TRANSITION ELEMENTS

Transition element:

Is an element that forms at least one stable ion with a partially filled d – orbital

Or

An element with a partially filled d – orbital in at least one of its stable oxidation states

This definition excludes elements such as zinc and scandium which although are d – block elements, they are not typically transition elements.

d – block element:

Is an element that has its highest energy electrons in the d –orbital

A table showing the d – block elements

Element	Symbol	Atomic number	Electronic configuration
Scandium	Sc	21	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$
Titanium	Ti	22	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$
Vanadium	V	23	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$
Chromium	Cr	24	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$
Manganese	Mn	25	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$
Iron	Fe	26	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
Cobalt	Co	27	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$
Nickel	Ni	28	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$
Copper	Cu	29	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$
Zinc	Zn	30	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$

Scandium is not transition because the stable ion of scandium, Sc^{3+}, has no electrons in the 3d sub-energy level.

Zinc is not transition because the stable ion of zinc, Zn^{2+}, has a fully filled 3d sub energy level.

Copper (I) does not exhibit transition properties because the copper(I) ion, Cu^{+}, has a fully filled 3d sub-energy level.

Periodic trends

1. Atomic radius

Elements	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic radius	1.44	1.32	1.22	1.17	1.17	1.16	1.16	1.15	1.17	1.25

The atomic radius decreases very slightly from scandium to nickel. This is because the increase in nuclear charge due addition of protons to the nuclei of the atoms is almost balanced by the increase in the screening effect due addition of electrons to the 3d sub energy level which is the penultimate energy level so that the increase in the nuclear charge is only very slight.

The slight increase in atomic from nickel to zinc is because the penultimate sub energy level is getting filled with electrons which increases the screening effect slightly more than increase in nuclear charge

***Qn:* Across the transition elements, atomic radius remains almost constant. Explain this observation**

Solution

Across the transition element series, the nuclear charge increases due to addition of a proton to atomic nucleus of each successive element. The electrons are added to the inner (penultimate) 3d sub-energy level, thus the screening effect increases. The increase in nuclear is balanced by the increase in screening effect. Thus nuclear attraction for the outermost electrons remains almost constant.

2. Melting points

Elements	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
M.P (°C)	1540	1680	1917	1890	1240	1535	1490	1452	1083	419

Generally, the melting points increase from scandium to vanadium and decrease from chromium to zinc.

From scandium to chromium, the number of unpaired 3d-orbital electrons that take part in metallic bonding increases, therefore the strength of the metallic bond increases resulting in increase in melting point.

From chromium to zinc, the number of unpaired 3d-electrons taking part in metallic boding decreases resulting into decrease the strength of metallic bond hence decrease in melting point from chromium to zinc.

Manganese and zinc have low melting point values than expected because of the half-filled and the fully filled 3d-orbitals are relatively stable and thus the electrons are not readily available for interatomic bonding.

Properties of transition elements

a. They are Paramagnetic

Atoms and cations of transition elements are weakly attracted into a magnetic field. The property arises because of the presence of unpaired electrons in the transition metal atoms and ions. These unpaired electron spin to generate a magnetic field that can be attracted by an external magnetic field.

The property increases with increase in the number of unpaired electrons.

Compounds of scandium and zinc are not paramagnetic because they don't have unpaired electrons and their magnetic moment is zero.

b. They have Catalytic activity

Transition metals and their compounds are used as catalysts. This is due to

- ✓ *Presence of partially filled d – orbitals* which allows the reacting particles to form partial bonds with them forming an unstable catalyst – reactant complexes that are more reactive.
- ✓ *Possession of variable oxidation states* which enables them to take part in electron transfer reactions.

These activated complexes can the react with each other to form the product which then leaves the catalyst.

c. They have variable oxidation states

Oxidation state*; Is the charge that an atom would have if all the bonds of the different elements in the compound were fully ionic.*

Or

The charge left on the central atom when all other atoms of the compound have been removed as ions

It can be negative, zero or positive.

Variable oxidation states are possible in these elements because

- ✓ Of the presence of empty orbitals and unpaired electrons

- ✓ The 3d and 4s – orbital electrons require little energy to promote in the empty orbitals to be used as valency electrons

d. They form coloured compounds and ions

The formation of coloured compounds and ions is associated with the presence of partially filled 3d – orbitals in the transition metal atoms and ions and the ability to promote electrons into these partially filled orbitals.

The energy used in the promotion of the electron is obtained by absorbing light of a particular wavelength hence colour.

The colour absorbed will be missing in the transmitted light, while the compound appears to have the colour of the light filtered through.

Cations with empty or fully filled 3d – orbitals do not possess colours because promotion of electrons is not possible.

e. They form interstitial compounds

Transition metals have metal lattices with spaces in between the atoms called *interstitial spaces.* These spaces can be occupied by atoms with small enough atomic radii such as carbon and nitrogen resulting into an *interstitial alloy* or *compound*. e.g. carbon steels are interstitial alloys.

f. They form complexes

Complex ion; *Is an ion consisting of a central metal ion datively bonded to electron rich molecules or ions called ligands.*

Formation of complexes is favoured by

- ✓ Availability of vacant or partially filled d – orbitals in the transition metal ions which can accommodate the lone pairs of electrons form the ligands
- ✓ Small ionic radius of the metal ions
- ✓ High charge of the metal ions.

High charge with small ionic radius gives the ion a high charge density resulting into strong attraction for the lone pairs of electrons on the ligands in order to form a stable complex.

The total number of ligands bonded to the central metal ion is called the *coordination number of the central metal ion*.

Nomenclature of complexes

1. The cation is always named first before the anion.
2. The names of the ligands come before the names of the central metal ion or atom
3. The number of ligands should be identified using prefixes such as di;- tri;- tetra;- penta;- hexa;- etc.
4. The names of anionic ligands end in *– o* for example
   Change the ending as follows
   -ide to ***-o***; ***-ate*** to ***-ato*** and ***-ite*** to ***–ito***

Ligand	Name	Ligand	Name
CN^-	Cyano	OH^-	Hydroxo
Br^-	bromo	Cl^-	Chloro
I^-	Iodo	F^-	fluoro
SO_4^{2-}	Sulphate	NO_3^-	Nitrato
NO_2^-	Nitrito	O^{2-}	Oxo

5. For neutral ligands, the common names are used with a few exceptions
   Common examples include

Ligand	Name	Ligand	Name
NH_3	Ammine	H_2O	Aqua
NO	Nitrosyl	CO	Carbonyl

6. In case there are more than one type of ligand, they are named as anionic ligands first and then neutral ligands. With each category if there is more than one type still, they are named inalphabetical order.
7. If the number prefix (di, tri, etc) is already used in the ligands, the prefix for the ligand then becomes bis;- tris;- tetrakis;- instead of di;- tri;- tetra;- etc.
8. Metals forming complex cations or neutral compounds are given their standard names.

9. Metals forming complex anions have their names changed ending in *–ate*. e.g.

   Ferrate for iron, *Cuprate* for copper, *Stannate* for tin, *Argentate* for silver

10. The oxidation number of the central metal atom or ion is written in Roman numerals in brackets immediately after its name.

Examples

$[Co(NH_3)_6]^{3+}$ is *hexaamminecobalt(III) ion*

$[Cu(NH_3)_4]^{2+}$ is *tetraamminecopper(II) ion*

$Ni(CO)_4$ is *tetracarbonylnickel(0) complex*

$[Zn(H_2O)_2(NH_3)_2]^{2+}$ is *diamminediaquazinc(II) ion*

$[PtCl_6]^{2-}$ is *hexachloroplatinate(II) ion*

$[Fe(CN)_6]^{3-}$ is *hexacyanoferrate(III) ion*

Hydrate (hydration) isomerism

The type of isomerism where the compounds differ in the number of water molecules directly bonded to the central metal ion.

For example, there are three isomers of the salt $CrCl_2.6H_2O$, hydrated chromium(III) chloride

$[Cr(H_2O)_6]Cl_3$ which is violet

$[Cr(H_2O)_5Cl]Cl_2.H_2O$ which is pale green

$[Cr(H_2O)_5Cl_2]Cl.2H_2O$ which is dark green.

If excess silver nitrate solution is added separately to each of the solutions of the above isomers:

- Isomer 1 gives three moles of silver chloride
- Isomer 2 gives two moles of silver chloride
- Isomer 3 gives one mole of silver chloride.

This is due to the difference in the number of chloride ions that are exchanged with the molecules in the complex compound.

