

# 08 d and f-Block Elements

## Subtopics

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| <p>8.0 Prominent scientists</p> <p><b><u>d-Block Elements</u></b></p> <p>8.1 General introduction and electronic configuration</p> <p>8.2 Occurrences and general characteristics of transition elements</p> <p>8.3 General trends in properties of the first row transition elements</p> | <p>8.4 Preparation and properties of <math>K_2Cr_2O_7</math> and <math>KMnO_4</math></p> <p><b><u>f-Block Elements</u></b></p> <p>8.5 General introduction and electronic configuration</p> <p>8.6 Lanthanoids</p> <p>8.7 Actinoids</p> |
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### 8.0 Prominent scientists

Scientists	Contributions	
Friedrich Wilhelm Ostwald (1853-1932) (German Chemist)	i.	Discovered Ostwald's dilution law.
	ii.	Gave the first modern definition of catalyst.
	iii.	Devised a method in 1900 to manufacture nitric acid by oxidizing ammonia.
	iv.	Got the Nobel prize in 1909 for catalysis.
	v.	Invented Ostwald viscometer.
Glenn Theodore Seaborg (1912-1999) (American Chemist)	i.	Discovered and isolated ten transuranic elements which includes Plutonium, Americium, Curium, Berkelium, Californium, Einsteinium, Fermium, Mendelevium, Nobelium and Seaborgium.
	ii.	Shared the Nobel prize with McMillan in 1951 for significant contributions in the field of transuranic elements.

### d-Block Elements

#### 8.1 General introduction and electronic configuration

\*Q.1. What are d-block elements?

**Ans:** The elements in which the last electron enters the d-orbital of the penultimate shell i.e.,  $(n-1)d$ -orbital where 'n' is the outermost shell, are called **d-block elements**.

Their general valence or outer electronic configuration is  $(n-1)d^{1-10}ns^{1-2}$ .



**\*Q.2. Explain the position of d-block elements in the periodic table.**

**Ans:** Position of d-block elements in the periodic table:

- The d-block elements lie in between s- and p-block elements, i.e., these elements are located in the middle part of the periodic table.
- The d-block elements are present in 4<sup>th</sup> period (Sc to Zn, 10 elements), 5<sup>th</sup> period (Y to Cd, 10 elements), 6<sup>th</sup> period (La, Hf to Hg, 10 elements) and 7<sup>th</sup> period (Ac, Rf to Uub, 10 elements)
- d-block elements are present from group 3 to group 12.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	s-block		d-block										p-block					
4	19	20	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31	32	33	34	35	36
5	37	38	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49	50	51	52	53	54
6	55	56	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81	82	83	84	85	86
7	87	88	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113	114	115	116	117	118

**Position of d-block elements in the periodic table**

**Q.3. Why are d-block elements called transition elements?**

(NCERT)

- Ans:**
- Transition elements* are defined as those elements which have partly or incompletely filled  $(n-1)d$  orbitals in their elementary state or in any of their common oxidation states.
  - The 3d, 4d, 5d and 6d series of the d-block elements correspond to the filling of 3d, 4d, 5d and 6d orbitals of the  $(n-1)$ <sup>th</sup> main shell. The last electron enters the  $(n-1)$  d-orbital.
  - d-block elements are called transition elements as they show transition in the properties from the most electropositive s-block elements to the less electropositive p-block elements.

**Q.4. \*Explain the meaning of transition series. OR**

**Explain in brief, four series of transition elements.**

- Ans:**
- d-block elements are also known as transition elements. The long form of periodic table contains four series of transition elements, known as transition series.
  - Four transition series are 3d, 4d, 5d and 6d series wherein orbitals of  $(n-1)$ <sup>th</sup> main shell gets filled.
    - The 3d series contains the elements from Sc ( $Z = 21$ ) to Zn ( $Z = 30$ ) belonging to the 4<sup>th</sup> period.
    - The 4d series contains the elements from Y ( $Z = 39$ ) to Cd ( $Z = 48$ ) belonging to the 5<sup>th</sup> period.
    - The 5d series begins with La ( $Z = 57$ ) and contains elements from Hf ( $Z = 72$ ) to Hg ( $Z = 80$ ) belonging to the 6<sup>th</sup> period.
    - The 6d series begins with Ac ( $Z = 89$ ) and contains elements from Rf ( $Z = 104$ ) to Uub ( $Z = 112$ ) belonging to the 7<sup>th</sup> period.

**Q.5. Give the general electronic configuration of four series of d-block elements.**

**Ans:** d-block elements have general valence electronic configuration  $(n-1)d^{1-10} ns^{1-2}$ .

The four series of d-block elements have the general electronic configuration as shown below:

- 3d series:  $[\text{Ar}] 3d^{1-10} 4s^{1-2}$
- 4d series:  $[\text{Kr}] 4d^{1-10} 5s^{0-2}$
- 5d series:  $[\text{Xe}] 5d^{1-10} 6s^2$
- 6d series:  $[\text{Rn}] 6d^{1-10} 7s^2$

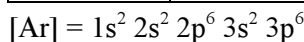
➤ **Electronic configuration of the elements belonging to the 3d series of d-block elements:**

3d series or first row transition series (Sc to Zn) belonging to the fourth period has the general electronic configuration  $[\text{Ar}] 3d^{1-10} 4s^{1-2}$ .



The following table lists the general electronic configuration of first row transition elements.

3d series or First Row Transition Series (Sc to Zn)				
Elements	Symbols	Atomic number	Expected electronic configuration	Observed electronic configuration
Scandium	Sc	21	[Ar] 3d <sup>1</sup> 4s <sup>2</sup>	[Ar] 3d <sup>1</sup> 4s <sup>2</sup>
Titanium	Ti	22	[Ar] 3d <sup>2</sup> 4s <sup>2</sup>	[Ar] 3d <sup>2</sup> 4s <sup>2</sup>
Vanadium	V	23	[Ar] 3d <sup>3</sup> 4s <sup>2</sup>	[Ar] 3d <sup>3</sup> 4s <sup>2</sup>
Chromium	Cr	24	[Ar] 3d <sup>4</sup> 4s <sup>2</sup>	[Ar] 3d <sup>5</sup> 4s <sup>1</sup>
Manganese	Mn	25	[Ar] 3d <sup>5</sup> 4s <sup>2</sup>	[Ar] 3d <sup>5</sup> 4s <sup>2</sup>
Iron	Fe	26	[Ar] 3d <sup>6</sup> 4s <sup>2</sup>	[Ar] 3d <sup>6</sup> 4s <sup>2</sup>
Cobalt	Co	27	[Ar] 3d <sup>7</sup> 4s <sup>2</sup>	[Ar] 3d <sup>7</sup> 4s <sup>2</sup>
Nickel	Ni	28	[Ar] 3d <sup>8</sup> 4s <sup>2</sup>	[Ar] 3d <sup>8</sup> 4s <sup>2</sup>
Copper	Cu	29	[Ar] 3d <sup>9</sup> 4s <sup>2</sup>	[Ar] 3d <sup>10</sup> 4s <sup>1</sup>
Zinc	Zn	30	[Ar] 3d <sup>10</sup> 4s <sup>2</sup>	[Ar] 3d <sup>10</sup> 4s <sup>2</sup>



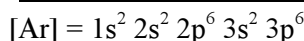
#Q.6. In which period of the periodic table, will an element, be found whose differentiating electron is a 4d electron?

Ans: Fifth period of the periodic table consist of elements in which the differentiating electron is a 4d electron.

Q.7. Write observed electronic configuration of elements from first transition series having half filled d-orbitals. [Oct 13]

Ans:

Element	Symbol	Atomic Number	Expected Electronic Configuration	Observed Electronic Configuration
Chromium	Cr	24	[Ar] 3d <sup>4</sup> 4s <sup>2</sup>	[Ar] 3d <sup>5</sup> 4s <sup>1</sup>
Manganese	Mn	25	[Ar] 3d <sup>5</sup> 4s <sup>2</sup>	[Ar] 3d <sup>5</sup> 4s <sup>2</sup>



[Any one example – 1 Mark]

Q.8. In what way is the electronic configuration of transition elements different from that of the non-transition elements? (NCERT)

Ans: Transition elements contain incompletely filled d subshell, i.e., their outer electronic configuration is (n-1) d<sup>1-10</sup> ns<sup>1-2</sup>, whereas non-transition elements have no d subshell or their d subshell is completely filled and they have the outer electronic configuration of ns<sup>1-2</sup> or ns<sup>2</sup> np<sup>1-6</sup>.

Q.9. Write down the electronic configuration of:

(NCERT)

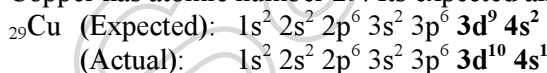
i. Cr<sup>3+</sup>                      ii. Cu<sup>+</sup>                      iii. Co<sup>2+</sup>                      iv. Mn<sup>2+</sup>

Ans: i. Cr<sup>3+</sup> = 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>3</sup>                      ii. Cu<sup>+</sup> = 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>10</sup>

iii. Co<sup>2+</sup> = 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>7</sup>                      iv. Mn<sup>2+</sup> = 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>5</sup>

\*Q.10. Why does copper show abnormal electronic configuration?

Ans: Copper has atomic number 29. Its expected and actual electronic configurations are:

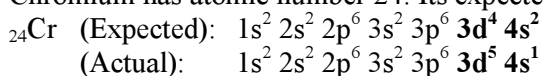


Explanation:

- The energy difference between the 3d and 4s orbitals is very low.
- The d-orbital being degenerate, acquires more stability when it is half-filled (3d<sup>5</sup>) or completely filled (3d<sup>10</sup>).
- Due to the inter-electronic repulsion, one electron from the 4s orbital is transferred to the 3d orbital in Cu so that Cu has completely filled 3d<sup>10</sup> orbital, thus acquiring more stability.

\*Q.11. Why chromium has electronic configuration 3d<sup>5</sup> 4s<sup>1</sup> and not 3d<sup>4</sup> 4s<sup>2</sup>?

Ans: Chromium has atomic number 24. Its expected and actual electronic configurations are:



**Explanation:**

- i. The energy difference between the 3d and 4s orbitals is very low.
- ii. The d-orbital being degenerate, acquires more stability when it is half-filled ( $3d^5$ ) or completely filled ( $3d^{10}$ ).
- iii. Electron – electron repulsion results in transfer of one electron from 4s orbital to 3d orbital of Cr. This results in half filled  $3d^5$  orbital which in turn results in extra stability.

## 8.2 Occurrences and general characteristics of transition elements

**Enrich Your Knowledge****Occurrence of d-block elements:**

- i. d-block elements occur in free state as well as in combined states.
- ii. Soft d-block elements occur as sulphide minerals. Roasting of sulphide minerals in air gives metal or metal oxide, which on reduction gives metal.
- iii. Hard d-block elements occur as oxide minerals. Reduction of oxide minerals with carbon gives metal. Hard d-block elements (metals) are more electropositive than soft d-block elements.
- iv. **Occurrence of some d-block elements:**
  - a. Titanium (in the combined state) is present in small quantities in coal, clay, rocks, sand, etc.  
**eg.** Rutile ( $TiO_2$ ), Ilmenite ( $FeTiO_3$ ).
  - b. Vanadium occurs in the ores vanadinite and carnotite. It is present in the form of vanadate of lead, zinc, copper, etc.
  - c. Some of the ores of chromium include chromite ( $FeO, Cr_2O_3$ ), chrom ochre ( $Cr_2O_3$ ), crocoisite ( $PbCrO_4$ ), etc.
  - d. Manganese is present in pyrolusite ore ( $MnO_2$ ) and other minerals. It is not present in free state.
  - e. Iron occurs in free and combined states. In the earth's crust, the abundance of iron is next to aluminium.
  - f. Cobalt is usually associated with nickel and arsenic and it is also found in traces in the soil.
  - g. Nickel is found in cobalt ores.
  - h. Copper is present in rocks, soil, sea, mineral waters. Some of the ores of copper include cuprite ( $Cu_2O$ ), malachite [ $CuCO_3, Cu(OH)_2$ ], azurite [ $2CuCO_3, Cu(OH)_2$ ], etc.
  - i. Zinc is found in association with silver, copper, lead and platinum and in their ores.

**Q.12. State the general characteristics of transition elements or d-block elements. OR**

**What are the characteristics of the transition elements?**

**(NCERT)**

**Ans: Characteristics of transition elements:**

- i. Most of the transition elements are metals and thereby they show metallic properties such as ductility, malleability, electrical conductivity, high tensile strength and metallic lustre.
- ii. Except mercury which is liquid at room temperature, other transition elements have typical metallic structures.
- iii. Their compounds generally contain unpaired electrons, hence they are paramagnetic in nature and form coloured compounds.
- iv. They show variable oxidation states.
- v. They have tendency to form large number of complexes.
- vi. They have higher densities as compared to the metals of groups 1 and 2 (s-block).
- vii. They are heavy metals with higher melting and boiling point as well as higher heats of vaporisation.
- viii. Transition elements are less reactive than s-block elements due to their higher ionisation energy.
- ix. Most of the transition metals such as Mn, Ni, Co, Cr, V, Pt, etc., and their compounds are used as catalysts.
- x. They have good thermal and electrical conductivity.
- xi. They form alloys with different metals.
- xii. They form interstitial compounds with elements such as hydrogen, boron, carbon, nitrogen, etc.
- xiii. They form organometallic compounds.

**Q.13. Why do transition metals possess high density and high melting and boiling points?**

- Ans:** i. The densities of d-block elements are relatively higher as compared to the s-block elements due to the decrease in the size of the atoms and the consequent increase in the nuclear charge, which results in the compact structure of the elements.
- ii. The density of the atoms increases with the decrease in the size of the atom. Therefore the density of the elements increases from left to right across a period.
- iii. Transition elements form strong metallic bond in which both (n-1) d and ns electrons take part.
- iv. Due to the notable covalent character of the strong metallic bond, considerable amount of energy is required to break the metallic bond in order to melt the metal. Hence, these metals possess high melting and boiling points.

**Note: Atomic properties of 3d series:**

Element	Density (g cm <sup>-3</sup> )	Radii (pm)			Ionization enthalpy (kJ mol <sup>-1</sup> )
		M <sup>+</sup>	M <sup>2+</sup>	M <sup>3+</sup>	
Sc – 21	2.99	164	–	73	631
Ti – 22	4.50	147	–	67	656
V – 23	5.96	135	79	64	650
Cr – 24	7.20	129	82	65	653
Mn – 25	7.21	137	82	65	717
Fe – 26	7.86	126	77	65	762
Co – 27	8.90	125	74	61	758
Ni – 28	8.90	125	70	60	736
Cu – 29	8.92	128	73	–	745
Zn – 30	7.14	137	75	–	906

**Q.14. All d-block elements are not transition elements. Explain. OR**

**Which of the d-block elements may not be regarded as the transition elements?**

(NCERT)

- Ans:** i. The d-block elements are those in which the last electron enters the d-orbital.
- ii. The transition elements are those elements which have incompletely filled (partly filled) d-subshells in their elementary state or in any one of their oxidation states.
- iii. Hence, only those d-block elements which have completely filled d-orbitals, (n-1)d<sup>10</sup> are not transition elements.
- eg.** Zn, Cd and Hg atoms have completely filled d-orbitals (3d<sup>10</sup>) in their ground state as well as in their oxidation states. Hence they are d-block elements, but not transition elements.

**8.3 General trends in properties of the first row transition elements****Q.15. Explain the metallic characters of the d-block elements.**

- Ans:** i. All the transition elements are metallic in nature. They either have hexagonal close pack (hcp), cubic close pack (ccp) or body centred cubic lattices which is a characteristic of true metal.
- ii. They are hard, lustrous, malleable and ductile with high melting and boiling points, and having good thermal and electrical conductivities.
- iii. Low ionization enthalpies and presence of vacant orbitals in the outermost shell results in metallic character due to formation of metallic bonds.
- iv. In addition to the electrons from outermost energy level, the unpaired d-electrons also contribute for the bond formation. So, greater the number of unpaired d-electrons, stronger is the bonding. This is due to the formation of covalent bonds by the overlapping of the d-orbitals containing unpaired electrons.

**Q.16. Why are Cr, Mo and W hard metals while Zn, Cd and Hg are not very hard metals?**

- Ans:** i. The d-orbitals containing unpaired electrons may overlap to form covalent bonds which are responsible for the hardness.
- ii. As the number of unpaired electrons increases, the number of covalent bonds and the strength of the metallic bonds increases. The increase in the number of covalent bonds result in increase in the strength and hardness of metal.



- iii. Cr, Mo and W have maximum number of unpaired d-electrons which makes them very hard due to increase in the number of covalent bonds.
- iv. Zn, Cd, and Hg on the other hand do not have unpaired d-electrons. Hence, they are not very hard.

**Q.17. Explain the trends in melting and boiling points of first row transition metals.**

- Ans:**
- i. Transition metals have hcp, ccp or bcc lattices. They are held together by strong metallic bonds with significant covalent character.
  - ii. To melt the metal, metallic bonds should be broken. This requires significant energy. Hence transition metals have very high melting and boiling points. The strength of metallic bonds, the melting and boiling points increases with increase in the number of unpaired electrons.
  - iii. In a given period of transition elements, the number of unpaired electrons in (n-1) d-orbital increases upto  $d^5$  configuration. This results in increase in the strength of metallic bonds and the melting and boiling points.
  - iv. Pairing of electrons results in decrease in the number of unpaired electrons from  $d^6$  to  $d^9$  configuration. This decreases the strength of metallic bonds and results in progressive decrease in the melting and boiling points, after the middle of the series.

In the first transition series, the number of unpaired electrons increases from Sc to Cr and then decreases. Thus, the strength of metallic bonds and the melting and boiling points increases from Sc to Cr and then decreases.

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Outer electronic configuration	$3d^14s^2$	$3d^24s^2$	$3d^34s^2$	$3d^54s^1$	$3d^54s^2$	$3d^64s^2$	$3d^74s^2$	$3d^84s^2$	$3d^{10}4s^1$	$3d^{10}4s^2$
No. of unpaired electrons	1	2	3	6	5	4	3	2	1	0

- Notes:**
- i. Zn, Cd, and Hg do not have unpaired d-electrons. Hence, they are soft and have low melting and boiling points. Mercury (Hg) is liquid at room temperature (melting point 234 K).
  - ii. Mn and Tc have unexpectedly lower melting points due to complicated lattice structure. They have low enthalpies of atomization.
  - iii. Osmium (Os) has the highest density ( $22.6 \text{ g cm}^{-3}$ ) whereas scandium (Sc) has the lowest ( $2.99 \text{ g cm}^{-3}$ ) and is the lightest transition element.

**Q.18. Define ionization enthalpy.**

**Ans:** *Ionization enthalpy is defined as the amount of energy required to remove the outermost electron completely from a gaseous atom in its ground state.*

**Q.19. Explain the trends observed in the ionization enthalpies of the d-block elements.**

- Ans:**
- i. The ionization enthalpies of transition elements are higher than the ionization enthalpies of s-block elements and lower than the ionization enthalpies of p-block elements. This is due to the trends in atomic radii and nuclear charge.
  - ii. The atomic radii of transition elements are lower than the atomic radii of s-block elements and higher than the atomic radii of p-block elements.
  - iii. The nuclear charges of transition elements are higher than the nuclear charges of s-block elements and lower than the nuclear charges of p-block elements.
  - iv. As the atomic number increases across a transition series, the first ionization energy increases with some irregularities.

