The *d*- and *f*- Block Elements - Part 3

Objectives

After going through this lesson, the learners will be able to understand the following:

- Explain the magnetic properties of the *d*–block elements;
- The formation of coloured ions and complex compounds;
- Know about the catalytic properties of the transition elements;
- Describe the formation of Interstitial compounds and alloys;
- Describe some of the important compounds of the transition elements like metal oxides and metal oxo-anions.

Contents Outline

- Magnetic Properties
- Formation of Coloured Ions
- Formation of Complex Compounds
- Catalytic Properties
- Formation of Interstitial Compounds
- Alloy Formation
- Some Important Compounds of Transition Elements: Oxides and Oxo-anions of Metals
- Summary

Magnetic Properties

When a magnetic field is applied to substances, mainly two types of magnetic behaviour are observed: diamagnetism and paramagnetism (Unit 1). Diamagnetic substances are repelled by the applied field while the paramagnetic substances are attracted. Substances which are attracted very strongly are said to be ferromagnetic. In fact, ferromagnetism is an extreme form of paramagnetism. Many of the transition metal ions are paramagnetic.

Paramagnetism arises from the presence of unpaired electrons, each such electron having a magnetic moment associated with its spin angular momentum and orbital angular momentum. For the compounds of the first series of transition metals, the contribution of the orbital angular momentum is effectively quenched and hence is of no significance. As explained in module 1, the *d* orbitals of the transition elements project to the periphery of an atom and are influenced by the surroundings as well as affecting the atoms or molecules surrounding them. These surroundings restrict the motion of electrons around the nucleus and the orbital angular momentum is effectively quenched. Hence, for the compounds of the first series of transition metals, the magnetic moment is determined by the number of unpaired electrons and is calculated by using the 'spin-only' formula, i.e.,

$$\mu = \sqrt{n(n + 2)}$$

where n is the number of unpaired electrons and μ is the magnetic moment in units of Bohr magneton (BM). A single unpaired electron has a magnetic moment of 1.73 Bohr magnetons (BM).

The magnetic moment increases with the increasing number of unpaired electrons. Thus, the observed magnetic moment gives a useful indication about the number of unpaired electrons present in the atom, molecule or ion. The magnetic moments calculated from the 'spin-only' formula and those derived experimentally for some ions of the first row transition elements are given in Table 1. The experimental data are mainly for hydrated ions in solution or in the solid state.

Table 1. Calculated and Observed Magnetic Moments (BM)

Ion	**Configuration**	**Unpaired electron(s)**	**Magnetic Moment**	
			Calculated	**Observed**
Sc^{3+}	$3d^0$	0	0	
Ti^{3+}	$3d^1$	1	1.73	0
Ti^{2+}	$3d^2$	2	2.84	1.75
V^{2+}	$3d^3$	3	3.87	2.76
Cr^{2+}	$3d^4$	4	4.90	3.86
Mn^{2+}	$3d^5$	5	5.92	4.80
Fe^{2+}	$3d^6$	4	4.90	5.96
Co^{2+}	$3d^7$	3	3.87	5.3 – 5.5
Ni^{2+}	$3d^8$	2	2.84	4.4 – 5.2
Cu^{2+}	$3d^9$	1	1.73	2.9 – 3.4
Zn^{2+}	$3d^{10}$	0	0	1.8 - 2.2

(Source: Table 8.7, page 221, Chapter 8, NCERT Chemistry Textbook)

Example 1: Calculate the magnetic moment of a divalent ion in aqueous solution if its atomic number is 25.

Solution: With atomic number 25, the divalent ion in aqueous solution will have d^5 configuration (five unpaired electrons). The magnetic moment, μ is

$$\mu = \sqrt{5(5 + 2)} = 5.92 BM$$

Example 2: Calculate the 'spin only' magnetic moment of $M^{2+}{}_{(aq)}$ ion (Z = 27).

Solution: The electronic configuration of the M^{2+} ion (Z = 27) would be [Ar] $3d^7$.

