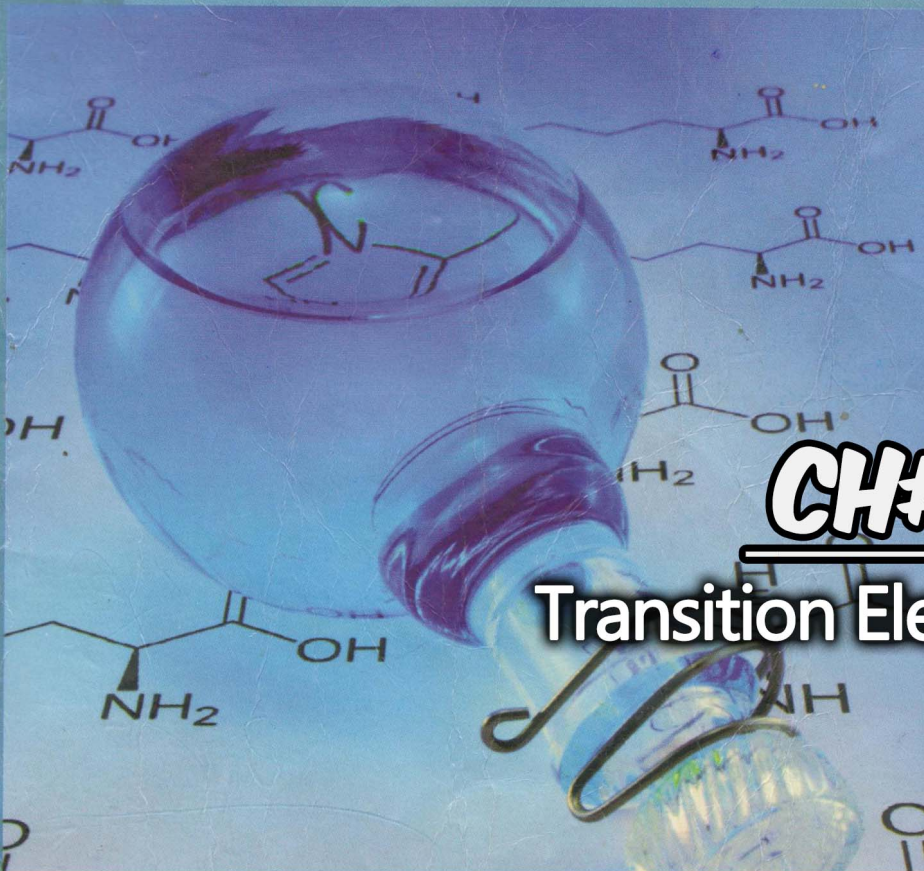


# CHEMISTRY

12



**CH#6**

**Transition Elements**



These Notes Have been Prepared  
and Developed By

**ADNAN SHAFIQUE**

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# Chapter 6

## TRANSITION ELEMENTS

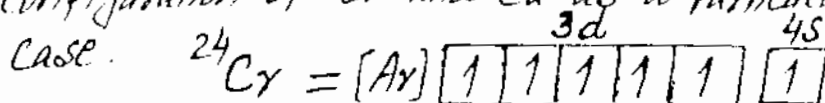
The elements which have partially filled d- or f-subshells in atomic state or in any of their oxidation state are called transition elements

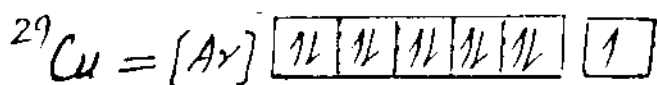
e.g. Fe, Cu, Mn, Co etc. The d-block and f-block elements are called transition elements. They are located between s-block and p-block elements. Their properties are in transition between metallic elements of s-block and non-metallic elements of p-block.

There are three series of d-block elements. Their electronic configuration is given in the following table.

3d block Elements	21 Sc [Ar] 3d <sup>1</sup> 4s <sup>2</sup>	22 Ti [Ar] 3d <sup>2</sup> 4s <sup>2</sup>	23 V [Ar] 3d <sup>3</sup> 4s <sup>2</sup>	24 Cr [Ar] 3d <sup>5</sup> 4s <sup>1</sup>	25 Mn [Ar] 3d <sup>5</sup> 4s <sup>2</sup>	26 Fe [Ar] 3d <sup>6</sup> 4s <sup>2</sup>	27 Co [Ar] 3d <sup>7</sup> 4s <sup>2</sup>	28 Ni [Ar] 3d <sup>8</sup> 4s <sup>2</sup>	29 Cu [Ar] 3d <sup>10</sup> 4s <sup>1</sup>	30 Zn [Ar] 3d <sup>10</sup> 4s <sup>2</sup>
4d block Elements	39 Y [Kr] 4d <sup>1</sup> 5s <sup>2</sup>	40 Zr [Kr] 4d <sup>2</sup> 5s <sup>2</sup>	41 Nb [Kr] 4d <sup>4</sup> 5s <sup>2</sup>	42 Mo [Kr] 4d <sup>5</sup> 5s <sup>1</sup>	43 Tc [Kr] 4d <sup>5</sup> 5s <sup>2</sup>	44 Ru [Kr] 4d <sup>6</sup> 5s <sup>2</sup>	45 Rh [Kr] 4d <sup>7</sup> 5s <sup>1</sup>	46 Pd [Kr] 4d <sup>10</sup> 5s <sup>0</sup>	47 Ag [Kr] 4d <sup>10</sup> 5s <sup>1</sup>	48 Cd [Kr] 4d <sup>10</sup> 5s <sup>2</sup>
5d block Elements	57 La [Xe] 5d <sup>1</sup> 6s <sup>2</sup>	72 Hf [Xe]4f <sup>14</sup> 5d <sup>2</sup> 6s <sup>2</sup>	73 Ta [Xe]4f <sup>14</sup> 5d <sup>3</sup> 6s <sup>2</sup>	74 W [Xe]4f <sup>14</sup> 5d <sup>4</sup> 6s <sup>2</sup>	75 Re [Xe]4f <sup>14</sup> 5d <sup>5</sup> 6s <sup>2</sup>	76 Os [Xe]4f <sup>14</sup> 5d <sup>6</sup> 6s <sup>2</sup>	77 Ir [Xe]4f <sup>14</sup> 5d <sup>7</sup> 6s <sup>2</sup>	78 Pt [Xe]4f <sup>14</sup> 5d <sup>9</sup> 6s <sup>1</sup>	79 Au [Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>1</sup>	80 Hg [Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup>

In first transition series, we explain electronic configuration of Cr and Cu as a particular case.





In Chromium one electron from s-subshell has been used to half fill d-subshell.

In copper one electron from s-subshell has gone to d-subshell to fill it completely. It is due to fact that half filled  $d^5$  shell and full  $d^{10}$  shell are more stable.

### Typical and Non-Typical Transition Elements

(The elements of the groups IB, IVB, VB, VIB, VII B and VIII B are called typical transition elements)

(The elements of groups IIB and IIIB are called non-typical transition elements)

The elements of group IIB

(Zn, Cd, Hg) have no partially filled d-subshell

The elements of group IIIB (Sc, Y, La) have

only one electron in d-subshell. But in ionic state they have no d-electron. Therefore they do not show the properties of transition elements.

**Coinage metals:** - The coinage metals (Cu, Ag, Au) are transition metals because  $\text{Cu}^{+2}$  has a  $3d^9$ ,

$\text{Ag}^{+2}$  has a  $4d^9$  and  $\text{Au}^{+3}$  has a  $5d^8$  configuration

-dc- The d-block elements are called **outer transition metals**. The f-block elements (Lanthanides and Actinides) are called **inner transition metals**.



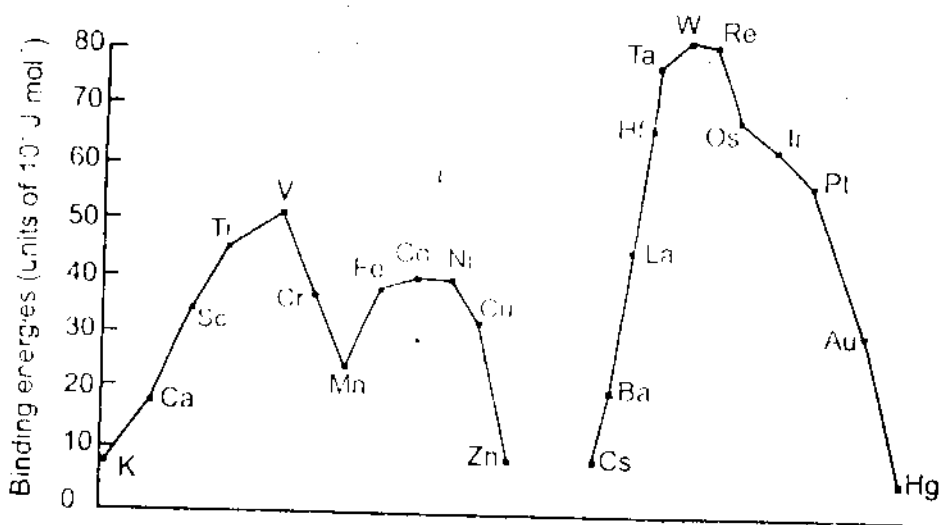
## Properties of transition elements

- (i) Transition elements are pure metals
- (ii) They are very hard with high melting and boiling points.
- (iii) They are good conductors of heat and electricity.
- (iv) They form alloys with one another
- (v) They show variable valency or oxidation state.
- (vi) Their compounds or ions are coloured in solid state or in solution form.

