

TRANSITION ELEMENTS

A transition element is defined as one which 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.

The bonding electrons are in the outer most s and inner d – orbitals.

d – block element:

Is an element whose outermost electrons are found in the d – orbital.

Below is an outline of transition elements and their electronic configuration.

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 a transition element because the stable ion of scandium, Sc^{3+} , has no electrons in the 3d sub-energy level i.e the Sc^{3+} has electronic configuration of $1s^2 2s^2 2p^6 3s^2 3p^6$

Also, zinc is a non-transition element because the stable ion of zinc, Zn^{2+} , has a fully filled 3d-sub energy level, i.e the ion formed has electronic configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$

Copper is only considered transition element in +2 oxidation state because the Cu^{2+} formed has electronic configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$. In +1 oxidation state, copper is considered non-transition because the ion formed has a fully filled d-orbital i.e Cu^+ has electronic configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$

Trends across transition elements

a) Atomic radius

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

Trend

The atomic radius decreases very slightly from scandium to nickel with a slight increase from cobalt to zinc.

Explanation

Across the elements, nuclear charge increases due addition of protons to the nuclei of the atoms, also screening effect increases 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 very small.

The partially filled 3d-subenergy level poorly shields the outer s-sub-energy level electrons from nuclear charge.

The increase in nuclear charge outweighs the increase in screening effect hence the effective nuclear attraction for the outermost electrons increases leading to the slight decrease in atomic radius.

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

b) 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

Trend

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

Explanation

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 bonding 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

- ✓ They are Paramagnetic

Paramagnetism is the attraction that occurs between transition metal ions and the magnetic field.

Atoms and cations of transition metal elements are weakly attracted to a magnetic field.

The property arises because of the presence of unpaired electrons in the transition metal atoms and ions. These unpaired electron spin about their axes to generate a magnetic field (magnetic moment) 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 manganese where it is maximum 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.

- ✓ They have act as catalysts

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.

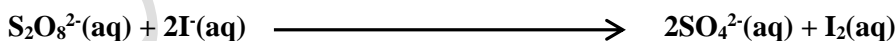
-Possession of variable oxidation states which enables them to take part in electron transfer reactions forming activated complexes of the reactants.

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

Some catalysis reactions involve heterogeneous catalysts in which the reactant molecules are adsorbed on the surface of the catalyst. It's likely that the 3d- electrons enable the transition metal to form temporally bonds in the reactant molecules. Examples of such reactions include;

- The contact process where vanadium pentaoxide V_2O_5 is a catalyst
- Haber process where finely divided iron is the catalyst
- Hydrogenation of unsaturated oils using nickel catalyst at 150°C

In homogeneous catalysis which is usually found in solution, the variable oxidation states of the transition metal may enable it to take part in a sequence of reaction stages and emerge unchanged at the end for example;



Iron(II) ions catalyses this reaction and it is thought that they may provide an alternative route for the reaction as follows;



Then;



- ✓ 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.

Transition elements have variable oxidation states because;

- Of the presence of empty orbitals and unpaired electrons. Manganese with the highest number of unpaired d – electrons shows the widest range of oxidation states and it's the only metal that exhibits oxidation state of +7. Elements/compounds with low oxidation states are strong reducing agents while those with high oxidation states are strong oxidizing agents.

+2 oxidation state

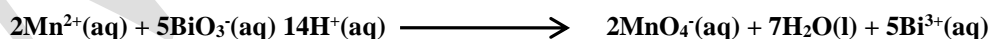
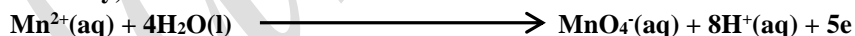
The divalent ions of vanadium, titanium, and chromium are all very strong reducing agents so that they reduce water to hydrogen.

Manganese(II) ion Mn^{2+} is formed more easily from the metal but its oxidation is less easily than expected, meaning that it has extra stability, this is because 3d – orbital in manganese is half full with electrons. Therefore, it can be oxidized by strong oxidizing agents like sodium bismuthate or lead(IV) oxide.



Dark brown solid dissolves to form a purple solution

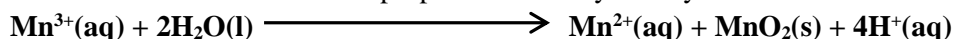
Similarly,



Colourless solution turns to purple solution

+3 oxidation state

Scandium exists only in +3 oxidation state but this state is very unstable for manganese, cobalt and nickel. The Mn^{3+} disproportionates very readily to Mn^{2+} and MnO_2 i.e



Higher oxidation states

Compounds with oxidation states of +4 for titanium, +5 for vanadium, +6 for chromium and +7 for manganese are particularly common for the element to achieve a stable

electronic configuration. These compounds are usually covalent and are strong oxidising agents.

Potassium permanganate and potassium dichromate(VI) are particularly well known oxidising agents and are widely used in volumetric analysis.

The manganate(VII) are stronger oxidising agents than the dichromate(VI) and are capable of oxidising water very slowly and for this reason not stored very well in aqueous solution, therefore standard solutions of potassium manganate(VII) must be freshly prepared and standardized.

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

✓ They form coloured compounds and ions

The formation of coloured compounds and ions is associated with the presence of partially/incompletely 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 wave length 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.

In an isolated transition metal atom, the 2d – orbitals are degenerate ie they are all at the same energy level. However, in a complex ion, the d-orbitals slightly differ in energy as a result of overlapping differently with ligands ie they are non-degenerate. The electrons can jump from d-orbitals to another orbital if they gain energy.

For most transition metal complexes, the frequency of the light absorbed in these electronic transitions is within the visible region of electromagnetic spectrum and the ion appears coloured, the colour of the ion is complementary to the colour absorbed

Zinc ion Zn^{2+} with a $3d^{10}$ configuration has no d-d electronic transitions and hence it is colourless.

Scandium Sc^{3+} with $3d^0$ configuration also has no d-d electronic transitions and is also colourless

✓ They form interstitial compounds

Transition metals have metallic lattices with spaces in between their atoms, these spaces are called interstitial spaces. These spaces can be occupied by atoms with atomic radii small enough such as carbon and nitrogen resulting into an interstitial alloy or compound for example carbon steels are interstitial alloys.

✓ They form complexes

A complex is an ion positive or negative in which atoms or groups of atoms with a negative charge or lone pair of electrons form coordinate/dative bonds with the central metal ion.

Or

It is an ion consisting of a central metal ion which is datively bonded to electron rich molecules or ions called ligands.

Transition metal elements form complexes by coordination which indicates the number of atoms.

Coordination number is the number of atoms/ligands forming coordinate bonds with the central metal ion. Common oxidation numbers are 2, 4 and 6.

Transition metals are able to form complexes because;

- They have vacant or partially filled d – orbitals in the transition metal ions which can accommodate the lone pairs of electrons from the ligands. This is because the d-orbitals require a small amount of energy to promote electrons from the ligands to be placed in them.
- They form cations with a high ionic charge and small ionic radius, high ionic 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.

A ligand is a negatively charged or neutral molecule with a lone pair of electrons and it uses these lone pairs to form coordinate bonds with the central metal ion.

Examples of neutral ligands include water and ammonia

Examples of negatively charged ligands include chloro Cl^- , cyano CN^- , thiocyanato SCN^- , etc.

Ligands are classified according to the number of donor atoms present in the molecule; they can be monodentate or polydentate ligands

Monodentate ligands

These are ligands which have one donor atom and hence form one dative bond with the central metal ion. Examples include aqua H_2O , ammine NH_3

Polydentate ligands

These are ligands with more than one donor atom and hence form more than one dative bond with the central metal ion. Examples include 1,2-diaminoethane $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$

Nomenclature of complexes

The following rules are used in naming 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 with o for example

- ✓ CN^- Cyano
- ✓ OH^- Hydroxo
- ✓ Br^- bromo
- ✓ Cl^- Chloro
- ✓ I^- Iodo
- ✓ F^- fluoro

- ✓ SO_4^{2-} Sulphate
- ✓ NO_3^- Nitrate
- ✓ NO_2^- Nitrite O^{2-} Oxo

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

- ✓ NH_3 Ammine
- ✓ H_2O Aqua
- ✓ NO Nitrosyl
- ✓ CO Carbonyl

6. In case there are more than one type of ligands, 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.

For example, 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 of complexes

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

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

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

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

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

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

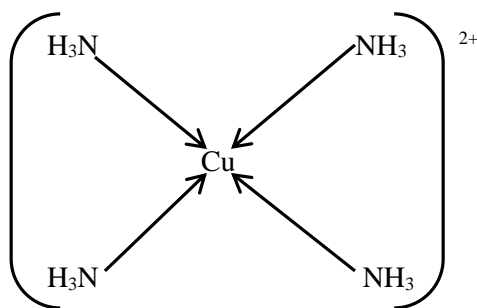
Shapes of complexes

The arrangement of bonds i.e dative bonds on the central ion in the complex determines the shape of the complex as follows.

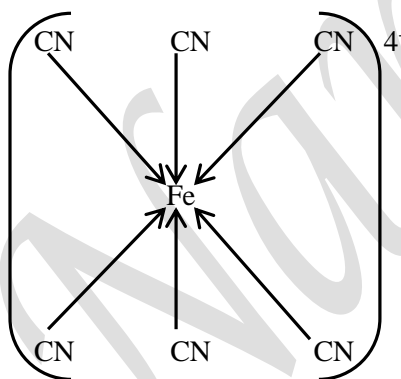
- ✓ Complexes of silver have a coordination number of 2 and are linear for example diamine silver ion $\text{Ag}(\text{NH}_3)_2^+$



- ✓ Complexes with coordination number of 4 are tetrahedral in shape for example tetraamminecopper(II) ion $[\text{Cu}(\text{NH}_3)_4]^{2+}$



- ✓ Complexes with coordination number of 6 are octahedral in shape for example hexacyanoferrate(II) ion $[\text{Fe}(\text{CN})_6]^{4-}$

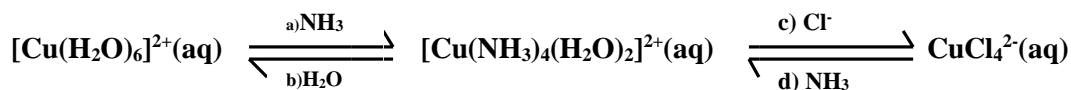


Displacement reactions of complexes

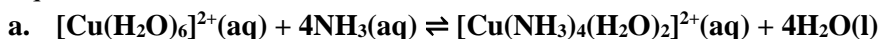
A ligand can be displaced by another and this results into a colour change; this colour change is used to identify the metal ion. The displacement reaction depends on the nature of the ligand and the concentration.

Examples

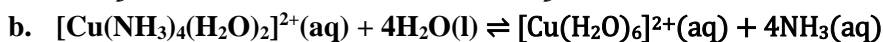
a) Copper(II) complexes



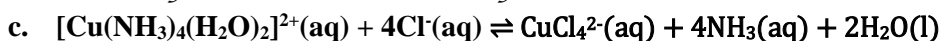
Equations of reactions are such that



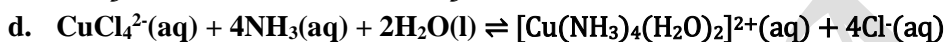
The pale blue solution turns deep blue



The deep blue solution turns pale blue

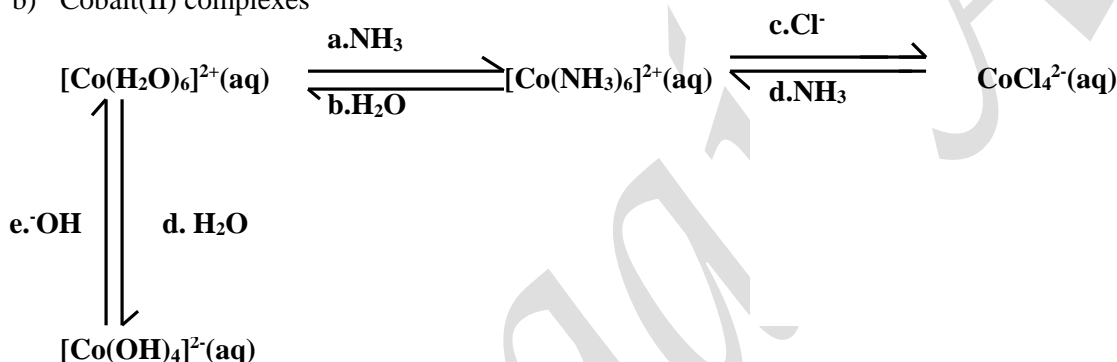


Deep blue solution turns yellow



Yellow solution turns deep blue

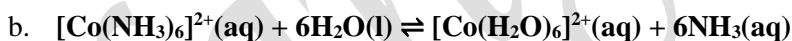
b) Cobalt(II) complexes



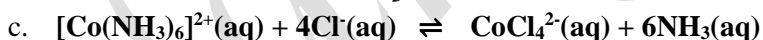
Equations for the reactions



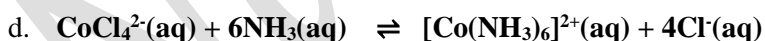
Pink solution turns brown



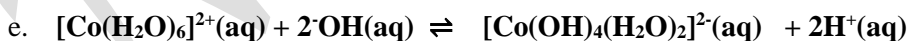
Brown solution turns pink



Brown solution turns blue

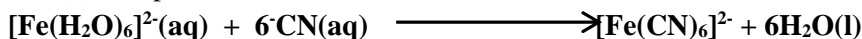


Blue solution turns brown



Pink solution turns blue

c) Iron(II) complexes



The order of ligand strength is such that $\text{CN}^- > \text{NH}_3 > \text{Cl}^- > \text{H}_2\text{O}$

Isomerism in complexes

Compounds which have the same molecular formula but different structural formulae are said to be isomers.