↑↓	↑↓	↑	↑	↑

[Ar]$3d^7$

It has 3 unpaired electrons i.e. n = 3, therefore its spin only magnetic moment is

$$\mu = \sqrt{3(3 + 2)} = 3.87 BM$$

Formation of Coloured Ions

In the compounds of transition metals, an electron from a lower energy *d* orbital is excited to a higher energy *d* orbital on absorption of light. The energy of excitation corresponds to the frequency of light absorbed (explanation will be discussed in modules of Unit 9). This frequency generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed. The frequency of the light absorbed is determined by the nature of the ligand. (The ion or molecule joined to the central atom in coordination entity; discussed in module 1, unit 9) In aqueous solutions where water molecules are the ligands, the colours of the ions observed are listed in Table 2. A few coloured solutions of *d*–block elements are illustrated in Fig. 1.

Fig. 1. Colours of some of the first row transition metal ions in aqueous solutions. From left to right: V^{4+}, V^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+}.

(Source: Fig 8.5, page no. 222, Chapter 8, Chemistry Textbook, NCERT)

Table 2. Colours of Some of the First Row (in aqueous medium) Transition Metal Ions

Configuration	Example	Colour
$3d^0$	Sc^{3+}	Colourless
$3d^0$	Ti^{4+}	Colourless
$3d^1$	Ti^{3+}	Purple
$3d^1$	V^{4+}	Blue
$3d^2$	V^{3+}	Green
$3d^3$	V^{2+}	Violet
$3d^3$	Cr^{3+}	Violet
$3d^4$	Mn^{3+}	Violet
$3d^4$	Cr^{2+}	Blue
$3d^5$	Mn^{2+}	Pink
$3d^5$	Fe^{3+}	Yellow
$3d^6$	Fe^{2+}	Green
$3d^6$	Co^{3+}	Blue
$3d^7$	Co^{2+}	Pink
$3d^8$	Ni^{2+}	Green
$3d^9$	Cu^{2+}	Blue
$3d^{10}$	Zn^{2+}	Colourless

(Source: Table 8.8, page 222, Chapter 8, NCERT Chemistry Textbook)

Formation of Complex Compounds

Complex compounds are those in which the metal ions bind a number of anions or neutral molecules giving complex species with characteristic properties. A few examples are: $[FeF_6]^{3-}$, $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, $[Cu(NH_3)_4]^{2+}$ and $[PtCl_4]^{2-}$. (The chemistry of complex compounds is dealt with in detail in modules of Unit 9). The transition metals form a large number of complex compounds. This is due to the comparatively smaller sizes of the metal ions, their high ionic charges and the availability of vacant d orbitals for bond formation.

Catalytic Properties

The transition metals and their compounds are known for their catalytic activity. This activity is ascribed to the ability of transition metals to adopt multiple oxidation states and to form complexes. Vanadium(V) oxide (in Contact Process), finely divided iron (in Haber's

Process), and nickel (in Catalytic Hydrogenation) are some of the examples. Catalysts at a solid surface involve the formation of bonds between reactant molecules and atoms of the surface of the catalyst (first row transition metals utilise 3*d* and 4*s* electrons for bonding). This has the effect of increasing the concentration of the reactants at the catalyst surface and also weakening of the bonds in the reacting molecules (the activation energy is lowering). Also because the transition metal ions can change their oxidation states, they become more effective as catalysts. For example, iron(III) catalyses the reaction between iodide and persulfate ions.

$$2\,I^{-} + S_2O_8^{2-} \rightarrow I_2 + 2\,SO_4^{2-}$$

An explanation of this catalytic action can be given as:

$$2\,Fe^{3+} + 2\,I^{-} \rightarrow 2\,Fe^{2+} + I_2$$

$$2\,Fe^{2+} + S_2O_8^{2-} \rightarrow 2\,Fe^{3+} + 2\,SO_4^{2-}$$

Formation of Interstitial Compounds

Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals. They are usually non stoichiometric and are neither typically ionic nor covalent, for example, TiC, Mn_4N, Fe_3H, $VH_{0.56}$ and $TiH_{1.7}$, etc. The formulas quoted do not, of course, correspond to any normal oxidation state of the metal. Because of the nature of their composition, these compounds are referred to as interstitial compounds. The principal physical and chemical characteristics of these compounds are as follows:

(i) They have high melting points, higher than those of pure metals.
(ii) They are very hard, some borides approach diamond in hardness.
(iii) They retain metallic conductivity.
(iv) They are chemically inert.

