

# UNIT

## 3

### d- and f-Block Elements

#### 3.1 Introduction

We have obtained the information about modern periodic table for classification of elements in standard 11 (semester I). In addition to this, we have also studied in detail the s- and p-block elements during semesters I to III. We know, the elements in modern periodic table are classified into s-, p-, d- and f-blocks and 1 to 18 groups. The elements of groups 1 and 2 and the groups 13 to 18 are known as s-block and p-block elements respectively; while elements of rest of the ten groups, group no 3 to 12 are called d-block elements because the last electron of the elements, enter into the available d-orbital. The position of these elements is between s-block and p-block elements. The properties of d-block elements show transition between the properties of representative elements of periodic table i.e. most electropositive elements of s-block (metal elements) and least electropositive elements of p-block (nonmetals, metalloids and metals). Hence, they are known as **transition elements**. This means that those elements have their properties which intermediate between those of s- and p-block elements. The two horizontal rows at the bottom of the modern periodic table are called f-block elements because the last electron enters into the available f-orbitals. Th ( $Z = 90$ ) has got the electronic structure  $[\text{Rn}] 5f^0 6d^2 7s^2$ . In Th, the last electron is not filled in f-orbital although the experimental results support the elements as f-block elements. Thus, it is included in f-block elements. These elements being part of the transition series of transition elements of periods 6 and 7; are called **innertransition elements**.

#### 3.2 Transition Elements – Elements of d-Block

**The elements which in their ground state or any one of its oxidation state, have incompletely filled d-orbitals with electrons are called the transition elements.** The elements whose ground state or any of its oxidation state have vacant 3d-orbitals are called **first transition series elements**, if 4d-orbitals are incompletely filled then **second transition series elements** and

5d-orbitals incompletely filled with electrons then they are called **third transition series elements**. In each of these series there are ten elements. Fourth transition series corresponding to the filling of 6d-orbital begins with actinium ( $Z = 89$ ) followed by element with atomic number 104 (Rf) onwards. Regarding fourth transition series, the research is continuing at present.

### 3.2.1 Electronic Configuration and Oxidation States of Transition Elements :

The general electronic configuration of transition elements is  $(n-1)d^{1-10}ns^{1-2}$ . Generally the stability of half filled or completely filled orbital is relatively more. Because of this the electronic configuration of Cr is considered  $[\text{Ar}]3d^54s^1$  instead of  $[\text{Ar}]3d^44s^2$ . In the same way the electronic configuration of Cu is considered  $[\text{Ar}]3d^{10}4s^1$  instead of  $[\text{Ar}]3d^94s^2$ . It is necessary here to note that the difference between energies of 3d and 4s orbital, is very less, hence this becomes possible.

When ions are formed from first transition series elements, the electron entering last in 3d-orbital is not removed first but both the electrons of 4s orbital are removed first and then the electrons of 3d-orbital are removed; because the electrons in the outermost orbital have relatively less attraction towards the nucleus in comparison to the electrons in the inner orbital. It is important to note here that the orbit having higher value of principal quantum number is considered as the outermost orbital. Thus, between the 3d-orbital ( $n = 3$ ) and 4s-orbital ( $n = 4$ ), 4s-orbital will be outermost orbital. Similarly, when ions are formed from the elements of second transition series, the electron of 5s-orbital is removed first and then the electron of 4d-orbital when ions of third transition elements, the electron is removed first from 6s-orbital and then the electron from 5d-orbital is removed; the electronic configuration of elements of first transition series in the ground state and their oxidation states are shown in table 3.1.

**Table 3.1. The electronic configuration of first transition series in ground state and their oxidation states**

Element	Atomic Number	Electronic configuration	Oxidation state
Sc	21	$[\text{Ar}]3d^14s^2$	(+3)
Ti	22	$[\text{Ar}]3d^24s^2$	+2, +3, (+4)
V	23	$[\text{Ar}]3d^34s^2$	+2, +3, (+4), +5
Cr	24	$[\text{Ar}]3d^54s^1$	(+2), (+3), +4, +5, (+6)
Mn	25	$[\text{Ar}]3d^54s^2$	(+2), +3, +4, +5, +6, (+7)
Fe	26	$[\text{Ar}]3d^64s^2$	(+2), (+3), +4, +5, +6
Co	27	$[\text{Ar}]3d^74s^2$	(+2), (+3), +4
Ni	28	$[\text{Ar}]3d^84s^2$	(+2), +3, +4
Cu	29	$[\text{Ar}]3d^{10}4s^1$	+1, (+2)
Zn	30	$[\text{Ar}]3d^{10}4s^2$	(+2)

Note: Stable oxidation state is shown in parenthesis.

The electronic configuration of Cu in ground state in first transition series is  $[\text{Ar}]3d^{10}4s^1$ . In it 3d-orbital is completely filled with electrons but electronic configuration of  $\text{Cu}^{2+}$  is  $[\text{Ar}]3d^9$ . Here, 3d-orbitals are incompletely filled with electrons and so Cu is considered transition element. The electronic configuration of Zn in ground state is  $[\text{Ar}]3d^{10}4s^2$ . In it, 3d-orbital is completely filled with electrons. In addition, the electronic configuration of  $\text{Zn}^{2+}$  is  $[\text{Ar}]3d^{10}$ . Here, also, the 3d-orbital is completely filled. Hence **Zn is not considered as a transition element**. The electronic configuration of elements of second transition series in the ground state and their oxidation states are shown in table 3.2.

**Table 3.2. Electronic configuration of elements of second transition series in ground state and their oxidation states**

Element	Atomic Number	Electronic configuration	Oxidation state
Y	39	[Kr]4d <sup>1</sup> 5s <sup>2</sup>	(+3)
Zr	40	[Kr]4d <sup>2</sup> 5s <sup>2</sup>	+2, +3, (+4)
Nb	41	[Kr]4d <sup>4</sup> 5s <sup>1</sup>	+3, (+5)
Mo	42	[Kr]4d <sup>5</sup> 5s <sup>1</sup>	+1, +3, +4, +5, (+6)
Tc	43	[Kr]4d <sup>5</sup> 5s <sup>2</sup>	(+4), +5, (+6)
Ru	44	[Kr]4d <sup>7</sup> 5s <sup>1</sup>	+2, (+3), +4, +6
Rh	45	[Kr]4d <sup>8</sup> 5s <sup>1</sup>	+2, (+3), +4
Pd	46	[Kr]4d <sup>10</sup> 5s <sup>0</sup>	(+2), +4
Ag	47	[Kr]4d <sup>10</sup> 5s <sup>1</sup>	(+1), +2, +3
Cd	48	[Kr]4d <sup>10</sup> 5s <sup>2</sup>	(+2)

Note: Stable Oxidation state is shown in parenthesis.

