



ELEMENTS OF d - BLOCK



- * Transition Elements
- * Compound of Transition Elements
- * Properties of Transition Metals
- * Lanthanides and Actinides

d-BLOCK ELEMENTS

5.1.1

Introduction

In d-block elements, differentiating electron enters into d-orbitals of penultimate shell

In the modern periodic table, elements are classified into four blocks on the basis of electronic configuration. Elements in which differentiating electron enter d-orbitals in penultimate shell are called d-block elements. These elements are placed in between s- and p- block elements in four series. They are 3d-, 4d-, 5d- and 6d-series. First three series of d- block are completely filled, with ten elements in each series and 6d- series is incomplete.

3d- series elements are scandium ($Z = 21$) to zinc ($Z = 30$), 4d- series elements are yttrium ($Z = 39$) to cadmium ($Z = 48$) and 5d - series elements are lanthanum ($Z = 57$), hafnium ($Z = 72$) to mercury ($Z = 80$). d-Block consists of ten groups: IIIB, IVB, VB, VIB, VIIB, VIII, IB and IIB. Names and atomic numbers of 3d-, 4d- and 5d- series elements are given in the Table 5.1.

Table 5.1 Atomic number (Z), names and symbols of d-block elements

3d-Series			4d-Series			5d-Series		
Z	Element	Symbol	Z	Element	Symbol	Z	Element	Symbol
21	Scandium	Sc	39	Yttrium	Y	57	Lanthanum	La
22	Titanium	Ti	40	Zirconium	Zr	72	Hafnium	Hf
23	Vanadium	V	41	Niobium	Nb	73	Tantalum	Ta
24	Chromium	Cr	42	Molybdenum	Mo	74	Tungsten	W
25	Manganese	Mn	43	Technetium	Tc	75	Rhenium	Re
26	Iron	Fe	44	Ruthenium	Ru	76	Osmium	Os
27	Cobalt	Co	45	Rhodium	Rh	77	Iridium	Ir
28	Nickel	Ni	46	Palladium	Pd	78	Platinum	Pt
29	Copper	Cu	47	Silver	Ag	79	Gold	Au
30	Zinc	Zn	48	Cadmium	Cd	80	Mercury	Hg

In a broader sense, d-block elements are called transition elements. This is because, d-block elements represent transition in properties from most electropositive s-block elements to least electropositive p-block elements.

IIB group elements are d-block elements but not transition elements

Ultimate and penultimate shells are incompletely filled with electrons in transition elements. Elements which have partially filled d-sub shells either in their elemental form or in any of their chemically significant oxidation state, are called transition elements. Thus IIB group elements (Zn, Cd and Hg) are d-block elements but not transition elements, because they do not have incompletely filled d-sub shell both in elemental form and in divalent state. So, except IIB group elements, remaining d-block elements are transition elements. All transition elements are d-block elements but all d-block elements are not transition elements.

**P.5.1****Solution**

What are coinage metals ? Are they transition elements ?

IIB group elements copper, silver and gold are called coinage elements. In olden days these metals are used to prepare coins.

They do not have incompletely filled subshell in elemental form but they have partially filled d-shell in their chemically significant oxidation states. Thus they are transition elements.

5.1.2 Electronic configuration

General electronic configuration of d-block elements is $(n-1)d^{1-10}ns^{1 or 2}$

General electronic configuration of d-block elements is $(n-1)d^{1-10}ns^{1 or 2}$. Here n values are 4 for 3d-series, 5 for 4d-, 6 for 5d- and 7 for 6d-series. Half filled and completely filled subshells give extra stability to the atom because of greater exchange energy. Thus in some transition elements, electrons move between ns- and $(n-1)d$ - sub shells and exhibit anomalous electronic configuration. These configurations are given in the Table 5.2.

Table 5.2 Anomalous electronic configurations of some elements

S.No.	Element	Symbol	Atomic number	Electronic configuration
1	Chromium	Cr	24	[Ar] $4s^13d^5$
2	Molybdenum	Mo	42	[Kr] $5s^14d^5$
3	Copper	Cu	29	[Ar] $4s^13d^{10}$
4	Silver	Ag	47	[Kr] $5s^14d^{10}$
5	Gold	Au	79	[Xe] $4f^{14}6s^15d^{10}$
6	Palladium	Pd	46	[Kr] $5s^04d^{10}$
7	Platinum	Pt	78	[Xe] $4f^{14}6s^15d^9$



P.5.2 Which element has pseudo inert gas electronic configuration?

Solution

Eighteen electrons in the valence shell is called pseudo inert gas electronic configuration. Palladium ($Z = 46$) has pseudo inert gas configuration in elemental form.

Electronic configuration of Pd ($Z = 46$) is $[Ar] 3d^{10} 4s^24p^64d^{10}$.



P.5.3 Elements with the general electronic configuration $(n-1)d^3ns^2$ belong to which group in the modern periodic table?

Solution

In case of d-block elements group number is equal to the sum of ns- and $(n-1)d$ - electrons. Elements with the electronic configuration $(n-1)d^3 ns^2$ belong to group 5 or VB group.

5.1.3**Occurrence**

3d- Series elements are more abundant than 4d- and 5d- series

When compared with 4d- and 5d- series elements, 3d- series elements are more widely distributed in the nature.

Another interesting point is, in 3d- series elements with even atomic numbers are largely available than the elements with odd atomic numbers. Iron is the fourth most abundant among all elements in the earth's crust.

The important mineral of iron is haematite (Fe_2O_3). Pyrolusite (MnO_2) and magnite ($\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$) are the main minerals of manganese. Chromite ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$) is the important mineral of chromium.

EXERCISE - 5.1.1

- Define transition elements. Give the names and symbols of the metals of the first transition series.
- Write the electronic configuration of the elements of first transition series.
- What are d-block elements? How many series the d-block elements are known? Give the outer electronic configuration of at least one element in each series.
- Name some d-block elements which have anomalous electronic configurations. Give their outer shell configurations.
- Write the configuration of the following metal ions : Cu^+ , Co^{2+} , Mn^{2+} , Ce^{4+} , Lu^{2+} and Th^{4+} .
- Name the minerals of chromium, manganese and iron. Write the composition of these minerals.

Transition elements have horizontal similarities in addition to vertical similarities

PROPERTIES OF TRANSITION METALS

There are greater horizontal similarities in the properties of the transition elements in contrast to the main group elements. However group similarities usually exist. We shall first study the general characteristics and their trends in the horizontal rows (particularly 3d series). General and characteristic properties of transition elements are:

- 1) Metallic nature and electropositivity,
- 2) High melting and boiling points,
- 3) Extremely hard,
- 4) Good conductors of heat and electricity,
- 5) Malleable and ductile,
- 6) Variable oxidation states,
- 7) Paramagnetic and ferromagnetic nature,
- 8) Formation of hydrated coloured ions and salts,
- 9) Alloy forming ability,
- 10) Complex compound forming ability,
- 11) Interstitial compound forming ability and
- 12) Catalytic property.

With the exceptions of Zn, Cd, Hg and Mn, transition elements have one or more typical metallic structures at normal temperatures.

Nearly all of these metals display typical metallic properties (Table 5.3). Some important general characteristics of 3d-series of transition elements are given in the Table 5.4.

Table 5.3 Some general characteristic properties of 3d-series elements

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
hcp (bcc)	hcp (bcc)	bcc	bcc (bcc, ccp)	x (hcp)	bcc (hcp)	ccp	ccp	ccp	x (hcp)
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
hcp (bcc)	hcp (bcc)	bcc	bcc	hcp	hcp	ccp	ccp	ccp	x (hcp)
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
hcp (ccp,bcc)	hcp (bcc)	bcc	bcc	hcp	hcp	ccp	ccp	ccp	x

Table 5.4 Some general characteristic properties of 3d-series elements

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number	21	22	23	24	25	26	27	28	29	30
Relative atomic mass	44.96	47.90	50.94	52.0	54.94	55.85	58.93	58.71	63.53	65.37
Electronic configuration	M	3d ¹ 4s ²	3d ² 4s ²	3d ³ 4s ²	3d ⁵ 4s ¹	3d ⁵ 4s ²	3d ⁶ 4s ²	3d ⁷ 4s ²	3d ⁸ 4s ²	3d ¹⁰ 4s ¹
	M ⁺	3d ¹ 4s ¹	3d ² 4s ¹	3d ³ 4s ¹	3d ⁵	3d ⁵ 4s ¹	3d ⁶ 4s ¹	3d ⁷ 4s ¹	3d ⁸ 4s ¹	3d ¹⁰ 4s ¹
	M ²⁺	3d ¹	3d ²	3d ³	3d ⁴	3d ⁵	3d ⁶	3d ⁷	3d ⁸	3d ⁹
	M ³⁺	[Ar]	3d ¹	3d ²	3d ³	3d ⁴	3d ⁵	3d ⁶	3d ⁷	---
Metallic radii, pm	M	164	147	135	129	137	126	125	125	128
Ionic radii, pm	M ²⁺	---	---	79	82	82	77	74	70	73
	M ³⁺	73	67	64	62	65	65	61	60	---
Density, g cm ⁻³		3.43	4.1	6.07	7.19	7.21	7.8	8.7	8.9	8.9
Electronegativity		1.2	1.3	1.45	1.55	1.60	1.65	1.70	1.75	1.75
										1.65

5.2.1**Atomic and ionic radii**

At the end of any transition series atomic radius increases due to higher inter electron repulsions

Atomic radii of 4d and 5d- series elements are nearly equal due to lanthanide contraction

Atomic radii of the d-block elements are intermediate between those of s- and p-block elements. Atomic and ionic radii of 3d-series elements are given in the Table 5.4.

Trend in series : The atomic radius decreases in a period in the beginning, because with increase in the atomic number, the nuclear charge goes on increasing progressively. However, we know that the electrons enter the penultimate shell, the added d-electrons increases and screening effect also increases. This neutralises the effect of increased nuclear charge due to increase in atomic number. Consequently, atomic radius remains almost unchanged after the middle of series.

At the end of any series, there are increased electron - electron repulsions between the added electrons in the same orbitals. These repulsions exceed the attractive forces due to increased nuclear charge. Therefore, electron cloud expands and the atomic radius increases at the end of any series. Slight irregularities in size have been ascribed to crystal field effects.

Trend in groups : In IIIB group from Sc to La, atomic radius increases. In the remaining groups of d-block, atomic radius increases from 3d-series element to 4d-series element. But atomic radius of 4d-series element and 5d-series element are nearly equal due to the effect of lanthanide contraction.

For example, atomic radius of IVB group elements Ti, Zr and Hf are 1.47A^0 , 1.60A^0 and 1.58A^0 respectively. Atomic radius of VB group elements V, Nb and Ta are 1.34 A^0 , 1.46 A^0 and 1.46 A^0 respectively. Atomic radii of d-block elements are represented in Fig 5.1.

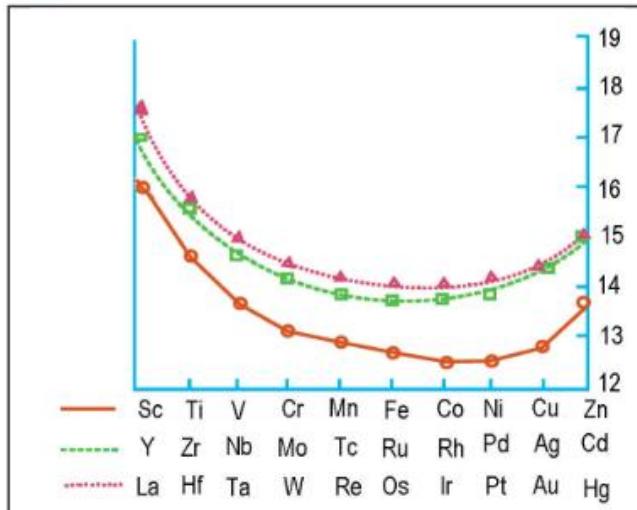


Fig 5.1 Trends in atomic radii of d-block elements

Ionic radii : The ionic radii follow the same trend as the atomic radii. Since the metals exhibit different oxidation states, the radii of ions also differ. The ionic radii of transition metals decreases, with increase in oxidation state. For the same oxidation state, in a series from left to right, ionic radius decreases due to increase in nuclear charge.



P.5.4 Among Cu, Ag, Zn and Cd which one is the biggest atom? why?

Solution At the end of any series atomic radius increases. Thus in between Cu and Zn, Zn is W bigger atom in between Ag and Cd, Cd is the bigger atom.

In a group from 3d-element to 4d-element atomic radius increase. Thus in between Zn and Cd, Cd is the bigger atom. So, among Cu, Ag, Zn and Cd, Cd is the biggest atom.



P.5.5 Why the decrease in atomic radius amongst a series of transition elements is less when compared with representative elements?

Solution

In transition elements differentiating electrons enter d-orbitals of penultimate shell. As the atomic number increases in a given series, though the nuclear charge increases, the electrons entering $(n-1)d$ orbitals reduces nuclear attraction on the outer electrons. Hence atomic radius decreases slightly as we move from left to right in a series of transition elements.

