Class-12 Chemistry Chapter-08: The d and f Block Elements

- **The d -Block elements:**
  a) The elements lying in the middle of periodic table belonging to groups 3 to 12 are known as d – block elements.
  b) Their general electronic configuration is (n – 1) d^{1-10} ns^{1-2} where (n – 1) stands for penultimate (last but one) shell.
- **Transition element:**
  a) A transition element is defined as the one which has incompletely filled *d* orbitals in its ground state or in any one of its oxidation states.
  b) Zinc, cadmium, mercury are not regarded as transition metals due to completely filled d – orbital.

1st Series

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Z	21	22	23	24	25	26	27	28	29	30
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10

2nd Series

	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Z	39	40	41	42	43	44	45	46	47	48
5s	2	2	1	1	1	1	1	0	1	2
4d	1	2	4	5	6	7	8	10	10	10

3rd Series

	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Z	57	72	73	74	75	76	77	78	79	80
6s	2	2	2	2	2	2	2	1	1	2
5d	1	2	3	4	5	6	7	9	10	10

4th Series

	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn
Z	89	104	105	106	107	108	109	110	111	112
7s	2	2	2	2	2	2	2	2	1	2
6d	1	2	3	4	5	6	7	8	10	10

- **The f-Block elements:**
  The elements constituting the *f* -block are those in which the 4 *f* and 5 *f* orbitals are progressively filled in the latter two long periods.
- **Lanthanoids**:

The 14 elements immediately following lanthanum, i.e., Cerium (58) to Lutetium (71) are called lanthanoids. They belong to first inner transition series. Lanthanum (57) has similar properties. Therefore, it is studied along with lanthanoids.

- **Actinoids:**
  The 14 elements immediately following actinium (89), with atomic numbers 90 (Thorium) to 103 (Lawrencium) are called actinoids. They belong to second inner transition series. Actinium (89) has similar properties. Therefore, it is studied along with actinoids.
- **Four transition series:**

a) 3d – transition series. The transition elements with atomic number 21(Sc) to 30(Zn) and having incomplete 3d orbitals is called the first transition series.

b) 4d – transition series. It consists of elements with atomic number 39(Y) to 48 (Cd) and having incomplete 4d orbitals. It is called second transition series.

c) 5d – transition series. It consists of elements with atomic number 57(La), 72(Hf) to 80(Hg) having incomplete 5d orbitals. It is called third transition series.

d) 6d – transition series. It consists of elements with atomic number 89(Ac), 104(Rf) to 112(Uub) having incomplete 6d orbitals. It is called fourth transition series.

- **General Characteristics of transition elements:**

  a) Metallic character:
  All transition elements are metallic in nature, i.e. they have strong metallic bonds. This is because of presence of unpaired electrons. This gives rise to properties like high density, high enthalpies of atomization, and high melting and boiling points.

  b) Atomic radii: The atomic radii decrease from Sc to Cr because the effective nuclear charge increases. The atomic size of Fe, Co, Ni is almost same because the attraction due to increase in nuclear charge is cancelled by the repulsion because of increase in shielding effect. Cu and Zn have bigger size because the shielding effect increases and electron- electron repulsions increases.

  c) Lanthanoid Contraction:

The steady decrease in the atomic and ionic radii of the transition metals as the atomic number increases. This is because of filling of 4f orbitals before the 5d orbitals. This contraction is size is quite regular. This is called lanthanoid contraction.It is because of lanthanoid contraction that the atomic radii of the second row of transition elements are almost similar to those of the third row of transition elements.

d) Ionization enthalpy:

There is slight and irregular variation in ionization energies of transition metals due to irregular variation of atomic size. The I.E. of 5d transition series is higher than 3d and 4d transition series because of Lanthanoid Contraction. The three reasons responsible for the value of ionization enthalpies are attraction of each electron towards nucleus, repulsion between the electrons and the exchange energy.

e) Oxidation state:

Transition metals show variable oxidation states due to tendency of (n-1)d as well as ns electrons to take part in bond formation. The elements with higher number of oxidation states are found in or near middle of the series. For example, Mn exhibits all the oxidation states from +2 to +7. Scandium appears as an exception to this as it does not show variable oxidation states other then +1.

f) Magnetic properties:

Most of transition metals are paramagnetic in nature due to presence of unpaired electrons. It increases from Sc to Cr and then decreases because number of unpaired and then decrease because number of unpaired electrons increases from Sc to Cr and then decreases. The magnetic moment increases with the increasing number of unpaired electrons.

