18

TRANSITION METALS

Student Learning Outcomes

[C-12- B-16 to C-12-B-46]

- Define a transition element as a d-block element which forms one or more stable ions with incomplete d orbitals.
- Identify the general physical and chemical properties of the first row of transition elements, titanium to copper.
- Identify the properties of transition elements (Some examples include:
  - a) they have variable oxidation states
  - b) they behave as catalysts
  - c) they form complex ions
  - d) they form coloured compounds
- Explain why transition elements have variable oxidation states in terms of the similarity in energy of the 3d and the 4s subshells.
- Explain why transition elements form complex ions in terms of vacant d orbitals that are energetically accessible.
- Explain why transition elements behave as catalysts in terms of having more than one stable oxidation state, and vacant d orbitals that are energetically accessible and can form dative bonds with ligands.
- Define the term complex as a molecule or ion formed by a central metal atom/ion surrounded by one or more ligands.
- Define the term ligand as a species that contains a lone pair of electrons that forms a dative covalent bond to a central metal atom/ion.
- State what is meant by coordination number.
- Use the term monodentate ligand including as examples H_2O, NH_3,, Cl^- and CN^-.
- Use the term bidentate ligand including as examples 1,2 diaminoethane, $H_2NCH_2CH_2NH_2$ and the ethanedioate ion, $C_2O_4^{2-}$.' polydentate ligand including as an example EDTA.
- Describe the geometry (shape and bond angles) of transition element complexes which are linear, square planar, tetrahedral or octahedral.
- Predict the formula and charge of a complex ion, given the metal ion, its charge or oxidation state, the ligand and its coordination number or geometry.
- Use the terms degenerate and non-degenerate d orbitals.
- Describe the splitting of degenerate d orbitals into two non-degenerate sets of d orbitals of higher energy, and use of ΔE in:
  - a) Octahedral complexes, two higher E and three lower E d orbitals
  - b) Tetrahedral complexes, three higher E and two lower E d orbitals
- Explain why transition elements form coloured compounds in terms of the frequency of light absorbed as an electron is promoted between two non–degenerate orbitals.
- Describe, in qualitative terms, the effects of different ligands on ΔE, frequency of light absorbed, and hence the complementary colour that is observed.

- Sketch the shape of a $3d_{xy}$ orbital and $3d_{z^2}$ orbital.
- Explain the reactions of transition elements with ligands to form complexes, including the complexes of copper(II) and cobalt(II) ions with water and ammonia molecules and hydroxide and chloride ions.
- Explain qualitatively that ligand exchange can occur, including the complexes of copper(II) ions and cobalt(II) ions with water and ammonia molecules and hydroxide and chloride ions.
- Use the complexes of copper(II) ions and cobalt(II) ions with water and ammonia molecules and hydroxide, chloride ions as examples of ligand exchange affecting the colour observed.
- Define the stability constant, K_{stab}, of a complex as the equilibrium constant for the formation of the complex ion in a solvent (from its constituent ions or molecules).
- Write an expression for a K_{stab} of a complex $[H_2O]$ should not be included).
- Use K_{stab} expressions to perform calculations.
- Explain ligand exchanges in terms of K_{stab} values and understand that a large K_{stab} is due to the formation of a stable complex ion."
- Describe the types of stereoisomerism shown by complexes, including those associated with bidentate ligands.
- Geometrical (cis-trans) isomerism, e.g. square planar such as $[Pt(NH_3)_2Cl_2]$ and octahedral such as $[Co(NH_3)_4(H_2O)_2]^{3+}$ and $[Ni(H_2NCH_2CH_2NH_2)_2(H_2O)_2]^{2+}$
- Deduce the overall polarity of complexes.
- Optical isomerism, e.g. $[Ni(H_2NCH_2CH_2NH_2)_3]^{2+}$ and $[Ni(H_2NCH_2CH_2NH_2)(H_2O)_2]^{2+}$.
- Predict, using E^0 values, the feasibility of redox reactions involving transition elements and their ions
- Analyse reactions involving MnO_4^- / $C_2O_4^{2-}$ in acid solution given suitable data (including describing the reaction and doing calculations).
- Analyse reactions involving MnO_4^-/ Fe^{2+} in acid solution given suitable data (including describing the reaction and doing calculations).
- Analyse reactions involving Cu^{2+}/ I^- given suitable data (including describing the reaction and doing calculations).
- Perform calculations involving other redox systems given suitable data.

Transition metals, found in d and f blocks of the modern periodic table, are characterized by their high density, conductivity, and ability to form colourful compounds. Iron stands as the backbone of human civilization; it has played a key role in the industrial revolution for the creation of durable tools and modern steel infrastructure. Copper, silver and gold are well known since ancient ages as symbols of wealth and prestige. They have been historically used for coinage and jewellery; they remain essential today in high-end electronics and dentistry due to their exceptional corrosion resistance and conductivity. From the steel in our cars to the gold in our smartphones, transition metals are highly valuable for our modern life. The transition metals can be classified on the basis of their electronic configuration into d-block (if their outermost electrons are being filled in d-orbitals) and f-block (if their outermost electrons are being filled in f-orbitals). However, as the d-block transition elements are more common in our daily life usage, and among them first row transition elements i.e., 3d-series, have a key role in human civilization and development, therefore, we shall focus on these 3d transition elements onwards in this chapter.

18.1 FIRST ROW TRANSITION ELEMENTS (3d)

First row transition elements are the elements found in the d block of the Periodic Table, having partially filled d-orbitals in any of their stable oxidation state. They are called transition elements because they show transitions between variable oxidation states. Although d-block elements are composed of groups 3 to 12, however, zinc and scandium cannot be classified as transition elements. Zn forms only one ion (Zn^{2+}), which has a complete 3d subshell, the electronic configuration of Zn^{2+} is [Ar] $3d^{10}\,4s^0$.

18.1.1 Electronic Configuration of Transition Metals and their Ions

Electronic configuration of the transition elements usually follows Aufbau principle, except in chromium and copper. These two elements show anomaly due to acquiring stability of half-filled (chromium; $3d^5$) and completely filled (copper; $3d^{10}$) d-subshell. This stabilizing factor makes the electron cloud of these two elements more symmetrical and provides a better shielding effect to nucleus. The electronic configuration of first row of transition elements in their neutral (M^0), dipositive (M^{2+}) and tripositive (M^{3+}) oxidation states are given in the following **Table 18.1**.

Table 18.1 Electronic configurations of first row transition elements

Element	Symbol	Atomic Number	Electronic Configuration		
			(M^0)	(M^{2+})	(M^{3+})
Titanium	Ti	22	[Ar] $3d^2\,4s^2$	[Ar] $3d^2\,4s^0$	[Ar] $3d^1\,4s^0$
Vanadium	V	23	[Ar] $3d^3\,4s^2$	[Ar] $3d^3\,4s^0$	[Ar] $3d^2\,4s^0$
Chromium	Cr	24	[Ar] $3d^5\,4s^1$	[Ar] $3d^4\,4s^0$	[Ar] $3d^3\,4s^0$
Manganese	Mn	25	[Ar] $3d^5\,4s^2$	[Ar] $3d^5\,4s^0$	[Ar] $3d^4\,4s^0$
Iron	Fe	26	[Ar] $3d^6\,4s^2$	[Ar] $3d^6\,4s^0$	[Ar] $3d^5\,4s^0$
Cobalt	Co	27	[Ar] $3d^7\,4s^2$	[Ar] $3d^7\,4s^0$	[Ar] $3d^6\,4s^0$
Nickel	Ni	28	[Ar] $3d^8\,4s^2$	[Ar] $3d^8\,4s^0$	[Ar] $3d^7\,4s^0$
Copper	Cu	29	[Ar] $3d^{10}\,4s^1$	[Ar] $3d^9\,4s^0$	[Ar] $3d^8\,4s^0$

18.2 PROPERTIES OF TRANSITION ELEMENTS

The first row of transition elements includes the metals from titanium to copper. The common physical and chemical properties arising due to their partially filled 3d orbitals are given as under.

18.2.1 Physical Properties

- The transition metals exist as hard and rigid solids.
- Except copper, which is reddish brown, others occur as silvery or grey lustrous metals.
- Their atomic radius usually decreases from left to right, however, at the end it increases a little. This increase may be associated to the stability acquired by copper due to its completely filled d-subshell.
- They have high melting and boiling points. The melting and boiling points of these elements show a variable trend from left to right as shown in **Figure 18.1**.
- They are good conductors of electricity and heat.
- They have high densities that generally increase across the row from titanium to copper. This is due to a regular build-up of nuclear charge and atomic size shrinkage.
- They possess a shiny surface, and are malleable (can be hammered into thin sheets), and ductile (can be drawn into wires).
- Most of them and their compounds are paramagnetic due to the presence of unpaired d electrons.

18.2.2 Chemical Properties

- Transition metals have variable oxidation states as they can lose varying number of electrons to form stable ions (e.g., Fe^{2+} and Fe^{3+}).
- They have a high tendency to form coordination compounds (complexes) by accepting lone pairs of electrons from ligands into vacant d-orbitals.
- They form coloured ions and complexes due to the transition of electrons from lower energy to higher energy level as a result of absorption of light.
- These metals and their compounds behave as catalysts because they can easily change oxidation states.

