Chapter
6

TRANSITION ELEMENTS

INTRODUCTION

"Elements of periodic table having partially filled d or f subshell in a common oxidation state (including zero oxidation state) are called transition elements."

Transition elements are located between s and p-block elements in periodic table. transition elements are divided into two types:

(1) d-Block Elements:

The elements having partially filled d-subshell are called d-block elements. Zinc, cadmium and mercury are also included in transition elements although they have no partially filled d-orbital. Properties of Zn, Cd and Hg are similar to transition elements and they are included in transition elements. Copper in zero state has no d-subshell partially filled but Cu^{2+} has configuration [Ar] $3s^2$, $3p^6$, $3d^9$ and transitional in character. Ag and Au also have no partially filled d-orbital in zero oxidation state. But Ag^{2+} has $4d^9$ and Au^{3+} has $5d^8$ electronic configuration. d-block elements are also called **transition elements**.

(2) f-Block Element:

"The elements have f-subshell partially filled in their common oxidation state are called f-block elements, f-block elements are also called inner transition elements."

f-block transition elements include two rows at the bottom of periodic table. First row is called **Lanthanides** while second row is called **Actinides**. All actinides are radioactive in nature.

ELECTRONIC CONFIGURATION OF d-BLOCK ELEMENTS

The electronic configuration of three series of d-block elements are given below:

Table – Electronic configurations of three series of d-block elements

3d-block element At. No. Electr. Config.	Sc 21 [Ar] $3d^1$ $4s^2$	Ti 22 [Ar] $3d^2$ $4s^2$	V 23 [Ar] $3d^3$ $4s^2$	Cr 24 [Ar] $3d^5$ $4s^1$	Mn 25 [Ar] $3d^5$ $4s^2$	Fe 26 [Ar] $3d^6$ $4s^2$	Co 27 [Ar] $3d^8$ $4s^2$	Ni 28 [Ar] $3d^8$ $4s^2$	Cu 29 [Ar] $3d^{10}$ $4s^1$	Zn 30 [Ar] $3d^{10}$ $4s^2$
4d-block element At. No. Electr. Config.	Y 39 [Kr] $4d^1$ s^1	Zr 40 [Kr] $4d^2$ $5s^2$	Nb 41 [Kr] $4d^4$ $5s^1$	Mo 42 [Kr] $4d^5$ $5s^1$	Te 43 [Kr] $4d^6$ $5s^2$	Ru 44 [Kr] $4d^7$ $5s^1$	Rh 45 [Kr] $4d^8$ $5s^1$	Pd 46 [Kr] $4d^{10}$ $5s^0$	Ag 47 [Kr] $4d^{10}$ $5s^1$	Cd 48 [Kr] $4d^{10}$ $5s^2$
5d-block elements At. No. Electr. Config.	La 57 [Xe] $5d^1$ $6s^2$	Hf 72 [Xe] $4f^{14}$ $5d^2$ $6s^2$	Ta 73 [Xe] $4f^{14}$ $5d^3$ $6s^2$	W 74 [Xe] $4f^{14}$ $5d^3$ $6s^2$	Re 75 [Xe] $4f^{14}$ $5d^5$ $6s^2$	Os 76 [Xe] $4f^{14}$ $5d^6$ $6s^2$	Ir 77 [Xe] $4f^{14}$ $5d^7$ $6s^2$	Pt 78 [Xe] $4f^{14}$ $5d^9$ $6s^1$	Au 79 [Xe] $4f^{14}$ $5d^1$ $6s^1$	Hg 80 [Xe] $4f^{14}$ $5d^{10}$ $6s^2$

The detailed electronic configuration of first series of d-block elements is given below. In this electronic configuration chromium and copper disobey the n + l rule. In case of chromium one electron from s-subshell have been used the half-fill d-subshell. Similarly in copper, one electron from s-subshell changes to the d-subshell to complete it. This are because half filled d-subshell (d^5) and full filled (d^{10}) d-subshell are most stable.

Table – Electronic configuration of first series of transition elements

Element	Symbol	At. Number	Electronic configuration
Scandium	Sc	21	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^1$
Titanium	Ti	22	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^2$
Vanadium	V	23	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^3$
Chromium	Cr	24	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^5$
Manganese	Mn	25	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^5$

Iron	Fe	26	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^6$
Cobalt	Co	27	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^7$
Nickel	Ni	28	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^8$
Copper	Cu	29	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^{10}$
Zinc	Zn	30	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}$

Table – Detail of d-subshell configuration (according to Hund rule)

Element	Atomic No.	Electronic configuration							
			4s	3d					
Sc	21	[Ar]	↿⇂	↿					
Ti	22	[Ar]	↿⇂	↿	↿				
V	23	[Ar]	↿⇂	↿	↿	↿			
Cr	24	[Ar]	↿	↿	↿	↿	↿	↿	
Mn	25	[Ar]	↿⇂	↿	↿	↿	↿	↿	
Fe	26	[Ar]	↿⇂	↿⇂	↿	↿	↿	↿	
Co	27	[Ar]	↿⇂	↿⇂	↿⇂	↿	↿	↿	
Ni	28	[Ar]	↿⇂	↿⇂	↿⇂	↿⇂	↿	↿	
Cu	29	[Ar]	↿	↿⇂	↿⇂	↿⇂	↿⇂	↿⇂	
Zn	30	[Ar]	↿⇂	↿⇂	↿⇂	↿⇂	↿⇂	↿⇂	

Non-typical Transition Elements:

"Elements of group IIB (Zn, Cd and Hg) and elements of group IIIB (Sc, Y and La) are called non-typical transition elements."

(1) Element of group IIB do not have partially filled d-subshell either as element or in any ionic state.

(2) Properties of these elements are some what different from transition elements e.g., they do not form coloured complexes.

(3) Elements of group IIIB (Sc, Y and Lu) are transition elements by definition because one electron is present in d-subshell.

(4) In compound, mostly occur in tri-positive ions and no d-electrons present in the d-sub-shell.

(5) They have variable valencies. They do not have properties of transition elements and behave like main group elements of sub-group A.

Typical Transition Elements:

"All the elements of d-block except the elements of group IIB and group IIIB are called typical transition elements."

We include coinage metals (Cu, Ag, Au) as transition elements because Cu^{2+} had $3d^9$ electronic configuration, Ag^{2+} has $4d^9$ and Au^{3+} has $5d^8$ configuration.

COMMON PROPERTIES OF TRANSITION ELEMENTS

Because of a similar electronic configuration, the d-block elements closely resemble one another in their physical and chemical properties. Some of the points of their resemblance are given below:

(1) They are all metals in true sense, some of which play important role in industry, Ti, Fe, Cr, Ni, Cu, Mo, W, Zr, Nb, Ta, Th etc.

(2) They are all hard and strong metals with high melting and boiling points. They are also good conductors of heat and electricity.

(3) They form alloys with one another and also with other elements.

(4) With few exceptions, they show variable valency or oxidation state.

(5) Their ions and compounds are coloured in solid state as well as in solution form, at least in one, if not all the oxidation states.

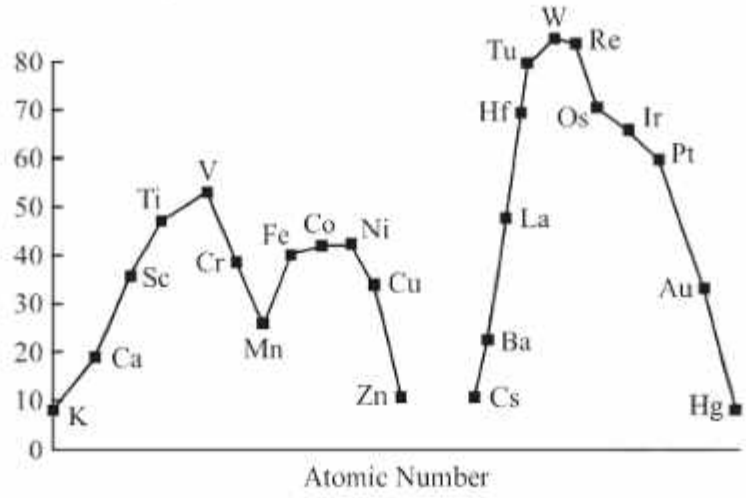
GENERAL CHARACTERISTICS OF TRANSITION ELEMENTS

(a) Binding Energies:

Transition metals show good mechanical properties. They are tough, malleable and ductile. The toughness of these metals indicate strong metallic binding. This is because, apart from s-electrons of the outer most shell, the electrons of underlying half-orbitals also participate in binding.

In moving from left to right in any transition series, the number of **unpaired electrons increases** up to group VB and VIB after that pairing takes place and number of unpaired electrons goes on decreasing until it becomes zero at group IIB.

