23

d-BLOCK AND *f*-BLOCK ELEMENTS

You have already learnt in lesson 4 on periodic classification, that each period (except the first period) of the periodic table starts with the filling of *ns* subshell and ends with the filling of *np* subshell (*n* is the principal quantum number and also the number of the period). The long form of the periodic table is based on the filling of electrons in various levels in order of increasing energy as given by Aufbau principle. In the fourth period, filling of the 4th shell commences with the filling of 4*s* subshell followed by 3*d* and 4*p* subshells. For the first time, we come across a group of elements in which a subshell of the previous principal quantum number (3*d*) starts getting filled instead of the expected subshell 4*p*. This group of elements that occurs in between the *4s* and *4p* elements is referred to as *3d* elements or elements of first transition series (see periodic table). *4f* Series consist of 14 members from Ce to Lu (At. No. 58-71), where the penultimate subshell, *4f* subshell is filled up. They have general electronic configuration [Xe] $4f^{1-14}\,5d^{1,2}\,6s^2$. La is also included in this series: it is the prototype for the succeeding 14 elements. In this lesson you will study more about these elements and also about the preparation, properties and uses of potassium dichromate ($K_2Cr_2O_7$) and potassium permanganate ($KMnO_4$).

Objectives

After reading this lesson, you will be able to:

- define transition metals and write their electronic configuration;
- list the general and characteristic properties of the transition elements;
- explain the properties of 3d transition series: metallic character, variable oxidation state, variation in atomic and ionic radii, catalytic properties, coloured ions, complex formation, magnetic properties, interstitial compounds and alloy formation;
- recall the preparation of potassium permanganate from pyrolusite ore;
- write the chemical equations illustrating the oxidizing properties of $KMnO_4$ in acidic, alkaline and neutral media (acidic: $FeSO_4$, SO_2, alkaline: KI and ethene, neutral: H_2S and $MnSO_4$);

- recall the preparation of potassium dichromate from chromite ore;
- write the oxidation reactions of potassium dichromate with SO_2 and ferrous sulphate in acidic medium;
- write electronic configuration of lanthanoides (4f-elements) and
- explain lanthanoide contraction.

23.1 *d*-Block Elements

d-Block elements occupy the middle portion of the periodic table i.e. between *s*- and *p*-block elements. They include elements from groups 3 to 12. In these elements the outermost shell contains one or two electrons in their outer most i.e, ns orbital but the last electron enters into the inner d-subshell i.e. (*n*-l) *d* orbital. The elements of the *d-block* are metallic in nature. Their general characteristic properties are intermediate between those of the s-block elements, on one hand and of the p-block elements on the other. We can say that *d*-block elements represent a change (or transition) from the most electropositive *s*-block elements to the least electropositive *p*-block elements and are, therefore, also named as transition elements.

Transition elements are elements in which the *d* subshell is partially filled either in atomic state or in ionic state.

There are four series of transition elements in the periodic table. The first transition series begins with scandium (At. No. 21) and ends at copper (At. No. 29) whereas the second, third and fourth series begin with yttrium (At. No. 39), lanthanum (At. No. 57) and actinium (At. No. 89) and end at silver (At. No. 47), gold (At. No. 79) and at the element having atomic number 112 (a synthetic element), respectively. These series are also referred to as *3d*, *4d*, *5d* and *6d* series, respectively. It may be noted that although elemental copper, silver and gold as well as Cu^{1+}, Ag^{1+} and Au^{1+} have a d^{10} configuration but Cu^{2+} has a $3d^9$, Ag^{2+} a $4d^9$ and Au^{3+} a $5d^8$ configuration and that is why these elements are classified as transition elements. On the other hand, zinc, cadmium and mercury do not have partially filled *d* subshell either in the elemental state or in any of their common ions. These elements, therefore, are not transition elements. However, zinc, cadmium and mercury are often considered along with *d*- block elements.

Intext Questions 23.1

1. What are transition elements?

   ....

2. How many elements comprise the first transition series? Give names of all these elements.

   ....

3. Whereas copper is a transition element, zinc is not included amongst transition elements. Explain.

   ....

4. Although Cu^{+}, Ag^{+} and Au^{+} have d^{10} configuration but Cu, Ag and Au are transition elements, why?

   ....