Alloy Formation

An alloy is a blend of metals prepared by mixing the components. Alloys may be homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other. Such alloys are formed by atoms with metallic radii that are within about 15 percent of each other. Because of similar radii and other characteristics of transition metals, alloys are readily formed by these metals. The alloys formed are hard and have often high melting points. The best known are ferrous alloys: chromium, vanadium, tungsten, molybdenum and manganese are used for the production of a variety of steels and stainless steel. Alloys of transition metals with non-transition metals such as brass (copper-zinc) and bronze (copper-tin), are also of considerable industrial importance.

Example 3: What is meant by 'disproportionation' of an oxidation state? Give an example.

Solution: When a particular oxidation state becomes less stable relative to other oxidation states, one lower, one higher, it is said to undergo disproportionation. For example, manganese (VI) becomes unstable relative to manganese(VII) and manganese (IV) in acidic solution.

$$3\,Mn^{VI}O_4^{2-} + 4\,H^+ \rightarrow 2\,Mn^{VII}O_4^- + Mn^{IV}O_2 + 2H_2O$$

Example 4: Explain why Cu^+ ion is not stable in aqueous solutions?

Solution: Cu^+ in aqueous solution undergoes disproportionation as follows:

$$2\,Cu^+\,(aq) \rightarrow Cu^{2+}\,(aq) + Cu\,(s)$$

The standard electrode potential value for the reaction is favourable.

Some Important Compounds of Transition Elements Oxides and Oxo-anions of Metals

These oxides are generally formed by the reaction of metals with oxygen at high temperatures. All the metals except scandium form MO oxides which are ionic. The highest oxidation number in the oxides, coincides with the group number and is attained in Sc_2O_3 to Mn_2O_7. Beyond group 7, no higher oxides of iron above Fe_2O_3 are known. Besides the oxides, the oxocations stabilize V^V as VO_2^+, V^{IV} as VO_2^+ and Ti^{IV} as TiO_2^+.

As the oxidation number of a metal increases, ionic character decreases. In the case of Mn, Mn_2O_7 is covalent green oil. Even CrO_3 and V_2O_5 have low melting points. In these higher oxides, the acidic character is predominant.

Thus, Mn_2O_7 gives $HMnO_4$ and CrO_3 gives H_2CrO_4 and $H_2Cr_2O_7$. V_2O_5 is, however, amphoteric though mainly acidic and it gives VO_4^{3-} as well as VO^{2+} salts. In vanadium there is gradual change from the basic V_2O_3 to less basic V_2O_4 and to amphoteric V_2O_5. V_2O_4 dissolves in acids to give VO^{2+} salts. Similarly, V_2O_5 reacts with alkalies as well as acids to give VO_4^{3-} and VO_4^+ respectively. The well characterised CrO is basic but Cr_2O_3 is amphoteric.

Potassium Dichromate ($K_2Cr_2O_7$)

Potassium dichromate is a very important chemical used in the leather industry and as an oxidant for preparation of many azo compounds. Dichromates are generally prepared from chromate, which in turn are obtained by the fusion of chromite ore ($FeCr_2O_4$) with sodium or potassium carbonate in free access of air. The reaction with sodium carbonate occurs as follows:

$$4\,FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to give a solution from which orange sodium dichromate, $Na_2Cr_2O_7$. $2H_2O$ can be crystallised.

$$2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$$

Sodium dichromate is more soluble than potassium dichromate. The latter is therefore, prepared by treating the solution of sodium dichromate with potassium chloride.

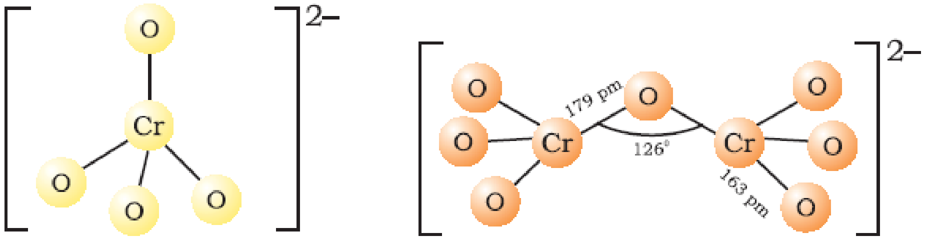
$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$$

Orange crystals of potassium dichromate crystallise out. The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution. The oxidation state of chromium in chromate and dichromate is the same.

