

# THE *d* BLOCK ELEMENTS. GENERAL CHARACTERISTICS

**The Transition Elements.** The transition elements may be broadly defined as those which as elements or as ions have partly filled *d* or *f* subshells. If the *d* subshell is partly filled, the elements are known as *d* block or transition elements. If the *f* subshell is partly filled, the elements are known as *f* block or inner transition elements. Both transition and inner transition elements have been discussed at an appropriate level in this book.

## THE TRANSITION ELEMENTS. THE *d* BLOCK ELEMENTS

**Electronic Configurations.** The *d* block elements consist of three rows called **first, second and third transition series**. The electronic configurations of these elements are discussed below.

**Elements of First Transition Series.** The elements from scandium ( $Z = 21$ ) to zinc ( $Z = 30$ ) constitute the First transition series. In the first element, scandium, the  $3d$  subshell starts filling up. Its electronic configuration is  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$ .

For reasons of space, we shall describe configurations of outer shells only, leaving aside the configuration upto  $3p$  level (argon configuration) which remains the same throughout the period. The outer electronic configuration of scandium may, thus, be written as  $3d^1 4s^2$ .

The next element, titanium ( $Z = 22$ ), has one more *d* electron added to it. Its outer electronic configuration is  $3d^2 4s^2$ . This procedure continues and the *d* orbitals get filled up more and more, step by step, on moving towards the right along this period. Accordingly, the outer electronic configurations of the succeeding elements, viz., vanadium ( $Z = 23$ ), chromium ( $Z = 24$ ), manganese ( $Z = 25$ ), iron ( $Z = 26$ ), cobalt ( $Z = 27$ ), nickel ( $Z = 28$ ), copper ( $Z = 29$ ) and zinc ( $Z = 30$ ), are as given below :

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$3d$	1	2	3	5	5	6	7	8	10	10
$4s$	2	2	2	1	2	2	2	2	1	2

The last element, zinc, has the maximum permissible number of electrons in the *d* orbitals. Its outer electronic configuration is  $3d^{10} 4s^2$ , as shown. But, the definition of *d* block elements based on the number of electrons in the *d* subshell excludes zinc from the First transition series of *d* block since neither zinc nor any of its common ions has a *partly filled d subshell*.

The atoms of chromium and copper, unlike the others, have a single electron in the  $4s$  orbital. This is due to the *additional stability* gained by the atom when the *d* subshell is *exactly half-filled* (i.e., it contains 5 electrons) or *completely filled* (i.e., it contains 10 electrons). Accordingly, one of the  $4s$  electrons moves to the  $3d$  level in the atoms of chromium and copper. The  $3d$  level in the case of chromium gets *exactly half-filled* and that in the case of copper gets *completely filled*.

**Elements of Second Transition Series.** The ten elements from yttrium to cadmium ( $Z = 39$  to  $48$ ) constitute the Second transition series. In yttrium,  $4d$  subshell begins filling up and its outer electronic



configuration is  $4d^1 5s^2$ . The filling up of the  $4d$  orbitals continues as we keep moving in this period towards the next nine elements, namely, zirconium ( $Z = 40$ ), niobium ( $Z = 41$ ), molybdenum ( $Z = 42$ ), technetium ( $Z = 43$ ), ruthenium ( $Z = 44$ ), rhodium ( $Z = 45$ ), palladium ( $Z = 46$ ), silver ( $Z = 47$ ) and cadmium ( $Z = 48$ ). In cadmium ( $Z = 48$ ), the  $4d$  subshell has now the maximum permissible number of 10 electrons, the configuration of the outer shell being  $4d^{10} 5s^2$ . The outer electronic configurations of these elements are given below.

	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
$4d$	1	2	4	5	5	7	8	9	10	10
$5s$	2	2	1	1	2	1	1	1	1	2

The number of  $4d$  electrons varies from 1 to 10 as we move from yttrium to cadmium.

According to the definition of  $d$  block elements already given, the nine elements from Y to Ag, may be taken as constituting the Second series of  $d$  block elements. The definition, based on the number of electrons in the  $4d$  subshell, excludes Cd from the Second transition series.

