UNIT 12 TRANSITION ELEMENTS

Structure

12.1 INTRODUCTION

As you already know, elements are classified on the basis of their electronic configuration into s–block, p–block, d–block and f–block elements. The s– and p–block elements together represent one of the major groups of the elements and are called main group elements. The d–block and the f–block elements represent the transition and the inner-transition elements, respectively. Most of the discussion so far has centered around the chemistry of main group elements having valence electrons in s and/or p orbitals only. From this unit onwards, we will start the study of rest of the elements of the periodic table, namely, the d–block or transition elements and the f–block or inner-transition elements. The name transition is given to the elements on the basis of their position in the periodic table and their properties, that is, they occupy a position between the highly electropositive elements on the left and the electronegative elements on the right. Their properties are also intermediate of the s– and p–block elements. Thus, in this unit we will describe the general features of the transition elements with the emphasis on the $3d$ series and also the periodic trends in their properties.

Here we would like to draw your attention to the fact that some chemists consider as transition elements only those which, either as neutral atoms or in any of their common oxidation states, have partly filled d–orbitals. According to this definition, the elements Zn, Cd and Hg are excluded from the list of transition elements. However, for the sake of completion of discussion on the d–block elements, the elements Zn, Cd and Hg will also be included in the discussion on transition elements in this unit.

Objectives

After studying this unit, you should be able to:

*   describe the electronic configuration of transition elements and their ions,

*   outline the general properties of transition elements,

*   describe the periodic trends in the properties of transition elements,

*   explain the colour, magnetic and catalytic properties of transition elements.

12.2 ELECTRONIC CONFIGURATION

Electronic configuration of the elements has been discussed in detail in Unit 1 of this course. Hence, we will concentrate here only on the features relevant to transition elements. You

already know that the electronic configuration of the argon atom is $1s^2 2s^2 2p^6 3s^2 3p^6$. In atoms of the successive elements from potassium to zinc, electrons can enter either $3d$ or $4s$ levels. In potassium and calcium atoms the differentiating electrons enter the $4s$ level, so the electronic configuration of calcium can be written as $[Ar]4s^2$. At scandium the $3d$ level begins to fill instead of $4p$ and the resulting configuration of the atoms of transition elements is shown in Table 12.1. The electronic configuration of the ions can be obtained by removing first the outer s electrons of the atom and then the outer d electrons until the total number of electrons removed is equal to the charge on the ion. For example Ni^{2+} will have the configuration as $[Ar]3d^8$.

Table 12.1: Electronic configurations of the free atoms and dipositive ions of the first transition series

Element	Free atom	Free M^{2+} ion	Element	Free atom	Free M^{2+} ion
Sc	$[Ar]3d^1 4s^2$	$[Ar]3d^1$	Fe	$[Ar]3d^6 4s^2$	$[Ar]3d^6$
Ti	$[Ar]3d^2 4s^2$	$[Ar]3d^2$	Co	$[Ar]3d^7 4s^2$	$[Ar]3d^7$
V	$[Ar]3d^3 4s^2$	$[Ar]3d^3$	Ni	$[Ar]3d^8 4s^2$	$[Ar]3d^8$
Cr	$[Ar]3d^5 4s^1$	$[Ar]3d^4$	Cu	$[Ar]3d^{10} 4s^1$	$[Ar]3d^9$
Mn	$[Ar]3d^5 4s^2$	$[Ar]3d^5$	Zn	$[Ar]3d^{10} 4s^2$	$[Ar]3d^{10}$

Now you may ask as to why the electrons in potassium enter $4s$ level rather than $3d$ and then later (from Sc to Cu) why $3d$ levels are filled prior to $4p$ level.

The radial dependence of the d orbitals is responsible for this order of filling of electrons in these elements. Fig. 12.1 shows the plot of radial probability functions introduced in Unit 2 of **Atoms and Molecules** course for a $3d$ and $4s$ electron in the hydrogen atom. Let us assume that the radial probability functions for $3d$ and $4s$ electron in a multi electron atom follow the same pattern as in the hydrogen atom.
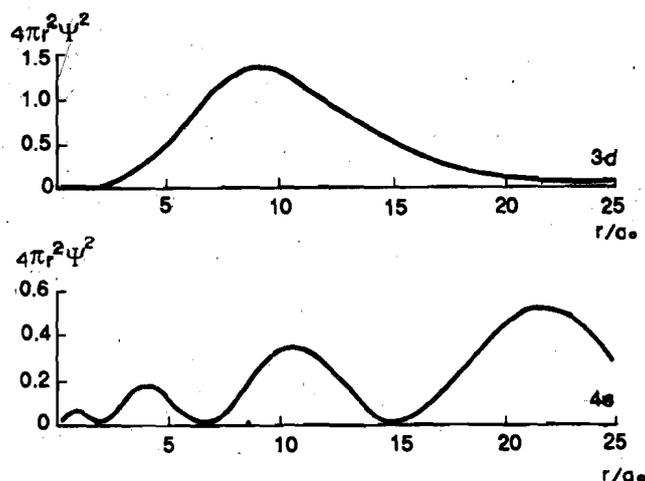

Fig. 12.1: Radial probability functions for $3d$ and $4s$ orbitals in hydrogen atom. a_0, the radius of first Bohr orbit is 52.9 pm.

You can see from Fig. 12.1 that significant humps in the $4s$ probability function occur close to the origin, and well inside the maximum of the $3d$ probability function. This suggests that the $4s$ electron penetrates significantly into the argon core and spends an appreciable portion of its time close to the nucleus. The average nuclear charge experienced by the $4s$ electron is, therefore, higher than that experienced by the $3d$ electron and thus after argon, in potassium and calcium the electrons enter the $4s$ orbital rather than the $3d$. As these two electrons are added the nuclear charge is also increased by two units. As the $3d$ orbitals penetrate the $4s$ orbital more than the $4p$ orbitals can penetrate the $4s$ orbital, the net result is that the effective nuclear charge for the $3d$ orbitals increases abruptly and they now drop well below the $4p$ orbitals to about the level of the $4s$ orbital. Moreover, as the atomic number increases, the $3d$ probability maximum progressively moves closer to the core and they continue to drop in energy. The next electron, therefore, enters the $3d$ orbital prior to the $4p$ orbital. The variation of the energies of the orbitals with increasing atomic number is shown very clearly in Fig. 12.2.
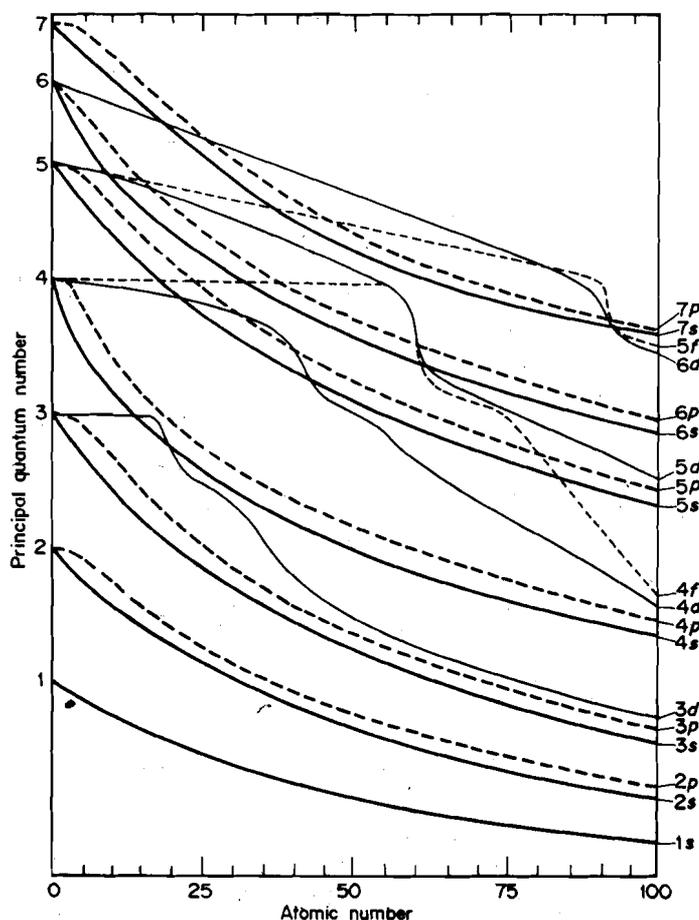
Fig. 12.2: The variation of the energies of atomic orbitals with increasing atomic number in neutral atoms