g) Catalytic properties:

Most of transition metals are used as catalyst because of (i) presence of incomplete or empty d – orbitals, (ii) large surface area, (iii) variable oxidation state, (iv) ability to form complexes, e.g., Fe, Ni, V2O3, Pt, Mo, Co and used as catalyst. For example: Vanadium oxide in contact process, finely divided Iron in Haber's process and Nickel in Catalytic Hydrogenation.

h) Formation of colored compounds:

They form colored ions due to presence of incompletely filled d – orbitals andunpaired electrons, they can undergo d – d transition by absorbing colour from visible region and radiating complementary color. The frequency of the light adsorbed is determined by the nature of the ligand.

i) Formation of complexes:

Complexes compounds are those in which the metal ions bind a number of anions or neutral molecules giving complex species with characteristic properties. Transition metals form complexes due to (i) presence of vacant d – orbitals of suitable energy (ii) smaller size (iii) higher charge on cations.

j) Interstitial compounds:

Transition metals have voids or interstitials in which C, H, N, B etc. can fit into resulting in formation of interstitial compounds. They are non – stoichiometric, i.e., their composition is not fixed, e.g., steel. They are harder and less malleable and ductile. The main physical and chemical properties of these interstitial compounds are as follows:

I. They have high melting points, higher than those of pure metals.
II. They are very hard, some borides approach diamond in hardness.
III. They retain metallic conductivity.
IV. They are chemically inert.

k) Alloys formation: an alloy is a blend of metals prepared by mixing the components. Alloys may be homogenous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other. They form alloys due to similar ionic size. Metals can replace each other in crystallattice, e.g., brass, bronze, steel etc.

The alloys so formed are hard and have often high melting points. The best known are ferrous alloys: Chromium, Vanadium, Tungsten, Molybdenum and manganese are used for the production of a variety of steels and stainless steels. The alloys of transition metals with non-transition metals such as brass(copper- zinc) and bronze (copper-tin) are of considerable industrial importance.

l) Chemical Reactivity: Many transition metals are electropositive. Hence, they dissolve in mineral acids. Few of them are noble and are unaffected by simple acids. Metals of the first series are relatively more reactive and are oxidized by 1MH^+.

- **Preparation of Potassium dichromate ($K_2Cr_2O_7$):**

  It is prepared by fusion of chromate ore ($FeCr_2O_4$) with sodium carbonate in excess ofair.

  $$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

  $$\underset{Sodium\ Chromate}{2Na_2CrO_4} + H_2SO_4 \rightarrow \underset{Sodium\ Dichromate}{Na_2Cr_2O_7} + H_2O + Na_2SO_4$$

  $$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$$

- **Effect of pH on chromate and dichromate ions:**

  The chromates and dichromates are inter-convertible in aqueous solution depending upon pH of the solution. The oxidation state of chromium in chromate and dichromate is the same.

  $$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$$

  $$Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$$

- **Potassium dichromate acts as a strong oxidizing agent in acidic medium:**

  $$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

- **Preparation of Potassium permanganate ($KMnO_4$):**

  a) Potassium permanganate is prepared by fusion of MnO_4 with alkali metal hydroxide (KOH) in presence of O_2 or oxidising agent like KNO_3. It produces dark green K_2MnO_4 which undergoes oxidation as well as reduction in neutral or acidic solution to give permanganate.

  $$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

  $$4H^+ + 3MnO_4^{2-} \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

  b) Commercially, it is prepared by the alkaline oxidative fusion of MnO_2 followed by the electrolytic oxidation of manganate (Vl).

  $$MnO_2 \xrightarrow{\text{Fused with KOH, oxidised with air or KNO3}} MnO_4^{2-}$$

  $$MnO_4^{2-} \xrightarrow{electrolytic\ oxidation\ in\ alkaline\ medium} MnO_4^- (Purple)$$

Green

c) In laboratory, Mn^{2+} salt can be oxidized by peroxodisulphate ion to permanganateion.

