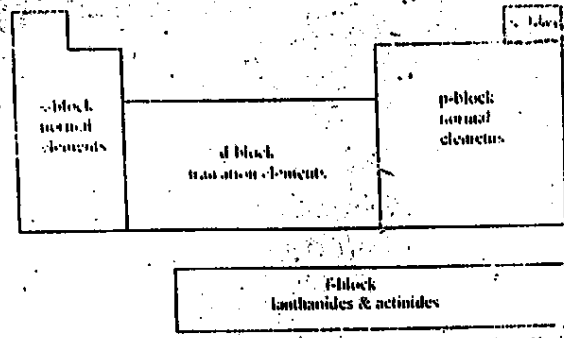


2004 to 2005

TRANSITION ELEMENTS

Elements which have partially filled d or f subshells in atomic state or in any of their commonly occurring oxidation states.

d-block, f-block are called transition elements. It is because these are present in between s and p-block elements in periodic table and their properties are in transition between metallic character of s-block elements and non-metallic character of p-block elements.



JAMSHED AKBAR
chemist@yahoo.com

ELECTRONIC CONFIGURATION

Electronic configuration of three series of d-block elements is shown below. Cr has $3d^5 4s^1$ configuration. Similarly Cu has $3d^{10} 4s^1$ configuration. It is due to extra stability of half-filled and full filled orbitals.

3d-block elements		4d-block elements		5d-block elements	
Elements	Electronic configuration	Elements	Electronic configuration	Elements	Electronic configuration
Sc (21)	[Ar] $3d^1 4s^2$	Y (39)	[Kr] $4d^1 5s^2$	La (57)	[Xe] $5d^1 6s^2$
Ti (22)	[Ar] $3d^2 4s^2$	Zr (40)	[Kr] $4d^2 5s^2$	Hf (72)	[Xe] $4f^{14} 5d^2 6s^2$
V (23)	[Ar] $3d^3 4s^2$	Nb (41)	[Kr] $4d^4 5s^1$	Ta (73)	[Xe] $4f^{14} 5d^3 6s^2$
Cr (24)	[Ar] $3d^5 4s^1$	Mo (42)	[Kr] $4d^5 5s^1$	W (74)	[Xe] $4f^{14} 5d^4 6s^2$
Mn (25)	[Ar] $3d^5 4s^2$	Tc (43)	[Kr] $4d^5 5s^2$	Re (75)	[Xe] $4f^{14} 5d^5 6s^2$
Fe (26)	[Ar] $3d^6 4s^2$	Ru (44)	[Kr] $4d^7 5s^1$	Os (76)	[Xe] $4f^{14} 5d^6 6s^2$
Co (27)	[Ar] $3d^7 4s^2$	Rh (45)	[Kr] $4d^8 5s^1$	Ir (77)	[Xe] $4f^{14} 5d^7 6s^2$
Ni (28)	[Ar] $3d^8 4s^2$	Pd (46)	[Kr] $4d^{10}$	Pt (78)	[Xe] $4f^{14} 5d^9 6s^1$
Cu (29)	[Ar] $3d^{10} 4s^1$	Ag (47)	[Kr] $4d^{10} 5s^1$	Au (79)	[Xe] $4f^{14} 5d^{10} 6s^1$
Zn (30)	[Ar] $3d^{10} 4s^2$	Cd (48)	[Kr] $4d^{10} 5s^2$	Hg (80)	[Xe] $4f^{14} 5d^{10} 6s^2$

	3d					4s
Sc (Ar)	1					1
Ti (Ar)	1	1				1
V (Ar)	1	1	1			1
Cr (Ar)	1	1	1	1	1	1
Mn (Ar)	1	1	1	1	1	1
Fe (Ar)	1	1	1	1	1	1
Co (Ar)	1	1	1	1	1	1
Ni (Ar)	1	1	1	1	1	1
Cu (Ar)	1	1	1	1	1	1
Zn (Ar)	1	1	1	1	1	1

TYPICAL AND NON-TYPICAL ELEMENTS

Elements which show typical properties of transition elements are called typical transition elements

While

Elements which do not show typical properties of transition elements are called non-typical transition elements

Explanation

Group IIB include Zn, Cd and Hg. These elements do not have partially filled d-orbital in atomic state or in their ionic state. Moreover these elements do not show typical properties of transition elements except complex formation.

Similarly group IIIB elements include Sc, Y and La. These elements do not show typical properties of transition elements. These mostly exist as tripositive ions. In this state their d-orbital is empty.

Hence elements of group IIIB and IIB are called non-typical transition elements. While other elements are called typical transition elements.

Coinage metals include Cu, Ag and Au. These are typical transition elements. Because Cu^{2+} has $3d^9$ configuration, Ag^{2+} has $4d^9$ configuration and Au^{3+} has $5d^8$ configuration.

Note:

f-block elements include Lanthanides and Actinides. These are called inner transition elements while d-block elements are called outer transition elements.

PROPERTIES OF TRANSITION ELEMENTS

Due to similar electronic configuration, transition metals show many similarities.

- They are all metals. Some of them are very important in industry e.g. Ti, Fe, Cr, Ni, Cu, Mo, Zr, Nb, Ta, Th etc.
 - They are hard with high m.p. and b.p.
 - They are good conductors of heat and electricity
 - They form alloys with one another and with other elements
 - Generally, they show variable valencies
 - Their ions and compounds are coloured in solid as well as in solution form.
- Typical transition elements have at least one coloured oxidation state.

Transition elements show following general properties

1. Binding Energies

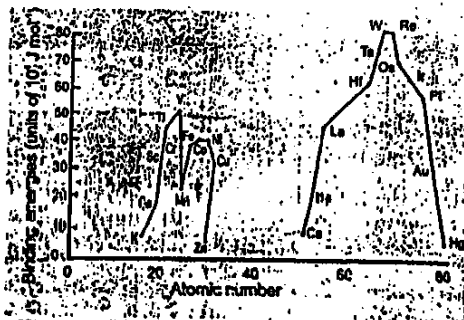
Transition metals show good mechanical properties. These are hard, malleable and ductile.

The hardness shows that these have strong metallic bonding. It is because s-electrons of outer shell as well as d-electrons of inner shell also take part in bonding.

In transition series, binding forces increases from left to right upto middle and then decreases.

It is because number of unpaired electrons increases upto VB and VIIB group and then decreases upto group IIB.