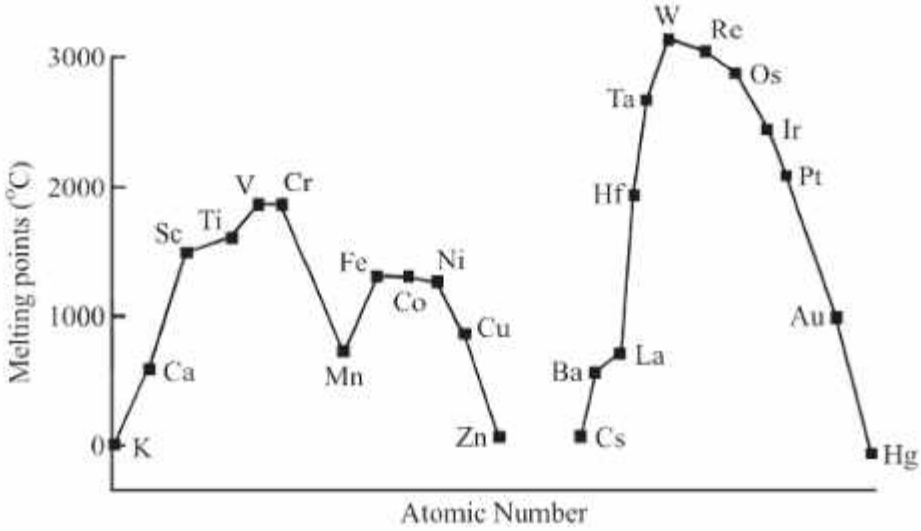
Therefore **binding is stronger up to group VIB and weakens progressively up to group IIB**. This trend of variation in binding energies is shown in figure. In the first transition series, the general increase in binding energy ends at vanadium. This is due to the change in metallic structure. Manganese has somewhat low binding energy. In the third transition series, the increase in binding energy ends at tungsten when all the 5d electrons contribute to binding.



Binding energies of the elements of the first and third transition series

(b) Melting Points and Boiling Points:

Transition metals have very high melting and boiling points due to strong binding forces present between their atoms. **Melting points increase up to the middle** of the series and then decrease to a minimum level at the end of the series.

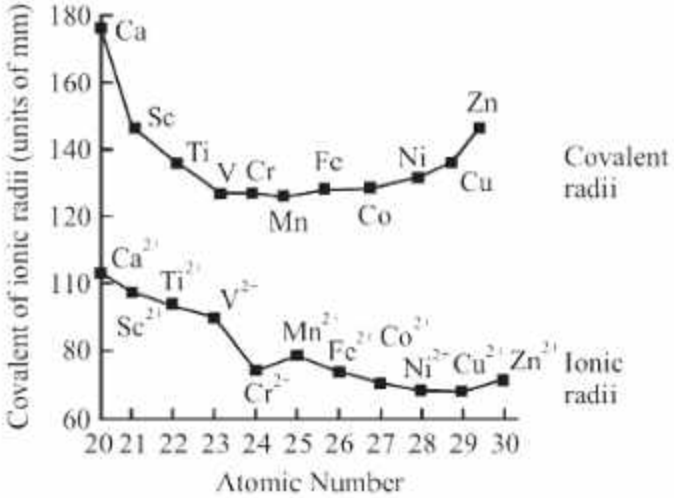


Melting points of the elements of the first and the third transition series

Melting points and boiling points of elements is directly related with the strength of inter-atomic forces. Greater is strength of bond, greater will be melting and boiling points.

(c) Covalent Radii and Ionic Radii:

The covalent radii decrease rapidly at the start of the series, then become almost constant, and finally begin to increase at the end of the series. The increase in covalent radii is possibly due to the fact that the filled 3d orbital have contracted into the electron core and so shield the outer 4s electrons more effectively from the nucleus.



Covalent radii and ionic radii (for M^{+2}) of first transition series elements

Changes in the ionic radii along the series are much less regular, so that periodic trends in the properties of these ions are difficult to rationalize.

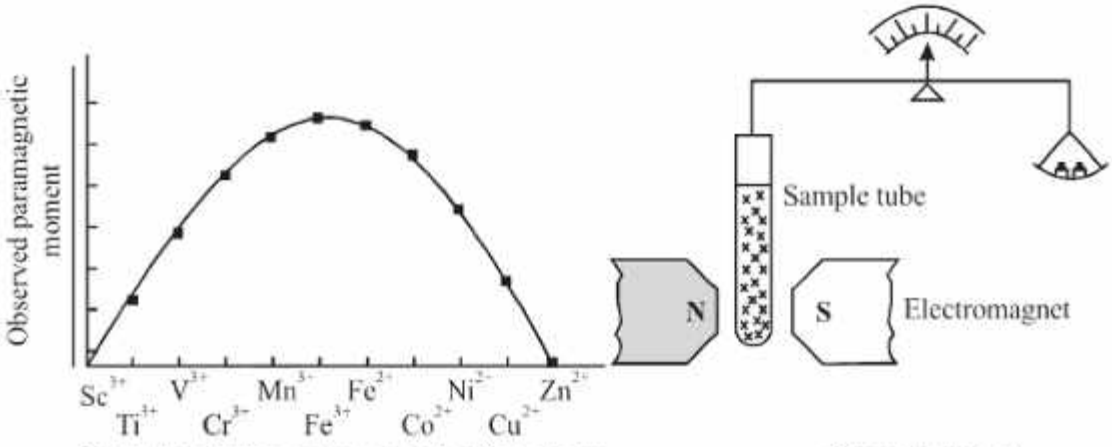
(d) Paramagnetism:

Substances which are weakly attracted by a strong magnetic field are called **paramagnetic substances**. Those substances which are weakly repelled by a strong magnetic field are called **diamagnetic substances**.

Paramagnetic behaviour is caused by the presence of **unpaired electrons** in an atom, molecule or ion because there is a magnetic moment associated with the spinning electron. It increases with increase in the number of unpaired electrons. When the electrons are paired in an orbital, then magnetic moments are cancelled out and the substances become diamagnetic.

The paramagnetic behaviour is the strongest for Fe^{3+} and Mn^{2+} and decreases on both sides of the first transition series. The reason is that both Mn^{+2} and Fe^{+3} have 5 unpaired electrons each. The number of unpaired electrons decreases gradually from left to right in transition and finally become zero. Paramagnetic trend in the first transition series and number of 5-unpaired d-subshell are shown below in the table. Graph indicates the paramagnetic moment of different ions.

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



Variation in the paramagnetic effect shown By the selected ions across the first transition series

(Gouy balance)

Guoy balance is used to determine the magnitude of paramagnetic nature and number of unpaired electrons of an atom. The sample in balance is weighed with electromagnetic field off and again with it on. The difference between the two weights is a measure of number of unpaired electrons in the sample.

(e) Oxidation State:

One of the most important property of transition elements is that they exhibit variable oxidation states. They show **variable valencies** because of the involvement of the unpaired d electrons in addition to s electrons in bond formation. All 3d series elements show an oxidation state of +2 in addition to higher oxidation states.

Table – Commonly occurring oxidation states of the 1st series of transition elements

			3d					4s	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]	$3d^5 4s^1$	↑	↑	↑	↑	↑	↑	2	3	4	5	6		
Mn	[Ar]	$3d^5 4s^2$	↑	↑	↑	↑	↑	↑↓	1 2	3	4	5	6	7	
Fe	[Ar]	$3d^6 4s^2$	↑↓	↑	↑	↑	↑	↑↓	1 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						

Period electrons enter the electron core

+2 oxidation state is shown when only the 2s electrons are involved in bonding. In the highest oxidation states of the first five elements, all the s and d electrons are used for bonding. Manganese has highest oxidation (+7) among the first transition series. After Mn, the number of oxidation states decreases as the d sub-shell fill up and fewer unpaired electrons are available for bond formation as shown in table.

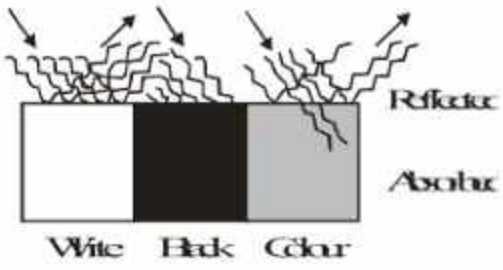
(f) Colour:

"Colour in compounds is produced due to absorption and emission of radiation in the visible region of spectrum."

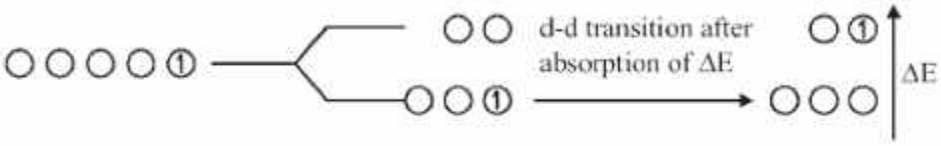
Compounds and ions of d-block elements are mostly coloured. When white light falls on a substance, if it is totally absorbed, it appears black, if it is totally reflected, it appears white. However, if certain wavelengths are absorbed and other are reflected, the substances appears coloured. In d-block elements, absorption of light is due to the presence of unpaired d-electrons in the ion. When d-orbital are involved in bonding, they

split up into two energy levels, one set has higher energy than the other. The electrons residing in the low energy d-orbital absorb a part of visible light and jump to high energy d-orbital. The process is called d-d transition.

The energy difference ΔE between ground state and excited state depends upon the ligand in coordination sphere and structure of ions. Thus every ion absorbs a different wavelength and reflect the remaining set of wavelengths which gives colours to the ions.



Schematic representation of light



Absorption of yellow light by $[Ti(H_2O)_6]^{3+}$ ion

In $[Ti(H_2O)_6]^{3+}$ ion, yellow light is absorbed while most of the blue and red lights are reflected. Therefore, the solution of $[Ti(H_2O)_6]^{3+}$ ions look violet in colour.

(g) Interstitial Compounds:

The empty spaces between atoms of transition metals in their crystal lattices are called **interstices** and small atoms, such as hydrogen, boron, carbon, nitrogen enter into these interstices to form non-stoichiometric compounds called **interstitial compounds**. These compounds have no definite composition and do not correspond to the normal oxidation state of metal. Interstitial compounds, some times also are called interstitial alloys.