There are two types of isomerism i.e structural and hydration isomerism.

Structural isomerism

This occurs in complex ions where the composition of the first coordination sphere may differ from one compound to another.

Structural isomerism is divided into two i.e ionisation and hydration isomerism

Ionisation isomerism

This type of isomerism occurs when compounds yield different ions in solution. For example;

$[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ Pentaamminemonobromocobalt(III) sulphate

And

$[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ Pentaamminemonosulphatecobalt(III) bromide

Hydration isomerism

This type of isomerism arises when 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 $\text{CrCl}_2 \cdot 6\text{H}_2\text{O}$, hydrated chromium(III) chloride i.e

$[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ hexaaquachromium(III) chloride which is violet

$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ pentaquachlorochromium(III) chloride which is pale green

$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ tetraquadichlorochromium(III) chloride 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

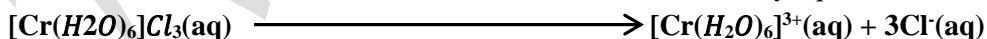
Isomer 2 gives two moles of silver chloride

Isomer 3 gives one mole of silver chloride.

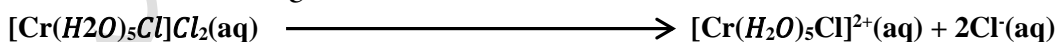
This is due to the difference in the number of chloride ions that are exchanged with the molecules in the complex compound.

Conductivity of the above isomer depends on the number of ions in solution, the higher the number of ions in solution, the higher the conductivity and the lower the number of ions in solution, the lower the conductivity. Therefore conductivity of the above isomers is in the order

$[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3 > [\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 > [\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$ as illustrated by equations below



It has 4 conducting ions hence most conductive



It has 3 conducting ions



It has 2 conducting ions hence least conductive

Guiding question

Chromium exhibits structural isomerism in some of its complexes $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ has at least 3 coloured isomers. When one of the isomers which is violet in colour reacts with silver nitrate solution, all the chlorine is precipitated as silver chloride. A second pale green isomer also reacts with silver nitrate solution but only 2/3 of chlorine is precipitated as silver chloride. The 3rd dark green isomer precipitates only 1/3 of its chlorine as silver nitrate.

- Write the structural formulae and the I.U.P.A.C names of each of the 3 isomers.
- Arrange the isomers in order of increasing conductivity and explain your answer.

Chemical properties of transition elements

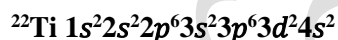
Scandium

Scandium does not show all transition metal properties because it forms Sc^{3+} ion which has no 3d electrons and it is colourless.

Scandium is similar to calcium in its reactivity with water where it reacts slowly with cold water to form scandium hydroxide and hydrogen gas as shown by the equation below.



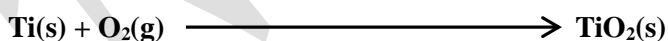
Titanium



Reactions of titanium

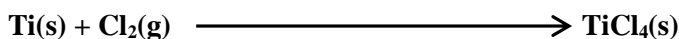
a) Reaction with air

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



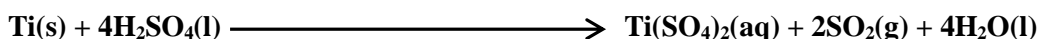
b) Reaction with chlorine

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



c) Reaction with acids

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



Compounds of titanium

Titanium forms compounds in the +2, +3 and +4 oxidation states.

Titanium(III) compounds

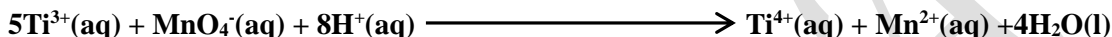
In the +3 oxidation state, the titanium ion still has one electron in the 3d-orbital and hence titanium(III) compounds are coloured and paramagnetic.

Titanium(III) compounds are reducing agents.

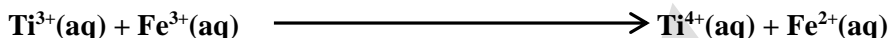


Titanium(III) salts are standardized by;

Titration with acidified potassium permanganate at 60°C



Titration with iron(III) solution using ammonium thiocyanate as an indicator

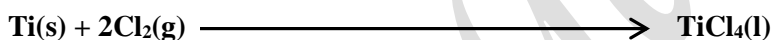


Titanium(IV) compounds

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) chloride

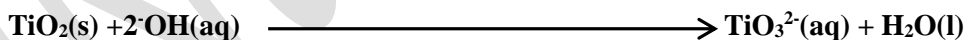
This can be prepared by heating titanium in a stream of dry chlorine.



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



The titanium(IV) oxide formed is amphoteric therefore reacts with both acids and bases as shown below;



Vanadium



Vanadium is resistant to chemical attack and at room temperature, it is not affected by air, water, non-oxidising acids and alkalis.

Reactions of vanadium

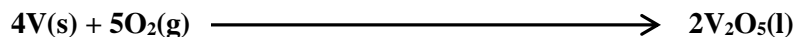
a) With chlorine

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



b) With air

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



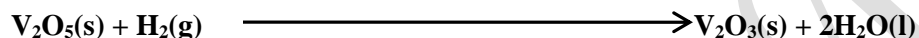
Compounds of vanadium

Vanadium forms compounds in the +2, +3, +4, and +5 oxidation states.

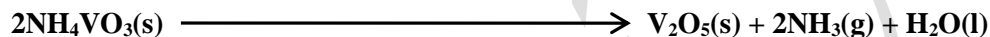
The +4 is the most stable oxidation state of all.

In +2 oxidation state, hexaaquavanadium(II) ion is violet

In +3 oxidation state is vanadium trioxide which is prepared by reducing vanadium pentaoxide with hydrogen



Vanadium pentaoxide is prepared by heating ammonium vanadate



Vanadium(V) oxide is an orange solid and amphoteric in nature, this implies that it is able to react with both acids and bases as shown in the below equations



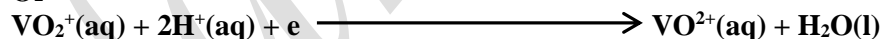
All the oxidation states of vanadium can be observed in the aqueous species formed when a solution of ammonium vanadate(V) is treated with dilute sulphuric acid and zinc amalgam. The colour of the solution changes from yellow to blue to green and then finally to violet.



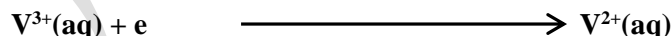
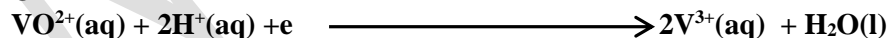
Or



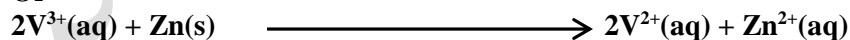
Or



Or



Or



Oxidation state	+5	+4	+3	+2
Colour in solution	Yellow	Blue	Green	Violet
Ion	VO_2^+	VO^{2+}	V^{3+}	V^{2+}
Name	Dioxovanadium(V) ion	Oxovanadium(IV) ion	Vanadium(III) ion	Vanadium(II) ion

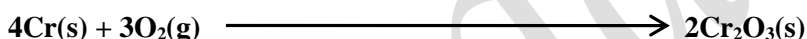
Chromium

^{24}Cr E.C $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$

Reactions of chromium

a) Reaction with air

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



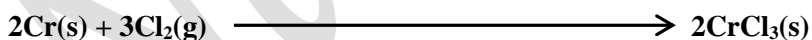
b) Reaction with water

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



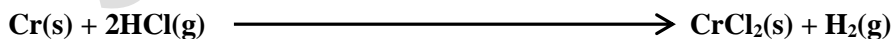
c) Reaction with chlorine

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



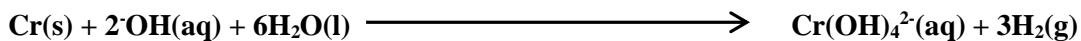
d) Reaction with hydrogen chloride gas

With dry hydrogen gas, chromium reacts on heating to form chromium(II) chloride and hydrogen gas.

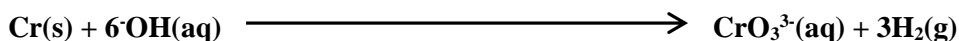


e) Reaction with alkalis

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



Or

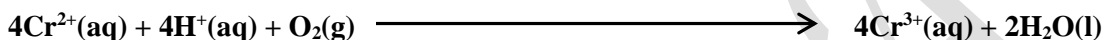


f) Reaction with acids

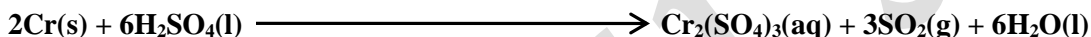
Chromium reacts with warm dilute sulphuric and hydrochloric acids to give the corresponding chromium(II) salts and hydrogen gas.



The chromium(II) salts formed are very unstable and are quickly oxidised to chromium(III) salts.



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



Chromium is rendered passive by concentrated nitric acid

Compounds of chromium

Chromium forms compounds in the +2, +3, and +6 oxidation states.

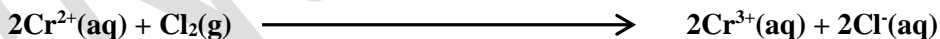
The +3 oxidation state is the most stable.

Chromium(II) compounds

Compounds of chromium in this oxidation state are very unstable and strong reducing agents.



Chromium(II) compounds are easily oxidised to chromium(III) by oxidising agents such as chlorine.



Chromium(II) chloride

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



Chromium(II) hydroxide

It's a yellow solid precipitated when small amounts of an alkali are added to a solution of chromium(II) salt



Chromium(III) compounds

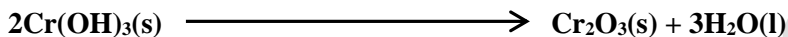
Chromium is more stable in +3 oxidation state, as oxidation state increases,

- ✓ Bonding changes from ionic to covalent because charge density increases
- ✓ Oxides change from basic through amphoteric to acidic

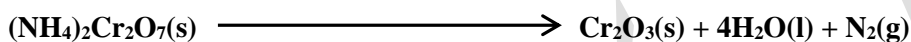
Compounds of chromium in +3 oxidation state and their reactions are studied below,]

Chromium(III) oxide

It is a green amphoteric solid that can be obtained by heating chromium(III) hydroxide.



It can also be prepared by heating ammonium dichromate(VI)



It is an amphoteric oxide, therefore reacts with both acids and bases(alkalis), it reacts with acids to form corresponding chromium(III) salts



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



Or

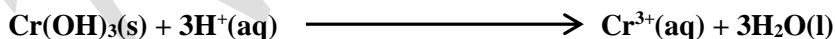


Chromium(III) hydroxide

It is a green amphoteric solid prepared through precipitation by reacting a solution of chromium(III) ions with ammonia solution/sodium (potassium) hydroxide solution in presence of ammonium chloride.



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



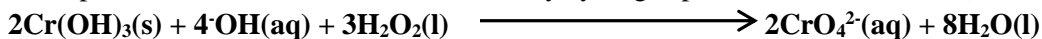
It reacts with alkalis to form chromate(III) salts which appear as a green solution.



Or



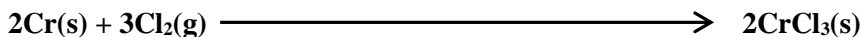
In the presence of excess alkali, it is oxidised by hydrogen peroxide to chromate(VI) ions on heating



Yellow solution

Chromium(III) chloride

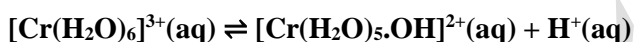
It is prepared by passing a stream of dry chlorine gas over heated chromium metal



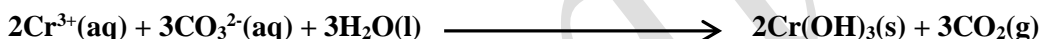
Hydrolysis of chromium(III) compounds

In aqueous solutions, chromium(III) salts exist as $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ which is violet in colour and octahedral in shape.

