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 from 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	$1s^22s^22p^63s^23p^63d^14s^2$
Titanium	Ti	22	$1s^22s^22p^63s^23p^63d^24s^2$
Vanadium	V	23	$1s^22s^22p^63s^23p^63d^34s^2$
Chromium	Cr	24	$1s^22s^22p^63s^23p^63d^54s^1$
Manganese	Mn	25	$1s^22s^22p^63s^23p^63d^54s^2$
Iron	Fe	26	$1s^22s^22p^63s^23p^63d^64s^2$
Cobalt	Co	27	$1s^22s^22p^63s^23p^63d^74s^2$
Nickel	Ni	28	$1s^22s^22p^63s^23p^63d^84s^2$
Copper	Cu	29	$1s^22s^22p^63s^23p^63d^{10}4s^1$
Zinc	Zn	30	$1s^22s^22p^63s^23p^63d^{10}4s^2$

- 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.

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

  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 in manganese and zinc respectively 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.
- Paramagnetism increases with increase in the number of unpaired electrons. Hence it increases from scandium to maximum at manganese due to increase in the number of unpaired electrons and then decreases to zinc due to electron pairing.
- 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. 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 forming activated complexes of the reactants.
- These activated complexes can then 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 valence 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 in alphabetical order.
7. If the number prefix (di, tri, etc) is already used in the ligands, the prefix for the ligand then becomes bis;- tris;- instead of di;- tri;- e.t.c
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*. *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(O) 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. Reaction with air

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

$$Ti(s) + O_2(g) \longrightarrow TiO_2(s)$$

b. Reaction with chlorine

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

$$Ti(s) + 2Cl_2(g) \longrightarrow TiCl_4(s)$$

c. With acids

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

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

Compounds of titanium

- Titanium forms compounds in the +3 and +4 oxidation states.
- In the +3 oxidation state, titanium still has one electron in the 3d-orbital and hence 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.

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

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

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

2. VANADIUM

Reactions of vanadium

a. With chlorine

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

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

b. With air

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

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

Compounds of vanadium

- Vanadium forms compounds in the +2, +3, +4, and +5 oxidation states. The +4 is the most stable oxidation state.
- 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.

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

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

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

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

- 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

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

b. With water

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

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

c. With chlorine

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

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

d. With alkalis

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

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

Or

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

e. With hydrogen chloride

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

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

f. With acids

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

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

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

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

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.

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

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

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

Chromium(II) chloride

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

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

Chromium(II) hydroxide

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

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

Chromium(III) compounds

Chromium(III) oxide

- It is a green ionic and amphoteric solid that can be obtained by heating chromium(III) hydroxide or ammonium dichromate

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

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

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

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

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

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

Or

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

Chromium(III) hydroxide

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

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

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

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

It reacts with alkalis to form chromate(III) salts

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

Or

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

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.

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

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

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

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

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

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

$$CrO_3(s) + H_2O(l) \longrightarrow H_2CrO_4(l)$$

It also reacts with alkalis to form chromates(VI)

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

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.

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

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

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

- 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

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

Dichromtes(VI)

- These are orange coloured salts containing the dichromate ion, $Cr_2O_7^{2-}$
- Dichromates can be obtained by adding dilute sulphuric acid to a solution of a chromate

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

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

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

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

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

- However, they are not strong enough to oxidise chlorides to chlorine therefore they can be used in the presence of hydrochloric acid in volumetric analysis. Reactions of dichromates include:

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

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

- *Observation:* The orange solution turns green

(b) *Oxidation of iodide ions to iodine*

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

- *Observation:* The colourless solution (of potassium iodide) turns brown

(c) *Oxidation of hydrogen sulphide to sulphur*

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

- *Observation:* The orange solution turns green, and a yellow precipitate is formed

(d) *Oxidation of sulphur dioxide to a sulphate*

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

- *Observation:* The orange solution turns green

(e) *Oxidation of sulphites to sulphates*

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

- *Observation:* The orange solution turns green

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

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

- *Observation*: The orange solution turns green

Qualitative analysis of Cr^{3+}

1. *Sodium carbonate solution*

- *Observation:* Green solid and bubbles (effervescence) of a colourless gas
- *Equation*

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

2. *Sodium hydroxide solution*

- *Observation*: Green precipitate soluble in excess to form a green solution
- *Equations*

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

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

3. *Ammonia solution*

- *Observation* Green precipitate insoluble in excess
- *Equation*

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

4. *Sodium hydroxide and hydrogen peroxide*

- *Observation:* A yellow solution on warming
- *Equation*

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

5. *Sodium hydroxide, hydrogen peroxide, butanol and dilute sulphuric acid*

- *Observation*: A blue solution in the organic layer
- *Equations*

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

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

4. MANGANESE

Reactions of manganese

a. With air

Heated manganese burns in air to form a mixture of trimanganese tetraoxide.