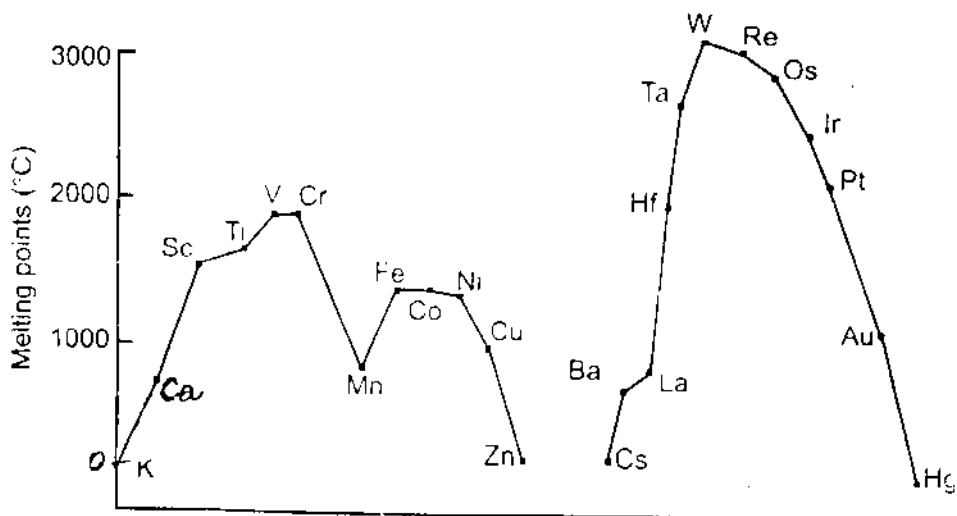
## General Characteristics of Transition Elements

(a) **Binding Energies:-** When we go from left to right of any transition series, then atomic binding becomes stronger upto group  $\text{VI B}$  and becomes weaker upto group  $\text{II B}$ . It is due to the increasing number of unpaired electrons up to group  $\text{VI B}$  and then number of unpaired electrons goes on decreasing to group  $\text{II B}$ . Therefore in the first transition series binding energy increases upto Vanadium and then decreases upto Zinc. Similarly in third series binding energy increases upto Tungsten when all the  $5d$ -electrons participate in bonding.

The Variation of binding energy in first and third transition series is shown below.



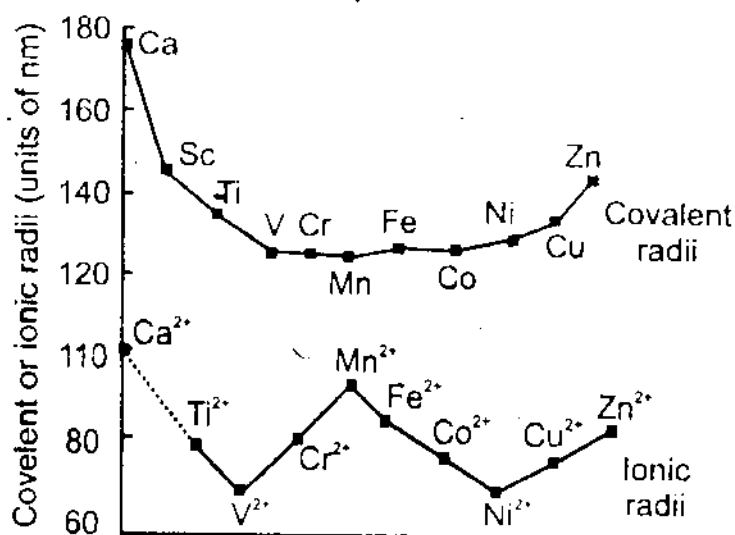
(b) Melting and boiling points. The melting and boiling points increase up to the middle of series and then decrease to a minimum level at the end of series. It is due to variation of interatomic



binding forces. It is shown in graphs.

(c) Covalent and Ionic Radii :-

In transition series the Covalent radii decrease at the start, then become constant and finally begin to increase at the end of series. The reason is that the filled 3d orbitals contract (shrink) into the electron core. Thus they shield the outer 4s electrons more effectively from the nucleus. It is shown in the graphs. In case of ionic radii the variation along the series is irregular. So we cannot explain periodic trend.

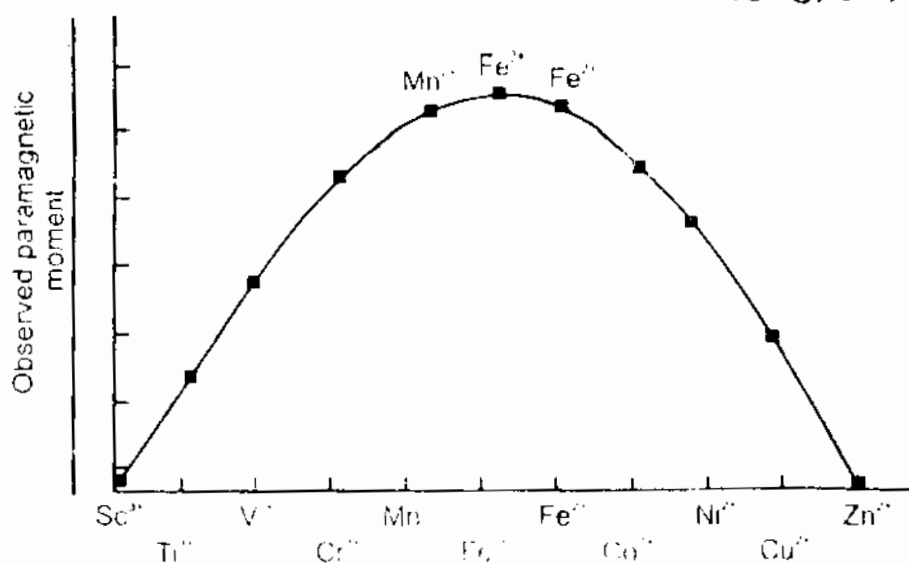


(d) Paramagnetism :- The substances which are weakly attracted by a strong magnetic field are called Paramagnetic substances.

e.g.  $Mn^{+2}$ ,  $Fe^{+3}$  etc. The Paramagnetic nature of a substance is due to presence of unpaired electrons in an atom, ion or molecule. The reason is that a spinning electron creates a magnetic field (magnetic moment). The substances which are weakly repelled by a strong magnetic field are called diamagnetic substances. e.g.  $Zn^{+2}$ ,  $Sc^{+3}$ . In first transition series  $Mn^{+2}$  and  $Fe^{+3}$  have maximum magnetic properties. The reason is that both  $Mn^{+2}$  and  $Fe^{+3}$  have five unpaired electrons each. The number of unpaired electrons decreases gradually to zero on both sides of series. The number of unpaired electrons in elements of first transition series are given in following table.

Ion	3d orbital electronic structure					No. of unpaired electrons
$Sc^{3+}$						0
$Ti^{3+}$	$\uparrow$					1
$V^{3+}$	$\uparrow$	$\uparrow$				2
$Cr^{3+}$	$\uparrow$	$\uparrow$	$\uparrow$			3
$Mn^{3+}$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$		4
$Mn^{2+}, Fe^{3+}$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	5
$Fe^{2+}$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	4
$Co^{2+}$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	3
$Ni^{2+}$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	$\uparrow$	2
$Cu^{2+}$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	1
$Zn^{2+}$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	0

The variation of Paramagnetic effect for the ions of first transition series is shown.

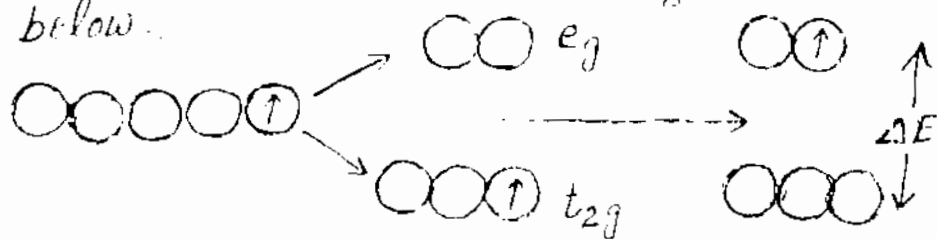


(e) **Oxidation State**:- Transition elements show variable valency or oxidation state. It is due to unpaired electrons in s and d orbitals which take part in bonding. The elements show +2 oxidation state when s-electrons involve in bonding. The elements show higher oxidation states when s and d-electrons involve in bonding. In first series of transition elements, the Mn shows a maximum number of oxidation states (+1 to +7). After Mn, the number of oxidation states decreases. The reason is that d-electrons are paired up and fewer (کمتر) unpaired.



electrons are available for bond formation

(f) **Colour:-** The ions of transition elements have specific colours. It is due to incomplete d-orbitals. During bond formation, the five d-orbitals split into two groups ( $t_{2g}$ ,  $e_g$  groups). The  $t_{2g}$  group contains three d-orbitals. It has lower energy. The  $e_g$  group contains two d-orbitals. It has high energy. When visible light falls, an electron from low energy d-orbital jumps to high energy d-orbital. It is called d-d transition. For example d-d transition for the ion  $[\text{Ti}(\text{H}_2\text{O})_6]^{+3}$  is shown below.



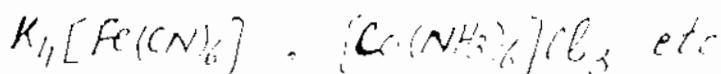
When visible light falls on solution of  $[\text{Ti}(\text{H}_2\text{O})_6]^{+3}$  ions, then yellow light is absorbed but blue and red lights are transmitted. It is the reason that aqueous solution of  $[\text{Ti}(\text{H}_2\text{O})_6]^{+3}$  ions has violet colour.

(g) **Interstitial Compounds:-** When small non-metallic atoms (H, B, C, N) enter into the interstices (holes) of transition

metals, the compounds formed are called **Interstitial Compounds**. They are also called interstitial alloys. e.g.  $VH_{0.56}$ ,  $TiH_{1.76}$ . They are nonstoichiometric. They are not true chemical compounds.