5.2.2

Ionization energies

Ionization energies of d-block elements are more than that of s-block elements and less than that of p-block elements. In a given series with an increase in the atomic number atomic size decreases and nuclear charge increases. As a result nuclear attraction over the valence electrons increases. Hence ionization energy increases in the series. In any series, ionization energy is highest for the last element. First three successive ionization energy values of 3d-series elements and first ionization energy of 4d- and 5d-series elements are given in the Table 5.5.

In III_B-group ionisation potential decreases from scandium to lanthanum, but in the remaining groups trend is not same. From 3d- to 4d-series element ionization potential decreases in some groups and increases to little extent in some other groups.

Table 5.5 Ionization energy values of d-block elements

3d-series	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
I.E. ₁	631	656	650	653	717	762	758	736	745	906
I.E. ₂	1235	1309	1414	1592	1509	1561	1644	1752	1958	1734
I.E. ₃	2393	2657	2833	2990	3260	2962	3243	3402	3556	3829
4d-series	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
I.E. ₁	616	674	664	685	703	711	720	804	731	876
5d-series	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
I.E. ₁	541	760	760	770	759	840	900	870	889	1007

From 4d - to 5d-series, ionization energy increased by great extent

In a group from 4d- to 5d-series element, no change in atomic radii but nuclear charge increases by 32 units. Thus from 4d- to 5d-series ionization energy increased by greater extent.

Chromium and copper have unusually high second ionization energy when compared with their neighbouring elements and with their first ionization energy. This is because Cr⁺ and Cu⁺ have d⁵ and d¹⁰ stable electronic configurations.

Second ionization energy of zinc is considerably low because removal of second electron from zinc leads to the stable d¹⁰ configuration. Removal of electron from the d⁵ configuration is difficult. Thus third ionization energy of manganese is higher than the neighbours. The higher third ionization energy values of Ni, Cu and Zn also indicate why it is difficult to obtain oxidation state greater than +2 for these elements.



P.5.6 Among 3d-, 4d- and 5d-series elements, which element has the least and which has the highest first ionisation energy?

Solution Among first three series of d-block, first ionisation energy is least for lanthanum and is highest for mercury.

5.2.3

Other general properties

Iridium has the highest density

IIB group elements are called volatile metals of d-block

Transition elements have high density due to their small size. In a period, densities increases as the atomic radii decreases. Density increases down the groups in transition elements. Densities of second transition series are higher and third transition series are still higher. Iridium has the highest density (22.7 g cm^{-3}) among all the elements. Osmium also has a very high density (22.6 g cm^{-3}).

All the transition elements are metals. They have high melting and boiling points, high tensile strength, ductility, malleability, hardness, high thermal and electrical conductivities and lustre. With the exceptions of Zn, Cd, Hg and Mn, d-block elements have one or more metallic structures at normal temperatures.

High melting points, boiling points and heat of atomisation values of transition elements are due to the involvement of $(n-1)d$ electrons in addition to ns electrons in the interatomic metallic bonding.

As we move along a transition series, the metallic bond strength increases upto the middle due to increase in number of unpaired d-electrons upto d^5 configuration. The metallic bond strength then decreases due to decrease in number of unpaired d-electrons. Therefore, in any transition series melting points of metals rise to a maximum at d^5 (except for anomalous values of Mn and Tc) and then falls regularly as the atomic number increases.

In any series of d-block, last element (IIB group) has the least melting and boiling points, because there is no unpaired d-electrons for metallic bonding. IIB group elements (Zn, Cd and Hg) are called volatile metals of d-block due to their less boiling points. Melting points of 3d-, 4d- and 5d- transition metals are given in the Fig 5.2.

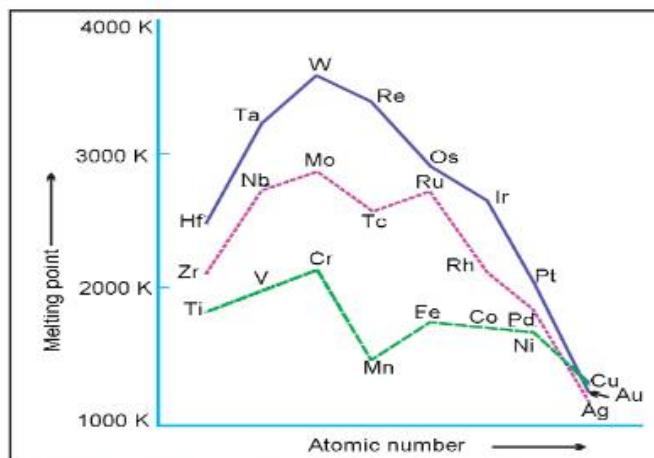


Fig 5.2 Trends in melting points of transition elements

Melting point is highest for w and least for Hg

In a group, generally melting point increases from 3d- to 5d- series element. Same trend is observed in heat of atomisation values. Since the alkali and alkaline earth metals have only one and two valence electrons available for metallic bond, their melting and boiling points are relatively low compared to transition elements. Among all metals tungsten has the highest melting point. Mercury is a liquid at room temperature.

In general, the resultant bonding will be stronger, with greater number of valence electrons. Enthalpy of atomisation is an important factor in determining the metal electrode potential. Metals with high enthalpy of atomisation tend to be noble in their reaction.

Metals of 4d- and 5d- series have greater enthalpies of atomisation than the corresponding 3d- metals (Fig 5.3). This is an important factor in accounting for the occurrence of much more frequent metal-metal bonding in compounds of the heavy transition metals.

All transition elements are metals and electropositive. They are all good conductors of electricity. Silver is the best conductor at room temperature.

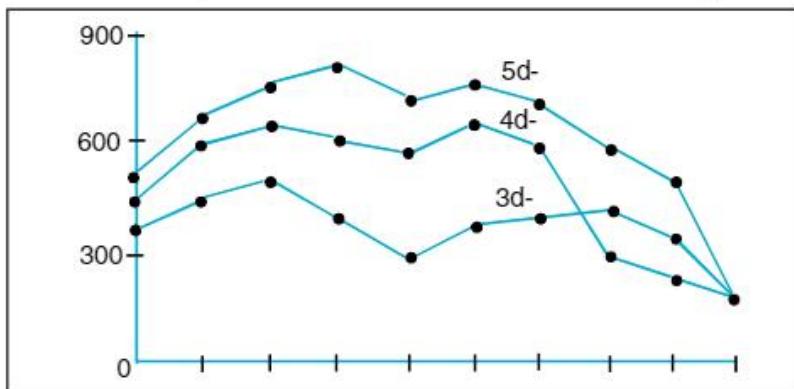


Fig 5.3 Enthalpy of atomisation of transition elements

5.2.4

Oxidation states

Transition elements exhibit variable oxidation states due to the involvement of ns- and (n-1) d-electrons

Transition elements exhibit variable oxidation states due to the involvement of (n-1)d electrons along with ns electrons in bonding. For example oxidation states of manganese are +2, +3, +4, +5, +6 and +7. Variable oxidation states of 3d-series elements are given in the Table 5.6.

Table 5.6 Electronic configurations and the oxidation states of 3d-elements*

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

* Bold denotes more stable oxidation state.

For transition elements, energy difference between ns electrons and (n-1)d electrons is very less. If more no of (n-1)d electrons are present, the energies differ considerably among themselves. As a result all ns electrons and variable number of (n-1)d electrons can be involved in bonding and exhibit more than one oxidation states. For example manganese ([Ar] 4s² 3d⁵) exhibit, +2 oxidation state by using two 4s- electrons, +4 oxidation state by using two 4s- and two of five 3d- electrons and +7 oxidation state by using two 4s- and all the five 3d- electrons in bonding.

d-Block elements exhibit the common oxidation state +2 by lossing two electrons from ns- subshell. Chromium and copper exhibit +1 oxidation state by lossing the lone 4s- electron.

In any d-series of elements, for the first five elements the minimum oxidation state is numerically equal to the number of ns electrons and the maximum oxidation state is numerically equal to the sum of ns and (n-1)d electrons. For the second five elements, the minimum oxidation state is numerically equal to the number of ns electrons and the number of unpaired (n - 1)d electrons.

In 3d, 4d and 5d-series Mn, Ru and Os respectively exhibit highest oxidation states

In 3d-series Mn exhibit the highest oxidation state +7 in the compound KMnO_4 . In 4d- and 5d- series Ru and Os respectively exhibit the highest oxidation state +8 in the compounds RuO_4 and OsO_4 . Some transition elements exhibit the lower oxidation state zero in their complex compounds with carbon monoxide. For example, oxidation state of nickel in $[\text{Ni}(\text{CO})_4]$ is zero.

In the +2 and +3 oxidation states, the bonds formed by transition metals are mostly ionic. In the compounds of higher oxidation states, the bonds are essentially covalent. For example, in MnO_4^- , Mn_2O_7 (oxidation state of manganese is +7) all the bonds are covalent. In the groups of p-block the lower oxidation states are favoured by the heavier members due to inert pair effect. The opposite is true in the groups of d-block. For example, in group 6, Mo (VI) and W (VI) are found to be more stable than Cr (VI). Thus Cr (VI) in the form of dichromate ion in acidic medium is a strong oxidising agent, where as MoO_3 and WO_3 are not.

Higher oxidation states are stable in oxides and in fluorides

Stability of higher oxidation state : d-Block elements exhibit their highest oxidation state fluorides and oxides. The oxides of 3d-metals are given in **Table 5.7**. The ability of oxygen to form multiple bonds with transition metals explain why transition metals exhibit the highest oxidation state in their oxides.

Table 5.7 Oxides of 3d- series metals

Oxidation number	Group number									
	3	4	5	6	7	8	9	10	11	12
+7					Mn_2O_7					
+6				CrO_3						
+5			V_2O_5							
+4		TiO_2	V_2O_4	CrO_2	MnO_2					
+3	Sc_2O_3	Ti_2O_3	V_2O_3	Cr_2O_3	Mn_2O_3	Fe_2O_3	Co_3O_4^*			
+2		TiO	VO	(CrO)	MnO	FeO	CoO	NiO	CuO	ZnO
+1									Cu_2O	

(*Mixed oxide)

The highest oxidation number in the oxides coincides with the group number upto 7th group. Beyond group 7, no higher oxides of element above M_2O_3 are known although ferrates (VI) (FeO_4^{2-}) are formed in alkaline medium but they readily decompose to give Fe_2O_3 and O_2 .

The ability of fluorine to stabilise the highest oxidation state is due to either higher lattice energy as in the case of ionic compounds like CoF_3 or higher bond energy as in the case of covalent compounds like VF_5 and CrF_6 . Another feature of fluorides is their instability in the lower oxidation state. eg: VX_2 , CuX ($\text{X} = \text{Cl}, \text{Br}$ or I). On the other hand, all Cu(II) halides are known except the iodide because Cu^{2+} oxidises I^- to I_2 . Halides of 3d- metals are given in Table 5.8.

Table 5.8 Halides of 3d- metals*

Oxidation number	Group number								
	4	5	6	7	8	9	10	11	12
+6			CrF_6						
+5		VF_5	CrF_5						
+4	TiX_4	VX_4^{I}	CrX_4	MnF_4					
+3	TiX_3	VX_3	CrX_3	MnF_3	FeX_3^{I}	CoF_3			
+2	$\text{TiX}_2^{\text{III}}$	VX_2^{III}	CrX_2	MnX_2	FeX_2	CoX_2	NiX_2	CuX_2^{II}	ZnX_2
+1								CuX^{III}	

* $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$; $\text{X}^{\text{I}} = \text{F}, \text{Cl}, \text{Br}$; $\text{X}^{\text{II}} = \text{F}, \text{Cl}$; $\text{X}^{\text{III}} = \text{Cl}, \text{Br}, \text{I}$

In aqueous solution Cu^{2+} is more stable than Cu^+ due to the higher hydration energy of Cu^{2+}

Many copper (I) compounds are unstable in aqueous solution and undergo disproportionation to Cu^{2+} and Cu. The stability of aqueous Cu^{2+} rather than aqueous Cu^+ is due to the more hydration energy of Cu^{2+} than Cu^+ , which compensates the second ionisation energy of Cu.

**P.5.7**

Name a transition metal which does not exhibit variable oxidation states.

Solution Scandium does not exhibit variable oxidation states, because it exhibits +3 oxidation state only. +2 oxidation state is doubtful.

**P.5.8**

Among ferrous and ferric ions, which one is more stable? Why?

Solution Electronic configuration of Fe(26) : [Ar]4s² 3d⁶

Ferrous ion Fe^{2+} : [Ar] 4s⁰ 3d⁶, Ferric ion Fe^{3+} : [Ar] 4s⁰ 3d⁵

Ferric ion is more stable than ferrous ion. This is because ferric ion has half filled d-subshell stable electronic configuration.

**P.5.9**

Arrange the MnO_4^- , $\text{Cr}_2\text{O}_7^{2-}$ and VO_2^+ ions in the increasing order of their oxidising power.

Solution Order of the oxidation ability: $\text{VO}_2^+ < \text{Cr}_2\text{O}_7^{2-} < \text{MnO}_4^-$.