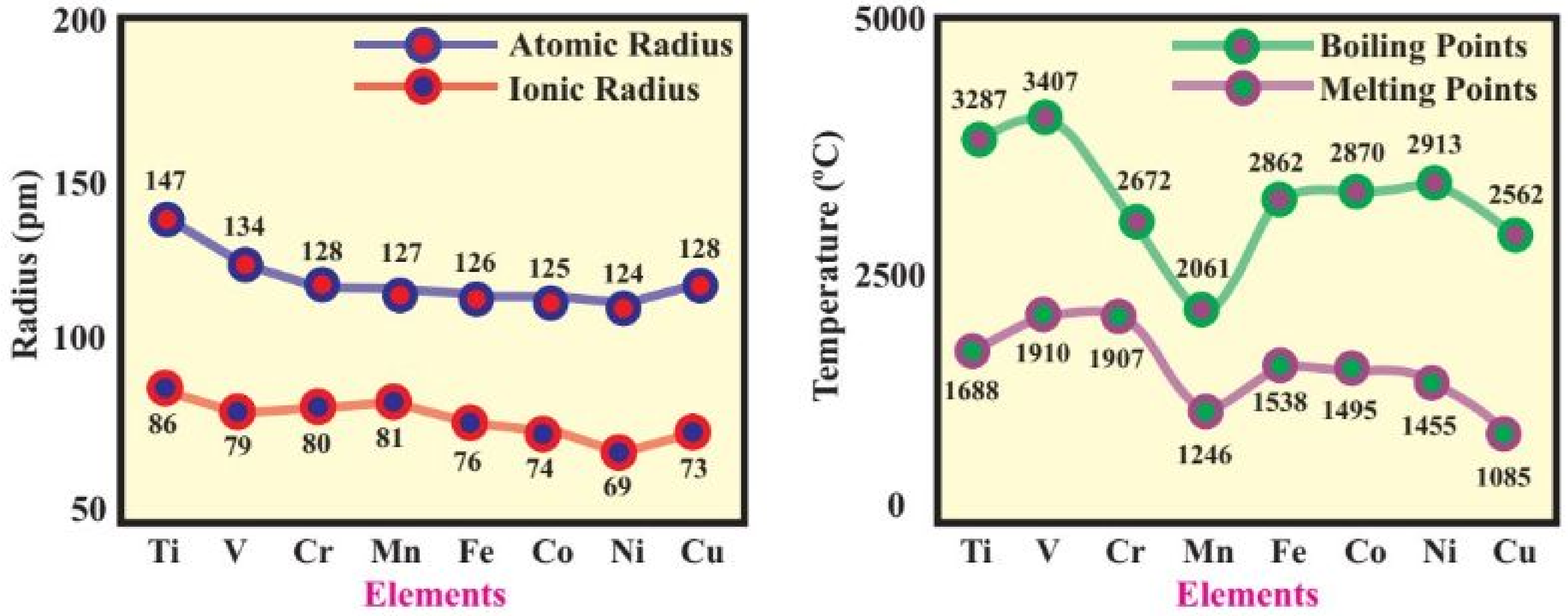


Figure 18.1 Atomic radii, ionic radii, melting points and boiling points of 3d transition elements

18.2.3 Variable Oxidation States

First row transition elements show variable oxidation states because the 3d and 4s subshells have comparable (very similar) energy. The energy difference between the inner 3d subshell and the outermost 4s subshell is very small. So, like 4s electrons, the 3d electrons can also easily be lost. This means that not only the electrons in the outermost 4s subshell but also the electrons in the partially filled 3d subshell are involved in chemical bonding.

A 3d metal atom can lose:

- Only the 4s electrons, usually giving the common +2 oxidation state.
- The 4s electrons plus a variable number of 3d electrons, giving the higher oxidation states.

Among these metals, Mn has the maximum oxidation state of +7. The oxidation state of transition elements varies in parabolic trend from left to right within d-block. The various oxidation states of 3d elements are provided in **Table 18.2.**

Table 18.2 Common oxidation states of 3d elements

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

Quick Check 18.1

a) Write down electronic configuration of Co^{2+} and Co^{3+}, and find the number of unpaired electrons in d- orbitals.

b) Why are the density and melting points of transition metals much higher than Group 1 metals?

c) The Sc^{3+} ion is $[Ar]\,3d^0\,4s^0$. Why is scandium not classified as a transition element?

18.2.4 Transition Metals as Catalysts

Transition elements act as effective catalysts to carry out various chemical reactions. They can easily switch between their different stable oxidation states (e.g., $Fe^{2+} \rightleftharpoons Fe^{3+}$). This allows the metal ion to form an unstable intermediate compound with a reactant molecule. The intermediate then quickly reacts to form the final product and regenerates the catalyst back to its original oxidation state, providing a reaction pathway with lower activation energy. This process usually occurs in homogenous catalysis. For example, nickel salts are used in the preparation of acrylic acid from acetylene, involve the oxidation states of Ni(0) and Ni(II).

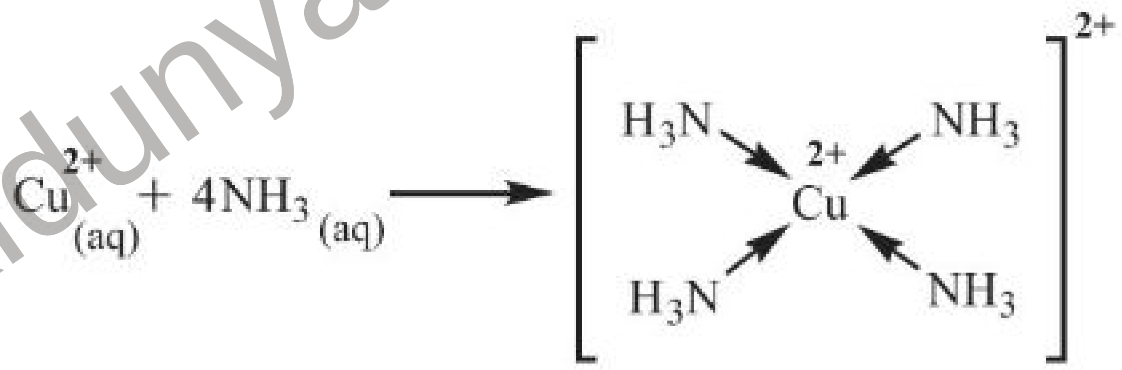
Another characteristic of transition metals is their vacant d-orbitals that are energetically accessible. Reactant molecules attach with the catalyst surface and form a temporary activated complex on the surface, which holds the reactants in the correct orientation, lowering the activation energy required for the reaction to occur. After the reaction, the products desorb, and the catalyst is ready for the next cycle. This process is generally observed in heterogeneous catalysis. A classic example of heterogeneous catalysis is the use of solid iron to accelerate the reaction between nitrogen and hydrogen gases to form ammonia in the Haber Process.

Quick Check 18.2

a) How Vanadium can show the range of oxidation states from +2 to +5?
b) What is the role of a ligand in forming a complex ion, and what type of bond is formed?
c) Why transition metals use both 4s and 3d electrons in bonding, unlike s-block elements.
d) Write the electronic configuration for Fe^{3+}. Why is the Fe^{2+}/ Fe^{3+}change useful in catalysis?
e) Which properties of transition metals enable them to be used as heterogeneous catalysts and homogeneous catalysts.

18.3 TRANSITION METAL COMPLEXES

Transition elements form complex ions because they have vacant (empty) d orbitals that are energetically accessible to accept electron pairs. The central transition metal ion (e.g., Fe^{3+} or Cu^{2+} has partially filled or empty (n-1)d orbitals.



The energy of these empty d-orbitals is low enough (accessible) to participate in bond formation. The vacant d-orbitals on the metal ion accept the lone pairs of electrons donated by the ligands, forming coordinate covalent bonds (or dative bonds). The electron pair donor species (molecules or ions, like H_2O, NH_3 or Cl^-) are called ligands. This donation and acceptance of electron pairs create a stable complex ion (or coordination compound).

A metal complex (or coordination compound) is a molecule or ion that forms when a central metal atom or ion is surrounded by a number of electron donor species (molecules or ions). A transition element acts as a Lewis acid (electron pair acceptor) in complex formation.

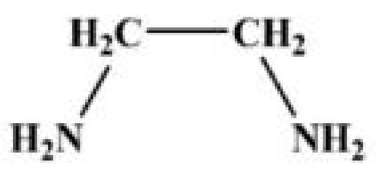
A ligand is a molecule or ion (for example, H_2O, NH_3 or Cl^-) that possesses at least one lone pair of electrons and forms a coordinate covalent bond (dative bond) to the central metal atom or ion in a complex. The word "ligand" originates from the Latin "*ligare*", meaning "to bind". It acts as a Lewis base because it donates an electron pair.

Ligands can be classified into different categories. The negatively charged electron pair donor species are called anionic ligands. These are the most abundant type of ligands. The most common examples are Cl^-, CN^-, OH^-, $C_2O_4^{2-}$ etc. Their names usually end at "-o", e.g., chloride becomes "chloro" and cyanide becomes "cyano" etc.