The chromium(III) cation has a high ionic charge and a small ionic radius giving it a high charge density thus in water, it becomes heavily hydrated in solution and undergoes hydrolysis as follows. 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.



When sodium carbonate solution is added to the resultant solution, a green precipitate is formed and bubbles of a colourless gas are given off which turn lime water milky.



When hydrogen carbonate solution is added, a green precipitate is formed and bubbles of a colourless gas are given off which turn lime water milky.



Analysis of chromium(III) ion in solution

a) Using sodium hydroxide solution

A green precipitate soluble in excess forming a green solution

Dropwise

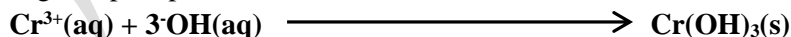


In excess



b) Using ammonia solution

A green precipitate insoluble in excess



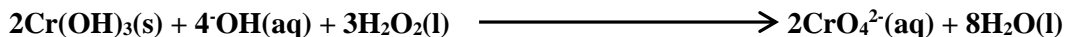
c) Using sodium/potassium carbonate solution

A green precipitate is formed and bubbles of a colourless gas are given off which turn lime water milky.



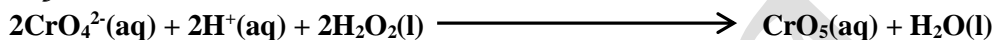
d) Using hydrogen peroxide in alkaline media followed by heat

A green precipitate which dissolves to form a yellow solution is formed



Note

If the resultant solution is added dilute acid then ether or butanol followed by hydrogen peroxide, a blue colour separates in the organic layer.



Chromium(VI) compounds

In +6 oxidation state,

- ✓ Chromium forms covalent bonds
- ✓ The compounds are acidic
- ✓ The compounds are strong oxidising agents and they tend to be reduced to chromium(III) ions

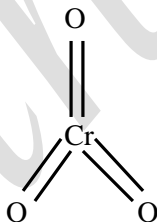
The compounds of chromium in +6 oxidation state include

Chromium(VI) oxide CrO_3

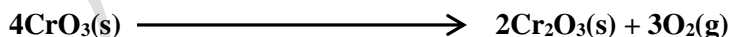
Chromium(VI) oxide is a dark red crystalline solid that can be prepared by adding concentrated sulphuric acid to a saturated solution of potassium dichromate



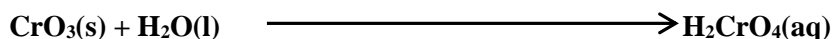
It is trigonal planar in shape



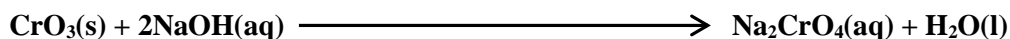
When heated it decomposes to give chromium(III) oxide and oxygen gas



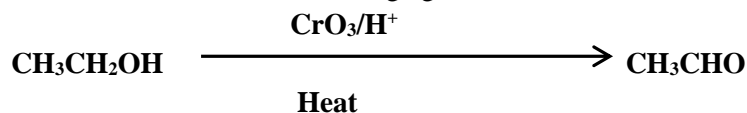
It is an acidic oxide therefore dissolves in water to form an acid i.e chromic(VI) acid



It also reacts with alkalis to form chromates(VI) and water

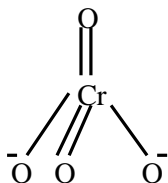


In acidic media, it is an oxidising agent



Chromate(VI) CrO_4^{2-}

This is a yellow crystalline solid with a tetrahedral shape



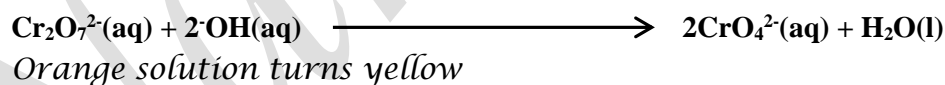
Chromate(VI) salts are derived from chromic(VI) acid.

They are generally insoluble in water except sodium, potassium and ammonium chromates which are soluble

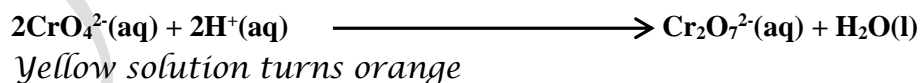
The insoluble chromates can be prepared by precipitation reactions.



Chromate(VI) can also be obtained by reacting sodium hydroxide solution and a solution of a dichromate(VI)



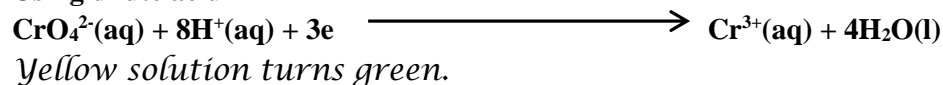
In acidic media, chromate(VI) dissolves forming a dichromate(VI)



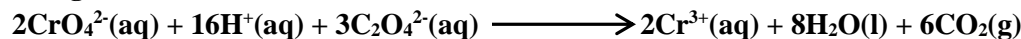
Chromate(VI) is used to confirm the presence of Pb^{2+} , Ba^{2+} , and Ag^+

Chromate(VI) ions are oxidising agents in which case they are reduced to chromium(III) ions by an acid (reducing agent), where the yellow solution turns green.

a) Using dilute acid

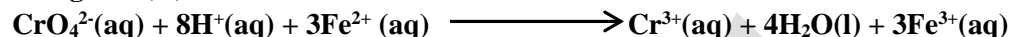


b) Using oxalic acid



Yellow solution turns green and bubbles of a colourless gas are given off

c) Using iron(II) ions



Yellow solution turns green

d) Using potassium iodide solution



Yellow solution turns green

e) Using hydrogen sulphide



Yellow solution turns green

f) Using nitrous acid



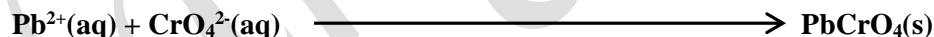
Yellow solution turns green

Analysis of chromate(VI) ions in solution

By precipitation using lead(II) nitrate and lead(II) acetate

A yellow precipitate soluble in sodium hydroxide solution

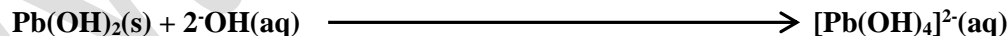
First



Then



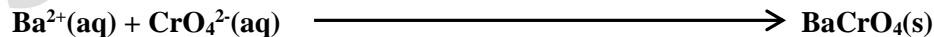
And



Using barium chloride/nitrate solution

A yellow precipitate insoluble in sodium hydroxide solution

First

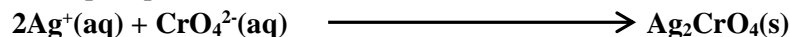


Then



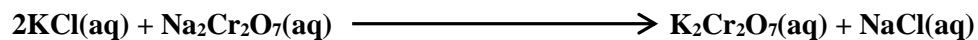
Using silver nitrate solution

A red precipitate is formed

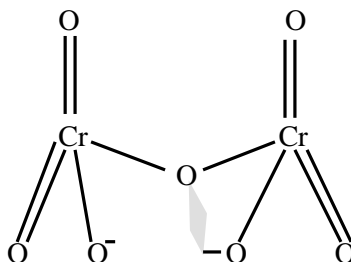


Dichromate(VI)

Potassium dichromate(VI) is an orange salt prepared by mixing hot concentrated solution of sodium dichromate and potassium chloride.



Any dichromate is an orange solid with the structure below;



Dichromate(VI) can be obtained by adding dilute sulphuric acid to a solution of a chromate(VI)



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



Dichromate(VI) ions are strong oxidizing agents in acid media, as shown by the following reactions.

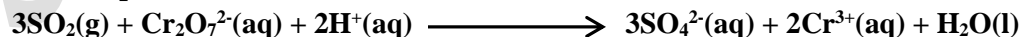
With hydrogen peroxide in acidic media, it behaves as a reducing agent



Orange solution turns blue

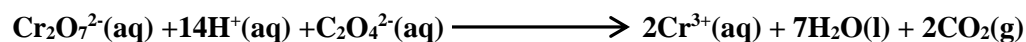
With other reducing agents, it behaves as an oxidising agent. However, it is not strong enough to oxidise chlorides to chlorine therefore they can be used in the presence of hydrochloric acid in volumetric analysis.

With sulphur dioxide



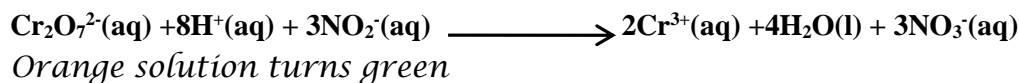
Orange solution turns green

With oxalate ions

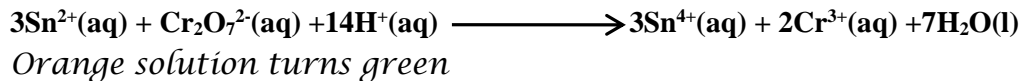


Orange solution turns green

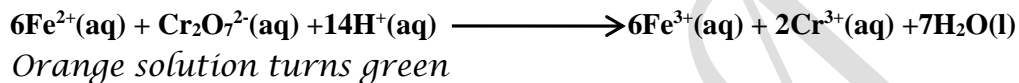
With nitrous acid



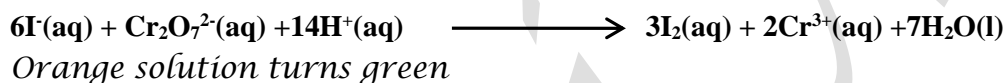
With tin(II) ions



With iron(II) ions



With iodide ions



With sulphite ions



With hydrogen sulphide



Note

Dilute nitric acid is not used to acidify a dichromate(VI) because the acid is a stronger oxidising agent.

Guiding question

A crystalline solid Z dissolves in water to form a violet solution. Addition of sodium hydroxide solution to the solution produces a grey-green solid which dissolves in excess alkali to form a deep green solution. The solution changed from green to yellow when sodium peroxide was added to it.

Name the cation in Z

Write equations for reactions which took place when sodium hydroxide solution was added to a solution of Z

Write the equation for the reaction leading to formation of the yellow species.

Manganese

Electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$

Manganese is a hard and brittle metal with a high melting point because it forms very strong metallic bonds. However, its melting point is lower than that of chromium because in manganese the 3d-subenergy level is half full hence relatively stable therefore electrons are less available for bonding unlike in chromium.

Manganese exists as pyrolusite (Manganese dioxide) MnO_2 and hausmannite (trimanganese tetraoxide) Mn_3O_4

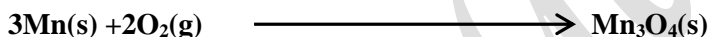
Oxidation states of manganese

- ✓ +2 oxidation state Mn^{2+} e.g manganese(II) oxide MnO , the ions are pink or colourless
- ✓ +3 oxidation state Mn^{3+} e.g manganese(II) oxide Mn_2O_3 , a brown solid
- ✓ +4 oxidation state Mn^{4+} e.g manganese(II) oxide MnO_2 a black solid
- ✓ +6 oxidation state Mn^{6+} e.g manganese(II) oxide MnO_4^{2-} green
- ✓ +7 oxidation state Mn^{7+} e.g manganese(II) oxide MnO_4^- purple

Chemical properties of manganese

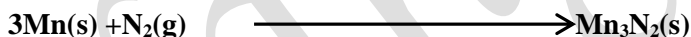
a) Reaction with air

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



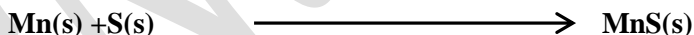
b) Reaction with nitrogen

Manganese reacts with dry nitrogen on strong heating to form manganese(II) nitride



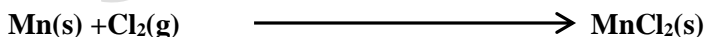
c) Reaction with sulphur

Manganese reacts with hot sulphur on strong heating to form manganese(II) sulphide



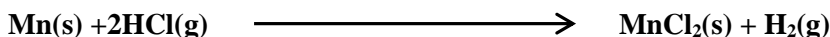
d) Reaction with chlorine

Manganese reacts with dry chlorine on strong heating to form manganese(II) chloride



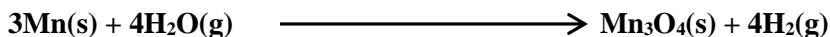
e) Reaction with hydrogen chloride

Manganese reacts with dry hydrogen chloride on strong heating to form manganese(II) chloride and hydrogen gas.