This process continues until the entire $3d$ shell is filled. Thus at Zn we have the configuration $[Ar]4s^23d^{10}$. Thereafter, the next lowest available orbitals are $4p$ which get filled in the next six elements. This same sequence of events for the filling of $5s$ and $4d$ orbitals is repeated again in the elements following krypton in the second transition series. This series starts with Y and is completed at Cd having the configuration $[Kr]4d^{10}5s^2$. After xenon, $[Kr]4d^{10}5s^25p^6$, the next available orbitals are $4f$, $5d$, $6s$ and $6p$ orbitals. The $4f$ orbitals are so slightly penetrating with respect to the xenon core that they have scarcely gained any stability, while the more penetrating $6s$ and $6p$ levels have gained a good deal of stability. Hence, in the next two elements, electrons are added to $6s$ orbitals giving Cs and Ba, respectively. However, the $6s$ electrons do not shield the $4f$ orbitals effectively, so the latter abruptly feel an increase in effective nuclear charge and thus suffer a steep drop in energy (Fig. 12.2). At the same time, with the addition of electrons in the $6s$ orbital, the $5d$ orbitals also drop in energy in the same manner as the $3d$ ones. This creates a situation in which $5d$ and $4f$ orbitals are of almost the same energy. The next electron in lanthanum thus enters the $5d$ orbital, but in the following element cerium, the electronic configuration is $[Xe]6s^2\,5d^1\,4f^1$. The electrons then continue to be added to the $4f$ orbital till we reach ytterbium which has the configuration $[Xe]6s^24f^{14}$. Now with the $6s$ and $4f$ shells full, the next lowest levels are the $5d$'s. Hence from lutecium onwards, the electrons enter the $5d$ orbital. This continues till we reach mercury which has the configuration $[Xe]6s^24f^{14}5d^{10}$. The electronic configurations of transition elements of $4d$ and $5d$ transition series are given in Table 12.2.

If the filling of the orbitals in transition elements takes place through the above scheme, then you may wonder why in the case of some elements e.g., Cr & Cu (belonging to the first transition series) and Mo & Ag (belonging to the second transition series) the electronic configuration is written as $[Ar]3d^54s^1$ & $[Ar]3d^{10}4s^1$ and $[Kr]4d^55s^1$ & $[Kr]4d^{10}5s^1$, respectively. This is because these configurations are considered to give more stability to the elements, rather than $[Ar]3d^44s^2$ & $[Ar]3d^94s^2$ and $[Kr]4d^45s^2$ & $[Kr]4d^95s^2$, respectively. This apparent stability can be associated with the high stability of exactly half filled and completely filled orbitals. Half-filled and completely-filled orbitals have an exchange energy considerably greater than the exchange energies associated with any other

7

configuration. This exchange energy is the driving force for these configurations to take an electron out of turn in order to achieve or maintain the half-filled or completely-filled configuration. Also these configurations provide the most symmetrical distribution of electrons which suffer the minimum mutual repulsion.

Table 12.2: Electronic configurations of elements of the second and third transition series

Elements of second transition series		Elements of third transition series	
Y	$[Kr]4d^1 5s^2$	La	$[Xe]5d^1 6s^2$
Zr	$[Kr]4d^2 5s^2$	Hf	$[Xe]4f^{14}5d^2 6s^2$
Nb	$[Kr]4d^4 5s^1$	Ta	$[Xe]4f^{14}5d^3 6s^2$
Mo	$[Kr]4d^5 5s^1$	W	$[Xe]4f^{14}5d^4 6s^2$
Tc	$[Kr]4d^6 5s^1$	Re	$[Xe]4f^{14}5d^5 6s^2$
Ru	$[Kr]4d^7 5s^1$	Os	$[Xe]4f^{14}5d^6 6s^2$
Rh	$[Kr]4d^8 5s^1$	Ir	$[Xe]4f^{14}5d^7 6s^2$
Pd	$[Kr]4d^{10}5s^0$	Pt	$[Xe]4f^{14}5d^9 6s^1$
Ag	$[Kr]4d^{10}5s^1$	Au	$[Xe]4f^{14}5d^{10}6s^1$
Cd	$[Kr]4d^{10}5s^2$	Hg	$[Xe]4f^{14}5d^{10}6s^2$

Exchange Energy

The exchange energy for any configuration is proportional to the total number of possible pairs of electrons with parallel spin in any orbital, i.e., $E_{ex} = K \times P$, where K is a constant and P is the number of possible pairs of electrons with parallel spin. If n is the number of electrons with parallel spin for any configuration, P will be equal to $^nC_2$. Accordingly values of P for different values of n are given below :

n	1	2	3	4	5	6	7
P	0	1	3	6	10	15	21

Let us compare the exchange energy for two possible configurations $3d^4 4s^2$ and $3d^5 4s^1$ for chromium.


$3d^4 4s^2$ or $3d^5 4s^1$
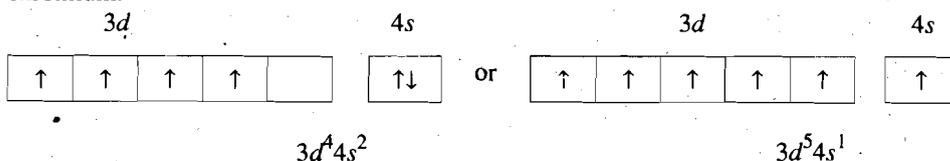
$^nC_2$ is the number of combinations that we can make out of the n objects taking 2 at a time

$$^nC_2 = \frac{n\,!}{2\,!(n-2)\,!}$$

where $n\,! = 1, 2, 3, 4 \ldots (n-1)\,.\,n$

$(n-2)\,! = 1, 2, 3, 4 \ldots (n-1)\,(n-2)$

$2\,! = 1, 2$

Electrons present in 4s orbital in two configurations contribute nothing to exchange energy as they do not constitute any pair with parallel spin. Four unpaired d-electrons in first configuration can make six pairs of electrons with parallel spin and thus contribute $6K$ towards exchange energy whereas five unpaired d-electrons in second configuration contribute $10K$ towards exchange energy because they can constitute 10 combinations of pairs of electrons with parallel spin. This gain of $4K$ in exchange energy would favour the $3d^5 4s^1$ configuration for chromium. But, you should remember that in achieving this configuration, there would be loss of energy in promoting an electron from 4s to 3d orbital. In case of chromium the gain in exchange energy is more than the loss in energy and therefore, $3d^5 4s^1$ is the favoured configuration.

Similarly you can compare the exchange energies for two possible configurations $3d^9 4s^2$ and $3d^{10}4s^1$ for copper.

$3d^9 4s^2$ or $3d^{10}4s^1$
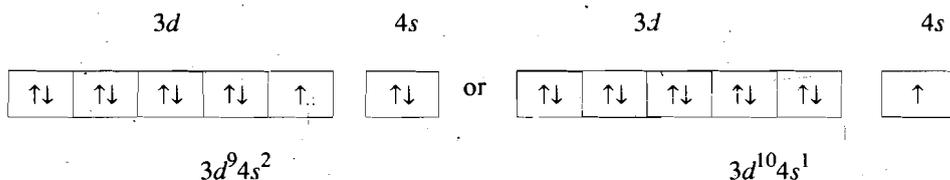
The former configuration has two sets of electrons with parallel spin — one set has five electrons represented by upward arrows and the other has four electrons represented by downward arrows.

These two sets of electrons will contribute $10K$ and $6K$ i.e. a total $16K$ towards exchange energy. On the other hand, the latter configuration has two sets of five electrons each with parallel spin which will contribute a total $20K$ towards exchange energy. Thus, there is a net gain of $4K$ in exchange energy if copper has the configuration $3d^{10}4s^1$. However, in achieving this configuration, there will again be a loss in energy in promoting an electron from $4s$ orbital to $3d$ orbital, which happens to be less than $4K$, the gain in exchange energy. Hence, the $3d^{10}4s^1$ configuration becomes more stable than $3d^9 4s^2$.

It is also worth mentioning here that though the $4s$ orbitals are occupied before $3d$ orbitals, we cannot say that they are always more stable. In fact, the ionisation of the transition elements takes place by the loss of ns electrons first. What happens actually is that when the electron is ionised from any transition element, say the one from $3d$ series, the effective nuclear charge experienced by the $3d$ electrons is greatly enhanced over that of any $4s$ electron as a direct consequence of the greater stability attained by the $3d$ orbitals in the due course of filling (cf. Fig. 12.2). Consequently, the $3d$ orbitals are expected to drop significantly in energy below the $4s$ orbital. Thus, ionisation of two or more electrons from an atom of a transition element will take place with the removal of s electrons in preference to the d electrons.