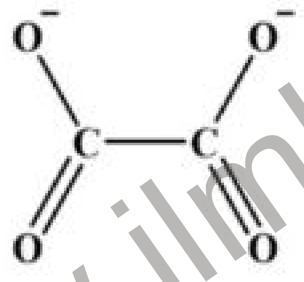
The neutral molecular species which are able to donate pair of electrons to form the transition metal complexes are called neutral ligands. For example, H_2O, NH_3, CO, etc. Their names usually remain the same, though some have special names like H_2O (aqua), NH_3 (ammine) and CO (carbonyl). The positively charged electron pair donating species are called cationic ligands. They are rare and their names often ends at "-ium". For example, NO^+ (nitrosonium), $NH_2\text{-}NH_3^+$ (hydrazinium) etc.

A monodentate ligand is a species that can donate only one pair of electrons to the central metal atom or ion. Some examples are H_2O, NH_3, CO, Cl^-, OH^- and CN^- etc. In each case, only a single atom on the ligand forms the dative covalent bond to the metal. Bidentate ligands can donate two electron pairs to the central metal atom/ion. Typical examples are 1,2-diaminoethane (also known as ethylenediamine) and ethanedioate (or oxalate) ion. In 1,2-diaminoethane ($H_2NCH_2CH_2NH_2$, abbreviated as ***en***), each of the two nitrogen (N) atoms donate a lone pair to the metal. In the ethanedioate ion ($C_2O_4^{2-}$), two oxygen (O) atoms, one from each carboxyl group, donate electron pairs.

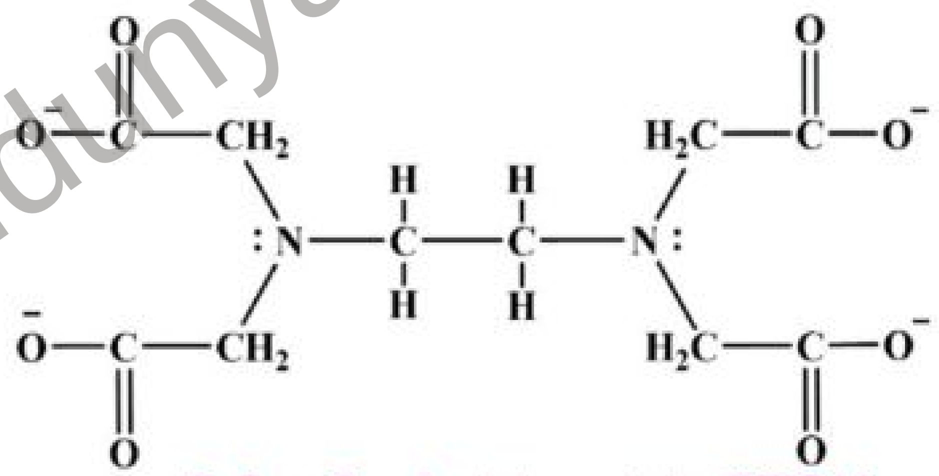
A polydentate ligand is a general term used for any ligand that forms more than two dative bonds to a single central metal atom/ion. Ethylenediaminetetraacetate ion (EDTA) is a common example. It is a hexadentate ligand because it can attach to a metal ion using six donor atoms (four oxygen and two nitrogen atoms).



1,2-diaminoethane



ethanedioate



ethylenediaminetetraacetate (EDTA)

The coordination number is the total number of dative bonds formed between ligands and the central metal atom or ion in a complex. For example, in the complex ion $[Fe(CN)_6]^{4-}$, the central metal ion Fe^{2+} is bonded to six CN^- ligands, so the coordination number of the metal ion is 6 as shown in **Figure 18.2**. The coordination number determines the overall structure of the complexes.

A coordination sphere is the central metal atom or ion and the directly bonded ligands (molecules or ions) surrounding it within a coordination compound. It defines the immediate chemical environment, is usually written inside square brackets [Complex].

The charge on coordination sphere is the arithmetic sum of the charges of central metal atom or ion and ligands. Whereas, the charge on the metal atom or ion will be the difference of the charge on sphere and total charge of ligands.

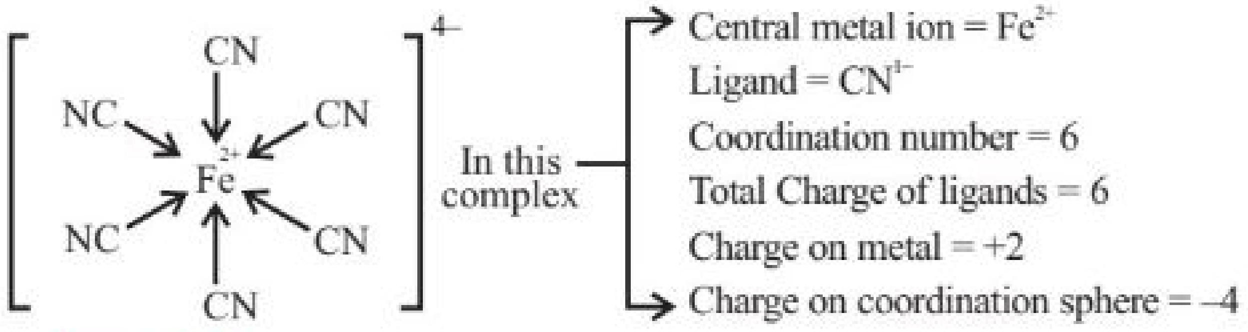


Figure 18.2 Hexacyanoferrate (II) complex and its components

18.4 PREDICTING FORMULA AND CHARGE OF A COMPLEX ION

The formula and charge of a complex ion are determined by combining the central metal ion, its oxidation state, and the ligands along with their charges. The general structure of a complex ion is $[\mathbf{M(L)_x}]^{\pm y}$. Where, M is the central metal ion, L is the ligand, x is the number of ligand (determined by the coordination number) and ±y is the overall charge of the complex ion.

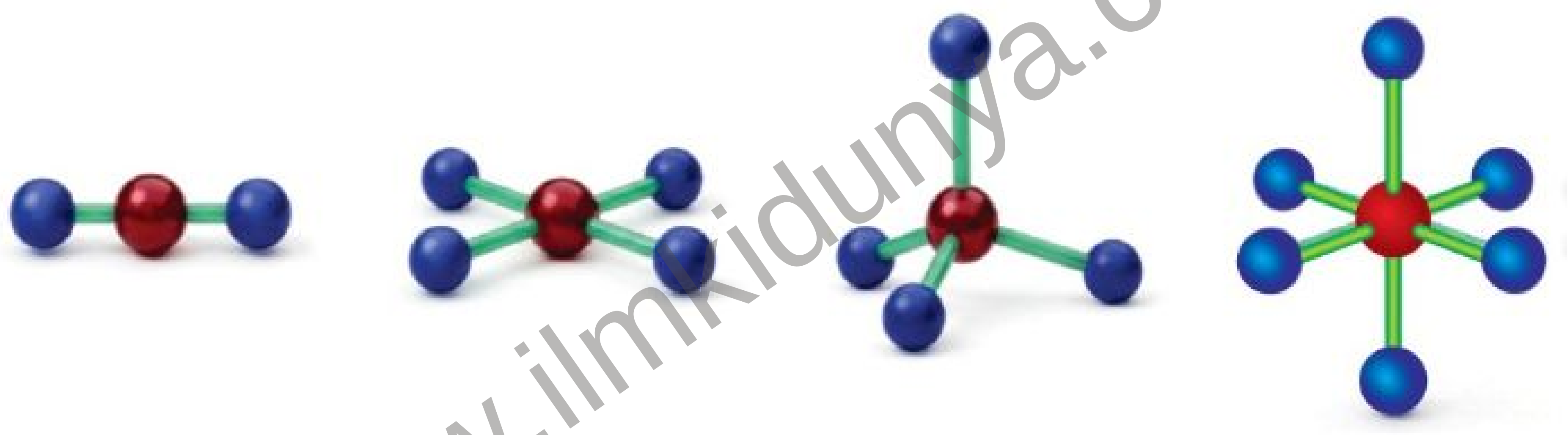
Table 18.3. Predicting formula and charge of a complex ion

Complex type	**Cationic Complex**	**Anionic Complex**	**Neutral Complex**
Metal Ion	Co	Fe	Ni
Oxidation state of metal	+3	+2	0
Ligand	NH_3 (Ammine)	CN^- (Cyano)	CO (Carbonyl)
Ligand type and charge	Neutral, 0	Anionic, -1	Neutral, 0
Coordination number	6	6	4
Determination of formula	Place Metal (Co) first, then Ligand (NH_3) with its number as a subscript (6), all inside square brackets [ ].	Place Metal (Fe) first, then Ligand (CN) with its number as a subscript (6), inside brackets [ ].	Place Metal (Ni) first, then Ligand (CO) with its number as a subscript (4), inside brackets [ ].
Calculate the charge	$(+3) + [6 \times (0)] = +3$	$(+2) + [6 \times (-1)] = -4$	$(0) + [4 \times (0)] = 0$
Explanation of charge calculation of complex	Metal charge (+3) + (Number of ligands × Ligand charge). A positive sum.	Metal charge (+2) + (Number of ligands × Ligand charge). A negative sum.	Metal charge (0) + (Number of ligands × Ligand charge). A zero sum.
Final form and charge	$\mathbf{[Co(NH_3)_6]^{3+}}$	$\mathbf{[Fe(CN)_6]^{4-}}$	$\mathbf{[Ni(CO)_4]}$

18.5 GEOMETRY OF TRANSITION METAL COMPLEXES

Transition metal complexes exhibit specific geometries (shapes) depending upon the electronic configuration and coordination number (number of donor atoms attached) of the metal, and the nature of the ligands. The common geometries found in transition metal complexes are explained below:

1. **Linear:** In this geometry, the two ligands are attached on opposite sides of the central metal ion at an angle of 180°. Typical examples of linear complexes are $[Ag(NH_3)_2]Cl$ and $K[Ag(CN)_2]$.
2. **Square planar:** In square planar shape, the central metal ion and the four ligands lie in the same plane, at the corners of a square with bond angle 90°. This geometry is characteristic of d^8 metal ions (e.g., Ni^{2+} and Pt^{2+}) with ligands like, NH_3 and CN^-). Examples are: $[Ni(CN)_4]^{2-}$ and $[Pt(NH_3)_4]^{2+}$.
3. **Tetrahedral:** In tetrahedral complexes, four ligands are directed at the corners of a tetrahedron with bond angle of 109.5°. Such shapes are common when the metal ion has a d^7, d^8 and d^{10} electron configuration for example, $[CoCl_4]^{2-}$ and $[MnCl_4]^{2-}$.



