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:
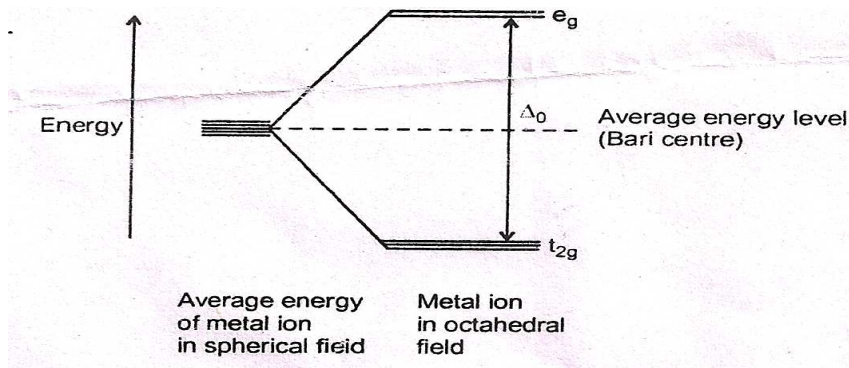

Fig. 1.1 *Bary centre*

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.

1.3.6 Formation of Interstitial and Non-stoichiometric Compounds:

The d-block elements form interstitial compounds with small non-metal atoms such as H, C, N, B, Si, etc. due to the ability of metal lattice to accommodate these non–metal atoms between the metal atoms without distortion of structure.

One of the striking properties of these metals is the formation of non-stoichiometric compounds which often exhibit semiconductivity, fluorescence and behave as heterogeneous catalysts. This non-stoichiometry is due to the defects in the solid structures.

1.3.7 Metallic Character and Alloy Formation:

All the d-block elements are metals, good conductors of heat and electricity, are malleable and ductile. All are solids except Hg (mercury) which exists as liquid at ordinary temperature.

These metals form alloys with each other due to almost similar sizes of the atoms. Thus the atoms of one metal can easily take up positions in the crystal lattice of the other. The alloys are usually harder and have higher melting points than the parent metals, are more resistant to corrosion than their constituents.

1.3.8 Periodic Properties and Their Variation along the Series:

The atomic radii, atomic volumes, ionic radii, melting and boiling points, ionization energies and reactivity, standard electrode potential and reducing properties, etc. are the important periodic properties of the d–block elements which vary and have a definite trend, in general, along each series. These will be discussed below:

a) Atomic Radii, Atomic Volumes and Ionic Radii.

The atomic radii generally decrease, with a few exceptions, on moving from left to right in each series of the transition elements due to increased nuclear charge at each step and constant value of the azimuthal quantum number (i.e. l) receiving the last electron.

The d-block elements have low atomic volumes as compared to those of the neighbouring s- and p-block elements. This is due to the fact that in these elements

(n-1) d-subshells are being filled and the increased nuclear charge pulls the electron cloud inwards.

The ionic radii of the d-block elements follow the same trend as the atomic radii, i.e. the radii of the ions having the same charge decrease with increasing atomic number. These properties will be discussed in detail for every series.

b) Melting and Boiling Points

The melting and boiling points of these elements are generally very high showing that they are held by strong forces. The melting and boiling points have the highest values in the middle of the series because, perhaps these elements have the maximum number of unpaired d-electrons available for bonding, detailed account of which will be given ahead for every series.

c) Ionization Energies and Reactivity

The ionization energy values of the d-block elements are fairly high and lie in between those of s- and p-block elements, i.e. these elements are less electropositive than s-block elements and more so than p-block elements. Hence, these elements do not form ionic compounds as readily as s-block elements and form covalent compounds as well. Because of the existence of covalent bonding, they have high heats of sublimation, i.e. a large amount of energy is required to convert them from solid to vapour state. The metal ions also do not get hydrated easily. Due to these parameters, the metal ions have a small tendency to react. Examples will be given in each series.

d) Standard Electrode Potentials and Reducing Properties

The standard reduction potential values of transition elements are generally lower (negative) than that of the standard hydrogen electrode (taken as zero). Thus they evolve H_2 gas from acids though most of them do that at low rate.

These metals are poor reducing agents which are contrary to the expected behaviour because of the high heats of vaporisation, high ionization energies and low heats of hydration. Example, if available will be given in each series.