On the basis of the table 3.2, it can be said that in this transition series the electronic configuration of Pd, Ag and Cd in ground state have 4d<sup>10</sup> that is 4d-orbital is completely filled with electrons; but in +2 of Pd and +2 of Ag, oxidation states, the electronic configurations, 4d-orbital is incompletely filled and so they are considered as transition elements but in the electronic configuration of Cd<sup>2+</sup>, 4d-orbital is completely filled (4d<sup>10</sup>). Hence **Cd is not considered as a transition element**. The electronic configuration of elements of third transition series in ground state and their oxidation states are shown in table 3.3.

**Table 3.3. Electronic configuration of third transition elements in ground state and their oxidation states**

Element	Atomic Number	Electronic configuration	Oxidation state
La	57	[Xe]5d <sup>1</sup> 6s <sup>2</sup>	(+3)
Hf	72	[Xe]4f <sup>14</sup> 5d <sup>2</sup> 6s <sup>2</sup>	+2, +3, (+4)
Ta	73	[Xe]4f <sup>14</sup> 5d <sup>3</sup> 6s <sup>2</sup>	+3, (+5)
W	74	[Xe]4f <sup>14</sup> 5d <sup>4</sup> 6s <sup>2</sup>	+1, +4, +5, (+6)
Re	75	[Xe]4f <sup>14</sup> 5d <sup>5</sup> 6s <sup>2</sup>	(+3), (+4), +5, (+6)
Os	76	[Xe]4f <sup>14</sup> 5d <sup>6</sup> 6s <sup>2</sup>	(+4), +5, +6
Ir	77	[Xe]4f <sup>14</sup> 5d <sup>7</sup> 6s <sup>2</sup>	(+3), (+4)
Pt	78	[Xe]4f <sup>14</sup> 5d <sup>9</sup> 6s <sup>1</sup>	(+2), (+4)
Au	79	[Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>1</sup>	+1, (+3), +5
Hg	80	[Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup>	+1, (+2)

Note: Stable oxidation state is shown in parenthesis.

On the basis of table 3.3, it can be said that in the electronic configuration of Au and Hg in ground state there is  $5d^{10}$  that is 5d-orbital is completely filled but in the electronic configuration of  $Au^{3+}$ , 5d-orbital is incompletely filled ( $5d^8$ ) and so Au is considered transition element while in electronic configuration of Hg, 5d orbital is completely filled ( $5d^{10}$ ) and so **Hg is not considered transition element.**

### 3.2.3 Occurrence of Transition Elements :

Definite transition metal is obtained from its definite mineral and a definite method is used for obtaining pure metal from the mineral. You have studied in unit 4 of semester III about the methods for the extraction of Cu, Fe and Zn from their minerals.

### 3.2.4 General Characteristics of Transition Elements :

- All the transition elements are metallic elements.
- These elements are hard and strong.
- Their melting points are high.
- These elements can form alloys with each other.
- Most of these elements dissolve in acid, but acid has no effect on certain noble elements.
- These elements possess various valencies.
- They possess property of malleability and ductility.
- They are good conductors of electricity and heat.
- Some of their ions possess paramagnetic property.

## 3.3 Periodic Trends in Properties of Elements of First Transition Series

(1) **Metallic property** : All the elements of first transition series possess metallic property. This point can be understood from the study of general characteristics of transition elements (see point 3.2.4)

(2) **Atomic radii and Ionic radii** : Generally in the periodic table, moving from left to right, there is decrease in atomic radii. This trend is observed in the transition elements, but this decrease in atomic radii is less. The tendency of ionic radii in transition elements is found to be similar to atomic radii. The atomic radii and ionic radii of first transition series elements are shown in tables 3.4 and 3.5 respectively.

Table 3.4 Atomic radii of first transition series elements

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic Radius (pm)	144	132	122	117	117	117	116	115	117	125

Table 3.5 Ionic radii of first transition series elements

Element	$Sc^{2+}$	$Ti^{2+}$	$V^{2+}$	$Cr^{2+}$	$Mn^{2+}$	$Fe^{2+}$	$Co^{2+}$	$Ni^{2+}$	$Cu^{2+}$	$Zn^{2+}$
Ionic Radius (pm)	-	90	79	82	82	77	74	70	73	75

As shown in table 3.4, the atomic radius decreases from Sc to V while the atomic radii from Cr to Cu is almost similar. In addition to this, instead of decreasing the atomic radius of Zn is found to be increasing. The reason for this is that, as we move from left side to right side in period, the positive electric charge of nucleus increases and the entering electron is added to 3d-orbital. This electron, increases the shielding effect for attraction of electron present in 4s-orbital due to increase in positive electric charge in the nucleus. As a result, the electrons present in 4s-orbital are not attracted more towards the nucleus (Relative to neighbouring transition element). Thus, the orbit does not contract hence the atomic radii remain same. 3d-orbital of Zn atom is completely filled. Hence, it decreases the attraction towards electron of 4s-orbital of positive electric charge of nucleus due to its shielding effect. Also repulsion between electron-electron in 3d orbital increases more than the value of attraction of electrons of 4s-orbital and nucleus. Hence, there is expansion of orbit; so the value of atomic radius of Zn is seen to be increasing.

**(3) Ionisation enthalpy :** Moving from left side to right side in first transition series elements, the nuclear electric charge increases and so the value of ionization enthalpy increases but the increase in this value, is not equal to the increase in enthalpy in the elements of the main group. Thus, there is not much change in the first ionization enthalpies of two neighbouring transition elements (table 3.6). The values of first, second and third ionization enthalpies are shown in table 3.6.

**Table 3.6 First, second and third ionization enthalpies ( $\text{kJ mol}^{-1}$ ) of first transition series elements**

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$\Delta_1 H_1$	631	656	650	653	717	762	758	736	745	906
$\Delta_1 H_2$	1235	1309	1414	1592	1509	1561	1644	1752	1958	1734
$\Delta_1 H_3$	2393	2657	2833	2990	3260	2962	3243	3402	3556	3829

As shown in table 3.6, there is not much difference seen in the values of second ionization enthalpies like the changes in the first ionization enthalpies of first transition series elements. But chromium and copper are found to be exceptions. The values of second ionization enthalpy of these two elements are more than those of their neighbouring elements, because both these elements attain the electronic configuration  $\text{Cr}^+ : [\text{Ar}]3d^5$  and  $\text{Cu}^+ : [\text{Ar}]3d^{10}$  after loss of one-one electron from these two elements. From Cr and Cu, the second electron is removed from half filled or completely fill 3d orbitals respectively having more stability. It is natural that more energy will be required for removal of such electrons.