There are evidently some pronounced irregularities in the configurations of these elements. The configurations of Mo ( $4d^5 5s^1$ ) and Ag ( $4d^{10} 5s^1$ ) can be easily understood on the basis of higher stability of exactly half-filled and completely filled subshells as is noticed in the case of Cr and Cu in the First transition series. This concept, however, cannot explain the anomalous configurations of Nb, Ru, Rh and Pd. As a matter of fact, no simple explanation for such anomalies can be offered. Suffice to say that nuclear-electron and electron-electron interactions play significant role in determining these configurations about which much cannot be said in the present volume.

**Elements of Third Transition Series.** The Third transition series starts from hafnium ( $Z = 72$ ) in which the filling of  $5d$  subshell begins\*. The outer electronic configuration of hafnium is  $4f^{14} 5d^2 6s^2$ . This process continues thereafter in tantalum ( $Z = 73$ ), tungsten ( $Z = 74$ ), rhenium ( $Z = 75$ ), osmium ( $Z = 76$ ), iridium ( $Z = 77$ ), platinum ( $Z = 78$ ), gold ( $Z = 79$ ) and mercury ( $Z = 80$ ). The  $5d$  subshell gets enlarged by the addition of one electron at each step and gets completed when mercury ( $Z = 80$ ) is reached, its outer electronic configuration being  $5d^{10} 6s^2$ . The outer electronic configurations of these elements are given below :

	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
$5d$	2	3	4	5	6	7	8	10	10
$6s$	2	2	2	2	2	2	2	1	2

Since mercury and its common ions have their  $d$  orbitals completely filled, it should, by definition, be excluded from the  $d$  block elements.

## IMPORTANT CHARACTERISTICS OF $d$ BLOCK ELEMENTS

Some of the important characteristics of the  $d$  block elements are given in Table 1.

**1. Metallic Character.** All the transition elements are metals. This is to be expected since the number of electrons in the outermost shell is very small being only 1 or 2 which can be readily lost. They are good conductors of heat and electricity. They are also malleable and ductile and form alloys with several other metals. They differ from non-transition metals, however, in being hard and brittle. Mercury is an exception. Although hardness and brittleness are associated with covalent bonding between

\* Lanthanum ( $Z = 57$ ) with outer electronic configuration  $5d^1 6s^2$  is, by definition, a  $d$  block element of Third transition series. However, in its physical and chemical properties, it closely resembles the series of 14 elements, viz., cerium ( $Z = 58$ ) to lutetium ( $Z = 71$ ) which follows it. These elements are called lanthanides. Therefore, lanthanum is considered as a member of the lanthanide series and is studied along with them.



**8. Oxidation States.** While discussing the chemistry of transition elements, it is more convenient to use the term oxidation state instead of valency. The transition elements show a large number of oxidation states which are related to their electronic configurations. This is illustrated below by taking into consideration the oxidation states of the elements of the First transition series.

The outer electronic configuration of scandium (Sc), the first element of the First transition series, is  $3d^1 4s^2$  (Table 4). It exhibits an oxidation state of +2 in those compounds in which it uses both of its 4s electrons. It can also exhibit an oxidation state of +3 when it uses its two 4s electrons as well as one 3d electron in chemical bonding.

Elements	Outer Electronic Configuration	Oxidation States
Sc	$3d^1 4s^2$	+ 2, + 3
Ti	$3d^2 4s^2$	+ 2, + 3, + 4
V	$3d^3 4s^2$	+ 2, + 3, + 4, + 5
Cr	$3d^5 4s^1$	+ 1, + 2, + 3, + 4, + 5, + 6
Mn	$3d^5 4s^2$	+ 2, + 3, + 4, + 5, + 6, + 7
Fe	$3d^6 4s^2$	+ 2, + 3, + 4, + 5, + 6
Co	$3d^7 4s^2$	+ 2, + 3, + 4
Ni	$3d^8 4s^2$	+ 2, + 3, + 4
Cu	$3d^{10} 4s^1$	+ 1, + 2
Zn	$3d^{10} 4s^2$	+ 2

The outer electronic configuration of titanium (Ti) is  $3d^2 4s^2$ . It shows an oxidation state equal to +2 when it uses both the 4s electrons, equal to +3 when both the s electrons and one d electron is used and +4 when both the s and both the d electrons are used in chemical bonding.