23.2 Electronic Configuration

The general electronic configuration of transition elements is (n-1) d^{1-10} ns^{1-2}. The (n-1) stands for inner shell and the *d*-orbitals may have one to ten electrons and the *s*-orbital of the outermost shell (n) may have one or two electrons. It is observed from the Fig. 23.1 that 4*s* orbital (l = 0 and n = 4) is of lower energy than 3*d* orbitals (l = 2 and n = 3) upto potassium (At. No.19). The energy of both these orbitals is almost same in case of calcium (At. No. 20), but the energy of 3*d* orbitals decreases with further increase of nuclear charge and becomes lower than *4s*, and 4*p*, (in case of scandium At. No.21). Thus after filling of 4*s* orbital successively with two electrons at atomic number 19 and 20, the next incoming electron goes to 3*d* orbital instead of 4*p*, as the former is of lower energy than the latter. This means that 21st electron enters the underlying principal quantum level with n = 3 rather than the outermost level with n = 4 which started filling at potassium (At. No.19), the first element of the fourth period. In the case of next nine elements following calcium, the incoming electron is filled in the *d*- subshell. Since half filled and completely filled subshells are stabler than the one in which one electron is short, an electron gets transferred from 4*s* to 3*d* in case of the elements with atomic number 24 and 29. Consequently, configuration of chromium and copper have only one 4*s* electron (Table 23.1).

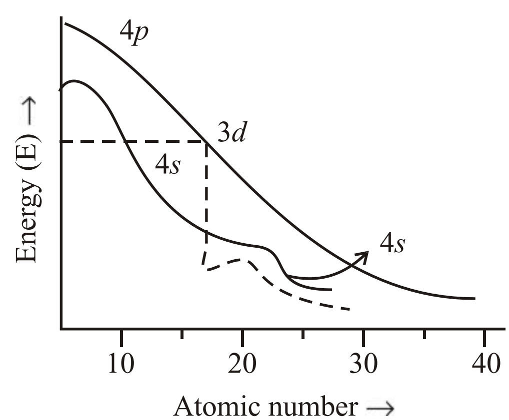


Fig. 23.1 : *Variation of energy of orbitals vs atomic number*

Table 23.1: Electronic configuration of first series(or 3*d*) transition elements

Element	Symbol	Z	Electronic Configuration
Scandium	Sc	21	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1\ 4s^2$
Titanium	Ti	22	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$
Vanadium	V	23	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$
Chromium	Cr	24	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$
Manganese	Mn	25	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$
Iron	Fe	26	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$
Cobalt	Co	27	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7\ 4s^2$
Nickel	Ni	28	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$
Copper	Cu	29	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$
Zinc	Zn	30	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2$

As can be seen, in case of zinc, the 30th electron goes to 4*s* level and not 3*d* level which is already full. Thus by definition, zinc cannot be called a member of *d*block elements. Besides, no compound of zinc is known to have a partially filled 3*d* subshell. Thus it does not fit into the definition of a transition element either. Hence zinc cannot be rightly called either a *d*-block element or transition element. However, zinc and other members of group 12, viz., cadmium and mercury are discussed along with 3*d*, 4*d* and 5*d* transition elements for the sake of convenience.

It is important to understand at this point, the process of ionization (i.e. oxidation) of transition elements. From what has been said above regarding filling of the orbitals, it is logical to conclude that during ionization electrons should be lost first from the (n-1) *d* subshells and then from the 4*s* level. This, however, is not the case. The reason for the deviation from the expected behavior is that once the filling of the *3d* subshell commences at scandium (At. No.21) energy of 3*d* subshell decreases and becomes lower than that of 4*s* subshell. Consequently, on ionization, the first row transition elements lose electrons from the 4*s* subshell followed by the loss from 3*d* level. For example vanadium (Z = 23) has electronic configuration V= $[Ar]3d^3 4s^2$ and the electronic configuration of V^{2+} is $[Ar]3d^3$, Similarly electronic configuration of V^{3+} and V^{4+} are $[Ar]3d^2$ and $[Ar]3d^1$, respectively. In some cases, however, for example scandium, all the electrons beyond the core of 18 electrons are lost in single step. It is important to note that though 3*d* orbitals are of higher energy than 4*s* orbitals (as is evident from the order of filling) the difference is so little that these are considered almost of same energy.

