the ore by floatation method**

The finely pulverized ore is mixed with water, containing ‘frothing’ agent (s).

Air is blown into the mixture, froth is produced and the earthly material is "wetted" and sinks.

The sulphide ore particles, rise to the surface in the froth and are skimmed off the surface.

Anti- frothing agent is added to break up the froth, the concentrated ore is filtered and dried.

2. Roasting

The ore is then roasted in a limited supply of air to convert the iron into iron (II) oxide.

$2CuFeS_2\,(s) + 4O_2\,(g) \rightarrow Cu_2S\,(s) + 3SO_2\,(g) + 2FeO\,(s)$

3. Addition of SiO_2 to remove impurities

Silica, SiO_2, is added to the mixture and heated in the absence of air to convert the iron (II) oxide into a slag of iron (II) silicate, $FeSiO_3$, which is poured away.

$FeO(s) + SiO_2 \rightarrow FeSiO_3(s)$ (slag)

4. Conversion of copper sulphide to copper

The copper (I) sulphide is reduced to copper by heating in a controlled amount of air.

$Cu_2S\,(s) + O_2\,(g) \rightarrow 2Cu\,(s) + SO_2\,(g)$

5. Purification of copper by electrolysis

Anode: Impure copper: $Cu(s) - 2e \rightarrow Cu^{2+}\,(aq)$

Cathode; pure copper strip: $Cu^{2+}(aq) + 2e \rightarrow Cu(s)$

Electrolyte: Copper sulphate

Trial 57

(a) Write the formulae of two ores of copper (1marks)

(b) (i) suggest one method by which the ores may be concentrated (1marks)

(ii) outline, giving equations, the process by which impure copper is obtained from the concentrated ore(6)

(c) (i) Name the method by which impure copper is purified (1mark)

(ii) Describe, giving equations the process of purification of copper in (i) above (4marks)

(d) Give two large scale uses of copper (1mark)

(e) 6.53 g of impure copper dissolved in excess nitric acid. The solution obtained was made up to 250cm^3 of solution with water. To 25cm^3 of this solution excess aqueous potassium iodide was added. The reaction that took place is given by the equation

$$2Cu^{2+}(aq) + 4I^-\,(aq) \rightarrow Cu_2I_2(s) + I_2(aq)$$

The iodine liberated reacted with 20cm^3 of 0.5M aqueous sodium thiosulphate according to the equation

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

Calculate the percentage by mass the purity of copper in sample (Cu=64) (6marks) [98%]

Trial 58

In extraction of copper from its ore, the ores are first concentrated and then roasted in air. The roasted material is then mixed with silica and heated by hot air in a blast furnace producing cooper

(a) Write the formula of one ore from which copper can be extracted (½ mark)
(b) Describe the process by which the ore named in (a) can be concentrated (4marks)
(c) Write an equation for the reaction that takes place when the ore is roasted in air (1½ marks)
(d) Write equation for the reaction that lead to the formation of copper in the blast furnace (3marks)

Properties and uses of copper

Copper has a melting point of 1083^0C and a density of 8.94gcm^{-3}. It is tough, malleable and ductile metal with attractive golden color. It has high electrical and thermal conductivity, thus used for electric cables and calorimeters.

Reaction of copper with air

Copper reacts slowly with air forming a mixture copper (I) and copper (II) oxides

$3Cu(s) + O_2(g) \rightarrow CuO(s) + Cu_2O(s)$

Reaction of copper with water

Copper does not react with water

Reaction of copper with dilute acids

Copper does not react with dilute or non-oxidizing acids

Reaction of copper with concentrated hydrochloric acid

With hot concentrated hhydrochloric acid copper form a dichlorocopper I complex ion

$2Cu(s) + 4HCl(aq) \rightarrow 2[CuCl_2]^-(aq) + 2H^+(aq) + H_2(g)$

Reaction of copper with concentrated sulphuric acid

Hot concentrated sulphuric acid oxidizes to copper sulphate, sulphur dioxide and water

$Cu (s) + 2H_2SO_4 (aq) \rightarrow CuSO_4 (aq) + SO_2 (g) + 2H_2O (l)$

Reaction of copper with concentrated nitric acid

Copper is oxidized by dilute and concentrated nitric acid to copper II ions as shown below

$$3Cu (s) + \underset{\text{dilute}}{8HNO_3 (l)} \rightarrow 3Cu(NO_3)_2 (aq) + 4H_2O (l) + 2NO (g)$$

$$Cu (s) + \underset{\text{conc.}}{4HNO_3 (l)} \rightarrow Cu(NO_3)_2 (aq) + 2H_2O (l) + 2NO_2 (g)$$

Uses of copper

- for the winding of dynamos and for conveying electrical power.
- Its resistance to chemical attack and its high thermal conductivity make it useful metal for the construction of condensers for chemical plants and car radiators.
- Finely divided copper is used as an industrial catalyst.