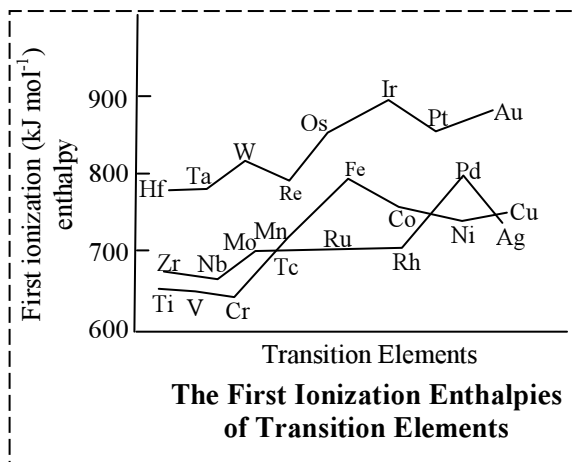
The irregularities are due to shielding of the valence electrons from the nucleus by the added (n-1) d-electrons. Thus, the effect of increased nuclear charge is opposed by the screening effect.

- v. The increasing order of the first ionization enthalpies of elements is:  
 First transition series < second transition series < third transition series  
 The third transition series comprises of elements having atoms which possess filled 4f-orbitals. On account of the peculiar diffused shape of 4f-orbitals, they exhibit poor shielding. Thus, the valence electrons experience greater nuclear attraction.



- vi. As a result, greater amount of energy is required to ionise the elements of the third transition series. Thus, the ionization enthalpies of the third transition series elements are much higher than those of the first and second series.

Note:



### Do You Know?

The energy required to remove first electron from gaseous atom in its ground state is called **first ionization enthalpy**, to remove second electron, it is called **second ionization enthalpy** and for removal of third electron it is called **third ionization enthalpy**.

### Q.20. Explain thermodynamic stability of transition metal compounds on the basis of ionization enthalpy.

- Ans: i. The thermodynamic stability of transition metal compounds can be predicted on the basis of their ionization enthalpy value.
- ii. When the sum of the ionization enthalpies required to attain a particular oxidation state of transition metal ions is small, the thermodynamic stability of the compounds of the metal in that oxidation state is high.

eg.

- a. Compounds containing Ni (II) are more stable than compounds containing Pt (II). Less amount of energy is required for the ionization of Ni to  $\text{Ni}^{2+}$ , than the energy required for the ionization of Pt to  $\text{Pt}^{2+}$ . This is because the sum of first and second ionization enthalpies ( $\text{IE}_1 + \text{IE}_2$ ) for nickel is lesser as compared to that of platinum.



- b. Compounds containing Pt (IV) are more stable than compounds containing Ni (IV). Less amount of energy is required for the ionization of Pt to  $\text{Pt}^{4+}$  than the energy required for the ionization of Ni to  $\text{Ni}^{4+}$ . This is because the sum of first four ionization enthalpies ( $\text{IE}_1 + \text{IE}_2 + \text{IE}_3 + \text{IE}_4$ ) for platinum is lesser as compared to that of nickel.



Note:  $\text{K}_2\text{PtCl}_6$  is a well known compound of Pt (IV). The corresponding compound of nickel is not known.

### \*Q.21. Explain the oxidation states of first row elements of transition series.

- Ans: i. The oxidation states of transition elements are related to the electronic configuration. Transition elements have last two orbitals incompletely filled i.e., they contain ns and (n-1)d orbitals.
- ii. Transition elements have variable oxidation states as both (n-1)d and ns electrons participate in bonding, due to nearly same energy levels.
- iii. Elements of first transition series show +1 and +2 as the lowest oxidation states due to presence of two 4s electrons, with the exception of copper and chromium which have only one 4s electron.



- iv. As the 3d electrons take part in the chemical bonding one after another, in addition to the +2 oxidation state, there are number of other oxidation states as illustrated below.

**Oxidation states of first transition (3d) series elements:**

Sc (3d <sup>1</sup> 4s <sup>2</sup> )	Ti (3d <sup>2</sup> 4s <sup>2</sup> )	V (3d <sup>3</sup> 4s <sup>2</sup> )	Cr (3d <sup>5</sup> 4s <sup>1</sup> )	Mn (3d <sup>5</sup> 4s <sup>2</sup> )	Fe (3d <sup>6</sup> 4s <sup>2</sup> )	Co (3d <sup>7</sup> 4s <sup>2</sup> )	Ni (3d <sup>8</sup> 4s <sup>2</sup> )	Cu (3d <sup>10</sup> 4s <sup>1</sup> )	Zn (3d <sup>10</sup> 4s <sup>2</sup> )
+2	+2	+2	+1	+2	+2	+2	+2	+1	+2
+3	+3	+3	+2	+3	+3	+3	+3	+2	
	+4	+4	+3	+4	+4	+4	+4		
		+5	+4	+5	+5	+5			
			+5	+6	+6				
			+6	+7					

- v. The common oxidation states are +2 and +3.  
vi. The number of oxidation states increases with increase in the number of unpaired 3d electrons.

**Q.22. Compare the stability of +2 oxidation state for the elements of the first transition series. (NCERT)**

- Ans:** i. In the beginning of 3d transition series, Sc<sup>2+</sup> is virtually not known or in other words it is not stable in comparison to Sc<sup>3+</sup>. Ti<sup>2+</sup>, V<sup>2+</sup>, Cr<sup>2+</sup> are known but less stable in comparison to their most common oxidation state of +3.  
ii. In the middle of the 3d transition series, Mn<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup> are known and quite common. Mn<sup>2+</sup> and Mn<sup>7+</sup> are most stable in Mn. Fe<sup>2+</sup> is less stable in comparison to Fe<sup>3+</sup>, due to fact that Fe<sup>2+</sup> tends to lose one electron to acquire d<sup>5</sup> structure, which has extra stability.  
iii. Co<sup>2+</sup> is less stable as compared to Co<sup>3+</sup>. Ni<sup>2+</sup> is most common and most stable among its +2, +3 and +4 states. Cu<sup>+</sup> is more stable and is most common species as compared to Cu<sup>2+</sup>.  
iv. At the end of the 3d transition series, Zn forms only Zn<sup>2+</sup> which is highly stable as it has 3d<sup>10</sup> configuration.

**Q.23. Write the different oxidation states of manganese. Why +2 oxidation state of manganese is more stable? [Mar 13] OR**

**Explain why Mn<sup>2+</sup> ion is more stable than Mn<sup>3+</sup>? (Given: Mn → Z = 25)**

**[Mar 14]**

**Ans:** Oxidation states of Mn: +2, +3, +4, +5, +6 and +7.

**Electronic configuration of Mn<sup>2+</sup>:** 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>5</sup> 4s<sup>0</sup>

Due to the presence of half filled 'd' orbital, the +2 oxidation state of manganese is more stable.

*[Mar 13: Oxidation states – 1 Mark, Electronic configuration – 1 Mark, Explanation – 1 Mark;*

*Mar 14: Electronic configuration – ½ Mark, Explanation – ½ Mark]*

**Q.24. What is the position of iron (Z = 26) in periodic table? Explain why is Fe<sup>3+</sup> more stable than Fe<sup>2+</sup>?**

**[Oct 15]**

**Ans:** Iron (Fe) is placed in the 4<sup>th</sup> period and group 8 of the modern periodic table. *[Explanation – 1 Mark]*

Electronic configuration of Fe<sup>2+</sup>: 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>6</sup> *[Electronic configuration – ½ Mark]*

Electronic configuration of Fe<sup>3+</sup>: 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>5</sup> *[Electronic configuration – ½ Mark]*

Due to the presence of half filled 'd' orbital, Fe<sup>3+</sup> is more stable than Fe<sup>2+</sup>. *[Explanation – 1 Mark]*

**Q.25. To what extent do the electronic configurations decide the stability of oxidation states in the first series of transition elements? Illustrate with example. (NCERT)**

**Ans:** In a transition series, the oxidation states which lead to noble gas or exactly half-filled or completely filled d-orbitals are more stable.

**eg.** In the first transition series, electronic configuration of Mn (Z = 25) is [Ar] 3d<sup>5</sup> 4s<sup>2</sup>. It shows oxidation states +2 to +7, but Mn (II) is most stable because it has the half-filled configuration [Ar] 3d<sup>5</sup>.

Similarly, Sc<sup>3+</sup> and Zn<sup>2+</sup> are more stable as illustrated below:

Sc = [Ar] 3d<sup>1</sup> 4s<sup>2</sup>, Sc<sup>3+</sup> = [Ar] i.e., noble gas configuration.

Zn = [Ar] 3d<sup>10</sup> 4s<sup>2</sup>, Zn<sup>2+</sup> = [Ar] 3d<sup>10</sup> i.e., completely filled configuration.

**Q.26. Why does scandium show only +2 and +3 oxidation states?**

**Ans:** i. Scandium (Sc) has electronic configuration, Sc: 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>1</sup> 4s<sup>2</sup>

ii. Due to the loss of two electrons from the 4s-orbital, Sc acquires +2 oxidation state.

Sc<sup>2+</sup>: 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>1</sup>





- iii. By the loss of one more electron from the 3d-orbital, it acquires +3 oxidation state.  
 $\text{Sc}^{3+} : 1s^2 2s^2 2p^6 3s^2 3p^6$
- iv. Since  $\text{Sc}^{3+}$  acquires extra stability of inert element [Ar], it does not form higher oxidation state.

**Q.27. #Why is manganese more stable in the +2 state than in the +3 state and the reverse is true for iron?**

OR

**Why  $\text{Mn}^{2+}$  compounds are more stable than  $\text{Fe}^{2+}$  towards oxidation to their +3 state? (NCERT)**

**Ans:** Electronic configuration of  $\text{Mn}^{2+}$  is [Ar]  $3d^5$  which is half filled and hence it is stable. So third ionization enthalpy of manganese is very high i.e., third electron cannot be easily removed. Whereas, in case of  $\text{Fe}^{2+}$ , the electronic configuration is [Ar]  $3d^6$ . Therefore,  $\text{Fe}^{2+}$  can easily lose one electron to form  $\text{Fe}^{3+}$  ( $3d^5$ ) which is more stable as it is half-filled.

Thus, manganese is more stable in the +2 state than in the +3 state and the reverse is true for iron.

**Q.28. Why Zn does not exist in variable oxidation states?**

**Ans:** The oxidation state of an element depends on its electronic configuration. Zn:  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$   
 When Zn loses two electrons from 4s-orbital thus acquiring +2 oxidation state, it gets a very stable electronic configuration wherein all the electrons in d-orbital are paired.  $\text{Zn}^{2+} : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$   
 Since d-orbitals are completely filled with paired electrons, it has a very stable electronic configuration. Therefore, Zn shows only one oxidation state of +2.

**#Q.29. Which element of 3d series of the transition metals exhibits the largest number of oxidation states and why? (NCERT)**

- Ans:** i. The electronic configuration of Mn is: Mn:  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$   
 ii. Manganese has maximum number of unpaired electrons.  
 iii. As the number of unpaired electrons in 3d subshell increases, the number of oxidation state increases.  
 iv. Hence, among transition metals, manganese exhibits the largest number of oxidation states ranging from +2 to +7.

**Notes:** i. Different oxidation states shown by Mn are:  $\text{MnCl}_2$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{MnO}_2$ ,  $\text{MnF}_5$ ,  $\text{K}_2\text{MnO}_4$ ,  $\text{KMnO}_4$   
 ii.  $\text{Mn}^{2+}$  state is very stable due to extra stability of half filled  $3d^5$  subshell.  
 iii.  $\text{Mn}^{7+}$  is a good oxidising agent, since it can be easily reduced to  $\text{Mn}^{4+}$  and  $\text{Mn}^{2+}$ .

**#Q.30. Explain why iron, cobalt and nickel do not show the expected highest oxidation states of +8, +9 and +10 respectively.**

- Ans:** i. The oxidation states of an element depends on its electronic configuration and the number of unpaired electrons.  
 ii. The electronic configuration of Fe, Co and Ni are as follows:

Element	Electronic configuration	Available electrons for excitation
Fe	[Ar] $3d^6 4s^2$	$6 + 2 = 8$
Co	[Ar] $3d^7 4s^2$	$7 + 2 = 9$
Ni	[Ar] $3d^8 4s^2$	$8 + 2 = 10$

- iii. Hence, the expected oxidation states of Fe, Co and Ni shall be +8, +9 and +10 respectively.  
 iv. Fe by the loss of two electrons from 4s subshell forms  $\text{Fe}^{2+}$  and further loss of one more electron from 3d-orbital forms  $\text{Fe}^{3+}$ , which is very stable due to half filled orbital,  $3d^5$ . Hence, there is no further loss of electrons from the 3d subshell and thus Fe does not show +8 oxidation.  
 v. Co forms  $\text{Co}^{2+}$  due to the loss of two electrons from 4s subshell and further loss of one more electron from 3d-orbital forms  $\text{Co}^{3+}$ . In cobalt, +2 and +3 oxidation states are more stable and it does not lose electrons further. Hence, Co does not show +9 oxidation state.  
 vi. Ni forms  $\text{Ni}^{2+}$  by the loss of two electrons from 4s-orbital and by the loss of one more electron from 3d-orbital, it forms  $\text{Ni}^{3+}$ . The amount of energy required for the ionization of Ni to  $\text{Ni}^{2+}$  is less when compared to that required for the ionization of Ni to  $\text{Ni}^{4+}$ . Hence,  $\text{Ni}^{2+}$  oxidation state is comparatively more stable. There is no further loss of electrons and therefore, Ni does not show +10 oxidation state.

**Q.31. Which metal in the first transition series exhibits +1 oxidation state most frequently and why? (NCERT)**

- Ans:** i. Copper metal in the first transition series exhibits +1 oxidation state most frequently.  
 ii. Copper has electronic configuration [Ar]  $3d^{10} 4s^1$ . It can easily lose one ( $4s^1$ ) electron to give stable  $3d^{10}$  configuration. Hence, it exhibits +1 oxidation state most frequently.



### Enrich Your Knowledge

No.	Name of Salt/Compound	Description	Example(s)
i.	Chromous salts	They are salts of chromium in +2 oxidation state.	Chromous chloride ( $\text{CrCl}_2$ ) and chromous sulphate ( $\text{CrSO}_4$ )
ii.	Chromic salts	They are salts of chromium in +3 oxidation state. They are also known as chromium salts.	Chromic chloride ( $\text{CrCl}_3$ )
iii.	Manganous salts	They are salts of manganese in +2 oxidation state. They are also known as manganese salts.	Manganese chloride ( $\text{MnCl}_2$ )
iv.	Ferrous compounds	They are compounds of iron in +2 oxidation state.	Ferrous sulphate ( $\text{FeSO}_4$ )
v.	Ferric compounds	They are compounds of iron in +3 oxidation state.	Ferric chloride ( $\text{FeCl}_3$ )
vi.	Ferrates	They are the compounds of iron in +6 oxidation state.	Potassium ferrate ( $\text{K}_2\text{FeO}_4$ )
vii.	Cuprous salts	They are salts of copper in +1 oxidation state.	Cuprous iodide ( $\text{Cu}_2\text{I}_2$ )
viii.	Cupric salts	They are salts of copper in +2 oxidation state. They are also known as copper salts.	Copper sulphate ( $\text{CuSO}_4$ ), Copper (II) chloride ( $\text{CuCl}_2$ )

**Q.32. Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only? (NCERT)**

**Ans:** Oxygen and fluorine have small size and high electronegativity, so they can easily oxidise the metal to its highest oxidation state.

**Q.33. Name the oxometal anions of the first series of the transition metals in which the metal exhibits the oxidation state equal to its group number. (NCERT)**

**Ans:**  $\text{MnO}_4^-$  (permanganate ion) : Oxidation state of Mn = +7 (Group No = 7)

$\text{CrO}_4^{2-}$  (chromate ion) : Oxidation state of Cr = +6 (Group No = 6)

- Note:**
- +8 oxidation state is shown by both Os and Rh. However, Os in  $\text{OsO}_4$  has the most stable oxidation state.
  - Atoms having high electronegativity such as O or F stabilize higher oxidation states. However, ligands which have the ability to accept electrons from the metal (such as CO) through  $\pi$  bonding stabilize lower oxidation states (zero or +1).
  - $\text{Fe}^{3+}$  has higher oxidizing power than  $\text{Fe}^{2+}$ .



### Check Your Grasp

**Comment on the statement that the “elements of the first transition series possess many properties different from those of heavier transition elements”. (NCERT)**

The given statement is true because:

- Atomic radii of the heavier transition elements (4d and 5d series) are larger than the corresponding elements of the first transition series though those of 4d and 5d series are very close to each other.
- For first transition series, +2 and +3 oxidation states are more common whereas for heavier transition elements, higher oxidation states are more common.
- Melting and boiling points of heavier transition elements are greater than those of the first transition series due to stronger intermetallic bonding (M–M bonding).
- Ionisation enthalpies of 5d series are higher than the corresponding elements of 3d and 4d series.
- The elements of the first transition series form low spin or high spin complexes depending upon the strength of the ligand field. However, the heavier transition elements form low spin complexes irrespective of the strength of the ligand field.



**\*Q.34. Explain the trend in atomic size of first row elements of transition series.**

- Ans:** i. The atomic radii for transition metals are smaller than their corresponding s-block elements.  
 ii. The atomic radii of the elements of a given series decrease with the increase in atomic number but this decrease becomes small after middle of the series.

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic radii (pm)	144	132	122	118	117	117	116	115	117	125

In the first transition series, the atomic radius gradually decreases from scandium to chromium but from chromium to copper, it is nearly the same. Similar behaviour has been observed in the second and third transition series.

- iii. The decrease in atomic radii in each series, in the beginning, is due to an increase in nuclear charge across the period, which tends to pull the ns electrons inward, i.e., it tends to reduce the size.  
 iv. The addition of extra electrons to (n-1) d-orbitals provides the screening effect. As the number of d-electrons increases, the screening effect increases. Thus, there are two operating effects namely screening effect and nuclear charge effect which oppose each other. In the midway onwards of the series, both these effects become nearly equal and thus, there is no change in atomic radii inspite of the fact that atomic number increases gradually.  
 v. The values of atomic radii at the end of each series are slightly higher which is due to electron-electron repulsions among (n-1) d-electrons. These repulsions become predominant at the end of each series and thus resulting in the increase in size.  
 vi. In a vertical row, the atomic radii is expected to increase from top to bottom. Therefore, the atomic radii of transition metals of second series have larger values than those of the first transition series. However, the transition metals of third series except the first member, lanthanum, have nearly the same radii as metals of second transition series above them which is due to the lanthanoid contraction.

**\*Q.35. Explain the trend in ionic size of first row elements of transition series.**

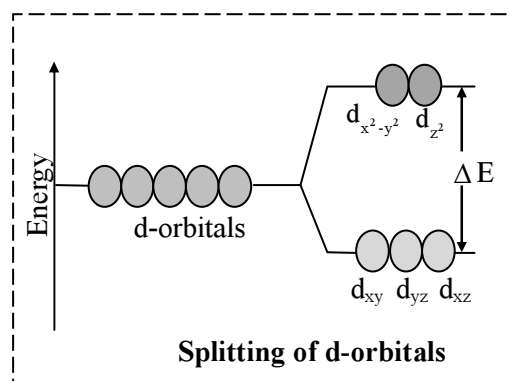
- Ans:** i. As the oxidation state increases, ionic radii decreases due to increase in effective nuclear charge.  
 ii. For a given oxidation state, as the nuclear charge increases, the ionic radii decreases.  
**eg.** With increase in the effective nuclear charge, the ionic radii decreases gradually from  $Ti^{2+}$  to  $Cu^{2+}$ .  
 iii. In a given period, transition elements have small ionic radii than representative elements.