Intext Questions 23.2

1. Write the general electronic configuration of transition elements.

   ....

2. Write down the electronic configuration of the following elements in ground state: Sc, Cr, Cu and Zn.

   ....

3. Write down the electronic configuration of the following ions: Cr^{3+}, Ti^{4+}, Ni^{3+} and Cu^{2+}.

   ....

4. Why the electronic configuration of Mn^{2+} is $3d^5$ and not $3d^2\,4s^2$?

   ....

23.3 Physical Properties

Some important physical properties of *d*-block elements are listed in Table 23.2. Like *s*-block elements, *d*-block elements are also metals. But properties of these elements are markedly different from those of *s*-block elements. The interesting feature of the chemistry of transition elements is that similarities in the properties of transition elements are much more marked as compared to those in *s*-block. Almost all transition elements show typical metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity and metallic lusture. All the transition elements have typical metallic structure except mercury, which is liquid at room temperature.

Transition elements show high melting and boiling points. They typically melt above 1356 K. It is due to the small atomic size and strong interatomic bonding. All the transition elements are hard except zinc, cadmium and mercury. They show high enthalpy of atomization (Table 23.2). Densities of transition elements are very high as compared to those of s-block elements. The density of the elements in a given transition series increases across a period and reaches a maximum value at groups 8,9 and 10. This trend can be explained on the basis of small radii and close packed structure of the elements.

Table 23.2: Some important physical properties of 1st transition series

Property	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number	21	22	23	24	25	26	27	28	29	30
Outer electronic configuration	$3d^1\ 4s^2$	$3d^2\ 4s^2$	$3d^3\ 4s^2$	$3d^4\ 4s^2$	$3d^5\ 4s^2$	$3d^6\ 4s^2$	$3d^7\ 4s^2$	$3d^8\ 4s^2$	$3d^9\ 4s^2$	$3d^{10}\ 4s^2$
Atomic radius (pm)	160	146	131	125	129	126	125	124	128	133
Ionic radius M^{2+} (pm)	–	90	88	84	80	76	74	72	69	79
Ionic radius M^{3+} (pm)	81	76	74	69	66	64	63	63	–	–
Crystal structure	fcc	hcp	bcc	bcc	bcc	bcc,fcc	hcp,fcc	fcc	fcc	hcp
Density (g ml^{-1})	3.1	4.5	6.1	7.2	7.6	7.9	8.7	8.9	8.9	7.1
Melting point (K)	1817	1998	2173	2148	1518	1809	1768	1726	1356	693
Boiling point (K)	3003	3533	3723	2138	2423	3273	3173	3003	2868	1179
Stable oxidation states	+3	+4	+3,+4,+5	+2,+3,+6	+2,+3,+4,+7	+2,+3	+2,+3	+2	+1,+2	+2
Ist ionization enthalpy (kJ mol^{-1})	632	659	650	652	717	762	758	736	745	906
Electronegatively	1.3	1.5	1.05	1.6	1.05	1.8	1.8	1.8	1.8	1.6
Heat of fusion (kJ mol^{-1})	15.9	15.5	17.6	13.8	14.6	15.3	15.2	17.6	13.0	7.4
Heat of vaporization (kJ mol^{-1})	338.9	445.6	443.6	305.4	224.7	353.9	389.1	380.7	338.9	114.6
Reduction potential $(E^0)M^{2+}/M(V)$	–	–1.63	–1.20	–0.91	–1.18	–0.44	–0.28	–0.25	+0.34	–0.76

Atomic radii

The radii of the elements decrease from left to right across a row in the transition series until near the end, then the size increases slightly. On passing from left to right, extra protons are placed in the nucleus and extra electrons are added. The *d*-orbital electrons shield the nuclear charge poorly. Thus the effective nuclear charge increases and, therefore, electrons are attracted more strongly, hence contraction in size occurs. There is an increase in atomic radii with increase in atomic number in a given group, for example Ti (146 pm), Zr (157 pm) and Hf (157 pm). The very close similarity between the radii of elements of second and third transition series is a consequence of the filling of the 4*f*- subshell (causing lanthanide contraction which you will study later in this lesson).

Notes

Intext Questions 23.3

1. Why do transition elements show higher melting and boiling points?

   ....

2. Why do the radii of transition elements decrease along a period?

   ....

3. Why do transition elements show higher density as compared to *s*-block elements?

   ....