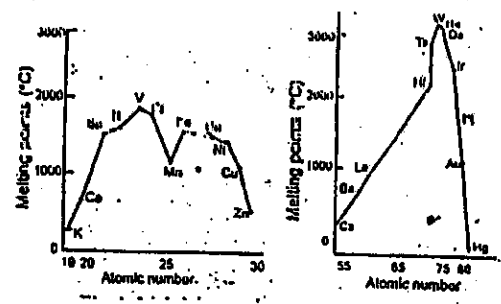
In third transition series, binding forces increases upto tungsten due to involvement of all 5d electrons.



2. Melting and Boiling Points

These have very high m.p. and b.p. due to strong binding forces.

Melting points increase upto middle and then decrease to a minimum at the end of series. It is due to increase in binding forces upto middle and then decrease upto end.

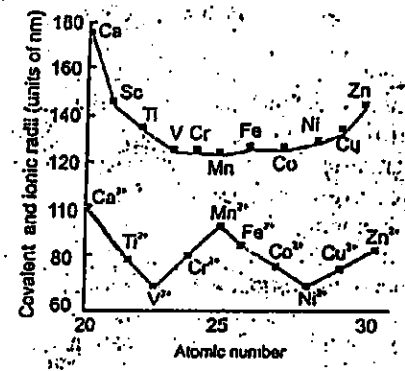


JAMSHIED AKBAR
E-mail: jamshed_chemist@yahoo.com

3. Covalent Radii and Ionic Radii

At the start of series, covalent radii rapidly decrease and then become almost constant.

At the end of series covalent radii shows a slight increase. This increase is because, at the end of series, inner d-orbital is contracted due to greater number of electrons and it has a greater shielding effect. Thus outer electrons are moved away from nucleus. Hence covalent radii increases. Periodicity of ionic radii is not much regular.



4. Paramagnetism

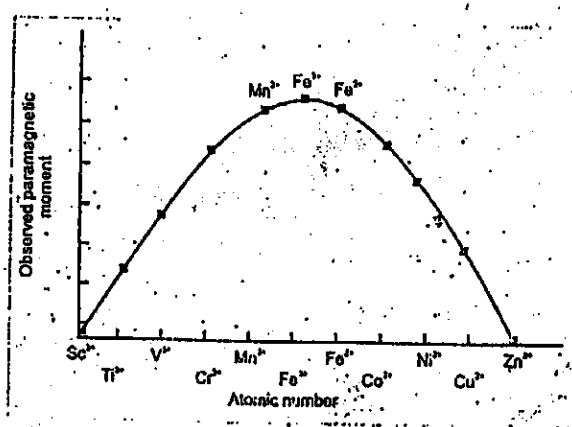
Substances which are weakly attracted by strong magnetic field are called paramagnetic substances.

While substances which are weakly repelled by strong magnetic field are called diamagnetic substances.

Paramagnetic behaviour is caused by unpaired electrons. It is because, moving electrons have magnetic moments. When electrons are paired, their magnetic moments cancel the effect of each other thus the substance become diamagnetic. However, if the electron is unpaired, it shows its magnetic moments. Thus the substance becomes paramagnetic.

Magnetic moment of a substance increases with increase in number of unpaired electrons. Thus maximum paramagnetic moment is shown by Fe^{3+} and Mn^{2+} while it decreases on both sides of these ions. It is because these ions have maximum unpaired electrons i.e. 5 each. On both sides of these ions number of unpaired electrons decreases to zero thus paramagnetic behaviour also decreases.

Ion	3d orbital electronic structure	No. of unpaired electrons
Sc ³⁺		0
Ti ³⁺	↑	1
V ³⁺	↑ ↑	2
Cr ³⁺	↑ ↑ ↑	3
Mn ³⁺	↑ ↑ ↑ ↑	4
Mn ²⁺ , Fe ³⁺	↑ ↑ ↑ ↑ ↑	5
Fe ²⁺	↑ ↑ ↑ ↑ ↓	4
Co ²⁺	↑ ↑ ↑ ↓ ↓	3
Ni ²⁺	↑ ↑ ↓ ↓ ↓	2
Cu ²⁺	↑ ↓ ↓ ↓ ↓	1
Zn ²⁺	↑ ↑ ↓ ↓ ↓	0



5. Oxidation State

Transition elements show variable oxidation state. It is because d-electrons of inner d-orbital are also involved in bonding in addition to outer s-electrons. Due to presence of larger number of unpaired electrons, these can show variable valency.

e.g. All elements of 3d series show a +2 oxidation state of +2 in addition to higher oxidation states.

+2 oxidation state is produced due to involvement of s-electrons in bonding. For higher oxidation states, d-electrons also become involve in bonding.

First five elements show highest oxidation state when all their s and d-electrons are involved in bonding. After Mn number of oxidation state decreases because d-orbital fill up with electrons and few unpaired electrons are available for bonding.

	Oxidation states						
Sc [Ar] 3d ¹ 4s ²	2	3					
Ti [Ar] 3d ² 4s ²	2	3	4				
V [Ar] 3d ³ 4s ²	2	3	4	5			
Cr [Ar] 3d ⁴ 4s ¹	2	3	4	5	6		
Mn [Ar] 3d ⁵ 4s ²	2	3	4	5	6	7	
Fe [Ar] 3d ⁶ 4s ²	2	3	4	5	6		
Co [Ar] 3d ⁷ 4s ²	2	3	4	5			
Ni [Ar] 3d ⁸ 4s ²	2	3	4				
Cu [Ar] 3d ¹⁰ 4s ¹	1	2	3				
Zn [Ar] 3d ¹⁰ 4s ²	2						

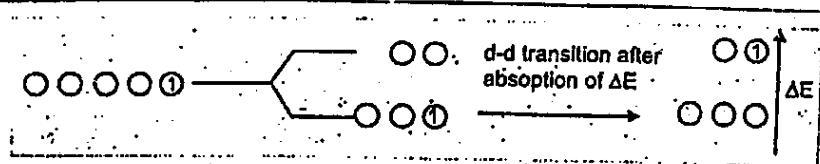
6. Color

Transition elements and their compounds show colors. The colors of these substances is due to d-orbitals.

During bond formation, d-orbitals of transition elements are split up into two sets of energy levels. One set of energy level has higher energy than other.

When light falls, an electron in lower set of energy level may absorb energy and it goes to higher energy set of d-orbitals. This is called d-d transition. The energy difference between two sets of d-orbitals varies from ion to ion. Thus each ion absorb a particular set of wavelengths while transmit the remaining set of wavelengths. Thus it give different colour to each ion.

e.g. In $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, yellow light is absorbed while blue and red light are transmitted. Thus the solution of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ shows violet colour.