**Note:** The trend in ionic radii is illustrated by the following table.

Element		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Ionic radii in pm	$M^{2+}$	—	90	88	84	80	76	76	72	72	74
	$M^{3+}$	81	76	74	69	66	64	63	—	—	—

**Q.36. Explain the splitting of d-orbitals in transition elements.**

- Ans:** i. In a free transition metal ion, the five (n-1)d orbitals are degenerate. This means that they have same energy.  
 ii. In transition metal compounds, the five (n-1)d orbitals of the transition metal ion split into two groups (**crystal field splitting**):  
 a. Lower energy level containing three orbitals  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$ .  
 b. Higher energy level containing two orbitals  $d_{x^2-y^2}$  and  $d_{z^2}$ .  
 iii. The groups linked to the metal ions cause the splitting of d-orbitals.  
 iv. The difference between the two energy levels ( $\Delta E$ ) is small.



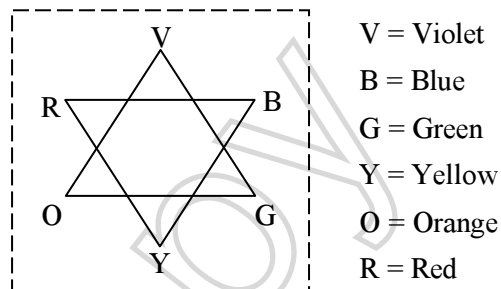
**Q.37. \*Explain, most of the transition metal compounds are remarkably coloured. OR**

**Explain giving reasons: The transition metals generally form coloured compounds. (NCERT)**

- Ans:** i. The colour of a substance is due to the absorption of light of a particular wavelength in visible region.  
 ii. Transition metal compounds contain partially filled (n-1) d-orbitals which become non-degenerate i.e., the energies of five d-orbitals are not same.



- iii. The amount of energy required to excite some of the electrons to the higher energy states within the same d-subshell, is quite small.
  - iv. In case of transition metal ions, the electrons can be easily promoted from one energy level to other within the same d-subshell. This transition is called the d-d transition.
  - v. The energy required for d-d transition falls within visible region. Hence, transition metal compounds are remarkably coloured.
  - vi. The colour observed is different from the colour absorbed. The colour observed is the colour transmitted and is complementary to the colour absorbed. In the following diagram, the complementary colours are placed diagonally opposite.
- eg. Absorption of red colour results in transmission of green colour. Thus, the transition metal compound appears green.



### Q.38. What are the factors responsible for colour of transition metal ions?

Ans: Factors responsible for colour of transition metal ions are as follows:

- i. The presence of incompletely filled d-orbitals in metal ions.
- ii. The presence of unpaired electrons in d-orbitals.
- iii. d-d transitions of electrons due to absorption of radiation in the visible region.
- iv. Nature of groups (anions or ligands) linked to the metal ion in the compound or a complex.
- v. Type of hybridisation in metal ion in the complex.
- vi. Geometry of the complex containing transition metal ion.

Note: Colour of 3d transition metal ions:

Ion	Outer electronic configuration	Number of unpaired electrons	Colour
Sc <sup>3+</sup>	3d <sup>0</sup>	0	Colourless
Ti <sup>3+</sup>	3d <sup>1</sup>	1	Purple
Ti <sup>4+</sup>	3d <sup>0</sup>	0	Colourless
V <sup>3+</sup>	3d <sup>2</sup>	2	Green
Cr <sup>3+</sup>	3d <sup>3</sup>	3	Violet
Mn <sup>2+</sup>	3d <sup>5</sup>	5	Light Pink
Mn <sup>3+</sup>	3d <sup>4</sup>	4	Violet

Ion	Outer electronic configuration	Number of unpaired electrons	Colour
Fe <sup>2+</sup>	3d <sup>6</sup>	4	Pale green
Fe <sup>3+</sup>	3d <sup>5</sup>	5	Yellow
Co <sup>2+</sup>	3d <sup>7</sup>	3	Pink
Ni <sup>2+</sup>	3d <sup>8</sup>	2	Green
Cu <sup>2+</sup>	3d <sup>9</sup>	1	Blue
Cu <sup>+</sup>	3d <sup>10</sup>	0	Colourless
Zn <sup>2+</sup>	3d <sup>10</sup>	0	Colourless

### Q.39. Why are some of the transition metal ions colourless?

- Ans: i. Transition metal ions exhibit colour due to the presence of unpaired electrons in (n-1)d-orbitals which undergo d-d transition.
- ii. The metal ions which do not have unpaired electrons i.e., (n-1)d<sup>0</sup> or which have completely filled d-orbitals i.e., (n-1)d<sup>10</sup> do not absorb radiations in visible region, since d-d transitions are not possible. Hence, they are colourless ions.
- eg. Cu<sup>+</sup> (3d<sup>10</sup>), Ag<sup>+</sup> (4d<sup>10</sup>), Zn<sup>2+</sup> (3d<sup>10</sup>), Cd<sup>2+</sup> (4d<sup>10</sup>), Hg<sup>2+</sup> (5d<sup>10</sup>), etc.

### Q.40. Predict which of the following will be coloured in aqueous solution?

Ti<sup>3+</sup>, V<sup>3+</sup>, Cu<sup>+</sup>, Sc<sup>3+</sup>, Mn<sup>2+</sup>, Fe<sup>3+</sup> and Co<sup>2+</sup>. Give reasons for each. (NCERT)

- Ans: i. Transition metal ions exhibit colour due to the presence of unpaired electrons in (n-1)d-orbitals which undergo d-d transition.
- ii. The metal ions which do not have unpaired electrons i.e., (n-1)d<sup>0</sup> or which have completely filled d-orbitals i.e., (n-1)d<sup>10</sup> do not absorb radiations in visible region, since d-d transitions are not possible. Hence, they are colourless ions.
- iii. Ti<sup>3+</sup>, V<sup>3+</sup>, Mn<sup>2+</sup>, Fe<sup>3+</sup> and Co<sup>2+</sup> contain 1, 2, 5, 5 and 3 unpaired electrons respectively in their (n-1) d-orbital. Hence, they are coloured in aqueous solution.
- iv. Cu<sup>+</sup> and Sc<sup>3+</sup> do not contain unpaired electrons. Hence, they are colourless.



**#Q.41. Why salts of  $\text{Sc}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{V}^{5+}$  are colourless?**

- Ans:** i. Electronic configurations of  $\text{Sc}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{V}^{5+}$  are:  $\text{Sc}^{3+}$ :  $[\text{Ar}] 3d^0$ ;  $\text{Ti}^{4+}$ :  $[\text{Ar}] 3d^0$ ;  $\text{V}^{5+}$ :  $[\text{Ar}] 3d^0$   
ii. The ions  $\text{Sc}^{3+}$ ,  $\text{Ti}^{4+}$  and  $\text{V}^{5+}$  have completely empty d-orbitals i.e., no unpaired electrons are present. Thus, their salts are colourless, as d-d transitions are not possible.

**\*Q.42. Explain why the compounds of copper (II) are coloured, but those of zinc are colourless.**

- Ans:** i. The electronic configuration of Cu:  $[\text{Ar}] 3d^{10} 4s^1$  and  $\text{Cu}^{2+}$ :  $[\text{Ar}] 3d^9$ .  
In copper (II) compounds,  $\text{Cu}^{2+}$  ions have incompletely filled 3d-orbital ( $3d^9$ ).  
ii. The presence of one unpaired electron in 3d-orbital results in d-d transition due to which,  $\text{Cu}^{2+}$  ions absorb red light from visible spectrum and emit blue light. Therefore, copper (II) compounds are coloured.  
iii. In case of zinc, the electronic configuration is Zn:  $[\text{Ar}] 3d^{10} 4s^2$  and  $\text{Zn}^{2+}$ :  $[\text{Ar}] 3d^{10}$ .  
iv. Since 3d subshell is completely filled and there are no unpaired electrons, d-d transition is not possible and hence,  $\text{Zn}^{2+}$  ions do not absorb radiation in visible region. Therefore, the compounds of zinc are colourless.

**Q.43. Explain why the solution containing hydrated  $\text{Ti}^{3+}$  ion is purple in colour.**

- Ans:** i. In  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ,  $\text{Ti}^{3+}$  has  $3d^1$  configuration.  
ii. This one electron will occupy one of the orbitals of lower energy and the complex (ion) will absorb suitable wavelength of white light and promote the electron from lower energy level to higher energy level.  
iii. Since the complex absorbs light around 500 nm region, yellow and green lights are absorbed to excite the electron and the transmitted light is of the complementary colour i.e., red blue (purple).  
iv. Hence, the solution containing hydrated  $\text{Ti}^{3+}$  ion is purple in colour.

**Q.44. Why is  $\text{Sc}^{3+}$  colourless while  $\text{Ti}^{3+}$  coloured? (Atomic number Sc = 21, Ti = 22)**

[Mar 16]

- Ans:** i. Electronic configuration of:  
 $\text{Sc}^{3+}$ :  $[\text{Ar}] 3d^0$ ;  $\text{Ti}^{3+}$ :  $[\text{Ar}] 3d^1$  *[Electronic configuration – ½ Mark each]*  
ii.  $\text{Sc}^{3+}$  ion has completely empty 3d-orbital, i.e., no unpaired electrons are present. As d-d transitions are not possible,  $\text{Sc}^{3+}$  ion is colourless.  
 $\text{Ti}^{3+}$  ion has one unpaired electron in 3d-orbital. As d-d transitions are possible,  $\text{Ti}^{3+}$  ion is coloured.  
*[Explanation – 1 Mark]*

**Q.45. Explain why copper sulphate is blue in colour when dissolved in water but turns yellow when treated with concentrated HCl.**

- Ans:** i. The electronic configuration of Cu:  $[\text{Ar}] 3d^{10} 4s^1$  and  $\text{Cu}^{2+}$ :  $[\text{Ar}] 3d^9$ .  
ii. In the aqueous solution of copper sulphate,  $\text{Cu}^{2+}$  forms blue hydrated complex  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  because it has one unpaired electron in 3d subshell. The complex has octahedral geometry.  
iii. When  $\text{CuSO}_4$  solution is treated with concentrated HCl solution, it forms a new complex  $[\text{CuCl}_4]^{2-}$ .  
$$[\text{Cu}(\text{H}_2\text{O})_6]^{2+} + 4\text{Cl}^- \longrightarrow [\text{CuCl}_4]^{2-} + 6\text{H}_2\text{O}$$
  
iv. The complex  $[\text{CuCl}_4]^{2-}$  has a tetrahedral geometry. Due to the change in geometry and hybridisation of the complex, the colour of the solution changes from blue to yellow.

**Q.46. Explain the colour of  $\text{MnO}_4^-$  ion.**

- Ans:** i.  $\text{MnO}_4^-$  ion is intense purple coloured in solution.  
ii. The colour is due to charge transfer. An electron is temporarily transferred from  $\text{O}^{2-}$  to  $\text{Mn}^{7+}$  in  $\text{MnO}_4^-$ .  
iii. Due to this, there is a temporary change in the oxidation state of oxygen from -2 to -1 and manganese from +7 to +6.  
iv. Charge transfer is possible when the energy levels on the two different atoms involved are appreciably close.

**Note:**  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{CrO}_4^{2-}$ ,  $\text{MnO}_4^-$ ,  $\text{Cu}_2\text{O}$  and Ni-DMG complex are coloured due to charge transfer transitions.

**Q.47. Explain catalytic activity of transition metals. OR**

**Explain giving reasons: Transition metals and their many compounds act as good catalyst. (NCERT)**

- Ans:** i. Many transition metals and complexes are used as catalysts which influence the rate of chemical reaction. The rate of a chemical reaction increases by the decrease in activation energy of the reactants. This decrease is caused by the catalyst which probably alter the path of the reaction.



- ii. Bonds are formed between reactant molecules and atoms on the surface of the catalyst (first row transition metals utilise 3d and 4s-electrons for bonding). This results in the formation of reaction intermediates which provides path of lower activation energy and therefore, increase the rate of the reaction.



- iii. These reaction intermediates decompose to form the product(s) and regenerate the original catalyst.  
iv. Many transition metals are used as catalysts for reactions. Fe, Co, Pt, Cr, Mn, etc., are the commonly used transition metal catalysts.

**Note:** Following table lists some reactions catalyzed by transition metals / transition metal compounds.

Catalyst	Reaction catalyzed
MnO <sub>2</sub>	Decomposition of KClO <sub>3</sub> to O <sub>2</sub>
Nickel	Hydrogenation of oils to fats
V <sub>2</sub> O <sub>5</sub>	Contact process for H <sub>2</sub> SO <sub>4</sub> manufacture
Fe (III)	Reaction between iodide and persulphate ions. $2 \text{I}^- + \text{S}_2\text{O}_8^{2-} \longrightarrow \text{I}_2 + 2 \text{SO}_4^{2-}$
Titanium chloride (Ziegler Natta catalyst)	Manufacture of high density polyethene $n \text{CH}_2 = \text{CH}_2 \longrightarrow \text{+CH}_2 - \text{CH}_2\text{+}_n$
Fe and Mo	Manufacture of ammonia
Co-Th alloy	Fischer Tropsch process for the synthesis of gasoline

**Q.48. Explain catalytic property of 3d series elements.**

- Ans:** i. Transition metals possess variable oxidation states. Hence, they can absorb and re-emit a wide range of energies. Thus, they can provide necessary activation energy.  
ii. Mechanism of  $2\text{I}^- + \text{S}_2\text{O}_8^{2-} \xrightarrow{\text{Fe}^{3+}} \text{I}_2 + 2\text{SO}_4^{2-}$  is as shown below.  
a.  $2\text{Fe}^{3+} + 2\text{I}^- \longrightarrow 2\text{Fe}^{2+} + \text{I}_2$       b.  $2\text{Fe}^{2+} + \text{S}_2\text{O}_8^{2-} \longrightarrow 2\text{Fe}^{3+} + 2\text{SO}_4^{2-}$   
iii. Transition metals possess free valencies on the surface. Hence, they can adsorb the reacting molecules. Thus, the concentration of the reactants increases on the surface. This increases the rate of reaction.

**Q.49. Transition metals and many of their compounds show paramagnetic behaviour. Explain. (NCERT)**

- Ans:** i. Paramagnetism is a property due to the presence of unpaired electrons.  
ii. In case of transition metals, as they contain unpaired electrons in the (n-1)d orbitals, most of the transition metal ions and their compounds are paramagnetic in nature.  
iii. The paramagnetic character increases with increase in the number of unpaired electrons.

**Q.50. Explain magnetic moment for transition elements and give formula for its calculation.**

- Ans:** i. The magnetic moment of an electron is partly due to its orbital motion and partly due to its spin motion.  
ii. In the compounds containing transition metal ions, the electrostatic field of other atoms, ions or molecules (which surround the metal ion) suppresses the orbital contribution to the magnetic moment. Thus, it is the spin of the electrons, that contributes towards the effective magnetic moment ( $\mu_{\text{eff}}$ ).  
iii. The expression for the effective magnetic moment ( $\mu_{\text{eff}}$ ) is,  
iv. Magnetic moment of a substance varies with the number of unpaired electrons present.

$$\mu_{\text{eff}} = \sqrt{n(n+2)} \text{ B.M.}$$

where, n is number of unpaired electrons. B.M. stand for Bohr magneton (unit of magnetic moment)

A paramagnetic substance is characterized by its effective magnetic moment ( $\mu_{\text{eff}}$ ).

$$1 \text{ B.M.} = \frac{eh}{4\pi mc}$$

where, 'h' represents Planck's constant, 'e' represents charge on electron, 'm' represents mass of an electron and 'c' represents the velocity of light.



**Q.51. The d-electronic configuration of  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  is  $d^7$  and  $d^9$  respectively. Which one of these ions will be more paramagnetic?**

**Ans:**  $\text{Co}^{2+}$ , (electronic configuration:  $3d^7$ ) contains three unpaired electrons while  $\text{Cu}^{2+}$ , (electronic configuration:  $3d^9$ ) contains only one unpaired electron. Greater the number of unpaired electrons present, more paramagnetic is the substance. So,  $\text{Co}^{2+}$  is more paramagnetic than  $\text{Cu}^{2+}$ .

**Q.52. Why does Mn(II) ion show maximum paramagnetic character amongst bivalent ions of the elements of 3d transition series?**

**Ans:** The electronic configuration of Mn(II) ion (atomic number of Mn = 25) is  $[\text{Ar}] 3d^5 4s^0$ .

It has five unpaired electrons in its d-orbitals which is a maximum value among the bivalent ions of the elements of 3d transition series. As the paramagnetic character increases with increase in the number of unpaired electrons, Mn(II) ion shows maximum paramagnetic character.

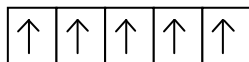
**#Q.53. Why are zinc metal and  $\text{Zn}^{++}$  ions diamagnetic?**

**Ans:** The atomic number of zinc is 30. The electronic configuration of Zn is  $[\text{Ar}] 3d^{10} 4s^2$  and  $\text{Zn}^{++}$  is  $[\text{Ar}] 3d^{10}$ . In zinc metal and  $\text{Zn}^{++}$  ions, all electrons are paired and hence, they are diamagnetic.

**Q.54. Calculate the magnetic moment of  $\text{Fe}^{3+}$  ion (atomic number of Fe = 26).**

**Ans:** Electronic configuration of  $\text{Fe}^{3+}$  ion is  $[\text{Ar}] 3d^5 4s^0$ .

So, d-orbital has following distribution of electrons,



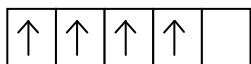
It has 5 unpaired electrons.

$$\therefore \text{Magnetic moment, } \mu = \sqrt{n(n+2)} = \sqrt{5(5+2)} = 5.9 \text{ B.M.}$$

**Q.55. Calculate the magnetic moment of divalent ion in aqueous solution if its atomic number is 24.**

**Ans:** The electronic configuration of the divalent ion (atomic number = 24) is  $[\text{Ar}] 3d^4$ .

So, d-orbital has following distribution of electrons.



It has 4 unpaired electrons.

$$\therefore \text{Magnetic moment, } \mu = \sqrt{n(n+2)} = \sqrt{4(4+2)} = 4.89 \text{ B.M.}$$

**#Q.56. Calculate the 'Spin only' magnetic moment of  $\text{M}^{2+}_{(\text{aq})}$  ion ( $Z = 26$ ).**

**Ans:** Atomic number = 26

Electronic configuration of M atom =  $[\text{Ar}] 3d^6 4s^2$ .

Electronic configuration of  $\text{M}^{2+}$  =  $[\text{Ar}] 3d^6$

So, d-orbital has following distribution of electrons.



There are 4 unpaired electrons.

$$\therefore \text{Spin only magnetic moment } (\mu) = \sqrt{n(n+2)} \text{ B.M.} = \sqrt{4(4+2)} \text{ B.M.} = 4.89 \text{ B.M.}$$

**Q.57. Calculate the 'Spin only' magnetic moment of  $\text{M}^{2+}_{(\text{aq})}$  ion ( $Z = 27$ ).**

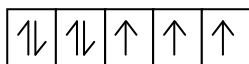
(NCERT)

**Ans:** Atomic number = 27

Electronic configuration of M atom =  $[\text{Ar}] 3d^7 4s^2$ .

Electronic configuration of  $\text{M}^{2+}$  =  $[\text{Ar}] 3d^7$

So, d-orbital has following distribution of electrons.