(h) **Alloy formation**:- Alloy formation is an important property of transition metals. The atoms of transition metals replace one another in the formation of lattice. The resultant products are called **substitutional alloys**. e.g. brass, bronze, alloy steels. In alloy steels iron atoms are substituted (replaced) by Chromium, Manganese, Nickel and Cobalt atoms.

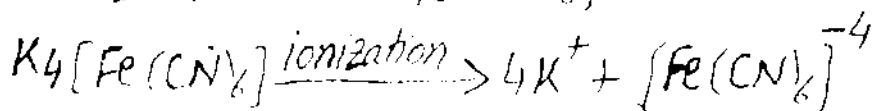
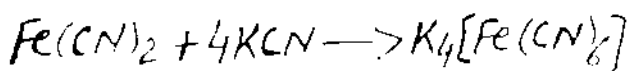
(i) **Complex formation**:- Complex formation is another important property of transition metals. Transition metals have incomplete d-orbitals and their ions have high charge density. It is the reason that transition metals form complexes. For example,



## **Complex Compounds**

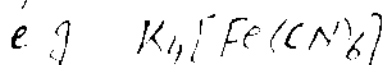
The compounds which contain complex molecules, or complex ions that can exist independently are called **Complex Compounds** or **Complexes**.



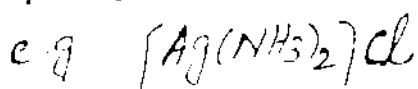


A Complex Compound may contain

(a) A Simple Cation and a Complex anion.



(b) A Complex Cation and a simple anion.



### Components of Complex Compounds.

(a) **Central metal ion**:- A metal atom or ion surrounded by a number of ligands is called Central metal atom or ion. For example

In  $\text{K}_4[\text{Fe}(\text{CN})_6]$ ,  $\text{Fe}^{+2}$  is central metal ion

In  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$ ,  $\text{Ag}^+$  is central metal ion.

(b) **Ligands**:- The atoms, ions or molecules which surround the central metal ion and donate electron pairs are called Ligands. They may be anions or neutral molecules. e.g.

In  $\text{K}_4[\text{Fe}(\text{CN})_6]$ , the  $\text{CN}^-$  ions are ligands

In  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$ , the  $\text{NH}_3$  molecules are ligands  
The ligands having one donor atom are called mono-dentate ligands. e.g.  $\text{CN}^-$ ,  $\text{NH}_3$ ,  $\text{NO}_2^-$

The ligands having two donor atoms are called

bidentate ligands. e.g. Oxalate ion  $\begin{matrix} \text{COO}^- \\ | \\ \text{COO}^- \end{matrix}$  is a bidentate ion.

### (C) Coordination number

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

In  $K_4[Fe(CN)_6]$ , the Coordination No. of  $Fe^{+2}$  is 6.

In  $[Ag(NH_3)_2]Cl$ , the Coordination No. of  $Ag^+$  is 2.

### (d) Coordination Sphere :-

The central metal atom or ion along with the ligands is called Coordination sphere. It is usually placed in square brackets. It may be anionic ( $3^-$ ), Cationic or neutral e.g.

In  $K_4[Fe(CN)_6]$ , Coordination sphere is  $[Fe(CN)_6]^{-4}$

In  $[Ag(NH_3)_2]Cl$ , Coordination sphere is  $[Ag(NH_3)_2]^+$

$[Ni(CO)_4]^0$  is a neutral Coordination sphere

### e) Charge on the Coordination Sphere :-

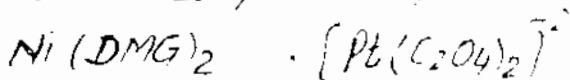
The algebraic sum of all the charges present on the central metal ion and the ligands is called Charge on the Coordination Sphere. e.g.

In  $K_4[Fe(CN)_6]$ , Charge on  $Fe = +2$

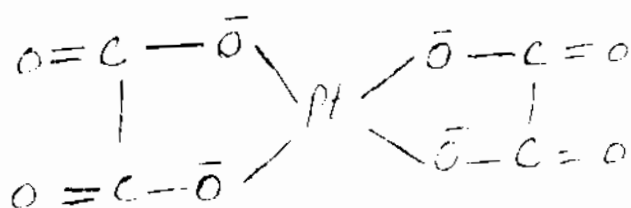
Total charge on six  $CN^-$  ions =  $-6$

Charge on Coordination Sphere =  $-6 + 2 = -4$

Chelates:- When a Polydentate ligand attaches (Coordinates  $\text{via } \delta^-$ ) with a metal ion, a Complex Compound having ring structure is formed. It is called a Chelate. The chelates are very stable Complex Compounds. For example,



The structure of  $[\text{Pt}(\text{C}_2\text{O}_4)_2]^{2-}$  is shown below.



dioxalato platinate(II) ion

The chelate formation is very important in volumetric analysis of some metals. e.g. DMG is used for estimation of Nickel.

## Nomenclature of Complex Compounds.

Inorganic Nomenclature Committee of IUPAC

has recommended a system for naming the Complex Compounds. This system has following rules

- (i) Cations are named before anions.
- (ii) In the coordination sphere, ligands are named first before the name of central metal ion. Moreover ligands are named in an alphabetical order (e.g.  $[\text{Co}(\text{en})_3]^{3+}$ ).



- (iii) The number of one kind of ligands is indicated by Prefix di, tri, tetra, Penta, hexa, hepta etc
- (iv) Anionic (negative) ligands name ends in suffix -o. e.g.  $\text{OH}^-$  as hydroxo,  $\text{Cl}^-$  as chloro,  $\text{CN}^-$  as cyano,  $\text{CO}_3^{2-}$  (carbonato)
- (v) Neutral ligands are named as molecules e.g.  $\text{H}_2\text{O}$  as aqua,  $\text{NH}_3$  as ammine.
- (vi) The name of anionic complex ends at the suffix -ate
- (vii) The oxidation number of metal ion is represented by a Roman number in small bracket (Parenthesis)

**Examples:-**

$\text{K}_4[\text{Fe}(\text{CN})_6]$  Potassium hexacyano ferrate(II)

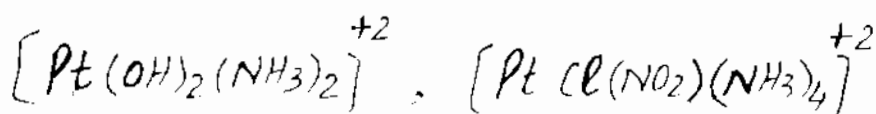
$\text{K}_2[\text{PtCl}_6]$  Potassium hexachloro platinate(IV)

$[\text{PtCl}(\text{NO}_2)(\text{NH}_3)_4]\text{SO}_4$  is  
Tetra ammine chloronitro Platinum(IV) Sulphate

$[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$  is Triammine trinitro Cobalt(III)

**Formula of Complex ion:-** In writing the formula of complex ion, first of all symbol of central metal atom is written, then symbols of ionic ligands and finally symbols

of neutral ligands are written in alphabetical order. The whole formula of Complex ion is enclosed in square brackets. e.g

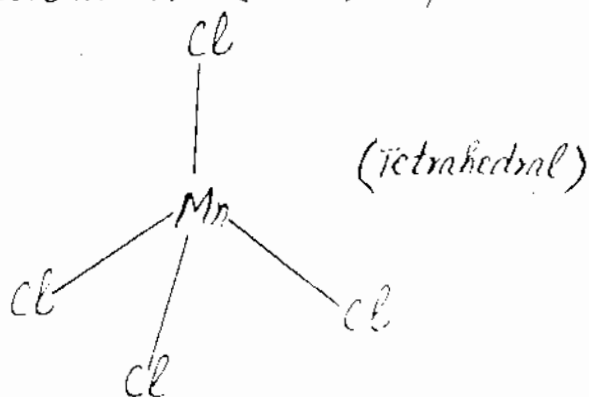


## Geometry of Complexes

Geometry (Shape) of Complexes depends upon  
(i) Coordination number of central metal ion  
(ii) Type of hybridization taking place in the valence shell of central metal atom.

There are four possible geometrical shapes in Complex Compounds.

(a) **Tetrahedral**:- When central metal atom shows  $sp^3$  hybridization, then complex has tetrahedral shape e.g  $Ni(CO)_4$ ,  $[MnCl_4]^{-2}$   
In this case Coordination number of the metal is 4.

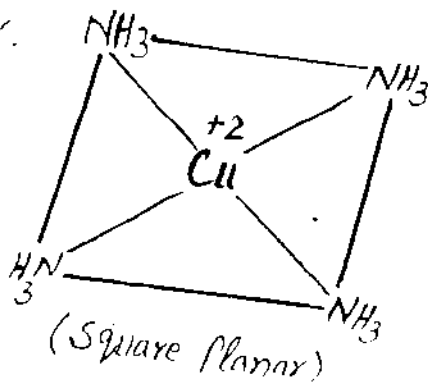


(b) **Square Planar**:- When central metal atom shows  $dsp^2$  hybridization, then the shape of

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complex is square planar.  
In this case Coordination  
number of metal is four.

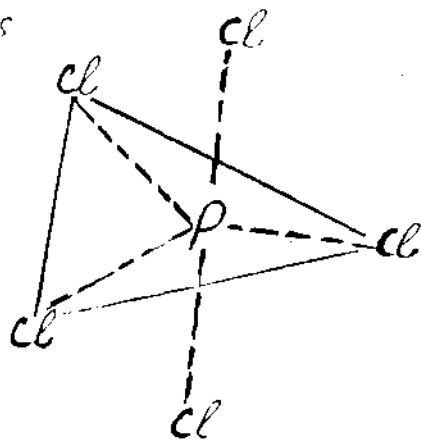
e.g.  $[\text{Ni}(\text{CN})_4]^{-2}$ ,  $[\text{Cu}(\text{NH}_3)_4]^{+2}$



(c) Trigonal bipyramidal:-

When central atom shows  
 $dsp^3$  hybridization, then  
shape of complex is  
trigonal bipyramidal.

