

Extraction of Metals.

These include; Al, Zn, Fe, and Cu

GENERAL PROCEDURES OF EXTRACTING METALS;

- (I) Concentrating the ore,
Removing unwanted particles (impurities) from the ore.
 - (i) Chemical methods like
 - Leaching with hot concentrated sodium hydroxide solution under pressure for example extraction of aluminium from bauxite.
 - Heating and roasting; used to drive out water in iron ores. Roasting in air is sometimes used to remove organic matter, and to convert sulphides and carbonates to oxides.
 - (ii) Physical methods like
 - Froth flotation; this is the method whereby the finely ground powdered ore is mixed with water having suitable oil. The oil wets the sulphide particles and the water wets mainly the impurities(gangue). Air is then blown through the mixture. The air bubbles attach themselves to the oiled particles and cause them to move up to the surface; therefore the major use of air is to agitate the mixture to form a froth at the surface, leaving the gangue at the bottom. The froth is skimmed off and acid is added to it to break the froth and the mixture is filtered and dried.
Froth flotation is mainly used to concentrate sulphide ores like copper pyrites, zinc blende.
 - By washing to remove sand
 - Magnetic separation; mainly used to separate the ore of tungsten sand.
- (2) Reduction

Reduction includes **two** processes
 - (i) High temperature reduction using carbon or carbon monoxide for example in the extraction of iron and zinc
 - (ii) By electrolysis of molten compound eg in the extraction of aluminium, the ore(pure aluminum oxide) is electrolysed in a graphite lined tank.
- (3) Purification(refining) eg copper, (blister, copper) is refined by **electrolysis**
Zinc is purified by **distillation in vacuum**.

EXTRACTION OF COPPER FROM COPPER PYRITES, CuFeS_2

Concentration

The finely powdered ore is concentrated by froth flotation. The powdered ore is treated with water containing suitable oil. The oil wets the ore whereas the water wets the impurities eg sand. Air is pumped into the mixture. The froth collects on the surface this carries with it the particles of the ore. The impurities sink to the bottom. The froth is skimmed off. It is made to overflow and then collected. The acid is added to the froth and then filtered.

Roasting

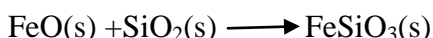
The ore is then roasted in air. The iron in the ore is converted into iron(II) oxide while the copper remains combined with sulphur, sulphur dioxide is also formed. Also other impurities like sulphur, arsenic, antimony are converted into their oxides.



The sulphur dioxide formed can be converted into sulphuric acid in the contact process. This explains why it is important to construct sulphuric acid manufacturing industry near a copper refinery.

Smelting

The iron(II) oxide formed during roasting is removed by heating the roasted mixture with sand (silicon) in a reverberatory furnace. In this furnace iron(II) oxide reacts with sand to form iron(II) silicate which is formed floats on top and is poured off.

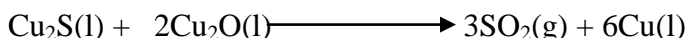


Reduction (conversion of copper(I) sulphide to blister copper)

More air is blown into the mixture part of the copper(I) sulphide in the mixture reacts with the air to form copper(I) oxide and sulphur dioxide



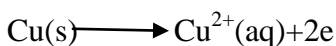
The remaining copper sulphide reacts with copper(I) oxide to form blister copper and sulphur dioxide



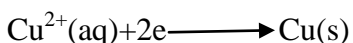
Purification/ refining of blister copper;

Blister copper is made the anode in the electrolysis cell. Pure copper is made the cathode. The electrolyte is acidified copper(II) sulphate solution. When the current is passed through, copper dissolves from the anode, and it is deposited at the cathode

Anode reaction



Cathode reaction



Extraction of iron

It is contained in its ores;

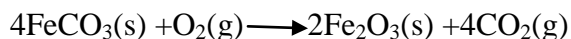
Siderite, spathic iron ore (FeCO_3)

Haematite (Fe_2O_3)

Magnetite (Fe_3O_4)

Procedure

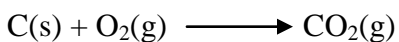
The ore is first roasted in air. Roasting converts the siderite into iron(III) oxide and carbon dioxide.



The roasted ore is then introduced into the blast furnace.

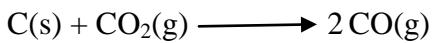
Hot air is fed from the bottom. The roasted ore (oxide of iron), limestone and coke are fed from the top of the furnace

Coke (carbon) burns in the air to produce carbon dioxide.