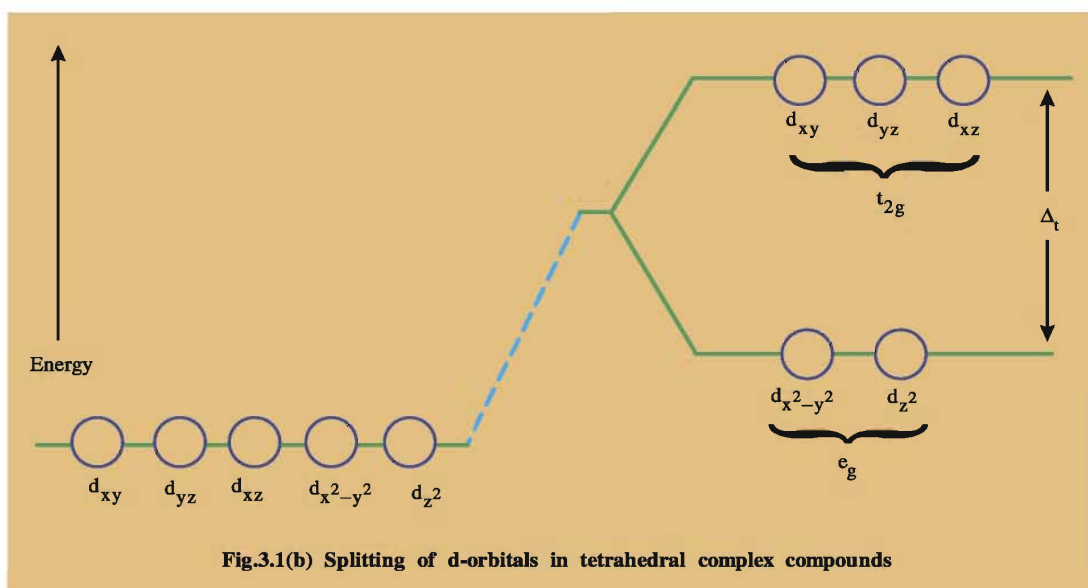
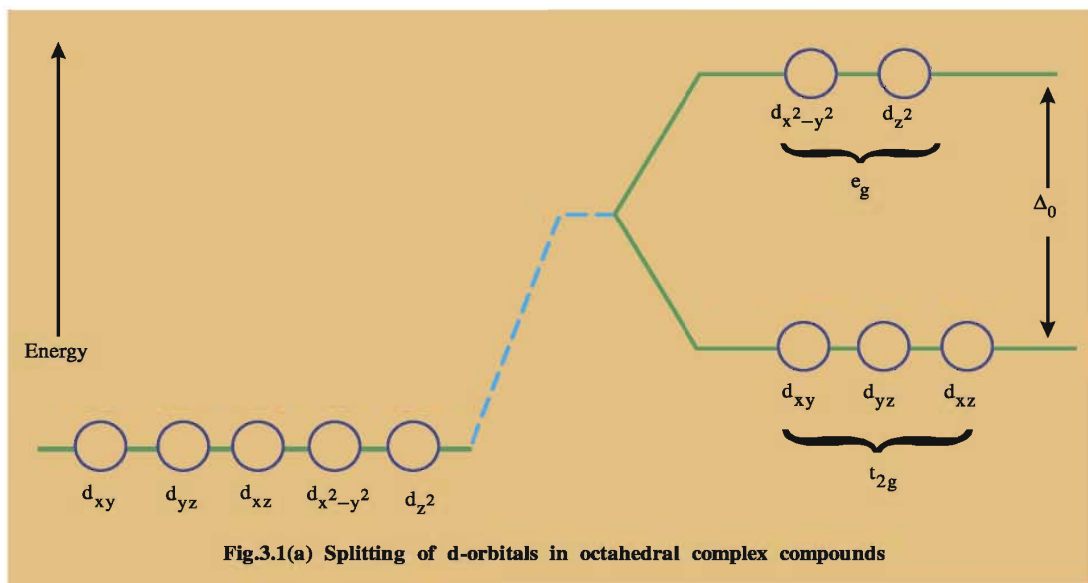
**(4) Electrode potential :** Thermodynamic stability of transition metals depends on their magnitude of ionization enthalpy. The compounds of metals having less ionization enthalpy are more stable, while the stability of compounds in solution is more dependent on relative electrode potentials.

The value of electrode potential is determined on the basis of the sum of the enthalpy changes ( $\Delta H_T$ ) of different reactions. The stabilities of different oxidation states of transition metal ions are determined on the basis of the electrode potentials. More negative the values of standard reduction potentials more will be the stability of ions in aqueous medium.

### 3.4 Characteristic Properties of Elements of First Transition Series

**(1) Colour :** Most of the ionic and covalent compounds of transition elements are coloured. It is due to the presence of incompletely filled d-orbitals. When visible light falls on transition metal ions, they absorb light of definite wavelength and emit the remaining light. Our eye catches the colour of this

emitted light as the colour of those ions. Hence, ions appear coloured. For example, when visible light passes through the aqueous solution of  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ , green colour is emitted and other colours are absorbed. Hence, the colour of this aqueous solution appears to be green. In the similar, when visible light passes through aqueous solution of  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , then red and green colours are emitted and other colours are absorbed. Because of the mixing of the emitted red and green colour, the colour of this solution appears to be yellowish orange. During absorption of light the electrons in d-orbital of ions receive energy and go to the d-orbital having higher energy. This transition of electrons is called **d-d transition**. It is necessary to note here, that generally the energy of all five d-orbitals is equal but according to crystal field theory, there is splitting of d-orbitals in different energy levels. The splitting of d-orbitals of different energy levels in transition compounds having tetrahedral and octahedral geometry are shown in figure 3.1.