Linear (2) Square Planar (4) Tetrahedral (4) Octahedral (6)

Figure 18.3 Shapes of Transition Metal complexes

4. **Octahedral:** In this geometry, the central metal ion is surrounded by six ligands, coming along the x, y and z axes. Four ligands form a square plane with an angle of 90°, and the other two are positioned above and below this plane at an angle of 180°. This is the most common geometry for transition metal complexes. The common examples are $[Cr(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$.

Quick Check 18.3

a) How Lewis acid base concept explains the transition metal complex formation?

b) Determine the overall charge of a complex ion formed from a Cr^{3+} metal ion with six neutral H_2O ligands and a coordination number of 6. Show your calculation.

c) Predict the likely geometry for the complex ion $[MnCl_4]^{2-}$, given that the central metal ion has a d^5 electron configuration and a coordination number of 4.

d) EDTA is described as a hexadentate ligand. Explain what "hexadentate" means in terms of coordinate covalent bonds formed with a single metal ion.

e) Identify the two essential features of a transition metal ion that enable it to form complex ions.

18.6 COLOUR OF COMPLEXES

The d-orbitals have a characteristic cloverleaf shape, generally resembling four lobes or two dumbbells in a plane, with five distinct orbitals d_{xy},d_{xz}, d_{yz}, $d_{x^2-z^2}$, and d_{z^2}. In an isolated atom, all five d orbitals have the same energy (degenerate), but their different shapes lead to different energies in complex ions (non-degenerate). Their spatial (in space) arrangements and energy levels decide the bonding, colour, and magnetic properties of transition metals. When ligands approach the metal ion to form an octahedral or a tetrahedral complex, they create an electric field that causes the five d orbitals to split into two groups with different energies, making them non-degenerate. The energy difference is related to the extent of splitting between the two sets of orbitals and is represented by Δ.

Octahedral Complexes

In octahedral complexes (with six ligands), like $[Ti(H_2O)_6]^{3+}$, the five d orbitals split into two sets; three lower-energy orbitals including, d_{xy}, d_{xz}, d_{yz} and two higher-energy orbitals; $d_{x^2-y^2}$, d_{z^2} **(Figure 18.4)**.

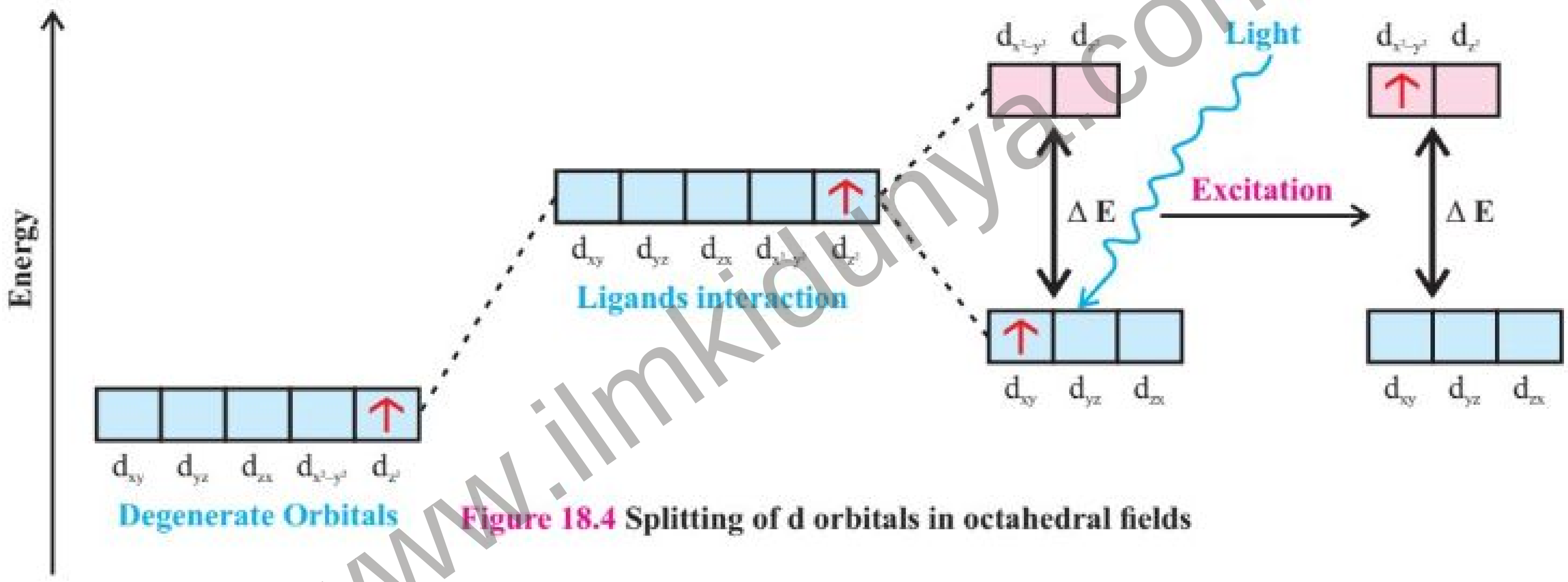


Figure 18.4 **Splitting of d orbitals in octahedral fields**

Tetrahedral Complexes

In tetrahedral complexes (with four ligands), like $[CuCl_4]^{2-}$, the splitting is inverted with three higher-energy orbitals d_{xy}, d_{xz}, d_{yz} and two lower-energy orbitals $d_{x^2-y^2}$, d_{z^2}. The magnitude of splitting in tetrahedral complexes is smaller than that in octahedral complexes **(Figure .18.5)**.

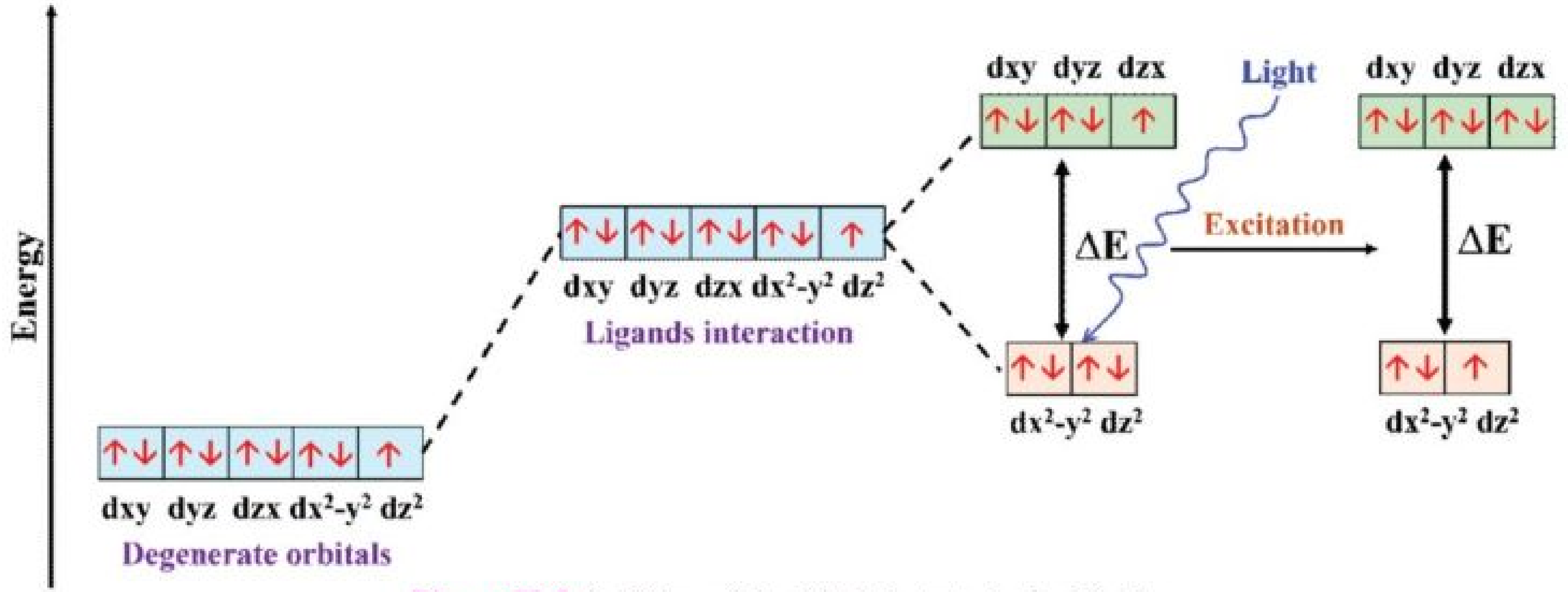


Figure 18.5 **Splitting of d orbitals in tetrahedral fields**

18.6.1 Colour Formation

When white light falls on the compound, it may get absorbed completely, and the complex appears black. The compound may reflect or transmit the whole light, and appears to be white. Another option is that the compound may absorb some of the light and reflect the remaining part, then complex shows different colours depending upon colour of the light reflected. The colour is produced in the substances due to absorption and emission of light in the visible region of the spectrum according the following colour scheme **(Figure 18.6)**.