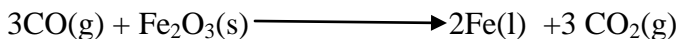


The reaction is exothermic.

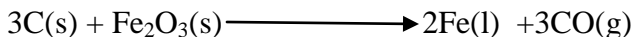
As carbon dioxide raises up the furnace, it is reduced to carbon monoxide by the coke.



Carbon monoxide reduces the roasted ore to form iron



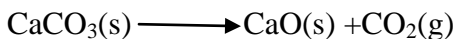
Some reduction takes place directly by carbon.



Drawing of the blast furnace

Function of the limestone

Limestone is decomposed by heat to calcium oxide(quicklime)



The calcium oxide reacts with sand the major impurity in the ore to form slag(calcium silicate)



The molten iron sinks to the bottom of the furnace as slag settles on top of it.

Therefore the major use of limestone is to remove sand which the major impurity in the ore

Zinc

Atomic number 30

Electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$

Extraction of zinc

It is contained in its ores;

Major ore **Zinc blende, ZnS**

Calamine ZnCO_3

Extraction of zinc from zinc blende

The ore contains large amounts of lead(II) sulphide PbS and other impurities like sand

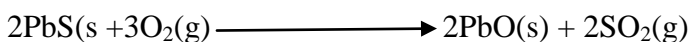
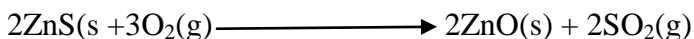
Procedure

Concentration

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Roasting

The sulphide ore is roasted in air. Zinc blende is oxidized by oxygen of the air.

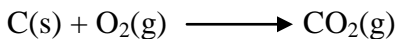


The sulphur dioxide formed can be converted into sulphuric acid in the contact process

Reduction of the zinc oxide

Hot air is fed from the bottom, the oxide of zinc and lead is mixed with limestone and coke are fed from the top of the furnace

Coke (carbon) burns in the air to produce carbon dioxide.

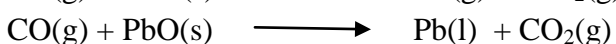
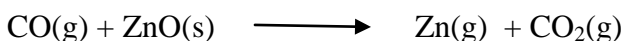


The reaction is exothermic.

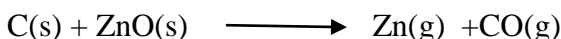
As carbon dioxide rises up the furnace, it is reduced to carbon monoxide by the coke.



Carbon monoxide reduces the roasted ore to form iron



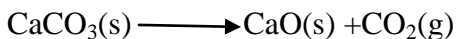
Some reduction takes place directly by carbon.



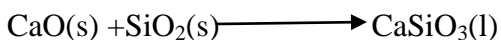
Zinc is more volatile than lead. Therefore, zinc is present as vapour. It leaves the furnace at the top whereas molten lead leaves the furnace from the bottom

Drawing of the blast furnace

Limestone is decomposed by heat to calcium oxide(quicklime)



The calcium oxide reacts with sand the major impurity in the ore to form slag(calcium silicate)



The molten iron sinks to the bottom of the furnace as slag settles on top of it.

Therefore the major use of limestone is to remove sand which the major impurity in the ore

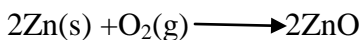
Uses of zinc

- Used to make alloys
- Used in dry electric batteries
- Used to galvanize iron

Properties of zinc

- ✓ Reaction with air/oxygen

Zinc reacts dry air at red heat to form zinc oxide.



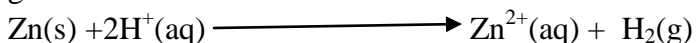
- ✓ Reaction with water

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

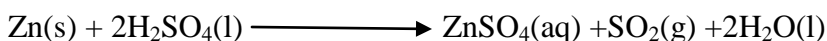


- ✓ With acids

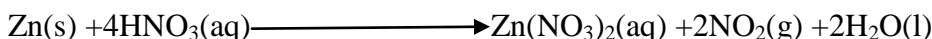
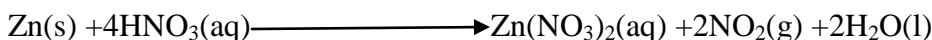
Zinc reacts with hydrochloric acid and dilute sulphuric acid to form a salt and hydrogen gas.