There are 3 unpaired electrons.

$$\therefore \text{Spin only magnetic moment } (\mu) = \sqrt{n(n+2)} \text{ B.M.} = \sqrt{3(3+2)} \text{ B.M.} = 3.87 \text{ B.M.}$$



**Q.58. What are interstitial compounds? Why are such compounds well known for transition metals?**

(NCERT)

- Ans:**
- Interstitial compounds* are those which are formed when small atoms like H, C, N, B, etc., are trapped inside the crystal lattice of metals.
  - Interstitial compounds have variable composition and are non-stoichiometric in nature.  
eg. TiC, TiH<sub>1.73</sub>, Mn<sub>4</sub>N, Fe<sub>3</sub>H, VH<sub>0.56</sub>, ZrH<sub>1.92</sub>, etc.
  - The chemical properties of interstitial compounds are similar to those of the parent transition metal.
  - Interstitial compounds are well known for transition metals because defects are present in the crystal lattice of transition metals. Due to this, vacant spaces (interstices) are present in the lattice of transition metals which can be easily occupied by small atoms such as H, C, N and B.

**Q.59. State the characteristics of interstitial compounds.**

**Ans: Characteristics of interstitial compounds:**

- The chemical properties of interstitial compounds are similar to those of the parent transition metal.
- They are hard and lustrous.
- They exhibit electrical and thermal conductivity.
- They have melting points higher than pure metals, due to stronger metal–non-metal bonds as compared to metal–metal bonds in pure metals.
- They have lower densities, when compared to parent metals.
- Transition metal hydrides are used as powerful reducing agents.
- Transition metallic carbides are chemically inert and extremely hard like diamond.

**Q.60. Explain alloy formation in case of transition elements.**

- Ans:**
- Alloys are formed by metals whose atomic radii differ by not more than 15% so that the atoms of one metal can easily take up the positions in crystal lattice of the other.
  - The transition metals have similar atomic radii and other characteristics, hence they form alloys very readily.
  - Alloys are generally solid solution which are formed by the cooling of the molten state solution of two or more transition metals.
  - Alloys are generally harder, have high melting points and more resistant to corrosion than the individual metals.
  - The metals chromium, vanadium, molybdenum, tungsten and manganese are used in the formation of alloy steels and stainless steels. Ferrous alloys are the most common alloys.
  - Some alloys of transition metals with non-transition metals are also very common.  
eg. Brass (Cu + Zn) and Bronze (Cu + Sn)

**\*Q.61. Why transition elements show tendency to form large number of complexes?**

- Ans:**
- All the transition metals have a tendency to form complexes. The tendency arises due to the following reasons:
    - They have small ionic radii.
    - They have high effective ionic charge.
    - Hence, they have high ratio of ionic charge to ionic radius.
    - Transition metals and ions have vacant d-orbitals which can accommodate the lone pairs of electrons from the ligands to form coordination compounds.
    - Transition metals show variable oxidation states.
    - After accepting the electrons from the ligands, metal ions acquire a stable electronic configuration of the nearest inert element and form stable complexes.  
eg. [Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>, [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>, [Ni(CN)<sub>4</sub>]<sup>2-</sup>, etc.
  - The stability of these complexes depends upon the nature of the metal ion, ligands and their bonding.

**\*Q.62. Explain, why Pt(IV) complexes are generally octahedral while Pt(II) complexes are square planar.**

- Ans:**
- In case of Pt(II) complexes, the central metal atom has d<sup>8</sup> configuration and it shows coordination number 4.
  - According to valence bond theory, central ion undergoes dsp<sup>2</sup> hybridisation which results in formation of square planar complexes.





- iii. In the Pt (IV) complexes, the central metal atom has  $d^6$  configuration and it shows coordination number 6.
- iv. According to valence bond theory, central ion undergoes  $d^2sp^3$  or  $sp^3d^2$  hybridisation which results in the formation of octahedral complexes.

#### 8.4 Preparation and properties of $K_2Cr_2O_7$ and $KMnO_4$

**Q.63. \*How is potassium dichromate prepared from chrome iron? OR**

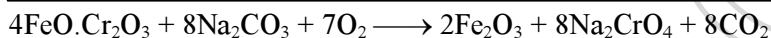
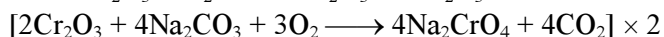
**Indicate the steps involved in the preparation of  $K_2Cr_2O_7$  from chromite ore ( $FeO.Cr_2O_3$ ). (NCERT)**

**Ans: Preparation of  $K_2Cr_2O_7$  from chromite ore/chrome iron ( $FeO.Cr_2O_3$ ):**

$K_2Cr_2O_7$  is prepared from chromite ore ( $FeO.Cr_2O_3$ ) which is also known as chrome iron ore. The following steps are involved:

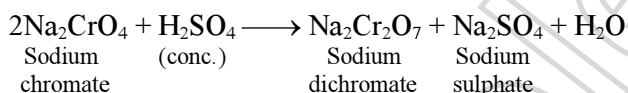
**Step I: Concentration of ore:** In a hydraulic classifier, powdered chromite ore is washed with water current. This process separates lighter gangue from the heavier chromite ore. The lighter gangue is washed away with water current. The heavier chromite ore is settled at the bottom.

**Step II: Conversion of chromite ore into sodium chromate (Roasting):** The chromite ore is converted to sodium chromate by roasting concentrated ore with soda ash (sodium carbonate) and lime stone (calcium carbonate) in reverberatory furnace, in presence of excess air. Water soluble sodium chromate (yellow coloured) is separated from water insoluble substances by extraction with water, followed by filtration.



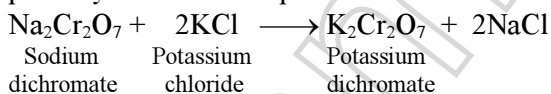
Addition of limestone makes the mass porous and aids easier oxidation.

**Step III: Conversion of sodium chromate into sodium dichromate:** The filtrate containing sodium chromate solution is treated with concentrated sulphuric acid. This converts sodium chromate into sodium dichromate.



On concentration, sodium sulphate being less soluble crystallizes out as decahydrate,  $Na_2SO_4.10H_2O$  and is separated by filtration. The filtrate obtained is concentrated solution of sodium dichromate.

**Step IV: Conversion of sodium dichromate into potassium dichromate:** Sodium dichromate is converted to potassium dichromate by treatment with calculated quantity of potassium chloride. This takes place by double decomposition.



The resulting solution is concentrated and then the hot solution is cooled. Orange red crystals of potassium dichromate are obtained by crystallisation. These crystals are further purified by recrystallisation. Sodium chloride (being more soluble than potassium dichromate) remains in the solution.

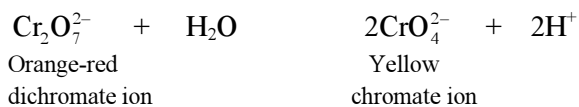
**Q.64. State physical properties of  $K_2Cr_2O_7$ .**

**Ans:**  $K_2Cr_2O_7$  is a orange coloured crystalline solid, soluble in water (readily soluble in hot water) and melts at 669 K.

**Q.65. Explain the action of alkali and acid on  $K_2Cr_2O_7$ .**

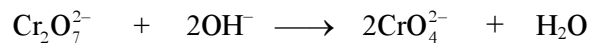
**Ans: Action of alkali and acid on  $K_2Cr_2O_7$ :**

- i. In neutral solution, water soluble orange red coloured potassium dichromate is in equilibrium with yellow coloured potassium chromate. In acid medium, chromate ion changes to dichromate ion and in basic medium, dichromate ion changes to chromate ion.



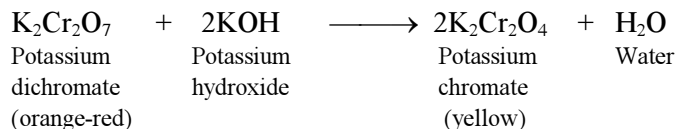


- ii. Addition of alkali shifts the equilibrium to right as  $\text{OH}^-$  combines with  $\text{H}^+$  to form water. Thus, chromate ions are formed which turn the solution yellow.



Orange-red dichromate ion	+ 2OH <sup>-</sup>	→	2CrO <sub>4</sub> <sup>2-</sup>	+ H <sub>2</sub> O
			Yellow chromate ion	

- iii. On addition of an acid, the  $\text{H}^+$  ion concentration increases and thereby the equilibrium shifts to the left, thus resulting in the formation of dichromate ions, which turn the solution orange-red.
- iv. On addition of potassium hydroxide solution to the orange red coloured solution of potassium dichromate, yellow coloured solution of potassium chromate is obtained.

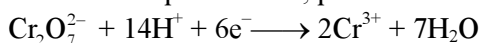


- v. On addition of hydrochloric acid to the yellow coloured solution of potassium chromate, orange-red coloured solution of potassium dichromate is obtained.



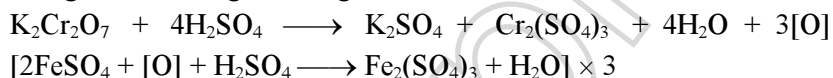
### Do You Know?

In acidic medium, Cr(VI) of potassium dichromate gains 3 electrons and is reduced to Cr(III) of chromium sulphate. Thus, potassium dichromate is a good oxidizing agent.

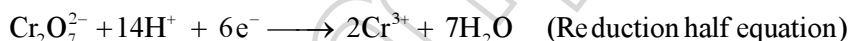


### Q.66. Explain the action of acidified potassium dichromate on ferrous sulphate.

**Ans: Action of acidified potassium dichromate on ferrous sulphate:** Ferrous sulphate is oxidized to ferric sulphate by acidified potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$  in presence of  $\text{dil.H}_2\text{SO}_4$ ). Colour of the solution changes from orange red to green.

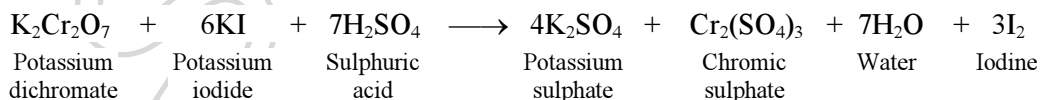


Ionic equations in which only active ions are written are given below:



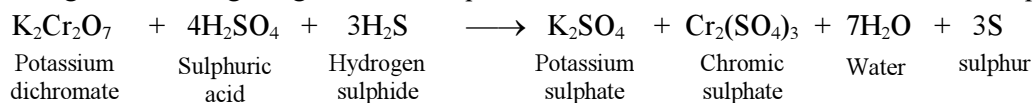
### Q.67. Explain the action of acidified potassium dichromate on potassium iodide.

**Ans: Action of acidified potassium dichromate on potassium iodide:** Potassium iodide is oxidized to iodine by acidified potassium dichromate. Colour of the solution changes to brown due to the liberated iodine.



### Q.68. Explain the action of acidified potassium dichromate on hydrogen sulphide.

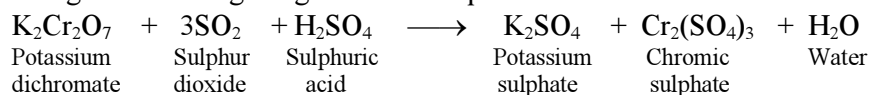
**Ans: Action of acidified potassium dichromate on hydrogen sulphide:** Hydrogen sulphide gas is oxidized to pale yellow precipitate of sulphur, when passed through acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution. Solution colour changes from orange to green because potassium dichromate is reduced to chromium sulphate.





**Q.69. Explain the action of acidified potassium dichromate on sulphur dioxide.**

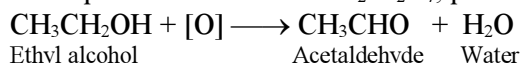
**Ans: Action of acidified potassium dichromate on sulphur dioxide:** Sulphur dioxide gas is oxidized to sulphuric acid when passed through acidified potassium dichromate solution. The colour of the solution changes from orange to green because potassium dichromate is reduced to chromic sulphate.



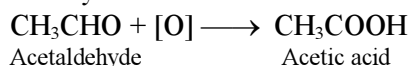
**Q.70. Explain the action of acidified potassium dichromate on alcohols.**

**Ans: Action of acidified potassium dichromate on alcohols:**

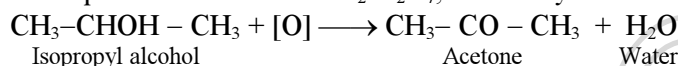
i. In the presence of acidified  $\text{K}_2\text{Cr}_2\text{O}_7$ , primary alcohols are oxidized to the corresponding aldehydes.



Aldehydes are further oxidized to the corresponding carboxylic acids.



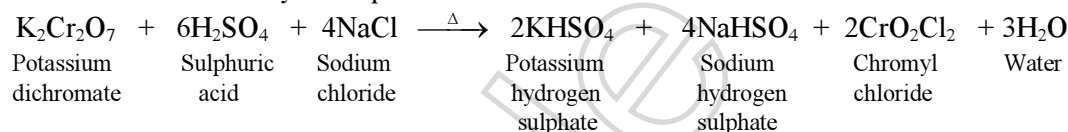
ii. In the presence of acidified  $\text{K}_2\text{Cr}_2\text{O}_7$ , secondary alcohols are oxidized to the corresponding ketones.



**Q.71. Explain formation of chromyl chloride ( $\text{CrO}_2\text{Cl}_2$ ) from potassium dichromate.**

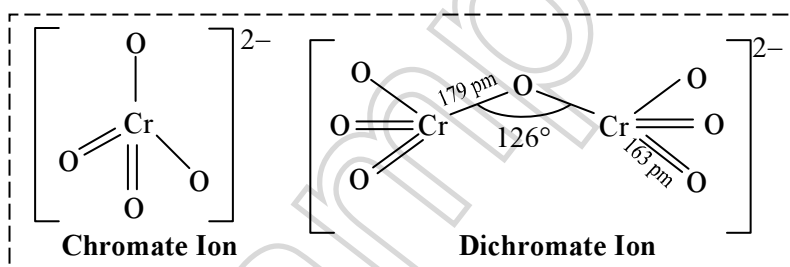
**Ans: Formation of chromyl chloride ( $\text{CrO}_2\text{Cl}_2$ ) from potassium dichromate:**

Chromyl chloride is obtained by heating a mixture of potassium dichromate crystals and sodium chloride in presence of concentrated sulphuric acid. First red vapours of chromyl chloride are evolved, which on condensation forms oily red liquid.



**Q.72. Describe structure of chromate ion and dichromate ion.**

**Ans: Structure of chromate and dichromate ions:**



- Chromate ion has tetrahedral structure.
- Dichromate ion has two tetrahedral units sharing one corner. The  $\text{Cr-O-Cr}$  bond angle is  $126^\circ$ .

**Q.73. State the uses of potassium dichromate.**

**Ans: Uses of  $\text{K}_2\text{Cr}_2\text{O}_7$ :**  $\text{K}_2\text{Cr}_2\text{O}_7$  is used

- in volumetric analysis, as a primary standard for the estimation of  $\text{Fe}^{2+}$  (ferrous ions) and  $\text{I}^-$  (iodides) in redox titrations.
- in the manufacture of chromium compounds such as lead chromate and chrome alum.
- in calico printing and dyeing.
- in the tanning of leather.
- as a powerful oxidising agent.
- in the chromyl chloride test for the detection of chloride ion.
- in the manufacture of pigments and inks.
- by dissolving in concentrated sulphuric acid resulting in the formation of chromic acid which is used as degrease glassware.

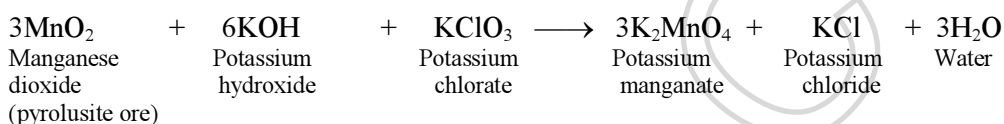
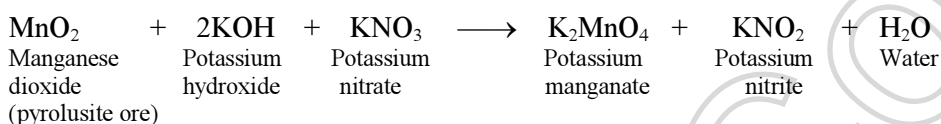
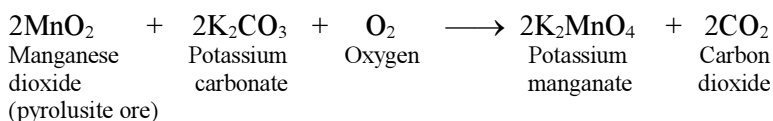
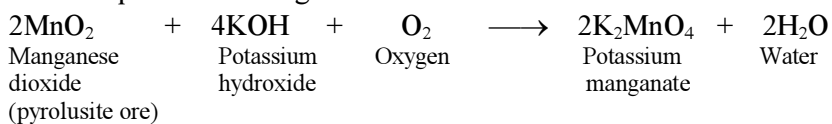


**Q.74. Indicate the steps involved in the preparation of  $\text{KMnO}_4$  from pyrolusite ore ( $\text{MnO}_2$ ). (NCERT) OR Describe the preparation of potassium permanganate. (NCERT)**

**Ans: Preparation of  $\text{KMnO}_4$  from pyrolusite ore ( $\text{MnO}_2$ ):**

**Step I: Conversion of pyrolusite ore ( $\text{MnO}_2$ ) into potassium manganate.**

The finely powdered pyrolusite mineral ( $\text{MnO}_2$ ) is fused with potassium hydroxide or potassium carbonate in the presence of air or oxidising agent such as potassium nitrate or potassium chlorate giving green coloured potassium manganate.



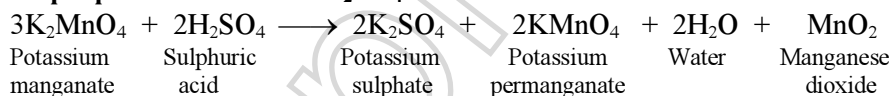
The reaction mixture containing  $\text{K}_2\text{MnO}_4$  (potassium manganate) is treated with water and then converted into  $\text{KMnO}_4$  (potassium permanganate) either by oxidation or by electrolysis.

**Step II: Oxidation of potassium manganate ( $\text{K}_2\text{MnO}_4$ ) to potassium permanganate ( $\text{KMnO}_4$ ).**

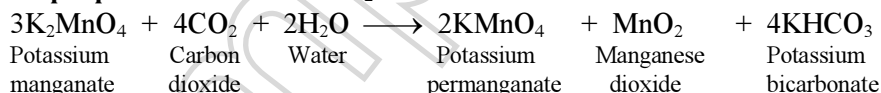
There are two methods for oxidation of potassium manganate.

i. **Chemical oxidation:** This can be achieved by any one of the following:

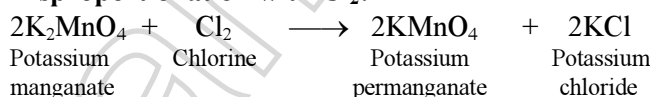
a. **Disproportionation with  $\text{H}_2\text{SO}_4$ :**



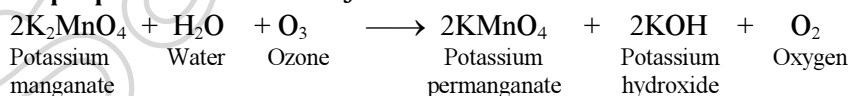
b. **Disproportionation with  $\text{CO}_2$ :**



c. **Disproportionation with  $\text{Cl}_2$ :**

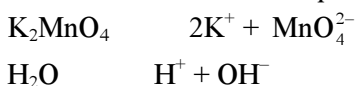


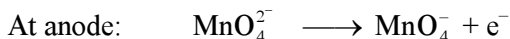
d. **Disproportionation with  $\text{O}_3$ :**



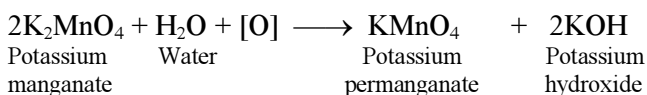
**Note:** The carbon dioxide process is uneconomical as one third of the original manganate is reconverted to manganese dioxide. However, this process has the advantage that the potassium carbonate formed as a byproduct can be used for the oxidative fusion of manganese dioxide. In the chlorine process, potassium chloride obtained as a byproduct is lost.

ii. **Electrolytic oxidation:** For manufacturing potassium permanganate commercially, the method of electrolytic oxidation is preferred. The alkaline manganate solution obtained in step (I) is electrolysed between iron electrodes separated by diaphragm. The reactions taking place are as follows:





Thus, manganate ions are oxidized to permanganate at the anode and hydrogen gas is liberated at the cathode.