Chemistry of the individual elements

1. Titanium

Reactions of titanium

a. With air

Heated titanium burns in oxygen to form titanium(IV) oxide

$$Ti(s) \;+\; O_2(g) \rightarrow \; TiO_2(s)$$

b. With chlorine

Heated titanium burns in dry chlorine to form titanium(IV) chloride

$$Ti(s) \;+\; 2Cl_2(g) \rightarrow \; TiCl_4(s)$$

c. With acids

Titanium is oxidized by hot concentrated sulphuric acid to titanium(IV) sulphate and the acid reduced to sulphur dioxide and water.

$$2Ti(s) + \; 6H_2SO_4(l) \rightarrow Ti_2(SO_4)_3(aq) \;+\; 3SO_2(g) \;+\; 6H_2O(l)$$

Compounds of titanium

Titanium forms compounds in which it shows +2; +3; and +4 oxidation states.

The +2 oxidation state is unstable and uncommon.

In the +3 oxidation state, titanium still has one electron in the 3d-orbital and because of this titanium(III) compounds are coloured are paramagnetic

In the +4 oxidation state, titanium has lost all the electrons in the 3d-orbital. Thus, titanium(IV) compounds are neither coloured nor paramagnetic.

Titanium(iv) compounds

Titanium(IV) chloride

This can be prepared by heating titanium in a stream of dry chlorine.

$$Ti(s) + 2Cl_2(g) \rightarrow TiCl_4(l)$$

It is a colourless fuming liquid that is readily hydrolysed in water.

$$TiCl_4(l) + 2H_2O(l) \rightarrow TiO_2(s) + 4HCl(g)$$

Question

(a) Write the electronic configuration of titanium (atomic number 22)

(b) Describe the reaction of titanium with

  (i) Air

  (ii) Chlorine

  (iii) Sulphuric acid

(c) Water was added to titanium(IV) chloride, state what was observed and write equation for the reaction

(d) Titanium(III) chloride is violet while titanium(IV) chloride is colourless. Explain the observation.

2. Vanadium

Reactions of vanadium

a. With chlorine

Heated vanadium reacts with chlorine to form vanadium(IV) chloride, a dark red covalent liquid

$$V(s) + \quad + 2Cl_2(g) \rightarrow VCl_4(l)$$

b. With air

Heated vanadium reacts with air to form vanandium(V) oxide, an orange solid

$$4V(s) + 5O_2(g) \rightarrow 2V_2O_5(s)$$

Compounds of vanadium

Vanadium forms compounds in the +2, +3, +4, and +5 oxidation states. The +4 is the most stable oxidation state. As with all the transition elements, the covalent character of the compounds increases with increasing oxidation number.

All the oxidation states of vanadium can be observed in the aqueous species formed when a solution of ammonium vanadate(V) is treated with dilute sulphuric acid and zinc metal.

$$VO_4^{3-}(aq) + 4H^+(aq) \rightarrow VO_2^+(aq) + 2H_2O(l)$$

$$2VO_2^+(aq) + 4H^+(aq) + Zn(s) \rightarrow 2VO^{2+}(aq) + Zn^{2+}(aq) + 2H_2O(l)$$

$$2VO^{2+}(aq) + 4H^+(aq) + Zn(s) \rightarrow 2V^{3+}(aq) + Zn^{2+}(aq) + 2H_2O(l)$$

$$2V^{3+}(aq) + Zn(s) \rightarrow 2V^{2+}(aq) + Zn^{2+}(aq)$$

Summary of the colour changes

Species	VO_2^+	VO^{2+}	V^{3+}	V^{2+}
Oxidation state	+5	+4	+3	+2
Colour	Yellow	Blue	Green	Violet

3. Chromium

Reactions of chromium

a. With air

Heated chromium reacts with air to form chromium(III) oxide

$$4Cr(s) + 3O_2(g) \rightarrow 2Cr_2O_3(s)$$

b. With water

Heated chromium reacts with steam to form chromium(III) oxide and hydrogen gas

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

c. With chlorine

Heated chromium reacts with dry chlorine to form chromium(III) chloride

$$2Cr(s) + \quad 3Cl_2(g) \rightarrow \quad 2CrCl_3(s)$$

d. With alkalis

Chromium reacts with hot concentrated sodium hydroxide solution forming a green solution of sodium chromate(III) and hydrogen gas

$$2Cr(s) \ + 2\bar{O}H \quad + \quad 2H_2O(l) \rightarrow 2CrO_2^-(aq) \quad + \quad 3H_2(g)$$

Or

$$2Cr(s) \ + 2\bar{O}H \quad + \quad 6H_2O(l) \rightarrow 2[Cr(OH)_4]^-(aq) \quad + \quad 3H_2(g)$$

e. With hydrogen chloride

Heated chromium reacts with dry hydrogen chloride gas to form chromium(II) chloride

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

f. With acids

Chromium reacts with warm dilute sulphuric and hydrochloric acids to give the corresponding chromium(II) salts and hydrogen gas

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

Chromium is oxidized by hot concentrated sulphuric acid to chromium(III) sulphate and the acid reduced to sulphur dioxide and water

$$2Cr(s) + \quad 6H_2SO_4(l) \rightarrow Cr_2(SO_4)_3(aq) \quad + \quad 3SO_2(g) + \quad 6H_2O(l)$$

Chromium is *rendered passive* by concentrated nitric acid

Compounds of chromium

Chromium forms compounds in the +2, +3, and +6 oxidation stated. The +3 oxidation state is the most stable.

Chromium(II) compounds

Compounds of chromium in this oxidation state are very unstable and strong reducing agents being converted into the more stable chromium(III) compounds

$$Cr^{2+}(aq) \rightarrow Cr^{3+}(aq) \quad + \quad e^-$$

Oxidizing agents like chlorine can oxidisechromium(II) to chromium(III)

$$2Cr^{2+}(aq) \quad + \quad Cl_2(g) \rightarrow 2Cr^{3+}(aq) \quad + \quad 2Cl^-(aq)$$

Chromium(II) chloride

It's a white solid prepared by heating chromium metal in dry hydrogen chloride

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

Chromium(II) hydroxide

It's a yellow solid precipitates when a little alkali is added to t solution of chromium(II) salt

$$Cr^{2+}(aq) \quad + \quad 2\bar{O}H(aq) \rightarrow \quad Cr(OH)_2(s)$$

Chromium(III) compounds

Chromium(III) oxide

It is a green ionic and amphoteric solid that can be obtained by

- ✓ Heating chromium in air

$$4Cr(s) \; + \; 3O_2(g) \rightarrow \quad 2Cr_2O_3(s)$$

- ✓ Heating chromium(III) hydroxide

$$2Cr(OH)_3(s) \rightarrow Cr_2O_3(s) \quad + \quad 3H_2O(l)$$

✓ Heating ammonium dichromate

$$(NH_4)_2Cr_2O_7(s) \rightarrow Cr_2O_3(s) \quad + \quad N_2(g) \quad + \quad 4H_2O(l)$$

It reacts with acids to form corresponding chromium(III) salts

$$Cr_2O_3(s) \quad + \quad 6H^+(aq) \rightarrow \quad 2Cr^{3+}(aq) \quad + \quad 3H_2O(l)$$

It reacts with hot concentrated alkalis to give chromate(VI) salts

$$Cr_2O_3(s) \quad + \quad 2\bar{O}H(aq) \quad + \quad 3H_2O(l) \quad \rightarrow \quad 2Cr(OH)_4^-(aq)$$

Or

$$Cr_2O_3(s) \quad + \quad 2\bar{O}H(aq) \rightarrow \quad 2CrO_2^-(aq) \quad + \quad H_2O(l)$$

When heated aluminium, it is reduced to chromium

$$Cr_2O_3(s) \quad + \quad 2Al(s) \rightarrow Al_2O_3(s) \quad + \quad 2Cr(s)$$

Chromium(III) hydroxide

It is a green amphoteric solid formed by precipitation when a little alkali is addedto a solution chromium(III) salt

$$Cr^{3+}(aq) \quad + \quad 3\bar{O}H(aq) \rightarrow \quad Cr(OH)_3(s)$$

It reacts with dilute acids to form chromium(III) salts

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

It reacts with alkalis to form chromate(III) salts

$$Cr(OH)_3(s) \quad + \quad \bar{O}H(aq) \rightarrow \quad Cr(OH)_4^-(aq)$$

Or

$$2Cr(OH)_3(s) \quad + \quad 2\bar{O}H(aq) \rightarrow \quad 2\,CrO_2^-(aq) \quad + \quad 4H_2O(l)$$

Chromium(III) salts

These are generally prepared by reacting chromium(III) oxide or hydroxide with acids.

Solutions of chromium(III) salts are acidic. This is because of hydrolysis of the hydrated chromium(III) cation.