The colour we see is the opposite (complementary colour) to the colour (frequency/wavelength) of light that is absorbed. For example, if a complex absorbs yellow light, it appears violet.

The electrons in a lower-energy d-orbital absorb light and are promoted (excited) to a higher-energy d-orbital. The light energy involved in the transition of electron is responsible for showing definite colour of the complex. The unabsorbed light is transmitted and it decides the nature of the colour. This process is called a d-d transition. The energy required for a d-d transition, corresponds to a specific frequency (υ) and wavelength (λ) of visible light according to the Planck's equation, $\Delta E = h\upsilon = hc/\lambda$ (h is Planck's constant and c is speed of light).

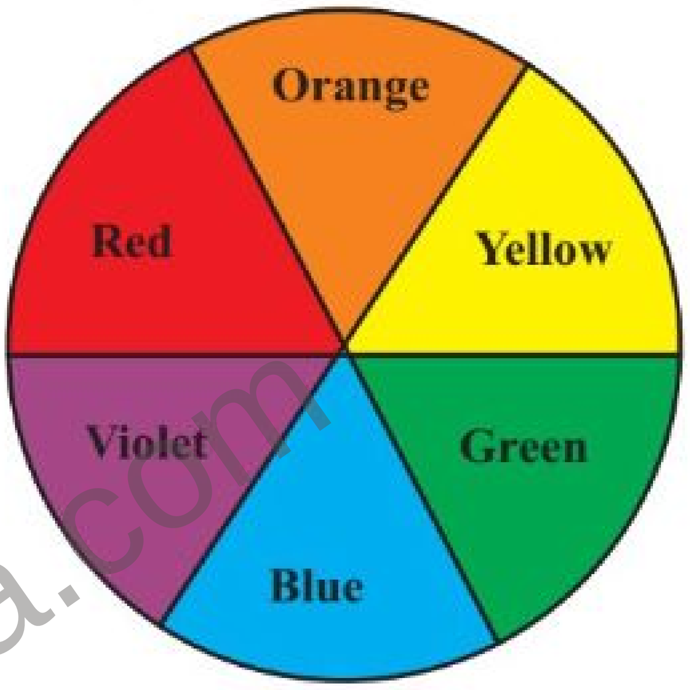


Figure 18.6 Colour wheel showing complementary colours

Effect of Different Ligands on ΔE and Colour

The nature of the ligand affects the magnitude of the splitting, ΔE. Some ligands like NH_3, CN^- cause larger splitting, increasing the energy gap (ΔE). Whereas, for some other ligands like Cl^-, I^-, ΔE is smaller. A larger ΔE means a higher frequency, (shorter wavelength) of light must be absorbed that is in the region of violet or blue colour. Corresponding to that a yellow light is reflected giving the compound a yellow colour. Some complexes absorb low-energy light (red/orange) and appear blue or green according to the complementary colour scheme. Ligands can be arranged in order of their ability to cause d-orbital splitting (from high ΔE to low ΔE):

$$CN^- > en > NH_3 > H_2O > OH^- > Cl^- > Br^- > I^-$$

Quick Check 18.4

a) How does the presence of ligands affect the degeneracy of d-orbitals in a complexion?
b) Describe the key difference in d-orbital splitting patterns between octahedral complexes and tetrahedral complexes.
c) Explain the relationship between the absorbed light energy (ΔE) and the observed colour of a transition metal complex. Reference Planck's equation ($\Delta E = h\upsilon = hc/\lambda$).
d) If a complex containing the ligand Cl^- absorbs light in the red/orange region of the spectrum, what general colour range would you expect the complex to appear?
e) Explain the phenomenon (d-d transitions) responsible for the colour of transition metal compounds.

18.7 LIGAND EXCHANGE REACTIONS OF COMPLEXES

If new complex to be formed is more stable than substitution of ligands occurs and it will changes the properties of the new complex, like colour, structure and reactivity. The complexes of copper(II) and cobalt(II) ions can be used to show ligand substitution reactions.

18.7.1 Ligand Exchange Reactions of Copper(II) Complexes

Whenever, we write $Cu^{2+}_{(aq)}$, we actually refer to the complex ion $[Cu(H_2O)_6]^{2+}$. This ion gives blue colour to the solution of a copper(II) salt, for example, copper sulphate. On adding sodium hydroxide to a copper(II) solution, a light blue precipitate is formed. Two water ligands are replaced by two hydroxide ions in this reaction.

$$\underset{\text{blue solution}}{[Cu(H_2O)_6]^{2+}_{(aq)}} + 2OH^-_{(aq)} \longrightarrow \underset{\text{light blue precipitate}}{[Cu(H_2O)_4(OH)_2]_{(s)}} + 2H_2O_{(\ell)}$$

If concentrated ammonia solution is added, the light blue precipitate dissolves resulting in a dark blue solution.

The structure of $[Cu(NH_3)_4(H_2O)_2]^{2+}_{(aq)}$ is shown in **Figure 18.7.** Water ligands in $[Cu(H_2O)_6]^{2+}$ can also be exchanged directly with ammonia by replacing four water molecules.

For simplicity, $[Cu(NH_3)_4(H_2O)_2]^{2+}$ is usually written as $[Cu(NH_3)_4]^{2+}$.

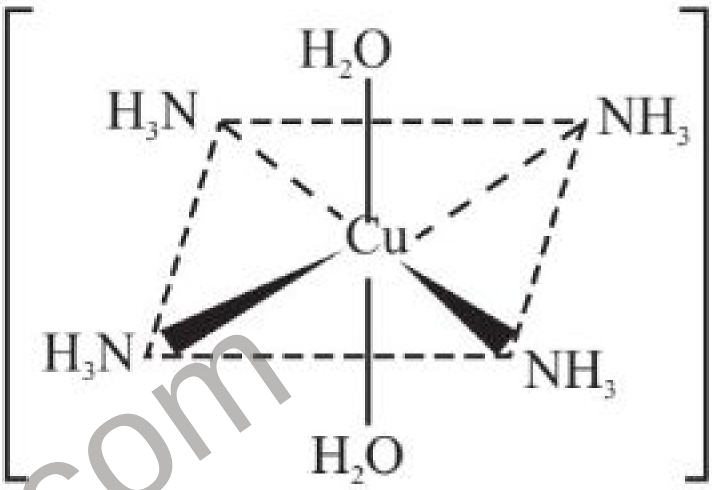


Figure 18.7 **Structure of $[Cu(NH_3)_4(H_2O)_2]^{2+}_{(aq)}$ ion**

$$[Cu(H_2O)_6]^{2+}_{(aq)} + 4NH_{3(aq)} \longrightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}_{(aq)} + 4H_2O_{(\ell)}$$

The chloride ions can also replace water ligands in $[Cu(H_2O)_6]^{2+}$ on addition of concentrated hydrochloric acid drop by drop. A yellow solution is obtained that contains the complex ion $[CuCl_4]^{2-}$ (**Figure 18.8**).

$$\underset{\text{blue solution}}{[Cu(H_2O)_6]^{2+}_{(aq)}} + 4Cl^-_{(aq)} \longrightarrow \underset{\text{yellow solution}}{[CuCl_4]^{2-}} + 6H_2O$$

$[CuCl_4]^{2-}$

This is yellow-green complex forms on adding conc. HCl.

$[Cu(H_2O)_6]^{2+}$

The well-known blue Cu^{2+} complex with water.

$[Cu(H_2O)_2(NH_3)_4]^{2+}$

This dark blue complex forms on adding conc. NH_3.