1.4 PROPERTIES OF THE ELEMENTS OF FIRST TRANSITION SERIES

As has already been mentioned in the beginning that the first transition series is also known as 3d-series because the last or the differentiating electron in the atoms of these elements enters the 3d-subshell. This series starts at scandium, the element of Group 3 and ends at zinc, the element of Group 12, containing a total of ten elements. Thus, this series of elements lies in between calcium (Ca, Z=20) and gallium (Ga, Z=31), the elements of Group 2 and Group 13. The ten elements of the first transition series are scandium (Sc, Z=21), titanium (Ti, Z=22), vanadium (V, Z=23), chromium (Cr, Z=24), manganese (Mn, Z=25), iron (Fe, Z= 26), cobalt (Co, Z= 27), nickel (Ni, Z=28), copper (Cu, Z= 29) and zinc (Zn, Z= 30). These elements are much more important than those of second transition series. All the characteristics properties of the d-block elements are shown by the elements of first transition series which are given below:

1.4.1 Electronic Configuration and Variable Oxidation States.

The general valence shell electronic configuration of these elements is $3d^x4s^y$ where x=1 to 10 and y= 1 or 2, i.e. the 3-d subshell has one to ten electrons from Sc to Zn and 4s-subshell, in general, has two electrons (i.e. $4s^2$) except in Cr and Cu which have only one 4s electron (i.e. $4s^1$). The exceptional valence shell configuration of Cr and Cu is attributed to the exchange energy effect and the extra stability of the resulting half–filled and completely–filled subshells. "The shifting of an electron from one subshell to another of similar or slightly higher energy in order to achieve the half-filled or completely-filled subshell is known as **exchange energy effect**". The state of affairs can be shown as follows:

Cr (Z= 24): $3d^44s^2$ (expected but unstable) $\longrightarrow$ $3d^54s^1$ (actual, more stable).

Cu (Z=29): $3d^94s^2$ (expected but unstable) $\longrightarrow$ $3d^{10}4s^1$ (actual, more stable).

As is evident, there is exchange of electrons from 4s to 3d subshell thereby increasing the stability of the valence shell configuration in Cr and Cu atoms. Thus, among 3d-series elements, only Cr and Cu exhibit irregular/anomalous electronic configurations.

The first transition series elements generally show variable (many) oxidation states in their compounds / ionic forms. The cause of showing different oxidation states is that these elements have several 3d electrons which are quite close to 4s – electrons in energy. The minimum oxidation state shown by all the elements of this series is +2 except Cr and Cu which show +1 oxidation state as well. The number of oxidation states shown increases from Sc to Mn and then decreases till Zn which shows the +2 oxidation state only. As a result, among these elements, Cr and Mn show the maximum number of oxidation states from +1 to +6 and +2 to +7, respectively. From Sc to Mn, the highest oxidation state shown by any element is equal to the group number but the latter elements do not follow this trend. This is evident from the following table:

Elements:	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Group number	3	4	5	6	7	8	9	10	11	12
Lowest oxidation state	+2	+2	+2	+1	+2	+2	+2	+2	+1	+2
Highest oxidation state	+3	+4	+5	+6	+7	+6	+4	+3	+2	+2

It has been observed that the lower (+2, +3, etc.) oxidation states generally dominate the chemistry of the first transition series. For an element the relative stability of various oxidation states can be explained on the basis of the stability of d^0, d^5 and d^{10} configurations, e.g. Ti^{4+} ion $(3d^0 4s^0)$ is more stable than Ti^{3+} $(3d^1 4s^0)$ because of the presence of $3d^0$ subshell. Similarly, Mn^{2+} $(3d^5 4d^0)$ ion is more stable than Mn^{3+} $(3d^4 4s^0)$ ion since Mn^{2+} ion has $3d^5$ subshell.

It has also been observed that first transition series elements form ionic oxides and chlorides in the lower oxidation states which are basic in nature. As the oxidation state of the elements increases, covalent character and acidic nature of these compounds also increases, e.g., MnO (+2) is basic, Mn_2O_3 (+3) and MnO_2 (+4) are amphoteric and Mn_2O_7 (+7) is acidic. Similarly, CrO (+2) is basic, Cr_2O_3 (+3) is amphoteric and CrO_3 (+6) is acidic. Also VCl_2 (+2) is basic and $VOCl_3$ (+5) is acidic.