The chromium(III) cation has a high charge density thus becomes heavily hydrated in solution. The coordinating water molecules are polarized weakening the oxygen-hydrogen bond so that the proton can easily be lost to the solution, making it acidic.

$$[Cr(H_2O)_6]^{3+}(aq) \quad \leftrightharpoons \quad [Cr(H_2O)_5(OH)]^{2+}(aq) \quad + \quad H^+(aq)$$

Chromium(VI) compounds

Chromium(VI) oxide, CrO_3

Chromium(VI) oxide is a dark red that can be prepared by adding concentrated sulphuric acid to a saturated solution of potassium dichromate

$$Cr_2O_7^{2-}(aq) \quad + \quad 2H^+(aq) \rightarrow \quad 2CrO_3(s) \quad + \quad H_2O(l)$$

When heated it decomposes to give chromium(III) oxide and oxygen gas

$$4CrO_3(s) \rightarrow \quad 2Cr_2O_3(s) \quad + \quad 3O_2(g)$$

It is an acidic oxide that dissolves in water to form chromic(VI) acid

$$CrO_3(s) \quad + \quad H_2O(l) \rightarrow H_2CrO_4(l)$$

It also reacts with alkalis to form chromates(VI)

$$CrO_3(s) \quad + \quad 2\bar{O}H(aq) \rightarrow CrO_4^{2-}(aq) \quad + \quad H_2O(l)$$

Chromates(VI)

These are salts derived from chromic(VI) acid. They are generally insoluble in water except sodium, potassium and ammonium chromates

The insoluble chromates can be prepared by precipitation reactions.

$$Ba^{2+}(aq) \quad + \quad CrO_4^{2-}(aq) \rightarrow BaCrO_4(s)$$

$$Pb^{2+}(aq) \quad + \quad CrO_4^{2-}(aq) \rightarrow PbCrO_4(s)$$

$$Ag^{+}(aq) \quad + \quad CrO_4^{2-}(aq) \rightarrow Ag_2CrO_4(s)$$

All the above chromates are yellow except silver chromate which is a dark red solid.

The chromate ions has a tetrahedral structure

Chromates are only stable in alkaline medium. In acidic medium, they convert to dichromates

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

Dichromtes(VI)

These are orange coloured salts containing the dichromate ion, $Cr_2O_7^{2-}$

In solution, dichromates can be obtained by adding dilute sulphuric acid to a solution of a chromate

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

Dichromates are only stable in acidic medium and in alkaline medium they convert to chromates

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

Potassium dichromate(VI) is used as an oxidizing agent in volumetric analysis and organic syntheses

Dichromate(VI) ions are strong oxidizing agents in acid medium

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

However, they are not strong enough to oxidise chlorides to chlorine therefore they can be used in the presence of hydrochloric acid unlike manganate(VII)

Examples:

(a) Oxidation of iron(II) to iron(III)

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

Observation

The orange solution turns green

(b) Oxidation of iodide ions to iodine

$$6I^-(aq) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow \quad 3I_2(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$$

Observation

The colourless solution (of potassium iodide) turns brown

(c) Oxidation of hydrogen sulphide to sulphur

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

Observation

The orange solution turns green, and a yellow precipitate is formed

(d) Oxidation of sulphur dioxide to a sulphate

$$3SO_2(g) + Cr_2O_7^{2-}(aq) + 2H^+(aq) \rightarrow 3SO_4^{2-}(aq) + 2Cr^{3+}(aq) + H_2O(l)$$

Observation

The orange solution turns green

(e) Oxidation of sulphites to sulphates

$$3SO_3^{2-}(g) + Cr_2O_7^{2-}(aq) + 8H^+(aq) \rightarrow 3SO_4^{2-}(aq) + 2Cr^{3+}(aq) + 4H_2O(l)$$

Observation

The orange solution turns green

(f) *Oxidation of tin(II) to tin(VI)*

$$3Sn^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 3Sn^{4+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$$

Observation

The orange solution turns green

Qualitative analysis of Cr^{3+}

1. *Sodium carbonate solution*

Observation

A green solid and bubbles (effervescence) of a colourless gas

Equation

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

2. *Sodium hydroxide solution*

Observation

A green precipitate soluble in excess to form a green solution

Equation

$$Cr^{3+}(aq) \;+\; 3\bar{O}H(aq) \rightarrow Cr(OH)_3(s)$$

$$Cr(OH)_3(s) \;+\; \bar{O}H(aq) \rightarrow Cr(OH)_4^-(aq)$$

3. *Ammonia solution*

Observation

A green precipitate insoluble in excess

Equation

$$Cr^{3+}(aq) \;+\; 3\bar{O}H(aq) \rightarrow \; Cr(OH)_3(s)$$

4. *Sodium hydroxide and hydrogen peroxide*

   Observation

   A yellow solution on warming

   Equation

$$2Cr^{3+}(aq) \;+\; 10\bar{O}H(aq) \;+\; 3H_2O_2(aq) \rightarrow 2CrO_4^{2-}(aq) \;+\; 8H_2O(l)$$

5. *Sodium hydroxide, hydrogen peroxide, butanoland dilute sulphuric acid*

   Observation

   A blue solution in the organic layer

   Equations

$$2Cr^{3+}(aq) \;+\; 10\bar{O}H(aq) \;+\; 3H_2O_2(aq) \rightarrow 2CrO_4^{2-}(aq) \;+\; 8H_2O(l)$$

$$CrO_4^{2-}(aq) \;+\; H_2O_2(aq) \;+\; 2H^+(aq) \;\rightarrow CrO_5(aq) \;+\; H_2O(l)$$

4. Manganese

Reactions of manganese

a. *With air*

   Heated manganese burns in air to form a mixture of trimanganesetetraoxide.

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

b. *With water*

Heated manganese reacts with steam to form trimanganesetetraoxide and hydrogen gas

$$3Mn(s) \quad + \quad 4H_2O(g) \rightarrow Mn_3O_4(s) \quad + \quad 4H_2(g)$$

c. *With acids*

Manganese reacts rapidly with cold dilute hydrochloric acid and sulphuric acid to form the corresponding manganese(II) salt and hydrogen gas

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

Manganese reacts with cold dilute nitric acid to form manganese(II) nitrate, nitrogen monoxide and water

$$3Mn(s) \quad + \quad 8HNO_3(aq) \rightarrow \quad 3Mn(NO_3)_2(aq) \quad + \quad 2NO(g) \quad + \quad 24O(l)$$

Manganese is oxidized by hot concentrated sulphuric acid to manganese(II) sulphate and the acid reduced to sulphur dioxide and water

$$Mn(s) \quad + \quad 2H_2SO_4(aq) \rightarrow \quad MnSO_4(aq) \quad + \quad 2SO_2(g) \quad + \quad 2H_2O(l)$$

Manganese is oxidized by cold concentrated nitric acid to manganese(II) nitrate and the acid reduced to nitrogen dioxide and water

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

d. *Chlorine*

Heated manganese reacts chlorine to form manganese(II) chloride

$$Mn(s) \quad + \quad Cl_2(g) \rightarrow \quad MnCl_2(s)$$

Compounds of manganese

Manganese exhibits oxidation states of +2, +3, +4, +6 and +7 in various compounds.

In the +2 oxidation state, the two 4s electrons are lost, leaving a half-filled 3d orbital which is stable. This makes the +2 oxidation state the most stable oxidation state of manganese

Manganese(II) compounds

Manganese(II) oxide, MnO

It's a green solid obtained by heating manganese(II) hydroxide, manganese(II) carbonate or manganese(II) oxalate in absence of air to prevent further oxidation

$$Mn(OH)_2(s) \rightarrow MnO(s) + H_2O(l)$$

$$MnCO_3(s) \rightarrow MnO(s) + CO_2(g)$$

$$MnC_2O_4(s) \rightarrow MnO(s) + CO_2(g) + CO(g)$$

It is a basic oxide, dissolving in acids to form manganese(II) salts

$$MnO(s) + 2H^+(aq) \rightarrow Mn^{2+}(aq) + H_2O(l)$$

Manganese(II) hydroxide $Mn(OH)_2$

It can be obtained as a white precipitate when sodium hydroxide or ammonia solution is added to a solution of o manganese()II salt

$$Mn^{2+}(aq) + 2\bar{O}H(aq) \rightarrow Mn(OH)_2(s)$$

The white precipitate turns brown due to oxidation by oxygen from air to form hydrated manganese(IV) oxide

$$2Mn(OH)_2(s) + O_2(g) \rightarrow 2MnO_2.H_2O(s)$$

Note: *hydrated manganese(IV) oxide is brown while anhydrous manganese(IV) oxide is black*

Manganese(II) salts

Most manganese(II) salts are pink. Manganese(II) carbonate is red

Manganese(II) chloride crystals ($MnCl_2.4H_2O$) can be obtained by heating manganese(IV) oxide with concentrated hydrochloric acid.