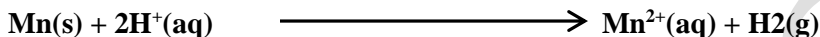
f) Reaction with water

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



g) Reaction with acids

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



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



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



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



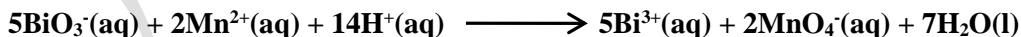
Compounds of manganese

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

Manganese(II) compounds

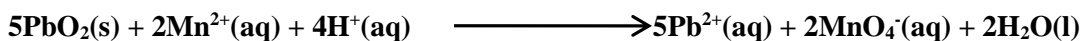
In the +2 oxidation state, the two 4s electrons are lost, leaving a half-filled 3d orbital which is stable. This makes the +2 oxidation state the most stable oxidation state of manganese

They can be oxidised by powerful oxidising agents like sodium bismuthate and lead(IV) oxide.



Colourless solution turns purple

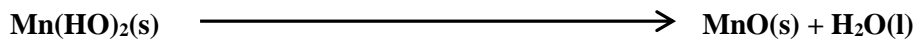
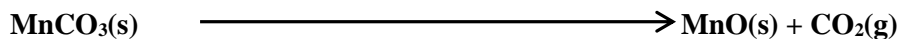
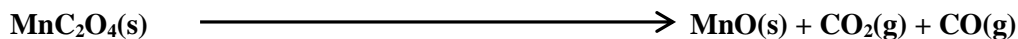
Or



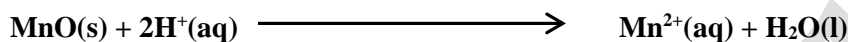
Colourless solution turns purple

Manganese(II) oxide, MnO

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



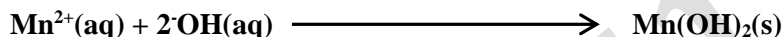
It is a basic oxide, hence dissolves in acids to form manganese(II) salts



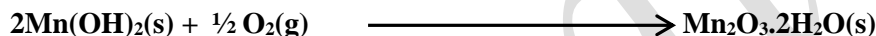
Manganese(II) hydroxide $\text{Mn}(\text{OH})_2$

It is a white precipitate obtained when sodium hydroxide or ammonia solution is added to a solution containing manganese(II) ions.

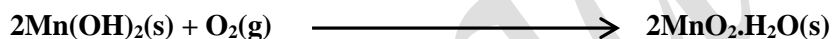
The observation is that a white precipitate insoluble in excess, turns brown on standing due to oxidation.



Then



Or



Manganese(II) nitrate

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



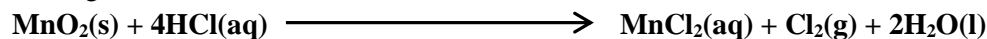
Manganese(II) carbonate

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

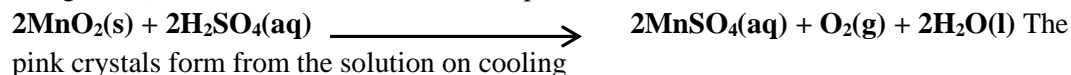


Note

- ✓ Most manganese(II) salts are pink, in solution they exist as hexaaquamanganese(II) ion $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
- ✓ Manganese(II) carbonate is red
- ✓ Manganese(II) chloride crystals ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) can be obtained by heating manganese(IV) oxide with concentrated hydrochloric acid. The pink crystals form from the solution on cooling

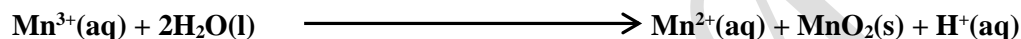


- ✓ Manganese(II) sulphate crystals ($\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$) can be obtained by heating manganese(IV) oxide with concentrated sulphuric acid



Manganese(III) compounds

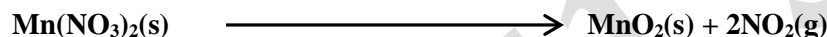
Compounds of manganese in this state are not common because disproportionate in water to form manganese(II) ion and manganese(IV) oxide.



Manganese(IV) compounds

Manganese(IV) oxide, MnO_2

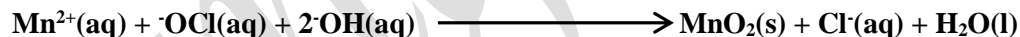
Anhydrous manganese(IV) oxide is a black solid prepared by heating manganese(II) nitrate



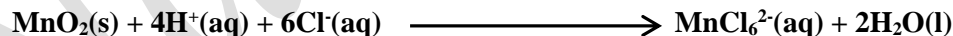
It can also be prepared by heating trimanganese tetraoxide in nitric oxide



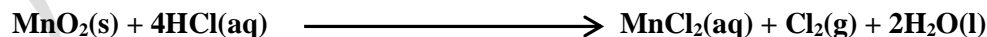
Its preparation can also be effected by oxidation of manganese(II) salts using sodium hypochlorite and sodium hydroxide



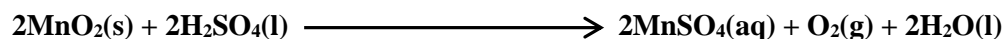
Manganese(IV) oxide is essentially ionic, it dissolves in cold concentrated hydrochloric acid to form hexachloromanganate(IV) complex



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



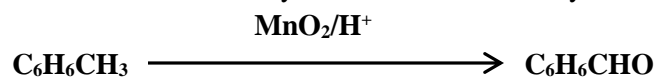
Manganese(IV) oxide reacts with hot concentrated sulphuric acid to liberate oxygen



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

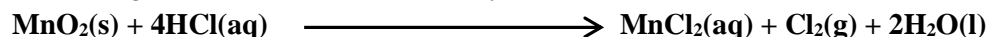


It is also oxidises methylbenzene to benzaldehyde

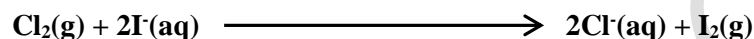


Experiment to determine the percentage of manganese(IV) oxide in pyrolusite

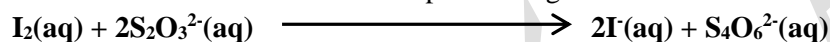
A known mass for pyrolusite (ore) is dissolved in excess hot concentrated hydrochloric acid. Manganese(IV) oxide reacts with hydrochloric acid to liberate chlorine



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



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



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

$$\text{Percentage of manganese(IV)oxide} = \frac{\text{mass of manganese(IV)oxide}}{\text{mass of ore}} \times 100\%$$

Manganese(VI) compounds

The only stable compound in +6 oxidation state is sodium/potassium manganate(VI) which is a dark green crystal.

Potassium manganate(VI) can be obtained as a green solution by fusing potassium hydroxide with manganese(IV) oxide in the presence of excess oxygen or potassium chlorate.

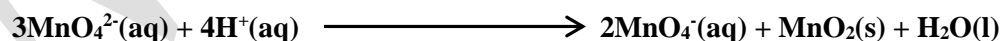


Or

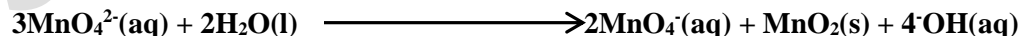


Manganate(VI) ion is only stable in alkaline medium.

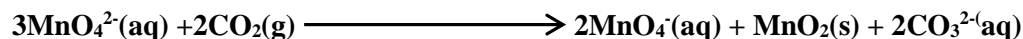
It disproportionates in the presence of an acid to form manganese(IV) oxide and permanganate ion. The green solution turns to a purple solution



In water, it undergoes hydrolysis as follows; green solution turns purple



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



Manganese(VII) compounds

Potassium manganate(VII) also called potassium permanganate

It is dark purple crystalline solid 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 a stronger oxidizing agent than potassium permanganate hence would compete with it during the reaction.

Hydrochloric acid is not used because it is easily oxidized to chlorine by the potassium permanganate.



It is prepared by heating a solid mixture of potassium hydroxide, potassium chlorate and manganese(IV) oxide to form a green solid of potassium manganate(VI)



The green solid is dissolved in water to form a green solution, this green solution is then acidified bubbling carbon dioxide through the mixture and a purple solution with a black solid is observed.



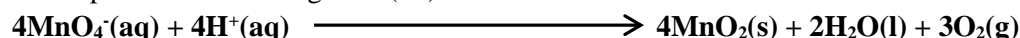
The solution is then filtered and the filtrate is crystallised to form purple crystals of potassium permanganate.

Advantages of using potassium permanganate in volumetric analysis

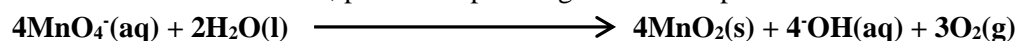
- ✓ It is a self – indicator
- ✓ It a high formula mass which minimizes the weighing errors
- ✓ It is highly soluble in water
- ✓ Most of its reaction can occur fast enough at room temperature

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

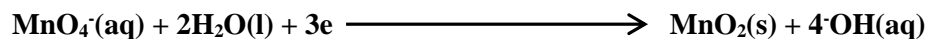
- ✓ It always found contaminated with manganese(VI) oxide
- ✓ It is not highly stable. In light, a solution of acidified potassium manganate(VII) decomposes to form manganese(IV) oxide



In alkaline/neutral medium, potassium permanganate decomposes as follows



In slightly alkaline medium, manganate(VII) is reduced to manganese(IV) oxide

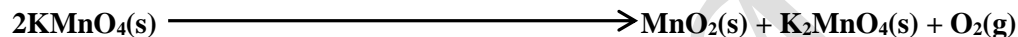


In strong alkaline, a manganate(VI) is formed



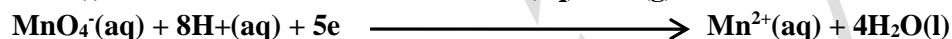
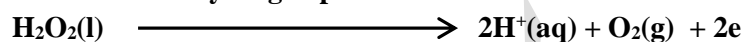
Reactions of potassium permanganate

When heated, it decomposes to form manganese(IV) and potassium manganate(VI) with oxygen gas.



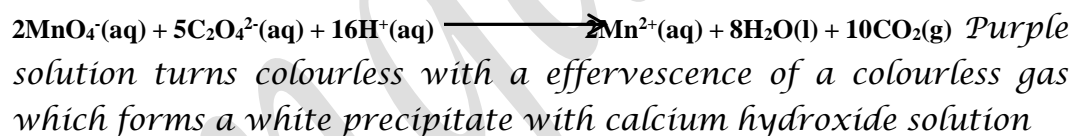
It is a strong oxidising agent in acidic media as shown in the following reactions

Reaction with hydrogen peroxide



Purple solution turns colourless with a effervescence of a colourless gas which rekindles a glowing splint

Reaction with oxalate ion



Reaction with iron(II) ion

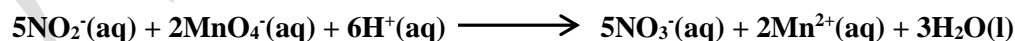


Purple solution turns colourless

Or

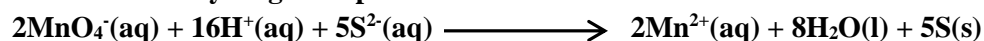
Green solution turns brown

Reaction with nitrous acid



Purple solution turns colourless

Reaction with hydrogen sulphide

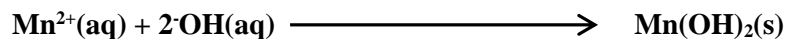


Purple solution turns colourless and a yellow solid is deposited

Qualitative analysis of Mn^{2+}

Using sodium hydroxide solution

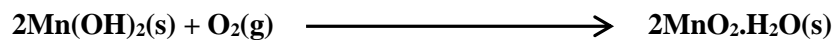
A white precipitate insoluble in excess, turns brown on standing



Then



Or

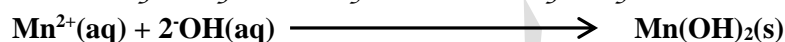


Using sodium hydroxide solution followed by hydrogen peroxide

A white precipitate insoluble in excess, turns brown on standing, on addition of hydrogen peroxide, effervescence of a colourless gas occurs, and a black solid is formed.

Using Ammonia solution

A white precipitate is formed, it rapidly turns to brown on standing.



Then



Or



Using concentrated nitric acid and solid sodium bismuthate (confirmatory test)

Colourless solution turns purple



Using concentrated nitric acid and solid lead(IV) oxide and warm

Colourless solution turned to a purple solution



Guiding question

A solution A contains a divalent metal ion, addition of excess ethane-1,2-dioic acid produces a pale pink precipitate P. On heating P in air it decomposes fast to a green solid in C, on further heating, a black solid D is formed. C is soluble in acid but D is not, when D is fused with solid potassium hydroxide solution and potassium chlorate, a green solid E is formed which gives a green solution in water. On acidifying the aqueous solution of E, the solution turns purple and a precipitate D also forms, the purple solution F reacts with iron(II) in acidic medium to give a solution containing A.

Identify all the species A to F

Give equations for all reactions occurring.