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

$$Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$$

The structures of chromate ion, CrO_4^{2-} and the dichromate ion, $Cr_2O_7^{2-}$ are shown in Fig. 2. The chromate ion is tetrahedral whereas the dichromate ion consists of two tetrahedra sharing one corner with Cr–O–Cr bond angle of 126°.



Chromate ion

Dichromate ion

Fig 2. Chromate and dichromate ion

(Source: page no. 225, Chapter 8, Chemistry Textbook, NCERT)

Sodium and potassium dichromates are strong oxidising agents; the sodium salt has a greater solubility in water and is extensively used as an oxidising agent in organic chemistry.

Potassium dichromate is used as a primary standard in volumetric analysis. In acidic solution, its oxidising action can be represented as follows:

$$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \rightarrow 2Cr^{3+} + 7H_2O\ (E^\ominus = 1.33\,V)$$

Thus, acidified potassium dichromate oxidises iodide to iodine, sulphides to sulphur, tin(II) to tin(IV) and iron(II) salts to iron(III). The half-reactions are noted below:

$$6\,I^- \rightarrow 3I_2 + 6\,e^-\ ; \qquad 3\,Sn^{2+} \rightarrow 3Sn^{4+} + 6e^-$$

$$3\,H_2S \rightarrow 6H^+ + 3S + 6e^-\ ; \qquad 6Fe^{2+} \rightarrow 6Fe^{3+} + 6e^-$$

The full ionic equation may be obtained by adding the half-reaction for potassium dichromate to the half-reaction for the reducing agent, for e.g.,

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

Potassium Permanganate ($KMnO_4$)

Potassium permanganate is prepared by fusion of MnO_2 with an alkali metal hydroxide and an oxidising agent like KNO_3. This produces the dark green K_2MnO_4 which disproportionates in a neutral or acidic solution to give permanganate.

$$2\,MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

$$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

Commercially it is prepared by the alkaline oxidative fusion of MnO_2 followed by the electrolytic oxidation of manganate (VI).

$$\underset{}{MnO_2} \xrightarrow[\text{with air or } KNO_3]{\text{Fused with KOH, oxidised}} \underset{\text{manganate ion}}{MnO_4^{2-}}\ ; \qquad \underset{\text{manganate}}{MnO_4^{2-}} \xrightarrow[\text{alkaline solution}]{\text{Electrolytic oxidation in}} \underset{\text{permanganate ion}}{MnO_4^-}$$

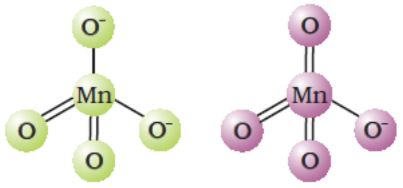
In the laboratory, a manganese (II) ion salt is oxidised by peroxodisulphate to permanganate.

$$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$$

Potassium permanganate forms dark purple (almost black) crystals which are isostructural with those of $KClO_4$. The salt is not very soluble in water (6.4 g /100 g of water at 293 K), but when heated it decomposes at 513 K.

$$2\,KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$

It has two physical properties of considerable interest: its intense colour and its weak temperature dependent paramagnetism. These can be explained by the use of molecular orbital theory which is beyond the present scope (Fig. 3).



Tetrahedral manganate (green) ion

Tetrahedral permanganate (purple) ion

Fig 3. Manganate and permanganate ion

(Source: page no. 226, Chapter 8, Chemistry Textbook, NCERT)

The manganate and permanganate ions are tetrahedral; the green manganate is paramagnetic with one unpaired electron but the permanganate is diamagnetic. The π-bonding takes place by overlap of p orbitals of oxygen with d orbitals of manganese.