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

The pink crystals form from the solution on cooling

Manganese(II) sulphate crystals ($MnSO_4.5H_2O$) can be obtained by heating manganese(IV) oxide with concentrated sulphuric acid

$$2MnO_2(s) + 2H_2SO_4(aq) \rightarrow 2MnSO_4(aq) + O_2(g) + 2H_2O(l)$$

The pink crystals form from the solution on cooling

Manganese(II) nitrate can be obtained by reacting dilute nitric acid and manganese(II) carbonate followed by crystallization.

$$MnCO_3(s) + 2HNO_3(aq) \rightarrow Mn(NO_3)_2 + CO_2(g) + H_2O(l)$$

Manganese(II) carbonate can be obtained by adding sodium hydrogen carbonate to a solution of manganese(II) salt.

$$Mn^{2+}(aq) + 2HCO_3^-(aq) \rightarrow MnCO_3(s) + CO_2(g) + H_2O(l)$$

Manganese(III) compounds

Compounds of manganese in this state are uncommon because of disproportionation

$$2Mn^{3+}(aq) + 2H_2O(l) \rightarrow Mn^{2+}(aq) + MnO_2(s) + 4H^+(aq)$$

Manganese(IV) compounds

Manganese(IV) oxide, MnO_2

Anhydrous manganese(IV) oxide is a black solid that can be prepared by heating manganese(II) nitrate

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

It can also be prepared by oxidation of manganese(II) salts using sodium hypochlorite and sodium hydroxide

$$Mn^{2+}(aq) + OCl^-(aq) + 2\bar{O}H(aq) \rightarrow MnO_2(s) + Cl^-(aq) + H_2O(l)$$

- ✓ Manganese(IV) oxide is essentially ionic and amphoteric. It dissolves in cold concentrated hydrochloric acid to form *hexachloromanganate(IV) complex*

$$MnO_2(s) \quad + \quad 4H^+ \quad + \quad 6Cl^-(aq) \rightarrow MnCl_6^{2-}(aq) \quad + \quad 2H_2O(l)$$

- ✓ Manganese(IV) oxide oxidizes hot concentrated hydrochloric acid to chlorine

$$MnO_2(s) \quad + \quad 4HCl(aq) \rightarrow MnCl_2(aq) \ + \ CL_2(g) \quad + \quad 2H_2O(l)$$

- ✓ Manganese(IV) oxide reacts with hot concentrated sulphuric acid to liberate oxygen

$$2MnO_2(s) \quad + \quad 2H_2SO_4(l) \rightarrow 2MnSO_4(aq) \quad + \quad O_2(g) \quad + \quad 2H_2O(l)$$

- ✓ Manganese(IV) oxide oxidizes oxalates to carbon dioxide in acidic medium

$$MnO_2(s) \quad + \quad C_2O_4^{2-}(aq) + \quad 4H^+(aq) \rightarrow Mn^{2+}(aq) \quad + \quad 2CO_2(g) \quad + \quad H_2O(l)$$

Determination of the percentage of manganese(IV) oxide the pyrulosite

- A known mass for pyrulosite (ore) is dissolved in excess hot concentrated hydrochloric acid
- Manganese(IV) oxide reacts with hydrochloric acid to liberate chlorine

$$MnO_2(s) \quad + \quad 4HCl(aq) \rightarrow MnCl_2(aq) \ + \quad Cl_2(g) \quad + \quad 2H_2O(l)$$

- The chlorine liberated is bubbled through excess potassium iodie solution to liberate iodine

$$Cl_2(g) \quad + \quad 2I^-(aq) \rightarrow I_2(aq) \ + \quad 2Cl^-(aq)$$

- A known volume of the solution containing the liberated iodine is then titrated with a standard solution of sodium thiosulphate using starch indicator

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

- The mass of manganese(IV) oxide is calculated and the percentage of the ore calculated as

$$Percentage\ of\ manganese(IV)oxide = \frac{mass\ of\ manganese(IV)oxide}{mass\ of\ the\ ore}$$

Manganese(VI) compounds

Sodium and potassium maganate(IV) are dark green crystals. Potassium manganate(VI) can be obtained by fusing potassium hydroxide with manganese(IV) oxide in the presence of excess oxygen.

$$2MnO_2(s) + 4KOH(s) + O_2(g) \rightarrow 2K_2MnO_4(s) + 2H_2O(l)$$

Manganate(VI) is only stable in alkaline medium. In acidic or neutral medium, it undergoes disproportionation

$$3MnO_4^{2-}(aq) + 4H^+ \rightarrow 2MnO_4^-(aq) + MnO_2\ (s) + 2H_2O(l)$$

Or

$$3MnO_4^{2-}(aq) + 2H_2O(l) \rightarrow 2MnO_4^-(aq) + MnO_2\ (s) + 4\bar{O}H(aq)$$

Even bubbling carbon dioxide through a solution of manganate(VI) causes the colour of the solution to change from green to purple with formation of a black solid

$$3MnO_4^{2-}(aq) + 2CO_2(g) \rightarrow 2MnO_4^-(aq) + MnO_2\ (s) + 2CO_3^{2-}(aq)$$

Manganese(VII) compounds

Potassium manganate(VII) is the most important compound manganese in the +7 oxidation state.

It is dark purple crystalline compound soluble in water forming a purple solution.

It is used in the laboratory for preparation of chlorine gas and testing for the presence of sulphur dioxide, unsaturated hydrocarbons and hydrogen sulphide

It is used in volumetric analysis and organic chemistry as an oxidizing agent

It can be used in neutral, alkaline and acidic medium. Only sulphuric acid is used to acidify potassium manganate(VII).

Nitric acid is not used because it is also an oxidizing agent hence will compete with potassium during the reaction.

Hydrochloric acid is not used because it is easily oxidized to chlorine by potassium manganate(VII)

$$2MnO_4^-(aq) + 16H^+(aq) + 10Cl^-(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5Cl_2(g)$$

Advantages of using potassium permanganate in volumetric analysis

- It acts as a its own indicator
- It a high formula mass which minimizes the weighing errors
- It is highly soluble in water
- Most of its reaction can occur fast enough at room temperature
- It oxidizes a wide range of substances

Why potassium manganate(VII) is not used as a primary

- it always found contaminated with manganese(VI) oxide
- It is not highly stable. In light, a solution of acidified potassium manganate(VII) will decompose to form manganese(IV) oxide

$$4MnO_4^-(aq) + 4H^+(aq) \rightarrow 2MnO_2(s) + 2H_2O(l) + 3O_2(g)$$

Even in alkaline medium, decomposition will occur as follows

$$4MnO_4^-(aq) + 2H_2O(l) \rightarrow 4MnO_2(s) + 4\bar{O}H(aq) + 3O_2(g)$$

Oxidizing properties potassium manganate(VII)

In neutral or slightly alkaline mediummanganate(VII) is reduced to manganese(IV) oxide

$$MnO_4^-(aq) + 2H_2O(l) + 3e^- \rightarrow MnO_2(s) + 4\bar{O}H(aq)$$

For example, oxidation of iodide to iodate

$$I^-(aq) + 6\bar{O}H(aq) \rightarrow IO_3^-(aq) + 3H_2O(l) + 6e^-$$

Overall equation

$$2MnO_4^-(aq) + H_2O(l) + I^-(aq) \rightarrow MnO_2(s) + 2\bar{O}H(aq) + IO_3^-(aq)$$

In strongly *alkaline* medium, manganate(VII) is reduced to green manganate(VI)

$$MnO_4^-(aq) + e^- \rightarrow MnO_4^{2-}(aq)$$

In strongly *acidic* medium, manganate(VII) is reduced to manganese(II) ions. Unless stated, the solution turns from *purple* to *colourless*

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

Examples

a. *Oxidation of nitrites to nitrates*

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

b. *Oxidation of hydrogen peroxide to oxygen*

$$2MnO_4^-(aq) + 16H^+ + 5H_2O_2(l) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5O_2(g)$$

c. *Oxidation of tin(II) to tin(IV)*

$$2MnO_4^-(aq) + 16H^+ + 5Sn^{2+}(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5Sn^{4+}(aq)$$

d. *Oxidation of iron(II) to iron(III)*

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

Observation

The solution turns from purple to brown

e. *Oxidation of hydrogen sulphide to sulphur*

$$2MnO_4^-(aq) + 16H^+ + 5S^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5S(s)$$

Observation

The solution turns from purple to colourless with formation of a yellow deposit (solid)

Qualitative analysis of Mn^{2+}

1. *Sodium carbonate solution*

Observation

A brown precipitate that rapidly turns brown on standing. (This is due to aerial oxidation of manganese(II) hydroxide to hydrated manganese(IV) oxide)

Equations

$$Mn^{2+}(aq) \ + \ 2\bar{O}H(aq) \rightarrow \ Mn(OH)_2(s)$$

$$2Mn(OH)_2(s) \ + \ O_2(g) \rightarrow \ 2MnO_2.H_2O(s)$$

2. *Ammonia solution*

Observation

A brown precipitate that rapidly turns brown on standing. (This is due to aerial oxidation of manganese(II) hydroxide to hydrated manganese(IV) oxide)

Equations

$$Mn^{2+}(aq) \ + \ 2\bar{O}H(aq) \rightarrow \ Mn(OH)_2(s)$$

$$2Mn(OH)_2(s) \ + \ O_2(g) \rightarrow \ 2MnO_2.H_2O(s)$$

3. *Conc. Nitric acid and solid sodium bismuthate*

Observation

A purple solution is formed.