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

b. With water

Heated manganese reacts with steam to form trimanganese tetraoxide and hydrogen gas

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

c. With acids

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

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

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

$$3Mn(s) \quad + \quad 8HNO_3(aq) \quad \longrightarrow \quad 3Mn(NO_3)_2(aq) \; + \; 2NO(g) \quad + \; H_2O(l)$$

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

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

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

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

d. Chlorine

Heated manganese reacts chlorine to form manganese(II) chloride

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

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

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

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

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

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

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

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

- Obtained as a white precipitate when sodium hydroxide or ammonia solution is added to a solution of o manganese(II)salt

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

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

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

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. The pink crystals form from the solution on cooling

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

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

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

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.

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

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

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

Manganese(III) compounds

Compounds of manganese in this state are uncommon because of disproportionation

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

Manganese(IV) compounds

Manganese(IV) oxide, MnO_2

- Anhydrous manganese(IV) oxide is a black solid prepared by heating manganese(II) nitrate

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

- Also by oxidation of manganese(II) salts using sodium hypochlorite and sodium hydroxide

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

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

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

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

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

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

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

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

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

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

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

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

$$Cl_2(g) \;+\; 2I^-(aq) \;\longrightarrow\; I_2(aq) \;+\; 2Cl^-(aq)$$

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

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

- 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.

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

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

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

Or

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

- 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

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

Manganese(VII) compounds

Potassium manganate(VII).

- 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
- 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 manganate(VII) during the reaction.
- Hydrochloric acid is not used because it is easily oxidized to chlorine.

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

Advantages of using potassium permanganate in volumetric analysis

- It is a self - 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

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

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

Even in alkaline medium, decomposition will occur as follows

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

__Oxidizing properties potassium manganate(VII)__

- In neutral or slightly alkaline medium manganate(VII) is reduced to manganese(IV) oxide

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

For example, oxidation of iodide to iodate

$$I^-(aq) + 6\bar{O}H(aq) \longrightarrow IO_3^-(aq) + 3H_2O(l) + s6e^-$$

Overall equation

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

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

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

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

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

a. *__Oxidation of nitrites to nitrates__*

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

b. *__Oxidation of hydrogen peroxide to oxygen__*

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

c. *__Oxidation of tin(II) to tin(IV)__*

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

d. *__Oxidation of iron(II) to iron(III)__*

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

- *__Observation__*

  The solution turns from purple to brown

e. *__Oxidation of hydrogen sulphide to sulphur__*

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

- *__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.

  (Due to oxidation of manganese(II) hydroxide to hydrated manganese(IV) oxide by atmospheric oxygen)

- *Equations*

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

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

2. *Ammonia solution*

- *Observation*

  A brown precipitate that rapidly turns brown on standing.

  (Due to oxidation of manganese(II) hydroxide to hydrated manganese(IV) oxide by atmospheric oxygen)

- *Equations*

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

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

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

- *Observation*

  A purple solution is formed.

  (Manganese(II) ions are oxidized to manganate(VII) ions by bismuthate)

- *Equation*

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

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)

- *Equation*

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

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.
- 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

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

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

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

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

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

- Limestone decomposes to calcium oxide and carbon dioxide

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

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

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

Reaction of iron

a. With water

- Heated iron reacts with steam to form triiron tetraoxide and hydrogen gas

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

b. With air

- Heated iron reacts with air to form triiron tetraoxide

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

c. **With acids**

i. ***Dilute acids***

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

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

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

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

ii. ***Concentrated acids***

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

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

- Concentrated nitric acid renders iron passive.

d. **With sulphur**

When a mixture of iron and sulphur is heated, a red glow is observed and black solid is formed

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

e. **With chlorine**

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

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

f. **With hydrogen chloride**

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

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

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 orbitals gives iron(III) ion.
- Because the 3d orbital is half filled, the iron(III) ion and the compounds are more stable than the iron(II) ion and compounds. This is why iron(II) compounds easily oxidize 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.

$$FeC_2O_4(s) \longrightarrow FeO(s) \ + \ CO(g) \ + \ CO_2(g)$$

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

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

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.