The colours of some metal ions are mentioned in table 3.7

**Table 3.7 Colours of some of the hydrated metal ions of first transition series**

Metal ions	Colour
Cu <sup>2+</sup> , Cr <sup>2+</sup> , Co <sup>3+</sup> , V <sup>4+</sup>	Blue
Ni <sup>2+</sup> , Fe <sup>2+</sup> , V <sup>3+</sup>	Green
V <sup>2+</sup> , Cr <sup>3+</sup> , Mn <sup>3+</sup>	Violet
Co <sup>2+</sup> , Mn <sup>2+</sup>	Pink
Fe <sup>3+</sup>	Yellow
Ti <sup>3+</sup>	Purple
Zn <sup>2+</sup> , Sc <sup>3+</sup> , Ti <sup>4+</sup> , Cu <sup>+</sup>	Colourless

Student friends, the verification of colour of certain metal ions mentioned in table 3.7 can be done in chemistry laboratory by observing easily the colours from the chemicals available- CuSO<sub>4</sub> · 5H<sub>2</sub>O, NiCl<sub>2</sub> · 6H<sub>2</sub>O, FeSO<sub>4</sub> · 7H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O, MnCl<sub>2</sub> · 4H<sub>2</sub>O, FeCl<sub>3</sub> and ZnCl<sub>2</sub>.

**(2) Catalytic property :** Transition metals and their certain compounds increase the rate of chemical reaction. Hence, they are useful catalysts. These substances used as catalyst are in solid state. The random and pointed peak points on the surface at the ends of the edges of their particles are responsible centres for catalysis work. The molecule-atom in the depth in the matter of solid substance are surrounded by similar other atoms. Hence, the magnetic field of their unpaired electrons is destroyed by the effect on each other, while atoms of the ends of the edges or the peak points, get affected by the magnetic field which are active centres for catalysis. The molecules of reactant are attracted by the magnetic field and so the required activation energy of the reaction decreases. As a result, the reaction rate increases viz. Ni in hydrogenation of vegetable oil, Fe in industrial production of NH<sub>3</sub> by Haber process, V<sub>2</sub>O<sub>5</sub> catalyst is used in obtaining SO<sub>3</sub> from SO<sub>2</sub> in contact process for manufacturing of H<sub>2</sub>SO<sub>4</sub>. You have studied in detail the point on catalysis in unit 2 : Surface Chemistry.

**(3) Magnetic property :** When a substance is placed in the magnetic field, then they possess two types of magnetic properties (i) Paramagnetism and (ii) Diamagnetism.

The molecule, atom or ion of a substances in which there are unpaired electrons, such substances possess paramagnetism, so they are called **paramagnetic substances**; while molecule, atom or ion in which all the electrons are paired, possesses diamagnetism. Hence, they are called **diamagnetic substances**. In the electronic configuration of transition elements, the (n-1)d-orbitals are incompletely filled; hence they possess unpaired electrons and so the atoms of these elements are paramagnetic. Because of paramagnetism they possess magnetic moment. Magnetic moment is produced due to rotation of unpaired electron on its axis and orbital rotation. In transition metal ions the unpaired electrons are present in the outermost orbit. Hence, in such cases axial rotation contribution is much more important than the orbit contribution. The value of magnetic moment based on only rotation on axis, can be calculated with the help of following formula :

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

where  $\mu$  = Magnetic moment, n = Number of unpaired electrons, BM = Bohr Magnetron (unit)

The value of magnetic moment increases with increase in number of unpaired electrons. Thus, through the measurement of magnetic moment we come to know about the number of unpaired electrons in atom, molecule or ion. Maximum five unpaired electrons can be in d-orbitals, so the theoretical values of magnetic moments are shown in table 3.8.

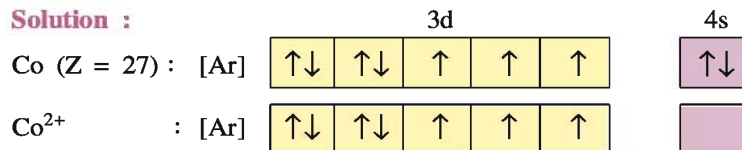
Table 3.8 Theoretical Value of Magnetic Moment

Number of unpaired electrons (n)	Magnetic moment $\mu$ (BM)
1	1.73
2	2.83
3	3.87
4	4.90
5	5.92

The magnetic moments of ions of transition elements or their compounds, are based on the axial rotation; so sometimes their values obtained experimentally are slightly more or less than the theoretical values. The reason for this is the rotation-orbital combination. This type of combination being directional, the value obtained is slightly more or less i.e. it depends on how these directional combinations occur. Earlier you have studied about diamagnetic or paramagnetic properties in semester III in unit 1 on Solid State.

**Example : 1** Calculate magnetic moment of  $\text{Co}^{2+}(\text{aq})$

**Solution :**



Here number of unpaired electrons  $n=3$

$$\begin{aligned} \text{Now, magnetic moment } \mu &= \sqrt{n(n+2)} \text{ BM} \\ &= \sqrt{3(3+2)} \text{ BM} \\ &= \sqrt{15} \text{ BM} = 3.87 \text{ BM} \end{aligned}$$

Thus, the value of magnetic moment of  $\text{Co}^{2+}(\text{aq})$  will be 3.87 BM

**(4) Capacity of transition metal ions to form complex compounds :** Transition metal ions combine with one or more anion or neutral molecule (ligand) and form complex species by co-ordinate covalent bond having definite characteristics which are called complex compounds. In depth, study of such **complex compounds** will be done in Unit 4 : complex compounds. The capacity of transition elements to form complex compounds is more than that with other elements; the reason of which is the below mentioned characteristics of transition metal ions.

- The size of transition metal ions is small.
- The nuclear electric charge and ionic electric charge of transition metal ions is comparatively more.
- The electronic configurations of transition metal ions is favourable for formation of complexes. In these metal ions, d-orbitals are vacant and so the electron pairs coming from the ligand can be accommodated.



- As very less difference is there between energy values of 3d, 4s, 4p or 4d orbitals, hybridization of different types can be possible with these orbitals. Thus, the different hybrid orbitals produced are helpful in formation of complex compounds.
- Due to formation of various types of hybridization and because of co-ordinate covalent bonds are directional, different types of geometrical shapes containing complex compound can be formed.
- Transition metal ions exhibit various oxidation states. Thus, varieties of complex compounds can be formed.