This is due to the increasing stability of the lower species to which they are reduced.

**P.5.10**

FeCl_3 is known but not FeI_3 . Why?

Solution I⁻ is a strong reducing agent, it reduces Fe^{3+} to Fe^{2+} (or) Fe^{3+} can oxidise I⁻ to I_2 but not Cl⁻ to Cl_2 . $2\text{Fe}^{3+} + 2\text{I}^- \rightarrow 2\text{Fe}^{2+} + \text{I}_2$. Thus FeCl_3 is known but not FeI_3 .

**P.5.11**

Why is Cr^{2+} acts as reductant and Mn^{3+} as oxidant even though both have d⁴ configuration?

Solution Cr^{2+} (d⁴) is less stable than Cr^{3+} (d³) because the latter having a half - filled t_{2g} level. Thus Cr^{2+} oxidises easily to Cr^{3+} and acts as reductant.

Mn^{3+} (d⁴) is less stable than Mn^{2+} (d⁵) because the latter has half-filled d-subshell stable electronic configuration. Thus Mn^{3+} easily reduced to Mn^{2+} and acts as oxidant.



P.5.12 Which is a stronger reducing agent among Cr^{2+} and Fe^{2+} ? Why?

Solution Cr^{2+} is stronger reducing agent than Fe^{2+} , because $d^4 \rightarrow d^3$ occurs in case of Cr^{2+} to Cr^{3+} but $d^5 \rightarrow d^4$ occurs in case of Fe^{2+} to Fe^{3+} . In aqueous solution, d^3 is more stable as compared to d^5 .



P.5.13 Why Ti^{3+} and Cr^{2+} are readily oxidised in air?

Solution Titanium is more stable in +4 oxidation state than +3. Chromium is more stable in +3 oxidation state than +2. Thus Ti^{3+} and Cr^{2+} undergo oxidation readily in air.

5.2.5

Electrode potentials

In addition to ionisation energy, the other factors such as enthalpy of atomisation and hydration energy determine the stability of a particular oxidation state in aqueous solution. This can be explained in terms of electrode potential values. The thermochemical parameters related to 3d-series metals are given in the Table 5.9.

Table 5.9 Thermochemical data (kJ mol^{-1}) and electrode potentials of 3d-elements

Element	$\Delta_a\text{H}^0(\text{M})$	$\Delta_1\text{H}_1^0(\text{M})$	$\Delta_1\text{H}_2^0(\text{M})$	$\Delta_{\text{Hyd}}\text{H}^0(\text{M}^{2+})$	ΔH^0 for $\text{M}_{(\text{s})}$ to M^{2+}	E^0, V (M^{2+}/M)	E^0, V ($\text{M}^{3+}/\text{M}^{2+}$)
Ti	469	661	1310	-1866	+574	-1.63	-0.37
V	515	648	1370	-1895	+638	-1.18	-0.26
Cr	398	653	1590	-1925	+716	-0.90	-0.41
Mn	279	716	1510	-1862	+643	-1.18	+1.56
Fe	418	762	1560	-1998	+742	-0.44	+0.77
Co	427	757	1640	-2079	+745	-0.28	+1.97
Ni	431	736	1750	-2121	+796	-0.25	-
Cu	339	745	1960	-2121	+923	+0.34	-
Zn	130	908	1730	-2059	+709	-0.76	-

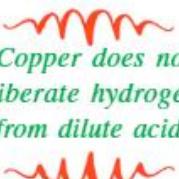
$E^0_{\text{M}^{2+}/\text{M}}$ values of d-block elements are higher compared to those of s-block metals. This is due to high enthalpy of atomisation and high ionization energy of transition elements. In general, across a transition series $E^0_{\text{M}^{2+}/\text{M}}$ values increases due to increase in sum of first and second ionisation energies. If the net enthalpy change in the conversion of $\text{M}_{(\text{s})}$ to $\text{M}^{2+}_{(\text{aq})}$ is more positive, then $E^0_{\text{M}^{2+}/\text{M}}$ is more (Fig 5.4).

$E^0_{\text{M}^{2+}/\text{M}}$ values of Mn and Zn are less than the expected. The stability of half-filled d subshell in Mn^{2+} and the completely filled d subshell in Zn^{2+} are related to their more negative $E^0_{\text{M}^{2+}/\text{M}}$ values.

$E^0_{\text{M}^{2+}/\text{M}}$ of copper is positive. This is because the high energy to transform $\text{Cu}_{(\text{s})}$ to $\text{Cu}^{2+}_{(\text{g})}$ is not balanced by hydration energy of Cu^{2+} . Copper does not liberate hydrogen from dilute acids at room temperature. This is due to its positive $E^0_{\text{M}^{2+}/\text{M}}$ value. Copper can react with oxidising acids like nitric acid and hot concentrated sulphuric acid.

High positive $E^0_{\text{M}^{3+}/\text{M}^{2+}}$ suggest that Mn^{3+} and Co^{3+} act as strong oxidants. Ti^{2+} , V^{2+} and Cr^{2+} act as strong reductants and will liberate hydrogen from acids.




Copper does not liberate hydrogen from dilute acids


Electrode potential is dependent on net enthalpy change

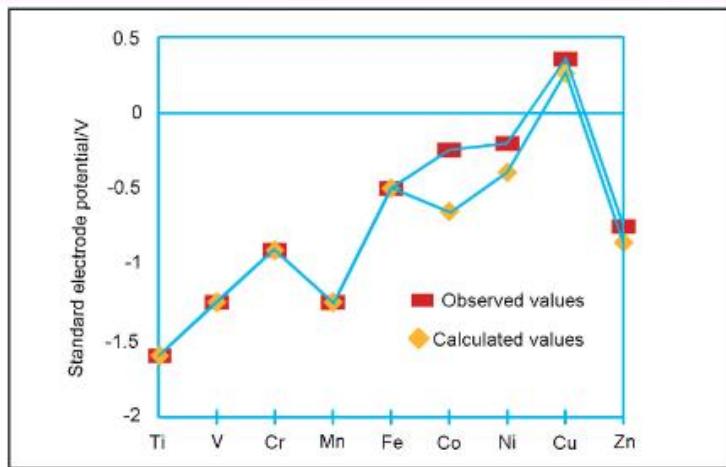



Fig 5.4 Trends in standard electrode potentials of 3d-elements



- P.5.14** Why is the E^0 value for the $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple much more positive than that for $\text{Cr}^{3+}/\text{Cr}^{2+}$ and $\text{Fe}^{3+}/\text{Fe}^{2+}$.

Solution One of the main factors that contributes to standard potential is ionisation enthalpy. Third ionisation energy of Mn is very high due to the greater stability of Mn^{2+} ion. Thus $E^0_{\text{Mn}^{3+}/\text{Mn}^{2+}}$ value is more positive.

5.2.6

Magnetic properties

When a magnetic field is applied on substances, mainly two types of behaviours are observed. They are diamagnetism and paramagnetism. Diamagnetic substances are repelled by the applied field. If permitted, diamagnetic substances move from stronger part of the field to a weaker part of the field. Magnetic lines of forces do not pass easily through the diamagnetic substance when compared with vacuum. The field strength (B) in these substances is less than the applied field (H). Substances having all the paired electrons behave as diamagnetic substances.

eg : Sc^{3+} , Ti^{4+} , Cu^+ , ZnO , KCl , $\text{K}_4[\text{Fe}(\text{CN})_6]$, O_3 , O_2^{2-} , etc.

Paramagnetic substances are attracted by the applied field. If permitted, they move from a weaker part of the field to a stronger part of the field. Magnetic lines of forces pass easily through the paramagnetic substance when compared with vacuum. The field strength (B) in the substance is greater than the applied field (H). Substances having at least one unpaired electron behave as paramagnetic substances.

eg : Ti^{3+} , V^{3+} , Cu^{2+} , Cr_2O_3 , O_2 , O_2^- , O_2^+ , NO , NO_2 , ClO_2 , $\text{K}_3[\text{Fe}(\text{CN})_6]$, etc.

Ferromagnetism is a special case of paramagnetism. Ferromagnetic substances are strongly attracted by the applied field and magnetised permanently. In ferromagnetic substances the magnetic moments of the individual atoms are aligned in the same direction. Thus in these substances the field strength (B) is very much greater than the applied field. Ferromagnetism is exhibited by some transition metals and their compounds.

eg : Fe, Co, Ni, CrO_2 , etc.

Ferromagnetism in the crystalline substances disappears in the solution form of the substance.


Fe, Co, Ni and CrO_2 are ferromagnetic substances


The magnetic moment is expressed in Bohr magnetons (BM). One Bohr magneton is equal to $9.273 \times 10^{-24} \text{ JT}^{-1}$.

The value of Bohr magneton is obtained from the relation, Bohr magneton = $\frac{e h}{4\pi m c}$
where e is charge of electron (in esu), h is Planck's constant (in erg.sec), m is mass of electron (in g) and c is light velocity (in cm/sec).

The magnetic moment of any substance arises from the spin and orbital motion of unpaired electrons. The magnetic moment (μ) can be calculated from the equation,

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

Here S is sum of the spin quantum numbers of all unpaired electrons and L is sum of the azimuthal quantum numbers of all the unpaired electrons.

In many compounds of the 3d-series elements, the angular momentum due to orbital motion of unpaired electrons is small and can be ignored. Therefore, the spin only magnetic moment,

$$\mu_S = \sqrt{4S(S+1)} \text{ BM (or)} \quad \mu_S = \sqrt{n(n+2)} \text{ BM,}$$

Here n is number of unpaired electrons in the substance.

Magnetic moment (μ) is zero, if number of unpaired electrons (n) is zero. Such a substance is diamagnetic. The spin only magnetic moment values of metal ions of 3d-series are given in the Table 5.10.

Table 5.10 Spin only magnetic moments for some of 3d-series ions

S.No.	Metal ion	Configuration of the ion	Number of unpaired electrons in ion (n)	Spin only magnetic moment (μ) in BM	
				Experimental value	Calculated value
1	Sc ³⁺	3d ⁰	0	0	0
2	Ti ³⁺	3d ¹	1	1.75	1.73
3	Ti ²⁺	3d ²	2	2.7 - 2.9	2.84
4	V ²⁺	3d ³	3	3.8 - 3.9	3.87
5	Cr ²⁺ (or) Mn ³⁺	3d ⁴	4	4.8 - 4.9	4.90
6	Mn ²⁺ (or) Fe ³⁺	3d ⁵	5	5.8 - 6.0	5.92
7	Fe ²⁺	3d ⁶	4	5.3 - 5.6	4.90
8	Co ²⁺	3d ⁷	3	4.4 - 5.2	3.87
9	Ni ²⁺	3d ⁸	2	2.9 - 3.4	2.84
10	Cu ²⁺	3d ⁹	1	1.8 - 2.1	1.73
11	Zn ²⁺	3d ¹⁰	0	0	0

For some ions like Co²⁺, μ_{obs} is greater than μ_{cal}

For some ions like Co²⁺, the observed magnetic moment is higher than the calculated magnetic moment. This suggests that there is an orbital contribution also to μ_S for these ions. In 4d- and 5d-series elements the orbital contribution is significant.



P.5.15 What is the value of one Bohr magneton in S.I. units?

Solution Bohr magneton (BM) is given in SI units as, $BM = 9.273 \times 10^{-24} \text{ J T}^{-1}$

$$\text{The value of BM is obtained from the relation } BM = \frac{e\hbar}{4\pi mc}$$

Here e is charge of electron (in coul), h is Planck's constant (in J.sec), m is mass of electron (in kg) and c is velocity of light.



P.5.16 Calculated spin only magnetic moment of Cr^{x+} is 4.9 BM. Find the 'x' value.

Solution Magnetic moment $\mu = 4.9 \text{ BM} = \sqrt{n(n+2)}$

Number of unpaired electrons = n = 4

with four unpaired electrons, the configuration is $3d^4 4s^0$.

Cr^{2+} ion posses 4 unpaired electrons, thus 'x' value is 2.



P.5.17 Calculate the spin only magnetic moment of Ti^{3+} in C.G.S. unit.

Solution Electronic configuration of Ti^{3+} ion is [Ar] $4s^0 3d^1$

Number of unpaired electrons in Ti^{3+} ion = (n) = 1

$$\text{Therefore, spin only magnetic moment, } \mu_s = \sqrt{n(n+2)} \text{ BM} = \sqrt{1(1+2)} = 1.732 \text{ BM}$$

$$1.732 \text{ BM} = 1.732 \times 9.273 \times 10^{-21} \text{ erg} = 1.6 \times 10^{-20} \text{ erg/gauss}$$

5.2.7

Coloured salts and solutions


Hydrated transition metal ion having unpaired d-electrons are coloured


Most of the compounds of s- and p-block are colourless but hydrated ions and compounds of many transition metals are coloured. eg: MnCl_2 is pink, CuCl_2 is blue, NiSO_4 is green, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is blue coloured, etc.

The colour of the hydrated transition metal ions and compounds may be attributed to the presence of unpaired d-electrons.

