CHAPTER 17

D- AND F-BLOCK ELEMENTS

17.1 D-BLOCK (TRANSITION ELEMENTS)

- Their general outer electronic configuration is (n – 1) d^{1-10} ns^{0-2} (where n is the outermost shell).

Known as	**Reason**
First transition series (3d-series)	Sc (At. No. 21) to Zn (At. No. 30)
Second transition series (4d-series)	Y (At. No. 39) to Cd (At. No. 48)
Third transition series (5d-series)	La (At. No. 57) to Hf (At. No. 72) to Hg (At. No. 80)
Fourth transition series (6d-series)	Ac (At. No. 89) to Rf (At. No. 104) to Cn (At. No. 112)

17.1.1 Electronic Configuration

The d-orbitals of the transition elements project to the periphery of an atom more than the other orbitals (i.e., s and p), hence they are more influenced by the surroundings as well as affecting the atoms or molecules surrounding them.

These elements exhibit certain characteristic properties such as display of a variety of oxidation states, formation of coloured ions and entering into complex formation with a variety of ligands.

In case of transition elements there is greater horizontal similarities in the properties. It is due to the fact that in a transition series there is no change in the number of electrons of outermost shell and only change occurs in the (n – 1) d electrons from member to member in a period.

17.1.2 Physical Properties

Presence of unpaired d-electrons favours covalent bond formation, hence greater the number of unpaired d-electrons, more is the number of covalent bonds resulting in hard metals.

The high melting points of these metals are attributed to the involvement of greater number of electrons from (n – 1)d in addition to the ns electrons in the interatomic metallic bonding. In any row, the melting points of these metals rise to a maximum at d^5. The maxima at about the middle of each series indicate that one unpaired electron per d-orbital is particularly favourable for strong interatomic interaction.

Cr, Mo and W are very hard metals as they have maximum number of unpaired orbitals while Zn, Cd and Hg are softer in nature as they do not have any unpaired d-orbitals.

All transition elements have higher melting points as compared to s-block elements due to strong metallic bonding as well as unpaired d-electron leading to covalence nature.

17.1.3 Variation in Atomic and Ionic Sizes

In general, ions of the same charge in a given series show progressive decrease in radius with increasing atomic number. This is due to the fact that effective nuclear charge increases gradually with ineffective shielding created by d-electrons.

When atomic sizes of one series are compared with those of the corresponding elements in the other series, the curves show an increase from the first (3d) to the second (4d) series of the elements but the radii of the third (5d) series are virtually the same as those of the corresponding members of the second series. This phenomenon is associated with the intervention of the 4f orbitals which must be filled before the 5d series of elements begin. The filling of 4f before 5d orbital results in a regular decrease in atomic radii called

lanthanoid contraction which essentially compensates for the expected increase in atomic size with increasing atomic number.

The net result of the lanthanoid contraction is that the second and the third d-series exhibit similar radii (e.g., Zr 160 pm and Hf 159 pm) and have very similar physical and chemical properties much more than that expected on the basis of usual family relationship. The shielding of one 4f electron by another is less than that of one d-electron by another, and as nuclear charge increases along the series, there is fairly regular decrease in the size of the entire $4f^n$ orbitals.

17.1.4 Density

The decrease in metallic radius coupled with increase in atomic mass results in a general increase in density. In a period on moving from left to right density increases significantly and then, decreases for the last element. However, while moving from top to bottom in a group of d-block density increases. Highest density is observed in case of osmium which is equal to 22.57g/cm^3.

17.1.5 Ionization Energy

Due to an increase in nuclear charge there is an increase in ionization enthalpy along each series of the transition elements from left to right. These values show that the successive enthalpies of these elements do not increase as steeply as in the main group elements. The magnitude of the increase in the second and third ionization enthalpies for the successive elements, in general is much higher, and removal of one electron alters the relative energies of 4s and 3d orbitals. So, the unipositive ions have d^n configurations with no 4s electrons. Due to transfer of electron from 4S to 3d oribital, exchange energy increases which compensate the ionization energy. Smaller the ionization enthalpy of a metal greater will be the thermodynamic stability of its compound.