7. Interstitial Compounds

Transition metals have close packed structure in which interstices are present. Small non-metallic atoms like H, B, C and N can enter into these interstices and adsorbed on the surface of metal atoms to form interstitial compounds. These are non-stoichiometric in nature and do not obey the laws of chemical combination. Sometimes they are also called interstitial alloys

8. Alloy Formation

Transition metals have almost same sizes. Thus these can replace each other in crystal lattice to form substitutional alloys.

e.g. Alloy steel is an alloy of iron with Cr, Mn and Ni. This alloys steel has many useful properties.

Other examples are brass, bronze, coinage alloys etc.

JAMSHED AKBAR

E-MAIL: JAMSHED_CHEMIST@YAHOO.COM

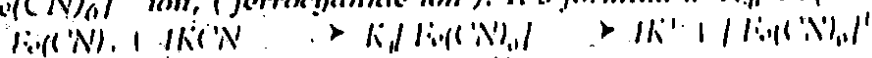
JAMSHED AKBAR
Email: jamshed_chemist@yahoo.com

COMPLEX COMPOUNDS

Compounds containing complex ions or complex molecules and can exist independently are called complex compounds or coordination compounds.

Example And Explanation

When an aqueous solution of $\text{Fe}(\text{CN})_2$ is mixed with an aqueous solution of KCN then a new compound is obtained. This new compound ionizes in water as K^+ ion and $[\text{Fe}(\text{CN})_6]^{4-}$ ion, (ferrocyanide ion). Its formula is $\text{K}_4[\text{Fe}(\text{CN})_6]$



$[\text{Fe}(\text{CN})_6]^{4-}$ is called complex ion. Thus $\text{K}_4[\text{Fe}(\text{CN})_6]$ is called complex compound.

A complex compound may contain

- A simple cation and a complex anion e.g. $\text{K}_4[\text{Fe}(\text{CN})_6]$
- A complex cation and a simple anion e.g. $[\text{Cr}(\text{NH}_3)_6] \text{Cl}_3$

TERMINOLOGY OF COMPLEX COMPOUNDS

CENTRAL METAL ION

A metal atom or ion (usually a transition element) surrounded by a number of ligands is called a central metal atom or ion.

Example

In $\text{K}_4[\text{Fe}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_6] \text{Cl}_3$, Fe and Cr are the central metal ions.

LIGAND

The atom or ions or neutral molecules which surround the central metal atom or ion by donating electron pairs are called ligands.

Examples

In $\text{K}_4[\text{Fe}(\text{CN})_6]$ and $\text{K}_4[\text{Fe}(\text{CN})_6]$, CN^- is the ligand.

In $[\text{Cr}(\text{NH}_3)_6] \text{Cl}_3$ and $[\text{Ag}(\text{NH}_3)_2] \text{Cl}$, NH_3 is the ligand

TYPES OF LIGANDS

Unidentate ligands

The ligands having only one donor atom are called unidentate ligand.

Examples

NH_3 , Cl^- , CN^- , I^- etc.

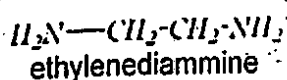
Polydentate ligands

Ligands having two or more donor atoms are called polydentate ligands

These ligands are further classified into bidentate, tridentate ligands etc, depending on the number of donor atoms.

Examples

Ethylenediamine (bidentate), EDTA (hexadentate) etc.



Oxalate ion is a bidentate ligand and its coordination with the metal ion occurs through its negatively charged oxygen atoms.

JAMSHED AKBAR

E-MAIL: JAMSHED_CHEMIST@YAHOO.COM

JAMSHED AKBAR
E-mail: jamshed_chemist@yahoo.com

6

COORDINATION NUMBER

The number of lone pair of electrons provided by the ligands to the central metal atom or ion is called the coordination number of the central metal atom or ion.

Examples

In $K_4[Fe(CN)_6]$, co-ordination number of Fe is 6.
 In $[Cu(NH_3)_4]SO_4$, co-ordination number of Cu is 4

2004 - 2005

COORDINATION SPHERE

The central metal atom or ion alongwith ligands is called the coordination sphere. It is placed in square brackets. It may be anionic, cationic or neutral

Examples

In $K_4[Fe(CN)_6]$, $[Fe(CN)_6]^{4-}$ is the anionic co-ordination sphere.
 In $[Cu(NH_3)_4]SO_4$, $[Cu(NH_3)_4]^{2+}$ is the cationic co-ordination sphere.
 In $[Ni(CO)_4]$, $[Ni(CO)_4]^0$ is the neutral co-ordination sphere.

CHARGE ON THE COORDINATION SPHERE

It is the algebraic sum of the charges present on the central metal ion and the total charge on the ligands.

Example



Charge on iron = +2
 Total charge on six CN^- ions = -6
 Charge on the coordination sphere = $-6 + 2 = -4$

JAMSHED AKBAR
 E-mail: jamshed_chemist@yahoo.com

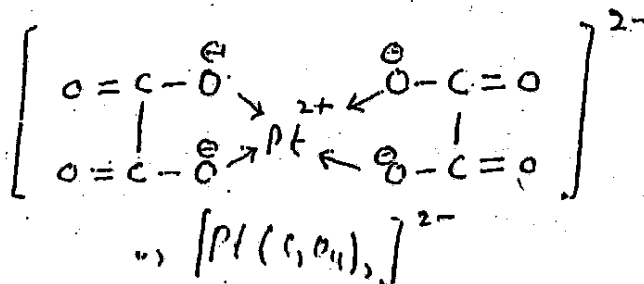
CHELATES

When all the donor atoms of a polydentate ligand are coordinated with the same metal ion, a complex compound is formed which contains one or more rings in its structure. It is called a Chelate.

Metal chelates are more stable metal complexes.

Example

When two oxalato ligands, $C_2O_4^{2-}$ (bidentate ligand) are coordinated with Pt^{+2} ion, dioxalato platinate (II) ion is obtained. Each oxalate ligand forms a five membered ring with the cation.



Dioxalatoplatinate (II) ion.

NOMENCLATURE:

Complex compounds are named according to the rules given by Inorganic nomenclature committee of IUPAC.