### 3.5 Interstitial Compounds

The atoms in solid state of transition metals are arranged in definite crystal structure. There are definite voids between atoms in such an arrangement. Hence, non-metallic atoms of smaller size viz. H, C, N and B can be easily arranged in the voids of crystal structure. The compounds formed in such a manner are called **interstitial compounds**; in which chemical bond is not formed between non-metal elements of smaller size arranged in the voids and the metal atom, hence the proportion of components in such compound is not definite. So interstitial compounds are not definite. In fact interstitial compounds are nonstoichiometric or non-proportionate compounds, e.g.,  $\text{TiH}_{1.7}$ ,  $\text{VH}_{0.56}$  etc. On the basis of the non-metal arranged in the interstitial void, they can be classified as hydrides, carbides, nitrides and borides, because elements like hydrogen, carbon, nitrogen and boron can be arranged in interstitial positions.

A notable change is observed in the characteristic properties of metals due to presence of non-metal elements like H,C,N and B in the voids of crystal structure. The small size of non-metal atoms present here in the void attract free electrons of metallic bond, hence free electrons of metallic bond are localised and so the strength of the bond increases. Hence, the properties of the metals like hardness, melting point resistance to wear, resistance to corrosion etc. are notably increased. Therefore, interstitial compounds are used in preparation of tools, machinery parts, vehicles etc. This type of compounds have not definite molecular formula. VN,  $\text{Fe}_3\text{N}$ ,  $\text{Fe}_3\text{C}$ ,  $\text{Cr}_3\text{C}_2$ ,  $\text{Mn}_3\text{C}$ , TiC, VB,  $\text{CrB}_2$  etc. are interstitial compounds.

### 3.6 Alloys

The characteristic properties like hardness, conductance, malleability, resistance to corrosion are essential for machineries, tools, vehicles and vessels of house-hold usages. There is no combination of all these properties and is not together found in any pure metal. Hence, instead of using pure metals in practice, alloys prepared from two or more metal-elements are used frequently..

Scientists **Hume** and **Rothery** presented rules as follows to obtain alloys of combination of useful properties :

- (1) The atomic size of two metals forming the alloy must be the same. There must not be more than 15 % difference in their atomic radii.
- (2) The chemical properties of the metals used for preparation of alloys must be same, that is, their electronic configurations of valence shell must be the same.
- (3) The crystal structures of pure metallic elements used for alloys must be similar.

22 carat gold ornaments is the best example of alloy. It is the alloy of Au and Cu. The difference between atomic size of Au (atomic size = 134 pm) and Cu (atomic size = 117 pm) is about 14.5 %. Both of them possess cubic close pack structure. Both of them being members of group-11 the electronic configuration of their valence shells is same. Thus best alloy can be prepared according to laws

suggested by Hume and Rothery. The difference in atomic sizes between Cr, Mn, Fe, Co, Ni, Cu metals, is less than 2%. There is much less difference in the electronic configuration of valence shell of these elements. Hence, these elements form number of alloys having different proportions which are very useful in practice. Certain important alloys, their components, properties and uses are shown in table 3.9.

**Table 3.9 Alloys, their components, properties and uses**

Alloy	Components	Properties	Uses
Stainless steel	Fe (70%), Cr (20%) Ni (10%)	No effect of air, water and alkali and does not get rusted	In preparation of utensils, blades, surgical instruments.
Brass	Cu (70%), Zn (30%)	Ductile, hard, corrosion resistant and can be shaped easily	In preparation of cooking vessels, parts of machine and musical instruments.
Bronze	Cu (90%), Sn (10%)	Very strong and possessing more corrosion resistance	In preparation of statues, currency coins and medals.
Nitinol	Ti (45%), Ni (55%)	Light in weight and strong and resists corrosion. It has marvellous property of memory.	Rivetting and useful in space research.
Cupronickel	Cu (75-85%), Ni (15-25%)	Strong and corrosion resistant.	In preparation of currency coins.
	Cu (50-55%), Ni (45-50%)	Electrical resistance is more.	In preparation of electric resistant wires.
German-silver	Ni (40-50%), Zn (25-30%) Cu (25-30%)	Possesses shining as silver	In preparation of household vessels, art models and resistant wires.
Nichrome	Ni (60%), Cr (40%)	Electrical resistance is very high	As electric resistant wire in electric furnaces and electric heaters.

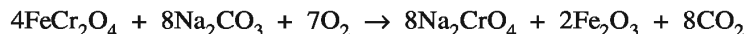
In addition, amalgam with mercury - alloy is also well known. In this alloy there are Hg (50%), Ag (35%), Sn (12%), Cu (3%) and Zn (0.2%). This alloy is, used in filling the cavity in the tooth. When this alloy is to be filled in cavity in the tooth, all these metals are mixed, some time before filling. This alloy is soft. By the time the dentist can fill in the cavity of tooth, it remains soft so that it becomes convenient for dentist to fill in the cavity. After filling in this alloy in cavity, it becomes hard and it does not expand.

### 3.7 Some Important Compounds of 3d-Transition Elements

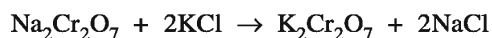
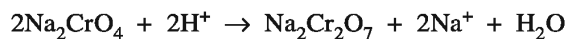
Many compounds of 3d-transition elements are familiar. We shall study here, preparation, properties and uses of only potassium dichromate ( $K_2Cr_2O_7$ ) and potassium permanganate ( $KMnO_4$ ).

### (1) Potassium dichromate ( $K_2Cr_2O_7$ ) :

**Preparation :** Sodium chromate ( $Na_2CrO_4$ ) and ferric oxide ( $Fe_2O_3$ ) are formed by fusion of chromite mineral ( $FeCr_2O_4$ ) with sodium carbonate and quick lime in presence of air. After the reaction, the roasted mass is extracted with water when  $Na_2CrO_4$  is completely dissolved while  $Fe_2O_3$  is left insoluble in presence of air.



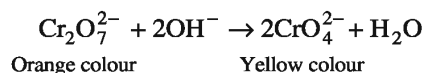
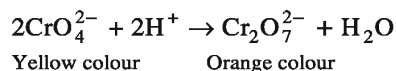
Filtering the yellow coloured solution of sodium chromate, it is acidified with  $H_2SO_4$ ; so that sodium dichromate ( $Na_2Cr_2O_7$ ) is formed, which reacts with potassium chloride and forms potassium dichromate and sodium chloride.  $K_2Cr_2O_7$  being much less soluble than  $NaCl$  it crystallizes out on cooling.