Thus, we see that it is the net effect of all the forces, comprising nuclear-electronic attraction, shielding of one electron by others from the nuclear charge, inter-electronic repulsion and exchange forces, that determines the stability of the electronic configuration.

SAQ 1

In the given space, explain :

a)   Why a transition series contains ten elements.

. . . .

. . . .

. . . .

. . . .

b)   Which of the two orbitals, $3d$ and $4s$ has higher energy at potassium.

. . . .

. . . .

. . . .

. . . .

12.3 GENERAL CHARACTERISTICS

In the preceding section you have learnt the electronic configuration of the transition elements and their position in the periodic table. Based on these two, the transition elements have certain common properties, which are given below :

*   All are metals and form alloys with one another and with other metallic elements.
*   They are hard, strong, ductile, malleable, high melting and high boiling. They are good conductors of heat and electricity.
*   Many of them are sufficiently electropositive to dissolve in mineral acids although a few are noble — that is, they have such low electrode potentials that they are unaffected by simple acids.
*   They usually exhibit multiple oxidation states.
*   They form coordination compounds/ions. In fact, the chemistry of the transition elements is mainly associated with the use of d as well as s and p orbitals in forming coordination compounds.
*   The transition metal complexes are usually coloured.
*   Most of their compounds are paramagnetic.
*   Many of these elements and their compounds act as catalysts for chemical reactions.

Let us now study some of these properties and their periodic trends in detail.

12.4 PERIODIC TRENDS IN PROPERTIES

In the previous section you have studied the important properties of transition metals in general. As you know the transition metals are an integral part of the periodic table, like the main group elements, the transition metals are also expected to exhibit periodicity in their properties. Let us see how their properties vary from one group to another and from one period to another.

Some of the important properties of the elements of 3d- series are listed in Table 12.3. If you study the data in the Table carefully, you will notice that along a period, these properties vary much less from one element to the other as compared to the main group elements. Although, the horizontal similarity amongst the d-block elements is well marked, yet the chemistry of the elements of first transition series differs considerably from that of the elements of the second and third transition series, which are incidentally more similar to each other. This difference in the trends in the properties of d-block elements from those of s–and p–block elements arises from a basic difference in their electronic configuration. While in the building up of elements from lithium to fluorine, the electrons are added to the outermost shell, in the case of transition metals, the electrons are added to inner $(n-1)d$ subshell. Let us see how this contributes to the variation in the properties of the elements.

Table 12.3: Some properties of d-block elements

Property	Scandium Sc 21	Titanium Ti 22	Vanadium V 23	Chromium Cr 24	Manganese Mn 25	Iron Fe 26	Cobalt Co 27	Nickel Ni 28	Copper Cu 29	Zinc Zn 30
Atomic weight	44.956	47.90	50.942	51.996	54.938	55.847	58.933	58.710	63.54	65.37
Metallic radius (pm)	164	147	135	130	135	126	125	125	128	137
*Ionic radius (pm)	81 (3+)	76, 68 (3+)(4+)	74, 60 (3+)(4+)	84,69 (2+)(3+)	80, 66 (2+)(3+)	76,64 (2+)(3+)	74,63 (2+)(3+)	72,62 (2+)(3+)	96,69 (1+)(2+)	74 (2+)
Covalent radius (pm)	144	132	122	118	117	117	116	115	117	125
Boiling point (K)	3000	3533	3673	2753	2370	3273	3173	3005	2868	1180
Melting point (K)	1812	1948	2173	2163	1517	1808	1768	1726	1356	692
Density $10^3 \times$ kg m^{-3}	3.0	4.5	6.11	7.2	7.44	7.86	8.86	8.90	8.92	7.13
Electronegativity (A/R)	1.2	1.3	1.45	1.55	1.6	1.65	1.7	1.75	1.75	1.65
Ionisation 1st energy 2nd (kJ mol^{-1}) 3rd	633 1235 2388	659 1309 2648	650 1414 2866	653 1591 2992	717 1509 3259	762 1561 2958	759 1644 3230	736 1751 3391	745 1958 3556	906 1732 3828
Electrode Potential (V)+	(III) −2.1	(III) (IV) −1.2–1.63	(II) (III) −1.2–0.86	(II) (III) −0.91–0.74	(II) (III) −1.18–0.28	(II) (III) −0.44–0.04	(II) (III) −0.28 +0.4	(II) −0.25	(I) (II) +0.52 +0.34	(II) −0.76

* Values in parantheses refer to oxidation states of the metal, + (III) refers to couple M^{3+}/M, etc.

12.4.1 Atomic Radii, Atomic Volume and Density

From Table 12.3, you can see that there is a gradual decrease in atomic radius across a row of transition elements. On passing from left to right, additional positive charges are placed on the nucleus and correspondingly electrons are added to the $(n-1)d$ orbitals. As the electrons in the d orbitals shield the ns electrons and also themselves from the nuclear charge incompletely, effective nuclear charge felt by them increases and hence a contraction in size occurs.

However, it is important to emphasise here that shielding of the outer ns electron(s) by $(n-1)d$ electron(s) is more efficient than the shielding of a ns electron by another ns electron (or that of a np electron by another np electron). This is why the decrease in atomic radius from sodium to chlorine is greater than that from scandium to copper. The elements which occur immediately after the transition elements are smaller than expected from simple

extrapolation from the group elements. This is due to the cumulative effect of incomplete shielding provided by $(n-1)d^{10}$ electrons and therefore, the effective nuclear charge felt by the outer electrons of the elements from gallium to krypton is greater than that if the d–orbitals-had not been gradually filled in transition elements.

The rate of decrease in size along the lanthanide series is even less than that in the transition series since in the lanthanides the electrons are added to the penultimate $[(n-2)f]$ shell and these shield the outer electrons much more effectively. The presence of $4f$ electrons in the lanthanides affects the atomic size and therefore, the chemistry of the elements following the lanthanides. The atomic radii of the elements of third transition series are much smaller than expected. This is due to the effect of the greater than expected effective nuclear charge felt by the electrons of the elements of the third row transition series, hafnium to gold, owing to the insertion of lanthanides.

Table 12.4: Metallic radii (pm) of some elements of Groups 1-13

1	2	3	4	5	6	7	8	9	10	11	12	13.
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga
235	197	164	147	135	130	135	126	125	125	128	137	141
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In
248	215	178	160	146	139	136	134	134	137	144	154	166
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl
267	222	188	160	149	141	137	135	136	139	146	157	171

This trend in the variation of the metallic radii in alkali, alkaline earth and transition metals is shown in Fig. 12.3. You can see in Fig. 12.3 that as we move from alkali metals to alkaline earth metals and from alkaline earth metals to the transition elements, the radii decrease steeply but within transition elements this rate of decrease is less. However, the data in Table 12.4 and Fig. 12.3 show that the general trend of decreasing size is reversed towards the end of the series. This could be due to an increase in inter-electronic repulsion after the addition of sufficient number of electrons in the d orbitals leading to the gradual increase in size.
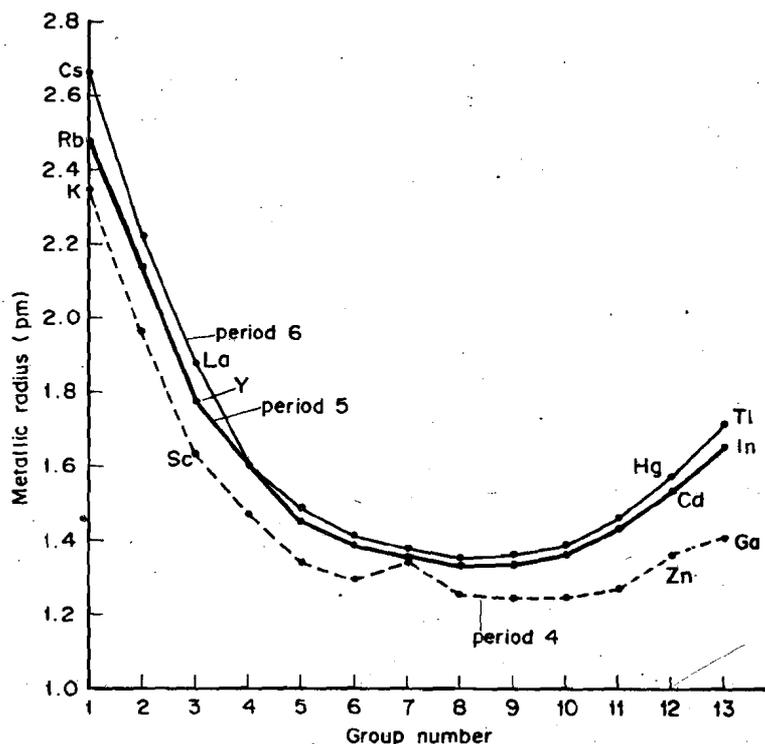

Fig. 12.3: Trends in metallic radii of alkali, alkaline earth and transition metals of fourth, fifth and sixth periods

The group trends in atomic radii of the transition elements are parallel to those observed in s– and p–block elements. As we go down the group, there is an increase in atomic size up to

the second transition series. This is not unexpected in view of the fact that electrons enter the $4d$ orbital in the second transition series. However, the size of the elements of third transition series is almost similar to that of the elements of second transition series because of the filling in of $4f$ orbitals in the lanthanides.