Trial 59

(a) State the condition under which copper reacts with the following acids and in each case write an equation for reaction:

(i) Sulphuric acid (03marks)

(ii) Nitric acid (03marks)

(b) State what would be observed and write equation which take place when the following reagents are added drop wise to a solution of copper (II) sulphate until in excess

(i) Concentrated hydrochloric acid (03marks)

(ii) Sodium hydroxide solution (02marks)

Copper compounds

Copper exhibits oxidation states +2 (the most common) and +1 (only stable in aqueous solution if part of a stable complex ion). A few compounds containing copper (III) are known, e.g., K_3CuF_6, but this ox-idation state of the metal is not important.

Simple covalent compounds of copper (II) are generally less thermally stable than corresponding copper (I) compounds. Where compounds with weakly electropositive groups are concerned, e.g., copper (II) iodide and copper (II) cyanide, the decomposition into corresponding copper (I) compound is spontaneous at room temperature.

$2CuI_2\ (s) \rightarrow 2CuI\ (s) + I_2\ (s)$

$2Cu(CN)_2\ (s) \rightarrow 2CuCN\ (s) + C_2N_2\ (g)$

With more electronegative groups, the decomposition requires a higher temperature, and many copper (II) compounds change into the corresponding copper (I) compounds on strong heating.

$2CuCl_2\ (s) \rightarrow 2CuCl\ (s) + Cl_2\ (g)$

$4CuO\ (s) \rightarrow 2Cu_2O\ (s) + O_2\ (g)$

$2CuS\ (s) \rightarrow Cu_2S\ (s) + S\ (s)$

In aqueous solution, the hydrated copper (I) ions are unstable and disproportionate into copper (II) ion and copper.

$2Cu^+\ (aq) \rightleftharpoons Cu^{2+}\ (aq) + Cu\ (s) \qquad E^\theta = +0.36V$

The positive e.m.f of the above cell reaction implies that hydrated copper (I) ions are thermodynamically unstable in solution with respect to copper and hydrated copper (II) ions. This is the reason why the chemistry of copper (I) compounds is largely that of its water insoluble compounds and of its stable complexes.

Copper (I) oxide, Cu_2O.

It is a dark red, insoluble solid made by partially reducing alkaline copper (II) solution. It is necessary to prevent the initial formation of a precipitate of copper (II) hydroxide. Experimentally, the following procedure is followed: a solution of copper (II) sulphate is added to an alkaline solution of sodium potassium tartrate to give a deep blue solution, the color being due to the presence of a copper (II) tartrate complex. This solution is then, warmed with a suitable reducing agent, e.g., ethanal or sugars to give a red precipitate of copper (I) oxide. This reaction is the basis of the qualitative and quantitative test for reducing sugars.

Copper (I) oxide is a covalent basic oxide; it reacts with acids to form copper (I) salts, but these immediately disproportionate into copper (II) salts unless they are insoluble, e.g.,

$$Cu_2O\ (s) + 2HCl\ (aq) \rightarrow 2CuCl\ (s) + H_2O\ (l)$$

$$Cu_2O\ (s) + H_2SO_4\ (aq) \rightarrow Cu_2SO_4\ (aq) + H_2O\ (l)$$

Then $Cu_2SO_4\ (aq) \rightarrow CuSO_4\ (aq) + Cu\ (s)$

Copper (I) sulphate, Cu_2SO_4

It is obtained as a white solid when copper (I) oxide is heated with anhydrous dimethyl sulphate.

$$Cu_2O\ (s) + (CH_3)_2SO_4\ (l) \rightarrow Cu_2SO_4\ (s) + (CH_3)_2O\ (l)$$

In the absence of moisture, it is stable. However, on dissolving it disproportionate rapidly into copper (II) sulphate and copper:

Copper (I) chloride, CuCl

It is prepared by boiling copper (II) chloride solution with excess copper and concentrated hydrochloric acid; copper (I) is present in this solution as the $CuCl_2^-$ (aq) complex ion:

$$2Cu(s) + 4HCl\ (aq) \rightarrow 2H^+(aq) + 2[CuCl_2]^-(aq) + H_2(g)$$

On pouring the solution into air free distilled water, copper (I) chloride precipitates as a white solid:

$$Cu\ (s) + Cu^{2+}\ (aq) + 2Cl^-\ (aq) \rightarrow 2CuCl\ (s)$$

It is oxidized by moist air to copper (II) chloride.

Other halides

Copper (I) bromide, CuBr, can be made by a method similar to that used for making copper (I) chloride. It resembles the chloride in most respects.

Copper (I) iodide, CuI, precipitates as a white solid when an aqueous solution of a copper (II) salt is treated with an aqueous solution of potassium iodide.

$$Cu^{2+}(aq) + 4I^-(aq) \rightarrow 2CuI(s) + I_2(s)$$

White ppt. brown solution

The above reaction can be used to estimate the concentration of a copper (II) salt, since the quantitative formation of iodine can be determined by titration with standard thiosulphate solution.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

Trial 60

State what would be observed and write equation for the reaction that takes place when the following compounds are reacted

Aqueous copper (II) sulphate with potassium iodide (2 ½ marks)

Copper (II) compounds

This is the most common oxidation state of copper and in aqueous solution copper (II) salts are blue, the color being due to the presence of $[Cu(H_2O)_6]^{2+}$ ions.

Copper (II) oxide, CuO

This is a black, insoluble covalent solid and may be obtained by heating the metal in air or oxygen or by heating the nitrate or carbonate of the metal

$$2Cu(s) + O_2(g) \rightarrow 2CuO(s)$$

$$CuCO_3(s) \rightarrow CuO(s) + CO_2(g)$$

$$2Cu(NO_3)_2(s) \rightarrow 2CuO(s) + 4NO_2(g) + O_2(g)$$

On heating to a temperature of above 800^0C, it decomposes into copper (I) oxide and oxygen.

$4CuO\ (s) \rightarrow 2Cu_2O\ (s) + O_2\ (g)$

It reacts readily with dilute mineral acids, on warming, with the formation of copper (II) salts. It is also easily reduced to copper on heating in a stream of hydrogen:

$CuO\ (s) + 2H^+\ (aq) \rightarrow Cu^{2+}\ (aq) + H_2O\ (l)$

$CuO\ (s) + H_2\ (g) \rightarrow Cu\ (s) + H_2O\ (l)$

The detection of carbon and hydrogen in organic compounds can be achieved by heating with dry copper (II) oxide, when carbon dioxide and water are formed.

Copper (II) hydroxide, $Cu(OH)_2$

Copper (II) hydroxide is precipitated as a blue-green gelatinous solid when an aqueous solution of copper (II) salt is made alkaline with sodium hydroxide

$Cu^{2+}\ (aq) + 2^-OH\ (aq) \rightarrow Cu(OH)_2\ (s)$

It can be filtered and dried at 100^0C to the composition of $Cu(OH)_2$. However, heating the unfiltered suspension to about 80^0 results in its decomposition into copper (II) oxide and water.

Copper (II) hydroxide is readily soluble in an aqueous solution of ammonia with formation of the intense blue $[Cu(NH_3)_4]^{2+}$ ions.

$Cu(OH)_2(s) + 4NH_3(aq) \rightarrow [Cu(NH_3)_4]^{2+}(aq) + 2OH^-(aq)$

It reacts readily with dilute acids to give copper (II) salts.

$Cu(OH)_2\ (s) + 2H^+\ (aq) \rightarrow Cu^{2+}\ (aq) + 2H_2O\ (l)$

Copper (II) carbonate, $aCuCO_3.bCu(OH)_2$

The pure substance is unknown and any method of preparation, e.g., the addition of either sodium carbonate or sodium hydrogen carbonate solution to a solution of copper (II) salt, results in formation of a blue-green basic carbonate. It naturally occurs as malachite, $CuCO_3.Cu(OH)_2$, and as a zurite, $Cu(OH)_2.2CuCO_3$.