1.4.2 Complex Formation Tendency:

The elements of first transition series fulfill all conditions of complex formation and are, thus, most suitable for this purpose. As a result, the cations of these elements have a strong tendency to form complexes with certain molecules (e.g. CO, NO, NH_3, etc.) or several ions (e.g. F^-, Cl^-, CN^- etc.). These molecules and ions are called ligands (L) and have one or more lone pairs of electrons on their donor atom (usually central atom) which they donate to the metal ion/atom (M) during the process of complex formation via M←L coordinate covalent bonds. This happens because the metal ions are electron deficient in most of their oxidation states or even the atoms are electron acceptors. Small size and high charge density of the metal ions facilitate the formation of the complexes which also depends on the basicity of the ligands. The complex formation tendency increases as the positive oxidation state of the metal ion increases.

The nature of the complexes depends on the orbitals available on the metal ion / atom for bonding. These orbitals are s, p and d type. The structures commonly found in the complexes of the elements of first transition series are linear, square planar, tetrahedral and octahedral. This shows that the metal orbitals are hybridized before bonding with the ligand orbitals, e.g. $[Ni(CN)_4]^{2-}$ ion is square planar while $[NiCl_4]^{2-}$ ion is tetrahedral (detail of the complexes have been given ahead in this section).

1.4.3 Magnetic Behaviour:

As has been mentioned earlier, there are several kinds of magnetism observed in the ions /compounds or complexes of transition metals. Among the transition metal compounds paramagnetism is common though some metals in the elemental form also show ferromagnetism.

Origin of Paramagnetism

The electrons being charged particles act as tiny magnets (or micro magnets) by themselves and determine the magnetic properties of the substances in two ways:

(a) Spin motion or spinning of the electron on its axis produces spin magnetic moment and

(b) Orbital motion or the movement of the electron round the nucleus produces orbital magnetic moment.

The resultant of the above two moments gives the total moment produced by an electron. The observed magnetic moment of the compounds is the sum of the moments of all the electrons present in them. If the two electrons with opposite spins are paired in the same orbital, the magnetic moment produced by one electron is cancelled by that caused by the other electron because both the electrons will have equal but opposite moment thereby giving zero resultant magnetic moment. Such substances which have paired electrons will not show paramagnetism, rather they are diamagnetic.

But if there are unpaired electrons in the ions/atoms of the substance it has the moment produced by all the unpaired electrons. The resultant or total moment in them is sufficiently high to overcome the magnetic moment induced by an approaching magnetic field. Hence, such substances instead of experiencing repulsion, are attracted in a magnetic field and are called paramagnetic substances.

The magnetic moments of atoms, ions and molecules are expressed in units called **Bohr Magneton** (B.M.) which is defined in terms of the fundamental constants as

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

where h = Planck's constant, e = electronic charge, c = velocity of light and m = mass of electron.

The magnetic moment of a single electron is given by the expression

$$\mu_s \text{ (B.M.)} = g\sqrt{S(S+1)} \text{ (According to wave mechanics)}$$

Where S= resultant spin quantum number and g = gyromagnetic ratio (called g-factor). The quantity $\sqrt{S(S+1)}$ is the value of the spin angular momentum of the electron and thus g is the ratio of magnetic moment to the angular momentum. For a free electron, g value is nearly 2 (i.e. 2.00023).

In transition metal compounds/complexes, the unpaired electrons are present in the outer shell of metal ions and in such cases the spin component is much more

significant than the orbital contribution because the orbital motion of these electrons is said to be quenched or suppressed. Therefore, the latter can be neglected in comparison to the former. In such cases, the total magnetic moment is, therefore, considered entirely due to the spin of the unpaired electrons and μ_s is given by

$\mu_s = 2\sqrt{S(S+1)} = \sqrt{4S(S+1)}$ BM (By putting the value of $g = 2$)

Now $S = n \times s$ where $n =$ number of unpaired electrons and $s =$ spin quantum number (irrespective of its sign)

$S = n \times \frac{1}{2} = \frac{n}{2}$

Putting this value of S in the above expression

$\mu_s = \sqrt{4 \frac{n}{2} \left(\frac{n}{2}+1\right)} = \sqrt{2n \left(\frac{n+2}{2}\right)}$ B.M.