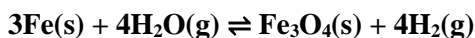
Iron

Electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$

Chemical properties of iron

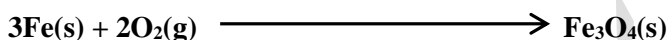
a) Reaction with water

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

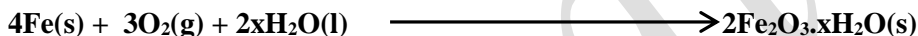


b) Reaction with air

Heated iron reacts with air to form triiron tetraoxide also called magnetite (an ore)



In the presence of water, iron reacts with air to form a reddish brown coat called rust whose chemical name is hydrated iron(III) oxide



c) Reaction with

Heated iron reacts with dry chlorine to form iron(III) chloride, which sublimes on strong heating

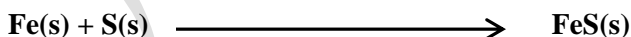


With hydrogen chloride gas, iron(II) chloride and hydrogen gas are formed



d) Reaction with sulphur

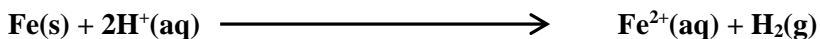
When a mixture of iron and sulphur is heated, a red glow spreads through the mixture and a black solid is formed, due to formation of iron(II) sulphide, which is used in the preparation of hydrogen sulphide gas



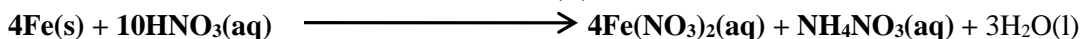
e) Reaction with acids

With dilute non oxidising acids

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

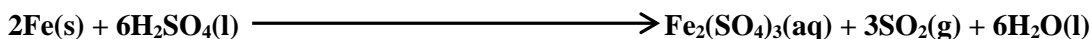


With dilute nitric acid, iron reacts to form iron(II) nitrate, ammonium nitrate and water



With concentrated acids

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



Iron is rendered passive by concentrated nitric acid

Compounds of iron

Iron forms compounds +2 and +3 oxidation states. +2 oxidation state arises from the loss of two electrons from the 4s orbital giving rise to iron(II) ion, Fe^{2+} while the loss of two electrons from the 4s and one electron from the 3d orbitals gives rise to Fe^{3+}

The iron(III) ion and the compounds formed in this oxidation state are more stable than those in +2 oxidation state, because the 3d orbital in +3 oxidation state is half filled and relatively stable, this explains why iron(II) compounds easily oxidize to iron(III) compounds.

Iron(II) compounds

Iron(II) oxide

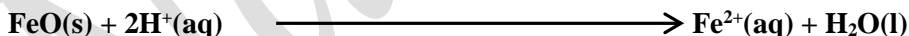
It is a black basic solid obtained by heating iron(II) oxalate in the absence of air.



On heating the solid product in air, the black solid turns to a brown solid



Since iron(II) is basic, it readily reacts with dilute acids to form iron(II) salts and water

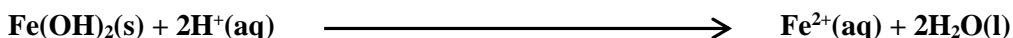


Iron(II) hydroxide

It is obtained as a green precipitate by adding an alkali such as sodium/potassium hydroxide solution to a solution of iron(II) salt. However, due to aerial oxidation its easily oxidised to iron(III) hydroxide which is a brown precipitate, due to this reaction, after some time, the green precipitate becomes dirty green.

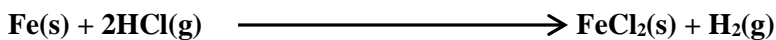


It is basic and hence reacts with dilute acids to form iron(II) salts and water



Iron(II) chloride

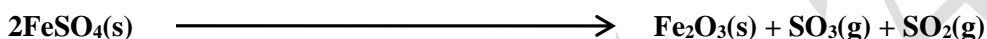
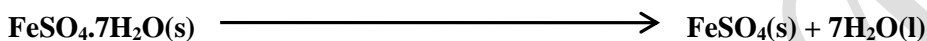
Anhydrous iron(II) chloride is a pale yellow solid prepared by heating iron in a stream of dry hydrogen chloride gas. Hydrated iron(II) chloride is obtained by crystallization



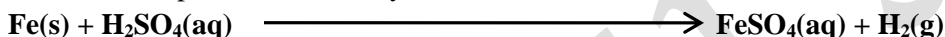
Iron(II) sulphate

It appears as green crystalline solid $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

On heating, it loses its water of crystallization, but on strong heating, it gives sulphur trioxide and sulphur dioxide.



In the laboratory, it is prepared by the action of dilute sulphuric acid on iron filings, the resulting solution is evaporated to form crystals



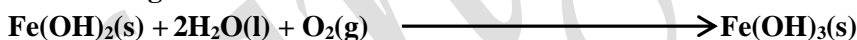
Analysis of iron(II) ions in solution

Using sodium hydroxide solution

Green precipitate insoluble in excess, turns brown on standing

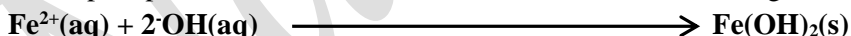


On standing

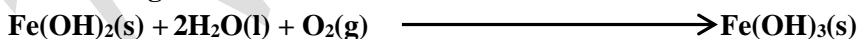


Using ammonia solution

Green precipitate insoluble in excess that turns brown on standing



On standing



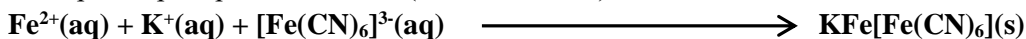
Using concentrated nitric acid (few drops)

Green solution turns yellow and brown fumes of a gas are given off



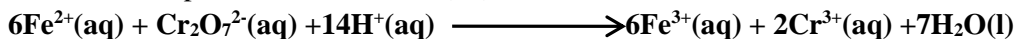
Using potassium hexacyanoferrate(III) solution

A deep blue precipitate is formed (Turnbull's blue)

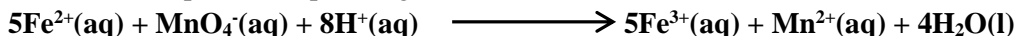


Redox reactions

With acidified potassium dichromate(VI) solution



With acidified potassium permanganate solution

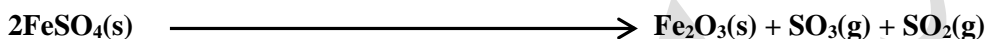


Iron(III) compounds

Compounds of iron in +3 oxidation state are very stable and are normally brown in colour. These compounds include;

Iron(III) oxide

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

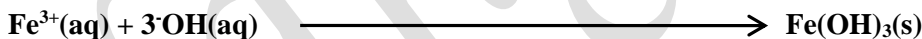


It is basic and readily reacts with hot dilute acids to form iron(III) salts and water

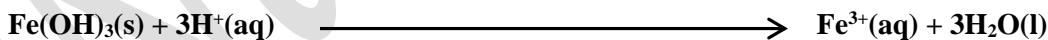


Iron(III) hydroxide

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

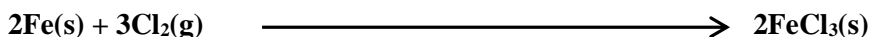


It is basic and reacts with dilute acids to form iron(III) salts and water

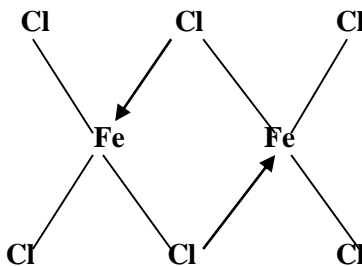


Iron(III) chloride

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

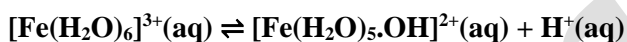
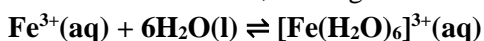


It is a covalent solid which exists as a dimer, Fe_2Cl_6 , in the vapour phase.



Hydrolysis of iron(III) salts in water

Solutions of iron(III) salts are acidic. The iron(III) cation has a high ionic charge and a small ionic radius which gives the iron(III) ion a high charge density thus in solution, it becomes heavily hydrated in solution and undergoes hydrolysis forming hexaaquairon(III) ion. 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 due to the hydrogen ions.



Or



Analysis of iron(III) ions in solution

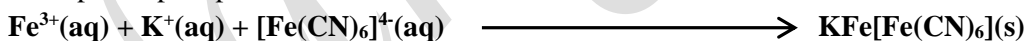
Using potassium/ammonium thiocyanate solution

A blood red colouration



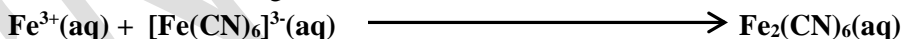
Using potassium hexacyanoferrate(II) solution

A deep blue precipitate



Action of potassium hexacyanoferrate(III) solution

Yellow solution turns green

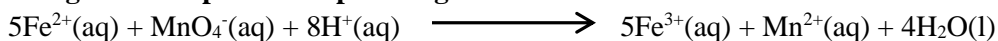


Fe^{2+} to Fe^{3+} conversions

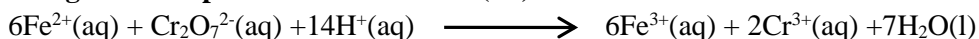
It is done by oxidising agents

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

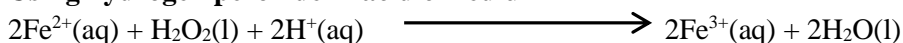
Using acidified potassium permanganate



Using acidified potassium dichromate(VI)



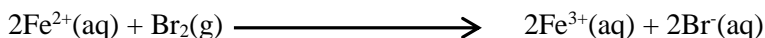
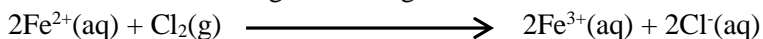
Using hydrogen peroxide in acidic medium



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 changes colourless



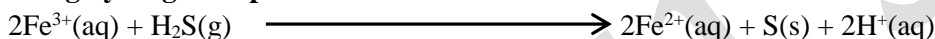
Fe³⁺ to Fe²⁺ conversions

It's done by reducing agents

Using potassium iodide



Using hydrogen sulphide



Using sulphur dioxide



Extraction of iron

Iron occurs as iron pyrites FeS_2 (concentrated by froth flotation), haematite Fe_2O_3 , magnetite Fe_3O_4 (concentrated in a magnetic field), siderate/spathic ore FeCO_3 (concentrated by roasting in air), limonite $\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$

The chief ore from which iron is extracted is haematite Fe_2O_3

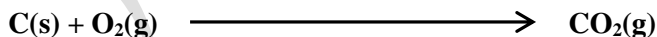
Extraction of iron from haematite

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

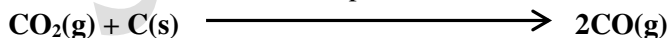
A mixture of the roasted ore, coke (carbon) and limestone (calcium carbonate) are fed into the blast furnace from the top.

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

Coke burns in the hot air to form carbon dioxide



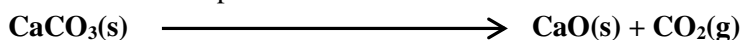
As the carbon dioxide rises up the furnace, it is reduced by the unburnt coke to carbon monoxide



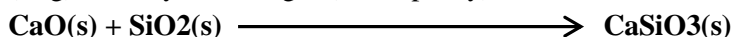
The carbon monoxide then reduces the iron ore to molten iron in the upper parts of the furnace.



Limestone decomposes to calcium oxide and carbon dioxide



Calcium oxide reacts with silicon(IV) oxide, the impurity, to form molten slag of calcium silicate (slag), thereby removing it (the impurity)



The molten iron sinks to the bottom since its denser than slag which floats on top, the slag also prevents oxidation of iron.

The iron obtained here is called pig iron because it is impure.

Uses of slag

- ✓ It is used in road surfacing since it forms hard surfaces
- ✓ It is used to fill quarries during land reclamation
- ✓ It is used to make fertilisers since it is rich in phosphates

Types of iron

There are three types of iron which are classified according to their percentage purity. The percentage purity also determines the strength and use of the iron. The types of iron are cast iron (pig iron), wrought iron and steel.

Cast iron

This is an impure iron which contains relatively high proportions of carbon (4%) and small proportions of other substances such as silicon, phosphorus and sulphur. Such impurities make cast iron to be hard, brittle and to have a lower melting point than pure iron.

It cannot be welded and has little tensile strength.

Cast iron can be used to make hot water pipes, Bunsen burner bases, cookers, in railings and other purposes where little strain is imposed.

Wrought iron

This is the purest form of iron (contains about 0.3% carbon) and it is obtained from cast iron by heating it with iron(III) oxide in a furnace by a process known as puddling.

The oxygen of the iron oxide oxidizes carbon and sulphur to their respective gaseous oxides, phosphorus to Phosphates(V) and silicon to silicates which form slag.