Figure 18.8 **Colour changes as a result ligand exchange reaction**

18.7.2 Ligand Exchange Reactions of Cobalt(II) Complexes

Cobalt(II) salts also form complex ions in aqueous solution. As mentioned in the case of copper(II), a $Co^{2+}_{(aq)}$ ion refers to the complex ion $[Co(H_2O)_6]^{2+}$. This ion gives a pink colour to the aqueous solution of cobalt(II) sulphate. On adding sodium hydroxide solution, we see a blue precipitate of cobalt(II) hydroxide, which may turn pink on standing.

$$\underset{\text{pink solution}}{[Co(H_2O)_6]^{2+}_{(aq)}} + 2OH^-_{(aq)} \longrightarrow \underset{\text{blue precipitate}}{[Co(H_2O)_4(OH)_2]_{(s)}} + 2H_2O_{(\ell)}$$

When excess ammonia solution is added to the cobalt(II) hydroxide precipitate, a ligand exchange reaction takes place. The ammonia ligands replace the water and hydroxide ligands, forming a soluble ammine complex, hexaamminecobalt(II) ions. The colour of the solution turns yellow (**Figure 18.9**).

$$\underset{\text{blue precipitate}}{[Co(H_2O)_4(OH)_2]_{(s)}} + 6NH_{3(aq)} \longrightarrow \underset{\text{yellow solution}}{[Co(NH_3)_6]^{2+}_{(aq)}} + 4H_2O_{(l)} + 2OH^-_{(aq)}$$

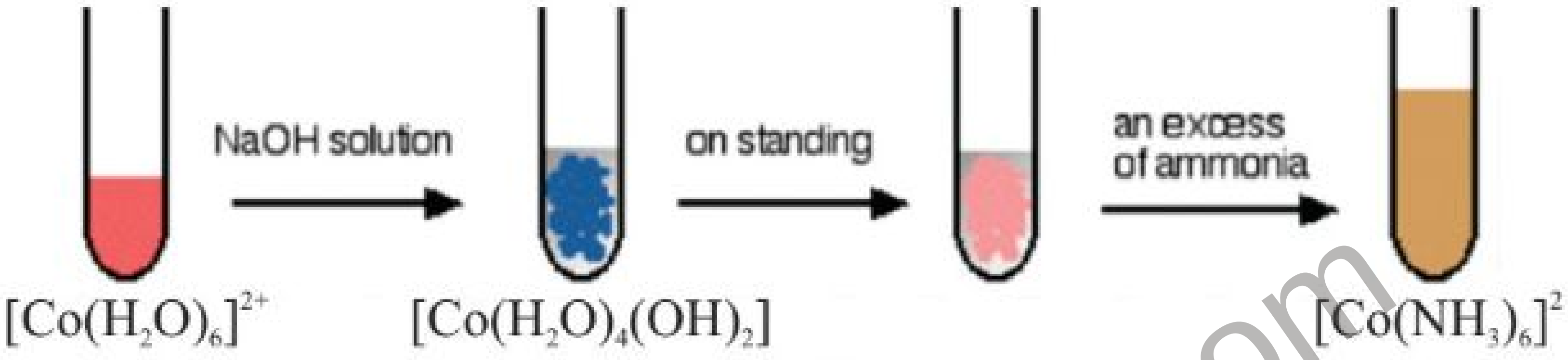


Figure 18.9 Colour changes in $[Co(H_2O)_6]^{2+}$ on addition of hydroxide and NH_3

Water ligands in $[Co(H_2O)_6]^{2+}$ can also be exchanged directly with ammonia ligands by adding concentrated ammonia solution.

$$[Co(H_2O)_6]^{2+}_{(aq)} + 6NH_{3(aq)} \longrightarrow [Co(NH_3)_6]^{2+}_{(aq)} + 6H_2O_{(\ell)}$$

The addition of concentrated hydrochloric acid drop by drop to an aqueous solution of cobalt(II) ions results in the formation of a blue solution containing the tetrahedral complex $[CoCl_4]^{2-}_{(aq)}$ (**Figure 18.10**).

$$[Co(H_2O)_6]^{2+}_{(aq)} + 4Cl^-_{(aq)} \longrightarrow [CoCl_4]^{2-}_{(aq)} + 6H_2O_{(\ell)}$$

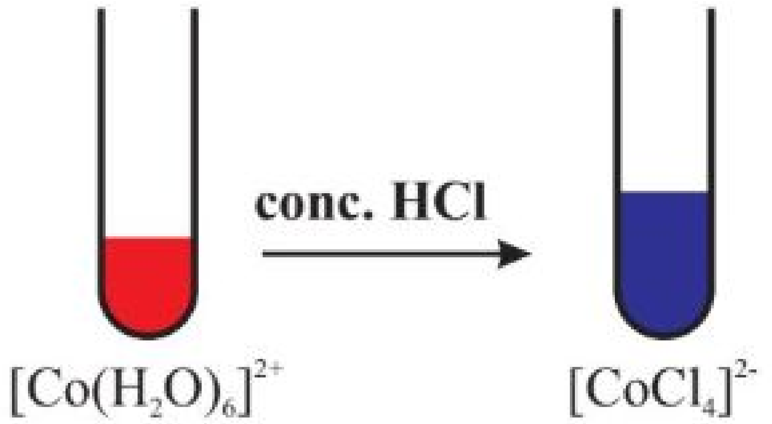


Figure 18.10 Exchange of water molecules by chloride ions in a Co(II) complex

Aqueous cobalt(II) ions usually form tetrahedral complexes with monodentate anionic ligands such as Cl^-, OH^- and SCN^-.

18.7.3 Effect of Ligand Exchange on the Colour of Complexes

The exchange of ligands in a complex changes the magnitude of splitting for the metal ion. As a result, the frequency of absorbed light also changes, leading to a change in the observed colour. In each case, the new complex has a different ΔE because the new ligands (NH_3 or Cl^-) makes more stable complex than the original H_2O ligands, leading to a different absorbed frequency and a different observed colour.

Table 18.4 Ligand exchange and colour change

Metal ion	Initial Colour of Complex	Ligand Exchange Reaction	Final Colour of Complex
Cu^{2+}	$[Cu(H_2O)_6]^{2+}$ (Blue)	Add conc. NH_3 solution	$[Cu(NH_3)_4(H_2O)_2]^{2+}$ (Deep Blue)
Cu^{2+}	$Cu(H_2O)_6]^{2+}$ (Blue)	Add conc. HCl solution	$[CuCl_4]^{2-}$ (Yellow/Green)
Co^{2+}	$[Co(H_2O)_6]^{2+}$ (Pink)	Add conc. NH_3 solution	$[Co(NH_3)_6]^{2+}$ (Yellow)
Co^{2+}	$[Co(H_2O)_6]^{2+}$ (Pink)	Add conc. HCl solution	$[CoCl_4]^{2-}$ (Blue)

Quick Check 18.5

a) Write the equation for the reaction, where $[Cu(H_2O)_4(OH)_2]_{(s)}$ dissolves in excess ammonia.

b) Pink $[Co(H_2O)_6]^{2+}$ turns blue with conc. HCl. Explain this colour change using d-orbital splitting.

c) **For the reaction:** $[Co(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CoCl_4]^{2-} + 6H_2O$, identify the coordination number and geometry of the product complex.

18.8 STABILITY OF COMPLEXES AND STABILITY CONSTANT, K_{stab}

The stability constant (K_{stab}) is an equilibrium constant (K_c) for the formation of a complex ion. In aqueous solutions, water is the initial ligand. When we add a new ligand, it competes with water to bind with the metal ion. Let us take the example of following equilibrium complexation reaction with its K_{stab} expression;

$$[Cu(H_2O)_6]^{2+} + 4Cl^-_{(aq)} \rightleftharpoons [CuCl_4]^{2-}_{(aq)} + 6H_2O_{(\ell)}$$

$$K_{stab} = \frac{[CuCl_4]^{2-}}{[Cu(H_2O)_6]^{2+}\ [Cl^-]^4}$$

Concentration of water $[H_2O]$ being solvent (remains constant) is omitted from the K_{stab} expression. Stability constants are usually provided on a $\log_{10}$ scale. This makes it easier to compare very large numbers. Higher the $\log_{10} K_{stab}$, more stable will be the complex and the equilibrium lies far to the right. And lower the $\log_{10} K_{stab}$, the complex is less stable, and the ligands can be easily displaced. The stability constant values ($\log_{10} K_{stab}$) of some copper (II) complexes are given **Table 18.5.**

Table 18.5 Stability constants of some Cu(II) complexes

Complex	$\log_{10} K_{stab}$
$[CuCl_4]^{2-}$	5.6
$[Cu(NH_3)_6]^{2-}$	13.1
$[Cu(EDTA)]^{2-}$	18.8

The data shows that complexes with polydentate ligands have higher stability constant values than those with monodentate ligands. This is called chelating effect of the ligands.

$$[Cu(H_2O)_{6(aq)}] + 3en \longrightarrow [Cu(en)_3] + 6H_2O_{(\ell)}$$

A ligand with a higher K_{stab} can displace a ligand with a lower K_{stab}. For example, adding ammonia to a chloride complex will turn the solution blue because the ammonia complex is significantly more stable.

$$[CuCl_{4(aq)}]^{2-} + 6NH_{3(aq)} \longrightarrow [Cu(NH_3)_6]^{2+} + 4Cl^-_{(aq)}$$

Similarly, if a stable complex is diluted with a massive amount of water, the equilibrium can be forced back to the left, re-forming the original hydrated ion.

Quick Check 18.6

a) Write the K_{stab} equilibrium expression for the formation of $[Cu(NH_3)_4]^{2+}$ from $[Cu(H_2O)_6]^{2+}$ and NH_3.

b) Explain why polydentate ligands form more stable complexes using K_{stab} data ($\log_{10}k_{stab}$) data for $[CuCl_4]^{2-}$ (5.6) and $[Cu(EDTA)]^{2-}$ (18.8).

c) Write the balanced equation for the first step of the stepwise substitution of water ligands by ammonia in $[Cu(H_2O)_6]^{2+}$.