Or $\mu_s = \sqrt{n(n+2)}$ B.M.

μ_s is also expressed as $\mu_{eff.}$ i.e. effective magnetic moment which is dependent only on the number of unpaired electrons and their spins. Hence, this formula of magnetic moment is also called **spin only formula.**

Thus, the permanent magnetic moment of 3d-transition elements gives important information about the number of unpaired electrons present in them and it varies with n. The calculated magnetic moments corresponding to 1, 2, 3, 4 and 5 unpaired electrons will be (using above formula) $\sqrt{3} = 1.73$ B.M., $\sqrt{8} = 2.83$ B.M., $\sqrt{15} = 3.87$ B.M., $\sqrt{24} = 4.90$ B.M. and $\sqrt{35} = 5.92$ B.M. , respectively.

The number of unpaired electrons evaluated from the magnetic moment value for a compound/complex gives the valuable information regarding the type of orbitals that are occupied as well as those available for hybridisation and also the structure of the molecules or complexes provided we have the idea of strength of the ligands (spectrochemical series). For example, here we discuss the structure of $[MnBr_4]^{2-}$ complex ion in which Mn is in +2 oxidation state and its coordination number is 4.

Mn atom (Z=25): [Ar] $3d^5 4s^2 4p^0$

Ground state of Mn

Excited state of Mn

Hybridization state
  of Mn^{+2}

SP^3 Hybridization
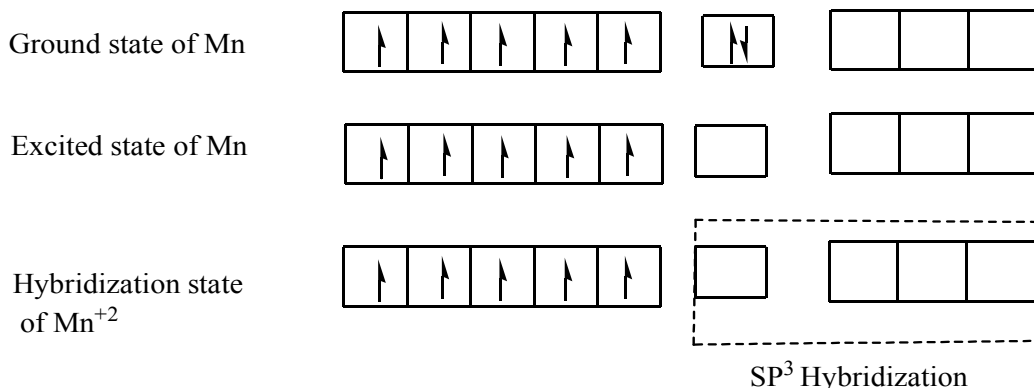
In the complex ion, Mn^{2+} ion is linked with four Br$^-$ ions as ligands which exert weak ligand field on the metal ion orbitals. As a result the five unpaired d-orbitals remain unaffected and one s and 3p empty orbitals of metal ion (only four hybrid orbitals are required) hybridise before bond formation producing sp^3 hybrid orbitals thus giving tetrahedral structure to the complex ion. The calculated magnetic moment of this complex is nearly 5.92 B.M. which indicates the presence of five unpaired electrons. If that is the situation, the tetrahedral structure of the complex ion is confirmed involving only s and p orbitals.

Similarly for the complexes with coordination number 6, i.e. six ligands are attached to the central metal ion, we can predict whether the complex is outer or inner orbital complex from the knowledge of weak and strong ligands, e.g. $[Co(H_2O)_6]^{2+}$ is an outer orbital complex and $[Co(NH_3)_6]^{2+}$ is an inner orbital complex having the central metal ion, Co^{2+} involving sp^{3}d^2 and d^{2}sp^3 hybridisation, respectively.