Atomic volume of an element is directly related to its size and, therefore, atomic volumes follow the same trend as the atomic size. Similarly density is also related to the size of the element. The smaller the size, the higher is the density of the element. Thus there is a general trend of increasing density across the elements of a transition series. This is well represented in Fig 12.4 which gives the variation of the densities of alkali, alkaline earth and the transition metals of the fourth, fifth and sixth periods. For $4d$ and $5d$ elements, this increase is not that regular as the increase in densities for $3d$ elements. Along the group also, the density increases (Fig. 12.4). The increase in density within the d block groups is greater than that within the s and p block groups.
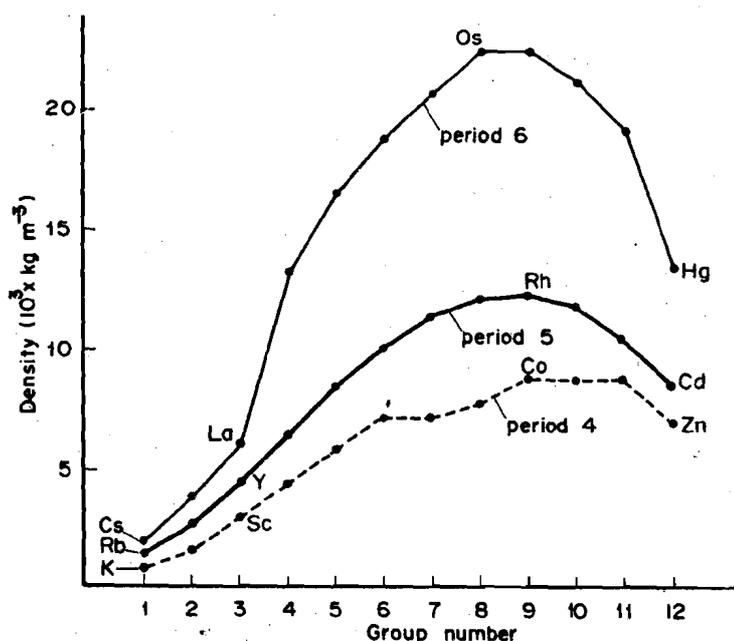

Fig. 12.4: Trend in densities of the alkali, alkaline earth and transition metals of the fourth, fifth and sixth periods.

SAQ 2

Of the following pairs, tick mark the element which is larger in size:

(i)   Calcium or scandium '

(ii)   Vanadium or titanium

(iii) Chromium or molybdenum

(iv)   Iron or osmium

12.4.2 Melting and Boiling Points

The melting and the boiling points of the transition elements are usually high. The melting points of the elements depend upon the strength of the metallic bond. As we know, the transition metals crystallise in the metallic lattices. The strength of the metallic bond increases with the availability of the electrons to participate in the bonding by delocalisation. Notice that between calcium and scandium (where d electron first appears), there is a jump of nearly 700 K in the melting point. The presence of one or more unpaired d electrons thus leads to higher interatomic forces and therefore, high melting and boiling temperatures. Thus, we can think that with the increasing availability of the unpaired d electrons, the strength of the metallic bond increases, resulting in higher melting points. But, we cannot generalise the argument because when we move across any period in the periodic table, the melting point increases upto the middle of each transition series and then it decreases with the beginning of electron pairing. For the elements of first transition series,
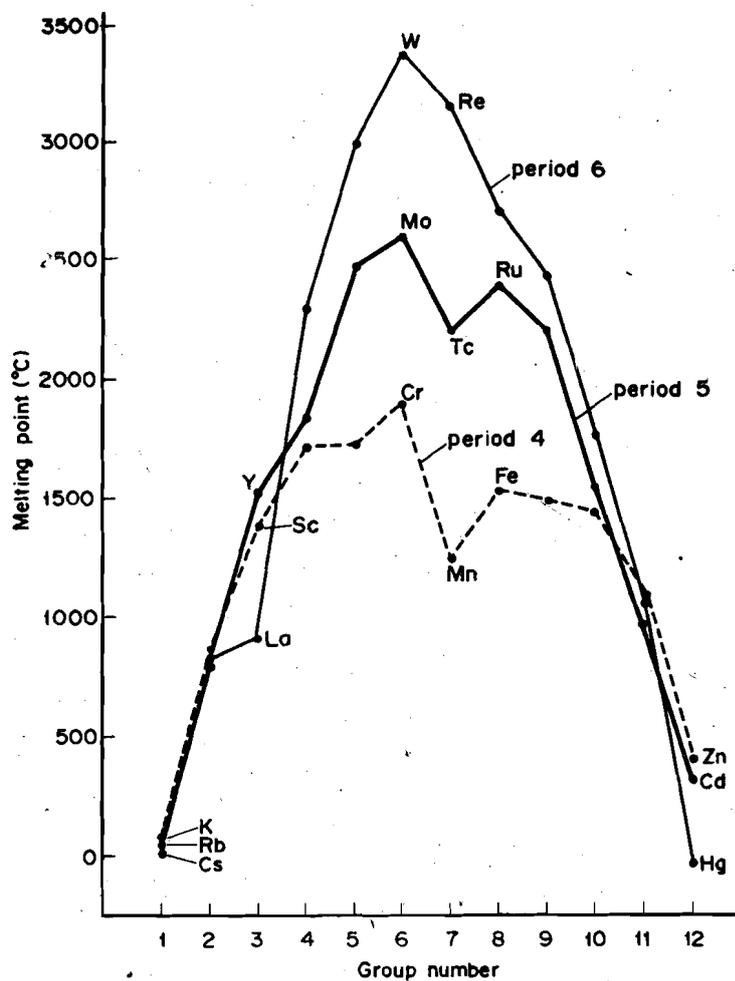
Fig. 12.5 : Trend in melting points of alkali, alkaline earth and transition metals of the fourth, fifth and sixth periods

there is a sharp decrease of melting point at manganese, which has five unpaired d electrons. However, the softness and low melting point of Zn, Cd and Hg (Hg is a liquid) in which all the electrons are paired up can tentatively be explained on the above basis. The melting points of the elements of the first transition series are comparatively lower than those of the elements of the second and third transition series. This trend is very well illustrated in the Fig. 12.5.

The periodic trends in the boiling points are similar to those in the melting points. As the process of boiling requires almost complete breaking of bonds and such metallic bonding exists in the liquid state to some extent, high temperatures are necessary. Therefore, the boiling points of the metals are much higher than their melting points.

SAQ 3

Explain briefly in the space given below, why zinc and cadmium are soft metals.

....

....

....

....

12.4.3 Ionisation Energy

You have already learnt about the concepts of ionisation energy and how it varies with the atomic size in Unit 2 on periodicity. In the case of transition metals also, the variation of ionisation energy across the periods and down the groups parallels quite closely the trend in atomic size. This is shown nicely in the Figure 12.6.