Similarly, vanadium (V), with electronic configuration  $3d^3 4s^2$ , shows oxidation states equal to +2, +3, +4, +5, depending on whether it uses the two s electrons only or also in addition to that, it uses one, two or three of its d electrons as well.

Chromium (Cr), the next element with outer electronic configuration  $3d^5 4s^1$ , has only one s electron. Accordingly, it can have an oxidation state of +1 when it uses only this electron in chemical bonding. In addition, it may have oxidation states equal to +2, +3, +4, +5 and +6 when it uses one, two, three, four or all the five of its d electrons as well. Similarly, manganese (Mn), having the outer electronic configuration  $3d^5 4s^2$ , may have oxidation states from +2 to +7.

It is clear from the above discussion that the first five elements of the First transition series upto Mn in which the 3d subshell is no more than half-filled, the minimum oxidation state is given by the number of electrons in the outer s subshell and the maximum oxidation state is given by the sum of the outer s and d electrons.

In the next elements, viz., iron ( $3d^6 4s^2$ ), cobalt ( $3d^7 4s^2$ ), nickel ( $3d^8 4s^2$ ), copper ( $3d^{10} 4s^1$ ) and zinc ( $3d^{10} 4s^2$ ), in which the number of 3d electrons is more than five, the minimum oxidation state is still equal to the number of the outer s electrons. The maximum oxidation state, however, is not related at all with the electronic configuration. In fact, the maximum oxidation state is rarely higher than +2 or +3. For example, the oxidation state of iron, which has outer electronic configuration as  $3d^6 4s^2$ , is largely confined to +2 or +3. The +4, +5 and +6 oxidation states are known but are rare and +8 oxidation state is unknown. The +8 oxidation state, however, is important in the chemistry of the other members of the iron family, namely, ruthenium and osmium.

particularly p-

**11. Colour.** Most of the compounds of transition metals are coloured in the solid or in solution states. This is unlike the compounds of *s* and *p* block elements which are usually colourless or in any case not strongly coloured.

Colour of a substance arises invariably from the property of the substance to absorb light of certain wave lengths in the region of visible light ( $\lambda = 3800 - 7600 \text{ \AA}$ ). If a substance absorbs wave length corresponding to, say, red light, the transmitted light will consist of wave lengths corresponding to other colours, of blue colour in particular. The substance will, therefore, appear blue. The transmitted light has complementary colour to that of the absorbed light. Hydrated copper (II) ion, for example, absorbs radiations corresponding to red light. The ion, therefore, transmits radiations of wave lengths corresponding to blue colour (which is complementary to red colour). Anhydrous cobalt (II) compounds also absorb red light and, therefore, appear blue. The hydrated cobalt (II) compounds, however, absorb radiations of wave lengths corresponding to blue colour and, therefore, appear red.



As discussed in Chapter 27, the energies of  $d$  orbitals of metal ions in their complexes are split into two sets of energy levels because of crystal field effects. The colour of transition metal ions arises from the excitation of electrons from the  $d$  orbitals of lower energy to the  $d$  orbitals of higher energy. Light radiations corresponding to such small amounts of energy which are required for the above mentioned  $d-d$  electron excitations, are available in the visible range. It is for this reason that transition metal ions have the property to absorb certain radiations from the visible region and exhibit the complementary colours.

The transition metal ions which have completely filled  $d$  orbitals are colourless. There are no vacant  $d$  orbitals to permit the above type of excitation of electrons. Thus,  $\text{Zn}^{2+}(3d^{10})$ ,  $\text{Cd}^{2+}(4d^{10})$  and  $\text{Hg}^{2+}(5d^{10})$  ions are colourless. The transition metal ions which have completely empty  $d$  orbitals are also colourless. Thus,  $\text{Sc}^{3+}$  and  $\text{Ti}^{4+}$  ions are colourless.

Colours and outer electronic configurations of important ions of the elements of the First transition series are given in Table 6.

The ions of  $s$  and  $p$  block elements are colourless because the excitation of electrons from the lower  $s$  or  $p$  orbital to the higher  $s$ ,  $p$  or  $d$  orbitals can only be carried out by the absorption of a very high amount of energy which is associated only with the radiation in the ultraviolet region. There is, therefore, no absorption of light from the visible region. As a result, the  $s$  and  $p$  block elements are colourless.