23.4 Characteristic Properties

These are the properties shown only by transition elements. On the basis of these properties transition elements can be distinguished from *s* and *p*-block elements.

23.4.1 Variable Oxidation States

s-block, *d*-block and *f*-block elements show positive oxidation states (except H which shows –1 oxidation state also) whereas, most of the *p*-block elements show both positive and negative states. The number of electrons used for bonding by an electropositive element is equal to its positive oxidation state. A characteristic property of *d*-block elements is their ability to exhibit a variety of oxidation states in their compounds. This is due to the fact that for bonding, in addition to ns electrons, these elements can use inner (n-1)d electrons as well because of very small difference in their energies. Thus, depending upon the number of d electrons involved in bonding, different oxidation states arise. The lowest oxidation state is usually equal to the number of *s*-electrons present (except Sc). For example, copper has an electronic configuration of $3d^{10}4s^{1}$ and shows oxidation state of + 1 besides the usual oxidation state of +2. The highest oxidation states are observed in compounds with fluorine and oxygen, which are the two most electronegative elements. The different oxidation states of elements of the first transition series are given below:

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

(* Given for comparison only.) Here the rare oxidation states are given in parentheses.

An examination of the common oxidation states given above, reveals the following:

Except for scandium, the most common oxidation state of 3*d* elements is +2 which arises from the loss of two 4*s* electrons. This means that after scandium, *d* orbitals become more stable than *s* orbital. Compounds having oxidation states +2 and +3 of these elements have ionic bonds whereas bonds are essentially covalent in higher oxidation states. For example, in case of permanganate ion, MnO_4^-, bonds formed between manganese and oxygen are covalent. Considering the acid base character of the oxides, it can be inferred that increase in oxidation state leads to decrease in basic character of the oxide and vice-versa. For example, MnO is a basic oxide whereas Mn_2O_7 is an acidic oxide.

Since transition metals exhibit multiple oxidation states, their compounds in the higher oxidation states are strong oxidizing agents as they tend to accept electrons and come to stable lower oxidation states.

23.4.2 Magnetic Properties

Substances possess two types of magnetic behaviour, either diamagnetism or paramagnetism. Diamagnetic substances are either repelled or remain unaffected by an applied magnetic field whereas, paramagnetic substances are attracted towards the applied field.

There is a strong co-relation between the magnetic behaviour, electronic configuration and oxidation state. Paramagnetism arises due to the presence of unpaired electrons (Table 23.3). Since transition metal ions generally contain unpaired electrons a large number of transition metal ions exhibit paramagnetic behavior.

Magnetic moment (μ) of paramagnetic material can be calculated (in B.M., Bohr Magneton) by using the expression: $\mu = \sqrt{n\,(n+2)}$ where n is the number of unpaired electrons.

For example, Ni^{2+} ion has two unpaired electrons (i.e. n = 2). The magnetic moment can be calculated as $\mu = \sqrt{2\,(2+2)} = \sqrt{8} = 2.83$ B.M The mangentic moments of some 3*d* metals ions are listed in Table 23.3 which shows that greater the number of unpaired electrons, greater is the magnetic moment.

Table 23.3 : Magnetic moments of some ions of the transition elements:

Ion	Electronic configuration	Number of unpaired electrons	Calculated magnetic moments (B.M.)
Sc^{3+}	$3d^0$	0	0
Ti^{3+}	$3d^1$	1	1.73
Ti^{2+}	$3d^2$	2	2.83
V^{2+}	$3d^3$	3	3.87
Cr^{2+}	$3d^4$	4	4.90
Mn^{2+}	$3d^5$	5	5.92
Fe^{2+}	$3d^6$	4	4.90
Co^{2+}	$3d^7$	3	3.87
Ni^{2+}	$3d^8$	2	2.83
Cu^{2+}	$3d^9$	1	1.73

Compounds containing Sc^{3+}, Ti^{4+}, V^{5+}, Cr^{6+}, Mn^{7+} and Cu^{+} ions are diamagnetic since these ions do not contain any unpaired electron.