Following are the rules

ORDER OF NAMING IONS

- Cations are named before anions

Examples

FeCl_2 : Iron (II) chloride

$[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$: Tetraammine copper (II) sulphate

- Non-ionic or Neutral molecules are given one word name

Examples

$[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$: Triamminedichlorocobalt (III)

$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$: Diamminedichloroplatinum (II)

NAMING OF LIGANDS

(i) NEUTRAL LIGANDS

Neutral ligands have no special ending. These are named as neutral molecule except NH_3 (ammine), H_2O (aqua), NO (nitrosyl), CO (carbonyl)

(ii) IONIC LIGANDS

Negative ligands has ending -o

Examples

Cl^- (chloro), CN^- (cyano), I^- (iodo), NO_2^- (nitro) etc.

Positive ligands has ending -ium

Examples

$\text{NH}_2 - \text{NH}_3^+$ (hydrazinium), NO_2^+ (nitronium), NO^+ (nitrosonium) etc.

- (iii) Prefixes di, tri, tetra etc are used to indicate the number of ligands of one type

NAMING OF CENTRAL METAL ION

- (i) If co-ordination sphere is positive or neutral, metal name is written as such
- (ii) If co-ordination sphere is negative, then suffix -ate is added to the metal name
- (iii) Oxidation state of central metal atom is indicated by Roman numeral in parenthesis at the end of metal name.

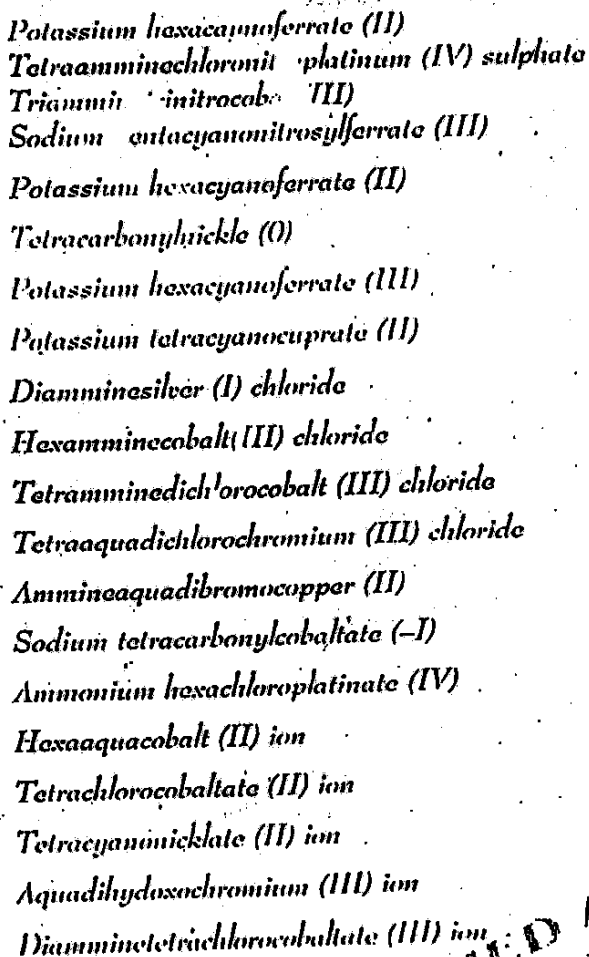
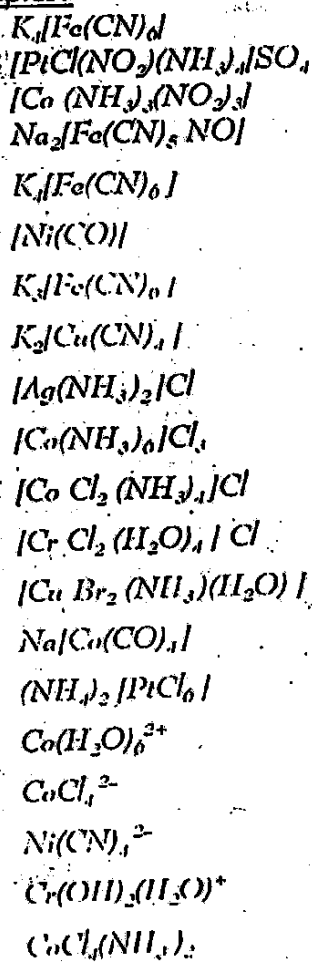
NAMING OF CO-ORDINATION SPHERE

- (i) Ligands are named first
- (ii) Ligands are named in alphabetical order, regardless of the charge and number of each
- (iii) Central metal atom is named last, followed by oxidation state with in parenthesis

Note

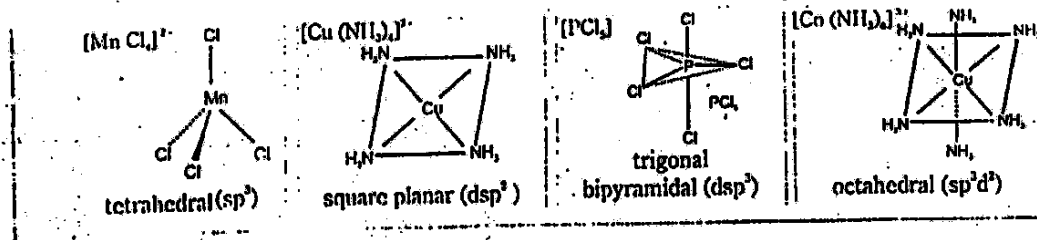
In writing the formula of a complex ion, the symbol of the central metal atom is placed first. It is followed by the names of the ionic ligands in alphabetical order, then neutral ligands in alphabetic order. The formula of the whole complex ion is enclosed in square brackets.

Examples:



GEOMETRY OF COMPLEXES

The geometry of complexes depends upon the type of hybridization taking place in the valence shell of the central metal atom. Following is the brief summary of geometry of complex compounds.



JAMSHED AKBAR
 the mail: jamshed_chemist@yahoo.com

IRONHistory

Iron has been known since prehistoric days. It was used in Egypt in 1500 B.C. Chinese also used iron as early as 2500 B.C. In subcontinent iron was produced around 600 B.C.

Ores of Iron

Following are the important ores of iron

Magnetite Fe_3O_4

Haematite Fe_2O_3

Limonite $Fe_2O_3 \cdot 3H_2O$, etc.

Commercial Forms Of Iron

Following three forms of iron are available commercially. They differ in carbon contents.