**12. Magnetic Properties.** Matter, in general, is associated with magnetic properties. Majority of substances are either *paramagnetic* or *diamagnetic*. A **paramagnetic substance** is one which is attracted into a magnetic field and a **diamagnetic substance** is one which is repelled by a magnetic field. The diamagnetic behaviour is due to the fact that small magnetic moments are induced into a substance when a magnetic field is brought in the vicinity of the substance. These magnetic moments are not normally present in the substance. The magnetic moments induced, however, are in **opposition** to the inducing field. This causes *repulsion* of the substance by the magnetic field.

**Paramagnetism** arises from the presence of unpaired electrons in atoms, ions, complex ions or molecules. We may recall from our knowledge of elementary physics that the motion of an electric charge creates a magnetic field. Thus, the motion (spin motion and orbital motion) of an electron, a charged particle, creates a magnetic field. Each electron may, in fact, be regarded as a micromagnet having a certain value of magnetic moment. The total magnetic moment of a substance is the resultant of the magnetic moments of all the individual electrons.

In substances in which electrons in their atoms are completely paired, the effects of individual electrons are mutually compensated. These substances, therefore, do not show paramagnetic behaviour. In fact, they show diamagnetic behaviour when placed in a magnetic field.

But if the atoms of a substance contain one or more unpaired electrons, the effects are not mutually compensated. The magnetic moments due to spin and orbital motion of such electrons get aligned parallel to the direction of external magnetic field applied. The magnetic moments due to unpaired electrons are of sufficiently high magnitude to overcome the small magnetic moments induced due to the paired electrons in the atoms by external magnetic field. Such a substance, therefore, instead of experiencing repulsion, experiences attraction in a magnetic field, i.e., it shows **paramagnetic behaviour**.

TABLE 6

Colour of Ions of the Elements of The First Transition Series

Ion	Outer Electronic Configuration	Number of Unpaired Electrons	Colour of the Ion
$\text{Sc}^{3+}$	$3d^0$	0	Colourless
$\text{Ti}^{3+}$	$3d^1$	1	Purple
$\text{Ti}^{4+}$	$3d^0$	0	Colourless
$\text{V}^{3+}$	$3d^2$	2	Green
$\text{Cr}^{3+}$	$3d^3$	3	Violet
$\text{Mn}^{2+}$	$3d^5$	5	Light Pink
$\text{Mn}^{3+}$	$3d^4$	4	Violet
$\text{Fe}^{2+}$	$3d^6$	4	Light green
$\text{Fe}^{3+}$	$3d^5$	5	Yellow
$\text{Co}^{2+}$	$3d^7$	3	Pink
$\text{Ni}^{2+}$	$3d^8$	2	Green
$\text{Cu}^{2+}$	$3d^9$	1	Blue
$\text{Cu}^+$	$3d^{10}$	0	Colourless
$\text{Zn}^{2+}$	$3d^{10}$	0	Colourless



As mentioned above, paramagnetism is shown by ions and molecules containing odd numbers of electrons. It is also shown by molecules containing even numbers of electrons provided there is one or more unpaired electrons in their structures (as, for example, the  $O_2$  molecule).

The magnetic moment of an electron, as discussed above, is partly due to its *spin motion* and partly due to its *orbital motion*. The total or **effective magnetic moment**  $\mu_{\text{eff}}$  of a substance containing an unpaired electron, is thus made up of *two components* :

- The component due to the orbital angular momentum of the electron,  $\mu_{\text{orbital}}$ , which is related to orbital angular momentum quantum number  $l$  and
- The component due to the spin angular momentum of the electron,  $\mu_{\text{spin}}$ , which is related to spin quantum number  $m_s$ .

In transition metal ions, the unpaired electrons are generally present in the outer orbitals. The orbital motion of such unpaired electrons is severely disturbed by the electrons of the surrounding ligands thereby 'quenching' the orbital angular momentum in the transition metal compounds. Therefore, in such cases, the  $\mu_{\text{spin}}$  contribution becomes much more significant than the  $\mu_{\text{orbital}}$  contribution so that the latter may be neglected in many cases. The effective magnetic moment,  $\mu_{\text{eff}}$ , in such cases may thus be given by the expression

$$\mu_{\text{eff}} = \mu_{\text{spin}} = \sqrt{n(n+2)}$$

where  $n$  is the number of unpaired electrons.