	$IE_1 + IE_2$ (MJ/mol)	$IE_3 + IE_4$ (MJ/mol)
Ni	2.49	8.8
Pt	2.66	6.7

From these values it is clear that Ni^{2+} compounds are more stable than Pt^{2+} compound but the Pt^{4+} compounds are more stable than Ni^{4+} compounds.

17.1.6 Standard Electrode Potentials

More the negative standard reduction potential of an ion greater will be its stability inside the solution.

Standard reduction potential value depends upon following factors:

(i) Heat of atomization
(ii) Ionization energy
(iii) Heat of hydration

$$\begin{tikzcd} M_{(s)} \arrow[r, "\Delta H^\circ_{ox}"] \arrow[d, "\Delta H^\circ_a"'] & M^+_{(aq)} \\ M_{(g)} \arrow[r, "\Delta H^\circ_i"'] & M^+_{(g)} \arrow[u, "\Delta H^\circ_{hyd}"'] \end{tikzcd}$$

$$\Delta H^\circ_{ox} = \Delta H^\circ_a + \Delta H^\circ{}_i + \Delta H^\circ_{hyd}$$

Metals having negative E° values have high enthalpy of atomization, high enthalpy of ionization and low enthalpy of hydration.

17.1.7 Oxidation State

The stability of a particular oxidation state depends upon the nature of the element with which the transition metal forms the compound. The highest oxidation states are found in fluorides and oxides. Since fluorine and oxygen are the most EN elements, their compounds posses highest lattice enthalpy as well as bond strength. Ruthenium in second transition series and osmium in third transition series has +8 oxidation states.

In case of transition elements their oxidation state differ by unity contrary to main group elements where oxidation state differ by two units. In case of p-block element while moving from top to bottom in the group stability of lower oxidation state increases, whereas in case of d-block element on moving from top to bottom in the group stability of higher oxidation state increases. M_n acquired +7 oxidation state in the form oxyfluoride MnO_3F rather than simple halide and beyond manganese no metal has trihalide except FeX_3 and CoF_3. However, fluorides are unstable in the lower oxidation state and similar result is observed. In case of CuX (X = Cl, Br, and I), on the other hand, all cupric halides are unknown except the iodide because Cu^{2+} oxidizes I^- to I_2.

$$2Cu^{2+} + 4I^{-} \rightarrow Cu_2I_{2(s)} + I_2$$

In aqueous solution, Cu^{2+} $^{-}$is more stable when compared to Cu^+ because of high hydration enthalpy of Cu^{2+}.

17.1.8 Complexes

Tendency to form complexes by transition metals is due to

- their smaller size
- higher nuclear charge
- presence of low energy vacant d-orbitals to accept lone pair of electrons donated by ligands
- Complexes where the metal is in +3 oxidation state are generally more stable than those where the metal is in +2 oxidation state.

17.1.9 Chemical Reactivity and E° values

They differ widely in terms of their chemical reactivity. The metals of first series with the exception of copper are relatively more reactive and oxidized by 1 M – H^+. However, the rate of liberation of H_2 is very poor because some of these metals get protected due to the formation of an inert oxide film on their surface e.g., Cr inspite of having highly –ve standard red potential values is SQ unreactive that it does not liberate H_2 on account of the formation of coating of Cr_2O_3 on its surface.

This general trend towards less negative $E^{\ominus}$ values is related to the increase in the sum of the first and second ionization enthalpies. It is interesting to note that the $E^{\ominus}$ values for Mn, Ni and Zn are more negative than expected from the general trend. However, the stabilities of half-filled d-subshell (d^0) in Mn^{2+} and completely filled d-subshell (d^{10}) in zinc are related to their E^e values; for nickel , E^0 value is related to the highest negative enthalpy of hydration. Mn^{3+} and Co^{3+} ions are the strongest oxidizing agents in aqueous solutions. The ions Ti^{2+}, V^{2+} and Cr^{2+} are strong reducing agents and will liberate hydrogen from a dilute acid.

17.1.10 Oxides/Hydroxides

Covalent character and acidity of oxides and hydroxides directly depend on oxidation state of transition metal atom present. As the oxidation state increases, their acidity and covalent character also increases.