As we move across a period, the effective nuclear charge experienced by ns^2 electrons goes on increasing causing the shells to shrink in size and thus making it difficult to remove the electrons. Thus along a period, the ionisation energy increases. This can be checked from the

13

values of the first ionisation energy of these elements given in Table 12.3. The second and the third ionisation energies follow the same pattern, except for the second ionisation energies of Cr and Cu which are comparatively higher due to the extra stability of $3d^5$ and $3d^{10}$ configurations. The ionisation energies of the elements of the second and the third transition series also follow the same trend along the period. As the decrease in the size of the transition metals is less than that of the main group elements along a period, the ionisation energies tend to increase along the series only slightly as compared to the main group elements (Fig. 12.6). Since *s* and the *d* electrons do not differ much in energy, the difference in the successive ionisation energies is relatively small.
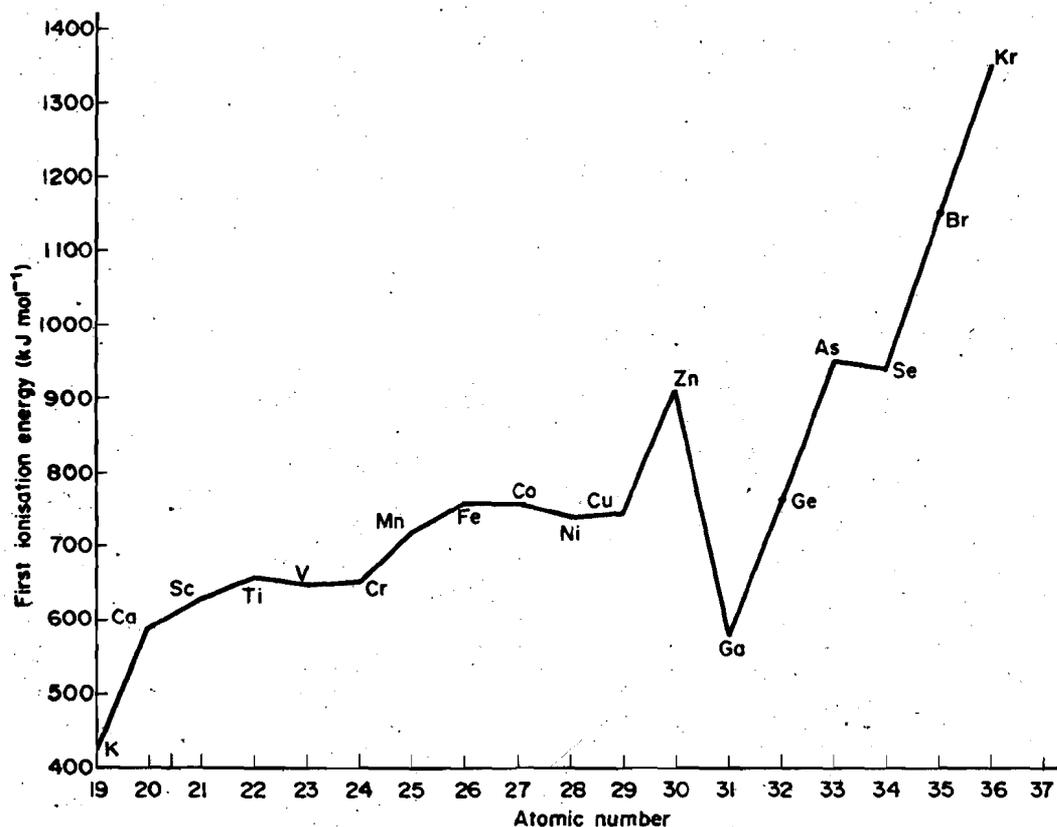

Fig. 12.6 : Variation in first ionisation energy of the elements of the fourth period

As we move down a group from the elements of first transition series to those of the second, there is a decrease in the ionisation energy. But it again increases when we move further down the group from second to the third transition series. This trend is consistent with relatively small size of the atoms of elements of the third transition series. This is due to the insertion of the lanthanides which causes the third row transition elements to have greater than expected effective nuclear charge.

12.4.4 Electronegativity

Transition elements have fairly low values of electronegativity. It increases from Sc to Cu with a fall at Mn and Zn. However, this increase in electronegativity is much slower because the additional electron is being added to an inner shell which provides relatively good shielding to the outer electrons from the nucleus. The increasing electronegativity from Sc to Cu means that the elements become slightly less metallic and this is reflected in the increasing positive electrode potentials of their ions M^{2+} and M^{3+} (Table 12.3).

12.4.5 Electrode Potential

Before going into the details of the variation in the electrode potential of the transition elements, let us discuss the concept of electrode potential first. When a metal is placed in a solution of its ions a potential difference is set up between the metal and the solution. There is a tendency for the metal ions to leave the metal lattice and go into the solution thus leaving an excess of electrons and hence a negative charge on the metal; there is also a reverse tendency for the metal ions from the solution to deposit on the metal leading to a positive charge on the metal. In practice one of these effects is greater than the other, bringing about a potential difference between the metal and the solution. The value of this

potential difference for a particular metal depends upon the nature of metal, the concentration of the metal ions in solution and the temperature. By convention, the potential difference set up in a 1M solution of metal ions at 298K is called the **standard electrode potential**. It is not possible to measure standard electrode potentials absolutely. Standard electrode potentials, therefore, have to be measured against some reference standard, the one adopted is the hydrogen electrode. This consists of hydrogen gas at one atmosphere pressure in contact with a 1M solution of its ions at 298 K.

In general, we can say that more negative the value of the electrode potential for the couple M^{n+}/M, more is the reducing power of the element. Similarly, more positive is the value of electrode potential for the couple M^{n+}/M, more is the oxidising power of the element. The values of some standard electrode potentials for the elements of first transition series are given in Table 12.3. Electrode potential is a measure of the electropositive character and the reactivity of the metals. In general along a period, there is a decrease in electropositive character. The reactivity of metals also decreases along a period and down a group. As you can see from Table 12.3, all the elements of the first transition series, except copper, have negative values and can react with acids (H^+) producing hydrogen. A plot of variation of the electrode potential of the transition elements of $3d$ series is shown in Fig. 12.7.
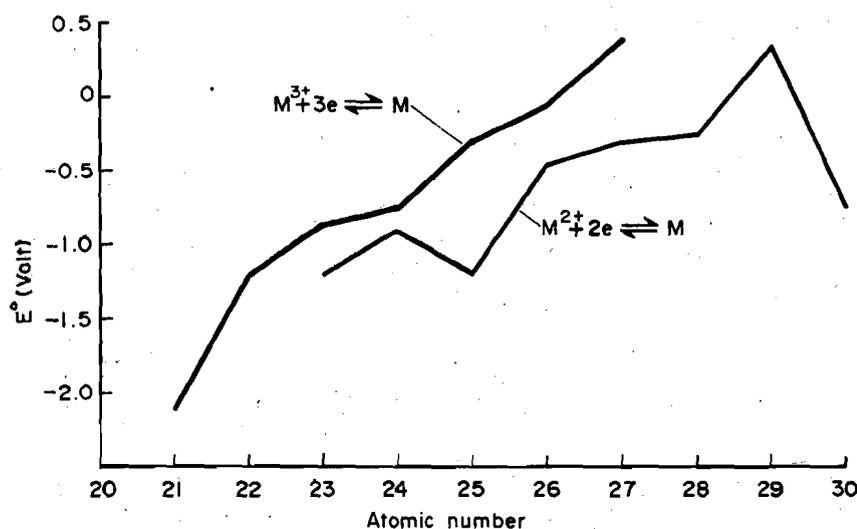

Fig. 12.7: Trends in electrode potentials of transition metals of $3d$ series

12.4.6 General Reactivity

Except in the unusual circumstances, metals act only as reducing agents. Generally, the reactivity of the transition metals as reducing agents tends to decrease as you go across the periodic table from left to right. The trend in their reactivity can be related to their electrode potentials. Group 3 metals including lanthanides and actinides are strong reducing agents. The metals of Groups 4-7 are moderately reactive as are iron, ruthenium, osmium, cobalt and nickel of Groups 8-10. The remaining metals of Groups 8-10, rhodium, iridium, platinum and palladium, as well as silver and gold have low reactivity. Because of this relative inertness, they are called **noble metals.**

12.4.7 Oxidation States

The concept of oxidation state has already been introduced in Unit 4 of this course. Therefore, here we will consider the oxidation states exhibited by transition metals only. Transition elements exhibit a wide range of oxidation states differing usually by units of one. This is due to the fact that $(n-1)d$ electrons may get involved along with ns electrons in bonding, as electrons in $(n-1)d$ orbitals are in an energy state comparable to ns electrons. From Table 12.5 you can see that there exists a general trend of lesser number of oxidation states at each end of the series and a higher number in the middle. The lesser number of oxidation states in the beginning of the series can be due to the presence of too few electrons

to lose or share, towards the end of series it can be ascribed to the presence of too many electrons and thus fewer empty orbitals to share electrons with the ligands

Table 12.5 : Oxidation states of transition elements of d–block (the most common oxidation states are in bold type)

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

Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
+3	+4	+3	+3	+4	+2	+3	+2	+1	+2
		+5	+4	+6	+3	+4	+3	+2	
			+5	+7	+4	+6	+4	+3	
			+6		+5				
					+6				
					+7				
					+8				

La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
+3	+4	+4	+2	+3	+2	+2	+2	+1	+1
		+5	+3	+4	+3	+3	+3	+3	+2
			+4	+5	+4	+4	+4		
			+5	+6	+6	+6			
			+6	+7	+8				

Another feature is the reduced tendency of higher oxidation states towards the end of the series. This could be due to steady increase in the effective nuclear charge along the series thus pulling the d orbitals into the electron core and not making them readily available for bonding. For example, the only oxidation state for Zn is Zn(II) where no d orbital is involved. On the other hand, early in the series, it is difficult to form species that do not utilise the d electrons i.e., Sc(II) is virtually unknown and Ti(IV) is more stable than Ti(II).