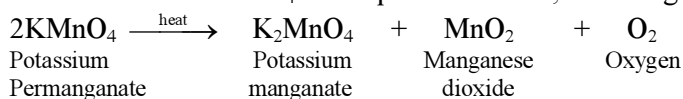
After the oxidation is complete, the solution is filtered and evaporated under controlled conditions to obtain the deep purple black crystals of potassium permanganate.

**Q.75. State physical properties of  $\text{KMnO}_4$ .**

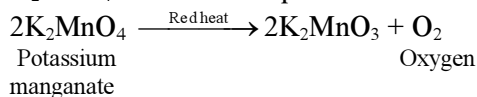
**Ans:**  $\text{KMnO}_4$  is a deep purple crystalline solid, having moderate solubility in water (6.4 g/100 g water) at room temperature and it is more soluble in hot water.

**Q.76. Explain the action of heat on  $\text{KMnO}_4$ .**

**Ans: Action of heat:**  $\text{KMnO}_4$  decomposes at 473 K, liberating oxygen.

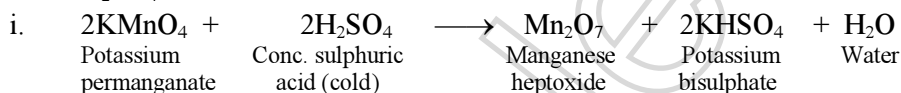


$\text{K}_2\text{MnO}_4$  further decomposes when red hot.

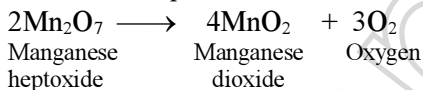


**Q.77. Explain action of cold conc.  $\text{H}_2\text{SO}_4$  on  $\text{KMnO}_4$ .**

**Ans: Action of cold conc.  $\text{H}_2\text{SO}_4$ :**  $\text{KMnO}_4$  is converted to  $\text{Mn}_2\text{O}_7$  (an explosive oil) upon reaction with cold conc.  $\text{H}_2\text{SO}_4$ .

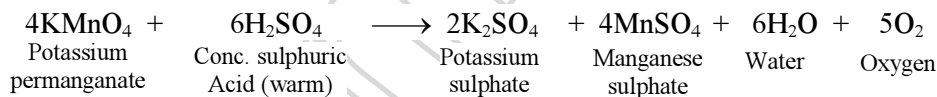


ii.  $\text{Mn}_2\text{O}_7$  decomposes to  $\text{MnO}_2$  on warming.



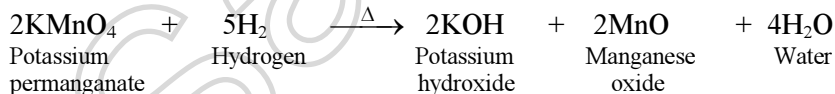
**Q.78. Explain action of warm conc. sulphuric acid on  $\text{KMnO}_4$ .**

**Ans:** Action of warm conc.  $\text{H}_2\text{SO}_4$  on  $\text{KMnO}_4$  results in conversion to  $\text{MnSO}_4$  with the evolution of  $\text{O}_2$  gas.



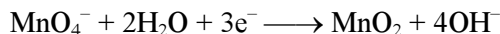
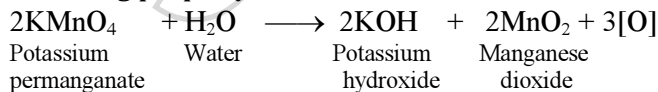
**Q.79. Explain action of  $\text{H}_2$  on  $\text{KMnO}_4$ .**

**Ans: Action of  $\text{H}_2$ :** Heating solid  $\text{KMnO}_4$  in a current of  $\text{H}_2$  results in formation of  $\text{MnO}$ ,  $\text{KOH}$  and water vapours.

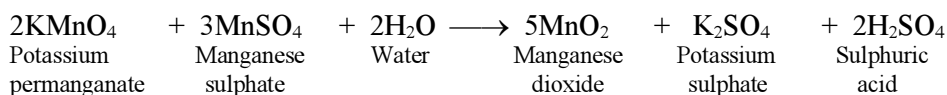


**Q.80. Explain oxidizing property of  $\text{KMnO}_4$  in neutral medium.**

**Ans: Oxidizing property in neutral medium:**



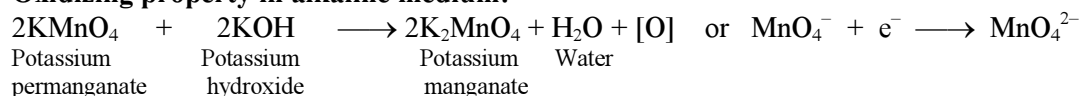
Manganous salt is oxidised to insoluble  $\text{MnO}_2$ .



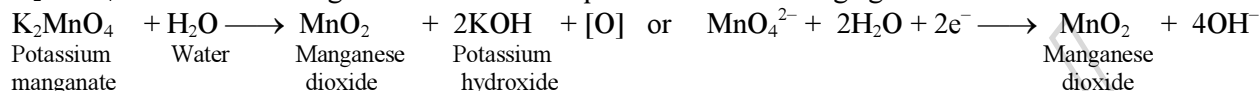


**Q.81. Explain oxidizing property of  $\text{KMnO}_4$  in alkaline medium.**

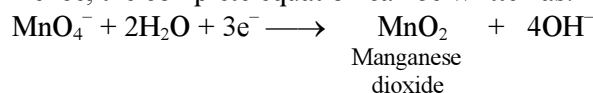
**Ans: Oxidizing property in alkaline medium:**



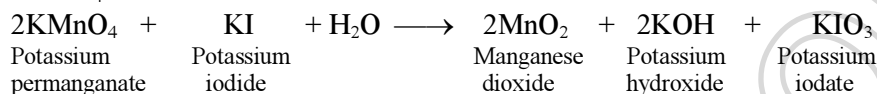
$\text{K}_2\text{MnO}_4$  is reduced to manganese dioxide in the presence of a reducing agent.



Hence, the complete equation can be written as:



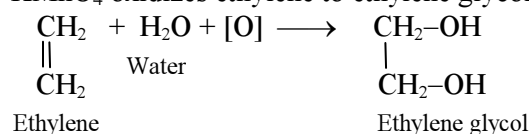
eg.  $\text{KMnO}_4$  oxidizes iodides to iodates.



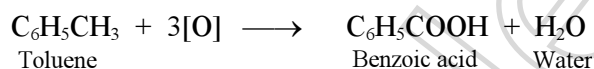
**Q.82. How does  $\text{KMnO}_4$  react with the following in alkaline medium:**

i. Ethylene ii. Toluene iii. Nitrotoluene?

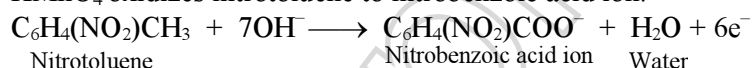
**Ans: i.**  $\text{KMnO}_4$  oxidizes ethylene to ethylene glycol.



ii.  $\text{KMnO}_4$  oxidizes toluene to benzoic acid.



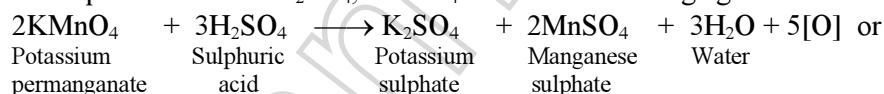
iii.  $\text{KMnO}_4$  oxidizes nitrotoluene to nitrobenzoic acid ion.



**Q.83. Explain oxidizing property of  $\text{KMnO}_4$  in acidic medium.**

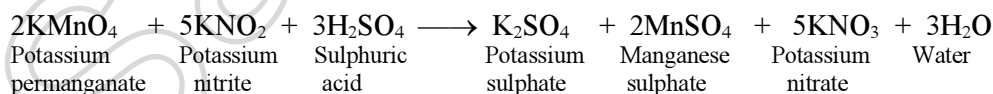
**Ans: Oxidizing property in acidic medium:**

In the presence of dil.  $\text{H}_2\text{SO}_4$ ,  $\text{KMnO}_4$  acts as an oxidizing agent. This is attributed to following reaction.

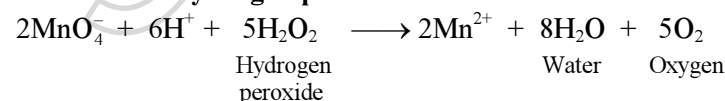


eg.

i. **Oxidation of nitrites:**



ii. **Oxidation of hydrogen peroxide:**



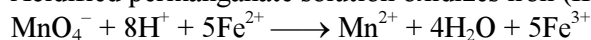
**Q.84. How does acidified permanganate solution react with:**

i. iron (II) ions ii.  $\text{SO}_2$  iii. oxalic acid?

**Write the ionic equations for the reactions.**

(NCERT)

**Ans: i.** Acidified permanganate solution oxidizes iron (II) salt to iron (III) salts.



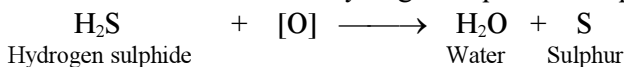


- ii. It oxidizes sulphur dioxide to sulphuric acid.  
 $2\text{MnO}_4^- + 5\text{SO}_2 + 2\text{H}_2\text{O} \longrightarrow 5\text{SO}_4^{2-} + 2\text{Mn}^{2+} + 4\text{H}^+$
- iii. It oxidizes oxalic acid to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .  
 $2\text{MnO}_4^- + 16\text{H}^+ + 5\text{C}_2\text{O}_4^{2-} \longrightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 10\text{CO}_2$

**Q.85. Give the balanced chemical equation for the oxidation of:**

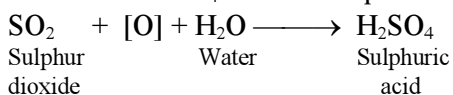
- i.  $\text{H}_2\text{S}$     ii.  $\text{SO}_2$     iii.  $\text{Na}_2\text{SO}_3$     iv.  $\text{KI}$     v.  $\text{HX}$  ( $\text{X} = \text{Cl, Br, I}$ )  
**when acidified potassium permanganate is used.**

**Ans:** i. Acidified  $\text{KMnO}_4$  oxidizes hydrogen sulphide to sulphur.

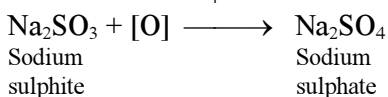


The nascent oxygen comes from acidified  $\text{KMnO}_4$ .

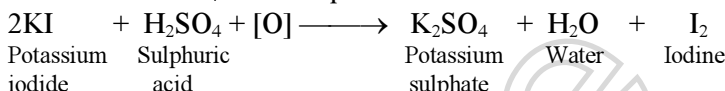
ii. Acidified  $\text{KMnO}_4$  oxidizes sulphur dioxide to sulphuric acid.



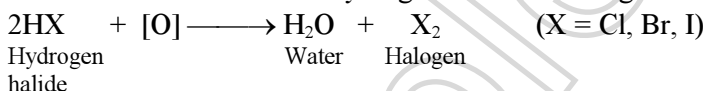
iii. Acidified  $\text{KMnO}_4$  oxidizes sodium sulphite to sodium sulphate.



iv. Acidified  $\text{KMnO}_4$  oxidizes potassium iodide to iodine.



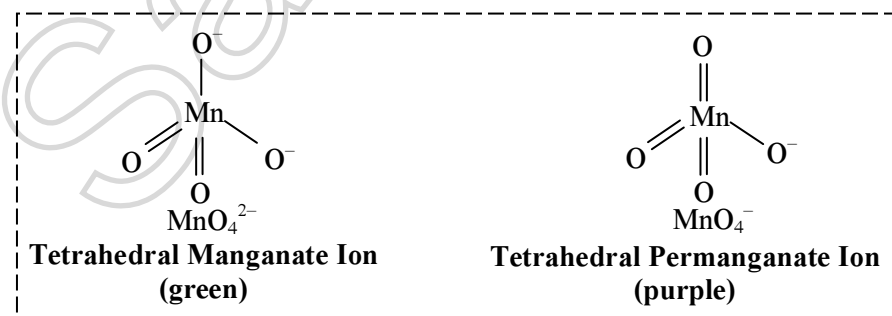
v. Acidified  $\text{KMnO}_4$  oxidizes hydrogen halides to halogens.



**Q.86. Explain the structures of manganate and permanganate ion.**

**Ans: Structures of manganate and permanganate ion:**

- i. Manganate ion has tetrahedral structure, green colour and paramagnetic properties (due to presence of one unpaired electron). Mn in  $\text{MnO}_4^{2-}$  is  $\text{sp}^3$  hybridized resulting in the tetrahedral arrangement of the four oxygen atoms around manganese.  $\pi$  bonds are formed due to overlap of p-orbitals of oxygen with d-orbitals of Mn.
- ii. Permanganate ion has tetrahedral structure, purple colour (due to charge transfer) and diamagnetic properties [due to  $d^0$  configuration of Mn(VII)].

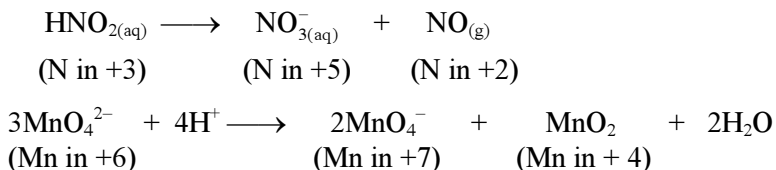


**Q.87. What is meant by disproportionation? Give two examples of disproportionation reaction in aqueous solution.** (NCERT)

**Ans:** A disproportionation reaction is a reaction in which an element in one oxidation state is simultaneously oxidized and reduced.



eg. N (III) and Mn (VI) species undergo disproportionation reaction as follows:



N in +3 oxidation state undergo disproportionation into its +5 and +2 states. Similarly, Mn in +6 oxidation state undergoes disproportionation into +7 and +4 oxidation states.

**Q.88. State the uses of potassium permanganate.**

**Ans:** Uses of  $\text{KMnO}_4$ :  $\text{KMnO}_4$  is used,

- in volumetric analysis for the estimation of ferrous salts, oxalates, iodides and hydrogen peroxide.
- as a strong oxidising agent in the laboratory as well as an effective oxidising agent in organic synthesis. Alkaline potassium permanganate is used for testing unsaturation in organic compounds and is known as Baeyer's reagent.
- as a disinfectant and germicide. A very dilute solution of permanganate is used for washing wounds and gargling for mouth sore. It is also used for purifying water of stinking wells.
- for bleaching of wool, cotton, silk and other textile fibres because of its strong oxidizing power and also for decolourisation of oils.

### f-Block Elements

#### 8.5 General introduction and electronic configuration

**\*Q.89. What are f-block elements?**

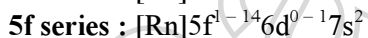
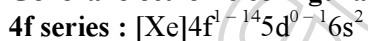
- Ans:**
- The elements in which the last electron enters into  $(n-2)$  f-orbital of the atoms are called **f-block elements**.
  - In these elements, the last electron enters in to the penultimate  $(n-2)$  shell (called antepenultimate).
  - The general valence electronic configuration is:  $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$ .

**Q.90. \*Explain the meaning of inner transition series. OR What are inner-transition elements? (NCERT)**

- Ans:**
- The last electron in the f-block elements enters into  $(n-2)$  f-orbitals, i.e., inner to the penultimate energy level and they form a transition series within the transition series (d-block elements). Hence, the f-block elements are known as inner transition series.
  - There are two series of inner transition elements:
    - Lanthanoids (atomic number 58–71)
    - Actinoids (atomic number 90–103).

**Q.91. Write the general electronic configuration of 4f and 5f series elements. [Mar 13 old course]**

**Ans: General electronic configuration:**



*[Electronic configurations – 1 Mark each]*

#### 8.6 Lanthanoids

**Q.92. What are lanthanoids?**

- Ans:**
- The series involving the filling of 4f-orbitals following lanthanum La ( $Z = 57$ ) is called **lanthanoid series**. The elements present in this series are called **lanthanoids**.
  - There are fourteen elements in this series starting with cerium, Ce ( $Z = 58$ ) and ending with Lutetium, Lu ( $Z = 71$ ). These elements are represented by the general symbol Ln. The name 'lanthanoid' has been derived from 'lanthanum' which is the prototype of lanthanoid.

**\*Q.93. Explain the position of lanthanoids in the periodic table.**

**Ans: Position of lanthanoids in the periodic table:**

- The 14 elements (from 58 to 71) of lanthanoid series have been placed along with lanthanum (at no. 57) in the third column and sixth period of the periodic table.





- ii. In the periodic table, as we move from one element to other, either from left to right or from top to bottom, the properties exhibit a gradual change. But these fifteen are so similar to one another, that they cannot be placed one after the other or one below the other.
- iii. As the fourteen elements i.e., Ce(58) to Lu(71) are closely similar to La(57), the best place for them is along with Lanthanum (La) i.e., third column and sixth period in the periodic table.
- iv. In case, these elements are given different position in order of their increasing atomic numbers, the symmetry of the periodic table would be disrupted.
- v. Due to this reason, the lanthanoids are placed at the bottom of the periodic table with a reference to the third group in the sixth period.
- vi. This position in the periodic table is justified due to following facts:
  - a. The number of valency electrons is same for all elements, i.e., one in 5d and two in 6s.
  - b. Group valency of all lanthanoids is 3.
  - c. Physical and chemical properties of all these elements are similar.
  - d. Atomic numbers of lanthanoids are in between lanthanum (57) and hafnium (72).

← GROUPS →

	H																	
1	1	2											13	14	15	16	17	18
2	← Transition Elements →																	
3	← s-block elements →																	
4	← d-block elements →												p-block elements					
5	← s-block elements →																	
6	La *																	
7	Ac **																	

f-block elements

*	58	59	60	61	62	63	64	65	66	67	68	69	70	71
Lanthanoids	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
**	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Actinoids	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

← Inner transition elements →

**Position of lanthanoids in the periodic table**

**Q.94. Briefly explain why electronic configurations of lanthanoids are not known with certainty.**

**Ans:** In the lanthanoids, 4f and 5d subshells are very close in energy. The outermost 6s-orbital remains filled with two electrons ( $6s^2$ ). The electrons can easily jump from 4f to 5d or vice-versa. Further, irregularities in electronic configurations are also related to the stabilities of  $f^0$ ,  $f^7$  and  $f^{14}$  occupancy of f-orbitals. Hence, their electronic configurations are not known with certainty.