(h) Alloy Formation:

"A solid solution of metals is called alloy". Due to the similarly in their sizes, some transition metal atoms are able to replace one another in the metallic lattice and form **substitutional alloys** among themselves. Alloy steels are an important example of this type of material in which iron atoms are substituted by chromium, manganese and nickel atoms, etc., to give the steel more useful properties. Other examples are brass, bronze, coinage alloys etc.

COMPLEX COMPOUND

"A substance formed when one or more anions or neutral molecules are bonded with a metal atom or ion is called complex."

In complex, coordinates covalent bond is present so it is called coordination compounds. The metal atom or cation which accept an electron pair is called Lewis acid and the anion or molecule which donate a pair of electrons is called Lewis base or **ligand**.

For example, when the aqueous solutions $Fe(CN)_2$ and KCN are mixed together and evaporated, a new compound is obtained which in aqueous solution does not ionize as Fe^{2+} and CN^- ions but ionizes as K^+ ion and $[Fe(CN)_6]^{4-}$ ion (Ferrocyanide ion). On this basis it has been given a formula $K_4[Fe(CN)_6]$.

$$Fe(CN)_2 + 4KCN \rightarrow K_4[Fe(CN)_6] \xrightarrow{\text{Ionization}} 4K^+ + [Fe(CN)_6]^{4-}$$

Here $[Fe(CN)_6]^{4-}$ is called a complex ion.

Such compounds containing the complex molecules or complex ions and capable of independent existence are called coordination compounds or complexes.

In $K_4[Fe(CN)_6]$ complex CN^- is ligand or Lewis base and Fe^{+2} ion is Lewis acid.

There are three types of complexes:

(1) A complex containing a simple cation and complex anion e.g., $K_4[Fe(CN)_6]$.

(2) A complex cation and simple anion, e.g., $[Cu(NH_3)_4]SO_4$.

(3) A neutral complex, e.g., $[Ni(CO)_4]$.

DIFFERENT COMPONENTS OF COMPLEXES

To understand the complexes, it is necessary to understand components of complexes.

(a) Central Metal Atom:

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

$K_4[Fe(CN)_6]$, $[Ag(NH_3)_2]Cl$

In above examples, Fe and Ag are central atoms or ions.

(b) Ligand:

"The ions or neutral molecule which donate electron pairs to central metal atom or ion is called ligand," e.g., In $K_4[Fe(CN_6)]$, CN^- is ligand, and in $[Ag(NH_3)_2]$ Cl, NH_3 is also a ligand. On the number of electron pairs which they donate, ligands are divided into following types.

Neutral ligands = NH_3, H_2O, CO

Monodentate Ligands:

"Ligands which donate one pair of electron to central metal atom or ion are called monodentate ligands." e.g.,

Cl^- (Chloro), Br^- (Bromo), I^- (Iodo), CN^- (Cyano) F^- (Fluoro), OH^- (Hydroxo), NO_2^- (Nitro), NO (Nitrosyl), H_2O (Aqua), NH_3 (Ammine).

Bidendate Ligands:

Ligands which donate two pairs of electrons to central metal atom or ion are called bidentate ligands. e.g.,

Symbol	Name	Formula
en	Ethlenediamine	$H_2N - CH_2 - CH_2 - NH_2$
Ox	Oxalato	$\begin{matrix} COO^- \\ \vert \\ COO^- \end{matrix}$

Note:

(1) If a ligand donate more than two pairs of electrons to central atom or ion is called polydentate ligand. e.g., EDTA (Ethylene Diamine Tetra Acetate).



(2) The name of negative ligand ends with –O. e.g., Chloro, Bromo, Sulphato etc.

(c) Coordination

"The number of electron pairs provided by the ligands to the central metal atom or ion is called coordination number." For example:

In $[Ag(NH_3)_2]Cl$ coordination number of silver is 2

In $[Cu(NH_3)_4]SO_4$ coordination number of cooper is 4

In $K_4[Fe(CN)_6]$ coordination number of iron is 6.

In $K_3[Fe(CN)_6]$ coordination number of iron is 6.

(d) Coordination Sphere:

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

$K_4[Fe(CN)_6]$, $[Cu(NH_3)_4]SO_4$, $[Ni(CO)_4]$

In the above examples, $[Fe(CN)_6]^{4-}$, $[Cu(NH_3)_4]^{2+}$ and $[Ni(CO)_4]^0$ are anionic, cationic and neutral coordination spheres respectively.

(e) 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.

$[Fe(CN)_6]^{4-}$

Charge on ion = +2

Total charge on six CN^- ions = –6

Charge on the coordination sphere = –6 + 2 = –4

NOMENCLATURE

Nomenclature of complex is given according to international union of pure and applied chemistry (IUPAC) rules. The rules for naming the complexes are given below:

(1) Name of positive ion is written before the name of negative ion like salt. e.g., NaCl, Sodium chloride.

$K_2[PtCl_4]$ potassium hexachloroplatinate (iv).

(2) The name of the ligand is written before the name of the metal which it is coordinated.

(3) The prefixes mono, di, tri, tetra, penta, hexa and so on are used indicate the number of ligands. Greek ;refixes bis, tris or tetrakis used with bidentate or polydentate ligands.

(4) The names of negative ligands end with O, as Chloro (Cl) Fluoro (F^-) Oxo (O^{2-}) hydroxo (OH^-) etc.

(5) Name of the neutral ligands remain unchanged, e.g., Aqua (H_2O), Carbonyl (CO), Ammine (NH_3) etc.

(6) If one type of ligands are present in a complex, they are named in alphabetic order. In case of different ligands, the order is anionic ligand, then neutral followed by cationic ligand.

(7) The oxidation number of metal atom is indicated by Roman numerals in parenthesis ( ) after the name of the metal.

(8) The suffix –ate comes after the name of the metal if metal is present in negative sphere. If metal is present in positive sphere its name will remain unchanged.

Metal	Name in +ive sphere	Name is –ive sphere
Cobalt	Cobalt	Coba tate
Chromium	Chromium	Chromate
Silver	Silver	Argentate
Iron	Iron	Ferrate
Nickel	Nickel	Nickelate
Platinum	Platinum	Platinate
Copper	Copper	Cuprate
Manganese	Manganese	Manganate

Examples:

(1) $[Ag(NH_3)_2]Cl$

Diamminesilver (I) chloride

(2) $[Cu(NH_3)_4]SO_4$

Tetraamminecopper (II) sulphate

(3) $[Co(NH_3)_6]^{3+}$

Hexaamminecobalt (III) ion

(4) $K_4[Fe(CN)_6]$

Potassium hexacyanoferrate (II)

(5) $K_3[Fe(CN)_6]$

Potassium hexacyanoferrate (III)

(7) $[Pt(NH_3)_4ClNO_2]SO_4$

Tetraammine chloro nitratoplatinum (IV) sulphate

(8) $[Fe(OH)_5]^{-3}$

Pentahydroxoferrate (II) ion

(9) $Ni(CO)_4$

Tetracarbonyl nickel (O)

(10) $[Co(NH_3)_4Cl_2]^{1+}$

Tetraamminedichloro cobalt (III) ion

(11) $[PtCl(NO_2)(NH_3)_4]SO_4$

Tetraamminechloronitroplatinum (IV) sulphate

(12) $[Co(NO_2)_3(NH_3)_3]$

Triamminetrinitrocobalt (III)

CHELATES

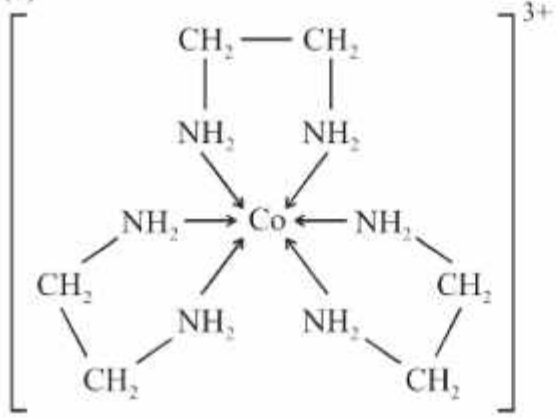
"The complex in which two or more different atoms of a polydentate ligand are coordinated with central metal atom or ion and form a ring is called chelate and this process is called chelation."

For example, when two oxalato ligands $C_2O_4^{2-}$, (bidentate ligand) get coordinated with Pt^{2+} ion, a chelate is formed. Each oxalato ligand forms a five members ring with the metal ion.

$[Pt(C_2O_4)_2]^{2-}$

Dioxalato platinate (II)

(b)



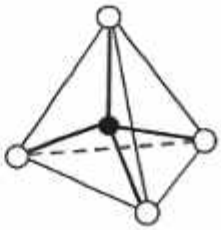
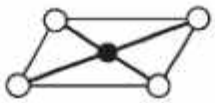
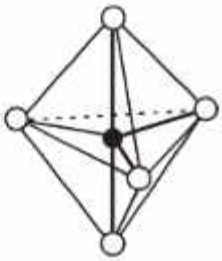
Example of chelationn: the complex ion $[Co(en)_3]^{3+}$

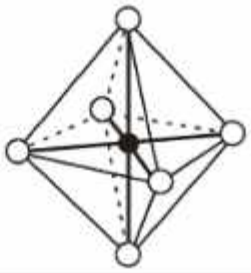


Dioxalato platinate (II) ion

GEOMETRY OF THE COMPLEXES

Geometry of a complex depends upon the type of hybridization taking place in the valence shell of central metal atom or ion.