23.4.3. Colour of Ions and Compounds

Most of the compounds of *d*-block elements are coloured or they give coloured solution when dissolved in water (Table 23.4). This property of transition elements is in marked contrast to that of the *s*- and *p*-block elements, which often yield white compounds. In transition metal compounds colour is generally associated with incomplete (n-1) *d* subshell of the transition metal. When white light, which has colored constituents, interacts with a substance, a part of it is absorbed by the substance. For example, if red portion of white light is absorbed by a substance, it would appear blue (the complementary colour of red). This is observed in case of copper sulphate solution. Since most compounds of transition elements are coloured, there must be energy transition, which can absorb some of the energy of the visible light. The colour of transition metal ions containing unpaired electrons is attributed to electronic transitions from one energy level to another in the *d*-subshell. In these metals the energy difference between the various *d*-orbitals is in the same order of magnitude as the energies of the radiation of white light (A. = 4000 to 8000 A).

Table 23.4 : Colours of hydrated ions of some transition elements

Hexahydrated ion of	Number of d electrons	Color of solid/solution
Ti^{3+}	1	Violet
V^{3+}	2	Blue
V^{2+}	3	Violet
Cr^{3+}	3	Green
Mn^{3+}	4	Violet
Fe^{3+}	5	Yellow/colorless
Mn^{2+}	5	Yellow/colorless
Fe^{2+}	6	Pale green
Co^{2+}	7	Pink
Ni^{2+}	8	Green
Cu^{2+}	9	Blue

23.4.4 Alloy and Interstitial Compound Formation

In the Table 23.2 it may be observed that the atomic size of the elements of first transition series is quite close to each other. Thus, in the crystal lattice, anyone of these elements can easily replace another element of similar size forming solid solutions and smooth alloys. Transition elements, therefore, form a number of alloys. Cr, V and Mn are used to produce alloy steel and stainless steel, copper forms brass, bronze etc. Besides, transition metals also form a number of interstitial compounds in which they take up atoms of small size, like hydrogen, carbon and nitrogen etc. These are located in the vacant spaces of metal lattices and are bound firmly there in. The products thus obtained are hard and rigid. For example, steel and cast iron become hard due to formation of an interstitial compound with carbon. In such compounds, malleability and ductility may marginally decrease but tenacity is considerably enhanced. Some examples of alloys are given in Table 23.5.

Table 23.5 : Examples of some alloys

Alloy	Composition
Brass	Cu (50%-80%) and Zn (50%-20%)
Bronze	Cu (90%-93%) and Sn (10%-7%)
Gun metal	Cu (88%), Sn (10%) and Zn (2%)
Bell metal	Cu (80%) and Sn (20%)

23.4.5 Complex Formation

Transition metals exhibit a strong tendency to form complexes with different ligands due to the following reasons:

1. Small size and high charge density.
2. Variable oxidation states.
3. Availability of vacant d-orbitals to accept electron pairs from ligands.

You will learn more about complexes in the next lesson

23.4.6 Catalytic Properties

The catalytic activity of transition metals and their compounds is associated with their variable oxidation states. Typical catalysts are vanadium(V) oxide (contact process for sulphuric acid), finely divided iron (Haber's process), nickel (catalytic hydrogenation) and palladium(II) chloride and a copper(II) salt for the production of ethanol from ethane and water (Wacker's process). Haemoglobin, a large molecule containing Fe(II), acts as a catalyst for the respiration process.

Catalysis at a solid surface involves the formation of bonds between reactant molecules and the catalyst surface atoms, this has the effect of increasing the concentration of the reactants at the catalyst surface and also of weakening the bonds in the reactant molecules (the activation energy is lowered).

Transition metal ions function as catalysts by changing their oxidation states, e.g., Fe(III) cations catalyse the reaction between iodide and peroxodisulphate ions:

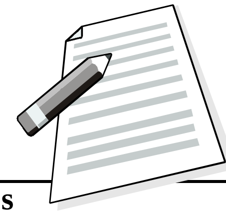
$$2I^-(aq) + S_2O_8^{2-}(aq) \xrightarrow{Fe^{3+}} I_2(aq) + 2SO_4^{2-}(aq)$$

An oversimplified, explanation of this catalysis reaction might be:

$$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$$

$$2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \rightarrow 2Fe^{3+}(aq) + 2SO_4^{2-}(aq)$$

It is known that both the above reactions can take place, and it would be expected that two reactions between ions of opposite charge would be faster than one reaction between ions of the same type of charge.



Notes

Intext Questions 23.4

1. Why do transition elements act as good catalysts?

   ....