Zinc reacts hot concentrated sulphuric acid to form sulphur dioxide, zinc sulphate and water

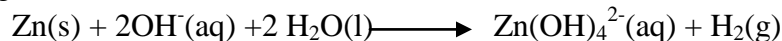


Zinc reacts with nitric acid to form oxides of nitrogen, zinc nitrate and water



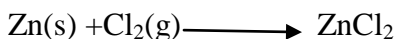
- ✓ Reaction with alkalis

Zinc reacts with hot concentrated sodium hydroxide solution to form sodium zincate and hydrogen gas.



- ✓ Reaction with non metals

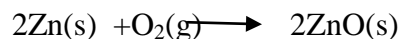
Zinc directly combines when heated with dry chlorine, dry oxygen, sulphur, and dry nitrogen to form zinc chloride, oxide, sulphide and nitride respectively



Compounds of zinc

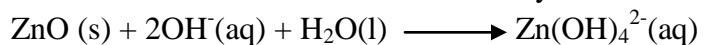
Zinc oxide, ZnO

Its prepared by heating zinc in dry oxygen gas



zinc oxide is amphoteric

It dissolves in hot concentrated sodium hydroxide to form a zincate

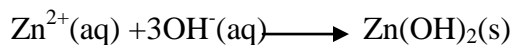


Or

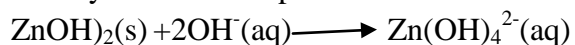


Zinc hydroxide

Its prepared as a white precipitate by adding sodium hydroxide solution or dilute aqueous ammonia to a solution of zinc salt.



zinc hydroxide is amphoteric



Transition elements

A transition element is one with partially filled d sub-shell in any of its oxidation state as well as the atomic state. Transition elements are called d -block elements because of their electronic structure.

d - block element is an element whose outermost electrons fill the d sub-shell.

In the periodic table the transition elements lie between the reactive elements of the s -block (which form mainly ionic compounds) and the least reactive p -block elements (which form mainly covalent compounds)

The table below shows the some of the d -block elements.

Elements	Symbol	Atomic number	Electronic structure
Scandium	Sc	21	
Titanium	Ti	22	
Vanadium	V	23	
Chromium	Cr	24	
Manganese	Mn	25	
Iron	Fe	26	
Cobalt	Co	27	
Nickel	Ni	28	
Copper	Cu	29	
Zinc	Zn	30	

✓ Electronic configuration

Chromium and copper have anomalous behavior in their electronic structure.

Quiz Write the electronic configuration of

Cu

Cu^+

Cr

Cr^{3+}

Cr^{6+}

Sc

Sc^{3+}

Zn

Zn^{2+}

Zinc is not a transition element because it has a completely filled $3d$ - subshell in both its stable oxidation state and atomic state.

Scandium forms a tripositive ion(Sc^{3+}) and this has no d electrons. Scandium therefore is not a transition element

✓ Atomic radii

Atomic radii of the atoms slightly vary from scandium to zinc. This is because the number of energy levels remain the same, the electron being added, enter an inner d shell and thereby increasing the primary screening effect. The nuclear charge increases with increasing atomic number. This increases the electric field attracting the electrons towards the nucleus. The increase in nuclear charge slightly outweighs the increase in screening effect and as a result the effective nuclear charge increases only slightly and this makes little change in the atomic radius

QUIZ

The table below shows the atomic radii of d - block elements

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic radius(nm)	0.144	0.132	0.122	0.117	0.117	0.116	0.116	0.115	0.117	0.125

(a) Plot a graph of atomic radius against element

(b) Explain the shape of the graph

Characteristics of transition elements

(1) Existence of variable oxidation states(variable valency)

Oxidation state is the charge left on the atom when all the other atoms of the compound have been removed as ions.

Transition elements show more than one oxidation state because;

- The presence of partially filled $3d$ orbitals.
- Similarity in the energies of the $3d$ and $4s$ orbitals in the neutral atoms of transition elements.

Calculating oxidation states.

Examples

The table below shows the possible oxidation states of transition elements.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+3	+4	+5	+6	+7	+6	+4	+4	+2	+2
	+3	+4	+5	+6	+3	+3	+2	+1	
	+2	+3	+4	+4	+2	+2			
		+2	+3	+3					
			+2	+2					
			+1						

Note

Bold ; means stable oxidation states.

Compounds of these metals in their higher oxidation states are covalent and act as oxidizing agents eg chromium(III) oxide is an ordinary basic oxide but chromium(VI) oxide is a covalent compound with very low melting points and soluble in organic solvents such as propane.