- Pig iron or cast iron 2.5 to 4.5% carbon
- Wrought iron 0.12 to 0.25% carbon
- Steel 0.25 to 2.5% carbon

WROUGHT IRON

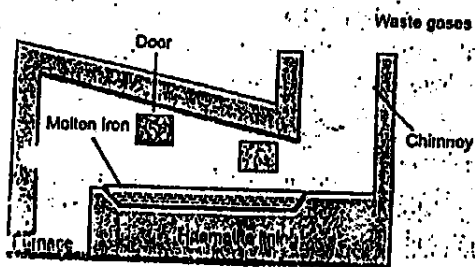
It is the purest form of commercial iron. It contains lowest percentage of carbon. It has upto 0.3% of impurities like S, P, Si and Mn, etc.

S = 0.2 to 0.15%, Mn = upto 0.25%, P = 0.04 to 0.2%

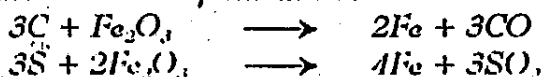
MANUFACTURE OF WROUGHT IRON FROM CAST IRON

It is manufactured from cast iron by puddling. In puddling cast iron is heated in a special type of reverberatory furnace called puddling furnace. Low roof of this furnace deflects hot gases and flames downwards and melts cast iron.

The hearth of furnace is lined with haematite (Fe_2O_3). Cast iron is placed on the hearth. It is melted by hot gases. It is stirred or puddled with long iron rods called rables through the doors to bring it in thorough contact with the lining of the hearth, i.e. Fe_2O_3 .



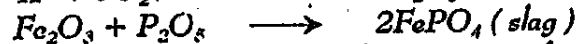
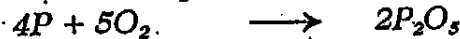
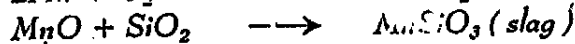
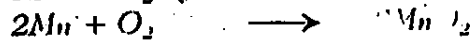
The haematite (Fe_2O_3) lining supplies oxygen. Oxygen oxidizes carbon, sulphur, silicon, manganese and phosphorus present in the cast iron to their oxides. Oxides of carbon and sulphur are volatile and escape out at high temperature.



JAMSHED AKBAR

E-MAIL: JAMSHED_CHEMIST@YAHOO.COM

While oxides of manganese, silicon and phosphorous form slags.



With the removal of impurities, melting point of metal rises and it becomes a semi-solid mass. It is then taken out in the form of balls or blooms on the ends of rabbles. It is hammered while hot to squeeze out as much of slag as possible. The product so obtained is called wrought iron.

STEEL:

It is an alloy of iron containing 0.25 to 2.5% of carbon and traces of S, P, Si and Mn. Carbon content of steel are intermediate between cast iron and wrought iron.

CLASSIFICATION OF STEEL:

Mild steel (0.1-0.2% C)

It is fairly soft, malleable and ductile. It can be forged (shaped by hammering and pressing while hot).

It is used in making tubes, nuts, bolts, bars and boiler plates.

Medium carbon steel (0.2-0.7% C)

It is harder than mild steel. It is malleable and ductile.

It is used in making rails, axles, castings.

High carbon steel (0.7-1.5% C)

It is hard. It can be forged when % of C is less than 1.0%.

Steel containing more than 1.0% carbon can not be forged.

It is used to make hammers, taps, dies, cutting tools, machine tools, hard steel parts of machinery and all sort of engines.

JAMSHED AKBAR
E-mail: jamshed_chemist@yahoo.com

MANUFACTURING OF STEEL

- It can be manufactured from cast iron by removing some carbon along with sulphur, phosphorus and silicon.
- It can be manufacture by adding required amount of carbon to wrought iron. Some special constituents are also added e.g. tungsten, chromium vanadium, molybdenum, manganese, nickel and cobalt. These give desired properties to the steel.

At present most of the steel is manufactured from cast iron.

Processes

Following processes are used to produce steel

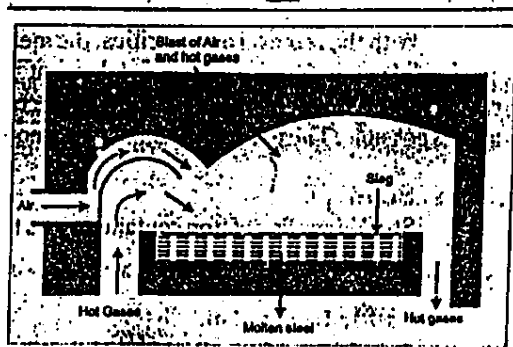
- Open hearth process (using cast iron, wrought iron or steel scarp)
- Bessemer process (using cast iron only)

Some other processes are also used to prepare special type of steel from pure wrought iron.

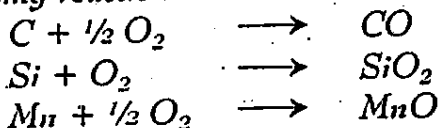
OPEN HEARTH PROCESS

It is the most modern method of manufacturing steel. It is carried out in an open hearth furnace. This furnace has low roof to deflect hot gases and flames downward to melt the charge. Open hearth furnace works on the regenerative principle of heat economy.

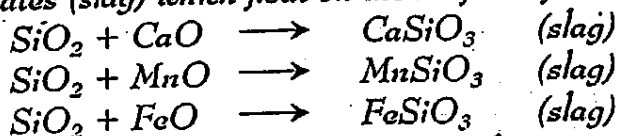
- Open hearth process is of two types.
 - When impurities are Mn, Si, etc. then furnace with acidic lining like SiO_2 is used.
 - When impurities are P and S, etc. then furnace with basic lining like dolomite (CaO , MgO) is used.

Process

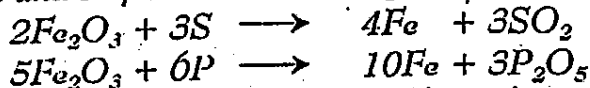
A mixture of cast iron, scrap steel and quick lime is charged into the furnace. At about 1600°C Si, Mn, C, S, and P are burnt out and removed according to the following reactions.



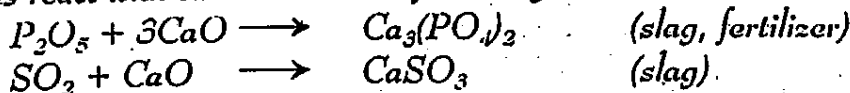
CO escapes in flue gases. Silica (SiO_2) combines with CaO, MnO and FeO to form silicates (slag) which float on the surface of the molten metal.