(Manganese(II) ions are oxidized to manganate(VII) ions by sodium bismuthate in acidic medium)

Equation

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

4. *Conc. Nitric acid and solid lead(IV) oxide and warm*

Observation

A purple solution is formed.

(Manganese(II) ions are oxidized to manganate(VII) ions by lead(IV) oxide in acidic medium)

Equation

$$2Mn^{2+}(aq) + 5PbO_2(s) + 4H^+(aq) \rightarrow 2MnO_4^-(aq) + 5Bi^{3+}(aq) + 2H_2O(l)$$

5. Iron

Extraction of iron

The chief ore from which iron is extracted is *haematite* Fe_2O_3.

The other ores of iron are

- Magnetite, Fe_3O_4 (concentrated by use a magnetic field)
- Iron pyrites FeS_2 (concentrated by froth flotation method)
- Siderite or spathic iron $FeCO_3$ (concentrated by roasting in air)

Extraction of iron from haematite

The iron ore is crushed into small particles which are roasted in air to drive out water and other volatile impurities as well as oxidizing iron(II) oxide to iron(III) oxide.

However, the roasted ore contains non-volatile impurities such as silicon(IV) oxide (silica)as the major impurity.

A mixture of the roasted ore, coke (carbon) and limestone (calcium carbonate) are fed into the blast furnace from the top.

Hot compressed air is driven into the furnace from the bottom.

Coke burns in the hot air to form carbon dioxide

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

As the carbon dioxide rises up the furnace, it is reduced by the unburnt coke to carbon monoxide

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

The carbon monoxide then reduces the iron ore to molten iron in the upper parts of the furnace.

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

Limestone decomposes to calcium oxide and carbon dioxide

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

Calcium oxide reacts with silicon(IV) oxide to form molten slag of calcium silicate.

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

NB: *extraction of iron from other sources such as* ***iron pyrites*** *and* ***spathic iron/ siderite*** *should also be considered*

Reaction of iron

a. **With water**

Heated iron reacts with steam to form triirontetraoxide and hydrogen gas

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

b. **With air**

Heated iron reacts with air to form triirontetraoxide

$$3Fe(s) \quad + \quad 2O_2(g) \quad \leftrightharpoons \quad Fe_3O_4(s)$$

c. **With acids**

i. ***Dilute acids***

Iron reacts with cold dilute sulphuric and hydrochloric acids to form hydrogen gas the corresponding iron(II) salt.

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

Iron reacts with dilute nitric acid to form a mixture of products.

$$4Fe(s) \quad + \quad 10HNO_3(aq) \rightarrow \quad 4Fe(NO_3)_2 \quad + \quad NH_4NO_3(aq) \quad + \quad 3H_2O(l)$$

ii. ***Concentrated acids***

Hotconcentrated sulphuric acid oxidizes iron to iron(III) sulphate and the acid is reduced to sulphur dioxide and water

$$2Fe(s) \quad + \quad 6H_2SO_4(l) \rightarrow Fe_2(SO_4)_3(aq) \quad + \quad 3SO_2(g) \quad + \quad 6H_2O(l)$$

Concentrated nitric acid renders iron passive.

d. With sulphur

When a mixture of iron and sulphur is heated, a red glow is observed leading to the formation of a black solid

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

e. With chlorine

Heated iron reacts with dry chlorine to form iron(III) chloride

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

f. With hydrogen chloride

Heated iron reacts with dry hydrogen chloride gas to form iron(II) chloride and hydrogen gas

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

Compounds of iron

The principal oxidation states of iron are +2 and +3. The loss of two electrons from the 4s orbital gives iron(II) ion, Fe^{2+}, while the loss of two electrons from the 4s and one electron from the 3d orbital gives iron(III) ion.

Because the 3d orbital is half filled, the iron(III) ion and the compounds of iron(III) are more stable than the iron(II) ion and the iron(II) compounds. This explains why iron(II) compounds are easily oxidized to iron(III) compounds.

Iron(II) compounds

Iron(II) oxide

It is a black solid that can be obtained by heating iron(II) oxalate in the absence of air.

$$FeC_2O_4(s) \rightarrow \ FeO(s) \quad + \quad CO(g) \quad + \quad CO_2(g)$$

It is a basic solid that readily reacts with dilute acids to formiron(II) salts and water

$$FeO(s) \quad + \quad 2H^+(aq) \rightarrow Fe^{2+}(aq) \quad + \quad H_2O(l)$$

Iron(II) hydroxide

It is obtained as a green precipitate by adding an alkali such as sodium hydroxide solution to a solution of iron(II) salt.

$$Fe^{2+}(aq) \quad + \quad 2\bar{O}H(aq) \rightarrow \quad Fe(OH)_2(s)$$

It is basic and reacts with dilute acids to form iron(II) salts and water

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

Iron(II) chloride

Anhydrous iron(II) chloride is pale yellow solid prepared by heating iron in a stream of dry hydrogen chloride gas.

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

Hydrated iron(II) chloride is obtained by crystallization method. It occurs as a pale green solid.

Iron(II) sulphate-7-water

In the laboratory, it is prepared by the action of dilute sulphuric acid on iron filings and crystallizing the salt from the solution.

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

$$FeSO_4(aq) \quad + \quad 7H_2O(l) \rightarrow \quad FeSO_4.7H_2O(s)$$

Hydrated iron(II) sulphate decomposes when heated, first to white anhydrous iron(II) sulphate.

$$FeSO_4.7H_2O(s) \rightarrow \quad FeSO_4(s) \quad + \quad 7H_2O(l)$$

On strong heating, it decomposes to iron(III) oxide (brown), sulphur dioxide and sulphur trioxide (which appear as white fumes)

$$2FeSO_4(s) \rightarrow Fe_2O_3(s) \quad + \quad SO_2(g) \quad + \quad SO_3(g)$$

Iron(III) compounds

Iron(III) oxide

It occurs as haematite in nature

In the laboratory, it can be obtained by heating

- Iron(II) sulphate

$$2FeSO_4(s) \rightarrow Fe_2O_3(s) \quad + \quad SO_2(g) \quad + \quad SO_3(g)$$

- Iron(III) hydroxide

$$2Fe(OH)_3(s) \rightarrow Fe_2O_3(s) \quad + \quad 3H_2O(l)$$

It is basic and readily reacts with hot dilute acids to form iron(III) salts and water

$$Fe_2O_3(s) \quad + \quad 6H^+(aq) \rightarrow \quad 2Fe^{3+}(aq) \quad + \quad 3H_2O(l)$$

Iron(III) hydroxide

It precipitated as a brown solid when an alkali such as sodium hydroxide is added to an aqueous solution of iron(III) salt.

$$Fe^{3+}(aq) \quad + \quad 3\bar{O}H(aq) \rightarrow \quad Fe(OH)_3(s)$$

It is basic and reacts with dilute acids to form iron(III) salts and water

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

Iron(III) chloride

Anhydrous iron(III) chloride is prepared as a black sublimate by passing dry chlorine over heated iron wire.

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

It is a covalent solid which exists as a dimer,Fe_2Cl_6, in the vapour phase.

Hydrolysis of iron(III) salts in water

Solutions of iron(III) salts are acidic. This is because of hydrolysis of the hydrated iron(III) cation.