Coordination number	Hybridization of metal	Shape	Diagram	Example
2	sp	Linear		$[Ag(NH_3)_2]Cl$
4	sp^3	Tetrahedral		$[MnCl_4]^{2-}$ $[Zn(NH_3)_4]^{3-}$
4	sp^2d	Square planar		$[Cu(NH_3)_4]^{2+}$ $[Ni(CN)_4]^{2-}$
5	sp^3d	Trigonal bipyramidal		$[Mn(CO)_4NO]$ $[Fe(CO)_5]$

6	sp^3d^2	Octahedral		$[Co(NH_3)_6]$ $[CoF_6]^{3-}$ $[Fe(CN)_6]^{4-}$ $[Fe(CN)_6]^{3-}$

IRON

Iron has been known since prehistoric days. It was used in Egypt in 1500 B.C. It is known that the Chinese also used iron as early as 2500 B.C. In the sub-continent iron was produced around 600 B.C.

Ores of Iron:

Magnetite	Fe_3O_4
Haematite	Fe_2O_3
Limonite	$Fe_2O_3.3H_2O$

Commercial Forms of Iron:

Iron is available commercially in the following three forms. They differ in carbon contents as follow:

(a)	Pig iron or cast iron	2.5 to 4.5% carbon
(b)	Steel	0.25 to 2.5% carbon
(c)	Wrought iron	0.12 to 0.25% carbon

WROUGHT IRON

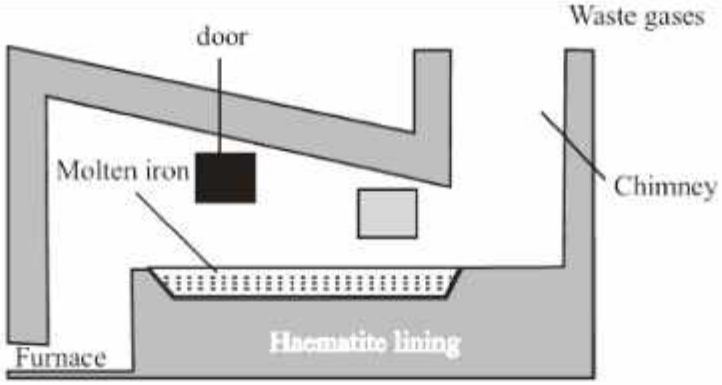
Composition:

It is the purest form of commercial iron and contains the lowest percentage of carbon and 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 BY PUDDLING

In this process cast iron is heated in a special type of **reverberatory furnace** called puddling furnance. This furnace has a low roof to deflect the hot gases and flames downwards and to melt cast iron. The hearth of the furnace is lined with haematite (Fe_2O_3). The cast iron is placed on the hearth, melted by hot gases and stirred or puddled with long iron rods called rabbles through the doors to bring it in thorough contact with the lining of the hearth, i.e., Fe_2O_3.



Puddling furnace for the manufacture of wrought iron

The haematite (Fe_2O_3) lining supplies oxygen, necessary for the oxidation of carbon, sulphur, silicon, manganese and phosphorus present in the cast iron. Oxides of carbon and sulphur, being volatile escape out at high temperature.

$$3C + Fe_2O_3 \longrightarrow 2Fe + 3CO$$

$$3S + 2Fe_2O_3 \longrightarrow 4Fe + 3SO_2$$

While those of manganese, silicon and phosphorus form slag. Thus

$$3Si + 2Fe_2O_3 \longrightarrow 4Fe + 3SiO_2$$

$$2Mn + SiO_2 \longrightarrow MnSiO_3$$

(Slag)

$$4P + 5O_2 \longrightarrow 2P_2O_3$$

$$Fe_2O_3 + P_2O_5 \longrightarrow 2FePO_4$$

(Slag)

With the removal of impurities, the melting point of the metal rises and it becomes a semi-solid mass. At this stag, it is taken out in the form of balls or blooms on the ends of rabbles. While still hot, these balls are subjected to hammering to squeeze out as much of slag as possible. The product so obtained is known as **wrought iron**.

STEEL

Steel is an alloy of iron containing 0.25 to 2.5% of carbon and traces of S, P, Si and Mn.

CLASSIFICATION OF STEEL

Steel is classified on the basis of percentage of carbon, present in it.

(1) Mild Steel (0.1 – 0.2% C):

It is fairly soft, malleable and ductile, can be forged (shaped by hammering and pressing while hot). It is used in making tubes, nuts, bolts, bars are boiler plates.

(2) Medium Carbon Steel (0.2 – 0.7% C):

It is harder than mild steel. It is also malleable and ductile. It is used in making rails, axels, castings.

(3) High Carbon Steel (0.7 – 1.5% C):

It is hard and can be forged when containing less than 1.0% carbon. Steel containing more than 1.0% carbon cannot be forged. It is used to make hammers, taps, dies, cutting tools, machine tools, hard steel parts of machinery and all sorts of engines.

Steel is intermediate in carbon contents between cast iron and wrought iron.

PRODUCTION OF STEEL FROM WROUGHT IRON OR CAST IRON

(i) Steel can be produced from cast iron by removing some carbon along with sulphur, phosphorus and silicon.

(ii) Steel can also be produced by adding the required amount of carbon to wrought iron, then adding some special constituents, e.g., tungsten, chromium, vanadium, molybedenum, manganese, nickel and cobalt which impart desired properties to the steel. At present most of the steel is manufactured from cast iron.

MANUFACTURE OF STEEL

In can be manufactured by the following processes:

(a) **Open hearth process** (using cast iron, wrought iron or steel scrap).

(b) **Bessemer's process** (using cast iron only).

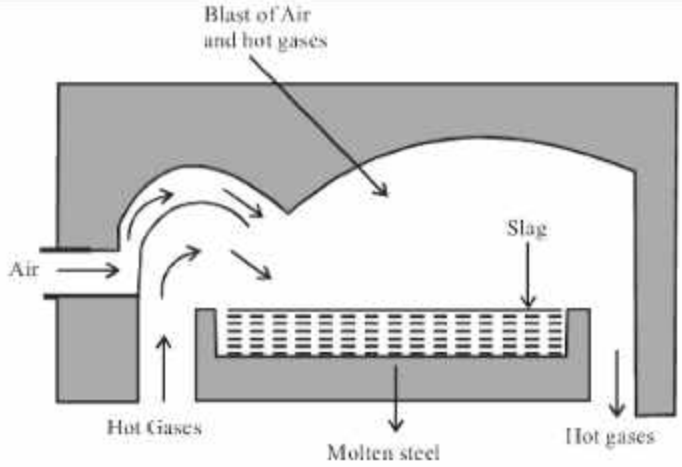
Some other processes are also used to prepare special type of steel from pure wrought iron.

(a) Open Heart Process:

This is the most modern method for the manufacture of steel. It is carried out in an open hearth furnace. This furnace has a low roof to deflect the hot gases and flames downward to melt the charge. The open hearth furnaces works on the regenerative principle of heat economy. Open hearth process is of two types:

(i) Furnace with acidic lining like SiO_2 is used when the impurities are Mn, Si etc.

(ii) Furnace with basic lining like dolomite (CaO, MgO) is used when the impurities are P and S, etc.



Open hearth furnace for the manufacture of steel from cast iron

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:

$$C + \tfrac{1}{2}O_2 \longrightarrow CO$$

$$Si + O_2 \longrightarrow SiO_2$$

$$Mn + \tfrac{1}{2}O_2 \longrightarrow MnO$$

CO escape in the flue gases. The gases which comes out from the furnace are called flue gases. Silica (SiO_2) combines with CaO, MnO and FeO to form silicates (slag) which float on the surface of the molten metal.

$$SiO_2 + CaO \longrightarrow CaSiO_3$$

$$SiO_2 + MnO \longrightarrow MnSiO_3$$

$$SiO_2 + FeO \longrightarrow FeSiO_3$$

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

$$2Fe_2O_3 + 3S \longrightarrow 4Fe + 3SO_2$$

$$5Fe_2O_3 + 6P \longrightarrow 10Fe + 3P_2O_5$$

These oxides react with calcium oxide to form slag.

$$P_2O_5 + 3CaO \longrightarrow Ca_3(PO_4)_2 \quad \text{(Fertilizer)}$$

$$SO_2 + CaO \longrightarrow CaSO_3$$

Samples are taken at intervals and the percentage of carbon in the steel is determined regularly. When this is reduced to about 0.1%, the calculated mass of

ferromanganese (Fe, Mn, C) is added. Manganese desulphurises the steel. Ferromanganese raises the carbon contents to the required values. After giving time for mixing, a little more ferromanganese is added, and the 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

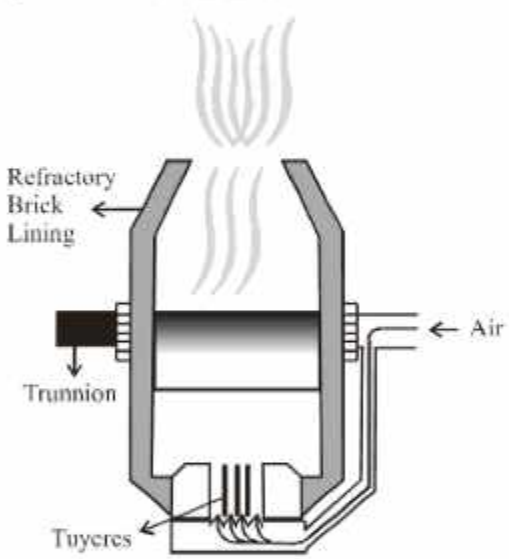
The furnace used in this process is called **Bessemer's Converter** which is a pear shaped vessel made of steel plates. At the bottom the converter is provided with a number of holes through which hot air is introduced. The converter is held on a central axis so that it can be tilted in any desired position 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 and hot air blast is injected through the perforated base. This oxidizes carbon, silicon, and manganese.

$$C + \tfrac{1}{2}O_2 \longrightarrow CO$$

$$Si + O_2 \longrightarrow SiO_2$$

$$2Mn + O_2 \longrightarrow 2MnO$$



Bessemer's converter for the manufacture of steel from cast iron

These oxides form a slag of $MnSiO_3$. The heat evolved during the oxidation is enough to keep iron in the molten state.

$$MnO + SiO_2 \longrightarrow MnSiO_3$$

(Slag)

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.

$$4Fe + 3O_2 \longrightarrow 2Fe_2O_3$$

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$

Within 10 to 15 minutes the flame due to CO subsides indicating that the 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 continued for a moment to ensure thorough mixing. The addition of Mn imparts increased hardness and tensile strength.