Element	Basic	Amphoteric	Acidic
V	VO, V_2O_3	VO_2	V_2O_5
Cr	CrO, $Cr(OH)_2$	Cr_2O_3, $Cr(OH)_3$	CrO_3 $CrO_2\ (OH)_2$ $H_2Cr_2O_7$
Mn	MnO	Mn_3O_4 Mn_2O_3 MnO	MnO_3 Mn_2O_7
Fe	FeO, Fe_2O_3 Fe_3O_4	---------	---------
Co, Ni, Cu, Zn	CoO, NiO CuO, ZnO	---------	---------

17.1.11 Colour

They form coloured compounds.The colour of transition metal ions arises from the excitation of electrons from the d-orbitals of lower energy to the d-orbitals of higher energy. The energy required for d–d electron excitations is available in the visible range. It is for this reason that transition metal ions have the property to absorb certain radiations from the visible region and exhibit the complementary colour. The colour of light absorbed directly depends upon the nature of ligand present.

17.1.12 Magnetic Properties

Different substances possess mainly two types of magnetic behaviour. Those which are repelled by applied magnetic field are diamagnetic, whereas those which are attracted by applied field are paramagnetic substances. Another kind of substances which are attracted very strongly are called ferromagnetic. Ferromagnetism is the extreme form of paramagnetism. Total magnetism of electrons due to its orbital and spin motion is given by $\mu_{(S+L)} = \sqrt{4S(S+1)+L(L+1)}$

S is total spin, i.e., sum of spin quantum number L is the sum of orbital angular momentum quantum number. In many compounds including those of the first row transition elements the orbital contribution is compensated by the electric field of the surrounding atoms and as an approximation the observed magnetic moment may be considered to arise only from unpaired spins. Putting L = O

$$\mu_s = \sqrt{4S(S+1)} = \sqrt{4\times\frac{N}{2}\times\left(\frac{N}{2}+1\right)} = \sqrt{N(N+2)}$$

$\because \quad S = N \times 1/2$

17.1.13 Interstitial Compounds

Interstitial compounds are those which are formed when small atoms like H,C or N are trapped inside the metallic crystal lattice.

C and N always occupy octahedral holes. Hydrogen is smaller and therefore, always occupy tetrahedral holes. As only transition metals form such compounds, the d-electrons are presumably involved in such bonding. The structure of a metal generally changes during the formation of such compounds.

17.1.14 Catalytic Properties

Compounds of transition metals are able to act as catalysts due to:

- utillisation of (n – 1)d and ns-orbitals
- their ability to adopt different oxidation states
- their ability to form complexes

17.1.15 Alloy formation

Alloy is homogeneous mixture of metals. In alloys, the atoms of one metal are distributed randomly among the atoms of the other. Alloys are formed readily by transition metals because of their similar atomic size. E.g.

Ferrous alloys: Contains Cr, V, W, Mo and Mn along with Fe

Brass: Cu + Zn

Bronze: Cu + Sn

Potassium permanganate ($KMnO_4$)

Preparation:

$$\underset{\text{pyrolusite}}{2MnO_2} + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

$$2MnO_2 + 2K_2CO_3 + O_2 \rightarrow 2K_2MnO_4 + 2CO_2$$

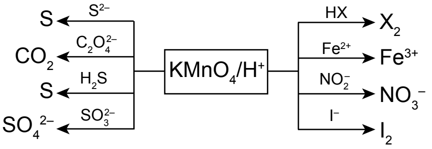
$$2K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$$

$$2K_2MnO_4 + H_2O + O_3 \rightarrow 2KMnO_4 + 2KOH + O_2$$

Properties:

It is a purple coloured crystalline substance. It is well soluble in water.

Colour of MnO_4^- is due to charge transfer by oxygen to Mn, because of which Mn changes from +7 to +6 with one unpaired e^- in 3d.



