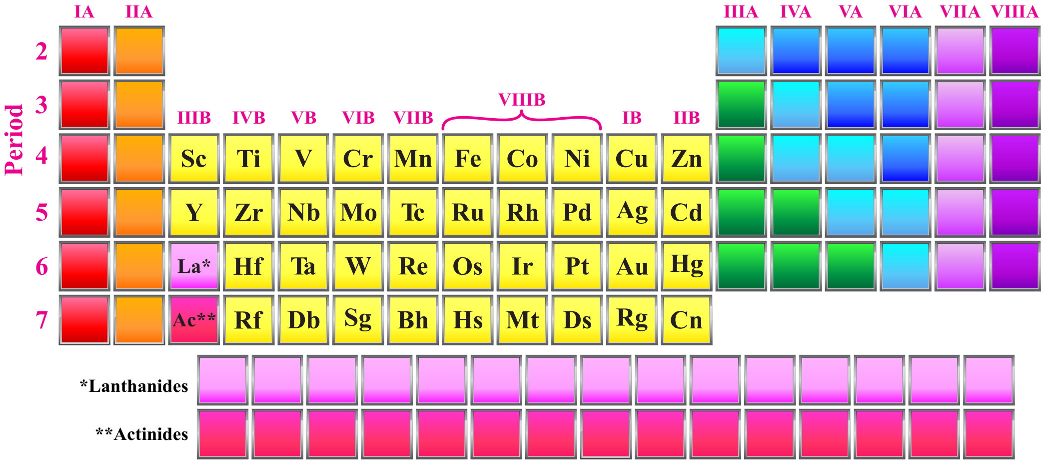
CHAPTER 2

CHEMISTRY OF OUTER TRANSITION ELEMENTS

Teaching Periods	**09**	**Assessment**	**01**	**Weightage %**	**07**



Students will be able to:

- ✓ Describe electronic structures of elements and ions of d-block elements. (Applying)
- ✓ Explain why the electronic configuration for chromium and copper differ from those assigned using the Aufbau principle. (Analyzing)
- ✓ Describe general features of transition elements (Understanding)
- ✓ Enlist oxidation states of Cr, Mn, Fe, Co. (Applying)
- ✓ Explain origin of colors and nomenclature of coordination compounds. (Applying)
- ✓ Describe important reactions and uses of Chromium, Manganese, Iron and Copper.
- ✓ Define an alloy and describe some properties of an alloy that are different from the metals that compose it. (Analyzing)
- ✓ Describe the Steel, types and its applications. (Understanding)
- ✓ Enlist alloys of d block elements and their applications in tabular form (Applying).
- ✓ Describe the reactions of potassium dichromate with oxalic acid and Mohr's salt. (Understanding)
- ✓ Describe the reactions of potassium permanagnate with ferrous sulphate, oxalic acid and Mohr's salt. (Understanding)
- ✓ Explain clearly the rules of nomenclature of coordination compounds with suitable examples (Applying)
- ✓ Enlist functions of some d-block elements and their important compounds in tabular form.

INTRODUCTION

The elements that possess partially occupied d-orbitals, either in their atomic state or any of their ionic states, are commonly referred as outer transition elements or d-block elements. These elements are positioned in the middle section of the periodic table and are recognized for their intermediate characteristics between s-block and p-block elements. The elements are called d-block elements because they possess partially filled d-electrons in their valence shell. These elements hold considerable significance across numerous domains of chemistry and industries due to their versatile oxidation states, catalytic activity, alloy forming ability, colour, complex forming ability, magnetic behavior and electrical conductivity. The unique electronic structure and broad range of oxidation states exhibited by these elements make significant contributions to the advancement of technology in industry and various scientific fields.

There are total four series of d-block elements found in the 4th, 5th, 6th and 7th periods.

3d – series:

This ten element series is located in the 4th period. It includes elements from scandium (Sc) to zinc (Zn).

4d – series:

This series is placed in 5th period and consists of elements from yttrium (Y) to cadmium (Cd).

5d – series:

This series is situated in the sixth period and consists of elements from lanthanum (La) to mercury (Hg).

6d – series:

This series consists of elements from actinium (Ac) to copernicium (Cn).

2.1 GENERAL FEATURES OF OUTER TRANSITION ELEMENTS

Outer transition elements typically exhibit metallic luster and shiny appearance. They possess hardness, high density and are malleable and ductile. These elements also have elevated melting and boiling points. Being situated in the middle of the periodic table, their atomic radii fall within an intermediate range, neither excessively large nor small.

The general physical properties of the first series of outer transition elements are summarized in Table 2.1.

Table 2.1 **Physical properties of 3d series of outer transition elements**

Elements	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic No. (z)	21	22	23	24	25	26	27	28	29	30
Atomic size (pm)	144	132	122	117	117	117	116	115	117	125
1st ionization potential (KJ/mol)	632	661	648	653	716	762	757	736	745	908
Melting Point (°C)	1539	1668	1760	1875	1245	1535	1480	1452	1083	419
Boiling point (°C)	3900	3130	3000	2480	2087	2450	2900	2900	2310	907
Electronegativity	1.3	1.5	1.6	1.6	1.5	1.8	1.8	1.8	1.9	1.6

2.1.1 Electronic Structure

d-block elements have valence electrons both in outer most and second outer most shells (penultimate) therefore the general valence electronic configuration of these elements is represented by $(n\text{-}1)d^{1-10}$, $ns^{1,2}$, where "n" is the outermost shell and n-1 is the penultimate shell.

In the context of the electronic configuration of the 3d series, the filling of electrons occurs in a sequential manner across the row (Sc to Zn). Typically the 4s orbital is filled prior to 3d orbitals. This pattern follows the guidelines set forth by Aufbau principle.

However, there are exceptions observed in chromium and copper where an electron is transferred from 4s orbital to 3d orbital in order to achieve more stable arrangement. Chromium contains four single parallel electrons in its 3d orbitals therefore one electron of 4s orbital jumps into 3d orbital to make it half-filled and reaches the more stable electronic configuration ($4s^1$, $3d^5$).