Basic copper (II) carbonate is insoluble in water but dissolves in ammonia solution, since the dark blue, $Cu(NH_3)_4^{2+}$ (aq) ion is formed and the reaction moves to the right.

$CuCO_3(s) + 4NH_3(aq) \rightarrow [Cu(NH_3)_4]^{2+}(aq) + CO_3^{2-}(aq)$

Copper (II) sulphide, CuS

It is made by gently heating powdered copper with excess sulphur or by passing hydrogen sulphide into an acidic solution of a copper (II) salt.

$$Cu^{2+}(aq) + H_2S(g) \rightarrow CuS(s) + 2H^+(aq)$$

It is a black solid, insoluble in water and is slowly oxidized in moist air to the sulphate and converted into copper (I) sulphide and sulphur on strong heating.

Copper (II) chloride, $CuCl_2$

It is predominantly covalent dark brown solid when anhydrous and is obtained by passing chlorine over heated copper.

$$Cu(s) + Cl_2(g) \rightarrow CuCl_2(s)$$

Copper (II) chloride is very soluble in water. A concentrated aqueous solution is dark brown to yellow, the color being due to the presence of complex ions such as $CuCl_4^{2-}$ (aq), but with dilution the color changes to green and then to blue.

$[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CuCl_4]^{2-}(aq) + 6H_2O(l)$

Blue green/yellow

These color changes are due to the successive replacement of chlorine ions in the complex by water molecules. The final color being that of the $Cu(H_2O)_6^{2+}$ (aq) ions. The dihydrate, $CuCl_2.2H_2O$, which is a green solid, can be obtained by crystallizing the solution.

Trial 61

Explain the following observations: To dilute solution of copper (II) sulphate was added concentrated hydrochloric acid drop wise until in excess. A student wrote the following equation for the reaction that took place

$$CuSO_4(aq) + 2HCl\ (aq) \rightarrow CuCl_2(aq) + H_2SO_4(aq)$$

Explain what is wrong with the equation *(4marks)*

Trial 62

Copper (ii) chloride dissolves in concentrate hydrochloric acid to form a brownish yellow solution; which on dilution with water turns green-blue and finally pale blue. Explain the observation.

Trial 63

To an aqueous solution of $CuSO_4.5H_2O$ was added concentrated hydrochloric acid drop wise until in excess

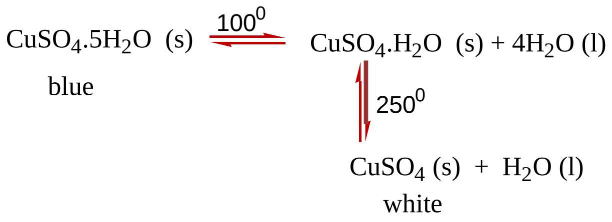
(a) *Name the copper species present in the solution before hydrochloric acid was added (1mark)*
(b) *Write the formula of the copper species in the solution, containing excess hydrochloric acid*
(c) *The solution containing excess hydrochloric acid was diluted with water*
  (i) *State the color changes that took place* *(1mark)*
  (ii) *Write an equation for the reaction that took place* *(2marks)*

Copper (II) sulphate, $CuSO_4.5H_2O$ (blue vitriol)

This prepared in the laboratory by addition of dilute sulphuric acid to copper (II) oxide, hydroxide or carbonate. The solution is heated to obtain a saturated solution and the blue solid pentahydrate separates on cooling (a few drops of dilute sulphuric acid are generally added before heating to prevent the hydrolysis). On industrial scale, copper (II) sulphate is obtained by oxidizing copper with air and the resulting oxide reacts with the acid

$$2Cu\ (s) + 2H_2SO_4\ (aq) + O_2\ (g) \rightarrow 2CuSO_4\ (aq) + H_2O\ (l)$$

Copper (II) sulphate pentahydrate loses four of its molecules of water of crystallization on heating to 100^0C, the fifth molecule of water is lost at a temperature of about 250^0C:



The anhydrous salt decomposes into black copper (II) oxide and sulphur trioxide on strong heating.

$$CuSO_4\ (s) \rightarrow CuO\ (s) + SO_3\ (g)$$

The sulphate is the most important copper (II) compound. It is used in electroplating, as a timber preservatives, in treating water, and in dyeing. Most of it is used as an agricultural fungicide, e.g., Bordeaux mixture ($CuSO_4$ and Ca $(OH)_2$) and Burgundy mixture ($CuSO_4$ and Na_2CO_3).