The iron(III) cation has a high charge density thus becomes heavily hydrated in solution. The coordinating water molecules are polarized weakening the oxygen-hydrogen bond so that the proton can easily be lost to the solution, making it acidic.

$$[Fe(H_2O)_6]^{3+}(aq) \quad \leftrightharpoons \quad [Fe(H_2O)_5(OH)]^{2+}(aq) \quad + \quad H^+(aq)$$

Fe^{2+}toFe^{3+}conversions

The green solutions turn to yellow (or brown) due to oxidation of iron(II) to iron(III) ions

a. ***Using chlorine or bromine (water)***

Cchlorine or bromine is added to a solution of iron(II) salt acidified with dilute sulphuric acid. The colour of the halogen is discharged.

$$2Fe^{2+}(aq) + Cl_2(g) \rightarrow 2Fe^{3+}(aq) + 2Cl^-(aq)$$

b. ***Using hydrogen peroxide in acidic medium***

$$2Fe^{2+}(aq) + H_2O_2(g) + 2H^+ \rightarrow 2Fe^{3+}(aq) + 2H_2O(l)$$

c. ***Using acidified potassium permanganate***

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

d. ***Using acidified potassium dichromate(VI)***

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

Fe^{3+} to Fe^{2+} conversions

a. ***Using potassium iodide***

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

b. ***Using hydrogen sulphide***

A yellow deposit of sulphur is observed. The solution turns from brown to green

$$S^{2-}(aq) + 2Fe^{3+}(aq) \rightarrow 2Fe^{2+}(aq) + S(s)$$

Or

$$2Fe^{3+}(aq) + H_2S(g) \rightarrow 2Fe^{2+}(aq) + S(s) + 2H^+(aq)$$

c. ***Using sulphur dioxide***

The yellow (or brown) solution turns green

$$2Fe^{3+}(aq) + SO_2(g) + H_2O(l) \rightarrow 2Fe^{2+}(aq) + SO_4^{2-}(aq) + 4H^+(aq)$$

Qualitative analysis of Fe^{2+}

1. *Sodium hydroxide solution*

Observation

Green precipitate insoluble in excess that turns brown on standing (this is due oxidation of iron(II) hydroxide to iron(III) hydroxide by atmospheric oxygen).

Equation

$$Fe^{2+}(aq) \ + \ 2\bar{O}H(aq) \rightarrow \ Fe(OH)_2(s)$$

$$4Fe(OH)_2(s) \ + \ O_2(g) \ + \ 2H_2O(l) \rightarrow \ 4Fe(OH)_3(s)$$

2. *Aqueous ammonia*

   Observation

   Green precipitate insoluble in excess that turns brown on standing (this is due oxidation of iron(II) hydroxide to iron(III) hydroxide by atmospheric oxygen).

   Equation

$$Fe^{2+}(aq) \ + \ 2\bar{O}H(aq) \rightarrow \ Fe(OH)_2(s)$$

$$4Fe(OH)_2(s) \ + \ O_2(g) \ + \ 2H_2O(l) \rightarrow \ 4Fe(OH)_3(s)$$

3. *Potassium hexacyanoferrate(III)*

   Observation

   A dark blue precipitate

   Equation

$$Fe^{2+}(aq) \ + \ K^+(aq) \ + \ [Fe(CN)_6]^{3-}(aq) \rightarrow \ KFe[Fe(CN)_6](s)$$

Qualitative analysis of Fe^{3+}

1. *Sodium hydroxide solution*

   Observation

   Brown precipitate insoluble in excess

   Equation

$$Fe^{3+}(aq) \ + \ 2\bar{O}H(aq) \rightarrow \ Fe(OH)_3(s)$$

2. *Aqueous ammonia*

Observation

Brown precipitate insoluble in excess

Equation

$$Fe^{3+}(aq) \quad + \quad 2\bar{O}H(aq) \rightarrow \quad Fe(OH)_3(s)$$

3. *Potassium (or ammonium) thiocyanate solution*

   Observation

   A dark red solution (coloration)

   Equation

$$Fe^{3+}(aq) \quad + \quad SCN^{-}(aq) \rightarrow [Fe(SCN)]^{2+}(aq)$$

4. *Potassium hexacyanoferrate(II) solution*

   Observation

   A dark blue precipitate

   Equation

$$Fe^{3+}(aq) \quad + \quad K^{+}(aq) \quad + \quad [Fe(CN)_6]^{4-}(aq) \rightarrow \quad KFe[Fe(CN)_6](s)$$

6. Cobalt

Reactions of cobalt

a. With air

Heated cobalt reacts with to form tricobalttetraoxide

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

b. With water

Heated cobalt reacts steam to form tricobalttetraoxide and hydrogen gas

$$3Co(s) \quad + \quad 4H_2O(g) \rightarrow \quad Co_3O_4(s) \quad + \quad 4H_2(g)$$

c. With acids

1. Dilute acids

Cobalt reacts slowly with hot dilute hydrochloric and sulphuric acid liberating hydrogen gas and forming the corresponding cobalt(II) salts in solution

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

2. Concentrated acids

Cobalt is oxidized by hot concentrated sulphuric acid to cobalt(II) sulphate and the acid reduced to sulphur dioxide and water

$$Co(s) + 2H_2SO_4(l) \rightarrow CoSO_4(aq) + SO_2(g) + 2H_2O(l)$$

Cobalt is rendered passive by concentrated nitric acid

d. With chlorine

Heated cobalt reacts with dry chlorine to form cobalt(II) chloride

$$Co(s) + Cl_2(g) \rightarrow CoCl_2(s)$$

e. With alkalis

Cobalt has no reaction with alkalis

Compounds of cobalt

Cobalt has two principle oxidation states, +2 and +3 oxidation states. The +2 oxidation state is the most stable while +3 is mainly found in complexes

Cobalt (II) compounds

1. Cobalt(II) oxide

It is a green solid that can be obtained by heating cobalt(II) hydroxide, carbonate or nitrate.

$$Co(OH)_2(s) \rightarrow CoO(s) + H_2O(l)$$

$$CoCO_3(s) \rightarrow CoO(s) + CO_2(g)$$

$$2Co(NO_3)_2 \rightarrow 2CoO(s) + 4NO_2(g) + O_2(g)$$

Cobalt(II) oxide is basic that reacts with dilute acids forming pink solutions of cobalt(II) salts

$$CoO(s) + 2H^+(aq) \rightarrow Co^{2+}(aq) + H_2O(l)$$

2. *Cobalt(II) hydroxide*

It is formed as a blue precipitate when aqueous sodium hydroxide is added to a solution of cobalt(II) salt.

$$Co^{2+}(aq) \quad + \quad 2\bar{O}H(aq) \rightarrow \quad Co(OH)_2(s)$$

It is also basic reacting with dilute acids to form cobalt(II) salts

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

3. *Cobalt(II) chloride*

The anhydrous slat is blue which can be obtained by heating cobalt in a stream of dry chlorine or hydrogen chloride

$$Co(s) \quad + \quad Cl_2(g) \rightarrow \quad CoCl_2(s)$$

$$Co(s) \quad + \quad 2HCl(g) \rightarrow \quad CoCl_2(s)$$

The hydrated salt is red or pink

Cobalt(II) chloride turns pink in water due to the formation of the hexaaqua cobalt(II) ion. $[Co(H_2O)_6]^{2+}$

When concentrated hydrochloric acid or a saturated solution of potassium chloride is added to the solution, it changes from pink to blue

$$[Co(H_2O)_6]^{2+}(aq) \; + \; 4Cl^-(aq) \; \leftrightharpoons \; [CoCl_4]^{2-}(aq) \; + \; 6H_2O(l)$$

This is called ligand exchange. This chloride ions have replaced water molecules as ligands in the complex resulting in colour change.

Diluting the solution results in reforming the pink solution.

Cobalt (III) compounds

Cobalt(III) does not occur in simple compounds but it is the stable form of many complexes which are formed by the oxidation of cobalt(II) complexes.

Qualitative analysis of Co^{2+} in solution

1. *Sodium hydroxide solution*

Observation

A blue precipitate insoluble in excess, turning pink on standing. (This due to aerial oxidation of cobalt(II) hydroxide to hydrated cobalt(III) oxide

Equations

$$Co^{2+}(aq) \; + \; 2\bar{O}H(aq) \rightarrow \quad Co(OH)_2(s)$$

$$Co(OH)_2(s) \quad + \quad 2O_2(g) \rightarrow Co_2O_3.2H_2O(s)$$

2. *Ammonia solution*

Observation

A blue precipitate, soluble in excess forming a yellow solution which turns red on standing (This is due to oxidation of hexaamminecobalt(II) complex to hexaammine cobalt(III))

Equations

$$Co^{2+}(aq) \; + \; 2\bar{O}H(aq) \rightarrow \quad Co(OH)_2(s)$$

$$Co(OH)_2(s) \quad + \; 6NH_3(aq) \rightarrow [Co(NH_3)_6]^{2+}(aq) \quad + \quad 2\bar{O}H(aq)$$

$$4[Co(NH_3)_6]^{2+}(aq) \; + \; O_2(g) \; + \; 2H_2O(l) \rightarrow \; 4[Co(NH_3)_6]^{3+}(aq) \; + \quad 4\bar{O}H(aq)$$

3. *Potassium thiocyanate(drops of conc. hydrochloric acid are added first)*

Observation

A blue solution (of tetrathiocyanatocobaltate(II) complex)

Equation

$$Co^{2+}(aq) + \quad 4SCN^-(aq) \rightarrow [Co(SCN)_4]^{2-}(aq)$$

If pentanol or ether is added to the resulting solution, the blue colour forms in the organic (upper) layer

4. *Potassium nitrite solution(ethanoic acid is added first)*

Observation

A yellow crystalline precipitate (potassium hexanitritocobaltate(III) complex)

Equation

$$Co^{2+}(aq) + 3K^{+} + 7NO_2^{-}(aq) + 2H^{+}(aq) \rightarrow K_3[Co(NO_2)_6](s) + NO(g) + H_2O(l)$$

5. *Potassium cyanide solution*

Observation

Reddish brown precipitate soluble in excess forming a reddish brown solution (containing hexacyanocobaltate(II) ion)

Equations

$$Co^{2+}(aq) \quad + \quad 2CN^{-}(aq) \rightarrow \quad Co(CN)_2(s)$$

$$Co(CN)_2(s) \quad + \quad 4CN^{-}(aq) \rightarrow [Co(CN)_6]^{4-}(aq)$$

7. Nickel

Reactions of nickel

a. With air

Heated nickel reacts with air to form nickel(II) oxide, a green solid.