A similar pattern is observed in the case of copper where a 4s electron is excited and moves into the 3d orbital, resulting in a completely filled 3d sub shell. The electron rearrangement makes a more stable configuration of copper ($4s^1$ $3d^{10}$).

Cr (z = 24) =	1	1	1	1	1	1	($4s^1$, $3d^5$)
	4s			3d			

Cu (z = 29) =	1	1⇂	1⇂	1⇂	1⇂	1⇂	($4s^1$, $3d^{10}$)
	4s			3d			

2.1.2 Binding Energy

"The amount of energy required to separate the constituents of a bound system, such as atoms, nuclei, or particles". It represents the strength of the attractive forces holding the system together.

The d-block elements have partially filled d orbitals, which contribute to their unique properties. Their binding energy is higher than that of other elements due to the strong attraction to their outermost d electrons. The binding energy increases across a period from left to right in the d-block elements due to increasing nuclear charge and decreasing atomic radius. The stronger positive charge attracts the d electrons more, requiring more energy to remove them.

Down a group, the binding energy tends to decrease in the d-block elements. This is because the increasing atomic size and shielding effect reduce the effective nuclear charge felt by the outermost d electrons, making them easier to remove.

2.1.3 Variable Oxidation States

The variable oxidation states displayed by transition elements are recognized as one of their distinctive properties. The oxidation states of transition metal ions are in the range of +1 to +7. **"This variation is due to very small energy difference between 3d and 4s orbitals"**. As a result, electrons of 3d as well as 4s orbitals take part in the bond formation. The oxidation states of 3d series of transition elements increase from scandium to manganese and then decrease up to zinc. The most common oxidation state of transition elements is +2 and the highest oxidation state is +7 for manganese as shown in Table 2.2.

Table 2.2 Oxidation states of the elements of 3d series

Elements	Outer Electronic Configuration	Oxidation States
Scandium (Sc)	$[Ar]3d^1\ 4s^2$	+2, +3
Titanium (Ti)	$[Ar]3d^3\ 4s^2$	+2, +3, +4
Vanadium (V)	$[Ar]3d^3\ 4s^2$	+2, +3, +4, +5
Chromium (Cr)	$[Ar]3d^5\ 4s^1$	+1, +2, +3, +4, +5, +6
Manganese (Mn)	$[Ar]3d^5\ 4s^2$	+2, +3, +4, +5, +6, +7
Iron (Fe)	$[Ar]3d^6\ 4s^2$	+2, +3, +4, +5, +6
Cobalt (Co)	$[Ar]3d^7\ 4s^2$	+2, +3, +4
Nickel (Ni)	$[Ar]3d^8\ 4s^2$	+2, +3, +4
Copper (Cu)	$[Ar]3d^{10}\ 4s^1$	+1, +2
Zinc (Zn)	$[Ar]3d^{10}\ 4s^2$	+2

Argon (Ar) 18 = $1s^2, 2s^2, 2p^6, 3s^2, 3p^6$

Self Assessment

Write down the electronic configurations of the following transition metals. Vanadium (V), Manganese (Mn), Nickle (Ni) and Titanium (Ti).

2.1.4 Catalytic Activity

Transition elements are well known for their significant catalytical activity. **"Most of the transition elements and their compounds serve as catalysts in numerous chemical reactions"**. For example nickel (Ni) is used in the addition reaction of alkene, iron is used in the synthesis of ammonia (NH_3) and vanadium pentaoxide (V_2O_5) is used in the manufacturing of sulphuric acid by contact process.

The property of transition metals to serve as catalyst can be explained by the following factors.

DO YOU KNOW?

Ruthenium (Ru) catalysts are being explored for water splitting reactions, which involve the conversion of water into hydrogen and oxygen through electrolysis. These catalysts play a vital role in renewable energy technologies like hydrogen production and fuel cells.

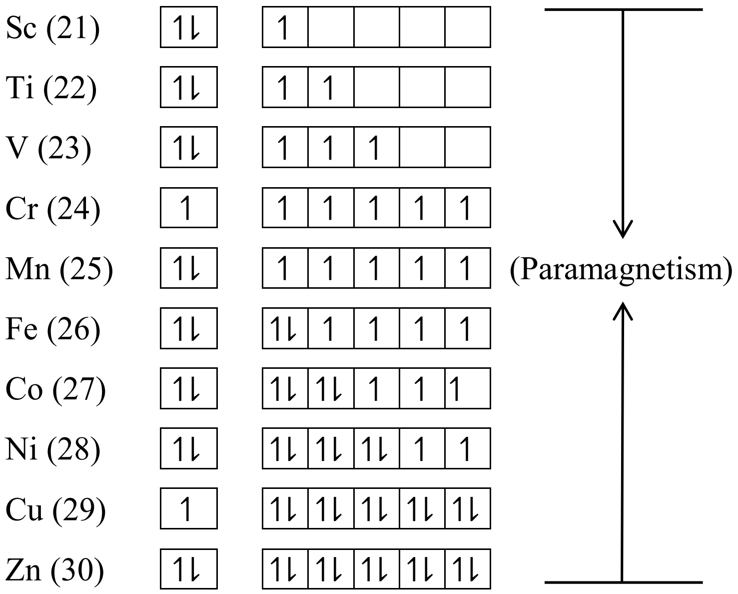
(i) Transition elements have variable oxidation states. They can easily withdraw or lend electrons from the reagent to form unstable intermediate which then changes into the final product.

(ii) The surfaces of transition metals offer many active sites where reactant molecules can adsorb.

2.1.5 Magnetic Behavior

Atoms, ions or molecules when exposed to a strong external magnetic field, exhibit two distinct behaviors, either they are weakly attracted or repelled by the magnetic field. **"The substances that are attracted by the magnetic field are called paramagnetic substances and those which are repelled by magnetic field are known as diamagnetic substances"**.

Most of the transition elements and their ions show paramagnetic behaviour. This is due to the fact that d-orbitals of these elements possess one or more unpaired electrons and the spinning of unpaired electrons generates a magnetic moment. This magnetic moment causes the ion to interact with the external magnetic field.