In the gaseous state or isolated state of metal ion all the five d-orbitals in a subshell are degenerate. But under the influence of anions in the compound or of water molecules in the hydrated metal ion, five degenerate orbitals are splitted into two sets of d-orbitals having different energies. This phenomenon is called crystal field splitting and it is indicated in Fig 5.5.

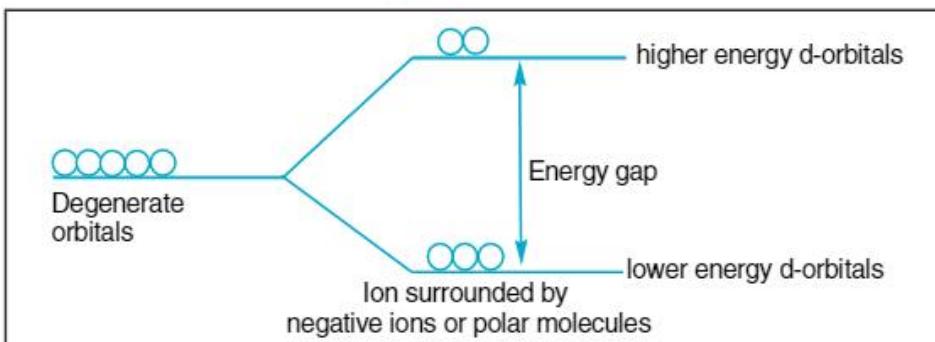


Fig 5.5 Splitting of the five degenerate d-orbitals

The excitation of electrons from a set of d-orbitals having less energy to another set of d-orbitals having high energy within the same d-subshell is called d-d transition. The amount of energy required for d-d transition is equal to the energy of any one of the colours in white light.


Colour of transition metal ions in solutions is due to d-d transitions



 $[Ti(H_2O)_6]^{3+}$ ions absorb green and yellow light and transmits red and violet light



Colour of MnO_4^- , $Cr_2O_7^{2-}$ or CrO_4^{2-} is due to charge transfer phenomenon


When white light falls on a hydrated transition metal ion having at least one unpaired d-electron, it absorbs a characteristic colour from visible region for d-d transition and transmit the complementary colour. Complementary colours are given in the Table 5.11.

Table 5.11 Colours of visible radiations

Colour absorbed	Wave length of absorbed colour	Complementary colour
Violet	400 - 450 nm	Yellow-green
Blue	450 - 490 nm	Yellow
Green blue	480 - 490 nm	Orange
Blue green	490 - 500 nm	Red
Green	500 - 560 nm	Purple
Yellow green	560 - 575 nm	Violet
Yellow	575 - 590 nm	Blue
Orange	590 - 625 nm	Green blue
Red	625 - 750 nm	Blue green

For example, $[Ti(H_2O)_6]^{3+}$ has a lone 3d electron. It absorbs green and yellow light ($\lambda = 500-570$ nm) from visible region and transmits a mixture of red and violet light ($\lambda = 400-450$ nm). Hence hydrated Ti^{3+} ion has purple colour. Similarly hydrated cupric ion (Cu^{2+}) absorbs orange red light from visible region and transmits its complementary colour greenish blue. Thus, cupric compounds have greenish blue colour. Colours of some hydrated ions of 3d-series metals are given in the Table 5.12.

Same metal exhibits different colours in the different oxidation states. For example, Fe^{2+} is green while Fe^{3+} is pinkish yellow. Similarly colours of Cr^{2+} and Cr^{3+} ions are blue and green respectively. Colours of Mn^{2+} , Mn^{3+} and Mn^{6+} ions are pink, blue and green respectively. Hydrated transition metal ions like Sc^{3+} , Ti^{4+} and V^{5+} with empty d-subshell and metal ions like Cu^+ , Zn^{2+} with completely filled d-subshell are colourless.

This is due to the absence of unpaired d-electrons. Even though Cr^{6+} and Mn^{7+} have no unpaired d-electrons, some of their oxo anions like $Cr_2O_7^{2-}$ (orange), CrO_4^{2-} (yellow) and MnO_4^- (purple) are coloured. These colours are due to a different process, known as charge transfer phenomenon.



P.5.18

$CuCl$ is colourless, while $CuSO_4 \cdot 5H_2O$ is coloured. Explain ?

Solution Electronic configuration of Cu^+ ion is $[Ar] 4s^0 3d^{10}$ and of Cu^{2+} ion is $[Ar] 4s^0 3d^9$

In $CuCl$, Cu^+ ion has no unpaired d-electron. Thus d-d transition is not possible in $CuCl$ and hence it is colourless.

In $CuI \cdot 8SO_4 \cdot 5H_2O$, the Cu^{2+} ion has one unpaired d-electron in 3d-subshell. Thus, d-d transition is possible and hence it exhibits colour.

Table 5.12 Colours of some hydrated of 3d-series metal ions

S.No.	Ion	3d electron configuration	Number of unpaired electrons	Colour exhibited
1.	Sc ³⁺	3d ⁰	0	Colourless
2.	Ti ³⁺	3d ¹	1	Purple
3.	V ³⁺	3d ²	2	Green
4.	Cr ³⁺	3d ³	3	Green
5.	Mn ³⁺	3d ⁴	4	Violet
6.	Fe ³⁺	3d ⁵	5	Yellow
7.	Mn ²⁺	3d ⁵	5	Pink
8.	Fe ²⁺	3d ⁶	4	Green
9.	Co ²⁺	3d ⁷	3	Pink
10.	Ni ²⁺	3d ⁸	2	Green
11.	Cu ²⁺	3d ⁹	1	Blue
12.	Cu ⁺	3d ¹⁰	0	Colourless



P.5.19 Eventhough Cu²⁺ has one unpaired d-electron, anhydrous copper sulphate is colourless. Why?

Solution Crystal field splitting is absent in anhydrous CuSO₄ due to the absence of water. Hence d-d transition is not possible. Thus anhydrous CuSO₄ is colourless.



P.5.20 Au(I) is diamagnetic, while Au(III) has a magnetic moment of 2.95 BM. Predict the colours of aurous and auric ions?

Solution Au⁺ (5d¹⁰) ion is colourless due to the absence of unpaired d-electron. Au³⁺ (5d⁸) ion is coloured due to the presence of unpaired d-electrons and d-d transitions.



P.5.21 Give some examples of the ions which are coloured but diamagnetic in nature.

Solution Dichromate ion (Cr₂O₇²⁻), chromate ion (CrO₄²⁻) and permanganate ion (MnO₄⁻) are diamagnetic, due to absence of unpaired electrons. But these are coloured due to charge transfer phenomenon.

5.2.8

Catalytic activity

Catalytic activity of transition elements is due to free valencies

Transition metals and their compounds act as catalysts. Some important catalysts and their industrial uses are given in the Table 5.13. The catalytic activity of transition elements is due to their ability to exhibit variable oxidation states and to form complex compounds. At a solid surface, catalysts involve in the formation of bonds between reactant molecules and atoms of the surface of the catalyst. This has the effect of increasing the concentration of the reactants at the catalyst surface and also weakening of the bonds in the reacting molecules. Transition metals become more effective catalysts, because the metal ions can change their oxidation states. In some cases catalyst forms unstable intermediates with the reactants.

In contact process for the manufacture of sulphuric acid, vanadium pentoxide or a vanadate is used as catalyst to oxidise sulphur dioxide to sulphur trioxide.

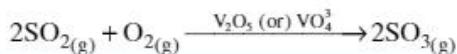
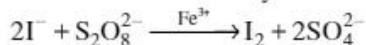


Table 5.13 Catalysts and their industrial uses

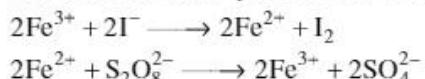
S.No.	Name of the catalyst and its composition	Applications
1	Powdered iron	Haber's process for the preparation of NH_3
2	Pt or V_2O_5	Contact process for the oxidation of SO_2 to SO_3
3	Pt, Ir mixture	Ostwald's process for oxidation of NH_3 to NO
4	Raney nickel	Catalyst in hydrogenation reactions
5	Fenton's reagent $\text{FeSO}_4 + \text{H}_2\text{O}_2$	Oxidation of benzene to phenol and primary alcohols to aldehydes
6	Ziegler-Natta catalyst $\text{TiCl}_4 + \text{Al}(\text{CH}_3)_2$	Polymerisation of ethylene and vinyl substances

This reaction takes place in two steps. In the first step SO_2 is oxidised to SO_3 and V^{5+} is reduced to V^{4+} . In the second step V^{4+} oxidised to V^{5+} .

Ferric ion acts as catalyst for the reaction between iodide and perdisulphate ions.



This reaction takes place in the following two steps.



5.2.9

Interstitial compounds

In interstitial compounds, hydrogen always occupies the tetrahedral holes

Interstitial compounds are those which are formed when small atoms like hydrogen, carbon or nitrogen are trapped in the holes or interstices of the metal lattice. For example steels and cast iron are interstitial compounds of iron and carbon. Some more examples are TiC , MoC , Mo_2C , $\text{VH}_{0.56}$, $\text{TiH}_{1.7}$ and Mn_4N .

Hydrogen always occupies the tetrahedral holes, whereas carbon and nitrogen occupy the larger octahedral holes in the lattice. In these compounds the metal lattice is not altered but the lattice may expand a little. Thus, the density of the interstitial compounds is less than that of the metals. Component elements do not combine in definite ratios and hence these compounds are also called non-stoichiometric compounds. The formulae of non-stoichiometric compounds do not correspond to any normal oxidation states of metal. The oxides and sulphides of transition metals which show variable oxidation states are generally non-stoichiometric compounds.

The interstitial compound of iron and oxygen is represented as $\text{Fe}_{0.93}\text{O}$. In the lattice of ferrous oxide, some iron (II) are replaced by iron (III). Some examples for interstitial compounds are $\text{WO}_{2.88-2.92}$, $\text{Fe}_{0.89-0.96}\text{S}$, etc. The principle physical and chemical properties of interstitial compounds are as follows:

- They retain metallic conductivity.
- They have high melting point than those of pure metals.
- They are very hard, some borides approach diamond in hardness.
- They are chemically inert.

5.2.10

Alloys

An intimate mixture of a metal with other metals or metalloids or sometimes non-metals, is called as an alloy. Alloys are generally prepared to modify the properties of metals like malleability, ductility, toughness, resistance to corrosion, etc.


Main constituent element in steel is iron metal


Alloys with iron are called ferrous alloys and without iron are called non-ferrous alloys. Composition and uses of some ferrous alloys are given in **Table 5.14**

The best known ferrous alloys are variety of steels. The main constituent element in steel is iron and the alloying element may be manganese, chromium, vanadium, tungsten, molybdenum, etc. Copper is an important constituent element in non-ferrous alloys. Some non-ferrous alloys are listed in **Table 5.15**.

Table 5.14 Some ferrous alloys

S.No.	Name of the alloy	Composition of the alloy	Common uses
1	Invar	It is nickel steel. 64% Fe; 35%Ni; trace amounts of Mn and C	It has a low temperature coefficient Used for pendulum rods
2	Nichrome	It is nickel chromium steel 60% Ni; 25% Fe; 15% Cr	It has high resistance to electric current. Used in heating elements of fire stoves and furnaces

Table 5.15 Some non-ferrous alloys

S.No.	Name of the alloy	Composition of the alloy	Common uses
1	Devarda's alloy	50% Cu; 45% Al; 5% Zn	Used to reduce nitrites or nitrates to ammonia gas
2	German silver	50 - 60% Cu; 10 - 30% Ni; 20 - 30% Zn	Used in spoons forks and utensils
3	Bell metal	80% Cu; 20%Sn	Used in Bells
4	Bronze	75 - 90% Cu; 10 - 25% Sn	Used in utensils, coins and statues
5	Gun metal	88% Cu; 10% Sn; 2% Zn	Used in bearings and guns
6	Brass	60 - 80% Cu; 20 - 40% Zn	Used in machiner parts
7	Solder metal	50% Sn, 48% Pb, 2% Sb	Used in electrical conductors

Alloys are formed by atoms with metallic radii that are within about 15 percent of each other of transition metals. Alloys are easily formed by transition metals, because of the similar atomic radii, crystal structure, similar valency and other characteristics.

Some methods of alloy preparation

- Alloys are prepared most commonly by melting a mixture of component metals in proper proportions and then cooling. Brass is prepared in this way.
- Some alloys like brass can be prepared by the simultaneous electrolytic deposition of metals during the electrolysis of complex compounds of the respective metal ions.
- In reduction method, a component metal is reduced in the presence of other metal. Iron-chromium alloy is prepared by reduction of chromite ore.
- Amalgams are the alloys of mercury with metals. Iron vessels are used generally to store mercury, because, amalgam is not formed by iron. Amalgamation process is used in the extraction of gold.