#### Properties :

- Potassium dichromate is orange coloured crystalline substance.
- It is soluble in water.
- It acts as a strong oxidizing agent in acidic medium.
- When an alkali is added to an orange coloured solution of potassium dichromate a yellow coloured solution results due to the formation of potassium chromate and on acidifying it, the colour again changes to orange due to the reformation of potassium dichromate.

Chromate and dichromate ions are interconvertible in aqueous solution; which depends on the pH of the aqueous solution; because the oxidation state of chromium in chromate and dichromate is the same.

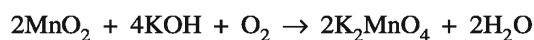


#### Uses :

- Potassium dichromate is mainly useful in leather industry and formation of azo compounds.
- As oxidizing agent used in synthesis of organic compounds, used as a reagent in chemical oxygen demand (COD) measurement in polluted water. In addition, the mixture of potassium dichromate with concentrated sulphuric acid which is known as chromic acid, is used for cleaning of glasswares in laboratory. It is corrosion inhibitor.
- It is used as titrant in redox titrations to determine the amount of metal ions like iron (II).

### (2) Potassium permanganate ( $KMnO_4$ ) :

**Preparation :** Dark green coloured potassium manganate ( $K_2MnO_4$ ) is formed by fusion of manganese dioxide ( $MnO_2$ ) with  $KOH$  in presence of air or oxidizing agent like  $KNO_3$ . Potassium permanganate is formed when sulphuric acid is added to this solution and made acidic.



(Green colour)



#### Properties :

- Potassium permanganate is dark purple coloured crystalline substance.
- It is soluble in water.
- It acts as oxidising agent in acidic, basic and neutral medium.

#### Uses :

- Potassium permanganate is used as strong oxidising agent in synthesis of organic compounds.
- It is used as bleaching agent for cotton cloth, silk and wood and in textile industries.
- An aqueous solution of potassium permanganate is used for gargling to keep mouth germfree as it is antiseptic.
- It is useful as titrant in redox titrations to know the proportion of metal ions like iron (II) and organic compounds like oxalic acid.

### 3.8 Application of d-Block Elements

- The alloys-stainless steel, brass, bronze, nitinol, cupronickel, german silver and nichrome prepared from elements of d-block elements are used for preparation of household utensils, currency coins, statues, and machinery.
- Some elements and compounds of these elements act as catalyst in chemical reaction e.g., Ni in hydrogenation of vegetable oil, Fe in Haber process of industrial production of  $\text{NH}_3$ ,  $\text{V}_2\text{O}_5$  catalyst for obtaining  $\text{SO}_3$  from  $\text{SO}_2$  in contact process for production of  $\text{H}_2\text{SO}_4$ .
- Alloy like mercury-amalgam is useful for filling in tooth cavity.
- Alloy of gold and copper is more appropriate for preparation of ornaments.
- Mercury is used in thermometer.
- The use of inert metal like platinum is made as electrodes in the experiments of electro-chemistry.
- Some compounds like  $\text{KMnO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$ , of d-block elements act as strong oxidizing agents in synthesis of organic compounds. They are used as titrant in redox titrations.
- $\text{MnO}_2$  is used in dry cell.
- To prevent water pipes and the roof on the house from corrosion they are changed in to galvanized form with the help of zinc metal.

### 3.9 Innertransition Elements (Elements of f-Block)

The f-block elements are distributed into two series : (A) Lanthanide series and (B) Actinide series. The series of fourteen elements immediately after lanthanum- Ce(Z = 58) to Lu (Z = 71) is called **lanthanide series**. The elements of this series are known as **lanthanoids**. Lanthanoids are expressed by general symbol Ln. As lanthanum has more similarity with lanthanoids, it is included in the lanthanide

series, during discussion. In the periodic table, series of fourteen elements immediately after actinium-Th (Z = 90) to Lr (Z = 103) is called **actinide series**. The elements of this series are known as **actinoids**. As actinium possesses more similarity with actinoids, it is included in the discussion of actinide series. **The general electronic structure of outermost electrons of elements of f-block is  $(n-2)f^{0-14}(n-1)d^{0-1}ns^2$ .**

### 3.10 Lanthanide Series

To understand the lanthanide series, we shall study here, its electronic configuration, oxidation state, atomic size, chemical reactivity and lanthanide contraction.

#### 3.10.1 Electronic Configuration and Oxidation State :

In the electronic configuration of elements of lanthanide series,  $6s^2$  is common in all the elements but the electrons in 4f-orbital keep changing. **All the lanthanoids and lanthanum element possess stable oxidation state + 3.** The electronic configuration and oxidation states of lanthanum and lanthanoids are shown in table 3.10.

**Table 3.10 Electronic configuration and oxidation states of lanthanum and lanthanoids**

Element	Atomic Number	Electronic configuration	Oxidation state
La	57	[Xe]5d <sup>1</sup> 6s <sup>2</sup>	(+3)
Ce	58	[Xe]4f <sup>1</sup> 5d <sup>1</sup> 6s <sup>2</sup>	(+3), +4
Pr	59	[Xe]4f <sup>3</sup> 6s <sup>2</sup>	(+3)
Nd	60	[Xe]4f <sup>4</sup> 6s <sup>2</sup>	+2, (+3)
Pm	61	[Xe]4f <sup>5</sup> 6s <sup>2</sup>	(+3)
Sm	62	[Xe]4f <sup>6</sup> 6s <sup>2</sup>	+2, (+3)
Eu	63	[Xe]4f <sup>7</sup> 6s <sup>2</sup>	+2, (+3)
Gd	64	[Xe]4f <sup>7</sup> 5d <sup>1</sup> 6s <sup>2</sup>	(+3)
Tb	65	[Xe]4f <sup>9</sup> 6s <sup>2</sup>	(+3), +4
Dy	66	[Xe]4f <sup>10</sup> 6s <sup>2</sup>	(+3), +4
Ho	67	[Xe]4f <sup>11</sup> 6s <sup>2</sup>	(+3)
Er	68	[Xe]4f <sup>12</sup> 6s <sup>2</sup>	(+3)
Tm	69	[Xe]4f <sup>13</sup> 6s <sup>2</sup>	+2, (+3)
Yb	70	[Xe]4f <sup>14</sup> 6s <sup>2</sup>	+2, (+3)
Lu	71	[Xe]4f <sup>14</sup> 5d <sup>1</sup> 6s <sup>2</sup>	(+3)

**Note :** Stable oxidation state is shown in parenthesis

It is apparent from the study of electronic configuration shown in table 3.10, that only in the lanthanoids like Ce, Gd and Lu electrons are filled in 5d orbital. In Gd, because of half filled orbital like 4f<sup>7</sup>, stability may be obtained and so newly added electron enters into 5d orbital, while in Lu, 4f orbital being completely filled, the added new electron enters into the 5d orbital. The filling of electron of Ce

in 5d-orbital is accepted at present as an exception. Thus, **the general electronic configuration of lanthanoids is  $[Xe]4f^{1-14}5d^{0-1}6s^2$** . Amongst lanthanoids, promethium (Pm) is a radioactive element.