$KMnO_4$ acts as an OA in acidic, neutral and alkaline media.
Oxidizing nature in acidic medium: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
Oxidizing nature in neutral medium:

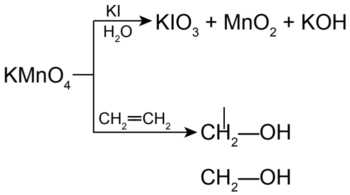
$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$

Oxidizing nature in neutral medium or dilute alkaline medium: $MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$

$MnO_4^- + e^- \rightarrow MnO_4^{2-}$ is a very strong alkaline medium.
While exposed to sunlight or heated: $2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$

$2KMnO_4 + conc.H_2SO_4 \rightarrow \underset{\text{Explosive oil}}{Mn_2O_7} + K_2SO_4 + H_2O$

(KMnO$_4$ is excess)



Potassium dischromate ($K_2Cr_2O_7$)
Preparation:

$\underset{\text{(Chromite ore)}}{FeCr_2O_4} + 8Na_2CO_3 + 7CO_2 \xrightarrow{\Delta} 8Na_2CrO_4 + Fe_2O_3 + 8CO_2$

$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

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

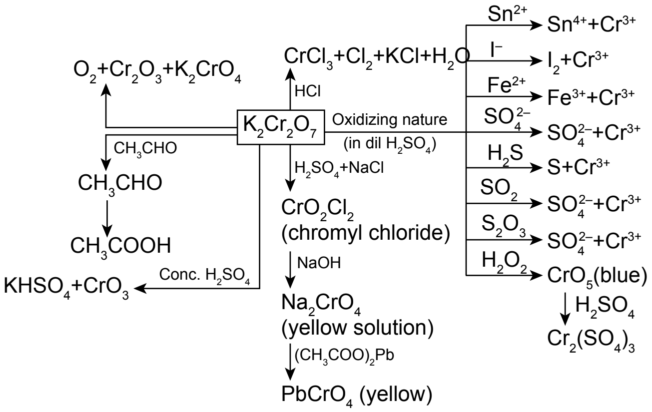
Properties:

Orange red coloured crystalline substance. Moderately soluble in cold water but freely soluble in hot water.

In alkaline solutions, orange colour of $Cr_2O_7^{2-}$ change into yellow colour due to formation of CrO_4^{2}.

Again, yellow changes to orange in an acidic medium of $pH > 7: Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$

If $pH < 7: 2CrO_4^{2-} + 2H^+ \rightarrow 2Cr_2O_7^{2-} + H_2O$



17.2 F-BLOCK (INNER-TRANSITION ELEMENTS)

- The F-block consists of two series of elements known as lanthanides and actinides.
- The general outer electronic configuration of the f-block elements is $(n-2)f^{1-14}\,(n-1)d^{0-1}\,ns^2$.

- Lanthanide ions with less than one electron have similar colour to those with (14 – x)f electrons. E.g., La^{3+} and Lu^{3+} are colourless, Sm^{3+} and Dy^{3+} are yellow coloured and Eu^{3+} and Tb^{3+} are pink coloured.
- Lanthanides differ from transition metals in the fact that their magnetic moments do not obey spin only formula. This is because in case of transition elements the orbital contribution is quenched by the electric field of the environment but in case of lanthanides 4f orbitals lie too deep to be quenched.
- Silvery white soft metals tarnish rapidly in air, samarium being steel hard, in this regard.
- General outer electronic configuration is $4f^{1-14}\,5d^{0-1}\,6s^2$.

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

- Many trivalent lanthanoid ions are coloured both in the solid state and in aqueous solutions. Colour of these ions may be attributed to the presence of f-electrons. Neither La^{3+} nor Lu^{3+} ion shows any colour but the rest do so. However, absorption bands are narrow, probably because of the excitation within f-level. The lanthanoid ions other than the f^0 type (La^{3+} and Ce^{4+}) and the f^{14} type (Yb^{2+} and Lu^{3+}) are all paramagnetic. The paramagnetism rises to maximum in neodymium.
- Their oxides are used in glass industry for polishing glass and for making coloured glasses for goggles as they gives protection against UV light and as phosphor for television screen and similar fluorescing surfaces.
- The best single use of the lanthanoids is for the production of alloy steels for plates and pipes. A (~95 per cent) and iron (~5 per cent) and traces of S, C, Ca and Al. A good deal of mischmetall is used in Mg-based alloy to produce bullets. Shell and lighter flint, mixed oxides of lanthaniods are employed as catalysts in petroleum cracking. Some individual Ln oxides are used as phosphors in television screen and similar fluorescing surfaces.

Lanthanide contraction: It is the decrease in size of atoms and ions with increase in atomic number in lanthanide series.