Amalgams is an alloy of Hg with metal


EXERCISE - 5.1.2

- What is meant by variable oxidation states? How does manganese show its variable oxidation states?
- The atomic radius along the 3d series decreases. Explain on the basis of their electron configuration.
- Explain the colour of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ion.
- How does a catalyst work in a chemical reaction? Discuss the catalysis with suitable examples.
- How do you classify magnetic substances? Give two examples each.
- What do you understand by non-stoichiometric compounds?
- What are alloys? How are they prepared?
- Mention any four alloys. Give the composition and uses.
- Discuss the colour of the transition metal compounds with suitable examples.
- Explain the magnetic properties of first transition series metal ions.
- Mention the characteristic properties of transition elements.
- The transition elements have high melting and boiling points. Why?
- $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ has pale blue colour while $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ is white. Discuss.
- Which of the following in aqueous solutions are coloured? Give reasons.
 Ti^{3+} , V^{3+} , Cu^+ , Sc^{3+} , Mn^{2+} , Fe^{3+} and Co^{2+} .
- The most common oxidation state of first transition series is +2. Explain.
- List out the characteristic properties of transition metals? Mention the reasons for these properties of metals.

COMPOUNDS OF TRANSITION ELEMENTS**5.3.1****Oxides**

The transition metals generally react with oxygen at high temperature to form oxides. Since the transition metals exhibit variable oxidation states, they form a large variety of oxides.

All the 3d-series elements except scandium form MO type oxides which are ionic as well as basic.

The highest oxidation number in the oxides, coincides with the group number upto group 7. Beyond group 7, no higher oxides of metal, above M_2O_3 are known.

As the oxidation number of a metal increases, ionic character decreases. In the case of manganese, Mn_2O_7 is a covalent green oil. In the case of chromium and vanadium, CrO_3 and V_2O_5 have low melting points. Transition metal oxides with lower oxidation state of metals are ionic oxides and are generally basic. As the oxidation number of a metal increases, acidic character increases.

In case of manganese MnO and Mn_2O_3 are basic, Mn_3O_4 and MnO_2 are amphoteric and Mn_2O_7 is acidic. In case of chromium CrO is basic, Cr_2O_3 and CrO_2 are amphoteric and CrO_3 is acidic. In case of vanadium VO , V_2O_3 and V_2O_4 are basic but V_2O_5 is amphoteric. V_2O_5 reacts with alkali as well as acids to give VO_4^{3-} and VO_2^+ respectively.

As the oxidation number of a metal in oxide increases, acidic character of oxide increases

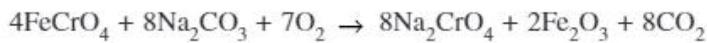


5.3.2**Oxoanions**

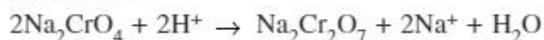
K₂Cr₂O₇ is manufactured from chromite ore, fused with Na₂CO₃ in air

Potassium dichromate

Preparation : K₂Cr₂O₇ is manufactured from chromite ore, FeO.CrO₃. Chromite ore is fused with sodium carbonate in free access of air.



The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to give a solution from which orange sodium dichromate, Na₂Cr₂O₇.2H₂O can be crystallised.

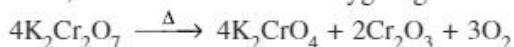


Sodium dichromate is more soluble in water than potassium dichromate. The latter is therefore, prepared by treating the solution of sodium dichromate with potassium chloride.

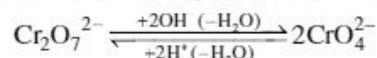


Properties : K₂Cr₂O₇ is orange red crystalline solid having melting point 670 K. It is moderately soluble in cold water but readily soluble in hot water.

Action of heat : When heated to a white heat, it decomposes to give potassium chromate, chromic oxide and oxygen gas.



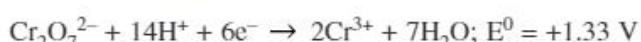
Action of alkalies and acids : When an alkali is added to an orange-red solution of K₂Cr₂O₇, a yellow solution of K₂CrO₄ results. This on acidification again gives back orange-red K₂Cr₂O₇. Dichromate in acidic solutions is called chromic acid. Dichromate ion, Cr₂O₇²⁻ and chromate ion, CrO₄²⁻ exist in equilibrium which are inter convertible by changing the pH of the solution. It indicates that the acidic solution contains Cr₂O₇²⁻ ions, while alkaline solution contains CrO₄²⁻ ions.



Chromyl chloride test : When K₂Cr₂O₇ is heated with concentrated sulphuric acid and a soluble metal chloride, deep red vapours of chromyl chloride are evolved.

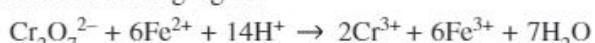


Oxidising properties : Potassium dichromate acts as powerful oxidising agent in acidic medium. Both Na₂Cr₂O₇ and K₂Cr₂O₇ are oxidising agents but K₂Cr₂O₇ is preferred because it is not hygroscopic and can be used as primary standard in volumetric analysis. In acidic solution, oxidising action of dichromate ion can be represented as follows.



Acidified K₂Cr₂O₇ will oxidise iodides to iodine, sulphides to sulphur, tin (II) to tin (IV) and iron (II) salts to iron (III) salts.

The full ionic equation may be obtained by adding half reactions of oxidising agent and reducing agent.



Structures of chromate ion, and dichromate ion, are given in Fig 5.6.

Dichromate and chromate ions are inter convertible by changing the pH.

Potassium dichromate acts as powerful oxidising agent in acidic medium

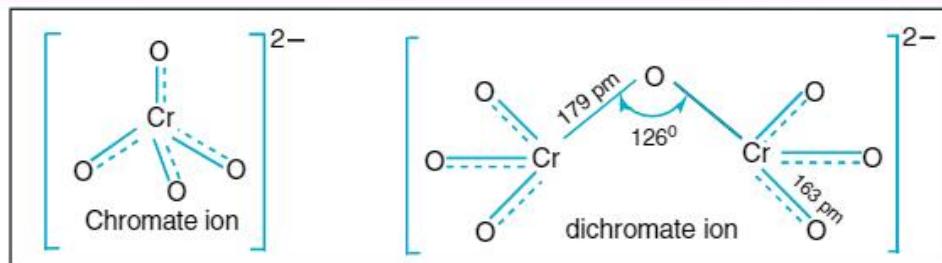


Fig 5.6 Structure of chromate and dichromate ions

Chromate ion is tetrahedral

Both in chromate and dichromate ions, chromium undergo sp^3 hybridisation. The chromate ion is tetrahedral whereas the dichromate ion consists of two tetrahedra sharing one corner with $Cr-O-Cr$ bond angle of 126° . In chromate ion chromium form $p_\pi - d_\pi$ bonds with two oxygens. In dichromate ion each chromium forms $p_\pi - d_\pi$ bonds with three oxygens.

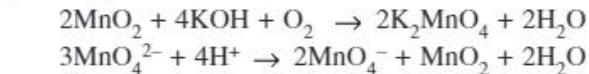
Uses : It is a very important chemical used in leather industry. It is used as an oxidant for preparation of many azo compounds.

Potassium permanganate

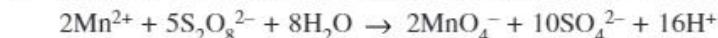
Potassium permanganate is the salt of permanganic acid, $HMnO_4$ which is an unstable acid and exists only in solution.

KMnO₄ is prepared from the pyrolusite

Preparation : $KMnO_4$ is prepared from the pyrolusite ore (MnO_2) in two steps. In the first step dark green K_2MnO_4 is prepared by fusing the finely powdered pyrolusite ore with an alkali metal hydroxide and oxidising agent like KNO_3 . In the second step K_2MnO_4 is acidified, then it disproportionates to give potassium permanganate.



Commercially potassium permanganate is prepared by the alkaline oxidative fusion of MnO_2 followed by the electrolytic oxidation of manganate ion. It is prepared by oxidation of manganese with peroxodisulphate, in laboratory.



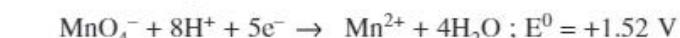
Properties : Potassium permanganate forms dark purple (almost black) lustrous crystals. It gives deep pink colour in solution.

Its solubility in water at $20^\circ C$ is only about 6.4 g per 100 g of water, but solubility increases with increasing the temperature. At a temperature of $240^\circ C$, potassium permanganate decomposes and gives off oxygen gas.



Permanganate ion is diamagnetic. The ion possess weak temperature dependent paramagnetism.

Oxidising properties : Potassium permanganate is a powerful oxidising agent in neutral, alkaline and acidic solutions. Permanganate ion is reduced to Mn^{2+} ion in acidic solutions, to manganate ion in strongly alkaline solutions and to MnO_2 in neutral or feebly alkaline solutions.



At $240^\circ C$ $KMnO_4$ decomposes and gives off O_2 gas

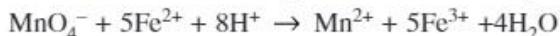
Hydrogen ion concentration of solution plays an important role in influencing the reaction. By considering redox potentials we can say that KMnO_4 can oxidise water at one molar proton concentration. But the reaction is very slow and the rate can be increased by increasing temperature or by taking manganese (II) ions.

Oxidising properties in acidic solutions : To acidify the KMnO_4 sulphuric acid to be used but not hydrochloric acid because it oxidises hydrochloric acid to chlorine.

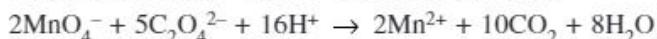
Permanganate oxidises iodide ions to iodine violet,



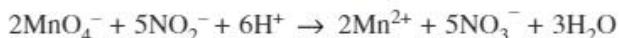
It oxidises ferrous ion (green) to ferric ion (yellow).



It oxidises oxalate ions to carbon dioxide gas,



It oxidises nitrite ions to nitrate ions.

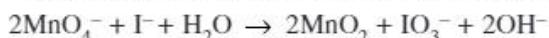


It oxidises sulphite or sulphurous acid to sulphate or sulphuric acid.



Oxidising properties in neutral or slightly alkaline solutions :

Permanganate oxidises iodide ion to iodate ion.



Permanganate oxidises thiosulphate ion to sulphate ion.



It oxidises manganous ion to manganese dioxide in the presence of zinc sulphate or zinc oxide catalyst.



Structures of manganate and permanganate ions : Permanganate ion is isostructural with perchlorate ion. Both in permanganate and manganate ions, manganese undergoes sp^3 hybridisation. Structures of permanganate and manganate ions both are tetrahedral and are given in Fig 5.7.

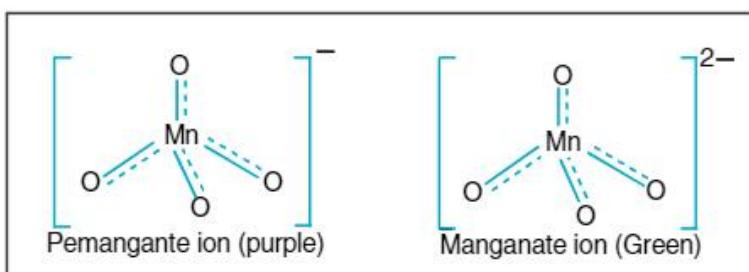


Fig 5.7 Structures of permanganate and manganate ions

In permanganate ion, three π bonds are formed by overlapping of d-orbitals of manganese and p-orbital of oxygen. In manganate ion, two π bonds are formed by overlapping of d-orbitals of manganese and p-orbital of oxygen. Permanganate ion is diamagnetic but manganate ion is paramagnetic with one unpaired d-electron.

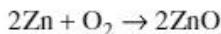
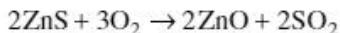
Uses : Permanganate is used in qualitative and quantitative analysis. Due to oxidising property, it is used for bleaching wool, cotton, silk and other textile fibres. It is also used for decolourisation of oils. Cold dilute alkaline potassium permanganate is used as oxidant in organic chemistry under the name Baeyer's reagent.

5.3.3

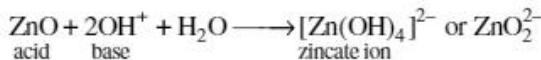
Compounds of zinc



Zinc oxide is formed when ZnS is oxidised. It is also formed on strong heating zinc hydroxide. Zinc on burning in air gives zinc oxide on a commercial scale.



Zinc oxide is white when it is cold, a property that has given it a use as a pigment in paints. However, it changes colour, when hot, to a pale yellow. This is due to change in the structure of lattice. It is soluble both in acid and alkali and is thus amphoteric in nature.



Zinc chloride is obtained by treating zinc oxide or zinc carbonate or zinc hydroxide with dilute hydrochloric acid as $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$.

The anhydrous zinc chloride is obtained by heating zinc in the atmosphere of dry chlorine or dry hydrogen chloride gas. On heating, hydrated zinc chloride forms zinc hydroxychloride or zinc oxychloride.

A white precipitate of zinc sulphide is formed when H_2S gas is passed through the solution. When NaOH is added, a white precipitate of zinc hydroxide is formed which dissolves in excess of sodium hydroxide forming sodium zincate.

A white precipitate of zinc hydroxide is formed with ammonium hydroxide which dissolves in excess of ammonia forming a complex salt.