Reaction of copper (II) salts with potassium hexacyanoferrate II

Copper (II) sulphate solution form brown precipitate with potassium hexacyanoferrate (II)

Trial 64

A green powder was dissolved in dilute hydrochloric acid to form a green solution. The solution was divided into three parts.

(a) To the first portion of the solution was added a few drops of potassium hexacyanoferrate (II) solution. A brown precipitate was formed. Name the cation in the powder (1mark)
(b) To the second portion of the solution was added concentrated hydrochloric acid drop wise until in excess

- *(i) State what was observed*
- *(ii) Write an equation for the reaction that took place (1 ½ marks)*

(c) Magnesium powder was added to the third portion of the solution and the mixture warmed

- *(i) State what was observed*
- *(ii) Write an equation for the reaction that took place (1 ½ marks)*

Similarities between Ni and Cu

(i) Both have coordination number 4

(ii) Their hydrate salts react with acid due hydrolysis

(iii) Basic carbonates with formula $XCO_3.X(OH)_2$ are precipitate on heating their salts solution with sodium carbonate.

(iv) Both are catalyst

$$2CH_3OH \xrightarrow{Cu,\ 500^0C} 2HCHO(l) + 2H_2O\ (l)$$

$$CH_2{=}CH_2 + H_2 \xrightarrow{Ni,\ 140^0C} CH_3{-}CH_3$$

(v) Both exhibit bivalency

(vi) Both form colored compounds

(vii) Both form black sulphides

(viii) Both form complex compounds e.g. $[Cu(NH_3)_4]SO_4$ and $[Ni(NH_3)_6]SO_4$

(ix) Their carbonates and nitrates decompose on heating to oxides

(x) Both form double salts of the following composition, $MSO_4.(NH_4)_2SO_4.6H_2O$

Zinc and it compounds

Electron configuration

$[Ar]3d^{10}4s^2$

Zinc compounds are generally white because it has a full d- orbital. Also zinc is not a transition element because it has got a full d-orbital.

Trial 65

Explain the following observations

(a) Although zinc belongs to the d-block elements in the periodic Table, it does not behave as a typical transition element (3marks)

Occurrence and extraction of zinc

The principal ore of zinc is zinc blende, ZnS, which occurs in Australia, Canada and the U.S.A., although the metal is also extracted from calamine, $ZnCO_3$.

In the extraction of zinc, zinc blende is first concentrated by the flotation process (as in the extraction of copper). The concentrated ore is then roasted in air to convert it into the oxide:

$$2ZnS\,(s) + 3O_2\,(g) \rightarrow 2ZnO\,(s) + 2SO_2\,(g)$$

$$ZnCO_3\,(s) \rightarrow ZnO\,(s) + CO_2\,(g)$$

The sulphur dioxide is used to manufacture sulphuric acid. The zinc oxide is reduced by heating with coke. The zinc is led off as a vapor, which is then cooled.

$$ZnO\,(g) + C\,(g) \rightarrow Zn\,(g) + CO\,(g)$$

Redistillation is used to purify the zinc and 99.99 percent pure metal is available commercially. Where there are cheap supplies of electricity, zinc is also purified by electrolysis of zinc sulphate, the solution being made from zinc oxide and sulphuric acid.

Trial 66

(a) Name one ore of zinc and give its formula (2marks)

(b) (i) Describe briefly how the ore you named in (a) is concentrated (3marks)

(ii) What further treatment of the ore is required immediately after concentration (1mark)

(c) Outline the process, giving equations for the production of zinc metal from the treated ore (5marks)

(d) Zinc belongs to the d-block in the periodic Table yet it is not a transition element. Explain this statement (3marks)

(e) Zinc chloride readily dissolves in water to form a solution with pH less than 7. Give reason for this observation and write equation for the reaction that takes place (3marks)

(f) A piece of zinc metal was suspended in a solution of copper (II) sulphate in water. State what was observed and write an equation for the change that took place (3marks)

Trial 67

(a)(i) Write the formula and name of one ore of zinc (2marks)

(ii) Briefly describe how pure zinc can be obtained from the ore you have named in (i) (7marks)

(b)(i) Name one reagent that can be used to distinguish between zinc ions and aluminium ions in solution (1) [dilute ammonia]