- (2) Transition metal ions and their compounds are colored because of the presence of incomplete $3d$ -orbitals, the elements are able to promote an electron from one level to another within the $3d$ -subshell.

The energy for this is obtained by absorbing light of a particular wavelength and the light that is obtained is reflected giving the color of the ion.

Ion

Sc^{3+} colourless

Ti^{3+} purple

V^{3+} green

Cr^{3+} violet

Mn^{3+} violet

Fe^{3+} yellow

Mn^{2+} pink

Fe^{2+} green

Co^{2+} pink

Ni^{2+} green

Cu^{2+} blue

Zn^{2+} colourless

- (3) Transition elements form complex ions.

A **complex ion** has a metal **ion** at its center with a number of other molecules or **ions** surrounding it. These can be considered to be attached to the central **ion** by coordinate (dative covalent) bonds

Transition metals ions form complex ions because they have a **small ionic radius** and comparatively **high charge of transition metal ion** favour the acceptance of a lone pair of electrons from the ligand molecule or ion. The ions metal have **vacant d -orbitals** which accommodate electron from ligands.

A ligand is an atom or molecule with lone pairs of electron which can form coordinate bonds with the central atom.

The number of atoms or molecules that form coordinate bonds with the central atom is as the coordination number.

Coordination number is the number of ligands surrounding the central atom.

A complex ion can be represented by the particular formula.

$(ML_n)^{y+}$ where

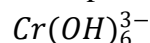
M = central atoms/ion

L = ligand

n = number of ligand

for y is the charge on the complex ion.

Example

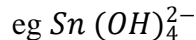


Coordination number = 6

Naming complex ions

Rules;

- The cation is always named first before the an ion.
- The ligand is always is always named before the central atom.
- The prefix is added to the ligand in the complex
- If the complex carries a negative charge, the name ends with “ate” and the metal will be given a latin name eg plumbate (Pb), Ferrate(Fe), cuprate(Cu), stannate (Sn)



tetrahydroxostannate(II) ion

For a complex carrying a positive charge or no change, the name of the central atom does not change

eg



- The oxidation state of the central atom is shown in roman numerals immediately after the name.
- The name of negatively charged ligands end with an “O”
eg sulphato(SO_4^{2-}), hydroxo(OH^-), bromo(Br^-), chloro(Cl^-)

For neutral ligands

H₂O – aqua

CO - carbonyl

NO- nitrosyl

NH₃- ammine

- Negatively charged ligands are named first followed by neutral ligands

eg



Monochloropentaaquachromium(III) ion

(4) Catalytic activity

- ✚ They act as catalysts because they have a high number of valence electrons.
- ✚ They also have available d subshell in the atoms to facilitate electron redistributions amongst reacting particles.
- ✚ They also provide an active surface for the reaction.

(5) They have a high melting point

They form strong metallic bonds due to the availability of d electrons

(6) Form interstitial compounds

Atoms of boron, hydrogen, carbon and nitrogen are able to fit into metal lattices of transition elements to form interstitial compounds which are hard compounds with no chemical formula.

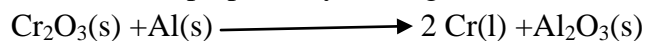
(7) Some are paramagnetic

Chromium

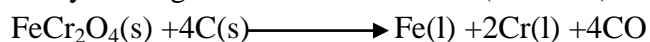
Atomic number 24

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

Chromium is prepared by heating a mixture of chromium(III) oxide and aluminium



Or by heating a mixture of chromite(FeCr_2O_4) and carbon



Uses of chromium

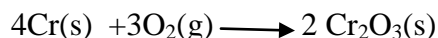
- ✓ As a constituent of alloys
- ✓ In electroplating

Properties of chromium

- Reaction with air

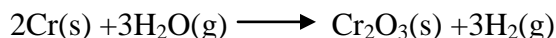
Chromium is unaffected by air at ordinary conditions.

Heated chromium is oxidized in air to form chromium(III) oxide.



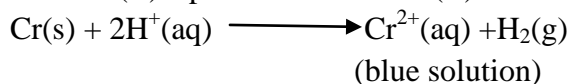
- Reaction with water

Chromium is unaffected by cold or hot water but it reacts at red heat with steam to form chromium(III) oxide and hydrogen gas.