In order to remove entrapped bubbles of gases (blow holes) such as O_2, N_2, CO_2, a little Al or ferrosilicon is also added. Al removes nitrogen as nitride and oxygen as oxide.

$$2Al + N_2 \longrightarrow 2AlN$$

$$4Al + 3O_2 \longrightarrow 2Al_2O_3$$

At the end of the operation, the molten steel is poured out into moulds for casting. Such casting are free from any defect.

CORROSION

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

Corrosion by Gases:

The simplest case of corrosion occurs when metals come into contact with gases of the atmosphere. The surface of metals becomes coated with compounds such as oxides, sulphides and carbonates. Such compounds sometime form a compact layer on the surface protecting the metal from further attack. e.g., Al.

Corrosion by Water:

The case would be different when the metal is in contact with water. The compounds formed in this case may dissolve in water, allowing the corrosion to penetrate further into the metal. Besides dissolving the compounds, water also promotes electrochemical process which is one of the main causes of rapid corrosion.

ELECTROCHEMICAL THEORY

Pure metals are not easily corroded, even iron hardly gets corroded if absolutely pure. The **impurities** present in the metal promotes corrosion.

To understand why impurities accelerate the corrosion of metals, consider what happens when two different metals come in contact with one another is moist air. Suppose, for instance, Cu is brought in contact with Al. After sometime, we shall notice that aluminium gets corroded while copper remains intact. This can be explained by the electrochemical theory.

According to this theory, moisture and CO_2 are present on the surface of the metal. Water ionizes into H^+ and OH^- ions. CO_2 dissolves in water forming H_2CO_3 which ionizes as follows:

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

Copper and aluminium are, in a sense, immersed in the solution containing H^+, OH^- and HCO_3^- ions.

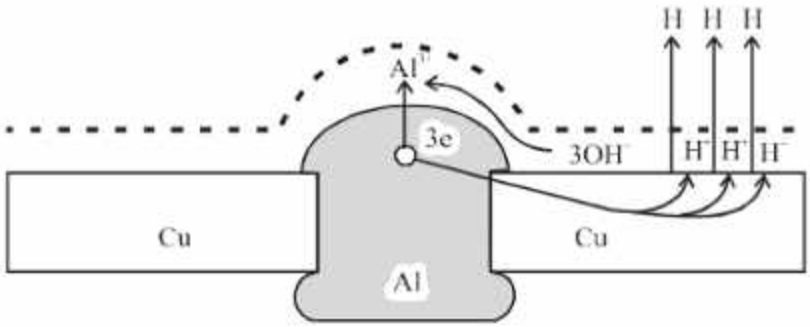


Diagram of the corrosion of aluminium in contact with copper

This forms a galvanic cell in which aluminium releases electrons and changes to Al^{+3} ion (being more reactive than Cu) i.e., it acts as negative electrode and Cu acts as a positive electrode as shown in the figure.

Anode: $Al \longrightarrow Al^{3+} + 3e^-$ (Oxidation)

$$Al^{+3} + 3OH^- \longrightarrow Al(OH)_3$$

Cathode: $2H^+ + 2e^- \longrightarrow H_2$ (Reduction)

Aluminium ions attract OH^- ion to form $Al(OH)_3$ i.e., it starts dissolving. The H^+ ions present on the Cu receive the electrons and released as H_2. In this way **aluminium corrodes rapidly** when in **contact with copper** which is lower in electrochemical series.

From this we can conclude that when an active metal Al (higher in the electrochemical series) comes in contact with less active metal Cu (lower in the electrochemical series) a galvanic cell is established. In this process active metal corrodes rapidly while the other intact.

PREVENTION OF CORROSION

It has been observed that the amount of iron destroyed each year by corrosion equal to about one fourth of its annual production. It is therefore necessary to prevent such a damaging process and avoid this loss.

Corrosion can be prevented by the following methods:

(1) Coating the Surface of Metal:

It is very simple method of prevention of corrosion. In this method, metal surface is coated with oil, paint, varnish or enamel. Environmental gases have no direct contact with metal.

(2) Alloying:

Mixture of two or more metals is called alloy. Alloying of metals serve to inhibit the corrosion.

(3) Metallic Coating:

Metallic coating is frequently used to prevent corrosion. e.g., tin plating, galvanizing.

(i) Tin Plating or Coating Iron with Tin (Cathode Coating):

The process of tin plating consists of dipping the clean sheet of iron in a bath of molten tin and the passing it through hot pairs of rollers. Such plates are used in the manufacture of tin canes, oil containers and other similar articles.

Tin itself is very stable and protects the metals effectively as long as its coating on the iron is intact.

If the protective coating is damaged then iron comes into contact with moisture. A galvanic cell is established in which tin acts as a cathode and iron acts as an anode. The electrons flow from iron to thin where they discharge H^+ ions, leaving behind OH^- in the solution. These hydroxide ions, react with iron forming $Fe(OH)_3$ which dissolves rapidly in ater.

$$H_2O \text{ (moisture)} \longrightarrow H^+ + OH^-$$

Anode: $Fe \longrightarrow Fe^{3+} + 3e^-$ (Oxidation)

$$Fe^{3+} + 3OH^- \longrightarrow Fe(OH)_3$$

Cathode: $2H^+ / Sn + 2e^- \longrightarrow H_2/Sn$ (Reduction)

From this we can conclude that plated iron gets rust more rapidly when the protective coating is damaged than the non-plated iron.

(ii) Galvanizing or Zinc Coating (Anode Coating):

"The coating of steel or iron with zinc to protect it from corrosion is called galvanizing."

Galvanizing is done by dipping a clean iron sheet in a zinc chloride bath and heating. The iron sheet is then removed, **rolled into zinc bath and air** cooled.

In this cause if a protective layer of zinc is damaged, a galvanic cell is established, in the presence of moisture. Iron serves as a cathode and zinc as an anode. Electrons flow from Zn to iron, as a result of which Zn decays while Fe remains intact. This is called **sacrificial corrosion**.

$$Fe^{+2} + Zn \longrightarrow Zn^{+2} + Fe$$

This is the way galvanizing helps protecting iron from rust. This process is used in water pipes, etc.

CHROMATES AND DICHROMATES

Chromates and dichromates are the salts of chromic acid, H_2CrO_4, and dichromic acid, $H_2Cr_2O_7$, respectively. Both acids exist only in aqueous solution and when attempts are made to isolate them from solution, they decompose immediately into chrommic anhydride (Cr_2O_3) and water. Their salts are, however, quite stable.

Potassium Chromate (K_2CrO_4):

Preparation:

(1) The chromates of alkali metals, which are soluble in water, are obtained by oxidizing trivalent chromium compounds in the presence of an alkali.

$$2KrCO_2 + 3Br_2 + 8KOH \longrightarrow 2K_2CrO_4 + 6KBr + 4H_2O$$

(Pot chromite)

(2) Chromates can also be produced by fusing Cr_2O_3 with an alkali in the presence of an oxidant, such as potassium chlorate.

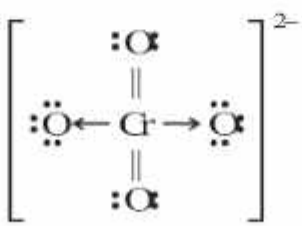
$$Cr_2O_3 + 4KOH + KClO_3 \longrightarrow 2K_2CrO_4 + KCl + 2H_2O$$

(3) Chromates are usually prepared from natural chromite ($FeO.Cr_2O_3$), if it is strongly heated with potassium carbonate in the presence of the oxygen. The resulting fused mass will contain potassium chromate which can be extracted with water.

$$4FeCr_2O_4 + 8K_2CO_3 + 7O_2 \longrightarrow 8K_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

Properties:

Structure of Chromate Ion:



Properties:

Almost all the chromates are yellow in colour. Some of them are used as pigments. For instance, insoluble lead chromate, $PbCrO_4$, is employed for the preparation of yellow oil colour called **yellow crown**.

$K_2Cr_2O_4$ and $K_2Cr_2O_7$ show similar properties because in an aqueous solution $Cr_2O_7^{2-}$ and CrO_4^{2-} ions exist in equilibrium.

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

If an alkali is added to such a solution the hydroxyl ions will bind the hydrogen ion in solution, the equilibrium will shift towards left and, as a result, dichromate ions will be converted into chromate ions. Similarly on adding an acid, the equilibrium will shift towards right and dichromate ions will be formed.