(ii) State what would be observed when zinc and aluminium ions are separately treated with the reagent. Write equations for the reactions (5marks)

(iii)Explain how zinc protects iron from rusting (5marks)

Properties of zinc

Reaction of zinc with air

Hot zinc reacts with air to form yellow zinc oxide when hot and white when cold

$2Zn(s) + O_2(g) \rightarrow 2ZnO(s)$

Reaction of zinc with water

Zinc does not react with water due to insoluble protective layer of zinc oxide. However, with steam it reacts temporarily to form zinc oxide

$Zn(s) + H_2O(g) \rightarrow ZnO(s) + H_2(g)$

Reaction of zinc with Acids

The pure metal is resistant to attack by dilute non-oxidizing acids (e.g., HCl, H_2SO_4), since they exhibit a high over potential to discharge of hydrogen (this appears to be due to high activation energy). Concentrated sulphuric acid attacks the metal with formation of sulphur dioxide. Oxides of nitrogen are formed by the action of both dilute and concentrated nitric acid.

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$

Reaction of zinc with nonmetals

Nonmetals such as oxygen, sulphur and halogens combine with the metals on heating

$$2Zn(s) + O_2(g) \rightarrow 2ZnO(s)$$

Reaction of zinc with sodium hydroxide

Zinc reacts slowly with sodium hydroxide solution liberating hydrogen because it is amphoteric.

$$Zn\ (s) + 2\,^{-}OH\ (aq) + 2H_2O\ (l) \rightarrow Zn(OH)_4^{2-}\ (aq) + H_2\ (g)$$

Uses of zinc

Zinc is used as a protective coating for steel from rusting by forming a protective coat but it also reduces iron salt to iron in case the coat is cracked.

In galvanization, the steel is first cleaned by dipping it in sulphuric acid and then coated by dipping it in molten zinc or by electroplating.

Zinc is also used in alloys such as brass.

Trial 68

(a) Describe using equations the reaction of zinc with

- *(i) Air*
- *(ii) Water*
- *(iii) Sodium hydroxide (10marks)*

(b) (i) Explain why is not considered a typical transition metal (3marks)

(ii) State three ways in which the chemistry of zinc is similar to that of magnesium (3marks)

(c) (i) State what is observed when dilute aqueous ammonia is added drop wise to the solution containing zinc ions (2marks)

(ii) Write equation(s) for the reaction that take place in (c)(i) (2marks)

Zinc compounds

The only characteristic that zinc has in common with transition metals is its ability to form complexes. Otherwise, it is different from transitional metals in as far as they exhibit oxidation state of +2

Zinc oxide, ZnO

These oxides may be obtained by burning the metals in air or by the thermal decomposition of the carbonate or nitrate, e.g.

$$Zn\ CO_3\ (s) \rightarrow ZnO\ (s) + CO_2\ (g)$$

Zinc oxide is a white solid which turns reversibly yellow on heating.

Zinc oxide readily react with dilute acids to give salts.

$$ZnO\,(s) + 2H^{+}\,(aq) \rightarrow Zn^{2+}\,(aq) + H_2O\,(l)$$

Zinc oxide dissolves in sodium hydroxide.

$$ZnO\,(s) + 2^{-}OH\,(aq) + H_2O\,(l) \rightarrow Zn(OH)_4^{2-}\,(aq)$$

Uses of zinc oxide

Zinc oxide is used as a white pigment, as a filter in rubber and as a component in various glazes, enamel and antiseptic ointments.

In combination with chromium (III) oxide, it is used as a catalyst in manufacture of methanal from synthesis gas.

Zinc hydroxide, $Zn(OH)_2$

The hydroxide is obtained as gelatinous white solids when sodium hydroxide solution is added to aqueous solutions of zinc salts.

$$Zn^{2+}\,(aq) + 2^{-}OH\,(aq) \rightarrow Zn(OH)_2\,(s)$$

Zinc hydroxide is amphoteric like the oxide, thus it will react with both dilute acid and sodium hydroxide solution

$$Zn(OH)_2\,(s) + 2H^{+}(aq) \rightarrow Zn^{2+}\,(aq) + 2H_2O\,(l)$$

$$Zn(OH)_2\,(s) + 2^{-}OH\,_{(}aq) \rightarrow [Zn(OH)_4]^{2-}\,(aq)$$

Zinchydroxide readily dissolve in excess ammonia, forming amine complexes.