The paramagnetic behaviour is more pronounced in the middle of 3d series due to the maximum spin of electrons. However, zinc is diamagnetic since it lacks unpaired electrons in its d-orbitals.

Self Assessment

Write down the valence electronic configurations of the following transition metal ions.

Cu^{+2}, Cu^{+1}, Fe^{+3}, Cr^{+3}, Fe^{+2}, Mn^{+2}, Co^{+2}

2.1.6 Alloy Formation

"Alloy is a homogenous mixture of two or more elements with at least one of them being a metal".

Transition elements have the tendency to form alloys because of their similarities in atomic size which enable them to mix easily with one another.

Alloys of transition metals exhibit greater rigidity, strength, light weight and shine compared to pure metals. Moreover, they possess enhanced resistance against corrosion. The composition and uses of some alloys are given in Table 2.3.

DO YOU KNOW?

Brass and Bronze both are copper-based alloys but they have different compositions and properties. Brass is yellowish coloured while bronze is reddish brown coloured. Brass is more resistant to corrosion than bronze.

Table 2.3 **Compositions and important uses of some alloys of transition-elements**

Alloys	Compositions	Important Uses
Stainless steel	Iron, Chromium and Nickel	In making cutlery, and surgical instruments.
Duralumin	Aluminum, Copper Magnesium and Manganese	In making utensils, aeroplane etc.
Brass	Copper and Zinc	In plumbing and automotive parts etc
Bronze	Copper and Aluminum	In making medals, statues, coins etc

2.1.7 Colour of Complexes

Transition elements possess partially filled d-orbitals. **“When a transition metal cation interacts with ligand, its five degenerate d-orbitals split into two sets of energy levels known as t$_2$g (lower energy level) and eg (higher energy level)”** as shown in figure 2.1.

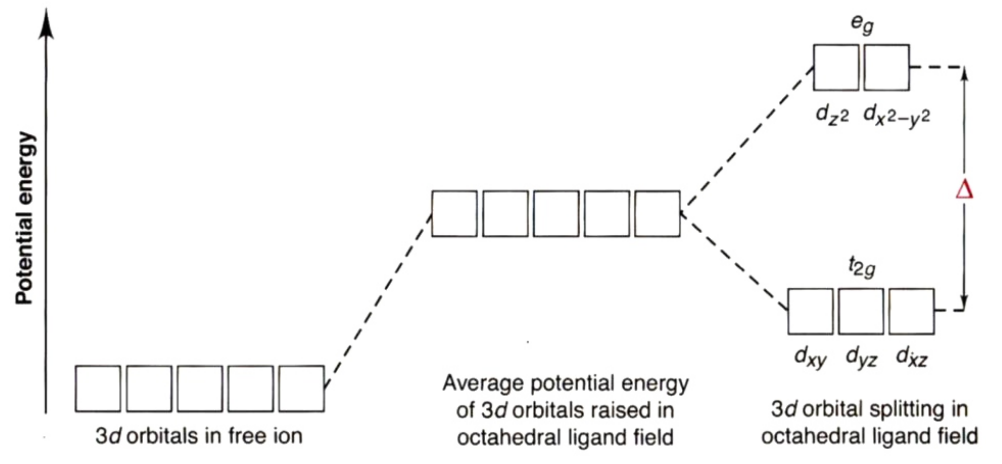


Fig 2.1: Splitting of five degenerate d-orbitals into t$_2$g and eg energy level

The energy difference between t$_2$g and eg orbitals is commonly known as crystal field splitting and is denoted by Δ_o (Δ_o = energy difference for octahedral splitting).

When visible light falls on a sample of a transition metal complex, electrons from the lower energy level (t$_2$g) are promoted to the higher energy level (eg) by absorbing light of specific wave length. The absorbed light corresponds to the energy difference between the two energy levels (d-d transition). The remaining wavelengths of light are transmitted, which gives characteristic colour.

Different complex ions of transition metals show different colours depending on the

DO YOU KNOW?

Visible light is composed of seven distinct colours when it interacts with transition metal ion, certain colours are selectively absorbed through d-d transitions while the rest pass through. For example Ti^{+3} complex absorbs yellow and green light while transmitting blue and red light, thereby giving rise to the perception of a violet colour.

oxidation state of the metal ion and the nature of ligands. Zinc complex ions are generally colourless since, there is no unpaired electron available in d-orbitals and hence d-d transition of the electron is not possible in zinc complexes. The Colours of certain transition metal ions are shown in figure 2.2.

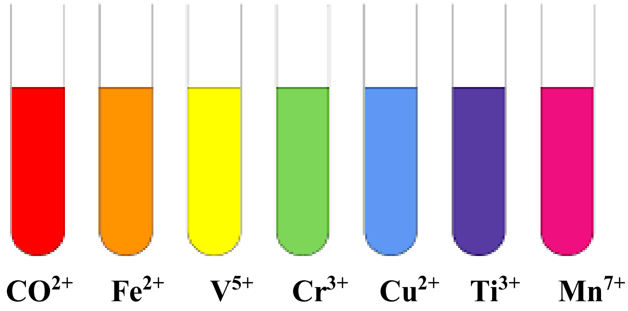


Fig 2.2: Colour of certain transition metal ions

For example when visible light fall on a tetraaminetitanium(III) $[Ti(NH_3)_4]^{+3}$ Complex ion, most of the component of light absorb in d-d transition while the waves of green colour are transmitted. This give rise to the green colour to the complex as shown in figure 2.3.