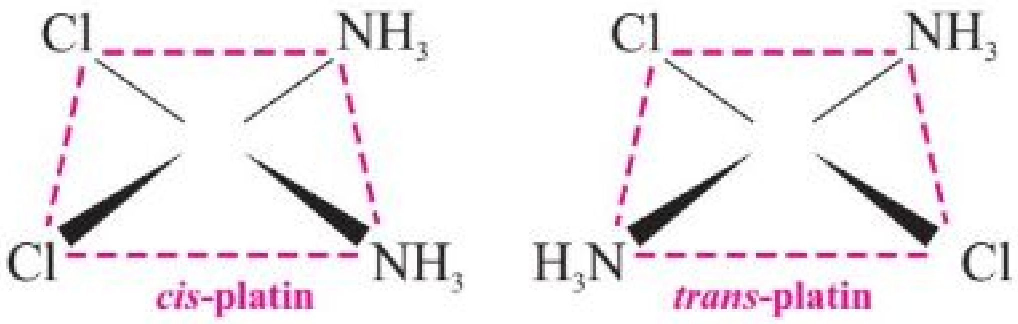
18.9 STEREOISOMERISM IN TRANSITION METAL COMPLEXES

The compounds that have the same chemical formula and bonds but differ with respect to the arrangement of ligands in space are called stereoisomers. There are two types of stereoisomerism: geometrical isomerism and optical isomerism.

18.9.1 Cis-Trans Isomerism

In these isomers, identical ligands are present at either adjacent (90° angle, cis) or opposite (180° angle, trans) positions. This is common in square planar (e.g., $[Pt(NH_3)_2Cl_2]$) and octahedral complexes (e.g., $[Co(NH_3)_4Cl_2]$).

The cis and trans isomers of $[Pt(NH_3)_2Cl_2]$ are shown in **Figure 18.11**. In *cis*-$[Pt(NH_3)_2Cl_2]$ (cisplatin), the chlorine atoms are adjacent to each other at the angle of 90° in the square complex but in *trans*-$[Pt(NH_3)_2Cl_2]$ (transplatin), they are opposite to each other at an angle of 180°. The properties of these geometrical isomers are different. It is interesting to know that cisplatin is used as an anti-cancer drug, while transplatin does not show such property.



cis-platin *trans*-platin

Figure 18.11 The geometrical isomers, cisplatin and transplatin

In transplatin, the individual bond dipoles of the identical ligands are pointed in opposite direction and cancel each other, making the molecule nonpolar. In cisplatin, the similar individual bond moments do not cancel out, resulting in a non-zero dipole moment that makes it polar.

MORE INFO

Interesting Information

Cisplatin, or *cis*-diamminedichloroplatinum(II), is a landmark inorganic anticancer drug. Its discovery was accidental, found when platinum electrodes inhibited bacterial cell division. It specifically targets rapidly dividing cancer cells by entering the cell and undergoing ligand exchange, where water replaces its chloride ions. The "activated" drug then binds to guanine bases in DNA, creating cross-links that link the double helix. This structural damage prevents DNA replication, triggering programmed cell death (apoptosis).

$[Co(NH_3)_4(H_2O)_2]^{3+}$ is an $[MA_4B_2]$ type octahedral complex. The cis and trans isomers of $[Co(NH_3)_4(H_2O)_2]^{3+}$ are shown in **Figure 18.12**. In the cis isomer, the two H_2O ligands occupy adjacent positions at a 90° angle with respect to each other, while in the trans isomer, they occupy opposite positions at a 180° angle to each other.

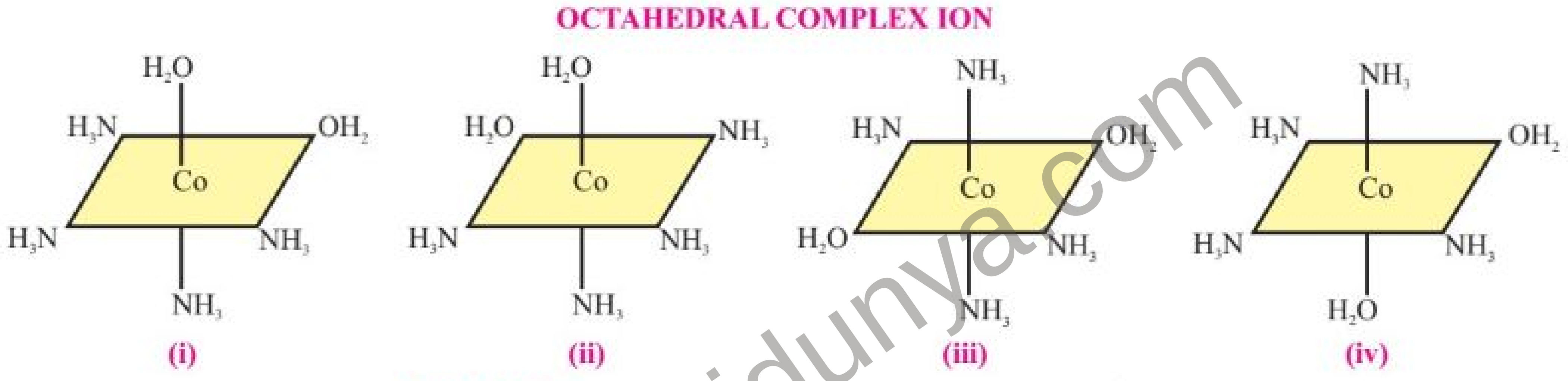


Figure 18.12 The geometrical isomers, $[Co(NH_3)_4(H_2O)_2]^{3+}$

18.9.2 Optical Isomerism

Optical isomers are non-superimposable mirror images of each other. Optical isomerism is commonly shown by octahedral complexes with bidentate ligands. An example is the nickel(II) complex containing 1,2-diaminoethane ($NH_2CH_2CH_2NH_2$) as the bidentate ligand (**Figure 18.13**). The two isomers are optical isomers because the two different molecules are mirror images of each other and cannot be superimposed. Such pairs of molecules are called enantiomers. The optical isomers rotate the plane of polarized light in opposite directions. The isomer that rotates the plane in right hand direction is called dextrorotatory "+", while the one that rotates in left hand direction is called laevorotatory "–".

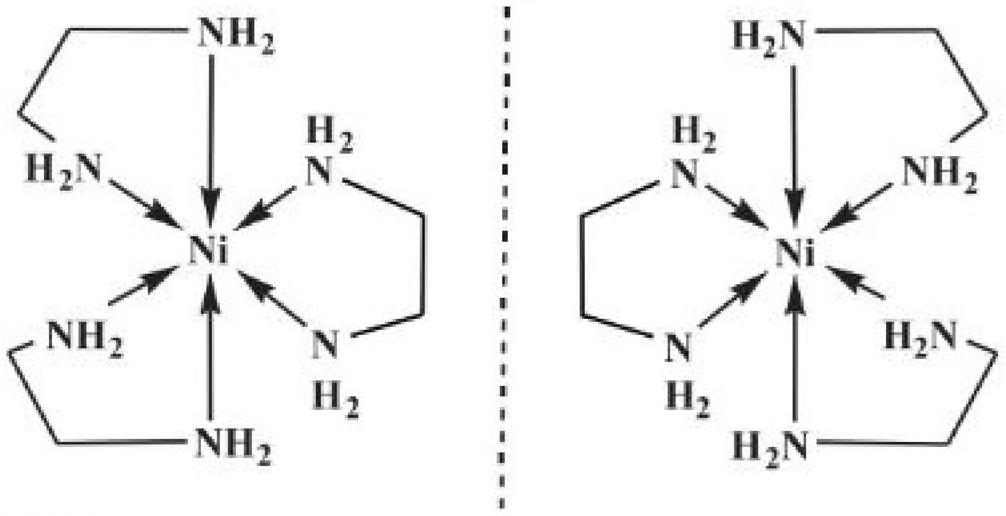


Figure 18.13 The two non-superimposable optical isomers of $[Ni(en)_3]^{2+}$

Quick Check 18.7

a) Which type of geometries shows cis-trans isomerism?

b) What type of ligand is most often required for a complex to show optical isomerism?

c) For the complex $[Ni(en)_3]^{2+}$, state the coordination number and the type of ligand.

d) Identify the type of isomerism displayed by the complex $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$, and describe how the two different isomers interact with plane-polarized light.

e) Define optical isomers (enantiomers) in terms of their mirror images and superimposability.

18.10 REDOX REACTIONS OF TRANSITION METALS

Transition elements are notable for their ability to exist in multiple oxidation states.The feasibility of a redox reaction is determined by comparing the standard electrode potentials (E^o) of the half-reactions involved. A reaction is feasible if the overall cell potential (E^o_{cell}) is positive.

$$E^o_{cell} = E^o_{reduction} - E^o_{oxidation}$$

In practice, the species with the more positive E^o value will be reduced (gain electrons). The species with the more negative (less positive) value will be oxidized (lose electrons).

18.10.1 Reaction of Acidified Manganate(VII) Ions (MnO_4^-) with Ethanedioate Ions ($C_2O_4^{2-}$)

Let us take the example of the reaction between acidified MnO_4^- and $C_2O_4^{2-}$, we compare the standard reduction potentials of the two half-reactions. The half-reaction with the more positive E^o value is more likely to undergo reduction (to proceed to the right). Based on the E^o values, the MnO_4^- ion is more likely to be reduced to Mn^{2+} (acting as the oxidizing agent), and the $C_2O_4^{2-}$ ion must be oxidized to CO_2 (acting as the reducing agent).

$$2CO_{2(g)} + 2e^- \longrightarrow C_2O_{4(aq)}^{2-} \qquad E^o = +0.49\ V$$

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O_{(\ell)} \qquad E^o = +1.52\ V$$

The reaction with higher reduction potential is likely to occur and proceed to the right and vice versa. The given reduction potential values indicate that Mn(VII) ion should be reduced to Mn(II) acting as an oxidizing agent while oxalate must be oxidized to CO_2 and behave as reducing agent.