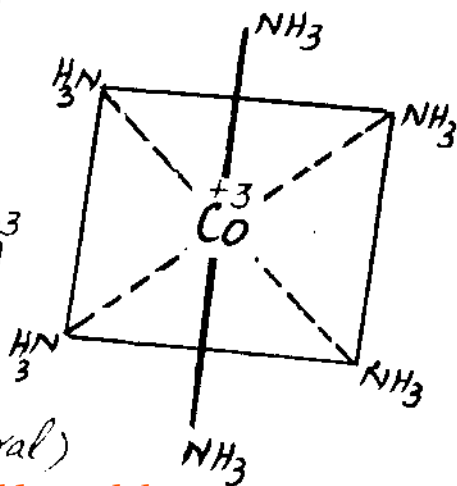
In this case Coordination  
number of central atom  
is five. e.g.  $\text{PCl}_5$ ,  $\text{SbCl}_5$



(d) Octahedral:-

When central atom shows  $d^2sp^3$  hybridization  
then shape of complex is  
octahedral. In this case  
coordination number of  
metal is six.

e.g.  $[\text{Co}(\text{NH}_3)_6]^{+3}$ ,  $[\text{Fe}(\text{CN})_6]^{-3}$



## الحديد (آئرن) IRON

Iron has been known since Prehistoric days. It was used in Egypt مصر in 1500 B.C. It was used by Chinese as early as 2500 B.C. In Subcontinent (برصغیر) it was used around 600 B.C.

### آئرن کی پیدافزا Ores of Iron

The important ores of iron are given below

Magnetite,  $Fe_3O_4$

Hematite,  $Fe_2O_3$

Limonite,  $Fe_2O_3 \cdot 3H_2O$

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### Commercial forms of Iron

Iron is available in three commercial forms. They differ in Carbon contents. مقدار

- (i) Pig iron or Cast iron 2.5 to 4.5% Carbon
- (ii) Wrought iron 0.12 to 0.25% Carbon
- (iii) Steel 0.25 to 2.5% Carbon

### Wrought Iron

Wrought iron is the purest form of iron. It contains the lowest Percentage of Carbon. 0.12 to 0.25% of Carbon. The or

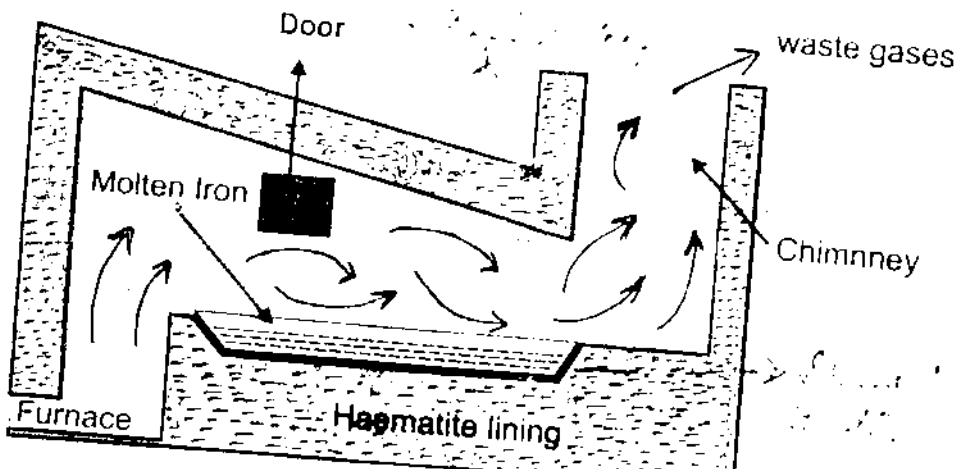
impurities are present upto 0.3%

$S = 0.2 \text{ to } 0.15\%$ ,  $Mn = \text{upto } 0.25\%$

$P = 0.04 \text{ to } 0.2\%$

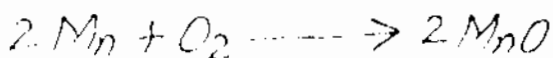
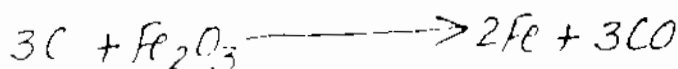
## Manufacture of Wrought Iron from Cast Iron

Wrought iron is prepared from Cast Iron by Puddling. The Puddling means melting and stirring the Cast iron to remove the impurities. It is done in a furnace (فرن) called **Puddling** furnace or **Reverberatory** furnace. The furnace has a hearth (تقران) which is lined with Haematite ( $Fe_2O_3$ ). The Cast iron is placed on the hearth. On one side of furnace Coal is burnt to give hot gases and long flames. These hot gases and long flames are deflected downward by the low sloping roof. (پائین کی طرف جھکا ہوا چھت) Thus Cast iron melts. This melted iron is

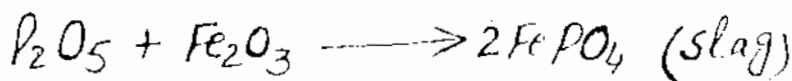
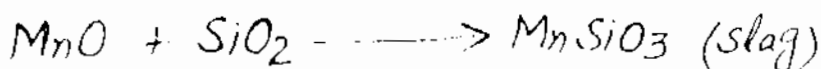




stirred or puddled with long iron rods (rables) through the doors. In this way melted iron comes in contact with haematite lining. So impurities like C, S, Si, Mn and P react with  $\text{Fe}_2\text{O}_3$  or  $\text{O}_2$  to form Oxides



The oxides of Carbon and Sulphur escape out and other oxides form slags.



After the removal of impurities, the melting point of iron rises and it becomes semi-solid mass. It is taken out in the form of balls or blooms on the ends of iron rods. These balls are removed from furnace and worked under a steam hammer to remove the slag. The product so obtained is called Wrought Iron.

## "Steel"

An alloy of iron containing 0.25—2.5% Carbon and traces of S, P, Si and Mn is called Steel. There are three classes of Steel.

(i) Mild steel:- It contains 0.1—0.2% C. It is soft. It is ductile and malleable. It can be forged. It is used to make nuts, bolts, bars, tubes and boiler plates.

(ii) Medium Carbon steel:-

It contains 0.2 — 0.7% Carbon. It is harder than mild steel. It can be forged. It is malleable and ductile. It is used to make rails, axels, Castings.

(iii) High Carbon Steel:-

It contains 0.7—1.5% Carbon. It is hard. It can be forged when contains less than 1% C. It can not be forged when contains more than 1% C. It is used to make hammers, tapes, die, machine tools, cutting tools, parts of engine and all parts of machinery.

**Forging of steel:-** When steel is hot, it can be shaped by pressing and hammering. It is called forging of steel. Steel containing less than 1% Carbon can be forged. The steel containing more than 1% C can not be forge.

## Steel From Cast and Wrought Iron :-

- (i) Steel can be Produced From Cast iron by removing some Carbon alongwith S, Si and P
- (ii) Steel can be Produced by adding the required amount of Carbon to wrought iron. Some special constituents can also be added to impart special Properties to the steel e.g. Ni, Co, Mn, Cr, W, V, Mo.

## Manufacture of Steel

Steel is manufactured by two processes

- (a) Open hearth Process
- (b) Bessemer Process

### (a) Open hearth Process

(Using Cast iron, wrought iron, or steel scrap)

It is modern method to produce steel

In this process, an open hearth furnace is used. The furnace has a low roof which deflects the hot gases and flames downward to melt the charge (Cast iron, steel scrap, lime).

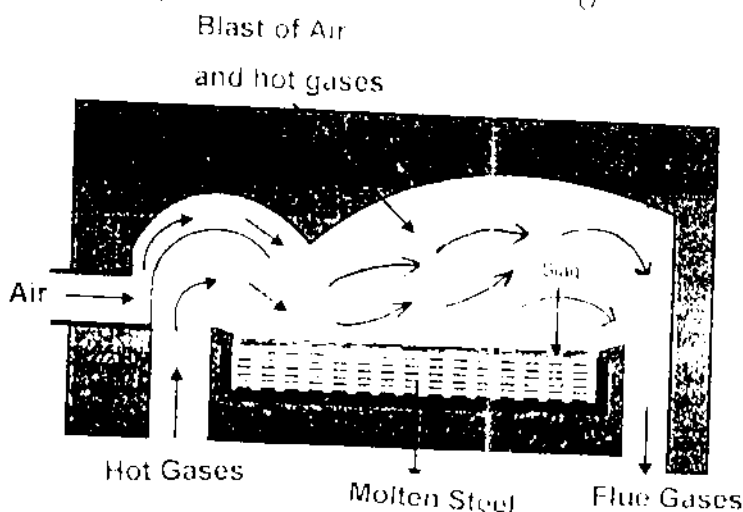
This furnace works on the regenerative principle of heat economy. The open hearth furnace is of two types

- (1) Furnace with acidic lining of  $\text{SiO}_2$  is used

When impurities are Si and Mn

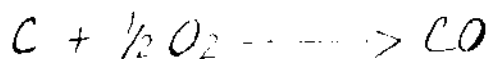
2) Furnace with basic lining of dolomite is used when impurities are S and P

An open hearth furnace is shown in figure

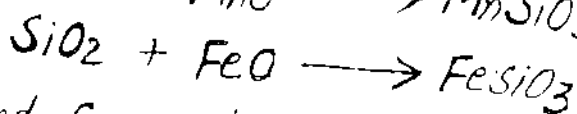
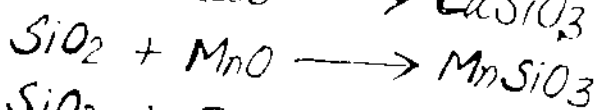
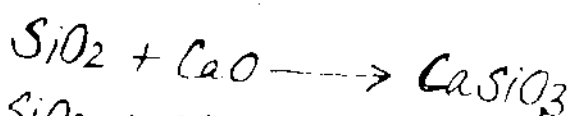