5.3.4

Compounds of iron

Ferrous oxide is nonstoichiometric and is metal deficient. It commonly has the formula $\text{Fe}_{0.95}\text{O}$. It may be formed as a black powder by strongly heating iron oxalate in a vacuum and then quenching to prevent its disproportionation.

Ferric chloride is formed on direct heating of elements. When Fe is dissolved in aqua-regia or Fe_2O_3 is dissolved in HCl , hydrate $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is formed.

Anhydrous FeCl_3 is black but hydrate $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is yellowish brown, highly deliquescent crystalline solid. It sublims at 300°C giving a dimeric gas. FeCl_3 dissolves in both ether and water giving solvated monomeric species.

Ferric solution gives blood red colour with SCN^- ions. This red colour also contains $[\text{Fe}(\text{SCN})(\text{H}_2\text{O})_5]^{2+}$, $[\text{Fe}(\text{SCN})_3]$ and $[\text{Fe}(\text{SCN})_4]^-$. However, when F^- is added, colour fades due to formation of $[\text{FeF}_6]^{3-}$.

Ferric solution also gives deep blue precipitate of Prussian blue with potassium ferrocyanide.

5.3.5**Compounds of copper**

Copper or cupric oxide on treating with hydrochloric acid gives cupric chloride

Cupric sulphate pentahydrate is blue vitriol

Copper sulphate crystals are efflorescent

Cupric oxide (CuO) is prepared by heating Cu_2O in air or by heating copper for a long time in air or cupric hydroxide or copper nitrate.

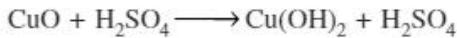
CuO is insoluble in water but dissolves in acids forming corresponding salts. When heated to $1100 - 1200^\circ\text{C}$, it is converted into cuprous oxide with evolution of oxygen. It is reduced to metallic copper by reductants like hydrogen, carbon and carbon monoxide.

Cupric chloride is prepared by dissolving copper metal or CuO or $\text{Cu}(\text{CH})_2$ or CuCO_3 in concentrated hydrochloric acid. Anhydrous cupric chloride is obtained when copper metal is heated in excess of chlorine gas.

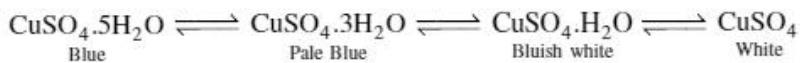
Cupric chloride is a deliquescent compound and is readily soluble in water. Its concentrated solution is green coloured but dilute solution is blue. The blue colour is due to complex cation $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ and yellow colour due to complex anion $[\text{CuCl}_4]^{2-}$ and green when both are present. Anhydrous salt on heating forms Cu_2Cl_2 and Cl_2 .

Cupric chloride is reduced to Cu_2Cl_2 by nascent hydrogen or Cu turings or SO_2 gas or hydrogen or SnCl_2 . With sodium hydroxide, a pale blue precipitate is formed due to the formation of $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$.

Copper sulphate exists as pentahydrate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ which is known as blue vitriol. It is prepared in the laboratory by dissolving cupric oxide or hydroxide or carbonate in dilute sulphuric acid and on evaporation, crystals are formed.



Copper sulphate crystals are efflorescent on exposure and converted into a pale blue powder; $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ and this on heating to 100°C , bluish white monohydrate is formed and this to anhydrous at 230°C .



With ammonium hydroxide solution, it first forms a soluble blue complex which dissolves in excess ammonia to form a complex. A pale blue precipitate of copper hydroxide is formed with alkali.



A black precipitate of copper sulphide is formed when H_2S gas is passed through CuSO_4 solution, which dissolves in concentrated nitric acid. With alkali metal sulphates and with ammonium sulphate, double salts are formed.



P.5.22 Potassium dichromate solution is used to test drunker driver ? Discuss.

Solution

Aqueous solution of potassium dichromate is orange. The driver is asked to breath into the solution. If the solution changes to green, the driver is in drunken state. This is because dichromate oxidises ethanol to acetic acid and itself is reduced to green chromic salt in solution.



P.5.23 Vanadium pentoxide is coloured. Why ?

Solution

Oxidation state of V in V_2O_5 is +5. It has d^0 configuration, but coloured. The colour arises due to defects in crystal structure of V_2O_5 in solid state.



P.5.24 Comment on the inter-conversion of dichromate and chromate

Solution Dichromate $\text{Cr}_2\text{O}_7^{2-}$ in aqueous solution is orange red chromate $\text{Cr}_2\text{O}_4^{2-}$ in aqueous solution is yellow. When an alkali is added to dichromate, it is converted to chromate. Acidification of chromate solution gives back dichromate. Both dichromate and chromate exist in equilibrium and are inter-converted by changing the pH value of the solution.

The inter-conversion of dichromate and chromate is a non-redox reaction.



P.5.25 What is chemical volcano?

Solution On heating crystals or red coloured ammonium dichromate a violent action accompanied by flashes of light and evolution of nitrogen takes place, leaving behind green coloured chromium sesquioxide. $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \xrightarrow{\Delta} \text{N}_2 + 4\text{H}_2\text{O} + \text{Cr}_2\text{O}_3$



P.5.26 How many moles of KMnO_4 are required to oxidise one mole of ferrous oxalate in acidic medium?

Solution Ferrous oxalate is a dual reducing agent. In acidic medium MnO_4^- oxidises ferrous ion to ferric ion and oxalate ion to CO_2 .

Thus balanced equation for the reaction between the permanganate ion and ferrous oxalate is
 $3\text{MnO}_4^- + 5\text{FeC}_2\text{O}_4 + 24\text{H}^+ \rightarrow 3\text{Mn}^{2+} + 5\text{Fe}^{3+} + 10\text{CO}_2 + 12\text{H}_2\text{O}$

Thus one mole of KMnO_4 can oxidise 1.67 moles of ferrous oxalate.



P.5.27 Why manganate ion (MnO_4^{2-}) undergo disproportionation in acidic solutions?

Solution In acidic solutions manganese (VI) becomes unstable relative to manganese (VII) and manganese (IV). Thus in acidic solution manganate ion undergo disproportionation to permanganate ion and manganese dioxide.



P.5.28 Nitric acid is not suitable to acidify potassium permanganate. Why?

Solution Nitric acid acts as oxidising agent. If potassium permanganate is acidified with nitric acid, the latter interferes in the oxidising property of potassium permanganate.

EXERCISE - 5.1.3

- How the acidic nature, covalent character changes with the oxidation state for oxides of a transition metal?
- Explain the preparation of potassium dichromate and potassium permanganate. Write their uses.
- Discuss on the structures of chromate, dichromate, manganate and permanganate ions.
- Write any four oxidising properties of potassium dichromate.
- Write the oxidation properties of KMnO_4 in acidic and neutral medium.

LANTHANIDES

5.4.1

Lanthanides

The fourteen elements from cerium ($Z = 58$) to lutetium ($Z = 71$) which come after lanthanum are called lanthanides. These elements are also called rare earth elements. The fourteen elements, from thorium ($Z = 90$) to lawrencium ($Z = 103$) which come after actinium are called actinides. Lanthanides belong to IIIB group and sixth period, actinides belong to IIIB group and seventh period in the modern periodic table.


Electronic configuration of lanthanoids is $[Xe]6s^25d^14f^n$


In the f-block elements differentiating electron enters f-subshell of the prepenultimate shell. These elements are placed separately at the bottom of periodic table to avoid excessively large width of the table. Since lanthanum closely resembles lanthanoids, it is usually included in any discussion of the lanthanides, with general symbol ‘Ln’. Monazite sand was the oldest source of lanthanides. It accounts for 78% of the total rare earths mined. Monazite sand contains, 60% of trivalent phosphates of La, Ce, Pr, and Nd, 30% of thorium phosphate and 10% of yttrium phosphate and phosphates of other heavier lanthanides.

Electronic configuration : Lanthanum has the electronic configuration $[Xe]5d^16s^2$. It might be expected that the 14 elements from cerium to lutetium would be formed by adding 1, 2, 3,, 14 electrons into the 4f level. However, it is energetically favourable to move the single 5d electron into the 4f level in most of the elements, but not in the case of Ce, Gd and Lu. The reason why Gd has $5d^1$ arrangement is that Gd has a half-filled 4f level, which gives extra stability.

Lu has $5d^1$ arrangement because the f-subshell is already full. The names, symbols, electronic configurations and radii are given in the **Table 5.16**.

Table 5.16 Electronic configuration of lanthanides and some of their cations

Element	Atomic number	Outer electronic configuration				Atomic radius (nm)	Radius of M^{3+} ion (nm)
		Ln	Ln^{2+}	Ln^{3+}	Ln^{4+}		
La	57	$5d^1$	$6s^2$	--	$[Xe]$	0.187	0.106
Ce	58	$4f^1$	$5d^1$	$6s^2$	--	0.183	0.103
Pr	59	$4f^3$	$6s^2$	--	$4f^2$	0.182	0.101
Nd	60	$4f^4$	$6s^2$	$4f^4$	$4f^3$	0.181	0.099
Pm	61	$4f^5$	$6s^2$	--	$4f^4$	0.181	0.098
Sm	62	$4f^6$	$6s^2$	$4f^6$	$4f^5$	0.179	0.096
Eu	63	$4f^7$	$6s^2$	$4f^7$	$4f^6$	0.199	0.095
Gd	64	$4f^7$	$5d^1$	$6s^2$	$4f^7$	0.180	0.094
Tb	65	$4f^9$	$6s^2$	-	$4f^8$	0.178	0.092
Dy	66	$4f^{10}$	$6s^2$	-	$4f^9$	0.177	0.091
Ho	67	$4f^{11}$	$6s^2$	-	$4f^{10}$	0.176	0.089
Er	68	$4f^{12}$	$6s^2$	-	$4f^{11}$	0.175	0.088
Tm	69	$4f^{13}$	$6s^2$	$4f^{13}$	$4f^{12}$	0.174	0.087
Yb	70	$4f^{14}$	$6s^2$	$4f^{14}$	$4f^{13}$	0.173	0.086
Lu	71	$4f^{14}$	$5d^1$	$6s^2$	$4f^{14}$	0.174	0.085

General electronic configuration of lanthanide atoms is $[Xe]6s^25d^14f^n$ or $[Xe]6s^25d^04f^{(n+1)}$, otherwise $[Pd]4f^n5s^25p^65d^16s^2$ or $[Pd]4f^{(n+1)}5s^25p^65d^06s^2$. General electronic configuration of trivalent lanthanide ion (Ln^{3+}) is $[Xe]4f^n$, where n increases gradually from 1 to 14.

Lanthanides are always stable in their common oxidation state +3

Ce⁴⁺ act as a strong oxidant reverting to the common state +3

Eu²⁺ and Yb²⁺ are reductants

The decrease in radius of Ln³⁺ ions is regular

Oxidation states : Lanthanides exhibit the common oxidation state +3. Even though some lanthanides exhibit +2 and +4 oxidation states, they are always less stable than +3 state. The higher oxidation states occur in the fluorides and oxides but the lower oxidation states occur in the other halides, particularly bromides and iodides.

The +2 and +4 oxidation states occur, particularly when they lead to either a noble gas configuration (Ce^{4+}) or a half-filled f subshell (Eu^{2+} and Tb^{4+}) or a completely filled f-subshell (Yb^{2+}). In addition, +2 and +4 states exist for the elements that are close to these stable electronic configurations. Thus Sm^{2+} and Tm^{2+} occur with f^6 and f^{13} configurations and Pr^{4+} and Nd^{4+} occur with f^1 and f^2 configurations.

The +3 state is only the most common and the most stable. Thus Ce^{4+} acts as a strong oxidant reverting to the common state +3. The E° value for $\text{Ce}^{4+}, \text{Ce}^{3+}$ is +1.74 V, suggests that Ce^{4+} can oxidise water but the reaction rate is very slow.

Similarly Tb^{4+} acts as oxidant. Eu^{2+} and Yb^{2+} act as reductants by reverting back to the common state +3.

The E° value for $\text{Ce}^{4+}/\text{Ce}^{3+}$ is +1.74 V which suggests that it can oxidise water. However, the reaction rate is very slow and hence Ce(IV) is a good analytical reagent. Pr, Nd, Tb and Dy also exhibit +4 state but only in oxides, MO_2 . Eu^{2+} is formed by losing the two s electrons and its f^7 configuration accounts for the formation of this ion. However, Eu^{2+} is a strong reducing agent changing to the common +3 state. Similarly Yb^{2+} which has f^{14} configuration is a reductant. Tb^{4+} has half-filled f-orbitals and is an oxidant.

Atomic and ionic radii : Atomic and ionic radii decrease gradually with increase in atomic number. The decrease in atomic (metallic) radii is not quite regular as it is in Ln^{3+} ions as shown in Fig 5.8.