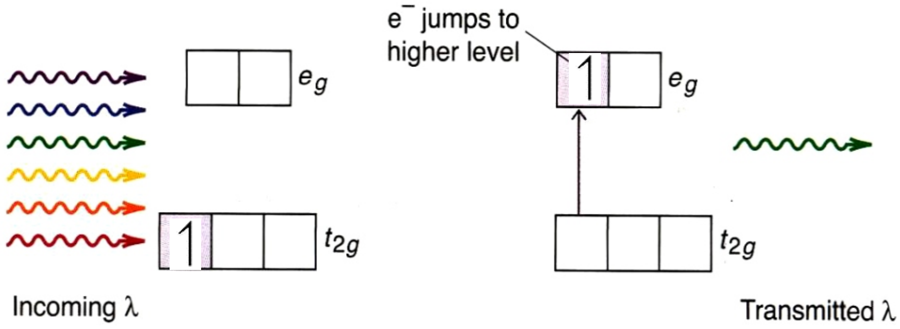


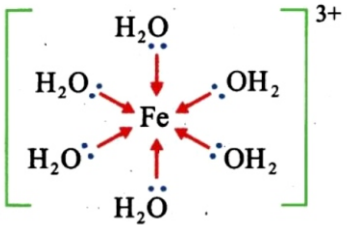
Fig 2.3: d-d transition of electron in $[Ti(NH_3)_4]^{+3}$ complex ion

Self Assessment

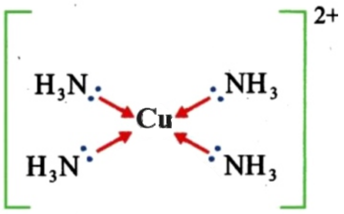
Explain why Tetraaminecopper(II) $[Cu(NH_3)_4]^{+2}$complex ion is blue but Tetrahydroxozincate(II) $[Zn(OH)_4]^{-2}$ is colourless?

2.2 NOMENCLATURE OF COORDINATION COMPOUNDS

Coordination compounds or coordination complexes are substances in which a central transition metal is surrounded by certain negative ions or neutral molecules known as ligands. These ligands possess one or more lone pairs of electrons that can be donated to the metal ion forming coordinate bond and the coordination number ranges 1-16. **"The number of coordinate bond exist between the metal ion and the surrounding ligands is known as coordination number"**.



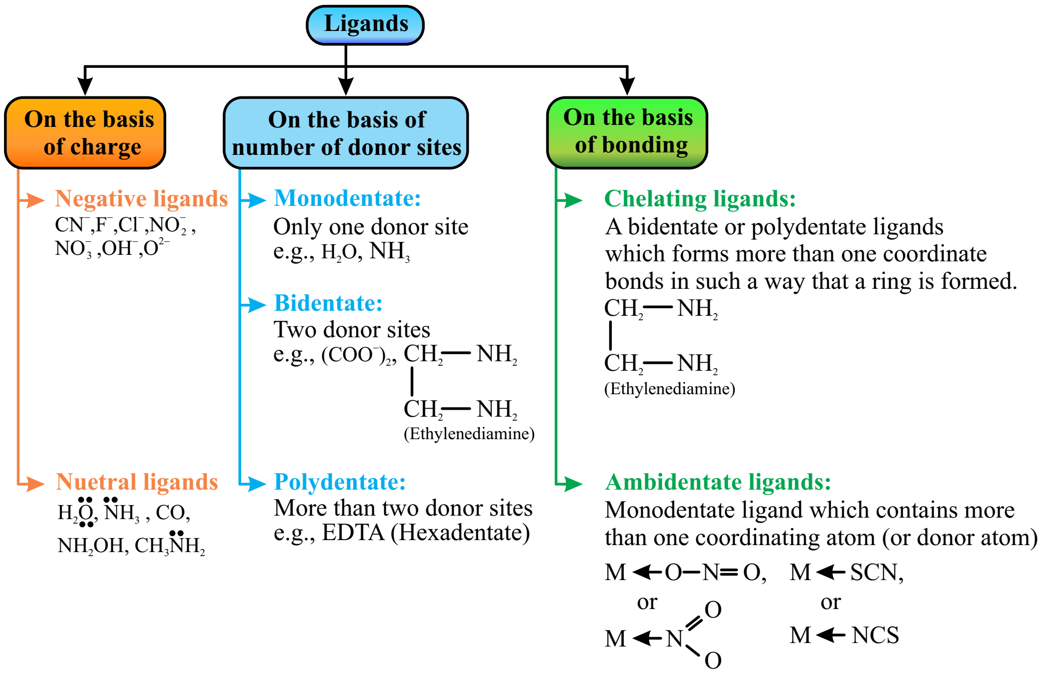
(**$[Fe(H_2O)_6]^{3+}$ Complex**)



(**$[Cu(NH_3)_4]^{2+}$ Complex**)

Ligands are the species that directly attached to the central atom or ion in the coordination complex and serve as coordinating group or Lewis base.

Classification of ligands



Ligands

On the basis of charge

- **Negative ligands**
  $CN^-, F^-, Cl^-, NO_2^-, NO_3^-, OH^-, O^{2-}$
- **Nuetral ligands**
  $H_2\ddot{\underset{\cdot\cdot}{O}}, \ddot{N}H_3$, CO, NH_2OH, $CH_3\ddot{N}H_2$

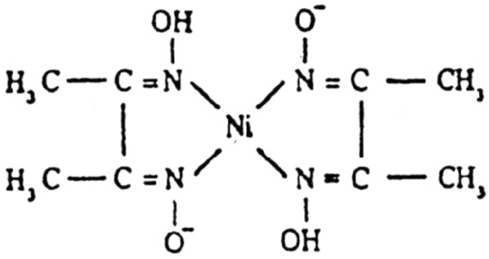
On the basis of number of donor sites

- **Monodentate:**
  Only one donor site
  e.g., H_2O, NH_3
- **Bidentate:**
  Two donor sites
  e.g., $(COO^-)_2$, $\begin{array}{l} CH_2-NH_2 \\ | \\ CH_2-NH_2 \end{array}$
  (Ethylenediamine)
- **Polydentate:**
  More than two donor sites
  e.g., EDTA (Hexadentate)

On the basis of bonding

- **Chelating ligands:**
  A bidentate or polydentate ligands which forms more than one coordinate bonds in such a way that a ring is formed.
  $\begin{array}{l} CH_2-NH_2 \\ | \\ CH_2-NH_2 \end{array}$
  (Ethylenediamine)
- **Ambidentate ligands:**
  Monodentate ligand which contains more than one coordinating atom (or donor atom)
  $M \leftarrow O-N=O$, or $M \leftarrow N\begin{matrix} {}^{/\!/}O \\ {}_{\setminus}O \end{matrix}$
  $M \leftarrow SCN$, or $M \leftarrow NCS$

Bidenate and Multidentate ligands are known as chelating agents because their multipoint attachment to metal ion form a ring structure that resembles the claws of a crab (chelate meaning claw) **"A chelate is a complex of multidentate ligand"**. An example of chelate is nickel dimethyl glyoximate.