(open hearth furnace)

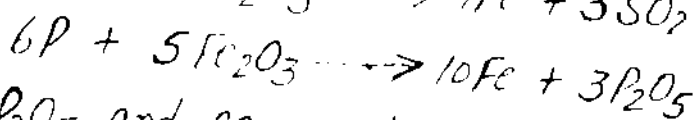
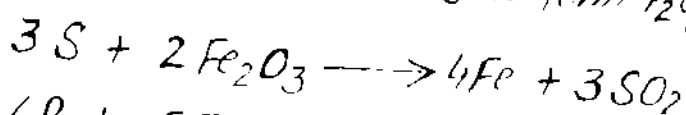
**Process:-** A mixture of cast iron - steel scrap and quick lime is charged into furnace. At about  $1600^{\circ}\text{C}$  Si, C, Mn, S and P burn and form oxides



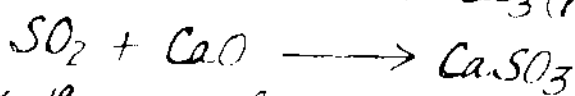
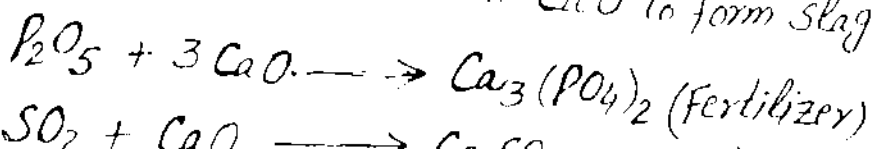
CO escapes in the flue gases. The  $\text{SiO}_2$  combines with  $\text{CaO}$ ,  $\text{MnO}$  and  $\text{FeO}$  to form silicates (slag). This slag floats on the surface of molten steel.



P and S react with  $\text{Fe}_2\text{O}_3$  to form  $\text{P}_2\text{O}_5$  and  $\text{SO}_2$



The  $\text{P}_2\text{O}_5$  and  $\text{SO}_2$  react with  $\text{CaO}$  to form slag.



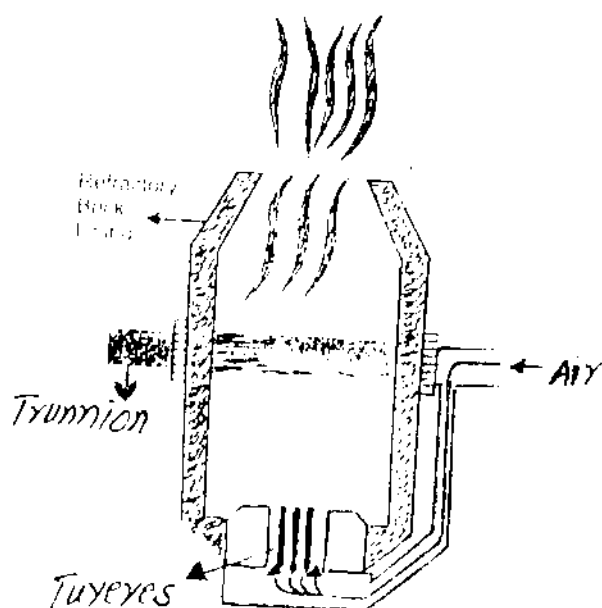
After the removal of impurities, the percentage of Carbon in steel is determined. When steel contains right percentage of Carbon, then some ferromanganese is also added. After the complete mixing the melted steel is run into moulds. This whole process completes in about 10 hours. In this process,  $\text{Ca}_3(\text{PO}_4)_2$  produced as a slag is sold as an important fertilizer.

**(b) Bessemer Process (using cast iron only)**

In this process, Bessemer's Converter is used as a furnace. It is pear shaped steel vessel. It is provided with a number of holes (tuyeres)

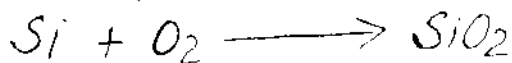
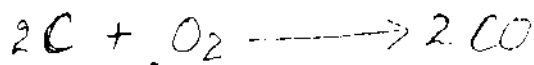


at the bottom to introduce air blast. The Converter is mounted on its central axis so that it can be tilted (like) in any position for charging, blowing and pouring. It is shown in figure.



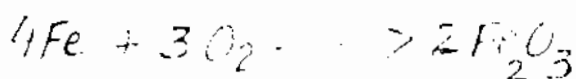
(Bessemer's Converter)

Molten Cast iron is fed into the Converter. The hot air blast is injected into the Converter through tuyeres. The Carbon, Silicon and Manganese are oxidized.



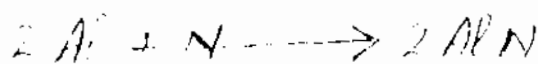
During oxidation reactions, large amount of

Heat is evolved. Due to this heat iron remains in molten state. The  $\text{SiO}_2$  and  $\text{MnO}$  form  $\text{MnSiO}_3$  as a slag. The  $\text{CO}$  produced in the Converter burns with blue flame. Following reactions also take place in the Converter:



The air blast is continued for 10-15 min. When all reactions are complete, then small amounts of ferromanganese ( $\text{Fe, Mn, C}$ ) and  $\text{Al}$  or ferro-silicon are also added.

The ferromanganese correct the percentage of carbon in steel and  $\text{Al}$  removes the entrapped gases ( $\text{N}_2, \text{O}_2, \text{CO}_2$ ) from steel.



At the end of the process molten steel is poured into moulds for casting.

## **CORROSION V. Imp**

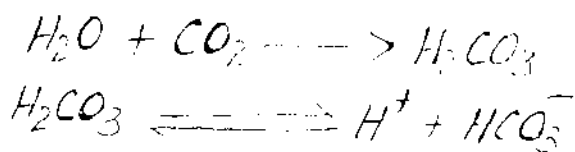
The chemical decay of metals due to the action of surrounding medium is called Corrosion. e.g. rusting of iron etc. The corrosion occurs due to the direct

Contact of metal with gases of atmosphere ( $O_2$ ,  $CO_2$ , moisture). The surface of metal is coated with oxides, sulphides, carbonates and their hydrates. Sometimes such compounds form a compact layer that further corrosion stops. During corrosion water plays important role. The reason is that water dissolves corrosion products and thus corrosion penetrates further into the metal. Moreover water promotes the corrosion by electrochemical process.

### **Electrochemical theory of Corrosion**

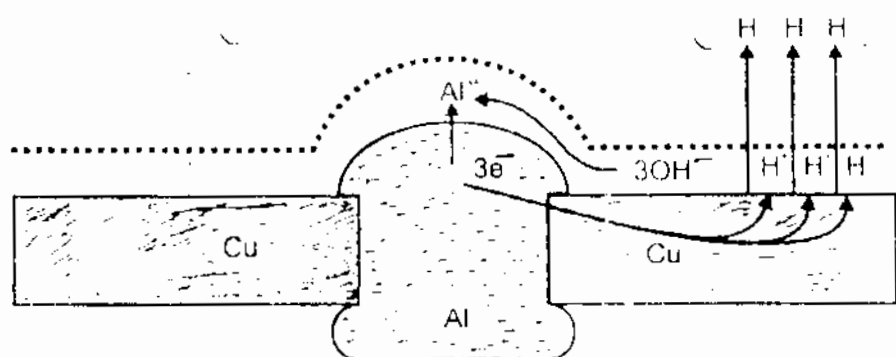
According to this theory corrosion is an electrochemical process. A small electrolytic (galvanic) cell is formed between two different metals joined. Thus flow of electron takes place which causes corrosion. For example when Cu comes in contact with Al in moisture, then Aluminum corrodes and Cu remains intact.

According to this theory moisture and  $CO_2$  are present on surface of metal. Following reactions occur on surface of two metals





Thus we say that Cu and Al are immersed in the solution containing  $H^+$ ,  $OH^-$  and  $HCO_3^-$  ions. Therefore a galvanic cell is formed between Al and Cu. It is shown in figure.



In this cell Al acts as an anode and Cu acts as Cathode. The Al loses electrons and changes to  $Al^{+3}$  ion. These electrons move from Al to Cu. The  $Al^{+3}$  ions react with  $OH^-$  ions to form  $Al(OH)_3$  which starts dissolving. On the Cathode  $H^+$  ions reduce to give Hydrogen. In this way Al is eaten away and corrodes but Cu remains intact.

From above discussion we say that when a more active metal and less active metal come in contact, a galvanic cell is established. In this process more active metal corrodes rapidly while less active metal remains intact.

## Prevention of Corrosion

Prevention of Corrosion is very essential, because large quantity of metals destroyed by Corrosion every year. It is observed that iron destroyed every year in corrosion is about  $\frac{1}{4}$ th of its annual Production. We prevent Corrosion by following methods.

- (i) Paint Coating
- (ii) Oil Coating
- (iii) Varnish Coating
- (iv) Enamel Coating
- (v) Alloying
- (vi) Metallic Coating.

Here we explain metallic Coating in detail.

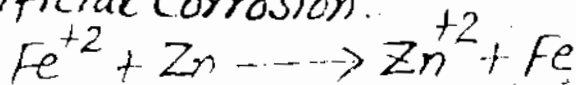
(a) **Tin Plating**:- The process in which a thin layer of tin is coated on metal (iron) sheet to stop corrosion is called tin plating. It is also called Coating iron with tin or Cathode Coating. It is done by dipping a clean sheet of iron in molten hot tin. e.g. Tin cans, oil containers, tooth paste tubes are coated by tin. Tin itself is very stable and protects other metals from corrosion. If the tin coating is damaged, then corrosion of iron



takes place more rapidly than the non-plated iron. It is explained as follows. When tin-plating damages, then galvanic cell is formed in which tin acts as Cathode and iron acts as anode. Thus electrons flow from iron to Tin. Therefore  $H^+$ ,  $OH^-$  and  $Fe^{+2}$  ions are produced in solution. Hence Fe is eaten away in the form of  $Fe(OH)_2$  rapidly.