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

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

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

Iron(II) chloride

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

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

- Hydrated iron(II) chloride is obtained by crystallization method.

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.

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

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

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

$$FeSO_4.7H_2O(s)\ \longrightarrow\ FeSO_4(s)\ +\ 7H_2O(l)$$

- On strong heating, it decomposes to iron(III) oxide (brown), sulphur dioxide and sulphur trioxide.

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

Iron(III) compounds

Iron(III) oxide

- It occurs as haematite in nature. In the laboratory, it can be obtained as a brown solid by heating Iron(II) sulphate or Iron(II) hydroxide

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

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

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

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

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.

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

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

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

Iron(III) chloride

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

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

- 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.

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

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

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

a. *Using acidified potassium permanganate*

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

b. *Using acidified potassium dichromate(VI)*

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

c. *Using hydrogen peroxide in acidic medium*

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

d. *Using chlorine or bromine (water)*

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

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

$$2Fe^{2+}(aq) + Br_2(g) \longrightarrow 2Fe^{3+}(aq) + 2Br^-(aq)$$

e. *__Using acidified potassium permanganate__*

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

f. *__Using acidified potassium dichromate(VI)__*

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

__$Fe^{3+}$to Fe^{2+}conversions__

a. *__Using potassium iodide__*

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

b. *__Using hydrogen sulphide__*

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

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

Or

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

c. *__Using sulphur dioxide__*

The yellow (or brown) solution turns green

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

__Qualitative analysis of Fe^{2+}__

1. __Sodium hydroxide solution__

- __Observation:__ Green precipitate insoluble in excess that turns brown on standing (Due oxidation of iron(II) hydroxide to iron(III) hydroxide by atmospheric oxygen).
- __Equation__

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

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

2. __Aqueous ammonia__

- __Observation:__ Green precipitate insoluble in excess that turns brown on standing
- __Equation__

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

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

3. __Potassium hexacyanoferrate(III)__

- __Observation:__ A dark blue precipitate
- __Equation__

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

Qualitative analysis of $\mathbf{Fe^{3+}}$

1. *Sodium hydroxide solution*

- *Observation:* Brown precipitate insoluble in excess
- *Equation*

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

2. *Aqueous ammonia*

- *Observation:* Brown precipitate insoluble in excess
- *Equation*

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

3. *Potassium (or ammonium) thiocyanate solution*

- *Observation:* A dark red solution (coloration)
- *Equation*

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

4. *Potassium hexacyanoferrate(II) solution*

- *Observation:* A dark blue precipitate
- *Equation*

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

6. COBALT

Reactions of cobalt

a. With air

Heated cobalt reacts with to form tricobalt tetraoxide

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

b. With water

Heated cobalt reacts steam to form tricobalt tetraoxide and hydrogen gas

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

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

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

2. *Concentrated acids*

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

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

Cobalt is rendered passive by concentrated nitric acid

d. With chlorine

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

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

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
- The +3 oxidation state 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.

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

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

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

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

2. *Cobalt(II) hydroxide*

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

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

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

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

3. *Cobalt(II) chloride*

- The anhydrous salt is blue obtained by heating cobalt in dry chlorine or hydrogen chloride

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

$$Co(s) + 2HCl(g) \longrightarrow CoCl_2(s)$$

- The hydrated salt is red or pink
- Cobalt(II) chloride turns pink in water due to the formation of the hexaaquacobalt(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.

Qualitative analysis of Co^{2+} in solution

1. *Sodium hydroxide solution*

- *Observation* Blue precipitate insoluble in excess, turning pink on standing.

  (Due to oxidation of cobalt(II) hydroxide to hydrated cobalt(III) oxide by atmospheric oxygen)
- *Equations*

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

$$Co(OH)_2(s) \;+\; 2O_2(g) \longrightarrow Co_2O_3.2H_2O(s)$$

2. *Ammonia solution*

- *Observation*

  A blue precipitate, soluble in excess forming a yellow solution which turns red on standing

  (Due to oxidation of hexaammine cobalt(II) complex to hexaammine cobalt(III)))
- *Equations*

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

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

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

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

- *Observation:* Blue solution (of tetrathiocyanatocobaltate(II) complex)
- *Equation*

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

- 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))

- *Equation*

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

5. *Potassium cyanide solution*

- *Observation*

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

- *Equations*

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

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

7. NICKEL

Reactions of nickel

a. With air

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

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

b. With water

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

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

c. With acids

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

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

Nickel is rendered passive by concentrated nitric acid

d. With chlorine

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

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

Compounds of nickel

- Nickel usually forms compounds in the +2 oxidation state.
- Nickel(II) compounds are generally green