➤ **Electronic configuration of lanthanum and 4f-series of f-block elements:**

- i. The 4f-series includes elements from cerium (Ce) to lutetium (Lu). The electronic configuration of these elements can be expressed in terms of its nearest inert gas Xe ( $Z = 54$ ).
- ii. Electronic configuration of Xe ( $Z = 54$ ) =  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$   
Therefore, general electronic configuration of 4f-series is  $[Xe] 4f^{1-14} 5d^{0-1} 6s^2$ .



iii. Lanthanum has electronic configuration  $[\text{Xe}]4f^0 5d^1 6s^2$ . It does not have any 4f electrons.

Element	Symbol	Atomic Number	Expected electronic configuration	Observed electronic configuration
Lanthanum	La	57	$[\text{Xe}] 4f^0 5d^1 6s^2$	$[\text{Xe}] 4f^0 5d^1 6s^2$
Cerium	Ce	58	$[\text{Xe}] 4f^1 5d^1 6s^2$	$[\text{Xe}] 4f^2 5d^0 6s^2$
Praseodymium	Pr	59	$[\text{Xe}] 4f^2 5d^1 6s^2$	$[\text{Xe}] 4f^3 5d^0 6s^2$
Neodymium	Nd	60	$[\text{Xe}] 4f^3 5d^1 6s^2$	$[\text{Xe}] 4f^4 5d^0 6s^2$
Promethium	Pm	61	$[\text{Xe}] 4f^4 5d^1 6s^2$	$[\text{Xe}] 4f^5 5d^0 6s^2$
Samarium	Sm	62	$[\text{Xe}] 4f^6 5d^1 6s^2$	$[\text{Xe}] 4f^6 5d^0 6s^2$
Europium	Eu	63	$[\text{Xe}] 4f^6 5d^1 6s^2$	$[\text{Xe}] 4f^7 5d^0 6s^2$
Gadolinium	Gd	64	$[\text{Xe}] 4f^7 5d^1 6s^2$	$[\text{Xe}] 4f^7 5d^1 6s^2$
Terbium	Tb	65	$[\text{Xe}] 4f^8 5d^1 6s^2$	$[\text{Xe}] 4f^9 5d^0 6s^2$
Dysprosium	Dy	66	$[\text{Xe}] 4f^9 5d^1 6s^2$	$[\text{Xe}] 4f^{10} 5d^0 6s^2$
Holmium	Ho	67	$[\text{Xe}] 4f^{10} 5d^1 6s^2$	$[\text{Xe}] 4f^{11} 5d^0 6s^2$
Erbium	Er	68	$[\text{Xe}] 4f^{11} 5d^1 6s^2$	$[\text{Xe}] 4f^{12} 5d^0 6s^2$
Thulium	Tm	69	$[\text{Xe}] 4f^{12} 5d^1 6s^2$	$[\text{Xe}] 4f^{13} 5d^0 6s^2$
Ytterbium	Yb	70	$[\text{Xe}] 4f^{13} 5d^1 6s^2$	$[\text{Xe}] 4f^{14} 5d^0 6s^2$
Lutetium	Lu	71	$[\text{Xe}] 4f^{14} 5d^1 6s^2$	$[\text{Xe}] 4f^{14} 5d^1 6s^2$

**Mnemonic:**

Lazy College Professors Never Prepare Superior Excellent Graduates To Dramatically Help Executives Trim Yearly Losses.

**Q.95. Write down the electronic configuration of**

- i.  $\text{Pm}^{3+}$       ii.  $\text{Ce}^{4+}$       iii.  $\text{Lu}^{2+}$

(NCERT)

Ans: i.  $\text{Pm}^{3+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^4$ .

ii.  $\text{Ce}^{4+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$ .

iii.  $\text{Lu}^{2+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^{14} 5d^1$ .

**Q.96. Use Hund's rule to derive the electronic configuration of  $\text{Ce}^{3+}$  ion, and calculate its magnetic moment on the basis of 'spin – only' formula.**

(NCERT)

Ans: The atomic number of Ce is 58. Its electronic configuration is  $[\text{Xe}] 4f^2 5d^0 6s^2$ .

It loses three electrons (one 4f and two 6s) to form  $\text{Ce}^{3+}$  ion with electronic configuration  $[\text{Xe}] 4f^1 5d^0 6s^0$ .

The electron distribution in 4f orbital is



4f

It contains one paired electron.

∴ Magnetic moment  $\mu = \sqrt{n(n+2)} = \sqrt{1(1+2)} = 1.73 \text{ B.M.}$

**Q.97. Why lanthanum, gadolinium and lutetium show different electronic configurations?**

- Ans: i. It is observed that lanthanum, gadolinium and lutetium show different electronic configuration because the 5d and 4f-orbitals are nearly of the same energy and the distinction between the two is difficult.
- ii. Due to this, some extra stability is achieved when the 4f is half-filled and completely filled so the next electron goes in 5d-orbital instead of 4f-orbital. 5d orbital contains one electron in 5d subshell in case of La, Gd and Lu while it is empty in case of other lanthanoids.
- iii.  $f^0$ ,  $f^7$  and  $f^{14}$  configurations have extra stability due to empty, half filled and completely filled f orbitals respectively.
- iv. The electronic configuration of  ${}_{57}\text{La}$ ,  ${}_{64}\text{Gd}$  and  ${}_{71}\text{Lu}$  in +3 oxidation state are as follows:  
 $\text{La}^{+3} : [\text{Xe}] 4f^0$  ;  $\text{Gd}^{+3} : [\text{Xe}] 4f^7$  ;  $\text{Lu}^{+3} : [\text{Xe}] 4f^{14}$ .

**Q.98.State the features of electronic configuration for lanthanoids.****Ans: Features of electronic configuration of lanthanoids:**

- The s-block element preceding La in period 6 is Ba with atomic number 56 and electronic configuration  $[\text{Xe}] 4f^0 5d^0 6s^2$ , where  $[\text{Xe}]$  is the electronic configuration of noble gas xenon in the period 5 and is  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$ .
- The electronic configuration of La is  $[\text{Xe}] 4f^0 5d^1 6s^2$ . The last electron enters 5d-orbital while the 4f orbital is empty.
- Cerium ( $Z = 58$ ) has expected electronic configuration,  $[\text{Xe}] 4f^1 5d^1 6s^2$  but the observed electronic configuration is  $[\text{Xe}] 4f^2 5d^0 6s^2$ . This can be explained on the basis of extra stability of empty 5d orbital. The electrons are successively added to 4f subshell.
- 5d orbital contains one electron in 5d subshell in case of La, Gd and Lu while it is empty in case of other lanthanoids. The filling up of 4f – orbitals is regular in idealised electronic configuration and irregular in observed electronic configuration. Single 5d electron is moved into 4f subshell in observed electronic configuration.
- $f^0$ ,  $f^7$  and  $f^{14}$  configurations have extra stability due to empty, half filled and completely filled f orbitals respectively.  
**eg.** La( $4f^0$ ) and Lu( $4f^{14}$ )
- Higher outer orbitals shield the 4f electrons in the  $(n-2)$  shell.

**Q.99. \*Explain the oxidation states of lanthanoids. OR****What are different oxidation states exhibited by the lanthanoids?****(NCERT)**

- Ans:**
- All lanthanoids exhibit a common stable oxidation state of +3.
  - In addition, some lanthanoids show +2 and +4 oxidation states also.
  - These are shown by those elements which by doing so attain the stable  $f^0$ ,  $f^7$  or  $f^{14}$  configurations i.e., empty, half-filled and completely filled 4f sub-shells.  
**eg.** Ce and Tb exhibit +4 oxidation states, Eu and Yb exhibit +2 oxidation states, while La, Gd and Lu exhibit only +3 oxidation states.

**Note: Oxidation states of Lanthanoids are as shown in following table:**

Element	Outer electronic configuration	Oxidation states		
		$M^{2+}$	$M^{3+}$	$M^{4+}$
Lanthanum	$4f^0 5d^1 6s^2$	–	3+	–
Cerium	$4f^2 5d^0 6s^2$	–	3+	4+
Praseodymium	$4f^3 5d^0 6s^2$	–	3+	4+
Neodymium	$4f^4 5d^0 6s^2$	2+	3+	4+
Promethium	$4f^6 5d^0 6s^2$	–	3+	–
Samarium	$4f^6 5d^0 6s^2$	2+	3+	–
Europium	$4f^7 5d^0 6s^2$	2+	3+	–
Gadolinium	$4f^7 5d^1 6s^2$	–	3+	–
Terbium	$4f^9 5d^0 6s^2$	–	3+	4+
Dysprosium	$4f^{10} 5d^0 6s^2$	–	3+	4+
Holmium	$4f^{11} 5d^0 6s^2$	–	3+	–
Erbium	$4f^{12} 5d^0 6s^2$	–	3+	–
Thullium	$4f^{13} 5d^0 6s^2$	2+	3+	–
Ytterbium	$4f^{14} 5d^0 6s^2$	2+	3+	–
Lutetium	$4f^{14} 5d^1 6s^2$	–	3+	–



**Q.100. Explain why Eu and Yb show oxidation state +2.**

- Ans:** i. In the +2 oxidation state, Eu donates two electrons from its 6s-orbitals. In  $\text{Eu}^{+2}$ , 4f-orbitals are half-filled i.e.,  $4f^7$  which is a more stable state.
- ii. Similarly in the +2 oxidation state, Yb donates two electrons from its 6s-orbitals. In  $\text{Yb}^{+2}$ , 4f-orbitals are completely filled i.e.,  $4f^{14}$  which is more stable.
- Therefore, Eu and Yb show +2 oxidation states.

**Q.101. La, Gd and Lu show only +3 oxidation state. Explain.**

- Ans:** i. The electronic configuration of  ${}_{57}\text{La}$ ,  ${}_{64}\text{Gd}$  and  ${}_{71}\text{Lu}$  in +3 oxidation state are as follows:  
 $\text{La}^{+3} : [\text{Xe}] 4f^0$  ;  $\text{Gd}^{+3} : [\text{Xe}] 4f^7$  ;  $\text{Lu}^{+3} : [\text{Xe}] 4f^{14}$ .
- ii. f-orbital acquires extra-stability when it is half filled or completely filled. Hence, La, Gd and Lu exhibit only +3 oxidation state.



### Brain Teaser

**Name the members of the lanthanoid series which exhibit +4 oxidation states and those which exhibit +2 oxidation states. Try to correlate this type of behaviour with the electronic configuration of these elements. (NCERT)**

- + 4 = Ce, Pr, Nd, Tb, Dy
- + 2 = Nd, Sm, Eu, Tm, Yb
- + 2 oxidation state is exhibited when the lanthanoid has the configuration  $5d^0 6s^2$  so that 2 electrons are easily lost.
- + 4 oxidation state is exhibited when the configuration left is close to  $4f^0$  (eg.  $4f^0$ ,  $4f^1$ ,  $4f^2$ ) or close to  $4f^7$  (eg.  $4f^7$  or  $4f^8$ )

**\*Q.102. Why do lanthanoids form coloured compounds?**

**Ans:** Unpaired electrons are present in the outermost 4f subshell of lanthanoid ions. Therefore, they can undergo f-f transitions and hence form coloured compounds.

**\*Q.103. Explain why  $\text{Gd}^{3+}$  is colourless.**

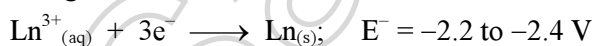
**Ans:** Lanthanoids show colour due to partially filled f-orbitals which allow f-f transitions.

$\text{Gd}^{3+}$  has electronic configuration  $[\text{Xe}] 4f^7$ .

$\text{Gd}^{3+}$  ion has exactly half filled electronic configuration. So, electrons for f-f transition are absent due to which it is colourless.

**Q.104. Explain the chemical reactivity of lanthanoids.**

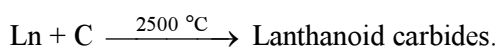
**Ans:** The chemical reactivity of earlier members of lanthanoid series is similar to that of calcium. This behaviour changes to that of aluminum as the atomic number increases.



For Eu,  $E^- = -2.0 \text{ V}$  (exceptional case)

**Q.105. Explain the reaction of lanthanoids with carbon.**

**Ans: Reaction with carbon:** Lanthanoids react with carbon at  $2500^\circ\text{C}$ , to form lanthanoid carbides having formulae  $\text{Ln}_3\text{C}$ ,  $\text{LnC}_2$  and  $\text{Ln}_2\text{C}_3$



**Q.106. Explain the reaction of lanthanoids with oxygen.**

**Ans: Reaction with oxygen:** Combustion of lanthanoids in presence of oxygen, gives lanthanide oxide ( $\text{Ln}_2\text{O}_3$ ).

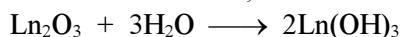




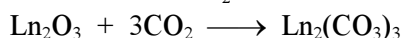
**Q.107. How do you bring about the following conversions:**

- i. Lanthanoid oxides to lanthanoid hydroxides?    ii. Lanthanoid oxides to lanthanoid carbonates?

**Ans:** i. Reaction with water, converts lanthanoid oxides to insoluble lanthanoid hydroxides.



- ii. Reaction with  $\text{CO}_2$  converts lanthanoid oxides to lanthanoid carbonates.



**Q.108. Explain the reaction of lanthanoids with nitrogen.**

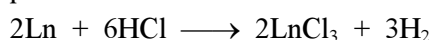
**Ans: Reaction with nitrogen:** Reaction of lanthanoids with nitrogen, gives lanthanide nitride ( $\text{LnN}$ ).



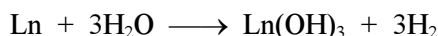
**Q.109. Explain the reaction of lanthanoids with the following:**

- i. Mineral acids    ii. Water    iii. Sulphur    iv. Hydrogen

**Ans: i. Reaction with mineral acids:** Reaction with mineral acids, liberates  $\text{H}_2$  gas as they have reduction potential of  $-2.0$  to  $-2.4$  V



- ii. **Reaction with water:** Reaction with water, forms ionic and basic lanthanide hydroxides with liberation of  $\text{H}_2$  gas.



- iii. **Reaction with sulphur:** Reaction with sulphur, forms lanthanide sulphide ( $\text{Ln}_2\text{S}_3$ ).



- iv. **Reaction with hydrogen:** The metals combine with hydrogen when gently heated in the hydrogen gas.



**Q.110. Write a short note on lanthanoid contraction.**

**Ans: Lanthanoid contraction:**

- The atomic and ionic radii of lanthanoids show gradual decrease with increase in atomic number. It is known as **Lanthanoid contraction**.
- There are 14 Lanthanoids from Ce to Lu. In Lanthanoids, after Lanthanum (La), the electrons are added to penultimate shell i.e., 4f-orbital.
- For each electron, one proton is also added to the nucleus of the atom of the element. Hence from Ce to Lu as atomic number increases, nuclear charge increases, therefore nuclear attraction increases. As atomic number increases, atomic volume or radius decreases as observed with all the elements along the period.
- But in case of Lanthanoids, this decrease in atomic volume or radius is comparatively very small. This is explained in terms of Lanthanoid contraction.

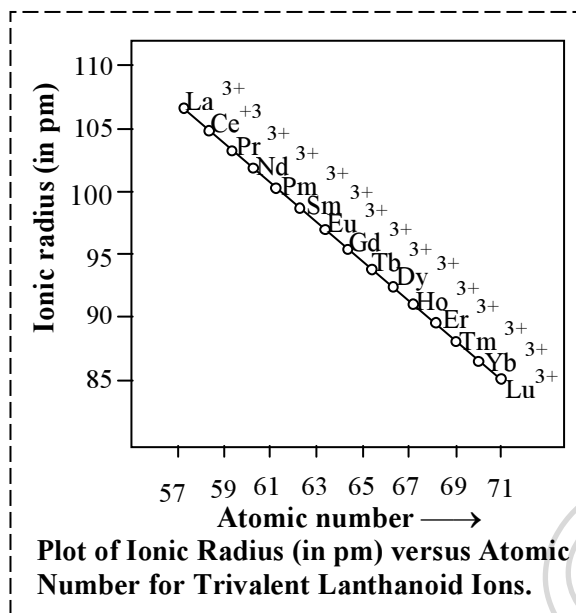
**Q.111. Explain the causes of the lanthanoid contraction.**

- Ans:**
- The nuclear positive charge increases by +1, when the atomic number increases by 1. An electron is added in the partly filled 4f orbital.
  - The shielding of 4f electrons is less effective than the shielding of 5d electron as 4f orbital is more diffused in shape than 5d orbital. Thus, greater effective nuclear charge is experienced with the increase in the atomic number. This results in slight pull of the valence shell towards the nucleus.
  - Thus, the atomic and ionic radii decrease slightly with increase in the atomic number, thereby causing lanthanoid contraction.
  - In a given lanthanoid series, atomic radii decrease by 10 pm and the ionic radii decrease by 18 pm. Thus, the extent of decrease is very small.



Note:

- i. The lanthanoid contraction of various trivalent lanthanoid ions is illustrated in the graph.



- ii. As we move from one element to other element, the contraction in size is small. However for the fourteen elements from Ce to Lu the net contraction is appreciable.
- iii. Atomic radii decrease with certain irregularities whereas the decrease in the ionic radii from La to Lu is steady.

**Variation of atomic and ionic radii (pm) of lanthanum and lanthanoids:**

Element	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Radii (Ln) pm	187	183	182	181	181	180	199	180	178	177	176	175	174	173	–
Radii (Ln <sup>3+</sup> ) pm	106	103	101	99	98	96	95	94	92	91	89	88	87	86	–

**Q.112. Explain the effects of lanthanoid contraction.**

**Ans: Effects of lanthanoid contraction:**

- i. **Decrease in basicity:**

- a. The size of Ln<sup>3+</sup> cation decreases with increase in the atomic number, due to lanthanoid contraction. This decreases the ionic character of M–OH bond and gradually increases the covalent character of M–OH bond.
- b. Therefore the basic strength of the corresponding hydroxides decreases from La(OH)<sub>3</sub> to Lu(OH)<sub>3</sub>. Thus, La(OH)<sub>3</sub> is most basic and Lu(OH)<sub>3</sub> is least basic.

**Note:** As per *Fajan's principle*, "With increase in the size of cation, the tendency of the hydroxide to dissociate, increases. This increases the strength of base."

- ii. **Ionic radii of post lanthanoids:**

- a. There is a regular increase in size from Sc to Y to La. But after the lanthanoids, the increase in radii from second to third transition series almost vanishes.
- b. Pairs of elements such as Zr–Hf (group 4), Nb–Ta (group 5), Mo–W (group 6) and Tc–Re (group 7) possess almost same size. These pair of elements are called 'chemical twins'. The properties of these elements are also similar. So due to lanthanoid contraction, elements of second and third series resemble each other.

**Note:**

- The elements which follow the lanthanoids in the third transition series are known as post-lanthanoids.
- The ionic radii of 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> transition series elements are listed in the following table.

**Ionic radii of 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> transition series elements:**

Group → Series ↓	4	5	6	7
1 <sup>st</sup> transition series	Ti (132 pm)	V (122 pm)	Cr (106 pm)	Mn (94 pm)
2 <sup>nd</sup> transition series	Zr (145 pm)	Nb (134 pm)	Mo (129 pm)	Tc (114 pm)
3 <sup>rd</sup> transition series	Hf (144 pm)	Ta (134 pm)	W (130 pm)	Re (114 pm)

- Similarity among lanthanoids:** Lanthanoids show very small change in radii so their chemical properties are quite similar. Thus it is very difficult to separate the elements in pure state.

**\*Q.113. What are chemical twins? Give examples.**

**Ans:** A pair of elements having similar properties due to similar number of valence electrons, atomic radii and almost same size are called **chemical twin elements**.