$$Zn(OH)_2\,(s) + 4NH_3\,(aq) \rightarrow [Zn(NH_3)_4]^{2+}\,(aq) + 2OH^{-}\,(aq)$$

Zinc sulphide, ZnS, and cadmium sulphide, CdS

Zinc sulphide occurs naturally as zinc blende. It can be formed by direct combination of heated metal and sulphur or by precipitation of the metal salts ions with hydrogen sulphide or ammonium sulphide.

$$Zn^{2+}\,(aq) + H_2S\,(g) \rightarrow ZnS\,(s)$$

Zinc sulphide, which is white readily dissolves in dilute hydrochloric acid.

Zinc sulphide is used in paint and, when impure, it is luminous.

Zinc chloride, $ZnCl_2$,

The anhydrous salt may be obtained by passing chlorine over the heated metal.

$$Zn (s) + Cl_2 (g) \rightarrow ZnCl_2 (g)$$

Zinc chloride is used as a wood preservative, as a catalyst or dehydrating agent in organic reactions.

Zinc sulphate, $ZnSO_4.7H_2O$

Zinc sulphate may be made by reacting its oxide, hydroxide or carbonate with dilute sulphuric acid followed by partial evaporation and crystallization; they are white solids.

Zinc sulphate is used in galvanizing iron and steel (the electrolytic process) and in the manufacture of lithopone, a white pigment:

$$ZnSO_4 (s) + BaS (s) \rightarrow \underbrace{\{BaSO_4 (s) + ZnS (s)\}}_{\text{lithopone}}$$

Zinc nitrate, $Zn (NO_3)_2.xH_2O$

It can be obtained by reacting its oxide, hydroxide or carbonate with nitric acid. Both It is very deliquescent and since it is soluble in ethanol it presumably possesses considerable covalent character. They decompose on heating into the metallic oxide, nitrogen dioxide and oxygen.

$$2Zn(NO_3)_2 (s) \rightarrow 2ZnO (s) + 4NO_2 (g) + O_2 (g)$$

Zinc carbonate, $ZnCO_3$

It is precipitate as white solids when hydrogen carbonate solution is added to an aqueous solution of the zinc salt, e.g.,

$$Zn^{2+} (aq) + 2HCO_3^- (aq) \rightarrow ZnCO_3 (s) + H_2O (l) + CO_2 (s)$$

Sodium carbonate which is more alkaline than the hydrogen carbonate precipitate basic carbonates.

$$2Zn^{2+} (aq) + 2CO_3^{2-} (aq) \rightarrow ZnO.ZnCO_3 (s) + CO_2 (s)$$

Complexes of Zn

Zinc forms many complexes, e.g., $[Zn(H_2O)_4]^{2+}$ (aq), and $[Zn(NH_3)_4]^{2+}$

Similarities between zinc and magnesium

- Both exhibit a valence of +2.
- Both react with air to form oxides
  $2Zn(s) + O_2(g) \rightarrow 2ZnO(s)$
- Both do not react with cold water but with steam to form oxides
  $Zn (s) + H_2O (aq) \rightarrow ZnO (s) + H_2 (g)$
- Their nitrate decompose into oxide nitrogen dioxide and oxide
  $2Zn(NO_3)_2 \rightarrow 2ZnO(s) + 4NO_2(g) + O_2(g)$
- Their carbonates decompose on heating into carbon dioxide
  $ZnCO_3(s) \rightarrow ZnO (s) + CO_2(g)$

Similarities between zinc and copper

(i) Both exhibit bivalency
(ii) Sulphide, phosphate and carbonates are insoluble
(iii) Their chloride and sulphates are soluble in water
(iv) Their carbonates and nitrates decompose on heating into oxides

$2Zn(NO_3)_2\ (s) \xrightarrow{heat} 2ZnO\ (s) + 4NO_2(g) + O_2(g)$

$CuCO3(s)\ (s) \xrightarrow{heat} CuO(s) + CO_2\ (g)$

(v) Both form complex compounds
$[Cu(NH_3)_4]SO_4$ and $[Zn(NH_3)_4]SO_4$

(vi) Both form double salts of the following composition;
$MSO_4.(NH_4)2SO_4.6H_2O$ where M = Cu or Zn

Thank you
Dr. Bbosa Science