In acidic medium: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

In neutral or faintly basic medium: $MnO_4^- + 3e^- + 2H_2O \rightarrow MnO_2 + 4OH^-$

- **Properties of Lanthanoids:**
  a) All the lanthanoids are silvery white soft metals and tarnish rapidly in air. Hardness increases with the atomic number.
  b) Their melting point ranges between 1000 to 1200 K with Samarium as an exception which melts at 1623 K.
  c) They liberate hydrogen gas from dilute acids and burns in halogens to form halides.
  d) +3 oxidation state is most common along with +2 and +4.
  e) Atomic size: the overall decrease in atomic and ionic radii from lanthanum to lutetium which is known as Lanthanide contraction is the unique feature of the lanthanides.
  f) Except Promethium, they are non – radioactive.
  g) The magnetic properties of lanthanoids are less complex than actinoids.

Table : electronic configuration of actinoids

Name of the element	Atomic number	Symbol	Electronic configuration
Actinium	89	Ac	[Rn] $5f^0$ $6d^1$ $7s^2$
Thorium	90	Th	[Rn] $5f^0$ $6d^2$ $7s^2$
Protactinium	91	Pa	[Rn] $5f^2$ $6d^1$ $7s^2$
Uranium	92	U	[Rn] $5f^3$ $6d^1$ $7s^2$
Neptunium	93	Np	[Rn] $5f^4$ $6d^1$ $7s^2$
Plutonium	94	Pu	[Rn] $5f^6$ $6d^0$ $7s^2$
Americium	95	Am	[Rn] $5f^7$ $6d^0$ $7s^2$
Curium	96	Cm	[Rn] $5f^7$ $6d^1$ $7s^2$
Berkelium	97	Bk	[Rn] $5f^9$ $6d^0$ $7s^2$
Californium	98	Cf	[Rn] $5f^{10}$ $6d^0$ $7s^2$
Einstenium	99	Es	[Rn] $5f^{11}$ $6d^0$ $7s^2$
Fermium	100	Fm	[Rn] $5f^{12}$ $6d^0$ $7s^2$
Mendelevium	101	Md	[Rn] $5f^{13}$ $6d^0$ $7s^2$
Nobelium	102	No	[Rn] $5f^{14}$ $6d^0$ $7s^2$
Lowrentium	103	Lr	[Rn] $5f^{14}$ $7s^2$ $7p^1$

- **Properties of Actinoids:**
  a) All actinoids are believed to have the electronic configuration of $7s^2$ with variable occupancy of the 5f and 6d subshells.
  b) The actinoids are silvery in appearance but show a variety of structures.
  c) Actinoids are highly reactive metals especially when finely divided.
  d) Actinoids also show higher oxidation states such as +4, +5, +6 and +7.
  e) They are radioactive.
  f) The magnetic properties of the actinoids are more complex than those of thelanthanoids.
  g) They are more reactive.

Element	Symbol	Electronic Configuration
Cerium	Ce	[Xe] $4f^1\ 5d^1\ 6s^2$
Praseodymium	Pr	[Xe] $4f^3\ 6s^2$
Neodymium	Nd	[Xe] $4f^4\ 6s^2$
Promethium	Pm	[Xe] $4f^5\ 6s^2$
Samarium	Sm	[Xe] $4f^6\ 6s^2$
Europium	Eu	[Xe] $4f^7\ 6s^2$
Gadolinium	Gd	[Xe] $4f^7\ 5d^1\ 6s^2$
Terbium	Tb	[Xe] $4f^9\ 6s^2$
Dysprosium	Dy	[Xe] $4f^{10}\ 6s^2$
Holmium	Ho	[Xe] $4f^{11}\ 6s^2$
Erbium	Er	[Xe] $4f^{12}\ 6s^2$
Thulium	Tm	[Xe] $4f^{13}\ 6s^2$
Ytterbium	Yb	[Xe] $4f^{14}\ 6s^2$
Lutetium	Lu	[Xe] $4f^{14}\ 5d^1\ 6s^2$

Applications of d- and f- block Elements

- Some compounds are manufactured for special purposes such as TiO for the pigment industry.
- MnO_2 is used in dry battery cells.
- $TiCl_4$ and Triethyl aluminum forms the basis of Zeigler Natta catalysts for manufacture of stereoselective polymers.
- Light sensitive properties of AbBr are used in photography industry.
- Many of the metals and/ or their compounds are used as essential catalysts in the chemical Industry.

- **Mischmetall**
  a) It is a well-known alloy which consists of a lanthanoid metal (~ 95%) and iron (~5%) and traces of S, C, Ca and Al.
  b) A good deal of mischmetall is used in Mg-based alloy to produce bullets, shell andlighter flint.