2. Name some of the common catalysts you have studied.

   ....

3. Which of the following compounds are expected to be diamagnetic: $CrCl_3$, $ScCl_3$, $CuSO_4$, $CoCl_2$, $TiCl_4$ and $ZnCl_2$?

   ....

4. Which of the following do you expect to be colored and why, Cr^+ and Cu^+?

   ....

5. Name any two alloys of transition elements.

   ....

6. Calculate in B.M., magnetic moments expected for the following ions:

   V^{4+}, Ni^{3+}, V^{4+}, Ni^{3+}, Cr^{3+} and Ti^{4+}.

   ....

23.6 *f*-Block Elements (Lanthanoides)

In addition to *d*-block elements, there are two rows of elements shown separately at the bottom of the periodic table. The elements from La to Lu (14 elements) are called lanthanoides. They are characterised by the filling up of the anti penultimate 4*f* orbitals. They are extremely similar to each other in properties. Earlier these were called the rare earths. This name is not appropriate because many of these elements are not particularly rare. Now these elements are known as inner transition elements (because they form transition series within the *d*-block transition elements) or lanthanoids.

23.6.1 Electronic Configuration

Lanthanum is the first member of the third transition series, and it has one 5*d* and two 6*s* electrons. The next element is cerium, which while still retaining two 6*s* electrons, has two electrons in the 4*f* orbitals and none in the 5*d* orbitals. There are 7 separate 4*f* orbitals, each of which can accommodate two electrons with opposite spins. The atoms of the elements from cerium to lutetium have two to fourteen electrons in 4*f*- orbitals, respectively. These elements constitute the first inner transition series known as lanthanides and, although lanthanum itself does not possess any 4*f* electrons, it is customary to include this element in this series.

The filling up of the 4*f* orbitals is regular with some exceptions (Table 23.6); the element europium has the outer electronic configuration $4f^7 5s^2 5p^6 5d^0 6s^2$ and the next element gadolinium has the extra electron in the 5*d* orbital. The element ytterbium has a full compliment of 4*f* electrons ($4f^{14} 5s^2 5p^6 5d^0 6s^2$) and the extra electron in the lutetium atom enters the 5d orbitals ($4f^{14} 5s^2 5p^6 5d^1 6s^2$). Except for lanthanum, gadolinium and lutetium, which have a single 5d electron, the lanthanoides do not have electrons in the 5*d* orbitals.

Table 23.6: Electronic configuration of lanthanides

Element	Symbol	Z	Electronic configuration
Lanthanum	La	57	$[Xe]4f^0 5d^1 6s^2$
Cerium	Ce	58	$[Xe]4f^2 6s^2$
Praseodymium	Pr	59	$[Xe]4f^3 6s^2$
Neodymium	Nd	60	$[Xe]4f^4 6s^2$
Promethium	Pm	61	$[Xe]4f^5 6s^2$
Samarium	Sm	62	$[Xe]4f^6 6s^2$
Europium	Eu	63	$[Xe]4f^7 6s^2$
Gadolinium	Gd	64	$[Xe]4f^7 5d^1 6s^2$
Terbium	Tb	65	$[Xe]4f^9 6s^2$
Dysprosium	Dy	66	$[Xe]4f^{10} 6s^2$
Holmium	Ho	67	$[Xe]4f^{11} 6s^2$
Erbium	Er	68	$[Xe]4f^{12} 6s^2$
Thulium	Tm	69	$[Xe]4f^{13} 6s^2$
Ytterbium	Yb	70	$[Xe]4f^{14} 6s^2$
Lutetium	Lu	71	$[Xe]4f^{14} 5d^1 6s^2$

23.6.2 The lanthanoide contraction

Each succeeding lanthanoide differs from its immediate predecessor in having one more electron in the 4*f* orbitals (except for some exceptions as discussed above) and one extra proton in the nucleus of the atom. The 4f electrons constitute inner shells and are rather ineffective in screening the nucleus; thus there is a gradual increase in the attraction of the nucleus for the peripheral electrons as the nuclear charge increases, and a consequent contraction in atomic radius is observed. For example, the ionic radii of the +3 cations decrease steadily from a value of 115 pm for La^{3+} to a value of 93 pm for Lu^{3+}. The regular decrease in atomic radii with increase in atomic number is known as lanthanoide contraction.