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

b. With water

Heated nickel reacts with steam to form nickel(II) oxide and hydrogen gas.

$$Ni(s) \quad + \quad H_2O(g) \rightarrow \quad NiO(s) \quad + \quad H_2(g)$$

c. With acids

Nickel reacts with hot dilute acids to form the corresponding nickel(II) salts and hydrogen gas

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

Nickel is rendered passive by concentrated nitric acid

d. With chlorine

Heated nickel reacts with dry chlorine to form nickel(II) chloride

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

Compounds of nickel

Nickelusually forms compounds in the +2 oxidation state.

Nickel(II) compounds are generally green and they contain the green hexaaquanickel(II) ion when hydrated or in aqueous solution. The complex ions has an octahedral structure.

Nickel(II) oxide

It is a green solid that can be obtained by heating nickel(II) carbonate nitrate or hydroxide.

$$Ni(OH)_2(s) \rightarrow \quad NiO(s) \quad + \quad H_2O(l)$$

$$NiCO_3(s) \quad \rightarrow \quad NiO(s) \quad + \quad CO_2(g)$$

It is a basic solid that reacts with dilute acids to form the corresponding nickel(II) salts and water

$$NiO(s) \quad + \quad 2H^+(aq) \rightarrow Ni^{2+}(aq) \quad + \quad H_2O(l)$$

Nickel(II) hydroxide

It is a green solid that can be obtained by precipitation when dilute sodium hydroxide is added to solution of nickel(II) salt.

$$Ni^{2+}(aq) \quad + \quad 2\bar{O}H(aq) \rightarrow Ni(OH)_2(s)$$

Qualitative analysis of Ni^{2+} in solution

1. *Sodium hydroxide solution*

   Observation

   A green precipitate insoluble in excess

   Equation

$$Ni^{2+}(aq) \quad + \quad 2\bar{O}H(aq) \rightarrow Ni(OH)_2(s)$$

2. *Ammonia solution*

   Observation

   A green precipitate soluble in excess forming a forming a blue solution

   Equation

$$Ni^{2+}(aq) \quad + \quad 2\bar{O}H(aq) \rightarrow Ni(OH)_2(s)$$

$$Ni(OH)_2(s) \quad + \quad 6NH_3(aq) \rightarrow [Ni(NH_3)_6]^{2+}(aq) \quad + \quad 2\bar{O}H(aq)$$

3. *Potassium hexacyanoferrate(II) solution*

Observation

A green precipitate soluble in ammonia solution

Equation

$$2Ni^{2+}(aq) \quad + \quad [Fe(CN)_6]^{4-}(aq) \rightarrow Ni_2[Fe(CN)_6] \ (s)$$

4. *Dimethylglyoxime solution in presence of ammonia solution*

Observation

A red precipitate

8. Copper

Extraction of copper

The chief ore from which copper is extracted is *copper pyrites,*$CuFeS_2$.

The other ores of copper are

- Cuprite,Cu_2O
- Copper glance,Cu_2S

Extraction of iron from copper pyrites,

The ore is crushed and concentrated by froth flotation, in which the finely powdered ore is mixed with water containing a frothing agent

A current of air is blown through the mixture producing a froth containing copper bearing particles, and the earthly impurities are wetted and they sink to the bottom of the tank. The froth is skimmed off, filtered and dried.

The ore is roasted in a limited supply of air to convert the ore to copper(I) sulphide, iron(II) oxide and sulphur dioxide

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

The product of roasting is then heated with sand (silica) in a closed furnace (absence of air). Iron(II) oxide reacts with silica to form iron(II) silicate which floats on top of the copper(I) sulphide formed and so is poured off

$$FeO(s) \; + \; SiO_2(s) \rightarrow \; FeSiO_3(l)$$

The molten copper(I) sulphide is then heated in limited (controlled) amount of air, causing the partial oxidation of copper(I) sulphide to copper(I) oxide

$$2Cu_2S(s) \ + \ 3O_2(g) \rightarrow \ 2Cu_2O(s) \ + \ 2SO_2(g)$$

The copper(I) oxide mixed with unchanged copper(I) sulphide is then heated strongly in the absence of air to form molten copper (blister copper) and sulphur dioxide gas

$$Cu_2S(s) \ + \ 2Cu_2O(s) \rightarrow \ 3Cu(l) \ + \ SO_2(g)$$

The blister copper is purified by electrolysis using a direct current, with blister copper is the anode and a pure sheet of copper as the cathode and copper(II) sulphate solution as the electrolyte

At the anode copper dissolves in the electrolyte.

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

At the cathode, pure copper is deposited

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

Reactions of copper

a. With air

Heated copper reacts with air to form copper(II) oxide

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

b. With water

Copper does not react with water

c. With chlorine

Heated copper reacts with dry chlorine gas to form copper(II) chloride

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

d. With alkalis

Copper does not react with alkalis

e. With acids

i. Dilute acids

Copper does not react with dilute acids

ii. *Concentrated acids*

- Copper is oxidized by hot concentrated sulphuric acid to copper(II) sulphate and the acid reduced to sulphur dioxide gas and water

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

- Copper is oxidized by concentrated nitric acid to copper(II) nitrate and the acid reduced to nitrogen dioxide and water

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

- Moderately concentrated nitric acid oxidizes copper to copper(II) nitrates and the acid reduced to nitrogen monoxide gas and water

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

Compounds of copper

Copper exhibits two principal oxidation states, +1 and +2.

By losing one electron from the 4s orbital, copper(I) ion, Cu^+,is formed. Because the 3d orbital id fully filled with electrons, copper(I) does not show typical transition metal properties.

The copper(II) ion, Cu^{2+}, is formed when two electrons, one from the 4s and the other from the 3d orbitals are lost. This gives copper(II) ion a partially filled 3d orbital and hence copper(II) shows typical transition properties in its compounds

From the electronic configuration, copper(I) is expected to be more stable than copper(II). However, this is not the case, and copper(II) is more stable than copper(I). This is because copper(II) has a higher charge density than copper(I), it produces more energy upon hydration enough to compensate for the second ionisation energy and forms stronger bonds in its compounds than copper(I).

Copper(I) compounds

The copper(I) ion is very unstable in water and undergoes disproportionation to form copper and copper(II) ions.

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

Copper(I) oxide

It is a dark red solid which can be obtained as a precipitate by reducing copper(II) sulphate using reducing compounds such as aliphatic aldehydes in alkaline medium.

$$2Cu^{2+}(aq) + CH_3CHO(aq) + 3\bar{O}H(aq) \rightarrow CH_3COO^-(aq) + Cu_2O(s) + H_2O(l)$$

It is insoluble in water but will disproportionate in dilute sulphuric acid

$$Cu_2O(s) \ + \ 2H^+(aq) \rightarrow \ Cu(s) \ + \ Cu^{2+}(aq) \ + \ H_2O(l)$$

Copper(I) chloride

It is a white covalent solid, insoluble in water. It can be prepared by boiling a mixture of copper(II) chloride and copper turnings with excess hydrochloric acid.

$$CuCl_2(aq) \ + \ Cu(s) \rightarrow \ 2CuCl(s)$$

It dissolves in conc. hydrochloric acid due to the formation of a complex, *dichlorocuprate(I) ion.*

$$CuCl(s) \ + \ Cl^-(aq) \rightarrow [CuCl_2]^-(aq)$$

It like silver chloride, copper(I) chloride is also soluble in ammonia solution forming a diamminecopper(I) ion

$$CuCl(s) \ + \ 2NH_3(aq) \rightarrow [Cu(NH_3)_2]^+(aq) \ + \ Cl^-(aq)$$

Copper(II)compounds

The hydrated hexaaquacopper(II) ion $[Cu(H_2O)_6]^{2+}$is blue.