The semi molten mass obtained is then hammered and rolled so that the slag is squeezed out and a mass of almost pure iron remains.

It is very tough, malleable and ductile and is therefore used to make iron nails, sheeting, ornamental work, horse shoes and agricultural implements.

Wrought iron is sometimes referred to as low carbon steel.

Steel

Steel is an alloy of mainly iron with carbon and other elements like manganese, chromium, silicon, cobalt and sometimes tungsten.

The quality of steel depends on the amount of carbon present and this in turn determines its intended use.

Steel is generally used in the construction of buildings, bridges, ships, car bodies, cutting and boring tools, crushing machines and stainless cutlery such as knives, forks etc.

Rusting

This is a chemical reaction between iron, oxygen and water to form a reddish brown coat called rust.

Rust is a reddish brown coat formed when iron reacts with oxygen in the presence of water. Its chemical name is hydrated iron(III) oxide.

Rusting is favoured by presence of impurities on the iron atom, its an electrochemical process with different parts of iron acting as anode and cathode.

Effects of dissolved substances on rusting

Presence of dissolved salts or acids in water tend to accelerate rusting while alkaline solutions tend to slow down rusting, therefore iron will rust faster in a salty or acidic solution than in tap water.

Advantages of rusting

- ✓ It helps in the decomposition of disposed iron and increases the iron content in the soil necessary for plants.
- ✓ It creates and increases market for the iron manufacturing industry.
- ✓ Rust is used for making paints
- ✓ Study purposes in the laboratory.

Disadvantages

- ✓ It weakens and wears the metal.
- ✓ It causes the metal to lose shape.
- ✓ It makes metals to appear dark.
- ✓ It increases friction in machines.
- ✓ It increases the maintenance costs of materials made of iron.
- ✓ It contaminates tinned food.

Prevention of rusting

Rusting can be controlled by preventing the iron from getting in to contact with air/ oxygen and water/ moisture. The following methods can be used.

- ✓ Oil and grease. When a layer of oil or grease is applied to the surface of iron, air and moisture are kept away and no rusting occurs. Oil and grease is applied to moving parts of machines.
- ✓ Paint or tar. Paint and tar keeps moisture and air away from contact with iron. Paint is used on window frames, doors, bicycles e.t.c. while tar is used on iron used in the construction of bridges and ships.
- ✓ Enamelling. Iron coated with enamel does not rust because moisture and air are kept away from the iron.
- ✓ Coating with other metals. The coating of iron with other metals is referred to as metal plating. The iron can be coated with zinc, tin, chromium, silver and nickel to prevent rusting from occurring.

Coating with zinc, the process of coating iron with zinc is called galvanization and iron coated with zinc is called galvanized iron. The galvanized iron is used for making iron sheets, bath buckets and pails.

Galvanized iron does not easily rust even when the zinc coat is scratched because zinc being more reactive than iron will react with air forming solids that seal off the scratch.

Coating with tin. This is called tin plating. Iron coated with tin is used to make tins that carry packed food, paints oil, e.t.c. Tin plated iron can rust when the tin coating is broken because iron is more reactive than tin and therefore will react with the air and moisture forming rust.

Coating with chromium. Chromium plated iron shines just like silver and can be used to make bicycle handle, car bumpers e.t.c.

Iron coated with nickel also prevents rusting from occurring.

- ✓ Alloying. In stainless steel, iron is mixed with carbon, chromium, nickel to prevent it from rusting.
- ✓ Sacrificial protection. The iron being protected from rusting is connected via a wire to a block of a more reactive metal (magnesium and zinc are commonly used). The magnesium/zinc being more reactive than the iron will react in preference to iron thus sacrificing to protect the iron from rusting.

This method is sometimes referred to as cathodic protection. i.e. the iron being protected acts as the cathode and the more reactive metal acts as the anode.

Corrosion

Corrosion is the reaction between metals and the atmosphere which causes metals to lose their structural properties like shape, color, strength e.t.c.

Examples of corrosion include: rusting of irons, reaction of copper metal with the atmosphere (oxygen and carbon dioxide) to form green solid of copper carbonate; reaction of aluminium with atmospheric oxygen to form aluminium oxide.

Self-protection from corrosion

Some metals are self-protected from corrosion e.g. magnesium and aluminium react with the air to form oxides which form a thin layer on the surface of the metal.

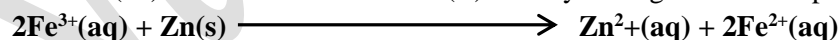
These oxide coatings prevent air from reaching the metal beneath it hence the metal is protected from further corrosion.

Unfortunately, iron cannot protect its self in this way because the rust formed is porous and can allow air and water to reach the metal below it causing further corrosion.

Experiment to determine the percentage of iron in an ore

A known mass of the ore is weighed and reacted with excess concentrated sulphuric acid, the acid converts iron(II) compounds to iron(III)

The iron(III) ions are reduced to iron(II) ions by adding excess zinc powder and heating.



The resultant solution is then diluted with a known volume of distilled water

A known volume of the solution is then pipetted and titrated against a standard solution of potassium dichromate(VI) using a suitable redox indicator.



Using ratios, the mass of iron can be calculated and its percentage got using the formula

$$\text{Percentage of iron} = \frac{\text{mass of iron}}{\text{mass of ore}} \times 100\%$$

Guiding question

Briefly describe how iron can be extracted from a named ore

Describe how the percentage of iron in an ore can be determined

Explain the reactions that take place when

a) a concentrated solution of sodium carbonate is added to a solution of iron(III) chloride

b) a solution of potassium thiocyanate is added to a solution of iron(III) chloride

Describe the reactions of iron with

a) air

b) water

c) sulphuric acid

Cobalt

Electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$

Chemical properties of cobalt

a) Reaction with air

Cobalt reacts with limited air on heating to form cobalt(II) oxide



In excess oxygen, heated cobalt reacts with to form tricobalt tetraoxide



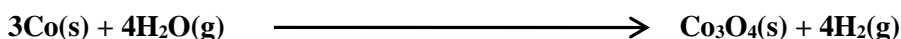
b) Reaction with chlorine

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



c) Reaction with water

Heated cobalt reacts steam to form tricobalt tetraoxide and hydrogen gas



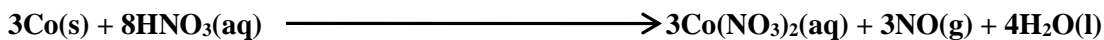
d) reaction with acids

With dilute acids

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

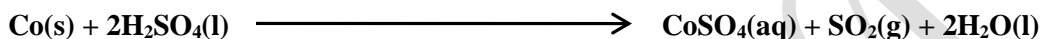


With dilute nitric acid, cobalt reacts to form cobalt(II) nitrate, nitrogen monoxide and water



With concentrated acids

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



Cobalt is rendered passive by concentrated nitric acid

Cobalt shows no reaction(s) with alkalis

Compounds of cobalt

Cobalt forms compounds in two oxidation states, i.e +2 and +3 oxidation states.

Compounds in +2 oxidation state more most stable than those in +3 oxidation state which is common in complexes

Cobalt (II) compounds

Cobalt forms cobalt(II) compounds which are pink in solution, and exist as hexaaquacobalt(II) ion $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$

Cobalt(II) oxide

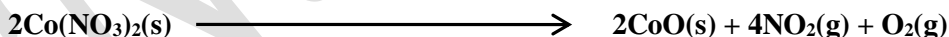
It is a green solid prepared by heating cobalt(II) hydroxide, carbonate or nitrate.



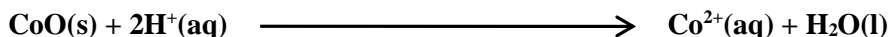
Or



Or

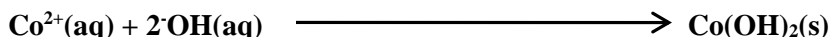


Cobalt(II) oxide is a basic oxide and reacts with dilute acids forming pink solutions of cobalt(II) salts

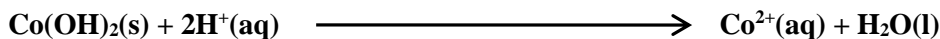


Cobalt(II) hydroxide

It is a blue precipitate prepared by reacting aqueous sodium hydroxide with a solution of cobalt(II) salt.

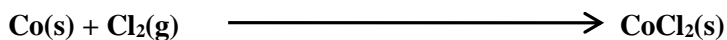


It is also basic and hence reacts with dilute acids to form cobalt(II) salts

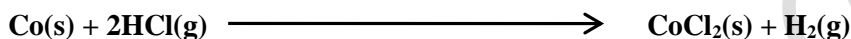


Cobalt(II) chloride

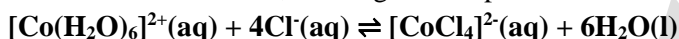
The anhydrous salt is blue obtained by heating cobalt in dry chlorine or hydrogen chloride. It is used to test for presence of water if it turns pink due to formation of hydrated cobalt(II) chloride



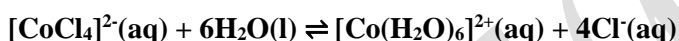
Or



Cobalt(II) chloride turns pink in water due to the formation of the hexaaquacobalt(II) ion $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$. When concentrated hydrochloric acid or a saturated solution of potassium chloride is added to the solution, it changes from pink to blue.



The chloride ions have replaced water molecules as ligands in the above complex resulting in colour change. This reaction is called ligand exchange. When blue solution is diluted, the pink solution is reformed.



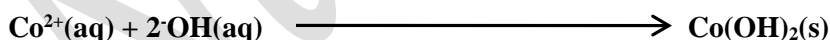
When cobalt is heated with carbon monoxide under high pressure, it gives dicobalt octacarbonyl $\text{Co}_2(\text{CO})_8$ which is used as a catalyst and reagent in organometallic chemistry and organic synthesis.



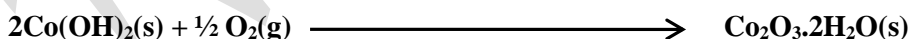
Analysis of Co^{2+} in solution

Using sodium hydroxide solution

Blue precipitate insoluble in excess, turns brown on standing (due to aerial oxidation/ also addition of hydrogen peroxide has a similar effect)

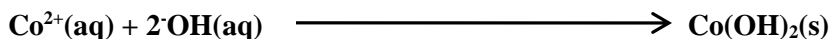


Then

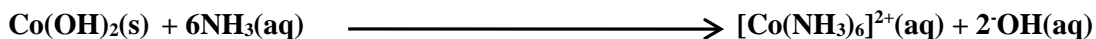


Using ammonia solution

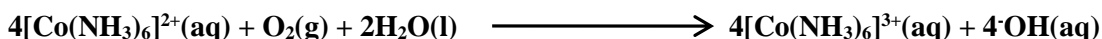
A blue precipitate, soluble in excess forming a (dark brown) yellow solution which turns reddish brown on standing



Then



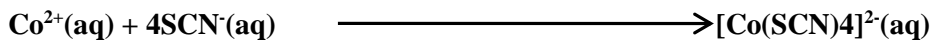
And



Using potassium/ammonium thiocyanate followed by ether or propanol

Usually few drops of concentrated hydrochloric acid are added first

Blue solution which separates in the organic layer

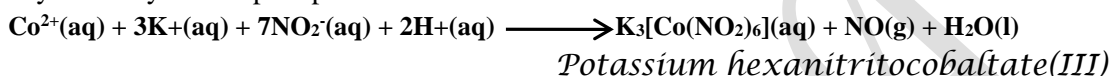


With no organic solvent is used, only a blue solution is formed

Using potassium nitrite solution

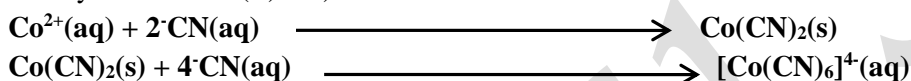
Usually ethanoic acid is added first then the reagent next

A yellow crystalline precipitate



Potassium cyanide solution

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



Nickel

Electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$

Chemical properties of nickel

a) Reaction with air

Heated nickel reacts with oxygen to form nickel(II) oxide which is a green solid.



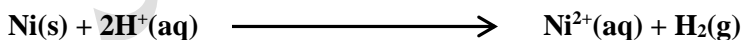
b) Reaction with water

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



c) Reaction with acids

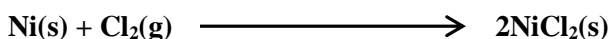
Nickel reacts with hot dilute acids to form the corresponding nickel(II) salts and hydrogen gas



Nickel is rendered passive by concentrated nitric acid

d) Reaction with chlorine

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



e) **Reaction with carbon monoxide**

When nickel is heated with carbon monoxide under pressure, tetracarbonylnickel(0) is formed.