Phosphorus and sulphur react with Fe_2O_3 to form P_2O_5 and SO_2 .



These oxides react with calcium oxide to form slag.



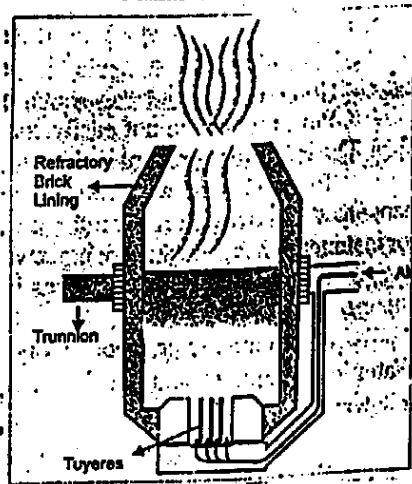
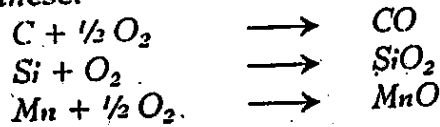
Percentage of carbon in steel is checked at regular intervals. When this is reduced to about 0.1%, then calculated amount of ferromanganese (Fe, Mn, C) is added. Manganese desulphurises the steel. Carbon raises the carbon contents to the required values. After giving time for mixing, a little more ferromanganese is added. Then charge is allowed to run into moulds where it solidifies to ingots.

The whole process takes about 10 hours. Slag contains calcium phosphate. It is ground to powder and sold as a fertilizer.

BESSEMER'S PROCESS

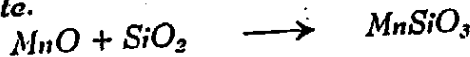
The furnace called Bessemer's converter. It is a pear shaped vessel made of steel plates. At the bottom the converter there are number of holes through which hot air can be introduced. The converter is held on a central axis. It can be tilted for feeding and pouring out the finished materials.

Molten pig or cast iron (25 to 30 tons) from the blast furnace is fed into the converter. Hot air blast is passed through the perforated base. This oxidizes carbon, silicon and manganese.

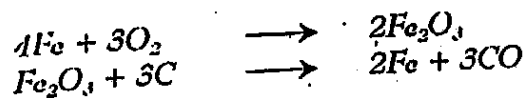


JAMSHED AKBAR
E-mail: jamshed_chemist@yahoo.com

These oxides form a slag of MnSiO_3 . Heat evolved during oxidation keep the iron in molten state.

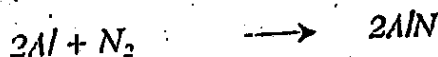


CO produced burns at the mouth of the converter with a blue flame. Iron is partly oxidized to ferric oxide (Fe_2O_3) which also extracts carbon from cast iron to form CO.



Within 10 to 15 minutes the flame due to CO subsides showing that carbon is completely oxidized. At this stage ferromanganese is added to correct the proportion of carbon to obtain the desired qualities. A blast of air is blown for few moments for thorough mixing. Addition of Mn gives increased hardness and tensile strength.

To remove entrapped bubbles of gases (below holes) such as O_2 , N_2 , CO_2 a little Al or ferrosilicon is added. Al removes nitrogen as nitride.



At the end of the operation, the molten steel is poured out into moulds for casting.

2004 - 2005

CORROSION

The process of chemical decay of metals due to the action of surrounding medium is called corrosion.

Explanation

When metals come in contact with atmospheric gases, the surface of metals is coated with oxides, sulphides, carbonates etc. sometimes these compounds form a compact layer on the surface. Thus metal is protected from further attack.

However, if water is present then layers of oxides, sulphides and carbonates are dissolved in water. Thus corrosion penetrates into the metal. Further water promotes electrochemical process which is the main cause of rapid corrosion.

THEORIES OF CORROSION

Two important theories of corrosion are

- Acid theory
- Electrochemical theory

JAMSHED AKBAR
E-mail: jamshed_chemist@yahoo.com

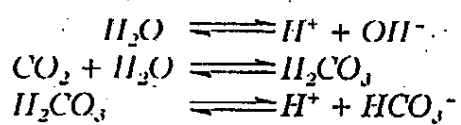
ELECTROCHEMICAL THEORY

100% pure metal does not corrode. Impurities present in metal promotes corrosion.

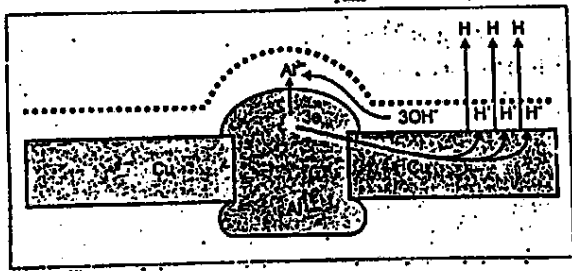
Consider an example

Let Al is present in contact with Cu

Moisture and CO₂ are present on the surface of metal. Water ionizes to H⁺ and OH⁻ ions. CO₂ is dissolved in water to produce H₂CO₃ which ionizes into H⁺ and HCO₃⁻ ions.

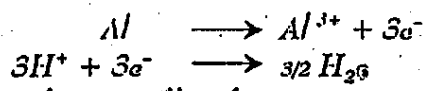


In other words, metals are actually immersed in a solution of H⁺, OH⁻ and HCO₃⁻ ions. Thus a Galvanic cell is set up.



In this cell, Al releases electrons and changes into Al³⁺ ion. It acts as -ve electrode while Cu acts as positive electrode. It is because Al is more reactive than Cu and is present above Cu in electrochemical series.

Al³⁺ ions combine with OH⁻ ions to form Al(OH)₃ ions, Thus Al starts dissolving.



Thus Al corrodes rapidly when in contact with Cu

Generally,

When an active metal (higher in electrochemical series) is in contact with less active metal (lower in electrochemical series). The active metal corrodes rapidly while other remains intact.

PREVENTION OF CORROSION

Prevention of corrosion is very important. In case of iron, its corrosion is about $\frac{1}{10}$ th of its annual production. Thus corrosion must be prevented.

Following methods are generally used

Coating Of Metals

It is the simplest method. In this metal surface is coated with oil, paint, varnish or enamel.

Alloying

Corrosion can be prevented by alloying of metal with other metals. e.g corrosion of Fe is prevented by alloying it with Ni, Cr etc.

Metallic Coating

A protective layer of another metal on the surface of metal can also prevent corrosion.