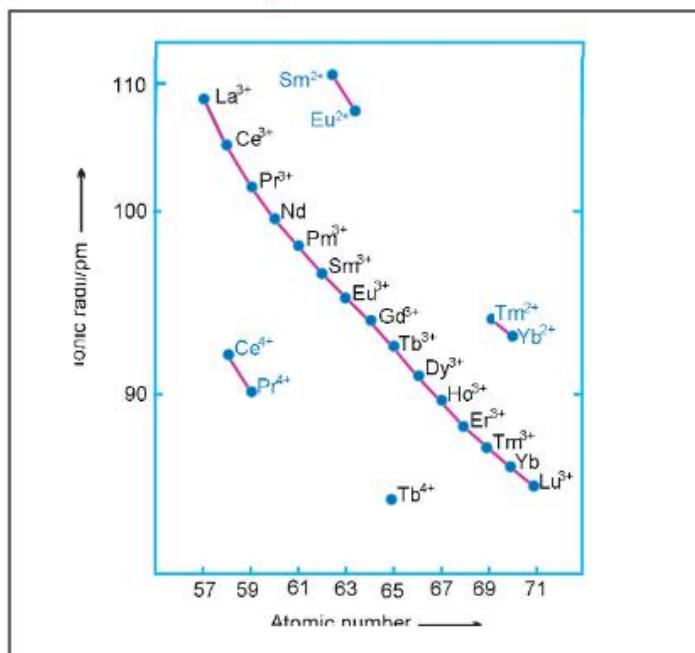


Fig 5.8 Ionic radius of lanthanides

The contraction in size is similar to that observed in transition series. It is attributed to the same cause, the imperfect shielding of one electron by another in the same sub-shell. However the shielding of one 4f-electron by another is less than one d-electron by another, with the increase in nuclear charge along the series. Thus there is fairly regular decrease in the size with increasing atomic number.

The cumulative effect of the contraction of the lanthanide series is known as lanthanide contraction. As a result of lanthanide contraction second and third transition series elements have nearly same atomic radii.

Nearly same size of pairs of elements, Zn and Hf, Nb and Ta, Mo and W is because of lanthanide contraction. Due to this reason, in a group second and third transition series elements resembles each other much more than the elements of first and second transition series.

As a result of lanthanide contraction ionization energy of third transition series elements is more than that of second transition series elements. Because of very small change in atomic radii of lanthanides, their chemical properties are quite similar. Thus it is very difficult to separate these elements from one another using simple chemical separation methods.

Ionisation energies: The first ionisation energies are about 1200 kJ mol^{-1} comparable with those of calcium. Lanthanum, gadolinium and lutetium have abnormally low values of the third ionisation energy. This is because of their stable M^{3+} ions.

Colour and magnetic properties : Many trivalent lanthanide ions are coloured both in the solid state and in aqueous solution. The colour of the ions is due to the presence of unpaired f-electrons. However absorption bands are narrow, probably because of the excitation within f-level. La^{3+} and Lu^{3+} are colourless due to the absence of unpaired f-electrons.

The colour of Ln^{3+} ion depends on the number of unpaired f-electrons. Ln^{3+} ion with 'n' 4f-electrons and Ln^{3+} ion with '(14 - n)' 4f-electrons have similar colour. For example Sm^{3+} ($4f^5$) and Dy^{3+} ($4f^9$) are yellow in colour. Colours of some trivalent lanthanide Ln^{3+} ions are listed compared in Table 5.17.

Table 5.17 Colour of some lanthanide ions

Ion	4f electrons	Colour	Ion	4f electrons	Colour
La^{3+}	0	colourless	Lu^{3+}	14	colourless
Ce^{3+}	1	colourless	Yb^{3+}	13	colourless
Pr^{3+}	2	green	Tm^{3+}	12	pale green
Nd^{3+}	3	lilac	Er^{3+}	11	pink
Pm^{3+}	4	pink	Ho^{3+}	10	pale yellow
Sm^{3+}	5	yellow	Dy^{3+}	9	yellow
Eu^{3+}	6	pale pink	Tb^{3+}	8	pale pink
Gd^{3+}	7	colourless	Gd^{3+}	7	colourless

Ln^{2+} and Ln^{4+} ions do not have colours similar to their isoelectronic Ln^{3+} ions. The lanthanide ions other than the f^0 type (La^{3+} and Ce^{4+}) and f^{14} type (Yb^{2+} and Lu^{3+}) are all paramagnetic. The paramagnetic behaviour is explained based on unpaired electrons in f subshells.

Zn and Hf have nearly same atomic radii due to lanthanide contraction

Ln^{3+} ion with 'n' 4f electrons and Ln^{3+} ion with '(14-n)' 4f electrons have similar colour

La^{3+} and Lu^{3+} are colourless


The hardness increases with increasing atomic number, samarium being steel hard



Properties of lanthanides are alike



Basic strength of oxides decreases from Ce to Lu


All the lanthanides are silvery white soft metals and tarnish rapidly in air. The hardness increases with increasing atomic number, samarium being steel hard. They have typical metallic structures and are good conductors of heat and electricity. Density and melting point increases smoothly across the series except for Eu and Yb.

Chemical properties : Properties of lanthanides are alike. This is due to electrons being filled into the low lying f- orbitals and similar outer electronic configuration. In lanthanoids 4f- electrons are very effectively shielded by 5s- and 5p- electrons. Consequently the 4f- electrons do not take part in bonding. This is one main difference between d- block and f- block elements.

Lanthanides in the monazite sand are first converted into chlorides or oxides. Then the metals are obtained either by the electrolysis of molten chlorides or by the reduction of anhydrous halides with strong electropositive metals like sodium, magnesium, zinc, potassium, calcium, etc.

In their chemical behaviour, in general, the earlier members of the series are quite reactive similar to calcium, but with increasing atomic number, they behave more like aluminium. $E^0_{M^{3+}/M}$ of lanthanides are in the range of -2.2 to -2.4 V.

Lanthanides react slowly with cold water and quickly with hot water to form hydroxides with liberation of hydrogen gas. These hydroxides are ionic and basic. They are less basic than $\text{Ca}(\text{OH})_2$ but more basic than $\text{Al}(\text{OH})_3$. The basic nature of the hydroxides decreases from $\text{Ce}(\text{OH})_3$ to $\text{Lu}(\text{OH})_3$ due to decrease in ionic radius. Lanthanides on heating in oxygen gas form Ln_2O_3 oxides. These oxides are ionic and basic in nature. Basic strength of oxides decreases from Ce to Lu.

Carbides like LnC_2 and $\text{Ln}_4(\text{C}_2)_3$ are formed when the metals are heated with carbon in inert atmosphere. They liberate hydrogen from dilute acids and burn in halogens to form halides. Lanthanides form nitrides LnN on heating with nitrogen gas and form sulphides Ln_2S_3 on heating with sulphur.

The lanthanide ions Ln^{3+} have a high charge, which favours the formation of complexes. But lanthanides can not form complex compounds as readily as d-block metals because of their larger sizes.

Complex compounds with chelating ligands are well known. In contrast to the transition elements, the most common coordination numbers of lanthanides are 7.

Basic nature of Lanthanides decreases with the increasing atomic number. Addition of a small amount of a base can precipitate the metal. The basic Lu is precipitated first. Ion exchange method is used to separate first the bigger hydrate ion followed by smaller hydrate ion. Solvent extraction method mainly depends on the solubility of lanthanide salts. Some of the lanthanide salts soluble in water and some of the lanthanide salts soluble in organic solvents.



P.5.29

Variability in the oxidation states of lanthanides is limited. Why?

Solution The common oxidation state of lanthanides is + 3. Existence of + 2 and +4 states is due to the fact that empty, half-filled or completely f-subshells provide lower energy and ions get stabilised. Ce^{4+} has f^0 , Tb^{4+} has f^7 , Eu^{2+} has f^7 and Yb^{2+} has f^{14} stable configurations.



P.5.30

In lanthanide series, which element is well known to exhibit +4 oxidation state? Why?

Solution Cerium is known to exhibit +4 state. Example of Ce^{4+} in compounds is CeF_4 or $\text{Ce}(\text{SO}_4)_2$. This is because Ce^{4+} has inert gas electronic configuration.



P.5.31 Why Ln^{2+} ions are reductants and Ln^{4+} are oxidants?

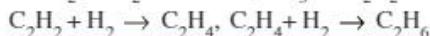
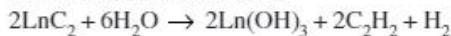
Solution Lanthanides are stable in +3 oxidation state only than in other oxidation states.

Thus Ln^{2+} ions are easily oxidised to Ln^{3+} ions and act as reductants. Ln^{4+} ions are easily reduced to Ln^{3+} ions and act as oxidants.



P.5.32 What are the hydrolysis products of LnC_2 ?

Solution LnC_2 react with water, giving ethyne. Small amounts of hydrogen, ethene and ethane are also formed during hydrolysis.



EXERCISE - 5.1.4

1. Write the names and outer electronic configurations of 4f-series elements.
2. What are the oxidation states exhibited by the Lanthanides? Write examples.
3. Write the chemical form and composition of monozite sand.
4. Write a note on the characteristics of lanthanides.
5. Mention important uses of lanthanides.

ACTINIDES

5.5.1

Actinides

All actinides are radioactive elements

Fourteen elements from thorium ($Z = 90$) to lawrencium ($Z = 103$) are actinides. The names, symbols and electronic configurations of actinium and actinides are given in the Table 5.18. In lanthanides promethium is the only radioactive element but all actinides are radioactive elements. In actinide series first three elements (Th, Pa and U) are naturally occurring elements but the remaining are man made elements. Natural radioactive elements have long half-lives but artificial radioactive elements have lower half-lives.

Table 5.18 Electronic configuration of actinides

Atomic number	Name	Symbol	Electronic configuration		
			of metal	of M^{3+} ion	of M^{4+} ion
89	Actinium	Ac	$6\text{d}^17\text{s}^2$	5f^0	---
90	Thorium	Th	$6\text{d}^27\text{s}^2$	5f^1	5f^0
91	Protactinium	Pa	$5\text{f}^26\text{d}^17\text{s}^2$	5f^2	5f^1
92	Uranium	U	$5\text{f}^36\text{d}^17\text{s}^2$	5f^3	5f^2
93	Neptunium	Np	$5\text{f}^46\text{d}^17\text{s}^2$	5f^4	5f^3
94	Plutonium	Pu	$5\text{f}^67\text{s}^2$	5f^5	5f^4
95	Americium	Am	$5\text{f}^77\text{s}^2$	5f^6	5f^5
96	Curium	Cm	$5\text{f}^76\text{d}17\text{s}^2$	5f^7	5f^7
97	Berkelium	Bk	$5\text{f}^97\text{s}^2$	5f^8	5f^7
98	Californium	Cf	$5\text{f}^{10}7\text{s}^2$	5f^9	5f^8
99	Einstenium	Es	$5\text{f}^{11}7\text{s}^2$	5f^{10}	5f^9
100	Fermium	Fm	$5\text{f}^{12}7\text{s}^2$	5f^{11}	5f^{10}
101	Mendelevium	Md	$5\text{f}^{13}7\text{s}^2$	5f^{12}	5f^{11}
102	Nobelium	No	$5\text{f}^{14}7\text{s}^2$	5f^{13}	5f^{12}
103	Lawrencium	Lr	$5\text{f}^{14}6\text{d}^17\text{s}^2$	5f^{14}	5f^{13}

The heaviest naturally available element is uranium. Elements with $Z > 92$ are all synthetic. Elements after uranium are called transuranic elements. Most of the transuranic elements were discovered by Seaborg. Some of the actinides are prepared only in nanogram quantities only. This factor render their study more difficult.

Electronic configuration : All the actinides are believed to have the electronic configuration of $7s^2$ and variable occupancy of the 5f- and 6d- subshells. The fourteen electrons are formally added to 5f, though not in thorium ($Z = 90$), but from protactinium onwards. The irregularities in the electronic configurations of the actinides, like those in the lanthanides are related to the stabilities of the f⁰, f⁷ and f¹⁴. Thus, the configurations of americium and curium are [Rn]5f⁷ 7s² and [Rn] 5f⁷ 6d¹ 7s². The 5f- orbitals extended into space beyond the 6s- and 6p- orbitals and participate in bonding. This is indirect contrast to the lanthanides where the 4f- orbitals are buried deep inside the atom and thus unable to take part in bonding. The participation of 5f- orbitals explains the higher oxidation states shown by the earlier actinide elements.

Atomic and ionic radii : Similar to lanthanides, actinides also exhibit actinide contraction. But actinide contraction is greater from element to element than lanthanide contraction. This is because the 5f- electrons themselves provide poor shielding from element to element in the series. Actinide contraction is less important because the chemistry of element succeeding the actinides are much less known at the present.

Oxidation states: Like the lanthanides, common oxidation state of actinide is +3. However, this is not always the most stable oxidation state in actinides. Oxidation states of actinides are given in the Table 5.19.

Table 5.19 Oxidate states of actinides* (stable state is given in bold)

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
+ 3		+ 3	+ 3	+ 3	+ 3	+ 3	+ 3	+ 3	+ 3	+ 3	+ 3	+ 3	+ 3	+ 3
	+ 4	+ 4	+ 4	+ 4	+ 4	+ 4	+ 4	+ 4						
		+ 5	+ 5	+ 5	+ 5	+ 5								
			+ 6	+ 6	+ 6	+ 6								
				+ 7	+ 7									

In contrast to lanthanides, the first half of the actinides exhibit a greater range of higher oxidation states. This may be due to the fact that 5f, 6d and 7s electrons have comparable energies and participate in bonding. The maximum oxidation state increases from +4 in Th to +5, +6 and +7 in Pa, U and Np respectively.