(Nickel dimethyl glyoximate)
(Chelate)

General rules of IUPAC naming of coordination compounds

International Union of Pure and Applied Chemistry (IUPAC) recommended following rules for the naming of coordination complexes.

(i) Cation is always named before anion and there should be a space between the names of cation and anion.

For example, in the complex $Na_3[Co(CN)_6]$, sodium (Na) is a simple cation and $[Co(CN)_6]$ is a complex anion, therefore according to the rule, the name of sodium is written first. Similarly, in the complex $[Cr(NH_3)_4]SO_4$, the $[Cr(NH_3)_4]^{+2}$ is a complex cation and SO_4^{-2} is a simple an ion therefore the name of $[Cr(NH_3)_4]^{+2}$ is written first before SO_4^{-2} ion.

(ii) The names of ligands are written in alphabetical order before the names of central metal atoms without any space between metal and ligand names.

(iii) While naming coordination sphere, the name of ligand is written prior to the name of metal.

(iv) Use Greek prefixes to indicate the number of each type of ligand, for example if there are four water molecules serving as ligand in the complex, use the term tetra. Similarly for six water molecules, it is written as hexa.

(v) Determine the oxidation state of metal and indicate it in parentheses ( ) by Roman numbers followed by the name of the metal.

(vi) The number of inorganic ligands are indicated by prefix such as di-, tri-, tetra, penta and hexa etc, while for organic ligands the prefix bis-, tris-, tetrakis-, etc are used to indicate the number of those ligands.

(vii) The names of negative ligands are modified to end in "O" for example fluoro (F), chloro (Cl^-), bromo (Br^-) thiocyanato (SCN^-), amido (NH_2^-), oxalato ($C_2O_4^{-2}$), carbonato (CO_3^{-2}), hydroxo (OH^-), thiosulphato ($S_2O_3^{-2}$) etc.

(viii) The name of neutral ligand usually remains unchanged for example amine (NH_3), carbonyl (CO), nitrosyl (NO). However, for water its name should be taken as "aquo".

(ix) In the case of anionic complex, the metal name will be written suffix "-ate" is added to the metal name after removing "-ium" or "-um" if present in Latin names.

(x) In case of cationic and neutral complexes, the metal name will be written as English name.

IUPAC naming of so--me coordination complexes

(i) $[Cu(NH_3)_4]SO_4$
Tetraaminecopper (II) sulphate

(ii) $[Cr(H_2O)_4Cl_2]NO_3$
Tetraaquodichlorochromium (III) nitrate

(iii) $K_4[Fe(CN)_6]$
Potassiumhexacyanoferrate (II)

(iv) $[Pt(NH_2 - CH_2 - CH_2 - NH_2)_3]Cl_4$
Trisethylenediamineplatinum (IV) chloride

(v) $[Co(NH_3)_3(NO_2)_3]$
Triaminetrinitrocobalt (III)

(vi) $[Zn(OH)_4]^{-2}$
Tetrahydroxozincate (II) ion

(vii) $[Cu(en)_2]^{+2}$
Bisethylenediaminecopper (II) ion

Self Assessment

Write the IUPAC names of the following complexes.

- $[Pt(H_2O)_5Cl](NO_3)_3$
- $[Cr(NH_3)_4]^{+3}$
- $K_2[Cu(CN)_4]$
- $[AlF_6]^{-3}$

2.3 CHEMISTRY OF SOME IMPORTANT TRANSITION ELEMENTS

2.3.1 Chromium

Chromium is the fourth member of 3d series of transition elements. It is characterized by its silvery grey colour and metallic luster. It is widely used as protective coating on metal surfaces to prevent them from corrosion.

Chromium exhibits various oxidation states (+2, +3, +4, +5, +6) due to the electronic configuration of its atom ($3d^5$, $4s^1$). The multiple oxidation states of chromium allow it to play a versatile role in redox reactions. In lower oxidation states, it serves as a reducing agent while in higher oxidation state it works as an oxidizing agent.

Chromium reacts with dilute hydrochloric acid to liberate hydrogen gas

$$2Cr_{(s)} + 6HCl_{(aq)} \longrightarrow 2CrCl_{3(aq)} + 3H_{2(g)}$$

Chromium reacts with oxygen to form chromium oxide

$$4Cr_{(s)} + 3O_{2(g)} \xrightarrow{\text{Heat}} 2Cr_2O_{3(s)}$$

Chromium reacts with steam at high temperatures to form chromium oxide with the liberation of hydrogen.

$$2Cr_{(s)} + 3H_2O_{(s)} \xrightarrow{\text{Heat}} Cr_2O_{3(s)} + 3H_{2(g)}$$

Chromium is used in the production of stainless steel, chrome plating, pigments and as a catalyst in certain chemical reactions.

2.3.1.1 Chemistry of Potassium dichromate

Potassium dichromate is a red crystalline solid that is highly soluble in water. If it dissolves in water at neutral pH, a chromate and dichromate equilibrium is formed which shows an orange red colour.

$$\underset{\textbf{(red)}}{Cr_2O_7^{-2}{}_{(aq.)}} + H_2O_{(\ell)} \rightleftharpoons \underset{\textbf{(yellow)}}{2CrO_4^{-2}{}_{(aq.)}} + 2H^+_{(aq.)}$$

This equilibrium between chromate and dichromate ions is pH sensitive. When an acid is added, the equilibrium shifts to the left, resulting in the formation of a red dichromate solution. On the other hand if a base is added, the equilibrium shifts to the right, leading to the formation of a yellow chromate solution.

The preparation of Potassium dichromate is commonly done by using chromates and these chromates are formed by the reaction of chromite ore with sodium or potassium carbonate.

Potassium dichromate is used as an oxidizing agent in various chemical reactions since it possesses the highest oxidation state of chromium (+6).