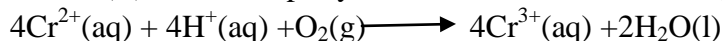


- Reaction with acids

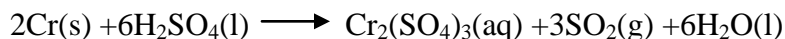
Chromium reacts with dilute sulphuric acid or dilute hydrochloric acid to form chromium(II) sulphate or chromium(II) chloride and hydrogen gas



The chromium(II) ions are rapidly oxidized to form chromium(III) salts(green solution)



Chromium reacts with hot concentrated sulphuric acid to form chromium(III) sulphate, water and sulphur dioxide gas.

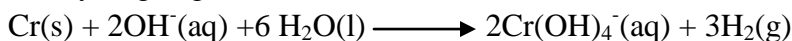


Cold or dilute or concentrated nitric acid has no action on chromium rendering it to be passive.

This is because of the formation of a thicker and tough film of chromium(III) oxide.

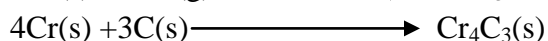
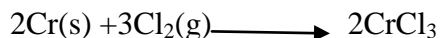
- Reaction with alkalis

Chromium reacts with hot concentrated sodium hydroxide solution to form sodium chromite and hydrogen gas.



- Reaction with non metals

Chromium directly combines when heated with dry chlorine, dry oxygen, sulphur, carbon and dry nitrogen to form chromium(III) chloride, oxide, sulphide, carbide and nitride respectively



Compounds of chromium

There are three common oxidation states of chromium +2, +3 and +6

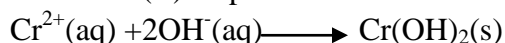
The +3 oxidation state is the most stable

Chromium in the +2 oxidation state

➤ Chromium(II) oxide, CrO, is a black solid

➤ Chromium(II) hydroxide is a yellow solid.

Its prepared as ppt by adding sodium hydroxide solution to chromium(II) chloride or chromium(II) sulphate solution.



➤ Chromium(II) chloride

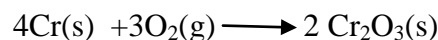
Its prepared by heating pure chromium in dry hydrogen chloride gas



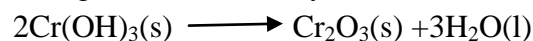
Chromium in the +3 oxidation state

Chromium(III) oxide, Cr₂O₃

Its prepared by heating chromium in dry oxygen gas



Or by heating chromium(III) hydroxide

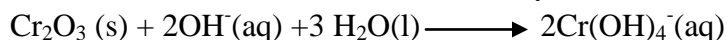


Or by heating ammonium dichromate

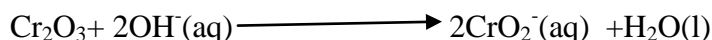


Chromium(III) oxide is amphoteric

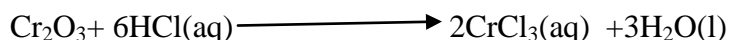
It dissolves in hot concentrated sodium hydroxide to form a chromite



Or

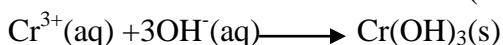


It dissolves in hot concentrated hydrochloric acid to form chromium(III) chloride and water

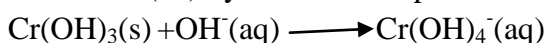


Chromium(III) hydroxide

Its prepared as a green precipitate by adding sodium hydroxide solution or dilute aqueous ammonia to a solution of chromium(III) salt.

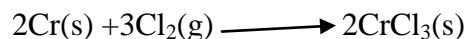


Chromium(III) hydroxide is amphoteric

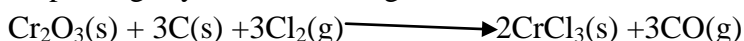


Chromium(III) chloride CrCl_3

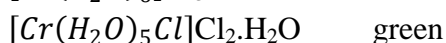
Its prepared by heating chromium in dry chlorine gas



Or passing dry chlorine through a heated mixture of carbon and chromium(III) oxide



Hydrated chromium(III) chloride, $(\text{CrCl}_3 \cdot 6\text{H}_2\text{O})$ exists in three isomeric forms

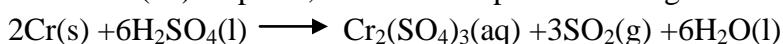


Although the isomers correspond to the same formula, they differ in their properties.

The violet on forms three moles of silver chloride when excess silver nitrate solution is added to it whereas $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ forms one mole of silver chloride when excess silver nitrate solution is added to it.