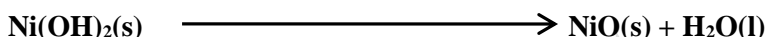


Compounds of nickel

Nickel forms compounds in the +2 oxidation state, most of its compounds are generally green and in solution, they exist as hexaaquanickel(II) ion which is also green, common compounds of nickel include;

Nickel(II) oxide NiO

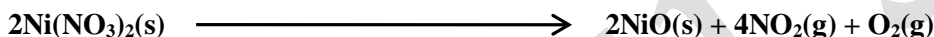
It is a green solid prepared by heating nickel(II) carbonate, nickel nitrate or nickel hydroxide.



Or



Or



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



Nickel (II) hydroxide

It is a green solid prepared through precipitation by adding sodium hydroxide solution to a solution containing nickel(II) ions. The resulting solution is then filtered and the residue dried.



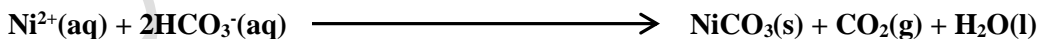
Nickel(II) sulphide

It's a black solid prepared by passing hydrogen sulphide gas through an alkaline solution containing nickel(II) ions.



Nickel(II) carbonate

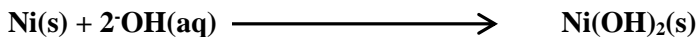
It is a green precipitate prepared by adding sodium hydrogen carbonate to a solution containing nickel(II) ions



Analysis of nickel(II) ions in solution

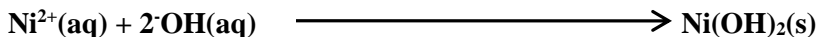
Using sodium hydroxide solution

Green precipitate insoluble in excess



Using ammonia solution/aqueous ammonia

Green precipitate soluble in excess forming a (pale) blue solution



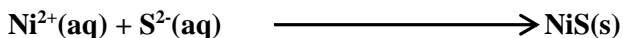
Then



Using hydrogen sulphide

Pass hydrogen sulphide through a solution of nickel ions

A black precipitate



Using potassium hexacyanoferrate(II) solution followed by ammonia solution

Green precipitate soluble in ammonia solution



Using dimethylglyoxime solution in presence of ammonia solution

Red precipitate forms

Using sodium hydrogen carbonate

A green precipitate and bubbles of a colourless gas that turns lime water milky



Guiding question

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

- a) identify compounds P to R*
- b) write equation for the reaction between*
 - Q and nitric acid*
 - R and sodium hydroxide*
 - S and ammonia*

Copper

Pure copper in elemental form is a brown solid whose electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

Chemical properties of copper

a) Reaction with air

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

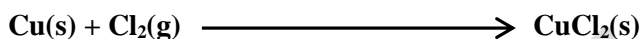


b) Reaction with water

Copper does not react with water

c) Reaction with chlorine

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



d) Reaction with acids

With dilute acids

Copper does not react with dilute acids i.e it is unable to displace hydrogen from acids because it is lower than hydrogen in the electrochemical series.

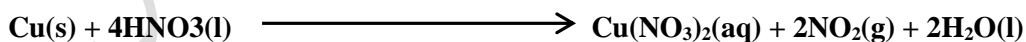
With concentrated acids

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



The brown solid dissolves forming a blue solution with evolution of a colourless gas that turns acidified potassium permanganate colourless from purple.

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



The brown solid dissolves forming a blue solution with evolution of brown fumes of a gas

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



Compounds of copper

Copper forms compounds in two oxidation states i.e +1 and +2

The +1 oxidation state is formed losing one electron from the 4s orbital, forming the copper(I) ion $\text{Cu}^+ 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^0$

However, since the 3d orbital in Cu^+ is fully filled with electrons, copper(I) does not show typical transition metal properties.

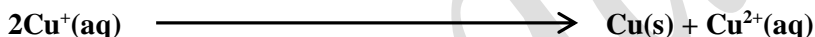
The +2 oxidation state Cu^{2+} is formed when two electrons, one from the 4s and also another one from the 3d orbitals are lost. This gives the copper(II) ion a partially filled 3d orbital $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s^0$ and hence copper(II) shows typical transition metal properties in all its compounds

Considering the electronic configuration of copper(I) and copper(II) ions, copper(I) ion is expected to be more stable than the copper(II) ion.

However, the copper(II) ion is more stable than copper(I) ion, because copper(II) has a higher charge density than copper(I), therefore it produces more energy on hydration, this energy then compensates for the second ionisation energy and forms stronger bonds in its compounds than in copper(I).

Copper(I) compounds

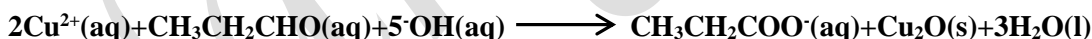
The copper(I) ion is very unstable in solution and undergoes disproportionation to form copper metal and copper(II) ions.



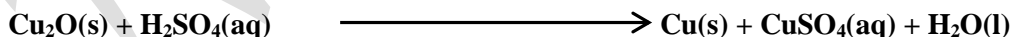
Copper(I) oxide

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.

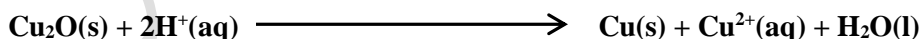
The solution is then filtered to obtain copper(I) oxide as a residue.



It is insoluble in water but disproportionates in dilute sulphuric acid forming copper metal, copper(II) sulphate and water

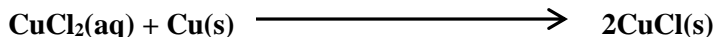


Or



Copper(I) chloride

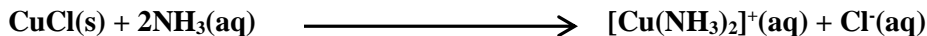
It is a white covalent solid which is insoluble in water. It is prepared by boiling a mixture of copper(II) chloride and copper turnings with excess hydrochloric acid.



It dissolves in concentrated hydrochloric acid forming a complex i.e dichlorocuprate(I) ion.

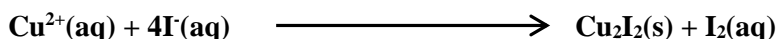


Just like silver chloride, copper(I) chloride too is soluble in ammonia solution forming a diamminecopper(I) ion.



Copper(I) iodide

It is a white precipitate prepared by adding aqueous potassium iodide to a solution of copper(II) ions. The observation is that a white precipitate in a brown solution is formed, the brown solution is due presence of iodine liberated.



Copper(II) compounds

Copper(II) compounds have a partially filled 3d-subenergy, also the copper(II) ion has a higher charge and in solution, its compounds exist as hexaaquacopper(II) ion $[\text{Cu(H}_2\text{O)}_6]^{2+}$ which is blue. Solutions of copper(II) are acidic because the copper(II) cation has a high ionic charge and a small ionic radius which gives the copper(II) ion a high charge density thus in solution, it becomes heavily hydrated in solution and undergoes hydrolysis forming hexaaquacopper(II) ion. The coordinating water molecules are polarized thereby weakening the oxygen-hydrogen bond therefore the proton can easily be lost to the solution, making it acidic due to the hydrogen ions.



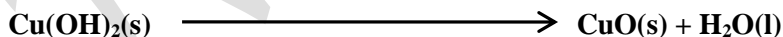
Or



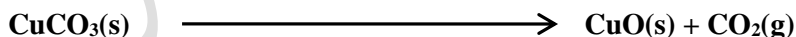
The following are some of the compounds of copper in +2 oxidation state

Copper(II) oxide

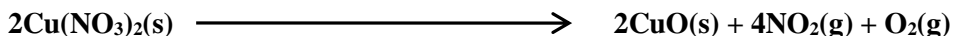
It is a black solid that can be obtained by heating copper(II) carbonate, hydroxide or nitrate.



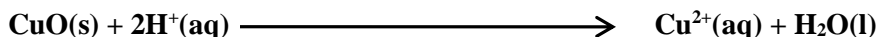
Or



Or

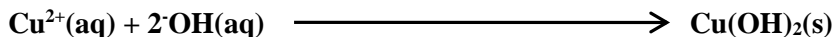


It is basic and reacts with dilute mineral acids to form the corresponding copper(II) salts and water

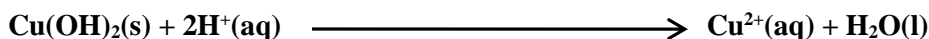


Copper(II) hydroxide

It is a blue solid prepared by the action of dilute sodium hydroxide on a solution containing copper(II) ions



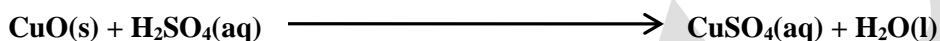
It is basic, and reacts with dilute acids to form the corresponding copper(II) salt and water



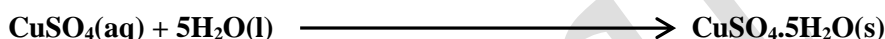
Copper(II) sulphate

It's a blue crystalline (the anhydrous solid is white) solid prepared by adding to dilute sulphuric acid the copper metal, its oxide or hydroxide while stirring until the solid dissolves no more.

The resulting solution is then filtered to obtain a saturated solution which is warmed until crystals begin to form. The heat source is then removed and the solution filtered again to obtain the crystals which can then be dried.



Then



When slightly heated, it loses its water of crystallization and the blue crystalline solid becomes white.



On strong heating, a black solid is formed



Extraction of copper

The chief ore from which copper is extracted is copper pyrites, CuFeS_2

Other ores are cuprite (Cu_2O), copper glance (Cu_2S) and malachite ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$)

The extraction process

The ore is crushed to a fine powder and then concentrated by froth flotation, in which the fine powder ore is mixed with water containing a frothing agent

A current of air is blown through the mixture thus producing a froth containing copper bearing particles; the earthly impurities are wetted and sink to the bottom of the tank.

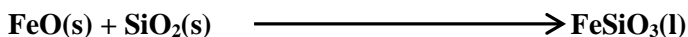
The froth is skimmed off, and dried.

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



The roasted ore is then heated with sand (silica) in a closed furnace (absence of air).

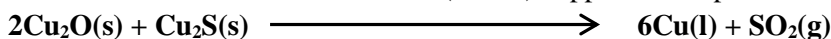
Iron(II) oxide reacts with silica to form iron(II) silicate which floats on top of the copper(I) sulphide formed and so is poured off



The molten copper(I) sulphide is then heated in limited (controlled) amount of air, to oxidise copper(I) sulphide to copper(I) oxide

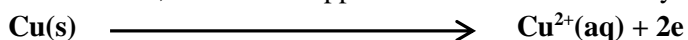


The copper(I) oxide mixed with unchanged copper(I) sulphide is then heated strongly in the absence of air to form molten blister (blister) copper and sulphur dioxide gas

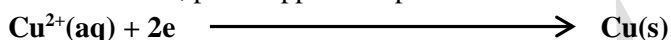


The blister copper is purified by electrolysis using direct current, during which blister copper is made the anode while a strip of pure copper is made the cathode and copper(II) sulphate solution as the electrolyte

At the anode, the blister copper dissolves in the electrolyte.

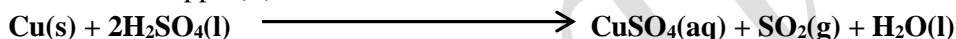


At the cathode, pure copper is deposited



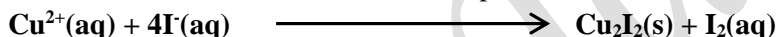
Experiment to determine the amount of copper in the ore

A known mass of impure copper is dissolved in excess concentrated sulphuric acid to the copper in the ore to copper(II) ions



The resultant solution is the neutralized with sodium hydrogencarbonate

The mixture is then reacted with excess potassium iodide to liberate iodine



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



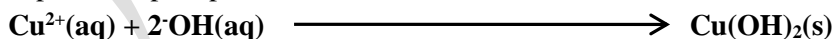
The concentration of iodine, copper(II) ions and hence mass of copper in the mixture is calculated and hence the mass of copper

$$\text{Percentage of copper} = \frac{\text{mass of copper}}{\text{mass of ore}} \times 100\%$$

Analysis of copper(II) ions in solution

Using sodium hydroxide solution

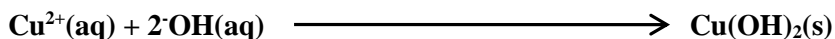
A pale blue precipitate insoluble in excess



Using ammonia solution

Blue precipitate soluble in excess forming a deep blue solution

First

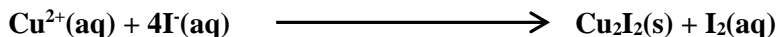


Then



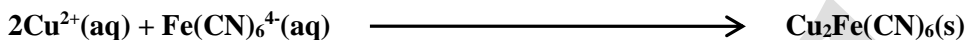
Using potassium iodide solution

White precipitate in a brown solution; turns colourless on addition of sodium thiosulphate solution.