The magnetic moment is expressed in *Bohr magneton*. A Bohr magneton (B.M.) is given by the expression

$$\text{B.M.} = eh/(4\pi mc)$$

where  $h$  is the Planck's constant,  $e$  is the electronic charge,  $c$  is the velocity of light and  $m$  is the mass of electron.

The effective magnetic moment of a substance thus depends mainly on the number of unpaired electrons present in it. If there is only one unpaired electron, the magnetic moment, evidently, will be approximately  $\sqrt{3}$  or 1.732 B.M. If there are two unpaired electrons, the magnetic moment will be approximately  $\sqrt{8}$  or 2.84 B.M. For 3, 4, 5 and 6 unpaired electrons, the values, as can be easily calculated from the above expression, will be approximately 3.87, 4.90, 5.92 and 6.93 B.M. respectively.

The calculated magnetic moments ( $\mu_{\text{spin}}$  values) of some of the ions of the elements of the First transition series are given in Table 7. The actual magnetic moments may differ slightly from these values depending upon the extent of quenching of orbital angular momentum of the electrons in the ions. This, in turn, depends upon the type of arrangement of the anions (or ligands) around the transition metal ions in their compounds (or complexes) and the extent of spin-orbit coupling.

In the case of iron, cobalt and nickel, the magnetic moment due to unpaired electron spins are aligned parallel to the

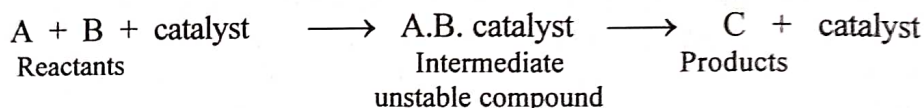
TABLE 7  
Magnetic Moments of the Ions of the Elements of the First Transition Series

Ion	Outer Electronic Configuration	Number of Unpaired Electrons	Calculated Magnetic Moment ( $\mu_{\text{spin}}$ ) (B.M.)
Sc <sup>3+</sup>	3d <sup>0</sup>	0	0
Ti <sup>3+</sup>	3d <sup>1</sup>	1	1.73
Ti <sup>2+</sup>	3d <sup>2</sup>	2	2.84
V <sup>2+</sup>	3d <sup>3</sup>	3	3.87
Cr <sup>2+</sup>	3d <sup>4</sup>	4	4.90
Mn <sup>2+</sup>	3d <sup>5</sup>	5	5.92
Fe <sup>2+</sup>	3d <sup>6</sup>	4	4.90
Co <sup>2+</sup>	3d <sup>7</sup>	3	3.87
Ni <sup>2+</sup>	3d <sup>8</sup>	2	2.84
Cu <sup>2+</sup>	3d <sup>9</sup>	1	1.73
Zn <sup>2+</sup>	3d <sup>10</sup>	0	0

external magnetic field more efficiently resulting in an exceptionally strong reinforcement of paramagnetism. These substances are, therefore, much more paramagnetic than the rest of the elements and are said to be **ferromagnetic**.

**13. Catalytic Properties.** Most of the transition metals and their compounds have good catalytic properties. Platinum, iron, vanadium pentoxide, nickel, etc., are important examples. Platinum is a general catalyst and is used particularly in the Contact process involving combination of sulphur dioxide and oxygen to yield sulphur trioxide. Vanadium pentoxide is also a good catalyst for the same reaction. Iron catalyses the combination of nitrogen and hydrogen in the Haber process for the manufacture of ammonia. Nickel is a good catalyst in hydrogenation processes.

According to the modern theory of catalysis, a catalytic substance is capable of forming an unstable intermediate compound which readily decomposes yielding the product and regenerating the catalyst :



The transition elements, on account of their variable valency, are able to form unstable intermediate compounds very readily.

**14. Tendency to form Complexes.** The transition metals are almost unique in their tendency to form coordination complexes. The tendency of cations of transition elements to form complexes is due to *two factors*. Firstly, these ions are very small in size and, therefore, have high positive charge density. This facilitates acceptance of lone pairs of electrons from other molecules. Secondly, they have vacant orbitals and these orbitals have the right type of energy to accept lone pairs of electrons. The formation and structures of the complex compounds have been discussed in details in Chapters 26 and 27.