Nickel(II) oxide

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

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

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

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

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

Qualitative analysis of Ni²⁺ in solution

1. *Sodium hydroxide solution*

- *Observation:* Green precipitate insoluble in excess forming a green solution
- *Equation*

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

2. *Ammonia solution*

- *Observation:* Green precipitate soluble in excess forming a forming a blue solution
- *Equation*

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

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

3. *Potassium hexacyanoferrate(II) solution*

- *Observation:* Green precipitate soluble in ammonia solution
- *Equation*

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

4. *Dimethylglyoxime solution in presence of ammonia solution*

- *Observation:* Red precipitate

8. COPPER

Extraction of copper

- The chief ore from which copper is extracted is *copper pyrites,* $CuFeS_2$
- Other ores are cuprite (Cu_2O) and copper glance (Cu_2S)

Extraction of iron from copper pyrites,

- The ore 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, the earthly impurities are wetted and sink to the bottom of the tank. The froth is skimmed off, 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

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

- 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

$$FeO(s) + SiO_2(s) \longrightarrow FeSiO_3(l)$$

- 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

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

- 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

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

- 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.

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

- At the cathode, pure copper is deposited

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

Reactions of copper

a. With air

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

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

b. With water

Copper does not react with water

c. With chlorine

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

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

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

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

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

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

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

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

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.

$$2Cu^+(aq) \ \longrightarrow \ Cu^{2+}(\mathrm{aq}) \ + \ Cu(s)$$

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.

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

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

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

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.

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

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

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

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

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

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.

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

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

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

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.

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

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

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

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

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

- ✓ 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*

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

2. *Ammonia solution*

- *Observation:* Pale blue precipitate soluble in excess forming a forming a deep blue solution
- *Equation*

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

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

3. *Potassium iodide solution*

- *Observation:* White precipitate in a brown solution
- *Equation*

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

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

4. *Potassium hexacyanoferrate(II) solution*

- *Observation:* Brown precipitate insoluble in ammonia solution
- *Equation*

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

9. ZINC

Extraction of zinc

- The chief ores from which zinc is extracted are Zinc blende, ZnS and Calamine, $ZnCO_3$

Extraction of iron from zinc blende

- The ore is concentrated by froth flotation method. In this method, the 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.

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

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

- 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

$$C(s) \quad + \quad O_2(g) \quad \longrightarrow \quad CO_2(g)$$

- Carbon dioxide is reduced by unburnt coke to carbon monoxide

$$C(s) \quad + \quad CO_2(g) \quad \longrightarrow \quad 2CO(g)$$

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

$$ZnO(s) \quad + \quad CO(g) \quad \longrightarrow Zn(g) \quad + \quad CO_2(g)$$

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

- 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.

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

$$CaO(s) \quad + \quad CO_2(g) \quad \longrightarrow \quad CaSiO_3(l)$$

Reactions of zinc

a. **With air**

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

$$2Zn(s) \quad + \quad O_2(g) \longrightarrow 2ZnO(s)$$

b. **With water**

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

$$Zn(s) \quad + \quad H_2O(g) \quad \longrightarrow ZnO(s) \quad + \quad H_2(g)$$

c. **With alkalis**

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

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

Or

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

d. With acids

i. Dilute acids

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

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

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

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

ii. Concentrated acids

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

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

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

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

e. With non-metals

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

$$3Zn(s) \quad + \quad N_2(g) \longrightarrow Zn_3N_2(s)$$

$$Zn(s) \quad + \quad Cl_2(g) \longrightarrow ZnCl_2(s)$$

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

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

- It is insoluble in water but it is amphoteric
- It reacts with dilute acids to form the corresponding zinc salt and water

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

- It reacts with hot concentrated alkalis to form a corresponding zincate

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

Or

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

Zinc hydroxide

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

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

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

Qualitative analysis of Zn^{2+} in solution

1. *Sodium hydroxide solution*

- *Observation*

  A white precipitate soluble in excess forming a colourless solution

- *Equation*

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

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

2. *Ammonia solution*

- *Observation*

  A white precipitate soluble in excess forming a colourless solution

- *Equation*

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

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

3. *Potassium hexacyanoferrate(II) solution*

- *Observation*

  A white precipitate soluble in aqueous ammonia

- *Equation*

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

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

- *Observation:* A White crystalline solid soluble in ammonia