Reactivity : Actinides are silvery white metals in appearance but display a variety of structures. The structural variability is obtained due to irregularities in metallic radii which are far greater than in lanthanides. Actinides are highly reactive metals, especially when finely divided. Hydrochloric acid attacks all metals but most of the metals are slightly affected by nitric acid due to the formation of protective oxide layers. Actinides do not react with alkalies.

Paramagnetism : Actinide ions are generally paramagnetic due to the presence of unpaired electrons. The magnetic properties of actinides are more complex than

All actinides have the electronic configuration $7s^2$

Common oxidation state of actinides is +3

Actinides are slightly affected by nitric acid due to the formation of protective oxide

those of the lanthanides. Although the variation in the magnetic susceptibility of the actinides with the number of unpaired 5f electrons is roughly parallel to the corresponding results for the lanthanides, the latter have higher values.

Ionisation potentials : Ionisation energies of early actinides are lesser than that of the early lanthanides. This is quite reasonable since it is to be expected that when 5f orbitals are beginning to be occupied, they will penetrate less into the inner core of electrons. The 5f- electrons, will therefore, be more effectively shielded from the nuclear charge than the 4f- electrons of the corresponding lanthanides. Actinides are relatively more reactive, because the outer electrons are less firmly held and are available for bonding. The properties are compared with these of lanthanides in Table 5.20.

Table 5.20 Comparison of properties of f-block elements

S.No.	Lanthanides	Actinides
1.	These exhibit mainly +3 oxidation state. In addition to +3, +2 and +4 are noticed.	These also exhibit +3 oxidation state. In addition to +3 states, higher oxidation states +3 to +7
2.	These show lanthanoid contraction.	These show actinoid contraction.
3.	These are separated by ion exchange behaviour	These also show ion exchange behaviour.
4.	These possess lesser tendency for complexation	These possess greater tendency for complexation
5.	Their compounds are less basic in nature	Their compounds are more basic in nature
6.	These are not radioactive (except promethium)	All these are radioactive and synthetic
7.	These are referred to as rare earths	These are referred as trans-uranic elements
8.	Their magnetic nature can be easily explained	Magnetic nature has not been easily explained

5.5.2

Applications

Iron and steels are the most important construction materials. Their production is based on the reduction of iron oxides, the removal of impurities and the addition of carbon and alloying metals such as Cr, Mn and Ni. Some compounds are manufactured for special purpose such as TiO for the pigment industry and MnO₂ for use in dry battery cells. The battery industry also requires Zn and Ni/Cd.

The elements of Group 11 are still worthy of being called the coinage metals, although Ag and Au are restricted collection items and the contemporary UK 'copper' coins are copper-coated steel. The 'silver' UK coins are a Cu/Ni alloy. Many of the metals and/or their compounds are essential catalysts in the chemical industry. V₂O₅ catalyses the oxidation of SO₂ in the manufacture of sulphuric acid. TiCl₄ with Al(CH₃)₃ forms the basis of the Ziegler catalysts used to manufacture polyethylene (polythene).

Iron catalysts are used in the Haber process for the production of ammonia from N₂/H₂ mixtures. Nickel catalysts enable the hydrogenation of fats to proceed. In the Wacker process the oxidation of ethyne to ethanal is catalysed by PdCl₂. Nickel complexes are useful in the polymerisation of alkynes and other organic compounds such as benzene. The photographic industry relies on the special light-sensitive properties of AgBr.





P.5.33 Why actinides are not affected by nitric acid?



Solution Actinide on reaction with concentrated nitric acid forms a protective oxide film. Hence it is slightly affected.



P.5.34 Actinides are called transuranic elements. Explain.



Solution Heaviest naturally available element is uranium. Elements with $Z > 92$ are called transuranic elements. They are all artificial and most of them were synthesised by Seaborg.



P.5.35 Why actinides are more reactive than lanthanides?



Solution All actinides have $7s^2$ outer electronic configuration. These s-electrons are less firmly held and are easily available for bonding. Hence actinides are more reactive.

The $6s$ -electrons of lanthanides are more firmly held and hence they are less reactive.



P.5.36 Complex compounds of transition metals are familiar, but not inner transition elements. Why?



Solution Transition metal ions have empty d-orbitals. Because the ions are small and highly charged the complex compounds formed are stable. Inner transition metal ions have empty f-orbitals. The ions are large and hence the complex compounds formed are relatively less stable.

EXERCISE - 5.1.5

1. What are actinides and transuranic elements?
2. Write the general configuration and reactivity of actinides.
3. Write four important differences between lanthanides and actinides.



1. Elements in which the differentiating electrons enters in d-orbitals are called d-block elements. Except IIB group all d-block elements are called transition elements.
2. General electronic configuration of d-block elements is $(n-1)d^{1-10} ns^1$ or 2 . Electronic configuration of chromium is $[Ar] 4s^1 3d^5$, copper is $[Ar] 4s^1 3d^{10}$ and palladium is $[Kr] 4d^{10}$.
3. In transition series atomic radius decreases across the series. But this decrease is less when compared with the representative elements.
4. 4d- and 5d- series elements have nearly same atomic radii due to lanthanide contraction.
5. Chromium and copper have high second ionisation enthalpy values than their neighbours due to the stable electronic configuration of Cr^+ and Cu^+ .
6. Transition elements exhibit variable oxidation states due to the involvement of both ns- and $(n-1)d$ - electrons in bonding.
7. Highest oxidation state is exhibited by Os or Ru in its compounds is +8.
8. Transition metal ions with unpaired d-electrons are paramagnetic and ions with no unpaired electrons are diamagnetic.

9. Among d-block elements Zn, Cd and Hg are diamagnetic and Fe, Co and Ni are ferromagnetic.
10. Magnetic moment is calculated using the formula $\mu = \sqrt{n(n+2)}$ BM, where n is number of unpaired electrons. One BM = 9.273×10^{-21} erg/gauss.
11. Hydrated transition metal ions with at least one unpaired electron are coloured. $ZnSO_4 \cdot 7H_2O$ is colourless due to the absence of unpaired d-electron in Zn^{2+} .
12. $[Ti(H_2O)_6]^{3+}$ absorbs, green light from visible region and transmits its complementary purple colour.
13. Colours of permanganate ion, dichromate ion and chromate ions are due to charge transfer phenomenon but not due to d-d transition.
14. Catalytic property of transition elements is due to their ability to exhibit variable oxidation states and to form complex compounds.
15. When small atoms like H, C, N, etc, are one trapped in the holes or nooks of metal, interstitial compounds are formed.
16. Alloys are easily formed by transition metals, because of similar size, crystal structure and valency.
17. In the oxides of a transition metals, with increase in the oxidation state, covalent character and acidic nature increases. MnO and Mn_2O_3 are basic, MnO_2 is amphoteric and Mn_2O_7 is acidic.
18. $K_2Cr_2O_7$ is prepared from chromite ore. $KMnO_4$ is prepared from pyrolusite ore.
19. Dichromate and chromate ions are inter convertible by changing pH value.
20. To acidify $KMnO_4$, sulphuric acid to be used but not hydrochloric acid, because $KMnO_4$ oxidises hydrochloric acid to chlorine.
21. Elements in which the differentiating electron enters f-orbitals of antepenultimate shell are called f-block elements and are also called inner transition elements. f-block consists of two series.
22. Fourteen elements from Ce ($Z = 58$) to Lu ($Z = 71$) are called lanthanides and from Th ($Z = 90$) to Lr ($Z = 103$) are called actinides. They are known as rare earths.
23. Monazite sand is important mineral of inner transition elements, consists of thorium phosphate.
24. The general electronic configuration of lanthanides is $[Xe] 6s^2 5d^1 4f^n$ or $[Xe] 6s^2 5d^0 4f^{n+1}$.
25. The common oxidation state of lanthanides in their compounds is + 3. Cerium exhibits + 4 state. Ce^{4+} is good oxidant because it is easily reduced back to + 3 state.
26. Due to ineffective shielding of inner f-electrons, the size of lanthanide atoms and their trivalent ions is abnormally decreased. This is called lanthanide contraction.
27. Actinides are very reactive metals, but their chemistry is limited due to their less abundance.

EXERCISE - 5.2

1. Give some examples for the ions with pseudo inert gas electronic configuration.
2. Iron is the most abundant d-block element in earth's crust. Why?
3. What is the crystal lattice structure of coinage metals? (Ans : ccp)
4. Compare the melting points of alkali metals and transition metals.
5. Explain the possible oxidation states of chromium by using electronic configuration.
6. How the maximum and minimum oxidation states of transition elements related to configuration?
7. What is the oxidation state of central metal in $[\text{Ni}(\text{CO})_4]$ and in $[\text{Fe}(\text{CO})_5]$?
8. Why higher oxidation states of some transition elements are stable?
9. How heat of atomisation changes in 3d-series elements are stable?
10. Why copper(I) compounds undergo disproportionation in aqueous solutions.
11. Formation of CuI_2 is not possible. Why?
12. Transition elements exhibit their highest oxidation states in oxides and fluorides. Discuss.
13. A brown precipitate is formed on long standing of aqueous ferric chloride. Why?
14. HgS precipitates in acidic medium, while ZnS precipitates in alkaline medium using H_2S as a reagent. Why?
15. Copper sulphate dissolves in NH_4OH , but not ferrous sulphate. Why?
16. Among Pr^{3+} , Eu^{3+} , Tm^{3+} and Tb^{3+} , which ion pairs can exhibit same colours? Why?
17. CrO is basic, but CrO_3 is acidic. Why?
18. Among Fe^{2+} and Cr^{2+} , which is stronger reductant? Why?
19. Ni^{2+} is more stable than Pt^{2+} , but Pt^{4+} is more stable than Ni^{4+} . Why?
20. Ferrous oxalate is used in developing black and white photographic film. Discuss.
21. In 3d-series which element has positive $E_{\text{M}^{2+}/\text{M}}^{\circ}$ value? Why? (Ans : Cu)
22. Titanium trichloride is coloured, but titanium tetrachloride is colourless. Why?
23. Fe^{3+} can oxidise halide ions. Discuss.
24. Why calculated magnetic moment of Co^{2+} is less than the experimental magnetic moment?
25. Mn^{x+} has a magnetic moment of 4.9 BM. Calculate the value of x in the given ion. (Ans : 3)
26. A salt of 3d metal gave a white precipitate with NH_4OH , but dissolves in excess NH_4OH . Name the 3d metal. (Ans : Zinc)
27. What is the percentage of number of ferric ions in the non-stoichiometric compound $\text{Fe}_{0.93}\text{O}$. (Ans : 15%)

28. Deverda's alloy is used for detection of nitrates and nitrites. Explain.
29. Ferric salts are more stable than ferrous salts. Why?
30. Addition of appreciable amount KMnO_4 in conc. H_2SO_4 explodes. Explain. (Hint : Mn_2O_7)
31. Aqueous yellow Na_2CrO_4 changes to orange red on passing CO_2 gas. Explain.
32. An aqueous solution of $\text{Al}_2(\text{SO}_4)_3$, FeSO_4 and chrome alum is heated with excess Na_2O_2 . A brown residue and an yellow filtrate are obtained. Discuss.
33. E° for Mn^{3+} , Mn^{2+} is more positive than that for Fe^{3+} , Fe^{2+} . Why?
34. Amongst the bivalent ions of 3d-elements, Mn(II) shows maximum paramagnetic character. Substantiate. (Hint : $\mu = 5.9 \text{ BM}$)
35. Copper is regarded as transition metal, though it has completely filled 3d-orbitals. Explain.
36. Compounds of iron are coloured and paramagnetic. Explain.
37. In 3d-series which element cannot displace hydrogen gas from dilute acids? Why ? (Ans : Cu)
38. Mn^{3+} is less stable than Mn^{2+} and Mn^{4+} ions. Why?
39. Acidified dichromate solution turns green when sodium sulphide is added to it. Explain.
40. How lanthanides differ from actinides in their oxidation states?
41. Is any actinide has no electrons in 5f-subshell? If so name it.
42. What is actinide contraction? How it differs from lanthanides contraction?
43. Only chelate complexes of lanthanides are known, other complexes are less stable. Substantiate.
44. Basic nature of $\text{Lu}(\text{OH})_2$ is less than that of $\text{La}(\text{OH})_3$. Why?
45. Which lanthanide is synthetic? Write its electronic configuration. (Hint : Pm)
46. Trivalent ions of Eu ($Z = 63$) and Tb ($Z = 65$) have same colours. Explain.
47. Eu^{2+} is good reductant, but Ce^{4+} is good oxidant. Explain.
48. The maximum oxidation state of lanthanides is +4, but actinides is +7. Explain.
49. Why 4f-electrons in lanthanides can not participate in bonding, but 5f-electrons in actinides can not participate in bonding?