POTASSIUM DICHROMATE ($K_2Cr_2O_7$) (SURKH KAHI)

Preparation:

(1) K_2CrO_4 is converted to $K_2Cr_2O_7$ by using H_2SO_4. By adding on acid to aqueous solution of K_2CrO_4 equilibrium will shift in the forward direction i.e., changing chromate ions into dichromate ions.

$$2K_2CrO_4 + H_2SO_4 \rightleftharpoons K_2Cr_2O_7 + K_2SO_4 + H_2O$$

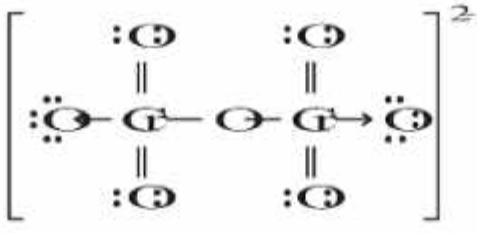
(2) Sometimes sodium dichromate is converted into potassium dichromate by reacting it with KCl.

$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$

Properties:

It is an orange red crystalline solid which melts of 396°C, it is fairly soluble in water.

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



(a) Reaction with H_2S:

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

$$3H_2S + 3[O] \longrightarrow 3H_2O + 3S$$

$$K_2Cr_2O_7 + 3H_2S + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$$

(b) Reaction with Ferrous Sulphate:

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

$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \longrightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O$$

(c) Reaction with Potassium Iodide:

Potassium dichromate also oxidizes KI in the presence of H_2SO_4.

$$K_2Cr_2O_7 + 8KI + 7H_2SO_4 \longrightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 3I_2 + 7H_2O$$

(d) Chromyl Chloride Test:

When solid potassium dichromate is heated with solid metal chloride in the presence of concentrated sulphuric acid chromyl chloride is produced. CrO_2Cl_2 is passed through NaOH and lead acetate is added. Yellow ppts of $PbCrO_4$ confirm chloride.

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \longrightarrow 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O$$

$$CrO_2Cl_2 + 2NaOH \longrightarrow Na_2CrO_4 + 2HCl$$

$$Na_2CrO_4 + Pb(CH_3COO)_2 \longrightarrow PbCrO_4 + 2CH_3COONa$$

Uses:

(a) $K_2Cr_2O_7$ finds extensive use in dyeing.

(b) It is used in leather industries for chrome tanning.

(c) It is used as oxidizing agent.

(d) For making insoluble chrome pigments.

POTASSIUM PERMANGANATE ($KMnO_4$)

This compound is the salt of permangantic acid, $HMnO_4$. It is an unstable acid and exists only in solution.

Preparation:

It is prepared by acidifying the solution of potassium manganate, K_2MnO_4 by H_2SO_4.

$$3K_2MnO_4 + 2H_2SO_4 \longrightarrow 2K_2SO_4 + 2KMnO_4 + MnO_2 + 2H_2O$$

On a large scale, it is prepared from the mineral pyrolusite, MnO_2. The finely powdered mineral is fused with KOH in the presence of air or an oxidizing agent like KNO_3 or $KClO_3$, etc. This treatment gives us green coloured potassium manganate, K_2MnO_4, in fused state.

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$

$$MnO_2 + 2KOH + KNO_3 \longrightarrow K_2MnO_4 + KNO_2 + H_2O$$

$$3MnO_2 + 6KOH + KClO_3 \longrightarrow 3K_2MnO_4 + KCl + 3H_2O$$

The fused potassium manganate K_2MnO_4 obtained as above is extracted with water and the solution, after filtration, is converted into potassium permanganate ($KMnO_4$) by any of the following methods.

(a) Stadeler's Process:

In this method, Cl_2 is passed through the green solution of K_2MnO_4 until it becomes purple due to the formation of $KMnO_4$. Here Cl_2 oxidizes K_2MnO_4 into $KMnO_4$.

$$2K_2MnO_4 + Cl_2 \longrightarrow 2KCl + 2KMnO_4$$

(b) In this processes CO_2 is passed though the green solution of K_2MnO_4 until it becomes purple.

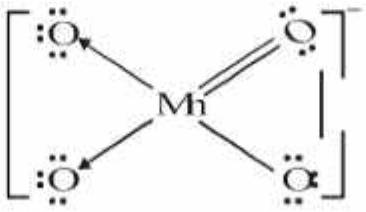
$$3K_2MnO_4 + 2H_2O + 4CO_2 \longrightarrow 2KMnO_4 + MnO_2 + 4KHCO_3$$

(c) Electrolytic Oxidation Process:

In this process magnate is converted in to permanganate by electrolytic oxidation. During electrolysis of an aqueous solution of K_2MnO_4, water is decomposed to evolve hydrogen gas at the cathode and oxygen gas at the anode. Oxygen liberated at the anode, oxidizes magnate ion $(MnO_4)^{2-}$ into permanganate ion $(MnO_4)^{1-}$ while hydrogen is liberated at the cathode.

$$2K_2MnO_4 + H_2O + [O] \longrightarrow 2KMnO_4 + 2KOH$$

The purple solution of $KMnO_4$ obtained as above is filtered through asbestos, concentrated and allowed to crystallize when $KMnO_4$ deposits as deep purple-red rhombic prisms.



Structure of permanganate ion

Properties:

(1) Potassium permanganate forms dark purple lustrous crystals giving deep pink colour in solution.

(2) Its solubility in water at 20°C is only about 7% while it dissolves more at higher temperature (25% at 63°C).

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

(a) Reaction with H_2S:

It oxidizes H_2S to sulphur.

$$2KMnO_4 + 3H_2SO_4 + 5H_2S \longrightarrow K_2SO_4 + 2MnSO_4 + 5S + 8H_2O$$

(b) Reaction with $FeSO_4$:

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

$$2KMnO_4 + 10FeSO_4.7H_2O + 8H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 78H_2O$$

(c) Reaction with Oxalic Acid:

It oxidizes oxalic acid to CO_2 and H_2O on heating.

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

(d) Reaction with KI:

$$2KMnO_4 + 10KI + 8H_2SO_4 \longrightarrow 6K_2SO_4 + 2MnSO_4 + 5I_2 + 8H_2O$$

Uses:

It is used:

(a) As an oxidizing agent.

(b) As a disinfectant and a germicide.

(c) In the manufacture of many organic compounds.

(d) In bleaching of pulp.

(e) In the manufacture of phamaceuticals.

EXERCISE

Q.1 Fill in the blanks:

(i) The property of paramagnetism is due to the presence of ———— electrons.

(ii) MnO_4^{-1} ion has ———— colour and $Cr_2O_7^{-2}$ has ———— colour.

(iii) When potassium chromate is treated with an acid ———— is produced.

(iv) The d-block elements are located between ———— and ———— block elements.

(v) Oxidation number of Fe in $K_4[Fe(CN)_6]$ is ———— while in $K_3[Fe(CN)_6]$ it is ————.

(vi) The presence of ———— in a metal promotes corrosion.

(vii) If copper is in contact with aluminium ———— gets corroded.

(viii) Complexes having sp^3d^2 hybridization have ———— shape.

(ix) In naming the complexes, all the ligands are named in ————.

(x) In an aqueous solution, CrO_4^{2-} and $Cr_2O_7^{2-}$ exist in the form of ————.

ANSWERS

(i)	unpaired	**(ii)**	purple, orange red	**(iii)**	potassium dichromate
(iv)	s, p	**(v)**	+2, +3	**(vi)**	impurities
(vii)	aluminium	**(viii)**	octahedral	**(ix)**	alphabetic order
(x)	equilibrium				

Q.2 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 the unplated iron.

(viii) The name of anionic ligands in a complex ends in suffix 'O'.

(ix) Pig iron contains greater percentage of carbon than steel.

(x) Complex compounds having dsp^2 hybridization have tetrahedral geometry.

ANSWERS

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

Q.3 Multiple choice questions. Encircle the correct answer:

(i) Which of the following is a non-typical transition element:

(a) Cr **(b)** Mn

(c) Zn **(d)** Fe

(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)** None is true

(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, Te, Re

(vi) Which is the formula of tetraammine chloro-nitro-platinum (IV) sulphate:

(a) $[Pt(NH_3)_4(NO_2)]SO_4$ **(b)** $[PtNO_2Cl(NH_3)_4]SO_4$

(c) $[PtCl(NO_2)(NH_3)_4]SO_4$ **(d)** $[Pt(NH_3)_4(NO_2)Cl]SO_4$

(vii) The percentage of carbon in different types of iron products is in the order of:

(a) $\overset{\text{Wrought iron}}{}$ > Steel > Cast iron **(b)** Cast iron > Steel > $\overset{\text{Wrought iron}}{}$

(c) Cast iron > $\overset{\text{Wrought iron}}{}$ > Steel **(d)** Cast iron > Steel > $\overset{\text{Wrought iron}}{}$

(viii) The colour of transition metal complexes is due to:

(a) d-d transition of electrons **(b)** Paramagnetic nature of transition elements

(c) Ionization **(d)** Loss of s-electrons

(ix) Coordination number of Pt in $[PtCl(NO_2)(NH_3)_4]^2$ is:

(a) 2 **(b)** 4

(c) 1 **(d)** 6

(x) The total number of transition element is:

(a) 10 **(b)** 14

(c) 40 **(d)** 58

ANSWERS

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

Q.4 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. Detailed question. See text book (Q.5 and Q.6 are on next page).

Q.5 Explain the following terms giving examples:

(a) Ligands **(b) Coordination sphere**

(c) Substitutional alloy **(d) Central metal atom**

Ans. Detailed question. See text book.

Q.6 Describe the rules for naming the coordination complexes and give examples.

Ans. Descriptive question. See text book.

Q.7 What is the difference between wrought iron and steel? Explain the Bessemer's process for the manufacture of steel.