The number of electrons lost must be equal to number of electrons gained. It is done by multiplying the two half reactions with different coefficients. Here, oxidation half equation is multiplied by 2 and reduction half equation by 5.

$$2 \times [MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O_{(\ell)}] \qquad E^o = +1.52\ V$$

$$5 \times [C_2O_{4\ (aq)}^{2-} \longrightarrow 2CO_{2(g)} + 2e] \text{ (The reaction and } E^o \text{ value written in opposite way)} \qquad E^o = -0.49\ V$$

$$2MnO_4^- + 5C_2O_{4\ (aq)}^{2-} + 8H^+ + \longrightarrow 5Mn^{2+} + 2CO_{2(g)} + 8H_2O_{(\ell)} \qquad E^o_{cell} = +1.03\ V$$

The large positive net E^o value (+1.03 V) indicates that the forward reaction is feasible.

18.10.2 Reaction of Manganate(VII) Ion (MnO_4^-) with Iron(II) Ion (Fe^{2+})

This redox reaction involves the reduction of MnO_4^- and the oxidation of Fe^{2+} as indicated by the potential values. The relevant half-reactions (in reduction form) are:

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O_{(\ell)} \qquad E^\circ = +1.52\ V$$

$$Fe^{3+} + e \longrightarrow Fe^{2+} \qquad E^\circ = -0.77\ V$$

Combine and balance the two equations and sum up their standard electrode potentials so that we can check feasibility of the overall reaction.

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O_{(\ell)} \qquad E^\circ = +\ 1.52\ V$$

$$5\times\ [Fe^{2+} \longrightarrow Fe^{3+} + e^-\ ] \qquad E^\circ = +\ 0.77\ V$$

$$MnO_4^- + 5Fe^{2+} \longrightarrow Mn^{2+} + 5Fe^{2+} + 4H_2O_{(\ell)} \qquad E^\circ = +\ 2.29\ V$$

The positive value of the standard electrode potential indicates that this reaction will proceed to the right, making this reaction feasible.

18.10.3 Reaction Between Copper(II) Ion (Cu^{2+}) and Iodide Ion (I^-)

When an excess of potassium iodide is added to an aqueous solution of copper(II) sulphate, the following reaction occurs:

$$2Cu^{2+}_{(aq)} + 4I^-_{(aq)} \longrightarrow \underset{\text{White ppt}}{2CuI_{(s)}} + \underset{\text{red-brown solution}}{I_{2(aq)}}$$

The reaction splits into the following half-equations:

$$\tfrac{1}{2}I_{2\ (aq)} + e^- \longrightarrow I^-_{(aq)} \qquad E^\circ = +0.54\ V$$

$$Cu^{2+}_{(aq)} + e^- \longrightarrow Cu^+_{(aq)} \qquad E^\circ = +0.15\ V$$

Typically, the I_2/I^- couple, with the higher E° value, would be more likely to undergo reduction. The Cu^{2+}/Cu^+ couple has a lower E°, suggesting Cu^+ is a better reducing agent than I^-.

However, the overall reaction proceeds forward despite a calculated **negative** net standard potential.

The reaction is driven forward because CuI formed is continuously precipitating out of the solution, which effectively removes the Cu^+ product and shifts the equilibrium to the right (Le Chatelier's principle). The amount of I_2 formed in this reaction can be quantified by titrating it with a thiosulfate solution.

Quick Check 18.8

a) State the principle used to determine the feasibility of a redox reaction using standard electrode potentials (E°), as described in the text.

b) For the reaction between MnO_4^- and Fe^{2+}, the relevant reduction potentials are MnO_4^-/Mn^{2+} (E°=+1.52 V) and Fe^{3+}/Fe^{2+} (E°=+0.77 V). Identify the oxidizing agent and the reducing agent in this specific feasible reaction.

c) Explain why water is omitted when calculating the E°_{cell} for the reaction between MnO_4^- and $C_2O_4^{2-}$ ions, even though it appears in the overall balanced equation.

Exercise

Q1. Multiple Choice Questions (MCQs)

I. Which statement about the general physical properties of the first-row transition elements (titanium to copper) is incorrect?

a) They generally have high densities.
b) They are typically soft solids at room temperature.
c) They are good conductors of heat and electricity.
d) They possess high melting and boiling points.

II. The ability of transition elements to behave as catalysts is primarily linked to which of their properties:

a) Their high density.
b) Their ability to easily change oxidation states.
c) Their shiny surface appearance.
d) Their formation of complex ions.

III. What is the reason for variable oxidation states in 3d transition metals?

a) High density.
b) Stable, filled 4s subshell.
c) Comparable energy of 3d and 4s subshells.
d) High ionization energies.

IV. Which ionic configuration represents a metal that lost only its 4s electrons?

a) Ti^{4+} ([Ar]) b) V^{5+}([Ar])
c) Fe^{2+}([Ar] $3d^6$) d) Sc^{3+}([Ar])

V. In the complex ion, $[Fe(CN)_6]^{4-}$, what is coordination number of central metal ion?

a) 2 b) 4
c) 6 d) 8

VI. The colour displayed by a transition metal complex is a result of electrons moving between d-orbitals. This process is called a:

a) p-p transition b) d-d transition
c) s-p transition d) Ligand-to-metal charge transfer

VII. Adding excess ammonia to pink $[Co(H_2O)_6]^{2+}$ gives a yellow solution. What other changes occur besides colour change?

a) Coordination number changes from 6 to 4
b) Oxidation state of Co changes form +2 to +3
c) d-orbital splitting magnitude (ΔE) changes
d) Complex becomes a precipitate

VIII. Which one of the following complex has different geometry than others?

a) $[CuCl_4]^{2-}$ b) $[Cu(H_2O)_4(OH)_2]$
c) $[Cu(H_2O)_6]^{2+}$ d) $[Cu(NH_3)_4(H_2O)_2]^{2+}$

IX. What geometry is typical when $Co^{2+}_{(aq)}$ reacts with six monodentate anionic ligands?

a) Octahedral b) Square Planar
c) Linear d) Tetrahedral

X. Optical isomers are characterized by their ability to rotate plane-polarized light. The isomer that rotates light to the right is called:

a) Laevorotatory (–) b) Superimposable
c) Dextrorotatory (+) d) Achiral

Q2. SHORT ANSWER QUESTIONS

a) Why is zinc not included in the transition metals, although it shows electronic configuration with d-orbitals and also the member of d-block?

b) What is the correlation between the ability of transition elements to exhibit variable oxidation states and their electron configuration.

c) How do transition metals function as effective catalysts. Give some examples.

d) Why the complex $[Cr(en)_3]^{3+}$ is more stable than $[Cr(H_2O)_6]^{3+}$?

e) Define a complex and the nature of the bond between its components.

f) What is the coordination number? Give this number for $[Fe(CN)_6]^{4-}$.

g) Define a bidentate ligand and state how many bonds it forms to the central ion.

h) Draw the structure of EDTA ligand and label its electron pair donating sites.

i) Draw the colour wheel used to predict the colour of transition metal complexes. Also pair up the complementary colours with each other.

j) Define K_{stab}. How it reflects the stability of coordination complexes?

k) How coordination number 4 has two shapes i.e., tetrahedral and square planar?

l) Illustrate the type of isomerism shown by $[PtNH_3)_2Cl_2]$ complex.

m) Give medicinal importance of cis-plantin.

n) What happens when excess of ammonia solution is added to Co(II) hydroxide precipitates?

o) Is there any effect of excessive dilution of complexes? If yes then justify how does dilution affect the position of equilibrium in ligand ion exchange reactions?

Q3. CONSTRUCTED RESPONSE QUESTIONS

a) Discuss the two types of stereoisomerism found in transition metal complexes. Use the examples $[Pt(NH_3)_2Cl_2]$ (square planar) and $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$ (octahedral) to illustrate the key structural differences that give rise to geometrical and optical isomerism, respectively.

b) The reaction between Cu^{2+} and I^- results in a solid precipitate of CuI and aqueous I_2.

a) Write down the two relevant reduction half-equations and their E^o values (provided in the text).

b) Explain why comparing only the E^o values suggests the reaction is *not* feasible as written.

c) Use Le Chatelier's principle to explain why the reaction proceeds forward in practice.

c) Using the examples $[Co(NH_3)_6]^{3+}$ and $[Fe(CN)_6]^{3-}$, demonstrate how to predict the formula and overall charge of a complex ion. Clearly explain the role of the central metal ion charge, ligand charge, and coordination number in determining the final result for both examples.

DESCRIPTIVE QUESTIONS

Q4. Explain the factors that determine the specific geometry (shape) of a transition metal complex.

Q3. Describe the splitting of d-orbitals and colour formation in octahedral and tetrahedral complexes.

Q4. Compare the reactions of conc. HCl with aqueous Cu^{2+} and aqueous Co^{2+}. Include equations, colour/geometry changes, and the reason for different colours.

Q5. Describe the various redox reactions that takes place in transition metal complex ions?

Q6. Explain the stereoisomerism with its types in transition metal complexes.