The redox titration of potassium dichromate with oxalic acid ($H_2C_2O_4$) and Mohr's salt ($Fe(NH_4)_2(SO_4)_2.6H_2O$) is commonly carried out in the laboratories for determining the concentration of analyte. The end point of this titration is indicated by the colour change from orange (Cr^{+6}) to green (Cr^{+3}).

$$\underset{\textbf{(orange)}}{2Cr_2O_7^{-2}} + 3H_2C_2O_4 + 8H^+ \longrightarrow \underset{\textbf{(green)}}{4Cr^{+3}} + 6CO_2 + 7H_2O$$

$$\underset{\textbf{(orange)}}{Cr_2O_7^{-2}} + 6Fe^{+2} + 14H^+ \longrightarrow \underset{\textbf{(green)}}{2Cr^{+3}} + 6Fe^{+3} + 7H_2O$$

2.3.2 Manganese

Manganese is a greyish white, hard and brittle metal. It ranks as the twelfth most prevalent element within the Earth crust.

It exists in various oxidation states. For example the oxidation state of manganese in potassium permanganate

($KMnO_4$) is +7 and in manganese dioxide (MnO_2) it is +4, where as in manganese chloride ($MnCl_2$) it is +2.
Manganese reacts with air to form manganese oxide Mn_3O_4.

$$3Mn_{(s)} + 2O_{2(g)} \longrightarrow Mn_3O_{4(s)}$$

Manganese reacts with chlorine to form manganese chloride.

$$Mn_{(s)} + Cl_2 \longrightarrow MnCl_{2(s)}$$

Manganese when dissolves in dilute sulphuric acid, it liberates hydrogen gas.

$$Mn_{(s)} + H_2SO_{4(aq)} \longrightarrow MnSO_{4(aq)} + H_{2(g)}$$

Manganese is used in the production of steel, alloys, batteries, ceramics and glasses etc. It is an essential nutrient and play vital role in metabolism, bone development and enzyme function.

2.3.2.1 Chemistry of Potassium Permanganate

Potassium permanganate is a deep purple crystalline solid. Commercially, potassium permanganate ($KMnO_4$) is prepared by mixing a solution of potassium hydroxide (KOH) with powdered manganese dioxide (MnO_2) along with an oxidizing agent such as potassium chlorate ($KClO_3$). It is highly soluble in water, forming a pink solution, potassium permanganate is a powerful oxidizing agent. It works either in acidic, alkaline or neutral medium.

In acidic solutions permanganate ion accept five electrons and change from MnO_4^- to Mn^{+2}.

$$MnO_4^- + 8H^+ + 5\bar{e} \longrightarrow Mn^{+2} + 4H_2O$$

In basic or neutral medium it accepts three electrons and changes from MnO_4^- to MnO_2.

$$MnO_4^- + 2H_2O + 3\bar{e} \longrightarrow MnO_2 + 4O\bar{H}$$

The reaction of potassium permanganate with ferrous sulphate and Mohr's salt is given as;

$$MnO_4^- + 5Fe^{+2} + 8H^+ \longrightarrow Mn^{+2} + 5Fe^{+3} + 4H_2O$$

The reaction of potassium permanganate with oxalic acid is given as

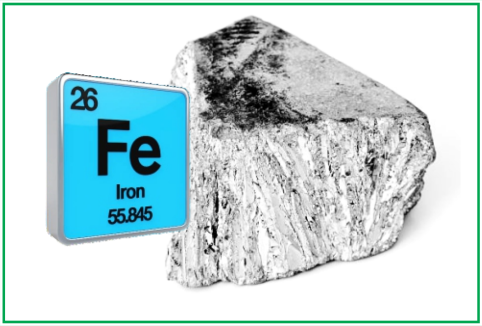
$$2MnO_4^- + 5C_2O_4^{-2} + 16H^+ \longrightarrow 2Mn^{+2} + 10CO_2 + 8H_2O$$

Potassium permanganate is used as a powerful oxidizing agent in various applications, including water treatment for purification and disinfection, and as a chemical reagent in organic synthesis and laboratory experiments.

Self Assessment

Explain why potassium dichromate and potassium permanganate are generally used in redox titration.

2.3.3 Iron



Iron is the fourth most abundant element in the Earth crust. Its strength and magnetic properties make it valuable in industries such as construction and manufacturing. Furthermore, iron is an indispensable component of haemoglobin, emphasizing its critical role in the biological system.

When iron is exposed to air, it oxidizes and forms an oxide film on its surface which is rusting of iron.

$$4Fe_{(s)} + 3O_{2(g)} \longrightarrow 2Fe_2O_{3(s)}$$

When it reacts with excess of chlorine, it forms ferric chloride.

$$2Fe_{(s)} + 3Cl_{2(g)} \longrightarrow 2FeCl_{3(s)}$$

Iron is mainly used in the construction of buildings and flyovers. It is used in industries for making tools, weapons, appliances, rail tracks, trains, automobiles etc.

2.3.3.1 Steel Types and Applications

Steel is a widely used alloy comprised primarily of iron combined with some other elements. By the inclusion of carbon and other alloying elements in steel enhances its mechanical, thermal and chemical properties compared with simple iron.

There are several types of steel each characterized by unique compositions and properties suited for specific applications.

Type of Steel	Applications
Carbon Steel	Construction tools, machinery, pipes, tubes, automotive etc.
Stainless Steel	Kitchen appliances, Cutlery and Medical equipment
Tool Steel	Cutting and drilling equipment
Alloy Steel	Fry pan, Toaster etc

2.3.4 Copper

Copper is a dense metal with a reddish brown colour. It is malleable and ductile, allowing it to be easily shaped and wired. Copper is known for its excellent electrical conductivity and it ranks as second highest (after silver) electrical conductor among pure metals.

Copper reacts with conc. sulphuric acid to form copper sulphate and sulphur dioxide.

$$Cu + 2H_2SO_{4(conc.)} \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

Copper reacts with conc. nitric acid to form copper nitrate and nitrogen dioxide.

$$Cu + 4HNO_{3(conc.)} \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

Copper is primarily used in making electric wires, cables, motors and other electrical equipments. It is also used in plumbing, piping, telecommunication, coinage and alloy formation.