Ans. **Wrought Iron and Steel:** Wrought iron is the purest form of commercial iron and contains 0.12% to 0.25% carbon which is lowest percentage of carbon while steel is an alloy of iron containing 0.25% to 2.5% of carbon.

Process for manufacture of steel see in text book.

Q.8 Explain the following giving reasons:

(a) Why does damaged tin plated iron get rusted quickly.

(b) Under what conditions does aluminium corrode?

(c) How does the process of galvanizing protect iron from rusting?

Ans.

(a) With iron alone galvanic cell cannot be established and rusting is slow but when tin plating gets damaged on the surface of iron then iron comes in contact with moisture of air and a galvanic cell is established due to which rusting proceeds more rapidly.

(b) The conditions necessary for aluminum corrosion are:

(i) Aluminum is in contact with less reactive metal like Cu.

(ii) Aluminum is provided with moisture by atmosphere or salt solution.

(c) When iron is coated with more reactive metal (like Zn) to prevent corrosion then iron is protected. Even when coating is damaged galvanic cell is established but iron remains intact because Zn will be rusted. In this way galvanizing or Zn coating protect iron from rusting.

Q.9 How chromate ions are converted into dichromate ions?

Ans. Chromate (K_2CrO_4) is converted into dichromate ($K_2Cr_2O_7$) in the presence of conc. H_2SO_4.

$$2CrO_4^{-2} + 2H^+ \rightleftharpoons Cr_2O_7^{-2} + H_2O$$

$$2K_2CrO_4 + H_2SO_4 \longrightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$$

The above reaction is a reversible reaction and equilibrium shift towards right according to Le-Chatelier's Principle changing chromate ions into dichromate ions.

Q.10 Describe the preparation of $KMnO_4$ and K_2CrO_4.

Ans. Descriptive question. Consult text book for details.

Q.11 Give systematic names to following complexes:

(a) $[Fe(CO)_5]$ **(b)** $[Co(NH_3)_6]Cl_3$

(c) $[Fe(H_2O)_6]^{2+}$ **(d)** $Na_3[CoF_6]$

(e) $K_2[Cu(CN)_4]$ **(f)** $K_2[PtCl_6]$

(g) $[Pt(OH)_2(NH_3)_4]SO_4$ **(h)** $[Cr(OH)_3(H_2O)_3]$

Ans.

(a)	$[Fe(CO)_5]$	Penta carbonyl iron (o)
(b)	$[Co(NH_3)_6]Cl_3$	Hexa ammine cobalt (III) chloride
(c)	$[Fe(H_2O)_6]^{2+}$	Hexa aqua iron (II) ion
(d)	$Na_3[CoF_6]$	Sodium hexa fluoro cobaltate (III)
(e)	$K_2[Cu(CN)_4]$	Potassium tetra cyano cuprate (II)
(f)	$K_2[PtCl_6]$	Potassium hexa chloro palatinate (IV)
(g)	$[Pt(OH)_2(NH_3)_4]SO_4$	Tetra ammine dihydroxo platinum (IV) sulphate
(h)	$[Cr(OH)_3(H_2O)_3]$	Triaqua trihydroxo chromium (III)

DO YOU KNOW?

(1) Formula of pyrolusite is MnO_2.

(2) Paramagnetic behaviour is due to the presence of unpaired electrons.

(3) The electrons in the low energy d-orbital absorb a part of visible light and jump to high energy d-orbital. This is called d-d transition.

(4) The ions or neutral molecules which donate electron pairs to the central metal atom or ion is called ligand. In $K_4[Fe(CN)_6]$, $\bar{C}N$ is ligand.

(5) The central metal atom or ion along with ligand is called coordination sphere.

(6) The number of electron pairs provided by the ligand to the central atom or ion is called coordination number. In $K_4[Fe(CN)_6]$, coordination number of Fe is 6.

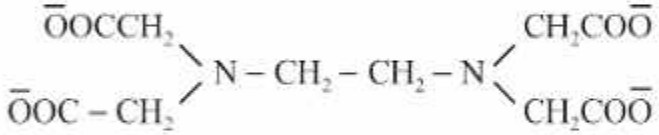
(7) Wrought iron is the purest form of iron.

(8) $KMnO_4$ is called pinky.

(9) $K_2Cr_2O_7$ is called "Surkh Kahi".

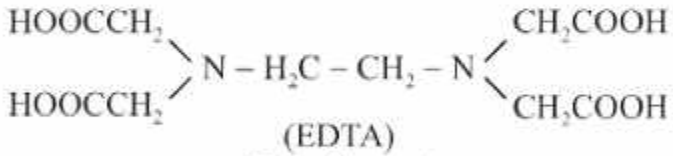
(10) Complexes having d^2sp^3 hybridization have octahedral shape.

(11)



(Ethylenediamine tetracetate)

(12)



(EDTA)
(Hexadentate)

CHAPTER 6

TRANSITION ELEMENTS

MULTIPLE CHOICE QUESTIONS

1. What is formula of haematite:

(a) FeS_2 (b) FeO_3

(c) Fe_2O_3 (d) Fe_3O_4

2. Which is non-typical transition elements:

(a) Cr (b) Mn

(c) Zn (d) Fe

3. Highest oxidation state of Mn in which compound:

(a) K_2MnO_4 (b) $KMnO_4$

(c) MnO (d) MnO_2

4. The trace metal present in insulin is:

(a) Mn (b) Co

(c) Fe (d) Zn

5. The hybridization of Ni in $[Ni(CN)_4]^{-2}$ ion is:

(a) sp^3 (b) dsp^3

(c) d^2sp^3 (d) dsp^2

6. Which of the following cation has maximum unpaired electron:

(a) Ni^{+2} (b) Co^{+2}

(c) Mn^{+2} (d) Fe^{2+}

7. Which is the configuration of Cr:

(a) $3d^4\ 4s^2$ (b) $3d^5\ 4s^1$

(c) $3d^6\ 4s^1$ (d) $2d^1\ 4s^2$

8. The black image on an exposed and developed photographic film is composed of:

(a) Ag (b) Ag_2O

(c) AgBr (d) $Ag[(SrO_3)_2]^-$

9. The strength of binding energy of transition elements depend upon:

(a) No. of $\bar{e}$-pair **(b)** No. of unpaired $\bar{e}$

(c) No. of neutron **(d)** No. of proton

10. Mild steel contain carbon:

(a) 0.1 – 0.2% **(b)** 0.2 – 0.7%

(c) 0.1 – 1.0% **(d)** 17

11. To prevent corrosion, iron pipes carrying drinking water are covered with Zn by process called:

(a) Alloy formation **(b)** Electroplating

(c) Galvanizing **(d)** Soldering

12. No. of $\bar{e}$-pairs accepted by the central atom in a transition metal complex is called:

(a) Co-ordination sphere **(b)** Co-ordination complex

(c) Co-ordination number **(d)** Chelate

13. Group VIB of transition elements contains:

(a) Zn, Cd, Hg **(b)** Fe, Ru, Os

(c) Cr, Mo, W **(d)** Mn, Te, Re

14. Which of the following is a typical transition metal:

(a) Sc **(b)** Y

(c) Ra **(d)** Co

15. Co-ordination number of Pt in $[Pt\ Cl(NO_2)(NH_3)_4^{2-}]$ is:

(a) 2 **(b)** 4

(c) 1 **(d)** 6

answers

1.	(c)	**2.**	(c)	**3.**	(b)	**4.**	(d)	**5.**	(d)
6.	(c)	**7.**	(b)	**8.**	(a)	**9.**	(b)	**10.**	(a)
11.	(c)	**12.**	(c)	**13.**	(c)	**14.**	(d)	**15.**	(d)

solved EXERCISE

Q.1 Fill in the blanks:

(i) The property of paramagnetism is due to the presence of ———— electrons.

(ii) MnO_4^{-1} ion has ———— colour and $Cr_2O_7^{-2}$ has ———— colour.

(iii) When potassium chromate is treated with an acid ———— is produced.

(iv) The d-block elements are located between ———— and ———— block elements.

(v) Oxidation number of Fe in $K_4[Fe(CN)_6]$ is ———— while in $K_3[Fe(CN)_6]$ it is ————.

(vi) The presence of ———— in a metal promotes corrosion.

(vii) If copper is in contact with aluminium ———— gets corroded.

(viii) Complexes having sp^3d^2 hybridization have ———— shape.

(ix) In naming the complexes, all the ligands are named in ————.

(x) In an aqueous solution, CrO_4^{2-} and $Cr_2O_7^{2-}$ exist in the form of ————.

answers

(i)	unpaired	**(ii)**	violet, orange red	**(iii)**	potassium dichromate
(iv)	s, p	**(v)**	+2, +3	**(vi)**	impurities
(vii)	aluminium	**(viii)**	octahedral	**(ix)**	alphabetic order
(x)	equilibrium				

Q.2 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 the unplated iron.

(viii) The name of anionic ligands in a complex ends in suffix 'O'.

(ix) Pig iron contains greater percentage of carbon than steel.

(x) Complex compounds having dsp^2 hybridization have tetrahedral geometry.

answers

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

Q.3 Multiple choice questions. Encircle the correct answer:

(i) Which of the following is a non-typical transition element:

(a) Cr **(b)** Mn

(c) Zn **(d)** Fe

(ii) Which of the following is a typical transition metal:

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answers

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

Q.4 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. Detailed question. See text book (Q.5 and Q.6 are on next page).

Q.5 Explain the following terms giving examples:

(a) Ligands **(b) Coordination sphere**

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Ans. Detailed question. See text book.

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Ans. Descriptive question. See text book.