Using potassium hexacyanoferrate(II) solution

A chocolate brown precipitate insoluble in ammonia solution



Uses of copper

- ✓ For wiring electrical circuits since it is a good conductor of electricity and is relatively cheap. The copper used for this purpose must be very pure since impurities increase electrical resistance.
- ✓ It is used for making ornaments like ear rings and pins, bangles e.t.c. because it is less attacked by air.
- ✓ It is used for making alloys like bronze (copper and tin) and brass (copper and zinc), copper coinage (copper and tin), German silver (copper, zinc and nickel)
- ✓ Used for making water pipes and boilers.
- ✓ Copper is used as a roofing material because it weathers to acquire a coating of green basic copper carbonate, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \cdot n\text{H}_2\text{O}$, which lends a colourful touch to the building.

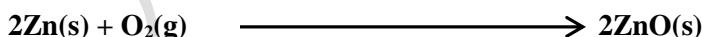
Zinc

Zinc has atomic number 30 and electronic configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$, it forms stable ions by loss of two electrons from the 4s sub energy level giving rise to Zn^{2+} with fully filled 3d-energy level $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ and as such, zinc is not considered as a transition metal and as such its ions are colourless.

Chemical properties of zinc

a) Reaction with air

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



b) Reaction with water

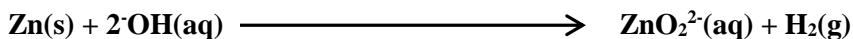
Zinc does not react with cold water; however heated zinc reacts with steam to form zinc oxide and hydrogen gas



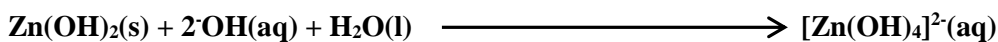
c) Reaction with alkalis

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

First

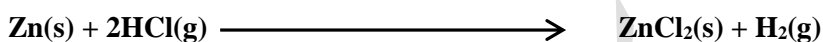
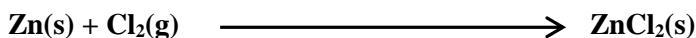


Then



d) Reaction with non-metals

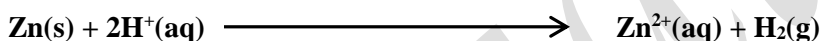
When heated, zinc reacts with non-metals like nitrogen, dry chlorine and hydrogen chloride to form zinc nitride, zinc chloride and hydrogen gas.



e) Reaction with acids

With dilute acids

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

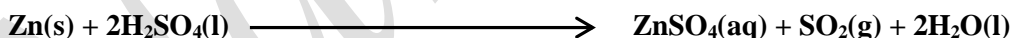


Zinc is oxidised by dilute nitric acid to zinc nitrate and the acid is reduced to ammonium nitrate and water

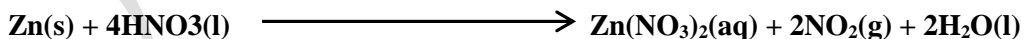


With concentrated acids

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



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



Moderately concentrated nitric acid oxidizes zinc to nitric(II) nitrate and the acid is reduced to nitrogen monoxide gas and water



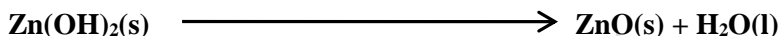
Compounds of zinc

Zinc forms compounds in the +2 oxidation states. In this state the zinc ion has a full 3d orbital $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$; therefore, it does not show typical transition metal properties and is not regarded as a typical transition element. Other reasons include

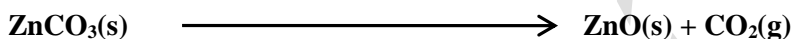
- ✓ Zinc does not have variable oxidation states as other transition metals
- ✓ Its compounds are colourless
- ✓ Zinc compounds have no paramagnetic properties

Zinc oxide

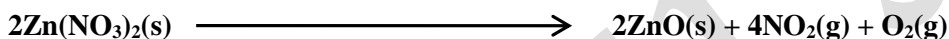
It is a white solid which is yellow when hot, but when cooled, it turns back to white. It can be prepared by heating zinc carbonate, zinc nitrate or zinc hydroxide.



Or



Or



It is an amphoteric oxide therefore is insoluble in water but reacts with alkalis and acids.

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



It reacts with hot concentrated alkalis to form a corresponding zincate

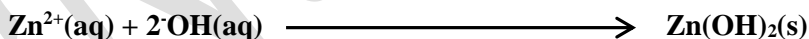


Or



Zinc hydroxide

It prepared by precipitation using aqueous sodium hydroxide and a solution containing excess zinc ions.



if the alkali is in excess, the white precipitate dissolves forming a colourless solution

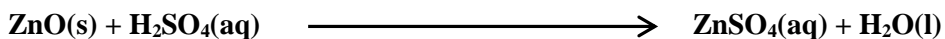


It reacts with dilute acids to form the corresponding zinc salts and water

Zinc sulphate

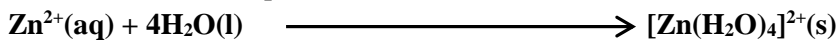
It is a white solid prepared by action of dilute sulphuric acid on a solution of zinc ions.

It can also be prepared by adding solid zinc metal, zinc oxide, or zinc hydroxide to dilute sulphuric acid with constant stirring until no more solid dissolves. The solution is filtered to obtain a saturated solution of zinc sulphate which can be concentrated by evaporation.



Hydrolysis of zinc compounds

Solutions of zinc compounds are acidic



Then

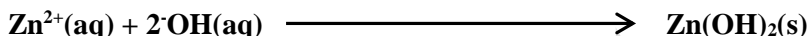


Analysis of zinc ions in solution

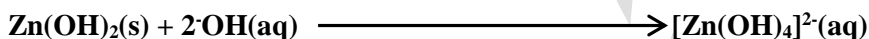
Using sodium hydroxide solution

White precipitate soluble in excess forming a colourless solution

First



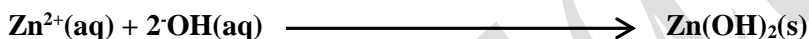
Then



Using ammonia solution

A white precipitate soluble in excess forming a colourless solution

First



Then



Using potassium hexacyanoferrate(II) solution followed by ammonia solution

A white precipitate soluble in aqueous ammonia



Solid ammonium chloride, disodium hydrogen phosphate and excess ammonia

A White crystalline solid soluble in ammonia

Extraction of zinc

The chief ores from which zinc is extracted are; zinc blende-ZnS and Calamine-ZnCO₃

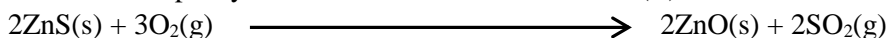
The extraction process

The ore is concentrated by froth flotation method during which the finely crushed ore is mixed with water containing a frothing agent.

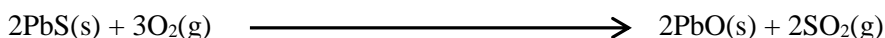
The mixture is then agitated by blowing air through it.

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

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

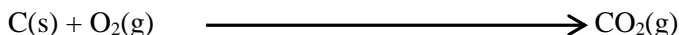


And

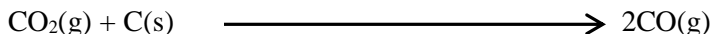


The solid product of roasting is now mixed with limestone and coke and then fed into the furnace and hot air blasted into it.

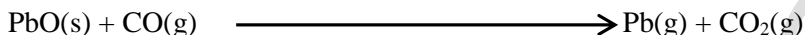
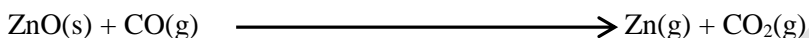
Coke (carbon) burns to form carbon dioxide



Carbon dioxide is reduced by unburnt coke to carbon monoxide

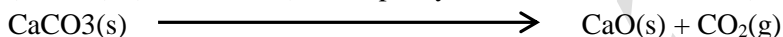


The carbon monoxide produced under high temperatures reduces zinc oxide to zinc, lead(II) oxide is also reduced to lead.



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.



Uses of zinc

- ✓ Used in the production of brass (copper and zinc)
- ✓ Used in galvanizing steel since it is higher than iron in the electrochemical series, even if the coating of zinc is scratched, it will continue to protect the iron underneath the rusting.

PRINCIPLES OF METAL EXTRACTION

For a metal to be extracted, its concentration in a given ore must be high. Therefore, it is necessary to concentrate (purify) the ore before the actual extraction process.

The method of metal extraction normally depends on the position of the metal in the electrochemical/reactivity series.

K	These are very reactive metals and therefore form very stable compounds.
Na	
Ca	
Mg	
Al	They are not found as free elements and can only be extracted from their compounds by electrolysis.
Zn	
Fe	
Pb	
Cu	These are moderately reactive metals. They usually occur as ores in form of oxides, sulphides, carbonates e.t.c. they are extracted by reduction of the ores using either carbon or carbon monoxide.
Hg	
Ag	
Au	
	They are not very reactive therefore found as free elements.
	They are the easiest to extract since they form unstable compounds e.g. they can be extracted by mere heating of the ore.
	Some may be found in natural state and can be extracted by mining

An ore is a naturally occurring substance from which an element can be extracted.

It can also be defined as is a rock which contains metallic compounds from which the metals can be extracted e.g. rock salt (NaCl) for sodium; spathic iron ore (FeCO_3) and iron pyrite (FeS_2) for iron.

A mineral is a naturally occurring free element which can be obtained by mining.

The chief ores in order of relative importance are,

- ✓ Oxides
- ✓ Sulphides
- ✓ Chlorides
- ✓ Carbonates

It is important to convert sulphides and carbonates into oxides before reduction because the oxides are more easily and effectively reduced than the sulphides.

The main features of the reduction process include

- ✓ High temperature reduction using carbon in form of coke or carbon monoxide
- ✓ Reduction of oxides using aluminium
- ✓ Electrolysis of molten compounds of the metal involving cathodic reduction of metal ions.

Metal extraction consists of concentration of the ore, roasting of the ore, reduction of the ore and purification (refining) the ore.

a) Concentration of the ore

This process involves removing impurities (unwanted earthly material- gangue) from the ore. Before concentration, the ore is finely crushed/ground/pulverized.

Impurities can be separated by physical means e.g. picking by hand, washing, and using a magnet or solvent extraction.

In the case of copper, the ore is first crushed and then mixed with water. Air is then blown through the mixture and the clean ore separates and collects at the surface as froth. This is referred to as froth floatation.

Methods of concentration

Concentration of an ore can be done using physical or chemical methods.

Physical methods

These are methods of concentrating an ore which do not involve chemical reactions but make use of the difference in the density and magnetic properties of the element to be extracted. These physical methods include;

- **Froth floatation**

After the ore is finely divided, it is mixed with water to which a suitable oil (frothing agent) has been added. It's common for ores with sulphides

Air is then blown through the mixture to agitate it thus producing froth.

The sulphide particles rise to the surface in the froth where they can be skimmed off

Acid is added to break up the froth; the ore is filtered and dried.

- **Washing**

Ores are usually denser than gangue, which can be washed away in a stream of water e.g. galena and limestone.

- **Using a magnet**

This is commonly used in the separation of wolframite the principle ore in tungsten from cassiterite within which it's found. The tungsten is attracted to the magnet while the cassiterite is not.

Chemical methods

It involves the following;

- Heating to drive out water
- Roasting in air to convert carbonates, sulphides, etc to oxides which are easy to reduce.
- Leaching, adding a solution (substance) which will react with the ore leaving behind impurities, e.g. in the extraction of aluminium from bauxite, the finely divided bauxite is heated under pressure with excess sodium hydroxide.

- Reduction which may be by smelting, electrolysis, etc.

Smelting is the reduction of an ore to the molten metal at high temperature using carbon monoxide or coke.

Fluxes whose role is to combine with the gangue to form slag which floats on the surface of the molten metal.

In some cases, e.g. in extraction of copper, reduction can be done using a suitable adjustment of the roasting process, oxidising some of the sulphides in the oxide and then by adding more of the ore to supply sufficient sulphur to react with the oxygen of the ore leaving the metal.

Electrolysis is used to obtain pure metal directly from its molten compound.

b) Roasting

The concentrated (pure) ore is roasted in air at high temperatures to produce oxides which are easier to reduce than carbonates or sulphides.

Sulphur is removed as sulphur dioxide and carbon dioxide driven off from the carbonates.

c) Reduction of the ore

The ore is usually heated in a furnace in the presence of a suitable reducing agent, usually coke (carbon) or carbon monoxide which converts the ore into the required metal.

d) Purification/refining of the metal.

Since the metal obtained is often impure, purification is normally done by electrolysis in the case of copper and zinc.

In other cases, the impure metal is heated in a hearth open to air where the impurities oxidize and rise to the surface as a scum and can be removed.