1.4.4 Formation of Coloured Ions/Compounds

The cause of the exhibition of colour by the ions/compounds/complexes of the d-block elements has been discussed earlier. The elements of first transition series form coloured ions/compounds/complexes due to the presence of unpaired electrons in them. For example, $[Co(H_2O)_6]^{2+}$ is pink, Cu$^+$ (d^{10}) ion and its salts are colourless but Cu^{2+} (d^9) ion and its compounds are coloured, $CuSO_4.5H_2O$ is blue which actually is represented as $[Cu(H_2O)_4]SO_4.H_2O$ and $[Cu(NH_3)_4]^{2+}$ is dark blue (almost violet). Similarly, $[Ni(NO_2)_6]^{4-}$ is red and $[Ni(NH_3)_6]^{2+}$ is blue. Among the other compounds VO_2^+ is pale yellow, CrO_4^{2-} is strongly yellow, MnO_4^- is purple in colour, and $[Ti(H_2O)_6]^{3+}$ is green coloured.

The colour of the complex ion depends on the nature of the ligands and type of complex formed. The metal ions with completely empty or completely filled d-subshell (as well as their compounds) are colourless, viz., Sc^{3+} ($3d^0$), Ti^{4+}($3d^0$), Cu^+($3d^{10}$), Zn^{2+}($3d^{10}$) etc.

1.4.5 Catalytic Activity

Elements of the first transition (3d) series and their compounds have been used in many industrial processes. Their availability in a variety of oxidation states makes them capable of forming intermediate products with various reactants and their tendency to form interstitial compounds which can absorb and activate the reacting species facilitate their application as catalyst. For example, finely divided Ni is used as a catalyst in hydrogenation reactions; MnO_2 catalyses the decomposition of H_2O_2; $TiCl_4$ is used as a catalyst for polymerisation of ethene in the manufacture of polythene; V_2O_5 is employed in the catalytic oxidation of SO_2 to SO_3 in the contact process of manufacture of H_2SO_4; Fe is used in the manufacture of NH_3 by Haber's process; Cu acts as a catalyst in the manufacture of $(CH_3)_2SiCl_2$ during the synthesis of silicones. Cu/V is used in the large scale production of Nylon-66. Fe(III) ions catalyse the reaction between iodide and peroxodisulphate ions.

1.4.6 Formation of Interstitial and Non-stoichiometric Compounds

Elements of the 3d-transition series are capable of forming interstitial compounds, e.g., Ti_2C, V_2C, ScN, TiN, Fe_4N etc. These compounds have the properties of alloys being hard and good conductors etc.

These elements also form non-stoichiometric compounds. For example, titanium forms TiO_x (x=0.65 - 1.25 and 1.998 - 2.000); vanadium forms VO_x (x= 0.79 - 1.29); manganese forms Mn_xO (x= 0.848 - 1.00); iron form Fe_xO (x = 0.833 - 0.957), etc. These compounds have variable composition and are formed due to the variability of oxidation states and solid defects. Sometimes the interstitial and non-stoichiometric compounds are the same.

1.4.7 Metallic Character and Alloy Formation

The metals of first transition series are hard, malleable and ductile. These exhibit face centered cubic (fcc), body centered cubic (bcc) or hexagonal close packed (hcp) type

of lattice structures. These metals are good conductors of heat and electricity. Copper and metals of the iron triad are softer than other metals.

The common alloys of these metals are as follows: brass (Cu-Zn), nichrome (Ni-Cr), monel metal (Cu-Ni), german silver (Cu-Ni-Zn), stainless steel (Fe-Cr-Ni-Mn), alnico steel (Fe-Ni-Co-Al), etc. These alloys are harder and have higher melting points than the parent metals. They are also more resistant to corrosion than their constituents.

1.4.8 Periodic Properties and Their Variation along the Series

The melting and boiling points, atomic and ionic radii, atomic volumes, ionization energies and standard electrode potentials along with reducing properties are the main periodic properties of these metals along the series from Sc to Zn, which are discussed below:

a) Atomic Radii, Atomic Volumes and Ionic Radii

As has been discussed earlier for d-block elements, the atomic radii of the elements of first transition series follow the same trend as is applied for other d-block elements. The values generally decrease along the series up to Ni then increase slightly for Cu but pronouncely for Zn. Thus Zn has exceptional value only lower than those for the first two elements and higher than those of others. This is evident from the following table:

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

This happens due to the increased attraction between the outer electrons and increasing nuclear charge along the period. The close values of the atomic radii from Cr to Cu are due to the existence of increased screening effect of 3d-electrons which are added in each step and which shield the 4s-electrons from the inward pull though the nuclear charge increases continuously in the series from one element to the other. The screening effect in Zn ($3d^{10}$) is maximum and hence has exceptional value.