## Galvanizing or Zinc Coating

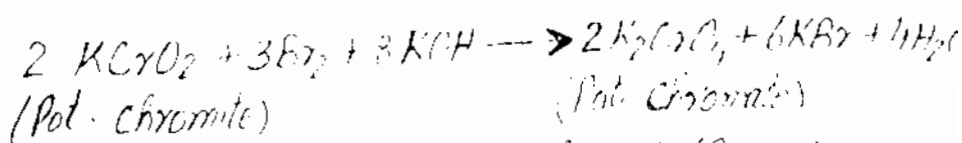
The Process in which a thin layer of Zinc is coated on iron sheet is called galvanizing. It is also called Zinc Coating or anode Coating. It is done by dipping a clean sheet of iron first in  $ZnCl_2$  bath and then in Zn-bath. When Zn-Coating is damaged, then galvanic cell is established between Zn and Fe. Here Fe acts as a Cathode and Zn acts as anode. The electrons flow from Zn to iron. Thus Zn is eaten (decay away) but iron remains unruined. It is called Sacrificial Corrosion.



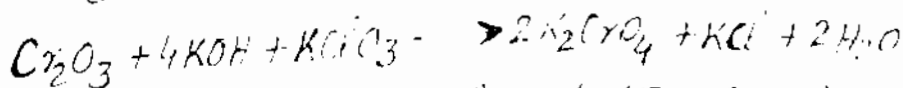
Hence Galvanizing protects iron from rust.

However Salts of these acids are very stable.

Preparation:- (i) Oxidation of Potassium Chromite ( $KCrO_2$ ) by  $Br_2$  in presence of an alkali gives Potassium Chromate.



(ii) Oxidation of Chromic anhydride ( $\text{Cr}_2\text{O}_3$ ) by  $\text{KClO}_3$  in presence of an alkali gives  $\text{K}_2\text{Cr}_2\text{O}_7$ .



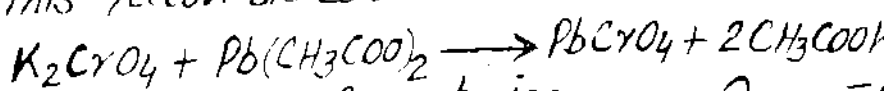
iii) When natural Ferrous Chromite ( $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ ) is strongly heated with  $\text{K}_2\text{CO}_3$  in presence of oxygen, then Potassium Chromate is produced.



**Properties:-** (i)  $K_2CrO_4$  is yellow crystalline solid

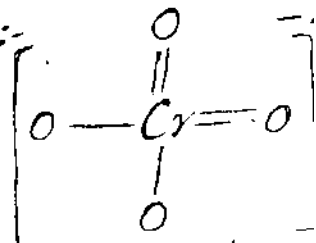
(ii) It is soluble in water

(iii)  $K_2CrO_4$  is used for preparation of Lead Chromate. The Lead Chromate  $PbCrO_4$  is used for preparation of yellow oil colour. This yellow oil colour is called Yellow Crow.



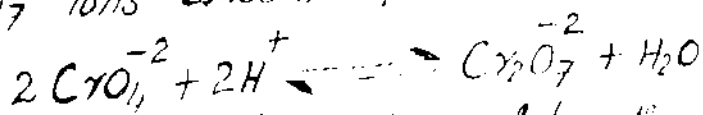
(v) Structure of Chromate ion:-

The structure of Chromate ion is shown in figure.



In this structure oxidation number of Chromium is +6 and oxidation number of Oxygen is -2.

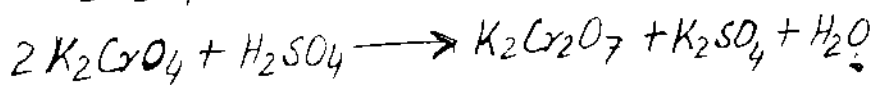
(vi) The properties of  $K_2CrO_4$  and  $K_2Cr_2O_7$  are similar because in aqueous solution  $CrO_4^{2-}$  and  $Cr_2O_7^{2-}$  ions exist in equilibrium.



When we add alkali in above solution then  $OH^-$  combine with  $H^+$  ions. So concentration of  $H^+$  ion decreases. Thus equilibrium will shift towards left and chromate ions will be formed. Similarly by adding acid to above equilibrium the equilibrium will shift towards right. The result is that dichromate ions will be formed.

## Potassium Dichromate ( $K_2Cr_2O_7$ )

Preparation:- (i) When  $K_2CrO_4$  reacts with  $H_2SO_4$ , then  $K_2Cr_2O_7$  is produced.



(ii) When Sodium dichromate reacts with  $KCl$ , then Potassium dichromate is produced.

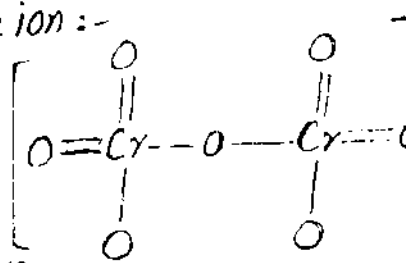


### Properties:-

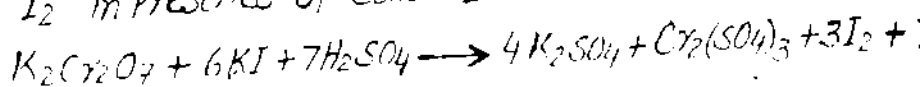
- (i)  $K_2Cr_2O_7$  is an orange red crystalline solid.
- (ii) Its melting point is  $396^\circ C$ .
- (iii) It is very soluble in water.
- (iv) It is very powerful oxidizing agent in an acidic solution. Here oxidation state of Chromium changes from +6 to +3.

(v) Structure of dichromate ion:-

In structure of dichromate ion, the oxidation number of  $Cr$  is +6 and that of oxygen is -2. It is shown in figure.

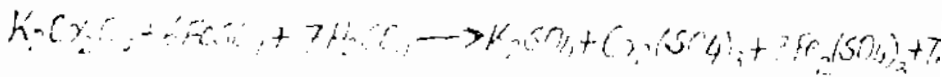


(vi) Oxidation Reaction:- (a)  $K_2Cr_2O_7$  oxidizes  $KI$ ,  $I_2$  in presence of conc  $H_2SO_4$ .



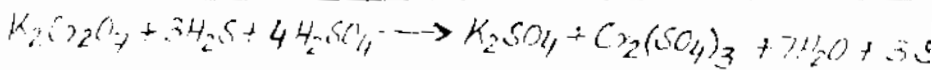
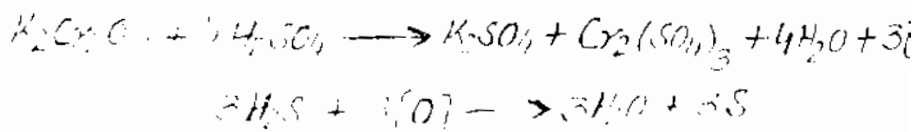
**(b) Oxidation of Ferrous Sulphate:-**

Potassium dichromate oxidizes Ferrous Sulphate into Ferric Sulphate in Presence of  $H_2SO_4$

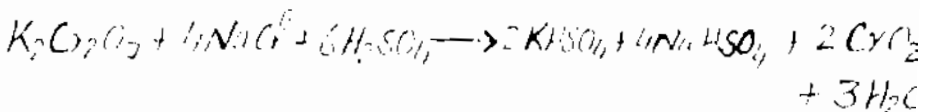


**(c) Oxidation of  $H_2S$ :-**

Potassium dichromate oxidizes  $H_2S$  into  $S$  in the Presence of Conc  $H_2SO_4$



**(d) Chromyl Chloride Test:-** It is a confirmatory test for Chloride radical. In this test solid  $K_2Cr_2O_7$  is heated with solid metal chloride in presence of Conc.  $H_2SO_4$ . The redish brown fumes of Chromyl Chloride are produced.



**USES of  $K_2Cr_2O_7$ :-**

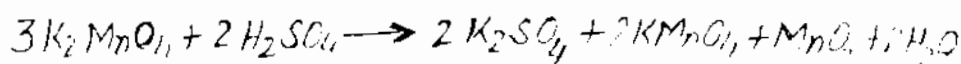
- (i)  $K_2Cr_2O_7$  is used as an oxidizing agent
- (ii) It is used in dyeing (رنگ)
- (iii) It is used in leather industries for Chrom tanning (رنگ چرم)
- (iv) It is used as an important reagent in our laboratory

## Potassium Permanganate ( $\text{KMnO}_4$ )

The Potassium salt of permanganic acid ( $\text{HMnO}_4$ ) is called Potassium Permanganate ( $\text{KMnO}_4$ ).

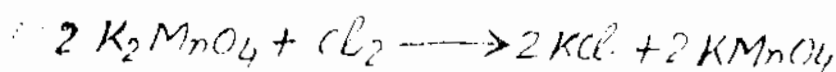
The permanganic acid is so unstable as it only exists in solution.

**Preparation:-** In laboratory  $\text{KMnO}_4$  is prepared by reaction of potassium manganate with  $\text{H}_2\text{O}_2$ .



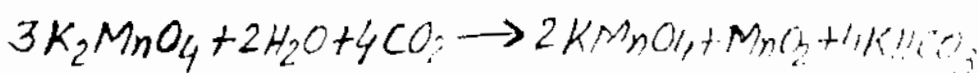
**Commercial Preparation:-** On large scale  $\text{KMnO}_4$  is prepared from  $\text{K}_2\text{MnO}_4$ .

