TDC Part II
Paper I, Group B
Inorganic Chemistry

Department of Chemistry

L.S COLLEGE MUZAFFARPUR
B. R. A. BIHAR UNIVERSITY
Dr. Priyanka

TOPIC: -Origin of Paramagnetism

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

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

Where S= re~~sultan~~t 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×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

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

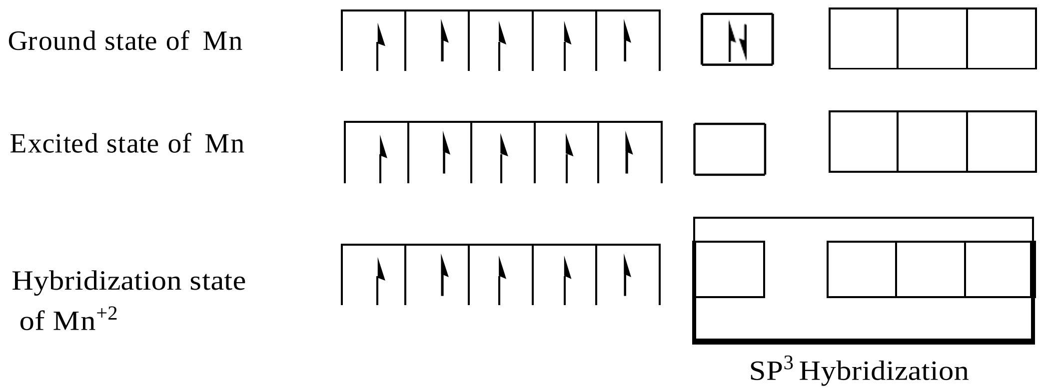
Or $\mu_s = \sqrt{n\,(n+2)}$ B.M.

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] $3d^5 4s^2 4p^0$



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^3d^2 and d^2sp^3 hybridisation, respectively.

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.

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.