TIN PLATING OR COATING IRON WITH TIN (Cathode Coating)

In this process, a clean sheet of iron is dipped in molten tin. It is then passed through hot pairs of rollers. Thus surface of iron is coated with a thin layer of tin. Tin itself is very stable. Thus it prevents the rusting of metal.

It is used in the manufacture of tin canes, oil containers and other similar articles.

If the protective layer is damaged then iron comes in direct contact with moisture. A galvanic cell is set up in which tin acts as cathode while iron acts as anode. Electrons flow from iron to tin. Iron is oxidised to Fe^{3+} which from $Fe(OH)_3$ on combining with OH^- ions. On the surface of tin H^+ ions are discharged to H_2 gas. Thus iron dissolves more rapidly.

Hence, it can be concluded that tin plated iron is rusted more rapidly than non-plated iron, if tin coating is damaged.

GALVANIZING OR ZINC COATING (Anode Coating)

It is done by dipping clean iron sheets in a $ZnCl_2$ bath and heating. Iron sheets are removed and rolled into Zn bath and air cooled.

If protective coating of Zn is destroyed then a galvanic cell is set up. In this cell Zn acts as anode and iron as cathode. Electrons flow from Zn to iron. Thus Zn decays while Fe remains intact. This is called sacrificial corrosion.



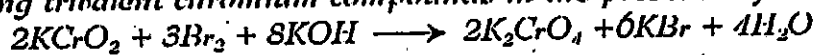
This type of galvanizing is used in water pipes.

CHROMATES AND DICHROMATESCHROMATES

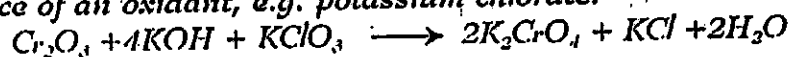
Chromates are the salts of chromic acid, H_2CrO_4 . This acid exist only in aq. solution. During isolation from solution they decompose immediately into chromic anhydride (Cr_2O_3) and water. However, their salts are quite stable.

POTASSIUM CHROMATE (K_2CrO_4)Preparation

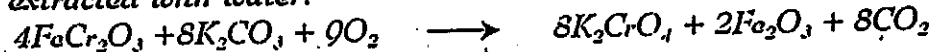
- Chromates of alkali metals are soluble in water. These are obtained by oxidizing trivalent chromium compounds in the presence of an alkali.



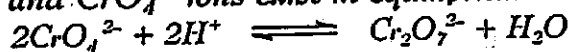
- Chromates can also be produced by fusing Cr_2O_3 with an alkali in the presence of an oxidant, e.g. potassium chlorate.



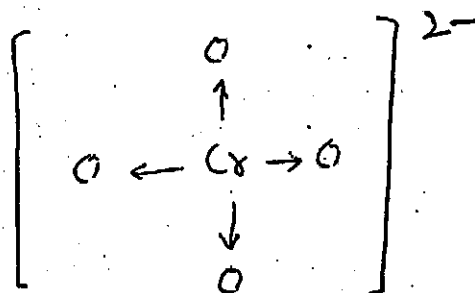
- Chromates are usually prepared from natural chromite ($FeO \cdot Cr_2O_3$). It is strongly heated with potassium carbonate in the presence of the oxygen. The resulting fused mass contains potassium chromate, which can be extracted with water.

Properties

- Almost all the chromates are yellow in colour.
- Some of them are used as pigments. e.g. insoluble lead chromate, $PbCrO_4$, is used for the preparation of yellow oil colour called yellow crown.
- K_2CrO_4 and $K_2Cr_2O_7$ show similar properties because in an aq. solution $Cr_2O_7^{2-}$ and CrO_4^{2-} ions exist in equilibrium.



If an alkali is added to this solution, hydroxyl ions will remove hydrogen ion in solution. Thus equilibrium will shift to left and dichromate ions will be converted into chromate ions. Similarly adding will shift equilibrium to right and dichromate ions will be formed.

Structure Of Chromate Ion

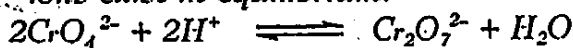
2004 - 2005

DICHROMATES AND DICHROMIC ACID

Dichromates are the salts of dichromic acid, $H_2Cr_2O_7$. This acid exist only in aq. solution. During isolation from solution it decompose immediately into chromic anhydride (Cr_2O_3) and water. However, its salts are quite stable.

POTASSIUM DICHROMATE ($K_2Cr_2O_7$)**PREPARATION****(1) From Potassium Chromate**

$K_2Cr_2O_7$ can be prepared from K_2CrO_4 in an aq. solution $Cr_2O_7^{2-}$ and CrO_4^{2-} ions exist in equilibrium.



In an acidic medium the equilibrium will shift in the forward direction. Thus chromate ions are changed into dichromate ions.

(2) From Sodium Chromate

Sometimes sodium dichromate is converted into potassium dichromate by reacting it with KCl .

**PHYSICAL PROPERTIES:**

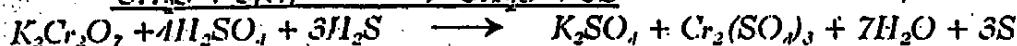
- It is an orange red crystalline solid
- It's m.p. is $396^\circ C$
- It is fairly soluble in water.

OXIDIZING PROPERTIES

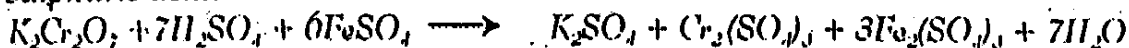
Dichromates are powerful oxidizing agents. Oxidation is carried out in an acid solution. In this process hexavalent chromium ion is reduced to trivalent chromium ion.

1. Reaction With H_2S

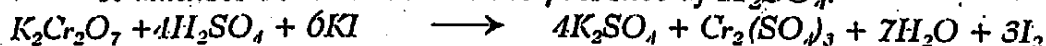
It oxidizes H_2S to free S in the presence of sulphuric acid

**2. Reaction With Ferrous Sulphate**

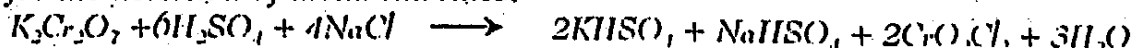
It oxidizes ferrous sulphate to ferric sulphate in the presence of sulphuric acid.