Copper(II) oxide

It is a black solid that can be obtained by heating copper(II) carbonate, hydroxide or nitrate.

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

It is basic and reacts with dilute mineral acids to form the corresponding copper(II) salts and water

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

Copper(II) hydroxide

It is a blue solid that can be obtained by the action of dilute sodium hydroxide on a solution of a copper(II) salt.

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

It is basic, and reacts with dilute acids to form the corresponding copper(II) salt and water

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

Determination of the amount of copper in impure (blister) copper

✓ A known mass of impure copper is dissolved in excess concentrated sulphuric acid

✓ The resultant solution is the neutralized with sodium hydrogencarbonate

✓ The mixture is then reacted with excess potassium iodide to liberate iodine according to the equation

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

✓ The liberated iodine is titrated with a standard solution of sodium thiosulphate using starch indicator.

✓ The concentration of iodine, copper(II) ions and hence mass of copper in the mixture is calculated.

✓ the percentage mass of copper in the mixture can the be calculated form the formula

$$percentage\ of\ copper = \frac{mass\ of\ copper}{mass\ of\ the\ impure\ sample} \times 100$$

Qualitative analysis of Cu^{2+} in solution

1. *Sodium hydroxide solution*

   Observation

   A pale blue precipitate insoluble in excess

   Equation

$$Cu^{2+}(aq) \quad + \quad 2\bar{O}H(aq) \rightarrow Cu(OH)_2(s)$$

2. *Ammonia solution*

   Observation

   A pale blue precipitate soluble in excess forming a forming a deep blue solution

   Equation

$$Cu^{2+}(aq) \quad + \quad 2\bar{O}H(aq) \rightarrow Cu(OH)_2(s)$$

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

3. *Potassium iodide solution*

   Observation

   A white precipitate in a brown solution

   Equation

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

   The brown solution turns colourless on addition of sodium thiosulphate solution.

4. *Potassiumhexacyanoferrate(II) solution*

   Observation

   A brown precipitate insoluble in ammonia solution

   Equation

$$2\,Cu^{2+}(aq) \quad + \quad [Fe(CN)_6]^{4-}(aq) \rightarrow Cu_2[Fe(CN)_6] \;\; (s)$$

9. Zinc

Extraction of zinc

The chief ores from which zinc is extracted are

- Zinc blende, ZnS
- Calamine, $ZnCO_3$

Extraction of iron from zinc blende

The ore is first crushed into a fine powder and then concentrated by froth flotation method. in this method, he finely crushed ore is mixed with water containing a frothing agent. The mixture is then agitated by blowing air through it.

The ore containing particles are carried on the surface as the froth which is removed, filtered and dried, and the earthly impurities are wetted and hence sink.

The dried ore is roasted in air converting it to zinc oxide. Lead(II) sulphide (galena) which is the main impurity is also oxidized to lead(II) oxide.

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

$$2PbS(s) + 3O_2(g) \rightarrow 2PbO(s) + 2SO_2(g)$$

(If calamine is used, it decomposes to zinc oxide and carbon dioxide)

The solid product of roasting is mixed with limestone and coke and fed into a furnace and hot air blasted into it.

Coke burns to form carbon dioxide

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

Carbon dioxide is reduced by unburnt coke to carbon monoxide

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

The carbon monoxide produced under high temperatures reduces zinc oxide to zinc. Lead(II) oxide s also reduced to lead.

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

$$PbO(s) + CO(g) \rightarrow Pb(l) + CO_2(g)$$

Zinc leaves the furnace as a vapour which is cooled by a spray of lead. Pure zinc solidifies and floats on top of molten lead.

Lime stone decomposes to calcium oxide and carbon dioxide. Calcium oxide combines with sand (silicon(IV) oxide/ silica), an impurity to form calcium silicate (slag) which flows off.

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

$$CaO(s) + CO_2(g) \rightarrow CaSiO_3(l)$$

Reactions of zinc

a. **With air**

Heated zinc burns in air with a blue flame to form zinc oxide

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

b. **With water**

Heated zinc reacts with steam to form zinc oxide and hydrogen gas

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

c. With alkalis

Zinc reacts with hot concentrated alkalis to a zincate complex and hydrogen gas

$$Zn(s) + 2\bar{O}H(aq) \rightarrow ZnO_2^{2-}(aq) + H_2(g)$$

Or

$$Zn(s) + 2\bar{O}H(aq) + 2H_2O(l) \rightarrow [Zn(OH)_4]^{2-}(aq) + H_2(g)$$

d. With acids

i. Dilute acids

Zinc reacts with dilute sulphuric acid and hydrochloric acid to form the corresponding zinc salt and hydrogen gas

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

Dilute nitric acid oxidizes zinc to zinc nitrate and the acid reduced to ammonium nitrate and water

$$4Zn(s) + 10HNO_3(aq) \rightarrow 4Zn(NO_3)_2(aq) + NH_4NO_3(aq) + 3H_2O(l)$$

ii. Concentrated acids

Hot concentrated sulphuric acid oxidizes zinc to zinc sulphate and the acid is reduced to sulphur dioxide and water

$$Zn(s) + 2H_2SO_4(l) \rightarrow ZnSO_4(aq) + SO_2(g) + 2H_2O(l)$$

Concentrated nitric acid oxidizes zinc to zinc nitrate and the acid reduced to nitrogen dioxide and water

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

e. With non-metals

Heated zinc reacts with non-metals such as nitrogen and dry chlorine to form zinc nitride and zinc chloride respectively

$$3Zn(s) + N_2(g) \rightarrow Zn_3N_2(s)$$

$$Zn(s) + Cl_2(g) \rightarrow ZnCl_2(s)$$

Compounds of zinc

Zinc forms compounds in the +2 oxidation states. In this state the zinc ion has a full 3d orbital, therefore, it does not show typical transition properties and not regarded as a typical transition element. Other reasons include

- Zinc has one oxidation state
- Zinc compounds are not coloured
- Zinc compounds a not paramagnetic

Zinc oxide

It is a white solid that turns yellow on heating. It can be obtained by heating zinc carbonate and zinc nitrate

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

$$2Zn(NO_3)_2(s) \rightarrow \quad 2ZnO(s) \quad + \quad 4NO_2(g) \quad + \; O_2(g)$$

It is insoluble in water but it is amphoteric

It reacts with dilute acids to form the corresponding zinc salt and water

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

It reacts with hotconcentrated alkalis to form a corresponding zincate

$$ZnO(s) \quad + \quad 2\bar{O}H(aq) \rightarrow \quad ZnO_2^{2-}(aq) \quad + \quad H_2O(l)$$

Or

$$ZnO(s) \quad + \quad 2\bar{O}H(aq) \;\; + \quad H_2O(l) \quad \rightarrow [Zn(OH)_4]^{2-}(aq)$$

Zinc hydroxide

It is precipitated as a white solid when aqueous sodium hydroxide is added to a solution of zinc salt

$$Zn^{2+}(aq) \;\; + \quad 2\bar{O}H(aq) \rightarrow \quad Zn(OH)_2(s)$$

It reacts with dilute acids to form the corresponding zinc salts and water

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

It reacts with dilute alkalis to form the corresponding zincate

$$Zn(OH)_2(s) \quad + \quad 2\bar{O}H(aq) \rightarrow [Zn(OH)_4]^{2-}(aq)$$

Qualitative analysis of Cu²⁺ in solution

1. *Sodium hydroxide solution*

   Observation

   A white precipitate soluble in excess forming a colourless solution

   Equation

$$Zn^{2+}(aq) \quad + \quad 2\bar{O}H(aq) \rightarrow Zn(OH)_2(s)$$

$$Zn(OH)_2(s) \quad + \quad 2\bar{O}H(aq) \rightarrow [Zn(OH)_4]^{2-}(aq)$$

2. *Ammonia solution*

   Observation

   A white precipitate soluble in excess forming a colourless solution

   Equation

$$Zn^{2+}(aq) \quad + \quad 2\bar{O}H(aq) \rightarrow Zn(OH)_2(s)$$

$$Zn(OH)_2(s) \quad + \quad 4NH_3(aq) \rightarrow [Zn(NH_3)_4]^{2+}(aq) \quad + \quad 2\bar{O}H(aq)$$

3. *Potassium hexacyanoferrate(II) solution*

   Observation

   A white precipitate soluble in aqueous ammonia

   Equation

$$2\,Zn^{2+}(aq) \quad + \quad [Fe(CN)_6]^{4-}(aq) \rightarrow Zn_2[Fe(CN)_6] \quad (s)$$

4. *Solid ammonium chloride, disodium hydrogen phosphate and ammonia solution*

   White crystalline solidsoluble in ammonia