Chromium(III) sulphate

It is prepared by adding chromium to hot concentrated sulphuric acid to form chromium(III) sulphate, water and sulphur dioxide gas.

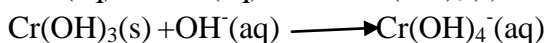
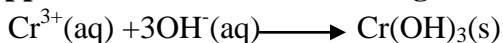


Chrome alums, potassium chromium(III) sulphate $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$

Test for Cr^{3+}

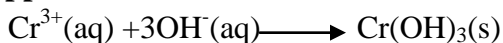
- ✓ Using sodium hydroxide solution

Green ppt soluble in excess to form a **green** solution



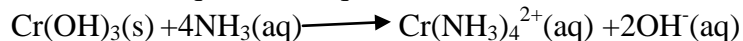
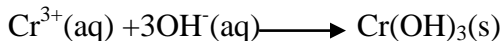
- ✓ Using dilute aqueous ammonia

Green ppt insoluble in excess



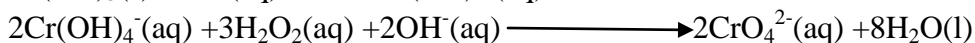
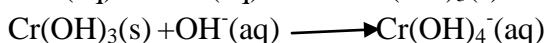
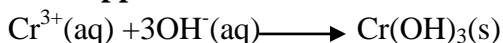
- ✓ Using concentrated ammonia solution

Green ppt soluble in excess to form a **green** solution



- ✓ Using sodium hydroxide dropwise until in excess followed by hydrogen peroxide

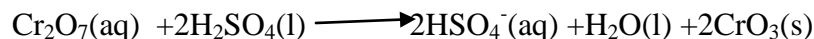
Green ppt soluble in excess to form a **green** solution which turns yellow



Chromium in the +6 oxidation state

Chromium(VI) oxide CrO_3 (Chromic anhydride) . they are red crystals

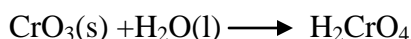
Its prepared by adding concentrated sulphuric acid to potassium dichromate



It decomposes on heating to form chromium(III) oxide



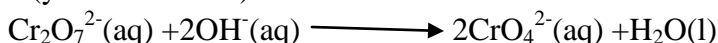
It dissolves in water to form chromic acid



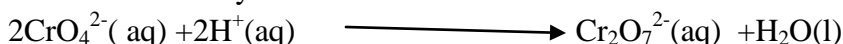
Chromates(CrO_4^{2-}) and dichromates($\text{Cr}_2\text{O}_7^{2-}$)

Relationship between a dichromate and chromate

Addition of alkali to a solution containing a dichromate ions (orange solution) converts them to chromate (yellow solution)



The process is reversed by the addition of an acid

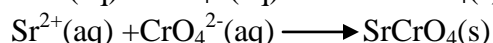
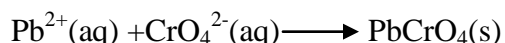
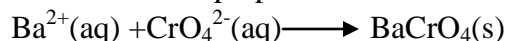


Sodium chromate

Potassium chromate

Is prepared by adding potassium hydroxide solution to a dichromate

It is used in the preparation of insoluble chromate(VI)



Sodium dichromate(VI), $\text{Na}_2\text{Cr}_2\text{O}_7$

Prepared by adding an acid to chromate

Potassium dichromate(VI), $\text{K}_2\text{Cr}_2\text{O}_7$

Oxidizing reactions of dichromates

Dichromates act as powerful oxidizing agent and its acidified using sulphuric acid

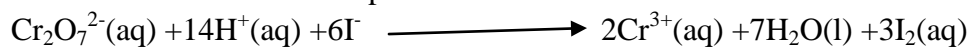


Examples of oxidizing actions

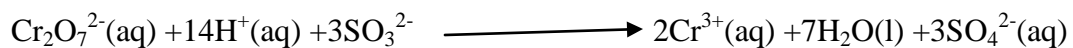
Conversion of iron(II) to iron(III)



Liberation of iodine from acidified potassium iodide solution



Oxidation of sulphite to sulphate ion



Quiz

Write equation for the reaction between acidified potassium dichromate solution and

- (i) ethanol
- (ii) methanoic acid
- (iii) hydrogen sulphide gas
- (iv) sulphur dioxide gas
- (v) sodium nitrite solution
- (vi) potassium oxalate solution