(i) **Stadeler's Process:-** In this process  $\text{KMnO}_4$  is prepared by oxidation of  $\text{K}_2\text{MnO}_4$  with  $\text{Cl}_2$ .



In this reaction green colour of  $\text{K}_2\text{MnO}_4$  becomes purple due to formation of  $\text{KMnO}_4$ .

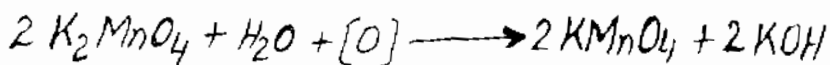
(ii) The oxidation of  $\text{K}_2\text{MnO}_4$  by  $\text{CO}_2$  also gives  $\text{KMnO}_4$ .



(iii) **By electrolytic Oxidation:-** The electrolytic oxidation of potassium manganate gives Potassium Permanganate. The electrolysis of aqueous solution of  $\text{K}_2\text{MnO}_4$  gives  $\text{H}_2$  at Cathode and  $\text{O}_2$  gas at anode. The oxygen oxidizes manganate ion  $\text{MnO}_4^{2-}$ .



to Permanganate ion ( $\text{MnO}_4^-$ )



The  $\text{KMnO}_4$  is obtained in form of Purple Coloured solution. It is filtered, Concentrated and allowed to crystallize. The crystals of  $\text{KMnO}_4$  are deep purple red rhombic prisms.

**Properties:-** (i)  $\text{KMnO}_4$  is deep purple crystalline solid. It has lustrous surface.

(ii) Its aqueous solution is deep pinky coloured.

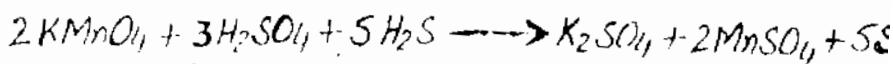
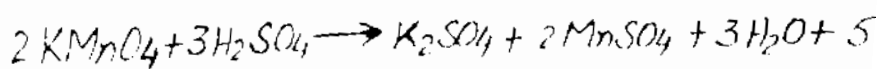
(iii) Its solubility  $\frac{\text{g}}{100 \text{ g}}$  in water at  $20^\circ\text{C}$  is only; and at  $6.3^\circ\text{C}$  its solubility is  $2.5\%$

(iv) It is a powerful oxidizing agent.

(v) Oxidation by  $\text{KMnO}_4$  is done in acidic medium

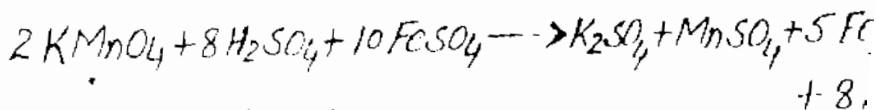
(vi) Oxidation of  $\text{H}_2\text{S}$ :-

$\text{KMnO}_4$  oxidises  $\text{H}_2\text{S}$  to Sulphur.



(vii) Oxidation of  $\text{FeSO}_4$ :-

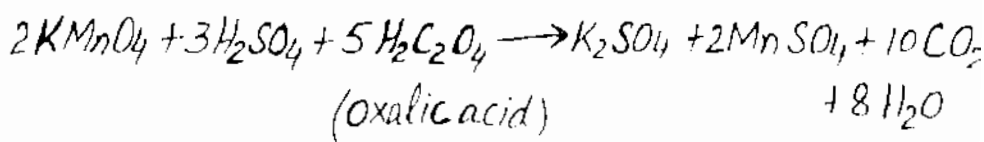
$\text{KMnO}_4$  oxidises  $\text{FeSO}_4$  into  $\text{Fe}_2(\text{SO}_4)_3$



In this reaction ferrous sulphate ( $\text{FeSO}_4$ ) is oxidized into ferric sulphate,  $\text{Fe}_2(\text{SO}_4)_3$ .

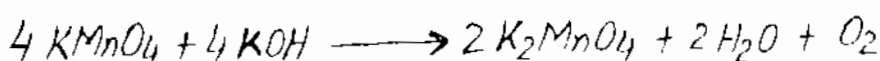
(viii) Oxidation of Oxalic acid:-

$\text{KMnO}_4$  oxidises oxalic acid into  $\text{CO}_2$  and  $\text{H}_2\text{O}$



(ix) Reaction with KOH

Reaction of  $\text{KMnO}_4$  with KOH gives  $\text{K}_2\text{MnO}_4$ .

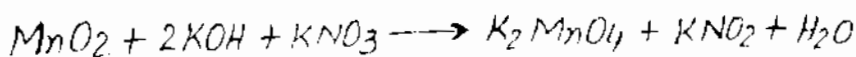
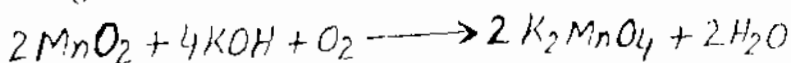


Uses of  $\text{KMnO}_4$ :-

- (i)  $\text{KMnO}_4$  is used as an oxidizing agent
- (ii) It is used as a disinfectant and a germicide
- (iii) It is used as a reagent in the laboratory.
- (iv) It is used for Preparation of many Compounds
- (v) It is used in bleaching and textile printing.

### Pyrolusite and Potassium Manganate

$\text{MnO}_2$  is called mineral Pyrolusite. Its Oxidation give Potassium Manganate. First of all  $\text{MnO}_2$  is finely Powdered. Then it is treated with KOH in Presence of Oxygen or Oxidizing agent ( $\text{KNO}_3$ ,  $\text{KClO}_3$ )



The  $\text{K}_2\text{MnO}_4$  is a green coloured fused Product. It is extracted with water. Then it is filtered and dark green crystals.

## EXERCISE

### Q1. Fill in the Blanks

- (i) The paramagnetic property is due to the presence of \_\_\_\_\_ electrons.
- (ii)  $MnO_2$  ion has \_\_\_\_\_ colour and  $Cr^{3+}$  has \_\_\_\_\_ colour.
- (iii) When potassium permanganate is treated with an acid \_\_\_\_\_ is produced.
- (iv) The d-block elements are located between \_\_\_\_\_ and \_\_\_\_\_ block elements.
- (v) Oxidation number of Fe in  $K_3[Fe(CN)_6]$  is \_\_\_\_\_ which in  $K_3[Fe(CN)_6]$  is \_\_\_\_\_.
- (vi) The presence of \_\_\_\_\_ in a metal promotes corrosion.
- (vii)  $Fe^{3+}$  ion in contact with Aluminium \_\_\_\_\_ gets corroded.
- (viii)  $d_{sp^2}$  hybridization has \_\_\_\_\_ shape.
- (ix) In naming the complexes, all the ligands are name in \_\_\_\_\_.
- (x) In an aqueous solution  $CrO_4^{2-}$  and  $Cr_2O_7^{2-}$  exist in \_\_\_\_\_.

### ANSWER

- |                         |                     |
|-------------------------|---------------------|
| (i) Unpaired            | (ii) Purple, Orange |
| (iii) Dichromate        | (iv) S & P          |
| (v) +2, +3              | (vi) Impurities     |
| (vii) Then Al           | (viii) Octahedral   |
| (ix) Alphabetical order | (x) Equilibrium     |

### Q2. Indicate True or False.

- (i) A substance which is attracted into a magnetic field is said to be diamagnetic.
- (ii) Compounds of the transition elements are mostly coloured.
- (iii)  $Fe^{3+}$  ions are blue when hydrated.
- (iv) An extreme case of paramagnetism is called diamagnetism.
- (v) Tin plating is used to protect iron sheets from corrosion.
- (vi) In Galvanizing, Zinc prevents corrosion of iron.
- (vii) Tin plated iron gets rusted more rapidly when the protective coating is damaged than un plated iron.

- (viii) The name of anionic ligands in a complex end in suffix 'O'.  
(ix) Pig iron contains great percentage of carbon than steel.  
(x) Complex compounds having  $dsp^2$  hybridization have tetrahedral geometry.

ANSWER

- |            |             |             |
|------------|-------------|-------------|
| (i) False  | (ii) True   | (iii) False |
| (iv) False | (v) True    | (vi) True   |
| (vii) True | (viii) True | (ix) True   |
| (x) False  |             |             |

**Q3. Multiple choice questions. Encircle the correct answer.**

- (i) Which of the following is a non-typical transition elements?
- |        |        |
|--------|--------|
| (a) Cr | (b) Mn |
| (c) Zn | (d) Co |
- (ii) Which of the following is a typical transition metal?
- |        |        |
|--------|--------|
| (a) Sc | (b) Y  |
| (c) Ra | (d) Co |
- (iii) f-Block elements are also called
- |                                      |
|--------------------------------------|
| (a) Non typical transition elements. |
| (b) Outer transition elements.       |
| (c) Normal transition elements       |
| (d) Inner transition elements.       |
- (iv) The strength of binding energy of transition elements depends upon.
- |                                   |
|-----------------------------------|
| (a) Number of electron pairs.     |
| (b) Number of unpaired electrons. |
| (c) Number of Neutrons.           |
| (d) Number of protons.            |
- (v) Group VIB of transition elements contains.
- |                 |                |
|-----------------|----------------|
| (a) Zn, Cd, Hg. | (b) Fe, Ru, Os |
| (c) Cr, Mo, W   | (d) Mn, Tc, Re |

- (vi) Which is the formula of tetraammine chloro-nitro-platinum (IV) sulphate?
- (a)  $[\text{Pt}(\text{NH}_3)_4(\text{NO}_2)\text{Cl}]\text{SO}_4$  (b)  $[\text{Pt}(\text{NO}_2)\text{Cl}(\text{NH}_3)_4]\text{SO}_4$   
 (c)  $[\text{PtCl}(\text{NO}_2)(\text{NH}_3)_4]\text{SO}_4$  (d)  $[\text{Pt}(\text{NH}_3)_4(\text{NO})^+\text{Cl}^+]\text{SO}_4$
- (vii) The percentage of carbon in different types of iron products is in the order of.
- (a) Cast iron > wrought iron > steel  
 (b) Wrought iron > steel > cast iron  
 (c) Cast iron > steel > wrought iron.  
 (d) Cast iron = Steel > wrought iron.
- (viii) The colour of transition metal complexes is due to
- (a) d-d-transitions metal complex is due to.  
 (b) Para magnetic nature of transition elements.  
 (c) Ionization  
 (d) Loss of s-electrons.
- (ix) Coordination number of Pt in  $[\text{PtCl}(\text{NO}_2)(\text{NH}_3)_4]^2$  is
- (a) -2 (b) 4  
 (c) 1 (d) 6
- (x) The total number of transition elements is .
- (a) 10 (b) 14  
 (c) 40 (d) More than 60

### ANSWER

- |       |   |        |   |       |   |
|-------|---|--------|---|-------|---|
| (i)   | c | (ii)   | d | (iii) | d |
| (iv)  | b | (v)    | c | (vi)  | c |
| (vii) | c | (viii) | a | (ix)  | b |
|       |   | (x)    | d |       |   |

Q4. How does the electronic configuration of valence shell affect the following properties of the transition elements.