This effect arises due to lanthanoid contraction.

**eg:** Zr and Hf, Nb and Ta, Mo and W, Tc and Re are a pair of chemical twins elements.

**Q.114. Write a short note on uses of lanthanoids.**

**Ans:** Uses of lanthanoids:

- Lanthanoids do not find any use in the pure state. The most important use of lanthanoids is in the production of alloy steels to improve the strength and workability of steel.
- Their oxides (**eg.** La<sub>2</sub>O<sub>3</sub>) are used in glass industry, for polishing glass and for making coloured glasses for goggles as they give protection against UV light and as phosphor for television screens and similar fluorescing surfaces. Mixed oxides of lanthanoids are used as catalysts in petroleum cracking.
- Because of their paramagnetic and ferromagnetic properties, their compounds are used in making magnetic and electronic devices.
- Ceric sulphate is a well known oxidizing agent in volumetric analysis.

**Q.115. What is Misch metal? Give its one use.**

**Ans:** Misch metal is an alloy of lanthanum metal and iron and traces of S, Ca, C or Al. It is used in making bullets and lighter flint.

**Q.116. What are alloys?**

(NCERT)

**Ans:** Alloys are homogeneous solid solutions in which the atoms of one metal are randomly distributed among the atoms of the other metal or non-metal.

**8.7 Actinoids****\*Q.117. What are actinoids?**

**Ans:** The series of elements from Thorium ( $Z = 90$ ) to Lawrencium ( $Z = 103$ ) in which 5f orbitals are progressively filled are called **actinoids**.

The elements are called actinoid because many physical and chemical properties are similar to actinium which is the prototype of the actinoids.

**\*Q.118.i. What are trans-uranic elements?**

[Mar 13 old course]

**ii. Write their names.**

- Ans:**
- Transuranic elements are the man-made elements, with atomic number higher than 92 (the atomic number of uranium), which are prepared by nuclear reactions involving transformation of naturally occurring elements. [Definition – 1 Mark]
  - The elements from atomic numbers 104 (Rf) to 112 (Uub) are identified. Elements upto atomic number 118 (Uuo) are synthesized.



## Transuranic elements:

Sr. no.	Name	Symbol	Atomic number
1.	Neptunium	Np	93
2.	Plutonium	Pu	94
3.	Americium	Am	95
4.	Curium	Cm	96
5.	Berkelium	Bk	97
6.	Californium	Cf	98
7.	Einsteinium	Es	99
8.	Fermium	Fm	100
9.	Mendelevium	Md	101
10.	Nobelium	No	102
11.	Lawrencium	Lr	103
12.	Rutherfordium	Rf	104
13.	Dubnium	Db	105

Sr. no.	Name	Symbol	Atomic number
14.	Seaborgium	Sg	106
15.	Bohrium	Bh	107
16.	Hassium	Hs	108
17.	Meitnerium	Mt	109
18.	Darmstadtium	Ds/Uun	110
19.	Rontgenium/Ununium	Rg/Uuu	111
20.	Copernicium/Ununbium	Cn/Uub	112
21.	Ununtrium	Uut	113
22.	Ununquadium	Uuq	114
23.	Ununpentium	Uup	115
24.	Ununhexium	Uuh	116
25.	Ununseptium	Uus	117
26.	Ununoctium	Uuo	118

\*Q.119. Explain the position of actinoids in the periodic table.

[Mar 14]

Ans: Position of actinoids in the periodic table:

- Actinoids belongs to the third group of periodic table in the seventh period.
- In the periodic table, as we move from one element to another, either from left to right or from top to bottom, the properties exhibit a gradual change. But these fifteen elements are so similar to one another, that they cannot be placed one after the other or one below the other.
- As the fourteen elements i.e. Th(90) to Lr(103) are closely similar to Ac(89), the best place for them is alongwith actinium(89) i.e., third group ( $3^{rd}$  column) and seventh period in the periodic table.
- In case these elements are given different positions in order of their increasing atomic numbers, the symmetry of the periodic table would be disrupted. Due to this reason, the actinoids are placed at the bottom of the periodic table with a reference to the third group in the seventh period i.e., the position of actinium.

[Explanation point i and iv – 1 Mark]

Note: For position, refer figure shown in Q. 93.

➤ **Electronic configuration of actinium and 5f-series of f-block elements:**

- The 5f-series includes elements from thorium (Th) to lawrencium (Lr).  
The electronic configuration of these elements can be expressed in terms of Rn ( $Z = 86$ ).
- Electronic configuration of Rn ( $Z = 86$ ) =  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 5d^{10} 5f^{14} 6s^2 6p^6$ .  
Therefore, General electronic configuration of actinoids :  $[Rn] 5f^{1-14} 6d^{0-1} 7s^2$
- The electronic configuration of actinium ( $Z = 89$ ) is  $[Rn] 5f^0 6d^1 7s^2$ . It does not contain any 5f electron.
- Thorium ( $Z = 90$ ) has expected electronic configuration  $[Rn] 5f^1 6d^1 7s^2$  and observed electronic configuration  $[Rn] 5f^0 6d^2 7s^2$ . This can be explained on the basis of extra stability of empty 5f orbital. The electrons are successively added to 5f subshell.

Element	Symbol	Atomic Number	Electronic configuration (Expected)	Electronic configuration (Observed)
Actinium	Ac	89	$[Rn] 5f^0 6d^1 7s^2$	$[Rn] 5f^0 6d^1 7s^2$
Thorium	Th	90	$[Rn] 5f^1 6d^1 7s^2$	$[Rn] 5f^0 6d^2 7s^2$
Protactinium	Pa	91	$[Rn] 5f^2 6d^1 7s^2$	$[Rn] 5f^2 6d^1 7s^2$
Uranium	U	92	$[Rn] 5f^3 6d^1 7s^2$	$[Rn] 5f^3 6d^1 7s^2$
Neptunium	Np	93	$[Rn] 5f^4 6d^1 7s^2$	$[Rn] 5f^4 6d^1 7s^2$
Plutonium	Pu	94	$[Rn] 5f^5 6d^1 7s^2$	$[Rn] 5f^6 6d^0 7s^2$
Americium	Am	95	$[Rn] 5f^7 6d^0 7s^2$	$[Rn] 5f^7 6d^0 7s^2$
Curium	Cm	96	$[Rn] 5f^7 6d^1 7s^2$	$[Rn] 5f^7 6d^1 7s^2$
Berkelium	Bk	97	$[Rn] 5f^8 6d^1 7s^2$	$[Rn] 5f^9 6d^0 7s^2$





Californium	Cf	98	[Rn] 5f <sup>9</sup> 6d <sup>1</sup> 7s <sup>2</sup>	[Rn] 5f <sup>10</sup> 6d <sup>0</sup> 7s <sup>2</sup>
Einsteinium	Es	99	[Rn] 5f <sup>10</sup> 6d <sup>1</sup> 7s <sup>2</sup>	[Rn] 5f <sup>11</sup> 6d <sup>0</sup> 7s <sup>2</sup>
Fermium	Fm	100	[Rn] 5f <sup>11</sup> 6d <sup>1</sup> 7s <sup>2</sup>	[Rn] 5f <sup>12</sup> 6d <sup>0</sup> 7s <sup>2</sup>
Mendelevium	Md	101	[Rn] 5f <sup>12</sup> 6d <sup>1</sup> 7s <sup>2</sup>	[Rn] 5f <sup>13</sup> 6d <sup>0</sup> 7s <sup>2</sup>
Nobelium	No	102	[Rn] 5f <sup>14</sup> 6d <sup>0</sup> 7s <sup>2</sup>	[Rn] 5f <sup>14</sup> 6d <sup>0</sup> 7s <sup>2</sup>
Lawrencium	Lr	103	[Rn] 5f <sup>14</sup> 6d <sup>1</sup> 7s <sup>2</sup>	[Rn] 5f <sup>14</sup> 6d <sup>1</sup> 7s <sup>2</sup>

**Q.120. Write down the electronic configuration of Th<sup>4+</sup>.**

(NCERT)

**Ans:** Electronic configuration of Th<sup>4+</sup> = [Rn] 5f<sup>0</sup> 6d<sup>0</sup> 7s<sup>0</sup>

**Q.121. The electronic configurations of actinoid elements are not known with certainty. Explain.**

**Ans:** In actinoids, 5f and 6d subshells are close in energy. The outermost 7s orbital remains filled with 2 electrons (7s<sup>2</sup>). The electron can easily jump from 5f to 6d or vice versa. Further, irregularities in electronic configurations are also related to the stabilities of f<sup>0</sup>, f<sup>7</sup> and f<sup>14</sup> occupancy of the 5f-orbitals. Hence, they show a large number of oxidation states (Moreover, they are radioactive with short half-lives. Hence, their properties cannot be studied easily).

**Q.122. \*Explain the oxidation states of actinoids. OR Write a short note on oxidation states of actinoids.**

- Ans:**
- Actinoids have variable oxidation states ranging from +2 to +7 due to availability of 5f, 6d and 7s orbitals.
  - The common oxidation state of actinoid elements is +3. +3 oxidation state is formed by loss of two 7s and one 5f or 6d electrons.
  - With increase in atomic number, +3 oxidation state becomes more and more stable.
  - Beside +3 oxidation state, actinoids show +2, +4, +5, +6 and +7 oxidation states.
    - Elements Am and Th show +2 oxidation state.  
**eg.** ThI<sub>2</sub>, ThS, ThBr<sub>2</sub>, etc.
    - Elements Th, Pa, U, Np, Pu, Am and Cm show +4 oxidation state.
    - Elements Th, Pa, U, Np, Pu and Am also show +5 oxidation state.
    - Elements U, Np, Pu and Am show +6 oxidation state.
- Note:** When the oxidation number increases to +6, the actinoid ions form oxygenated ions due to high charge density.  
**eg.** UO<sub>2</sub><sup>2+</sup>, NpO<sub>2</sub><sup>2+</sup>, etc.
- Np and Pu show +7 oxidation states.
  - Actinoids exhibit large number of variable oxidation states because all the electrons in 5f, 6d and 7s orbitals can take part in bond formation due to very small energy gap between these orbitals.
  - Actinoids have more compounds in +3 oxidation state than in +4 oxidation state. However, compounds of actinoids in +3 and +4 oxidation states have tendency to undergo hydrolysis.

**Note: Oxidation states of actinium and actinoids:**

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
+2	+2					+2								
+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3
+4	+4	+4	+4	+4	+4	+4	+4	+4						
	+5	+5	+5	+5	+5	+5								
			+6	+6	+6	+6								
				+7	+7									



### Check Your Grasp

**Which is the last element in the series of the actinoids? Write the electronic configuration of this element. Comment on the possible oxidation state of this element.**

(NCERT)

Last element : Lawrencium (Z = 103); Electronic Configuration : [Rn] 5f<sup>14</sup> 6d<sup>1</sup> 7s<sup>2</sup>; Possible oxidation state : +3



\*Q.123. Differentiate between lanthanoids and actinoids.

Ans:

	Lanthanoids	Actinoids
i.	In lanthanoids, last differentiating electron occupies 4f orbital.	In actinoids, last differentiating electron occupies 5f orbital.
ii.	They are the elements of first inner transition series.	They are the elements of second inner transition series.
iii.	They are present in period 6.	They are present in period 7.
iv.	Most of lanthanoids (with exception of promethium) occur in nature.	Most of actinoids (with exception of uranium and thorium) are prepared in laboratory.
v.	Most of lanthanoids (with exception of promethium) are non-radioactive.	All the actinoids are radioactive.
vi.	Lanthanoids do not form oxo cation.	Actinoids form oxo cation such as $\text{UO}_2^{2+}$ , $\text{PuO}^{2+}$ , $\text{UO}^+$ .
vii.	4f orbitals in lanthanoids have higher binding energy.	5f orbitals in actinoids have lower binding energy.
viii.	Contraction in atomic and ionic radii is relatively less in lanthanoids.	Contraction in atomic and ionic radii is relatively greater in actinoids due to poor shielding of 5f electrons.
ix.	Lanthanoids shows +2, +3 and +4 oxidation states.	Actinoids show +3, +4, +5, +6, +7 oxidation states.
x.	Lanthanoids have less tendency to form complexes.	Actinoids have greater tendency to form complexes.
xi.	Some ions of lanthanoids are coloured.	Most of the ions of actinoids are deeply coloured.
xii.	Lanthanoid hydroxides are less basic in nature.	Actinoid hydroxides are more basic in nature.

Q.124. #The extent of actinoid contraction is greater than lanthanoid contraction, explain. OR

Actinoid contraction is greater from element to element than lanthanoid contraction. Why? (NCERT)

Ans: Actinoid contraction is greater than lanthanoid contraction:

- The size of the atoms or ions of actinoids decrease regularly along the series with the increase in atomic number from actinium to lawrencium. This steady decrease in the ionic radii with the increase in atomic number is called **actinoid contraction**.
- The actinoid contraction is due to the **imperfect shielding** of 5f-electron. Despite of the imperfect shielding of 5f-orbitals, the effective nuclear charge increases which results in contraction of the size.
- It may be noted that in actinoid contraction, there are bigger jumps in ionic size between the consecutive members as compared to lanthanoids.
- This is due to lesser shielding of 5f-electrons (as compared to shielding of 4f-electrons in lanthanoids) which results in greater increase in the effective nuclear charge and therefore, larger attraction.

Q.125. Write a short note on uses of actinoids.

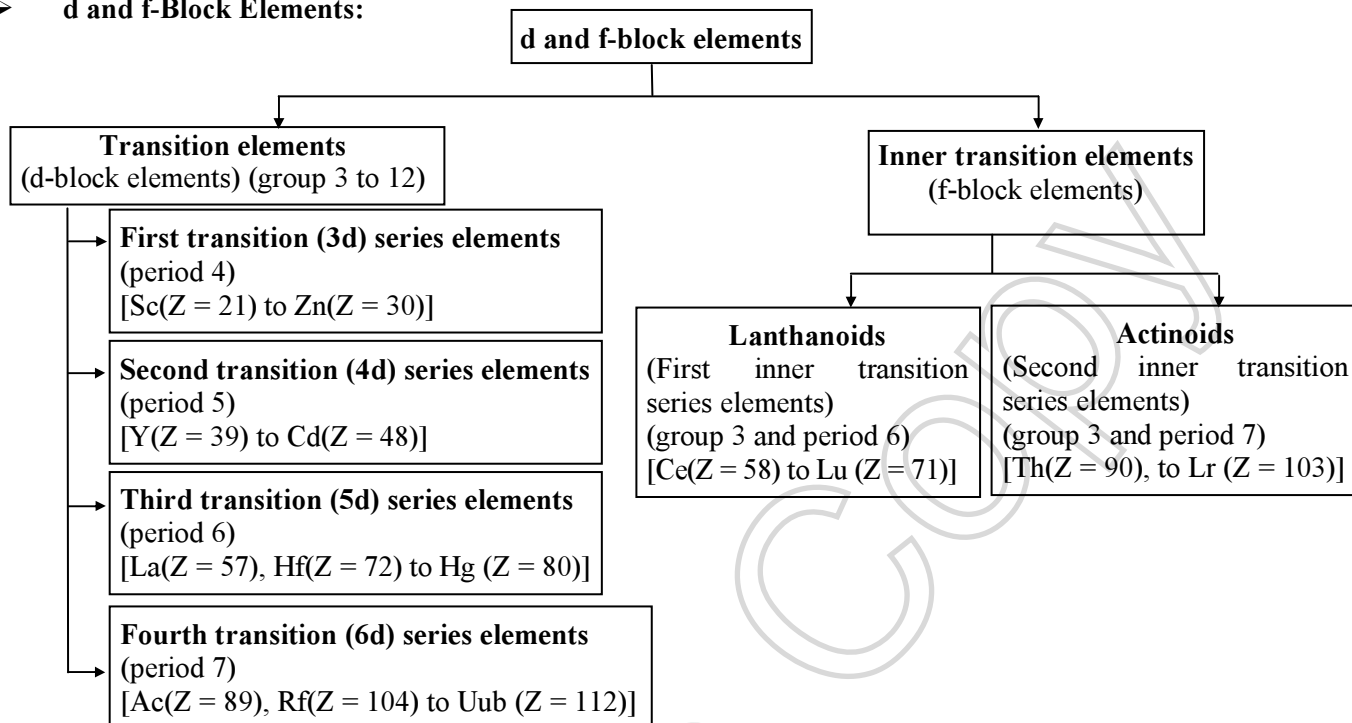
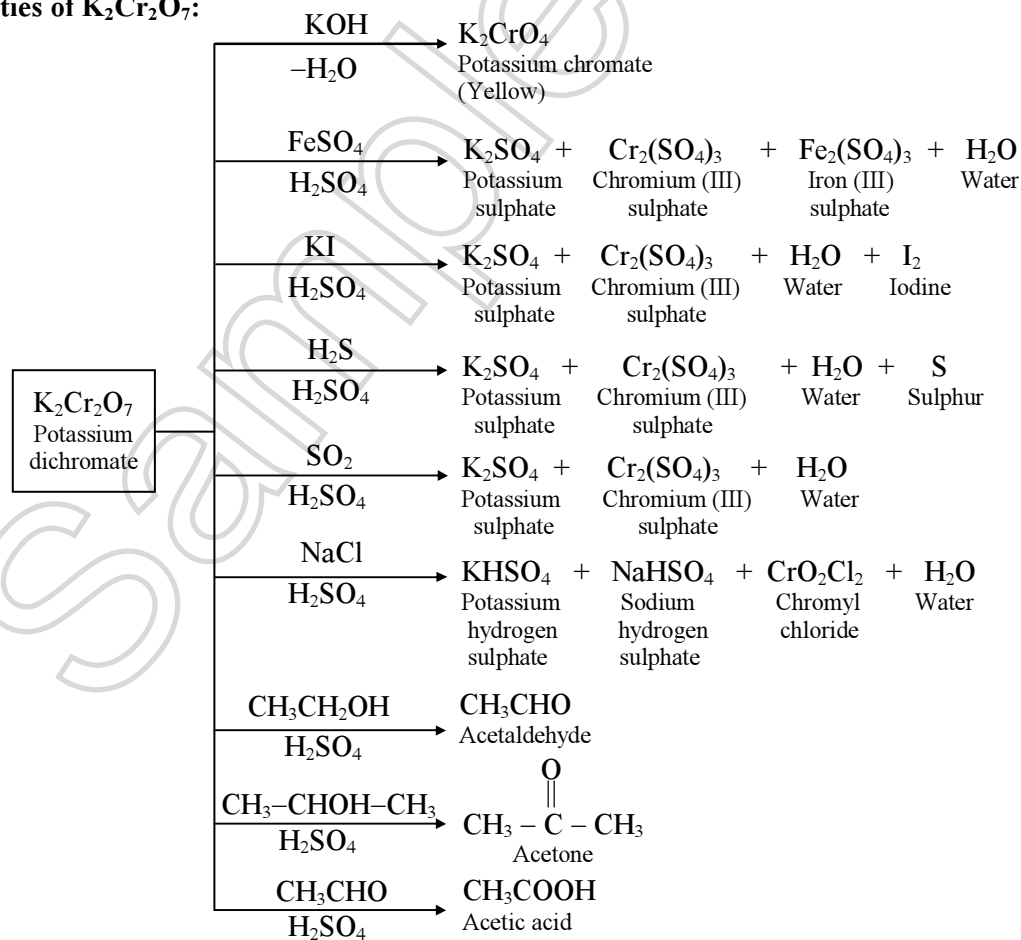
Ans: **Uses of actinoids:** The three most important actinoids which find uses as such or in the form of their compounds are thorium, uranium and plutonium.