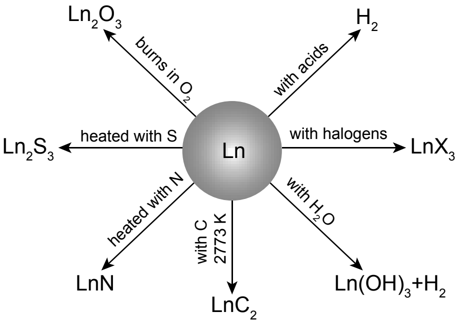
- Consequences of lanthanide contraction
  Similar chemical properties
  Decrease in basicity with decrease in the size
  Similarly of II and III transition series
- **Low ionization energies**
- Lanthanides have low values of first and second ionization energies (IE_1 and IE_2) which are closer to alkaline earth metals specially to calcium. On account of fairly low ionization energy and large atomic size, lanthanoides are strong electropositive elements

17.2.1 Oxidation States

Lanthanoids show limited number of oxidation states because the energy gap between 4f and sd subsshell is range

The E^0 value of Ce^{4+}/Ce^{3+} is +1.74 V, which suggest that it can oxidize water. However, the reaction rate is very slow and hence Ce(IV) is a good analytical reagent.

- **Coloured ions:** Due to partially filled f-orbitals which allow f–f transitions.
- La^{3+} ($4f^0$), Gd^{3+} ($4f^7$), Lu^{3+} ($4f^{14}$) → Colourless
- Ce^{3+} ($4f^1$) and Yb^{3+} ($4f^{13}$) → Colourless despite of having unpaired electrons (exceptions)
- **Chemical reactivity:** The oxides are ionic and basic.
- With air: forms M_2O_3 type oxides, (except Ce which forms CeO_2)
- With hydrogen: forms MH_3 type hydrides
- With halogen: forms MH_3 type halides
  Fluorides → insoluble
  Chlorides → deliquescent and soluble



17.2.2 Actinides

- General outer electronic configuration is $5f^{1-14}\,6d^{0-1}\,7s^2$.

Element	Atomic Number	Electronic Configuration	Oxidation Number
Ac	89	$[Rn]\ 6d^1, 7s^2$	+3
Th	90	$[Rn]6d^2, 7s^2$	+3, +4
Pa	91	$[Rn]5f^2, 6d^1, 7s^2$	+3, +4, +5
U	92	$[Rn]5f^3, 6d^1, 7s^2$	+3, +4, +5, +6
Np	93	$[Rn]5f^4, 6d^1, 7s^2$	+3, +4, +5, +6, +7
Pu	94	$[Rn]5f^6\ 7s^2$	+3, +4, +5, +6, +7
Am	95	$[Rn]5f^7, 7s^2$	+3, +4, +5, +6
Cm	96	$[Rn]5f^7\ 5d^1\ 6s^2$	+3, +4

Element	Atomic Number	Electronic Configuration	Oxidation Number
Bk	97	$[Rn]5f^9\ 7s^2$	+3, +4
Cf	98	$[Rn]5f^{10}, 7s^2$	+3
Es	99	$[Rn]5f^{11}, 7s^2$	+3
Fm	100	$[Rn]5f^{12}, 7s^2$	+3
Md	101	$[Rn]5f^{13}, 7s^2$	+3
No	102	$[Rn]5f^{14}, 7s^2$	+3
Lr	103	$[Rn]5f^{14}, 6d^1, 7s^2$	+3

- Actinide contraction is similar to lanthanide contraction.
- The ions having 2 to 6 electrons in 5d orbitals are coloured, both in crystalline and in aqueous solution, due to f–f transition.
- Ions with $5f^0$, $5f^7$ and $5f^{14}$ configurations are colourless.

Unlike lanthanoids, actinoids show a large number oxidation states. This is because of very small energy gap between 4f, 6d and 7s subshells; hence, all these electrons can take part in bonding.

The actinoids are highly reactive metals, especially when finely divided. The action of boiling water on them, for example, gives a mixture of oxide and hydride and combination with most nonmetals takes place at moderate temperatures. Hydrochloric acid attacks all metals but most are slightly affected by nitric acid owing to the formation of protective oxide layers, whereas, alkalies have no action in this regard.