### 3.10.2 Atomic Size and Lanthanide Contraction :

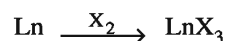
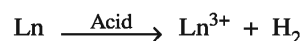
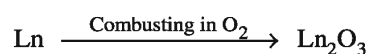
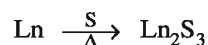
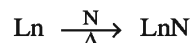
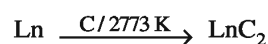
Like the elements in any period of periodic table, in elements of lanthanide series going from cerium(Ce) to lutetium (Lu), the atomic radii and ionic radii go on decreasing. In the elements of this series, with the increase in atomic number the addition of new electron is in inner orbit  $4f(n = 4)$  instead of last orbit ( $n = 6$ ). Hence, with the increase in positive electric charge, the electrons in 4f-orbital possess more attraction towards it. Hence, there is contraction of atom. i.e. atomic radius decreases. This contraction occurring in lanthanide elements, is called **lanthanide contraction**. The effect of this lanthanide contraction is observed on the atomic radii of the elements after lanthanide series. The atomic radii of some of the elements of third transition series after lanthanide series are equal to the atomic radii of some elements of second transition series earlier to this, which can be understood from table 3.11.

**Table 3.11 Atomic radii (pm) of elements of second and third transition series**

<b>Second Transition Series</b>	Y 162	Zr 145	Nb 134	Mo 129	Tc -	Ru 124	Rh 125	Pd 128
<b>Third Transition Series</b>	Lanthanoids	Hf 144	Ta 134	W 130	Re 128	Os 126	Ir 126	Pt 129

### 3.10.3 Chemical Reactivity :

As lanthanoids possess (+3) oxidation state they form hydroxides of the type  $Ln(OH)_3$ . These hydroxides are less basic than  $Ca(OH)_2$  but more basic than  $Al(OH)_3$ . The carbonates and nitrates of these elements decompose faster into their oxide by heating. The size of ion decreases on going from  $Ce^{3+}$  to  $Lu^{3+}$ , hence their basicity decreases, that is  $Ce(OH)_3$  is most basic and  $Lu(OH)_3$  is least basic. These elements possess similarity in physical and chemical properties so their separation is carried out on the basis of the difference in their basicity.  $Ln_2O_3$  type oxides of these elements are ionic and basic. The property of basicity decreases with ionic size. Some ions of these elements possess paramagnetic property because of unpaired electrons in f-orbital. Their certain ions are coloured and give coloured solution. The general chemical reactions of lanthanoids are shown below :



### 3.11 Actinide Series

We shall study electronic configuration and oxidation states to understand the actinide series.

#### 3.11.1 Electronic Configuration and Oxidation State :

In the electronic configuration of elements of actinide series,  $7s^2$  is common in all the elements but electrons keep on changing in 5f orbital. Irregularity is found more in the electronic configuration of actinoids. Actinoids possess more than one oxidation states. The electronic configuration and the oxidation states of actinium and actinoids are shown in table 3.12.

Table 3.12 Electronic configuration and oxidation states of actinium and actinoids

Element	Atomic Number	Electronic configuration	Oxidation state
Ac	89	$[Rn]6d^17s^2$	(+3)
Th	90	$[Rn]6d^27s^2$	(+4)
Pa	91	$[Rn]5f^26d^17s^2$	+3, +4, (+5)
U	92	$[Rn]5f^36d^17s^2$	+3, +4, +5, (+6)
Np	93	$[Rn]5f^46d^17s^2$	+3, +4, (+5), +6, +7
Pu	94	$[Rn]5f^67s^2$	+3, (+4), +5, +6, +7
Am	95	$[Rn]5f^77s^2$	(+3), +4, +5, +6
Cm	96	$[Rn]5f^76d^17s^2$	(+3), +4
Bk	97	$[Rn]5f^97s^2$	(+3), +4
Cf	98	$[Rn]5f^{10}7s^2$	(+3)
Es	99	$[Rn]5f^{11}7s^2$	(+3)
Fm	100	$[Rn]5f^{12}7s^2$	(+3)
Md	101	$[Rn]5f^{13}7s^2$	(+3)
No	102	$[Rn]5f^{14}7s^2$	(+2), +3
Lr	103	$[Rn]5f^{14}6d^17s^2$	(+3)

Note : Stable oxidation state is shown in parenthesis

In the electronic configuration of elements Th to Np as shown in table 3.12, irregularity is found to be more in comparison to other elements which is at present accepted as an exception, while in Cm and Lr, the half filled 5f-orbital and completely filled 5f-orbitals respectively, to attain stability, the new added electron is filled in 6d-orbital.

Thus general electronic configuration is  $[Rn]5f^{0-14}6d^{0-2}7s^2$ . All the actinoids are radioactive.

### 3.12 Comparison of Actinoids with Lanthanoids

- Actinoids are like silver in appearance. More irregularity is observed in the metallic radii in actinoids than lanthanoids. Hence, diversity is found in the structures of actinoids.
- As the outermost orbit in actinoids is far from the nucleus in comparison to lanthanoids, their electron can be easily removed. Hence, the values of ionization enthalpy of actinoids are less than the values of ionisation enthalpies of lanthanoids.

- The stable oxidation state of all the lathanoids is (+3). In actinoids, oxidation states (+2) to (+6) are seen.
- In lanthanoids only promethium is radioactive but all the actinoids are radioactive.

### 3.13 Applications of f-Block Elements

- Pyrophoric Misch metal (50 % Ce +40 % La + 7 % Fe + 3 % other metals) is used as reducing agent and as stones in gas lighters.
- $\text{CeO}_2$  is useful in pigments.
- Ceric compounds are used as oxidizing agent in volumetric analysis.
- Oxides of lanthanoids are useful in preparation of optical glass of camera having high refractive index.
- Gadolinium sulphate is used to produce very low temperature by magnetic effect.
- Metals like, uranium, plutonium, and thorium are useful in production of atomic energy. Electrical energy can be obtained from nuclear energy.