Now let us see the trend in the oxidation states as we go down the group. A full range of oxidation states of the transition elements is shown in Table 12.5. The trend in the stability of oxidation states with in the groups is different for the transition elements and the main group elements (s and p block elements). For the main group elements, the higher oxidation state becomes less-stable going down a group because of inert pair effect. However, for the transition elements the stability of the higher oxidation states increases going down a group.

To illustrate this trend, let us first look at Group 6. It is composed of Cr, Mo and W. We have seen that chromium in +6 oxidation state as in K_2CrO_4 is a good oxidising agent forming Cr^{3+} as the product. This means that in many instances Cr(III) is more stable than Cr(VI). In contrast, molybdenum and tungsten are not easily reduced when they are in +6 oxidation state in K_2MoO_4 and K_2WO_4. This implies that lower oxidation states, e.g., Mo(III) and W(III) are not as easy to form as Cr(III), making the +6 oxidation state more stable. Thus the stability of the +6 state for Group 6 elements will be $W^{6+}>Mo^{6+}>Cr^{6+}$. We find the same trend in Group 4 which is composed of Ti, Zr and Hf. For all the three elements, most stable oxidation state is +4. However Ti(II) and Ti(III) can be formed from Ti(IV) by the use of good reducing agents but lower oxidation states of Zr and Hf are extremely difficult to prepare. Table 12.6 shows how various oxidation states of some elements of period 4 tend to react with respect to oxidation and reduction.

Going from left to right across period 4, $M^{2+}(aq)$ ions are known for the last seven elements from V to Cu and $M^{3+}(aq)$ ions are known for the first seven elements from Sc and Co. Thus, there is an overall increase in stability of $M^{2+}(aq)$ with respect to oxidation as one moves across the series. However, in the case of iron, $Fe^{2+}(aq)$ is less stable than $Fe^{3+}(aq)$ because of the extra stability associated with half-filled (d^5) orbitals in the case of $Fe^{3+}(aq)$.

The highest oxidation states are often stabilised in the oxide and fluoride compounds, e.g., MnO_4^-, CrO_4^{2-}, VO_2^+, VF_5, etc. In these compounds O^{2-} and F^- are difficult to be oxidised by the central metal because O and F are strong oxidising agents.

Table 12.6 : Reactivity of some oxidation states of first transition series elements in aqueous solution

Reducing agents ———————→	Most stable ←———————	Oxidising agents
	Sc^{3+}	–
Ti^{2+}, Ti^{3+}	Ti^{4+}	–
V^{2+}, V^{3+}	V^{4+}	V^{5+} (slightly)
Cr^{2+}	Cr^{3+}	Cr^{6+}
	Mn^{2+}	$Mn^{3+}, Mn^{4+}, Mn^{7+}$
Fe^{2+}	Fe^{3+}	–
–	Co^{2+}	Co^{3+}
–	Ni^{2+}	–
Cu^+	Cu^{2+}	–

SAQ 4

Explain, briefly in the space provided below, the existence of OsO_4 in terms of trends in oxidation states.

....

....

....

....

....

12.5 FORMATION OF COMPLEXES

By now you must be familiar with the word 'complexes'. The chemistry of the transition metals is dominated by their tendency to form complex ions. This is because the transition elements form small, highly charged ions which have vacant orbitals of suitable energy to accept lone pairs of electrons donated by other groups or ligands. In case of transition metals in high oxidation states, highly charged ions can strongly bind electrostatically a wide variety of negative or polar ligands. In the case of transition metals in low oxidation states, the electrons in the d orbitals become involved in π bonding with ligands. The majority of transition metal ion complexes contain six ligands surrounding the central ion octahedrally. Some elements contain four ligands which are either arranged tetrahedrally or less frequently at the corners of a square. Besides these geometries, other geometries like trigonal bipyramid, pentagonal bipyramid, etc., are also present occasionally. The bonding between the ligand and the transition metal ion can either be predominantly electrostatic or covalent or in many cases intermediate between the two extremes. Some of the typical complexes of the transition metals are $[Fe(CN)_6]^{3-}$, $[Ni(NH_3)_4]^{2+}$, $[Cu(CN)_4]^{3-}$, $[Cu(NH_3)_4]^{2+}$, etc. The nature of these complexes and the important theories of bonding related to them are discussed in Unit 14 of this block.

12.6 COLOUR OF TRANSITION METAL COMPOUNDS

Compounds of transition elements are usually markedly coloured, in contrast to compounds of $s-$ and $p-$ block elements which are mostly white or colourless unless the anion is coloured. As you know, substances appear coloured when they absorb light of a particular wavelength in the visible region of the spectrum and transmit light of other wavelengths. The colour which we see is the colour of the transmitted wavelengths. In other words, the colour of the compound observed by us is the complementary colour of the colour absorbed by the compound. You know that the transition metals as such or in the form of ions have partly filled d–orbitals which are degenerate, i.e., they are of equal energy. You will study in Unit 14 that in transition metal complexes the d– orbitals do not remain degenerate, but these split into sets of orbitals of different energies. By absorbing energy, electrons can move from a d–orbital of lower energy to that of higher energy. This transition of electron

from one d–orbital to another corresponds to a fairly small energy difference, therefore, light is absorbed in the visible region of spectrum. For example, the aqua ion $Ti(H_2O)_6^{3+}$, which has one electron in the $3d$ orbital absorbs light of wavelength in the yellow-green region of spectrum and therefore, appears reddish violet in colour. Table 12.7 gives the relationship between the colour and the wavelength of light.

Table 12.7 : Relationship between the colour and wavelength

Wavelength absorbed in nm	Colour absorbed	Colour observed
<400	UV region	White/colourless
400–435	Violet	Yellow-green
435–480	Indigo	Yellow
480–490	Green-blue	Orange
490–500	Blue-green	Red
500–560	Green	Purple
560–580	Yellow-green	Violet
580–595	Yellow	Indigo
595–605	Orange	Green-blue
605–750	Red	Blue-green
>750	Infra-red	White/colourless

Whenever the d–orbitals are completely filled or empty, there is no possibility of electronic transitions within the d–orbitals. In such cases, the ions will not show any colour. For example, the compounds of Sc^{3+}, Ti^{4+}, Cu^+ and Zn^{2+} are white or colourless. Table 12.8 gives the colour and oxidation states of the metal ions present in some hydrated ions of transition elements.

Table 12.8 : Oxidation states and observed colours for some aqua species

Element	+2	+3	+6	+7
Sc		Colourless $[Sc(H_2O)_6]^{3+}$		
Ti		Violet $[Ti(H_2O)_6]^{3+}$		
V	Violet $[V(H_2O)_6]^{2+}$	Green $[V(H_2O)_6]^{3+}$		
Cr	Blue $[Cr(H_2O)_6]^{2+}$	Violet/green $[Cr(H_2O)_6]^{3+}$	Orange/yellow $Cr_2O_7^{2-}$, CrO_4^{2-}	
Mn	Pink $[Mn(H_2O)_6]^{2+}$	Red $[Mn(H_2O)_6]^{3+}$	Green MnO_4^{2-}	Purple MnO_4^-
Fe	Pale green $[Fe(H_2O)_6]^{2+}$	Yellow/brown $[Fe(H_2O)_6]^{3+}$		
Co	Pink $[Co(H_2O)_6]^{2+}$	Blue $[Co(H_2O)_6]^{3+}$		
Ni	Green $[Ni(H_2O)_6]^{2+}$			
Cu	Blue $[Cu(H_2O)_6]^{2+}$			
Zn	Colourless $[Zn(H_2O)_6]^{2+}$			

In the s– and p– block elements there cannot be any d–d transitions and the energy needed to promote s or p electron to a higher level is much greater and may correspond to ultraviolet region, in which case the compound will not appear coloured to the eye.

