

The d-block elements have a valence shell electronic configuration of  $(n-1)d^{1-10}ns^{0-2}$  where  $(n-1)$  stands for inner shell whose d-orbitals may have one to ten electrons and the s-orbitals of the outermost shell ( $n$ ) may have no electron or one or two electrons. The filling of d-orbitals takes place after the s-orbital of next higher shell has already filled as has been discussed in Aufbau principle in Unit 1 (BCH-101). This is because ns orbitals have lower energy than  $(n-1)d$  orbitals. But during ionization of the elements (oxidation), the electrons are first lost from ns level followed by the expulsion from  $(n-1)d$  subshell (deviation from the expected behaviour) because  $(n-1)d$  subshell becomes of the lower energy than ns subshell once the filling of electrons commences in  $(n-1)d$  subshell.

Most of the d-block elements show several oxidation states (variable) in their compounds due to the availability of d-electrons in the valence shell which comprises of the two subshells, *viz.*,  $(n-1)d$  and ns whose orbitals are quite close together in energy and hence the electrons can be used from both the subshells for bonding and under different conditions different number of electrons can be used by them. The variability in the oxidation states increases towards the middle of the series from both ends, i.e. left  $\rightarrow$  middle  $\leftarrow$  right. It has been observed that the d-block elements can form ionic bonds in their lower oxidation states and the ionic character of the bond decreases as well as the covalent character increases with increasing oxidation state. As a result, with decreasing ionic character the acidic character of the oxides and chlorides increases.

### 1.3.2 Complex Formation Tendency:

The cations of d-block elements are unique in their tendency to form complexes with several molecules such as ammonia, water, etc. or different ions such as cyanide,  $NO_2^-$ , halide ions, etc. These molecules or ions are called ligands. The complex forming tendency of these elements is attributed to the following factors:

- (a) Small size and high positive charge density,
- (b) Availability of vacant d-orbitals of right energy to accept the lone pairs of electrons from the approaching ligands,
- (c) Exhibition of variable oxidation states.

The detailed account of this tendency will be given in the respective sections mentioned ahead.

### 1.3.3 Magnetic Properties:

Many compounds of d-block elements exhibit magnetic properties. Qualitatively speaking, there are several kinds of magnetism. The substances which are weakly repelled by the strong magnetic field are termed as **diamagnetic** while those which are weakly attracted by the strong magnetic field are called **paramagnetic**. These substances lose their magnetism on removing the magnetic field. Diamagnetism is the property of the completely filled electronic subshells and is shown by all substances to more or less extent. Paramagnetism is produced by the presence of unpaired electrons and because most of the d-block metal atoms and ions have unpaired electrons, they are paramagnetic in behaviour.

In some transition metals (e.g. Fe, Co, Ni) unpaired electron spins are more pronounced and show much more paramagnetism than the other d-block metals. Such metals are called **ferromagnetic** metals and magnetic property shown by them is known as ferromagnetism. Such metals can be permanently magnetized. The detailed account will be given in the section 1.4 of this unit and in subsequent units.

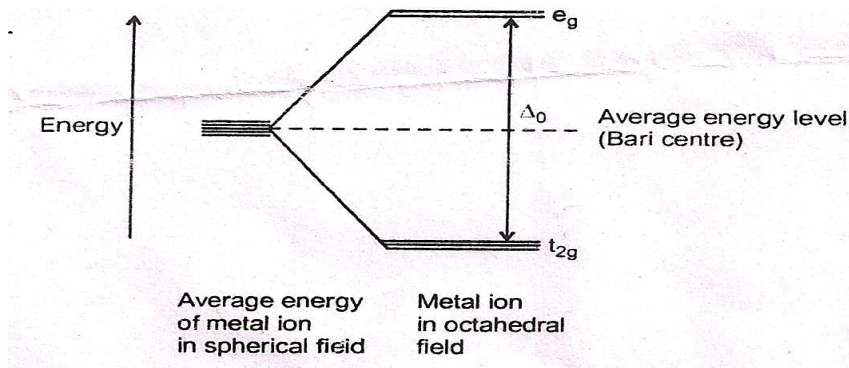
### 1.3.4 Formation of Coloured Ions/ Compounds:

The majority of compounds of d-block elements, whether ionic or covalent, are coloured in solid or solution state. This property of d-block elements is in marked difference from those of s or p-block elements which are white or light coloured.

The colour of a substance arises from the property of the substance to absorb light of certain wavelength in the region of visible light (white light) when the latter interacts with the substance. The colour of the substance is the colour of the transmitted light component and is complementary to the colour of light component absorbed. The colour of d-block metal ions is associated with

- (a) an incomplete d-subshell in the metal ion,
- (b) the nature of surrounding groups around the metal ion.

The whole act of exhibition of colour by d-block ions/compounds can be explained as follows. In a free gaseous or isolated ion the five d-orbitals are degenerate, i.e. of same energy. Since five d-orbitals are oriented differently in space, the surrounding groups affect the energy of some orbitals more than others in the compounds. This destroys their degeneracy. For example, in the simplest case of an octahedral complex, they form two groups of orbitals of different energy:



*Fig. 1.1 Bary centre*

Thus, in d-block metal ions with partially filled d-subshell, it is possible to promote electron(s) from one set of d-orbitals to another set (group) of higher energy by fairly small energy absorbed from the visible light. The colour of the compounds depends on the energy difference (gap) between the two groups (sets) of d-orbitals. This in turn depends on the nature of ligands and their arrangement around the metal ion in the compound / complex.

### 1.3.5 Catalytic Activity:

The catalytic activity of d-block elements and their compounds is associated with their variable oxidation states and their capability of forming interstitial compounds. A number of d-block metals and their compounds are known to catalyse various reactions of industrial importance, e.g., vanadium (V) oxide in the manufacture of sulphuric acid by contact process, etc. An important view of the mechanism of catalysis is that at solid surface of the catalyst, bonds would be formed between the molecules of the reactants and atoms of the catalysts thereby increasing the concentration of the reactants at the surface. This weakens the bonds of the reactant molecules due to lowering of the activation energy.