- (a) Binding energy      (b) Paramagnetism  
(c) Melting Points      (d) Oxidation States

Ans. See on Page No. 201, 202, 203, 205,

Q5. Explain the following terms, giving examples.

- (a) Ligands      (b) Coordination sphere  
(c) Substitutional Alloy      (d) Central metal atom

Ans. See on Page No. 207, 208, 209

Q6. Describe the rules for naming the coordination complexes and give examples.

Ans. See on Page No. 210, 211

Q7. What is the difference between wrought iron and steel. Explain the Bessemer process for the manufacture of steel.

Ans. See on Page No. 214, 215, 221

Q8. Explain the following giving reasons.

- (a) Why damaged tin plated cause should be avoided?  
(b) Under what conditions aluminium corrodes?  
(c) How does the process of galvanizing protect iron from rusting?

Ans. (a) When iron sheet is coated by Tin, it does not corrode. But when tin coating is damaged, then a galvanic cell is formed between Tin and iron. Here Tin acts as cathode and iron acts as anode. Thus electrons flow from iron



to tin. Therefore  $H^+$ ,  $OH^-$  and  $Fe^{+3}$  ions are present in solution. Hence iron forms  $Fe(OH)_3$  and Corrodes. the result is that after damaged tin plating, the Corrosion of iron takes place more rapidly.

(b) When Al is brought in contact with Cu, it shows Corrosion. In this case a galvanic cell is formed between Al and Cu. Here Al acts as anode and Cu acts as Cathode. Thus Al loses electrons and forms  $Al^{+3}$  ions. the electrons move from Al to Cu. the  $Al^{+3}$  ions react with  $OH^-$  ions to form  $Al(OH)_3$  which starts to dissolve. In this way Al is eaten away and shows Corrosion but Cu remains intact

(C)

Q9. How chromate ions are converted into dichromate ions?

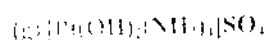
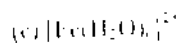
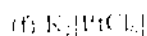
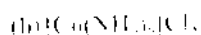
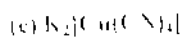
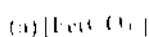
Ans. See on Page No 228

Q10. Describe the preparation of  $KMnO_4$  and  $K_2CrO_4$

Ans. See on Page No 227, 231

گلدسته  
[www.guldasta.pk](http://www.guldasta.pk)

Q. 11. Give systematic names to following complexes.

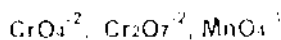


Ans. (a)  $[Fe(CO)_5]$  is Penta Carbonyl Iron (0)

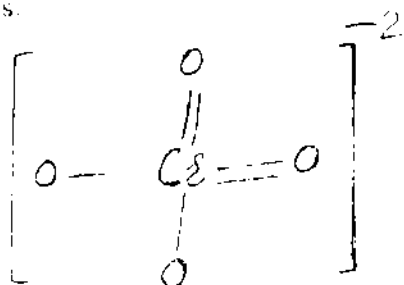
(b)  $[Co(NH_3)_6]Cl_3$  Hexa ammine Cobalt(III) Chloride

- (c)  $[\text{Fe}(\text{H}_2\text{O})_6]^{+2}$  Hexa aqua Iron(II) ion
- (d)  $\text{Na}_3[\text{CoF}_6]$  Sodium hexa fluoro Cobaltate(III)
- (e)  $\text{K}_2[\text{Cu}(\text{CN})_4]$  Potassium tetra cyano Cuprate(II)
- (f)  $\text{K}_2[\text{PtCl}_6]$  Potassium hexa Chloro Plutinate(IV)
- (g)  $[\text{Pt}(\text{OH})_2(\text{NH}_3)_4]\text{SO}_4$   
Tetra ammine dihydroxo Platinum(IV) Sulphate
- (h)  $[\text{Cr}(\text{OH})_3(\text{H}_2\text{O})_3]$  Triquo trihydroxo Chromium(III)

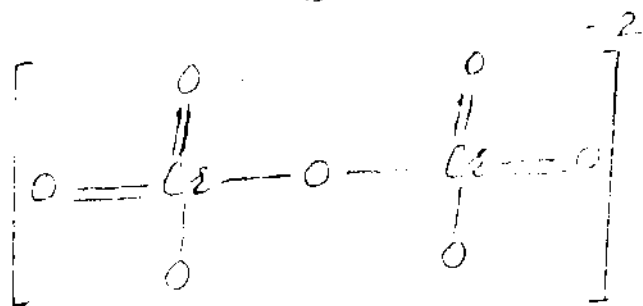
Q12. Draw Structures of following ions.



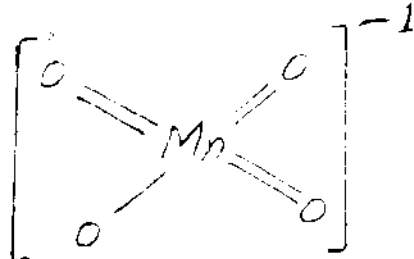
Ans. (i)  $\text{CrO}_4^{2-}$  ion  
Chromate ion



(ii)  $\text{Cr}_2\text{O}_7^{2-}$   
dichromate ion



(iii)  $\text{MnO}_4^-$   
Permanganate ion



گلدستہ ڈاٹ پی کے کی جانب سے خوش آمدید

## السلام علیکم ورحمۃ اللہ وبرکاتہ

### مختصر تعارف

کافی عرصہ سے خواہش تھی کہ ایک ایسی ویب سائٹ بناؤں جس پر طالب العلموں کیلئے کچھ تعلیمی مواد جمع کر سکوں۔ اللہ تعالیٰ نے توفیق دی اور میں نے ایک سال کی محنت کے بعد ایک سائٹ ”گلدستہ ڈاٹ پی کے“ کے نام سے بنائی جو کہ قرآن و حدیث، اصلاحی، دلچسپ، تاریخی قصے واقعات، اردو انگلش تحریریں، شاعری و اقوال زریں، F.Sc اور B.Sc کے مضامین کے آن لائن نوٹس، اسلامک، تفریحی، معلوماتی وال پیپرز، حمد و نعت، فرقہ واریت سے پاک اسلامی بیانات، پنجابی نظمیں و ترانے اور کمپیوٹر و انٹرنیٹ کی دنیا کے بارے میں ٹپس، آن لائن کمائی کرنے کے مستند طریقہ کار۔ کے ساتھ ساتھ اور بھی بہت سی چیزوں پر مشتمل ہے۔ اور انشاء اللہ میں مزید وقت کے ساتھ ساتھ اضافہ کرتا جاؤں گا۔ آپ کی قیمتی رائے کی ضرورت ہے۔ **عمران شفیق**

### اہم نوٹ

ذیل میں جو نوٹس مہیا کیے گئے ہیں وہ کئی گھنٹوں کی لگاتار محنت کے مرتب ہوئے ہیں۔ اور آپ کو بالکل مفت مہیا کر رہے کیے جا رہے ہیں۔ آپ سے ان کی قیمت صرف اتنی سی متوقع ہے کہ ایک بار **دروڈ ابراہیمی** اپنی زبان سے ادا کر دیں۔



# دُرود شریف

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

اللَّهُمَّ صَلِّ عَلَى مُحَمَّدٍ وَعَلَى آلِ مُحَمَّدٍ كَمَا

اے اللہ! رحمت بھیج حضرت محمد پر اور حضرت محمد کی آل پر

صَلَّيْتَ عَلَى إِبْرَاهِيمَ وَعَلَى آلِ إِبْرَاهِيمَ

جس طرح تو نے رحمت بھیجی حضرت ابراہیم پر اور حضرت ابراہیم کی آل پر

إِنَّكَ حَمِيدٌ مُّجِيدٌ

بے شک تو تعریف کیا گیا بزرگ ہے۔

اللَّهُمَّ بَارِكْ عَلَى مُحَمَّدٍ وَعَلَى آلِ مُحَمَّدٍ كَمَا

اے اللہ! برکت دے حضرت محمد کو اور حضرت محمد کی آل کو جس

بَارَكْتَ عَلَى إِبْرَاهِيمَ وَعَلَى آلِ إِبْرَاهِيمَ

طرح پر برکت دی تو نے حضرت ابراہیم کو اور حضرت ابراہیم کی آل کو

إِنَّكَ حَمِيدٌ مُّجِيدٌ

بے شک تو تعریف کیا گیا بزرگ ہے۔