- Thorium:** It is used in atomic reactors and in the treatment of cancer. Its salts are used in making incandescent gas mantles.
- Uranium:** It is used as a nuclear fuel. Its salts are used in glass industry (for imparting green colour), textile industry, ceramic industry and in medicines.
- Plutonium:** It is used as a fuel for atomic reactors as well as for making atomic bombs.



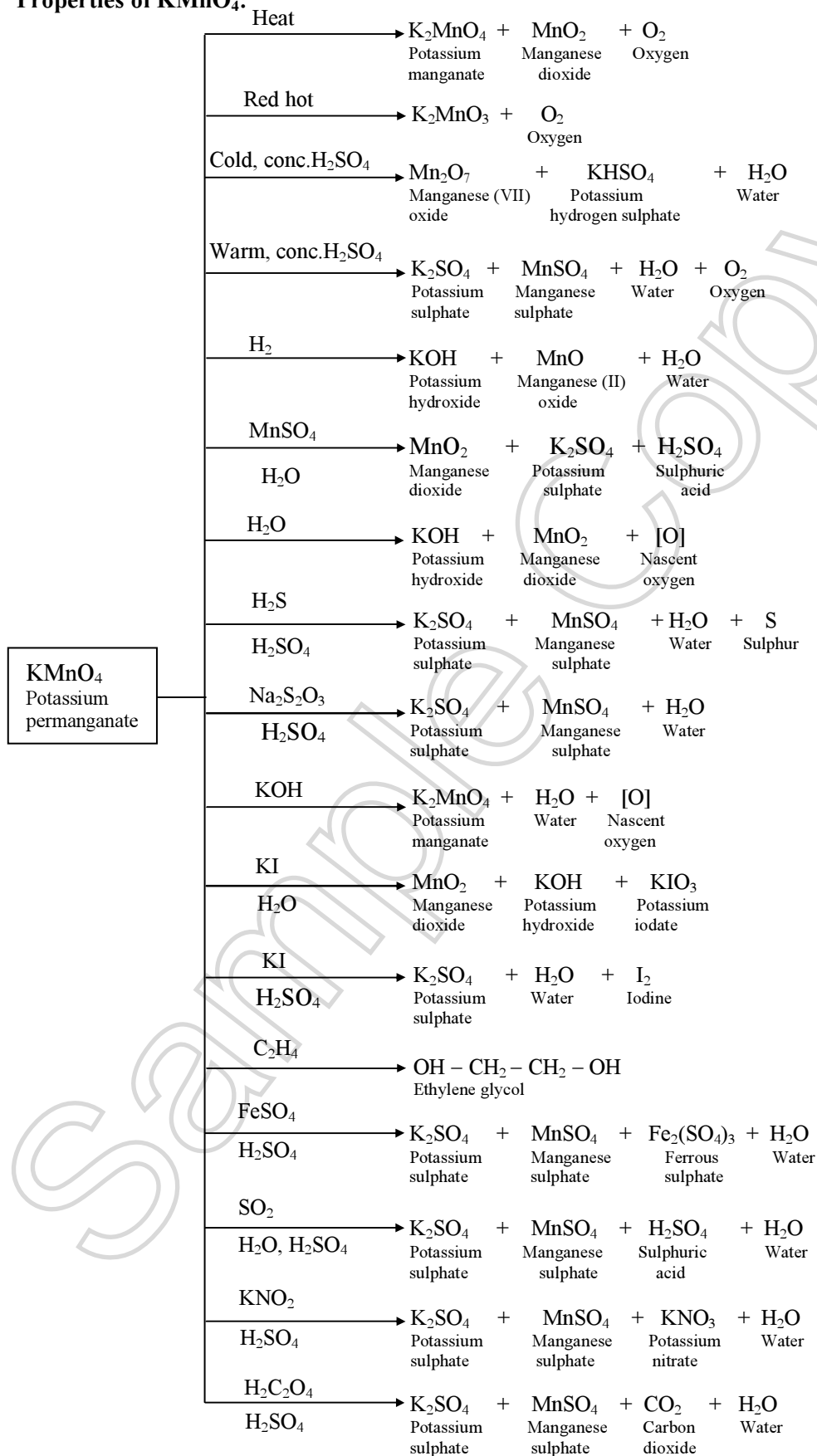
## Quick Review

## ➤ d and f-Block Elements:

➤ Properties of  $K_2Cr_2O_7$ :

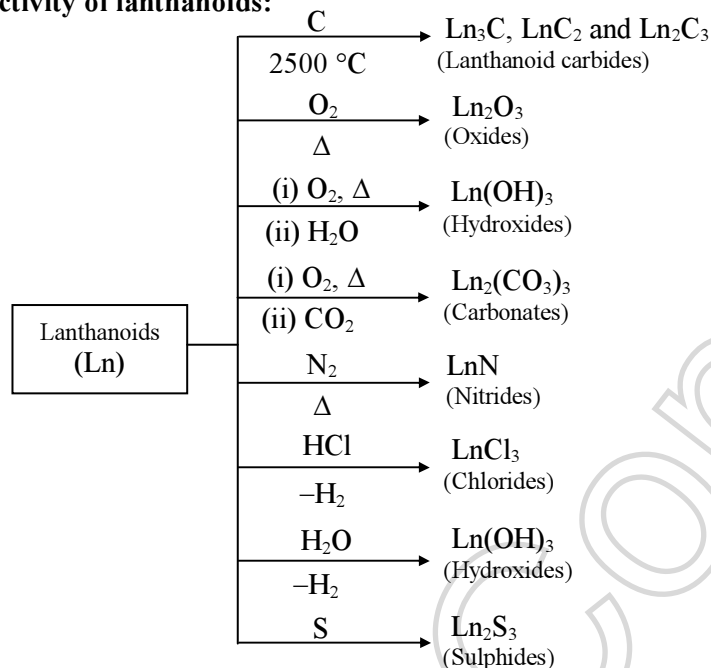


➤ Properties of  $\text{KMnO}_4$ :





## ➤ Chemical reactivity of lanthanoids:

**Additional Theory Questions**

- Q.1. Calculate magnetic moment of Fe<sup>2+</sup><sub>(aq)</sub> ion (Z = 26). [Mar 13]  
Refer Q.56. [Electronic configuration – ½ Mark, No. of unpaired electrons – ½ Mark, Formula – ½ Mark, Calculation + Final answer – ½ Mark]
- Q.2. Explain the term: Interstitial compounds. Refer Q.58.i, ii. [Explanation – 1 Mark] [Mar 16]
- Q.3. What are interstitial compounds? Why do these compounds have higher melting points than corresponding pure metals? Refer Q.58.i. and Q.59. iv. [Definition – 1 Mark, Explanation – 1 Mark] [Mar 15]
- Q.4. Write reactions involved in preparation of potassium dichromate from chrome iron ore. Refer Q.63. Step II, III and IV : Reactions. [Chemical reaction – 1 Mark] [July 16]
- Q.5. What is the effect of increasing pH on a solution of potassium dichromate? Refer Q.65.i,ii. (NCERT)
- Q.6. What is the action of acidified potassium dichromate on:  
i. SO<sub>2</sub>? Refer Q.69      ii. KI? Refer Q.67.ii. [Explanation + Chemical reaction – 1 Mark each] [Oct 14]
- Q.7. Draw structure of dichromate ion. Refer Q.72  
[Structure of dichromate ion with bond angle and bond length – 1 Mark] [Oct 14]
- Q.8. Describe the conversion of pyrolusite ore (MnO<sub>2</sub>) into potassium manganate. Refer Q.74. Step I (Any one reaction)
- Q.9. Describe chemical oxidation of potassium manganate to potassium permanganate. Refer Q.74. Step II i. (Any one chemical oxidation method)
- Q.10. Describe electrolytic oxidation of potassium manganate to potassium permanganate. Refer Q.74. Step II ii.
- Q.11. Write balanced chemical equations for action of potassium permanganate on:  
i. Hydrogen. Refer Q.79.      ii. Warm conc. sulphuric acid. Refer Q.78.  
[Chemical reactions – 1 Mark each] [Mar 14]
- \*Q.12. Write the preparation, properties and uses of potassium permanganate. Refer Q.74,75 to 85 and 88.
- Q.13. What are f-block elements? Refer Q.89. i. [Definition – 1 Mark] [Mar 16]
- Q.14. What are lanthanoids? Refer Q.92. i. [Definition – 1 Mark] [Mar 14]



- \*Q.15. Explain the trends in atomic and ionic sizes of lanthanoids. Refer Q.111.
- Q.16. i. What is lanthanoid contraction? Refer Q.110. i. [Definition – 1 Mark]  
 ii. Explain the cause and effects of lanthanoid contraction. Q.111. i to iii. and Q.112. i., ii. [Causes – 1 Mark, Effects: Any two points – 1 Mark each] [Oct 13]
- Q.17. i. Define lanthanoid contraction. Refer Q.110. i. [Definition – 1 Mark]  
 ii. Explain its effects. Refer Q.112. i., ii. [Any two points – 1 Mark each] [Mar 15]
- Q.18. What are chemical twins? Write 'two' examples. Refer Q.113. [Definition – 1 Mark, Any two examples – ½ Mark each] [Oct 14]
- Q.19. Write names of 'two' transuranic elements. Refer Q.118. ii. Table. [Any two elements – ½ Mark each] [Mar 13 old course]
- Q.20. Distinguish between lanthanoids and actinoids. Refer Q.123. [Any four distinguishing points – ½ Mark each] [Oct 15; Mar 16]
- Q.21. Write four points of distinction between lanthanoids and actinoids. Refer Q.123. [Any four distinguishing points – ½ Mark each] [July 16]

### Multiple Choice Questions

- The general outer electronic configuration of transition elements is \_\_\_\_\_.  
 (A)  $(n-1) d^{1-10} ns^1$  (B)  $(n-1) d^{10} ns^2$   
 (C)  $(n-1) d^{1-10} ns^{1-2}$  (D)  $(n-1) d^5 ns^1$
- Which of the following is a lanthanoid?  
 (A) Ta (B) Th  
 (C) Lu (D) Rh
- Which of the following belongs to the actinoid series?  
 (A) U (B) Yb  
 (C) Lu (D) Tb
- Lanthanoid contraction implies \_\_\_\_\_.  
 (A) decrease in density  
 (B) decrease in mass  
 (C) decrease in ionic radii  
 (D) decrease in radioactivity
- Which one of the following does NOT show different oxidation states?  
 (A) Iron (B) Copper  
 (C) Zinc (D) Manganese
- When KOH solution is added to potassium dichromate solution the colour of solution changes to yellow, because \_\_\_\_\_. [Oct 13]  
 (A) chromate ion changes to dichromate ion  
 (B) dichromate ion changes to chromate ion.  
 (C) oxidation number of chromium changes from + 6 to + 4.  
 (D) oxidation number of chromium changes from + 4 to +6.
- In  $KMnO_4$ , oxidation number of Mn is \_\_\_\_\_.  
 (A) +2 (B) +4  
 (C) +6 (D) +7
- Which of the following would be diamagnetic?  
 (A)  $Cu^{2+}$  (B)  $Ni^{2+}$   
 (C)  $Cd^{2+}$  (D)  $Ti^{3+}$
- Which among the following pairs is NOT a chemical twin? [Mar 13 old course; Mar 14]  
 (A) Mo - W  
 (B) Nb - Mo  
 (C) Nb - Ta  
 (D) Zr - Hf
- Which of the following has the maximum number of unpaired electrons?  
 (A)  $Fe^{2+}$  (B)  $Cr^{3+}$   
 (C)  $Fe^{3+}$  (D)  $Co^{2+}$
- Which of the following is a component of Ziegler-Natta catalyst?  
 (A)  $V_2O_5$  (B)  $TiCl_4$   
 (C)  $CuCl_2$  (D)  $NiCl_2$
- Which of the following ions has the highest magnetic moment?  
 (A)  $Ti^{3+}$  (B)  $Sc^{3+}$   
 (C)  $Mn^{2+}$  (D)  $Zn^{2+}$
- Which lanthanoid has the smallest atomic radius?  
 (A) Gadolinium  
 (B) Scandium  
 (C) Lutetium  
 (D) Cerium



14. The lanthanoid contraction is responsible for the fact that Zr and \_\_\_\_\_.  
(A) Y have about same radius  
(B) Nb have similar oxidation state  
(C) Hf have about same radius  
(D) Zn have same oxidation state
15. The atomic number of an element is 22. The highest oxidation state exhibited by it in its compounds is \_\_\_\_\_.  
(A) 1 (B) 2  
(C) 3 (D) 4
16. A reduction in atomic size with increase in atomic number is a characteristic of \_\_\_\_\_.  
(A) inert gases  
(B) inner transition elements  
(C) halogens  
(D) all of these
17. The elements belonging to the first transition series have atomic number from \_\_\_\_\_.  
(A) 19 to 37 (B) 22 to 32  
(C) 24 to 30 (D) 21 to 30
18. The variable valency in transition elements occurs due to \_\_\_\_\_.  
(A) difference in the energies between the  $(n - 1)$  d and np electrons  
(B) similarity in the energies between the ns and np electrons  
(C) similarity in the energies between the ns and  $(n - 1)$  d electrons  
(D) difference in the energies between the ns and  $(n - 1)$  d electrons
19. Zinc is a member of 12<sup>th</sup> group of periodic table. The other members of this group are \_\_\_\_\_.  
(A) boron and aluminium  
(B) cadmium and mercury  
(C) silver and gold  
(D) tin and lead
20. Which one of the following ions is colourless?  
(A)  $\text{Cu}^+$  (B)  $\text{Co}^{2+}$   
(C)  $\text{Ni}^{2+}$  (D)  $\text{Fe}^{3+}$
21. The d-block elements include \_\_\_\_\_.  
(A) both metals and non-metals  
(B) only non-metals  
(C) only metals  
(D) metals, non-metals and metalloids
22. The most abundant transition metal is \_\_\_\_\_.  
(A) Zn (B) Fe  
(C) Hg (D) Au
23. Which of the following statement is NOT TRUE?  
(A) Colourless compounds of transition elements are paramagnetic.  
(B) Coloured compounds of transition elements are paramagnetic.  
(C) Colourless compounds of transition elements are diamagnetic.  
(D) Transition elements form the complex compounds.
24. The maximum oxidation state shown by actinoids is \_\_\_\_\_.  
(A) +6 (B) +7  
(C) +5 (D) +4
25. The element with the electronic configuration  $[\text{Xe}] 4f^{14} 5d^1 6s^2$  is a/an \_\_\_\_\_.  
(A) trans-uranic element  
(B) transition element  
(C) lanthanoid  
(D) actinoid
26. With increase in atomic number, the ionic radii of actinoids, \_\_\_\_\_.  
(A) contract slightly  
(B) increase gradually  
(C) show no change  
(D) change irregularly
27. 5d orbital contains one electron in 5d subshell in case of \_\_\_\_\_.  
(A) La, Gd and Lu  
(B) Tb, Nd and Ho  
(C) Ce, Pr and Sm  
(D) Tm, Yb and Dy
28. The Lanthanoid ions are coloured due to \_\_\_\_\_.  
(A) d-d transition (B) d-f transition  
(C) f-f transition (D) All of these
29. What is the geometry of chromate ion?  
[Mar 15]  
(A) Tetrahedral (B) Octahedral  
(C) Trigonal planar (D) Linear
30. Actinoids \_\_\_\_\_.  
(A) are all synthetic elements  
(B) include element 104  
(C) are non-radioactive  
(D) have variable valency
31. Ni has valuable catalytic properties in process involving \_\_\_\_\_.  
(A) halogenation (B) oxidation  
(C) hydrogenation (D) nitration



32. Which ion has the highest ionic radii?  
 (A)  $\text{Cr}^{3+}$  (B)  $\text{Mn}^{3+}$   
 (C)  $\text{Fe}^{3+}$  (D)  $\text{Co}^{3+}$
33. Actinoid and Lanthanoid are placed respectively in \_\_\_\_\_.  
 (A) third group and 6th and 7th period of periodic table  
 (B) fourth group and 7th and 6th period of periodic table  
 (C) third group and 7th and 6th period of periodic table  
 (D) fourth and third group of the periodic table
34. \_\_\_\_\_ is paramagnetic in nature.  
 (A)  $\text{La}^{3+}$  (B)  $\text{Lu}^{3+}$   
 (C)  $\text{Gd}^{3+}$  (D)  $\text{Ce}^{4+}$
35. Which of the following factors may be regarded as the main cause of lanthanoid contraction?  
 (A) The extent of shielding for electrons is less in 4f subshell as compared to electrons in 5d subshell.  
 (B) The extent of shielding for electrons is more in 4f subshell as compared to electrons in 5d subshell.  
 (C) The extent of shielding for electrons is less in 6s subshell as compared to electrons in 5d subshell.  
 (D) The extent of shielding for electrons is more in 6s subshell as compared to electrons in 5d subshell.
36. Cerium can show the oxidation state of +4 because, \_\_\_\_\_.  
 (A) it resembles alkali metals  
 (B) it has very low value of I.E.  
 (C) of its tendency to attain noble gas configuration of xenon  
 (D) of its tendency to attain  $4f^7$  configuration
37. Which is the strongest base among the following?  
 (A)  $\text{La}(\text{OH})_3$  (B)  $\text{Lu}(\text{OH})_3$   
 (C)  $\text{Ce}(\text{OH})_3$  (D)  $\text{Yb}(\text{OH})_3$
38. Contraction in atomic and ionic radii is shown by \_\_\_\_\_.  
 (A) lanthanoids but not actinoids  
 (B) actinoids but not lanthanoids  
 (C) both lanthanoids and actinoids  
 (D) neither lanthanoids nor actinoids
39. Chemical formula of pyrolusite is \_\_\_\_\_.  
 (A)  $\text{Mn}_2\text{O}_3$  (B)  $\text{MnO}_3$   
 (C)  $\text{MnO}_2$  (D)  $\text{Mn}_2\text{O}_7$
40. Which one of the following ions is coloured?  
 (A)  $\text{Sc}^{3+}$  (B)  $\text{Ti}^{4+}$   
 (C)  $\text{Zn}^{2+}$  (D)  $\text{V}^{2+}$
41. In which of the following pair highest oxidation states of transition metals are found? [Mar 13]  
 (A) nitriles and chlorides  
 (B) fluorides and chlorides  
 (C) fluorides and oxides  
 (D) nitriles and oxides
42. What is the molecular formula of chromyl chloride? [Oct 15]  
 (A)  $\text{CrO}_2\text{Cl}_2$  (B)  $\text{CrOCl}_2$   
 (C)  $\text{CrCl}_3$  (D)  $\text{Cr}_2\text{OCl}_2$
43. Which one of the following oxidation state of manganese is unstable? [July 16]  
 (A) +2 (B) +4  
 (C) +5 (D) +7

#### Answers to Multiple Choice Questions

1. (C) 2. (C) 3. (A) 4. (C)  
 5. (C) 6. (B) 7. (D) 8. (C)  
 9. (B) 10. (C) 11. (B) 12. (C)  
 13. (C) 14. (C) 15. (D) 16. (B)  
 17. (D) 18. (C) 19. (B) 20. (A)  
 21. (C) 22. (B) 23. (A) 24. (B)  
 25. (C) 26. (A) 27. (A) 28. (C)  
 29. (A) 30. (D) 31. (C) 32. (A)  
 33. (C) 34. (C) 35. (A) 36. (C)  
 37. (A) 38. (C) 39. (C) 40. (D)  
 41. (C) 42. (A) 43. (C)