#### SUMMARY

Position in periodic table	Block
Groups 1 to 2	s-Block
Groups 13 to 18	p-Block
Groups 3 to 12	d-Block
Two horizontal rows at the bottom of the periodic table	f-Block

- d-block elements are in periods 4 to 7.
- f-block elements are in periods 6 and 7.

#### Elements of d-block (Transition metal elements)

- The elements which in their ground state or any one of their oxidation states, d-orbital is incompletely filled are called transition elements.
- Amongst the d-block elements Zn, Cd and Hg do not act as transition elements.
- All the transition elements are metallic elements.
- In the first transition series, atomic radii decrease from Sc to V, while atomic radius remains same in elements Cr to Cu and the atomic radius of Zn is found increasing instead of decreasing.
- Not much difference is observed in first and second ionization enthalpies of two neighbouring transition elements but the value of second ionization enthalpy of Cr and Cu are more than those of their neighbouring elements.
- Most of the ionic and covalent compounds of transition elements are coloured.





- (3) The aqueous solution of which of the following ions is green coloured ?  
 (A)  $\text{Co}^{2+}$                       (B)  $\text{Zn}^{2+}$                       (C)  $\text{Ni}^{2+}$                       (D)  $\text{Cr}^{2+}$
- (4) What will be the order of energy of d-orbitals during their division in tetrahedral complex compounds ?  
 (A)  $d_{xy} \cong d_{yz} \cong d_{xz} < d_{x^2-y^2} \cong d_{z^2}$       (B)  $d_{x^2-y^2} \cong d_{z^2} < d_{xy} \cong d_{yz} \cong d_{xz}$   
 (C)  $d_{xy} \cong d_{z^2} < d_{yz} \cong d_{xz} \cong d_{x^2-y^2}$       (D)  $d_{x^2-y^2} \cong d_{xz} < d_{xy} \cong d_{yz} \cong d_{z^2}$
- (5) Which of the following ions in its aqueous solution possesses the value of magnetic moment as 3.87 ?  
 (A)  $\text{Cu}^{2+}$                       (B)  $\text{Cr}^{3+}$                       (C)  $\text{Co}^{3+}$                       (D)  $\text{Fe}^{3+}$
- (6) Which of the following is the alloy of iron ?  
 (A) Stainless steel    (B) Brass                      (C) Bronze                      (D) Nichrome
- (7) Which of the following compounds of transition elements is used in dry cell ?  
 (A)  $\text{V}_2\text{O}_5$                       (B)  $\text{KMnO}_4$                       (C)  $\text{K}_2\text{Cr}_2\text{O}_7$                       (D)  $\text{MnO}_2$
- (8) Which of the following elements is radioactive ?  
 (A) Pr                      (B) Pm                      (c) Gd                      (D) Tm
- (9) What is the general electronic configuration of actinide series ?  
 (A)  $[\text{Xe}] 4f^{0-14} 5d^{0-1} 6s^2$                       (B)  $[\text{Xe}] 4f^{0-14} 5d^{0-10} 6s^2$   
 (C)  $[\text{Rn}] 5f^{0-14} 5d^{0-2} 6s^2$                       (D)  $[\text{Rn}] 5f^{0-14} 6d^{0-2} 7s^2$
- (10) Which of the following statements is incorrect ?  
 (A) Atoms of all the transition elements are paramagnetic.  
 (B) All the transition elements are metal elements.  
 (C) All the elements of d-block are transition elements.  
 (D) The position of d-block is between s and p-block element in the periodic table.

**2. Answer the following questions in brief :**

- (1) Innertransition elements are the members of which period ?
- (2) Elements of which block are called innertransition elements ?
- (3) Which of the elements of the first transition series (Sc to Zn) do not act as transition element ?
- (4) Which are the elements of first transition series elements having  $d^5$  and  $d^{10}$  electronic configurations ?
- (5) Aqueous solutions of which ions of first transition elements are blue coloured ?
- (6) Write unit of magnetic moment.
- (7) Which non-metal elements form interstitial compounds with elements of first transition series ?
- (8) Which centres are responsible for catalytic function of catalyst ?
- (9) Which alloy is filled in tooth cavity ?
- (10) Which alloy is used for preparation of electric resistant wire ?

- (11) Cupronickel is the alloy of which metals ?
- (12) Which compound of transition elements acts as strong oxidizing agent in acidic and basic media ?
- (13) By which common symbol, the elements of lanthanide series are shown ?
- (14) Write general electronic configuration of lanthanide series elements.
- (15) Which compound of f-block elements is useful in pigment ?
- (16) Give definitions :
  - (i) Transition elements
  - (ii) d-d transition
  - (iii) Interstitial compounds
  - (iv) Alloy
  - (v) Lanthanide series
  - (vi) Actinide series

**3. Write answers of following questions :**

- (1) Write electronic configuration of Cr and Cu.
- (2) Write formula to determine magnetic moment and give identification of symbols in it.
- (3) Write two properties and two uses of  $\text{KMnO}_4$ .
- (4) Write two properties and two uses of  $\text{K}_2\text{Cr}_2\text{O}_7$ .
- (5) Write four applications of f-block elements.
- (6) Write three laws presented by scientists Hume and Rothery for preparation of alloys.
- (7) **Explain giving reason :**
  - (i) The values of second ionization enthalpy of Cr and Cu are found to be more than their neighbouring elements.
  - (ii) The atomic radius of Zn in first transition series increases instead of decreasing.
  - (iii) The atomic radii of elements Cr to Cu in first transition series are almost same.
  - (iv) In electronic configuration of Pd, Ag and Cd,  $d^{10}$  electrons are present even then Pd and Ag are considered transition elements, while Cd is not considered transition element.
- (8) Calculate magnetic moments :  $\text{Sc}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{V}^{4+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cr}^{6+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$

**4. Answer the following questions in detail :**

- (1) Mention the general properties of transition elements.
- (2) Discuss catalytic and magnetic properties of transition elements.
- (3) Describe the characteristic capacity of transition metal ions to form complex compounds.
- (4) Mention the preparation of potassium dichromate and potassium permanganate.
- (5) Describe applications of d-block elements.
- (6) Compare actinide elements with lanthanide elements.
- (7) **Write short notes :**
  - (i) Interstitial compounds
  - (ii) Alloys
  - (iii) Chemical reactivity of lanthanide elements
  - (iv) Lanthanide contraction