DO YOU KNOW?

Copper deposits of considerable significance are present in Pakistan, notably in the province of Balochistan. Two prominent copper mining projects in the country are the Saindak copper-gold mine and the Reko-diq copper-gold mine.

2.3.4.1 Metallurgy of Copper

Copper is present in Earth's crust in the combined form referred to as ore. The most abundant ore of copper is chalcopyrite ($CuFeS_2$). The process of extracting metal like copper from its ore is called metallurgy. The metallurgical operations associated with chalcopyrite ore include series of steps: such as crushing, grinding, Concentration, roasting, smelting and refining.

Concentration

In this stage, the objective is to eliminate gangue impurities from the powdered chalcopyrite ore. This is accomplished through a froth floating process, where the ore is blended with water that has pine oil added to it. Subsequently, air is introduced into the water, causing the ore particles to become coated with froth, while the gange particles settle to the bottom as shown in figure 2.4.

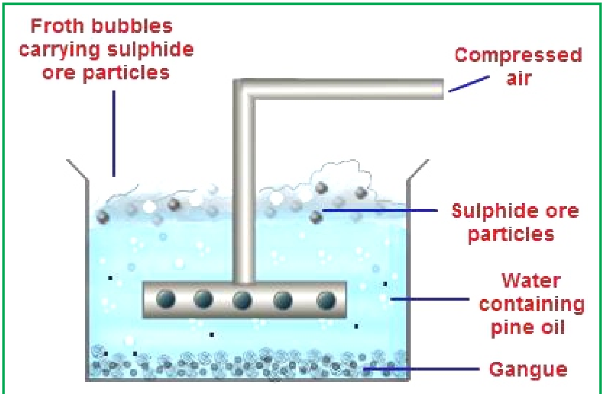


Fig 2.4: Concentration process of copper ore

Roasting

This process involves the heating of ore in the presence of excess air at an elevated temperature in a roasted kiln. As a result, the impurities oxidizes and the ore undergoes decomposition, leading to the formation of cupreous sulphide and ferrous oxide while sulphur dioxide is simultaneously eliminated.

$$2CuFeS_2 + 4O_2 \longrightarrow Cu_2S + 2FeO + 3SO_2$$

Smelting

Roasted ore along with silica and coal is charged into a blast furnace. The combustion of coal elevates the furnace temperature to approximately 1200°C to 1500°C. Within this environment, ferrous oxide (FeO) present in the ore reacts with silica, resulting in the formation of iron silicate ($FeSiO_3$) commonly referred to as slag. The slag floats on the surface of the molten matte while the matte (consisting of Cu_2S and some impurities) is separately collected from the slag.

$$\underset{\textbf{(Iron oxide)}}{FeO} + \underset{\textbf{(Silica)}}{SiO_2} \xrightarrow{1200°C - 1500°C} \underset{\textbf{(Slag)}}{FeSiO_3}$$

Bessemerization

The matte is subsequently fed into a pear shaped Bessemer converter, where hot gases are introduced from the mid lower portion. Within this converter, cuperous sulphide (Cu_2S) is partly converted into cuperous oxide (Cu_2O), which then reacts with the remaining cuperous sulphide, resulting in the production of molten metallic copper.

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$$

The copper thus produced is called blister copper because as it solidifies hidden sulphur dioxide gas escapes producing blisters on its surface. It is about 99% pure. The blister copper contains impurities mainly iron but small amount of arsenic, zinc, lead, silver and gold. Blister copper is not suitable especially for electrical purposes; therefore, it undergoes a refining process to remove all remaining impurities as shown in figure 2.5.

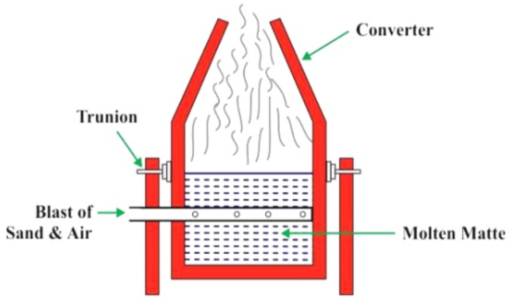


Fig. 2.5: Structure of Bessemer Converter

Refining of Copper

Copper is refined by electrolysis in an electrolytic tank. The blocks of blister copper are used as anodes and thin sheets of pure copper act as cathodes as shown in figure 2.6. The electrolyte is copper sulphate which is acidified with sulphuric acid. By passing electricity through the electrolytic solution, the blister copper undergoes oxidation and the Cu^{+2} ions produced in this oxidation process are then deposited onto cathode. The impurities are left behind which fall to the bottom of the cell as anode mud.

$$\underset{\textbf{(Blister copper)}}{Cu} \longrightarrow Cu^{+2} + 2\bar{e} \text{ (oxidation at anode)}$$

$$Cu^{+2} + 2\bar{e} \longrightarrow Cu \qquad \text{(reduction at cathode)}$$

Copper obtained after electrolytic refining is 99.99% pure.

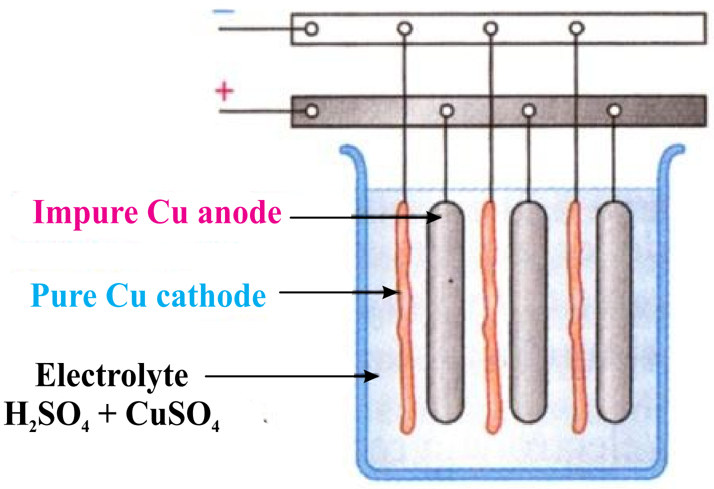


Fig 2.6: Electrolytic refining of blister copper

Table 2.4 **Commercial applications of some common transition elements**

Transition Elements	Commercial Applications
Titanium	In making artificial joints, bone plates, screws and dental implants.
Vanadium	Use in batteries, as a catalyst and as a pigment in glass making
Iron	Building and bridge construction and tool making.
Copper	In making copper wires, alloys and sanitary works.
Zinc	Galvanizing, alloying and also use in batteries
Platinum	In making jewellery and also serves as a catalyst.
Mercury	Use in thermometers, B.P. apparatus, and amalgam formation