SAQ 5

Explain briefly why $CuSO_4$ is blue while $ZnSO_4$ is white.

....

....

12.7 MAGNETIC PROPERTIES

When you place an iron piece near a magnet, you will see that it is immediately drawn towards the magnet. However, some elements are repelled by the magnets. The property of an element to be attracted or repelled by a magnet differs from element to element. Substances which are weakly repelled by a magnetic field are called **diamagnetic**, while the substances which are weakly attracted by the magnetic field and lose their magnetism when removed from the field are called **paramagnetic**. If the force of attraction is very large and the permanent magnetisation is retained, the substance is said to be **ferromagnetic**, e.g., iron and some iron compounds.

Electrons determine the magnetic properties of matter in two ways. From the pre-wave mechanical view point, the electron may be regarded as a small sphere of negative charge spinning on its axis. Then from the completely classical considerations, the spinning of charge produces a magnetic moment. Secondly, an electron travelling in a closed path (orbit) around a nucleus, again according to pre-wave mechanical picture, will also produce a magnetic moment. The magnetic properties of any individual atom or ion will result from some combination of these two properties, that is, the inherent spin moment of the electron and the orbital moment resulting from the motion of the electron around the nucleus.

The magnetic moment is usually expressed in units called **Bohr magnetons** (BM). The general equation for the magnetic moment is given by :

$$\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)}$$

In the above expression , S is the sum of the spin quantum numbers and L is the sum of orbital angular momentum quantum numbers of all the electrons. In many compounds including those of the first row transition elements, the orbital contribution is quenched out by the electric fields of the surrounding atoms and as an approximation, the observed magnetic moment may be considered to arise only from unpaired spins. Putting $L=0$ in the above expression, you can get the spin-only magnetic moment μ_S.

Thus, $\mu_S = \sqrt{4S(S+1)}$

The spin-only magnetic moment, μ_S can also be related to the number of unpaired electrons, n, in any species, as the total spin quantum number $S = n/2$.

Hence, $\mu_S = \sqrt{4S(S+1)} = \sqrt{4n/2\,(\,n/2 + 1)}$

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

Above expression gives the value of magnetic moment in Bohr magnetons which can be converted into SI unit of Ampere square meter (A m^2) by the following relationship:

$$1 \text{ BM} = 9.274 \times 10^{-24} \text{ A m}^2$$

The magnetic moment is measured by weighing the sample in the presence and absence of magnetic field using a magnetic balance called Gouy balance (Fig. 12.8). Diamagnetic
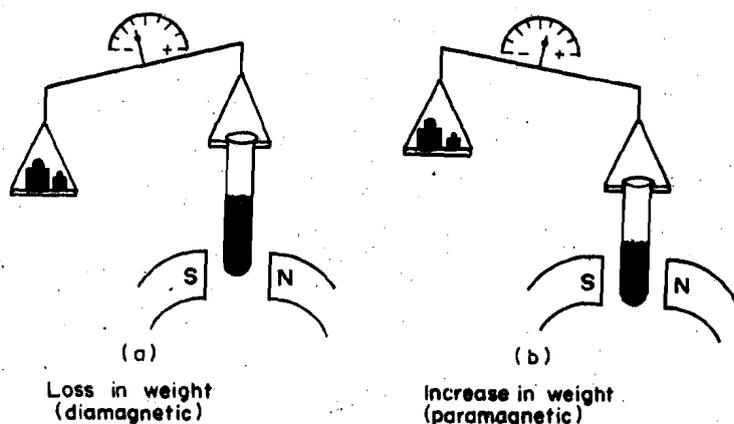

Loss in weight
(diamagnetic)

Increase in weight
(paramagnetic)

Fig. 12.8: Measurement of molecular paramagnetism using a Gouy balance

19

materials have no magnetic moment and show a slight decrease in weight on weighing in the presence of magnetic field. On the other hand, paramagnetic materials show an apparent increase in weight. The magnetic moment can be calculated from the change in weight.

In some cases (e.g., Mn^{2+}, or Fe^{3+}, in which all the d orbitals are occupied singly by electrons for which $m_l = 2, 1, 0, -1$ and -2, giving $L = 0$) the observed magnetic moment values agree very well with the spin-only value as given in Table 12.10. But generally, experimental values differ from the spin-only values. This is because the orbital motion of the electron also makes some contribution to the moment. More details on the magnetic properties of the transition elements can be studied in higher courses on the subject.

Table 12.9 : Predicted and observed magnetic moment values of some transition metal hydrated ions

Ion	Electronic configuration	Unpaired electrons	Magnetic moment (BM) Calculated Experimental (μ_s)
$[Ti(H_2O)_6]^{3+}$	$3d^1$ ↑	1	1.73 1.75
$[V(H_2O)_6]^{3+}$	$3d^2$ ↑ ↑	2	2.84 2.75
$[V(H_2O)_6]^{2+}$	$3d^3$ ↑ ↑ ↑	3	3.87 3.86
$[Cr(H_2O)_6]^{2+}$	$3d^4$ ↑ ↑ ↑ ↑	4	4.90 4.80
$[Mn(H_2O)_6]^{2+}$	$3d^5$ ↑ ↑ ↑ ↑ ↑	5	5.92 5.96
$[Fe(H_2O)_6]^{2+}$	$3d^6$ ↑↓ ↑ ↑ ↑ ↑	4	4.90 5.00
$[Co(H_2O)_6]^{2+}$	$3d^7$ ↑↓ ↑↓ ↑ ↑ ↑	3	3.87 4.40
$[Ni(H_2O)_6]^{2+}$	$3d^8$ ↑↓ ↑↓ ↑↓ ↑ ↑	2	2.84 2.90
$[Cu(H_2O)_6]^{2+}$	$3d^9$ ↑↓ ↑↓ ↑↓ ↑↓ ↑	1	1.73 1.80

SAQ 6

In $[Co(H_2O)_6]^{2+}$ the observed magnetic moment is higher than the spin-only value. Explain the reason for this in the space provided below.

....

....

....

....

12.8 CATALYTIC PROPERTIES

Many transition metals and their compounds have catalytic properties. These metals can function as catalysts because they can utilise both d and s electrons for the formation of bonds between reactant molecules and the surface catalyst atoms. This increases the concentration of the reactants at the catalyst surface and weakens the bonds in the reactant molecules with the result that the activation energy is lowered. Compounds of transition metals are able to act as catalysts because of the ease with which the metal can adopt different oxidation states and also because of their ability to form complexes. Some of the common catalysts used for important reactions are :

a. $FeSO_4$ and H_2O_2 as Fenton's reagent for the oxidation of alcohols to aldehydes

b. Pd for hydrogenation, e.g., phenol to cyclohexanol

c. Fe/Mo in manufacture of ammonia by Haber process

d. Pt/PtO as Adians catalyst for reductions

e. Pt/Rh in oxidation of NH_3 to NO in the manufacture of nitric acid

f. V_2O_5 in oxidation of SO_2 to SO_3 in the manufacture of sulphuric acid by contact process

g. Ni (Raney nickel) in reduction processes

h. $TiCl_4$ as (Ziegler Natta Catalyst) for polymerisation of ethene.

Transition metals are important catalysts in biological systems. A number of transition elements present in very small quantities in plants and animals are essential for the enzymes to function. For example, a cobalt atom lies at the centre of the vitamin B_{12} coenzyme. Iron atoms are importantly involved in hemoglobin of blood and in the ferredoxins of photosynthetic process. Both molybdenum and iron are contained in nitrogen fixing enzymes.

An enzyme is a biological catalyst which can bring about specific chemical reactions. It is known that several transition metal ions. e.g., iron, manganese, cobalt, zinc and molybdenum ions are involved in various processes.