**3. Reaction With Potassium Iodide**

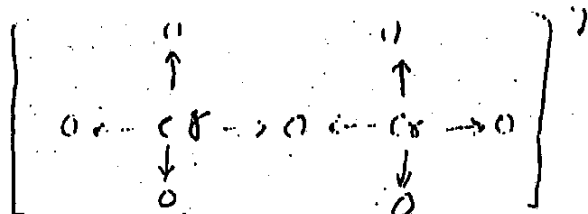
It oxidizes KI to iodine in the presence of H_2SO_4 .

**4. Chromyl Chloride Test**

When solid potassium dichromate is heated with solid metal chloride in the presence of conc. sulphuric acid chromyl chloride is produced. This test is used for the detection of metal chlorides.



Structure Of Dichromate Ion



USES:

1. It is used in dyeing.
2. It is used in leather industries for chrome tanning.
3. It is used as an oxidizing agent.

JAMSHED AKBAR
E-mail: jamshed_chemist@yahoo.com

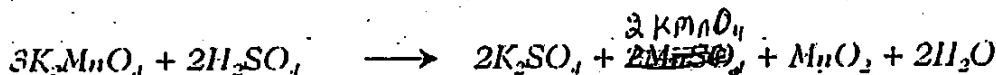
POTASSIUM PERMANGANATE (KMnO₄)

It is salt of permanganic acid, HMnO₄. It is an unstable acid and exists only in solution.

PREPARATION

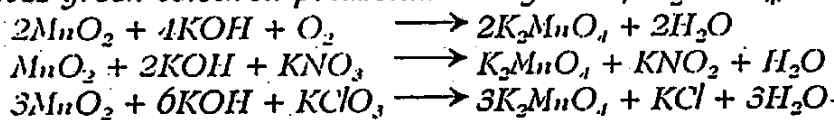
Laboratory Preparation

It is prepared by acidifying the solution of potassium manganate, K₂MnO₄ by H₂SO₄.



Industrial Preparation

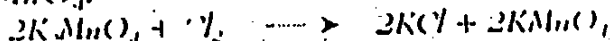
It is prepared from mineral pyrolusite, MnO₂. Finely powdered mineral is fused with KOH in the presence of air or an oxidizing agent like KNO₃ or KClO₃, etc. This gives green coloured potassium manganate, K₂MnO₄, in fused state.



The fused K₂MnO₄ obtained is extracted with water. The solution, after filtration, is converted into potassium permanganate (KMnO₄) by any of the following methods:

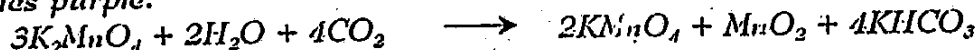
• Stadeler's process:

In this method Cl₂ is passed through green solution of K₂MnO₄ until it becomes purple due to the formation of KMnO₄. Hence Cl₂ oxidizes K₂MnO₄ into KMnO₄.



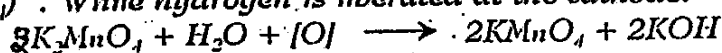
• By Passing CO₂

In this process CO₂ is passed through the green solution of K₂MnO₄ until it becomes purple.



• Electrolytic oxidation process:

In this process an aqueous solution of K₂MnO₄ is electrolyzed. Water is decomposed to give hydrogen gas at cathode and oxygen gas at anode. Oxygen liberated at anode oxidizes manganate ion (MnO₄)²⁻ into permanganate ion (MnO₄)⁻. While hydrogen is liberated at the cathode.



Purple solution of $KMnO_4$ obtained is filtered through asbestos. It then concentrated and allowed to crystallize. Crystals of $KMnO_4$ deposits deep purple-red rhombic crystals.

PHYSICAL PROPERTIES

- It forms dark purple lustrous crystals which gives deep pink colour in solution.
- Its solubility in water at $20^\circ C$ is only about 7%. It dissolves more at high temperature (25% at $63^\circ C$).

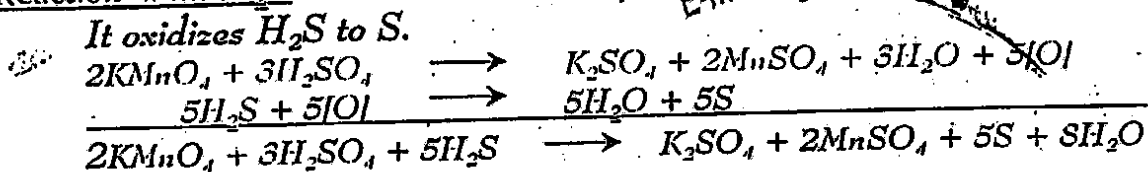
OXIDIZING PROPERTIES

Potassium permanganate is a powerful oxidizing agent. Oxidation is usually carried out in an acid solution.

JAMSHED AKBAR
Oxidation
Email: jamshed_chemist@yahoo.com

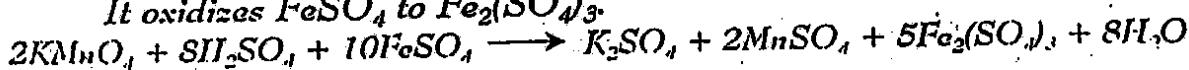
1. Reaction With H_2S

It oxidizes H_2S to S .



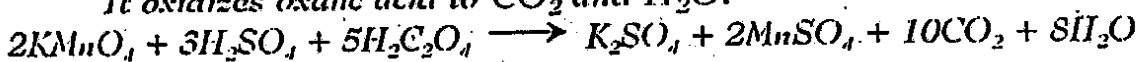
2. Reaction With $FeSO_4$

It oxidizes $FeSO_4$ to $Fe_2(SO_4)_3$.



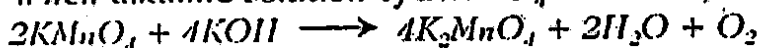
3. Reaction With Oxalic Acid

It oxidizes oxalic acid to CO_2 and H_2O .

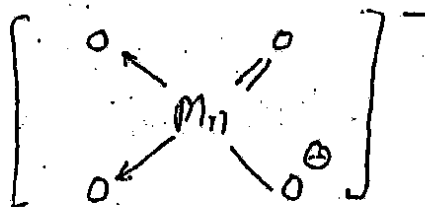


4. Reaction With KOH

When alkaline solution of $KMnO_4$ is heated, O_2 gas is evolved



Structure Of Permanganate Ion



USES:

- It is used as an oxidizing agent.
- It is used as a disinfectant and a germicide.
- It is used in the manufacture of many organic compounds.

2004 - 2005