SOCIETY, TECHNOLOGY AND SCIENCE

Use of transition metals in paints

Transition elements are widely used in the formulation of paints. They are often employed as pigments. For example, titanium dioxide is used as a white pigment, while iron oxide is used as a brown pigment. Certain transition metals such as zinc and chromium are added to paint formulations for corrosion inhibition. Additionally, certain transition metals, including various forms of zinc and titanium, are used to protect paint surfaces from the damaging effects of ultra violet light.

SUMMARY

- The elements that possess partially filled d-orbitals in their atomic or any of their ionic states are called outer transition elements.
- Transition elements are located in the mid portion of periodic table and cover up 4th, 5th, 6th and 7th periods.
- The general valence electronic configuration of transition elements is $(n - l)\ d^{1\text{-}10}, ns^{1,2}$.
- Chromium and copper deviate from the general trend of electronic configuration in 3d series of transition elements because of achieving extra stability.
- Binding energy of Mn^{+2} and Fe^{+3} are highest because they possess maximum unpaired electrons in their 3d orbitals.
- The most common oxidation number of transition metal cations is +2.
- Paramagnetic behavior of transition elements is due to the availability of unpaired electrons in their 3d orbitals.
- The colour phenomena of transition elements is due to the excitation of electron from t_{2g} to e_g energy levels by the absorption of light of specific wavelengths.

- Coordination number is the number of coordinate bonds formed between ligands and the transition metal in a complex molecule or ion.
- The complexes of multidentate ligands are known as chelates.
- Potassium dichromate and potassium permagnate are powerful oxidizing agents.
- Transition elements have ability to form alloys with each other due to the similarities in their atomic sizes.
- Stainless steel is the most common alloy of iron. It is made up of iron, chromium and nickel.
- The most common ore of copper is chalcopyrite ($CuFeS_2$).
- Refining of copper is carried out in an electrolytic tank where thick plates of blister copper serve as anode and thin sheets of pure copper act as cathode.

EXERCISE

Multiple Choice Questions

(i) Zn^{+2} ion is colourless because:
(a) Its undergoes d-d transition of electron
(b) Its 3d orbitals have all unpaired electrons
(c) Its 3d orbitals have all paired electrons
(d) Its d orbitals split up into t_2g and eg

(ii) The coordination number of cobalt in $Na_4[Co(C_2O_4)_3]$ is:

(a) 3	(b) 4
(c) 6	(d) 7

(iii) An example of a bidentate ligand among the following is:

(a) $O\bar{H}$	(b) $C_2O_4^{-2}$
(c) Cl^-	(d) $C\bar{N}$

(iv) A highly paramagnetic ion among the following is:

(a) Fe^{+2}	(b) Fe^{+3}
(c) Co^{+2}	(d) Cr^{+3}

(v) The highest oxidation state of chromium is:
(a) +4 (b) +5
(c) +6 (d) +7

(vi) The element is not used for electroplating:
(a) Zinc (b) Tin
(c) Chromium (d) Manganese

(vii) The steel is typically used in making Fry pans:
(a) Carbon steel (b) Stainless steel
(c) Tool Steel (d) Alloy Steel

(viii) The step which involved in the extraction of copper from chalcopyrite ore in the elimination of gangue impurities is:
(a) Concentration (b) Roasting
(c) Smelting (d) Bessemerization

(ix) 5d series of outer transition elements is:
(a) Sc to Zn (b) Y to Cd
(c) La to Hg (d) Ac to Cn

(x) Oxidation of manganese in air gives the following oxide:
(a) MnO (b) MnO_3
(c) Mn_2O_3 (d) Mn_3O_4

Short Questions

1. Write the IUPAC names of the following:
   - (i) $Na_2[Pt(OH)_4]$
   - (ii) $K_2[Fe(CN)_5NO]$
   - (iii) $[Zn(NH_3)_4]^{+2}$
   - (iv) $[Ni(SCN)_4]^{-2}$
2. Give reasons for the following:
   - (i) Why do transition elements show variable oxidation states?
   - (ii) Why transition elements have ability to form alloys?
   - (iii) Why Cu^{+2} ion is blue but Zn^{+2} is colourless?

(iv) Why chromium exists in $4s^1\ 3d^5$ configuration but not in $4s^2\ 3d^4$?
(v) Why binding energy of zinc is least in 3d series?

3. Write down the balanced chemical equations for the following reactions.
   (i) Reaction of conc. nitric acid with copper
   (ii) Reaction of conc. sulphuric acid with copper
   (iii) Reaction of permanganate with oxalic acid
   (iv) Reaction of dichromate with ferrous sulphate
   (v) Reaction of manganese with dilute sulphuric acid
   (vi) Reaction of iron with chlorine

4. Why d-block elements are called outer transition elements?

5. Write down the effect of pH changes on dichromate equilibrium in water.

6. Melting point of d-block elements increase up to middle of the series and then decrease why?

7. Give the composition and applications of stainless steel, brass and bronze.

Descriptive Questions

1. Explain the trend of following properties of 3d-series of transition elements.
   (a) Paramagnetic behavior
   (b) Variable oxidation state
   (c) Colour formation.

2. How can you define a coordination complex and a chelating ligand? Explain various types of ligands with examples.

3. Describe how 99.99% pure copper is obtained from its chalcopyrite ore.

4. Explain why transition elements and their compounds serve as catalysts in many chemical reactions.
5. What is meant by binding energy? Write down the trend of binding energy in 3d series of transition elements.