Acidified permanganate solution oxidises oxalates to carbon dioxide, iron(II) to iron(III), nitrites to nitrates and iodides to free iodine. The half-reactions of reductants are:

$$5(COO)^{2-} \rightarrow 10CO_2 + 10e^-$$

$$5Fe^{2+} \rightarrow 5Fe^{3+} + 5\,e^-$$

$$5NO_2^- + 5H_2O \rightarrow 5NO_3^- + 10H^+ + l0e^-$$

$$10I^- \rightarrow 5I_2 + 10e^-$$

The full reaction can be written by adding the half-reaction for $KMnO_4$ to the half-reaction of the reducing agent, balancing wherever necessary. If we represent the reduction of permanganate to manganese, manganese dioxide and manganese(II) salt by half-reactions,

$$MnO_4^- + e^- \rightarrow MnO_4^{2-}\ (E^{\Theta} =+\ 0.56\ V)$$

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O\ (E^{\Theta} =+\ 1.69\ V)$$

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O\ (E^{\Theta} =+\ 1.52\ V)$$

We can very well see that the hydrogen ion concentration of the solution plays an important part in influencing the reaction. Although many reactions can be understood by consideration of redox potential, kinetics of the reaction is also an important factor. Permanganate at $[H^+]$ =

1 should oxidise water but in practice the reaction is extremely slow unless either manganese(ll) ions are present or the temperature is raised.

A few important oxidising reactions of $KMnO_4$ are given below:

- **In acid solutions:**
  - Iodine is liberated from iodide:

    $10I^- + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5I_2$
  - Fe^{2+} ion (green) is converted to Fe^{3+} (yellow):

    $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$
  - Oxalate ion or oxalic acid is oxidised at 333 K:

    $5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 10\,CO_2$
  - Hydrogen sulphide is oxidised, sulphur being precipitated:

    $H_2S \rightarrow 2H^+ + S^{2-}$

    $5S^{2-} + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5S$
  - Sulphurous acid or sulphite is oxidised to a sulphate or sulphuric acid:

    $5SO_3^{2-} + 2MnO_4^- + 6H^+ \rightarrow 2Mn^{2+} + 3H_2O + 5SO_4^{2-}$
  - Nitrite is oxidised to nitrate:

    $5NO_2^- + 2\,MnO_4^- + 6H^+ \rightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$

- **In neutral or faintly alkaline solutions:**
  - A notable reaction is the oxidation of iodide to iodate:

    $2MnO_4^- + H_2O + I^- \rightarrow 2MnO_2 + 2OH^- + IO_3^-$
  - Thiosulphate is oxidised almost quantitatively to sulphate:

    $8MnO_4^- + 3S_2O_3^{2-} + H_2O \rightarrow 8\,MnO_2 + 6SO_4^{2-} + 2OH^-$
  - Manganous salt is oxidised to MnO_2; the presence of zinc sulphate or zinc oxide catalyses the oxidation:

    $2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2 + 4H^+$

***Note*:** Permanganate titrations in presence of hydrochloric acid are unsatisfactory since hydrochloric acid is oxidised to chlorine.

Uses: Besides its use in analytical chemistry, potassium permanganate is used as a favourite oxidant in preparative organic chemistry. Its uses for the bleaching of wool, cotton, silk and other textile fibres and for the decolourisation of oils are also dependent on its strong oxidising power.

Summary

In this module, we learnt that the transition elements exhibit paramagnetic behaviour, catalytic properties and tendency for the formation of coloured ions, interstitial compounds and complexes. The transition elements vary widely in their chemical behaviour. Many of them are sufficiently electropositive to dissolve in mineral acids, although a few are 'noble'. Of the first series, with the exception of copper, all the metals are relatively reactive. The transition metals react with a number of non-metals like oxygen, nitrogen, sulphur and halogens to form binary compounds. The first series transition metal oxides are generally formed from the reaction of metals with oxygen at high temperatures. These oxides dissolve in acids and bases to form oxometallic salts. Potassium dichromate and potassium permanganate are common examples. Potassium dichromate is prepared from the chromite ore by fusion with alkali in presence of air and acidifying the extract. Pyrolusite ore (MnO_2) is used for the preparation of potassium permanganate. Both the dichromate and the permanganate ions are strong oxidising agents.