12.9 INTERSTITIAL COMPOUNDS

Transition metals can trap some small atoms like hydrogen, boron, carbon, nitrogen, etc., in vacant spaces in their crystal lattice forming interstitial compounds. Carbon and nitrogen always occupy octahedral holes; hydrogen is smaller and always occupies tetrahedral holes. As only transition metals form such compounds, the d electrons are, therefore, presumably involved in the bonding. The structure of the metal often changes during the formation of such compounds. The composition of these compounds is generally non-stoichiometric, e.g., $TiH_{1.73}$, $PdH_{0.56}$, $VH_{0.56}$, but may approach regular stoichiometry and a regular structure, e.g., TiC and VN. The later transition elements of the first series form non-stoichiometric carbides with irregular structures, such as Cr_7C_3, which are more reactive than the interstitial carbides of the early transition elements. These interstitial compounds are of much importance, e.g., carbon steels are interstitial iron-carbon compounds in which the interstitial carbon prevents the iron atoms from sliding over one another, making iron harder, stronger but more brittle.

12.10 SUMMARY

Let us now summarise what we have learnt in this unit. This unit focuses on the transition metals and their characteristics. We have learnt about the electronic configuration of the transition elements and how the filling of the orbitals takes place with the increase in atomic number. We learnt that unlike the main group elements, the differentiating electron enters the penultimate $(n-1)d$ orbital in transition metals. This reflects in the properties of the transition metals and the periodicity in their properties. In this unit we have studied the variation of size, density, volume, melting and boiling points, ionisation energy, electronegativity, electrode potential, oxidation states and reactivity of the transition metals. Besides these, a few of their properties like colour, magnetic properties, complex formation, catalytic properties and formation of interstitial compounds have also been discussed. Thus, besides gaining the basic understanding of transition metals, we have also learnt about their applications. We now understand why silver and gold are so extensively used in jewellery, why transition metals are used as catalysts, etc. Thus this unit outlines a broad aspect of the transition metals.

12.11 TERMINAL QUESTIONS

1. How do the following properties vary in the transition elements?

   a) Atomic size

   b) Ionisation energy

   c) Stability of various oxidation states.

2. Why gold and silver are used for making ornaments?

3. Explain the following

   a) Mercury is a liquid.

   b) TiO_2 is white but $TiCl_3$ is violet.

4. Predict the spin-only magnetic moment for :

   a) Fe^{2+}

   b) Mn^{7+}

   c) Cu^+

   d) Ti^{3+}

5. Arrange each of the following groups of elements in order of increasing atomic size :
(a) iron, osmium, ruthenium (b) molybdenum, strontium, zirconium (c) scandium, lanthanum, yttrium.

6. Which one of the following pairs is more stable?

   a) CrO_3, WO_3

   b) MnO_4^-, ReO_4^-

   c) Cr^{2+}, Cr^{3+}

   d) Mn^{2+}, MnO_4^-

   e) CrO_4^{2-}, MoO_4^{2-}

   f) Mn_2O_7, Re_2O_7

   g) V^{2+}, VO_4^{3-}

7. Which of the following tend to be an oxidising agent or a reducing agent?

   a) Ti^{2+}

   b) CrO_4^{2-}

   c) Cu^+

   d) MnO_4^-

8. Yttrium with chlorine does not form YCl or YCl_2 but only YCl_3. How does this agree with the trends in stability of oxidation states?

9. Write a balanced equation for the reaction of each of the following elements with oxygen:
a. Scandium   b. Titanium   c. Vanadium   d. Chromium   e. Manganese   f. Nickel   g. Copper

12.12 ANSWERS.

Answers to Self Assessment Questions

1. a) In transition series, the electrons enter the *d* orbitals which can accommodate ten electrons and therefore, there are ten elements in one transition series.
   b) $3d$ is at higher energy than $4s$ at potassium, that is why the electron enters the $4s$ orbital instead of $3d$ orbital.

2. (i) Calcium
   (ii) Titanium
   (iii) Molybdenum
   (iv) Iron

3. Zn and Cd have electronic configuration $[Ar]3d^{10}4s^2$ and $[Kr]4d^{10}5s^2$, respectively. Therefore, there is no unpaired electron for metallic bonding. Thus, these metals are soft.

4. The oxidation number of osmium in OsO_4 is +8. The stability of higher oxidation states increases as we go down the group of the transition metals. Osmium being in third transition series is, therefore, stable in oxidation state +8 and exists as OsO_4.

5. Cu^{2+} in $CuSO_4$ has $[Ar]3d^94s^0$ configuration and its electron can be promoted to the half filled *d* orbital. Thus it can undergo *d–d* transition which absorbs mainly in the red region of the visible light and $CuSO_4$ appears blue in colour (blue is complementary colour of red). Because Zn^{2+} in $ZnSO_4$ has the configuration $[Ar]3d^{10}4s^0$, the transition of electron from one *d* orbital to another is not possible and no light is absorbed in the visible region of spectrum by $ZnSO_4$ and therefore, it appears white.

6. The observed magnetic moment at times differs from that of the calculated spin-only

magnetic moment due to the contribution of orbital motion of the electrons. The observed magnetic moment for $[Co(H_2O)_6]^{2+}$ has contribution from the spin as well as orbital angular momentum and thus the observed magnetic moment is higher than the calculated spin-only magnetic moment.

Answers to Terminal Questions

1. See the trends in properties.

2. Because of their noble nature gold and silver are used for making ornaments.

3. a) No metallic bond formation

   b) Ti(IV) has d^0 configuration

4.

Ion	Electronic configuration	Number of unpaired electrons	Magnetic moment
a) Fe^{2+}	$[Ar]3d^64s^0$	4	4.90 BM
b) Mn^{7+}	$[Ar]3d^04s^0$	0	0 BM
c) Cu^+	$[Ar]3d^{10}4s^0$	0	0 BM
d) Ti^{3+}	$[Ar]3d^14s^0$	1	1.73 BM

5. a) Fe < Ru < Os

   b) Mo < Zr < Sr

   c) Sc < Y < La

6. (a) WO_3 (b) ReO_4^- (c) Cr^{3+} (d) Mn^{2+}

   (e) MoO_4^{2-} (f) Re_2O_7 (g) VO_4^{3-}

7. a) Reducing agent

   b) Oxidising agent

   c) Reducing agent

   d) Oxidising agent

8. Stability of high oxidation state as we go down a group.

9. a) $4Sc(s) + 3O_2(g) \longrightarrow 2Sc_2O_3(s)$

   b) $Ti(s) + O_2(g) \longrightarrow TiO_2(s)$

   c) $4(V)(s) + 5O_2(g) \longrightarrow 2V_2O_5(s)$

   d) $4Cr(s) + 3O_2(g) \longrightarrow 2Cr_2O_3(s)$

   e) $Mn(s) + O_2(g) \longrightarrow MnO_2(s)$

   f) $2Ni(s) + O_2(g) \longrightarrow 2NiO(s)$

   g) $2Cu(s) + O_2(g) \longrightarrow 2CuO(s)$

UNIT 13 INNER-TRANSITION ELEMENTS

Structure

13.1 INTRODUCTION

In the preceding unit, you studied the main features of the chemistry of the transition elements of the d-block. You learnt that in addition to the usual vertical relationship, the transition elements show a horizontal similarity in their physical and chemical properties. In this unit you will study the salient features of the chemistry of the transition elements of the f-block. Because of filling of electrons in the f-orbitals of an inner shell, these elements are also termed as inner-transition elements. The f-block elements comprise two series of elements — the lanthanide series and the actinide series. You will observe that in comparison to the elements of d-block transition series, the members of lanthanide series resemble one another much more closely. They have generally one common stable oxidation state and occur together in the same ores in nature. Because of the similarity in their chemical properties their separation from one another is very difficult. Therefore, special techniques of solvent extraction and ion exchange are employed for their separation. On the other hand, the chemistry of the actinides is quite complicated because they exhibit more than one oxidation state and their radioactivity creates problems in the study of their properties. However, the actinides do exhibit some similarities with one another and with their lanthanide congeners in a particular oxidation state. Therefore, these elements are discussed as a class in one unit. In this unit you will study the general features of the chemistry of lanthanide and actinide elements with emphasis on periodicity in their properties.

Objectives

After studying this unit you should be able to :
- distinguish between transition and inner-transition elements,
- define the terms lanthanides and actinides,
- compute the electronic configurations of lanthanide and actinide ions from the electronic configurations of free atoms,
- discuss the ways in which actinide elements resemble their lanthanide congeners,
- discuss the ways in which the actinides resemble more closely d-block transition elements,
- explain lanthanide and actinide contraction,
- describe general characteristics of lanthanide and actinide elements and bring out periodicity in their properties.

13.2 GENERAL CHARACTERISTICS

You know that the fourteen elements from cerium ($Z = 58$) to lutetium ($Z = 71$), which