The lanthanoide contraction considerably influences the chemistry of the elements, which succeed the lanthanides in the periodic table; for instance the atomic radii of zirconium (At. No. 40) and hafnium (At. No. 72) are almost identical and the chemistry of these two elements is strikingly similar. Incidentally, the density of hafnium (which immediately follows the lanthanides) is almost twice the density of zirconium (which is in the same group).

Intext Questions 23.7

1. How many elements constitute lanthanoide series?

   ....

2. Why Zr and Hf show almost same properties?

   ....

3. Write down the electronic configuration of the following in the ground state: Gd, Lu, Ho, Er.

   ....

4. Write down the electronic configuration of the following ions: Eu^{3+}, $Y6^{3+}$, Ce^{4+}.

   ....

What You Have Learnt

- Transition elements have partially filled *d*-orbitals either in atomic or ionic state.
- They show general electronic configuration $(n-1)d^{1-10}ns^{1,2}$.
- They show high M.P. and B.P. due to strong inter-atomic bonding.
- They show variable oxidation states.
- They form colored ions and compounds.
- They show paramagnetic behaviour.
- They form complexes.

- They form alloy and interstitial compounds.
- Manufacture of $K_2Cr_2O_7$ and $KMnO_4$.
- $K_2Cr_2O_7$ and $KMnO_4$ act as oxidizing agents.

  These compounds are used in volumetric analysis.
- Electronic configuration of lanthanoids.
- Lanthanoid contraction.

Terminal Exercises

1. What distinguishes a transition metal from a representative metal?
2. Why is zinc not considered a transition metal?
3. Explain why atomic radii decrease very gradually from Sc to Cu.
4. Write down the ground state electronic configuration of the first row transition elements. Explain the irregularities.
5. Write down the electronic configuration of the following ions:

   V^{5+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Cu^{2+}, Sc^{3+} and Ti^{4+}
6. Why do transition elements have more oxidation states than other elements?
7. Give the highest oxidation states for the elements from Sc to Cu.
8. How would you define transition elements? List the properties associated with transition elements.
9. How do the following properties vary in transition elements?

   (a) Stability of the various oxidation states.

   (b) Ability to form complexes.
10. What do you understand by the terms paramagnetism and diamagnetism? Predict the magnetic moments for Fe^{2+}, Co^{3+}, Ni^{3+} and Cu^{+} ions.
11. 4*s* sub-shell is filled prior to 3*d*- sub-shell but on ionization 4*s* electrons are removed first. Explain.
12. Why does Mn(II) show maximum paramagnetic character amongst the bivalent ions of first transition series?
13. Why is Cu^{2+} ion colored and paramagnetic while Zn^{2+} ion is colorless and diamagnetic.
14. Why do transition elements.

    (a) show variable oxidation states?

    (b) form a large number of coordination compounds?

    (c) give colored and paramagnetic ions?

    (d) exhibit good catalytic properties?

15. Discuss the main characteristic features of the transition elements with special reference to their atomic size, variable oxidation states, magnetic and catalytic properties.

16. Explain the trends of variations of:

    (a) melting and boiling points.

    (b) atomic radius in the first transition series.

17. A solution of $KMnO_4$ on reduction yields either a colorless solution or a brown precipitate or a green solution depending on the pH of the solution. What different stages of the reduction do these represent and how are they carried out?

18. A black color compound [X] of manganese when fused with KOH under atmospheric oxygen gave a green colored compound [Y]. When the compound [Y] was treated with an oxidizing agent (chlorine or ozone), it gave a purple colored solution [Z]. Identify X, Y, Z and write the chemical equation.

19. Compound [A] of chromium when treated with sodium carbonate in the presence of atmospheric oxygen gave a yellow colored compound [B]. Compound [B] on treatment with acid gave an orange colored compound [C]. [B] can also be obtained by treatment of [C] with alkali. Identify the compound A, B, C and write the chemical equations.

20. Why do transition elements form a large number of alloys and interstitial compounds?

21. What are lanthanides? Why are they called inner transition elements?

22. What is lanthanide contraction and what are its consequences?

23. Write the electronic configurations of the following in ground state:

    Eu, Ho and Gd.

24. Describe two oxidizing properties of potassium dichromate.

25. Describe two oxidizing properties of potassium permanganate.