Q.7 What is the difference between wrought iron and steel? Explain the Bessemer's process for the manufacture of steel.

Ans. **Wrought Iron and Steel:** Wrought iron is the purest form of commercial iron and contains 0.12% to 0.25% carbon which is lowest percentage of carbon while steel is an alloy of iron containing 0.25% to 2.5% of carbon.

Process for manufacture of steel see in text book.

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(a) Why does damaged tin plated iron get rusted quickly.

(b) Under what conditions does aluminium corrode?

(c) How does the process of galvanizing protect iron from rusting?

Ans.

(a) When iron is alone galvanic cell cannot be established and rusting is slow but when tin plating gets damaged on the surface of iron then iron comes in contact with moisture of air and a galvanic cell is established due to which rusting proceeds more rapidly.

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Q.9 How chromate ions are converted into dichromate ions?

Ans. Chromate (K_2CrO_4) is converted into dichromate ($K_2Cr_2O_7$) in the presence of conc. H_2SO_4.

$$2CrO_4^{-2} + 2H^+ \rightleftharpoons Cr_2O_7^{-2} + H_2O$$

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Ans. Descriptive question. Consult text book for details.

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(a) $[Fe(CO)_5]$ **(b)** $[Co(NH_3)_6]Cl_3$

(c) $[Fe(H_2O)_6]^{2+}$ **(d)** $Na_3[CoF_6]$

(e) $K_2[Cu(CN)_4]$ **(f)** $K_2[PtCl_6]$

(g) $[Pt(OH)_2(NH_3)_4]SO_4$ **(h)** $[Cr(OH)_3(H_2O)_3]$

Ans.

(a)	$[Fe(CO)_5]$	Penta carbonyl iron (o)
(b)	$[Co(NH_3)_6]Cl_3$	Hexa ammine cobalt (III) chloride
(c)	$[Fe(H_2O)_6]^{2+}$	Hexa aqua iron (II) ion
(d)	$Na_3[CoF_6]$	Sodium hexa fluoro cobaltate (III)
(e)	$K_2[Cu(CN)_4]$	Potassium tetra cyano cuprate (II)
(f)	$K_2[PtCl_6]$	Potassium hexa chloro palatinate (IV)
(g)	$[Pt(OH)_2(NH_3)_4]SO_4$	Tetra ammine dihydroxo platinum (IV) sulphate
(h)	$[Cr(OH)_3(H_2O)_3]$	Triaqua trihydroxo chromium (III)

DO YOU KNOW?

1. Formula of pyrolusite is MnO_2.
2. Paramagnetic behaviour is due to the presence of unpaired electrons.
3. The electrons in the low energy d-orbital absorb a part of visible light and jump to high energy d-orbital. This is called d-d transition.
4. The ions or neutral molecules which donate electron pairs to the central metal atom or ion is called ligand. In $K_4[Fe(CN)_6]$, $\overline{C}N$ is ligand.
5. The central metal atom or ion along with ligand is called coordination sphere.
6. The number of electron pairs provided by the ligand to the central atom or ion is called coordination number. In $K_4[Fe(CN)_6]$, coordination number of Fe is 6.
7. Wrought iron is the purest form of iron.
8. $KMnO_4$ is called pinky.
9. $K_2Cr_2O_7$ is called "Surkh Kahi".
10. Complexes having d^2sp^3 hybridization have octahedral shape.

SHORT QUESTIONS

Q.1 Why most of the transition metal ions are coloured?

Ans. Metal ions are coloured due to the excitation of electrons. These ions absorb particular wavelengths of visible light for excitation of electrons. Thus remaining wavelengths are reflected and give some colour.

Q.2 Why some transition metals are paramagnetic in nature?

Ans. Paramagnetic nature of metals and metals ions is due to presence of unpaired electrons present in them. Fe^{+3} and Mn^{+2} have strong paramagnetic behaviour due to the presence of five unpaired electrons in them.

$$Mn_{25}^{+2} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^0, 3d^5$$

$$Fe_{26}^{+3} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^0, 3d^5$$

Q.3 What is the trend of melting points in transition series?

Ans. The melting point of metals depends upon the binding force between the bonded atoms. In transition series, the binding force increases upto the middle due to the increase in unpaired electrons and melting point increases upto middle of transition series. The binding force is maximum upto group VI-B and then decreases due to the decrease in no. of unpaired electrons.

Q.4 Differentiate between paramagnetism and diamagnetism.

Ans. The substance which is weakly attracted by the strong magnetic field is called paramagnetic. Paramagnetism is due to the presence of unpaired electrons. The substance which is weakly repelled by the strong magnetic field is called diamagnetic substance. The substance in which all atoms have paired spin are diamagnetic. O_2 is paramagnetic and N_2 is diamagnetic.

Q.5 What is trend in paramagnetic behaviour in the transition series of 4^{th} period?

Ans. The paramagnetic nature of a substance depends upon the number of unpaired electrons. In the transition series, number of unpaired electrons increase upto the middle and then decreases. So the paramagnetic behaviour increases upto the middle and then decreases.

Q.6 How the entrapped air of molten iron is removed?

Ans. The entrapped air in iron is removed by adding small amount of aluminum in it. N_2 and O_2 of air react with Al to form AlN and Al_2O_3 respectively.

$$2Al + N_2 \longrightarrow 2AlN$$

$$4Al + 3O_2 \longrightarrow 2Al_2O_3$$

Q.7 What is sacrificial corrosion?

Ans. Less reactive metal (Fe) is protected by coating it with more reactive metal (Zn). If this coating is damaged, a galvanic cell is established in the presence of moisture. Then active

metal (Zn) acts as anode and is oxidized and corroded. Less reactive metal (Fe) remain intact. This is called sacrificial corrosion.

Anode: (oxidation) $Zn \longrightarrow Zn^{+2} + 2e^-$

Cathode: (reduction) $Fe^{+2} + 2e^- \longrightarrow Fe$

Overall reaction: $Zn + Fe^{+2} \longrightarrow Zn^{+2} + Fe$

Q.8 $K_2Cr_2O_7$ acts as strong oxidising agent. Support this statement with two equations.

Ans. (i) $K_2Cr_2O_7$ oxidies $FeSO_4$ to $Fe_2(SO_4)_3$ in the presence of H_2SO_4.

$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \longrightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + 7H_2O + 2H_2SO_4$$

(ii) $K_2Cr_2O_7$ reacts with KI to form I_2 in the presence of H_2SO_4.

$$4K_2Cr_2O_7 + 6KI + 7H_2SO_4 \longrightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 3I_2 + 7H_2O$$

Q.9 What is chromyl chloride test for which radical this test is performed?

Ans. Chromyl chloride test is performed for Cl^- radical. In this test conc. H_2SO_4 is added to solid salt and solid $K_2Cr_2O_7$. An orange coloured gas CrO_2Cl_2 is evolved. This CrO_2Cl_2 is called chromyl chloride gas. It is passed into NaOH and lead acetate is added yellow ppts of $PbCrO_4$ is formed.

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \longrightarrow 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O$$

$$CrO_2Cl_2 + 2NaOH \longrightarrow Na_2CrO_4 + 2HCl$$

$$Na_2CrO_4 + Pb(CH_3COO)_2 \longrightarrow PbCrO_4 + 2CH_3COONa$$

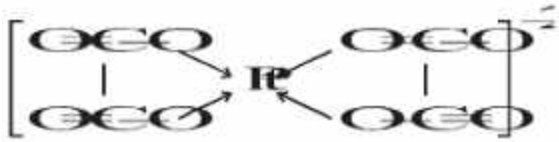
Q.10 "$KMnO_4$ is a strong oxidising agent". Support the statement with two chemical reactions.

Ans. $2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \longrightarrow K_2SO_4 + MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$

$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$

Q.11 Define chelate with one example.

Ans. The complex in which two or more different atoms of a polydentate ligands are coordinated with central metal atom or ion and form a ring is called chelate and this process is called chelation.



Diethylenediaminetetraacetatoferrate(II) ion

Q.12 What is difference between mild steel and medium steel?

Ans. (i) The steel in which percentage of C is 0.1 – 0.2% is called mild steel. It is fairly soft, malleable and ductile and can be forged into different shapes.

(ii) The steel which contain 0.2 – 0.7% of carbon in it is called medium steel.

Q.13 What is difference between pig iron and steel?

Ans. The percentage of carbon in pig iron is 2.5 – 4.5% and in steel is 0.25 – 2.5%.

Q.14 Name the following complexes.

Ans.

$[Fe(CO)_5]$	Pentacarbonyl iron (O)
$[Co(NH_3)_6]Cl_3$	Hexa ammine cobalt (III) chloride
$[Fe(H_2O)_6]^{+2}$	Hexa aqua iron (II) ion
$Na_3[CoF_6]$	Sodium hexa fluoro cobaltate (III)
$K_2[Cu(CN)_4]$	Pot-tetra cyano cuprate (II)
$K_2[PtCl_6]$	Pot-hexa chloroplatinate (IV)
$[Pt(OH)_2(NH_3)_4]SO_4$	Tetra ammine dihydroxo platinum (IV) sulphate
$[Cr(OH)_3(H_2O)_3]$	Tri aqua trihydroxo chromium (III)
$[Ag(NH_3)_2]Cl$	Diammine silver (I) chloride
$[Cu(NH_3)_4]SO_4$	Tetra ammine copper (II) sulphate
$K_4[Fe(CN)_6]$	Pot-hexa cyano ferrate (II)
$Ni(CO)_4$	Tetra carbonyl nickel (O)
$[MnCl_4]^{-2}$	Tetra chloro manganate (II) ion