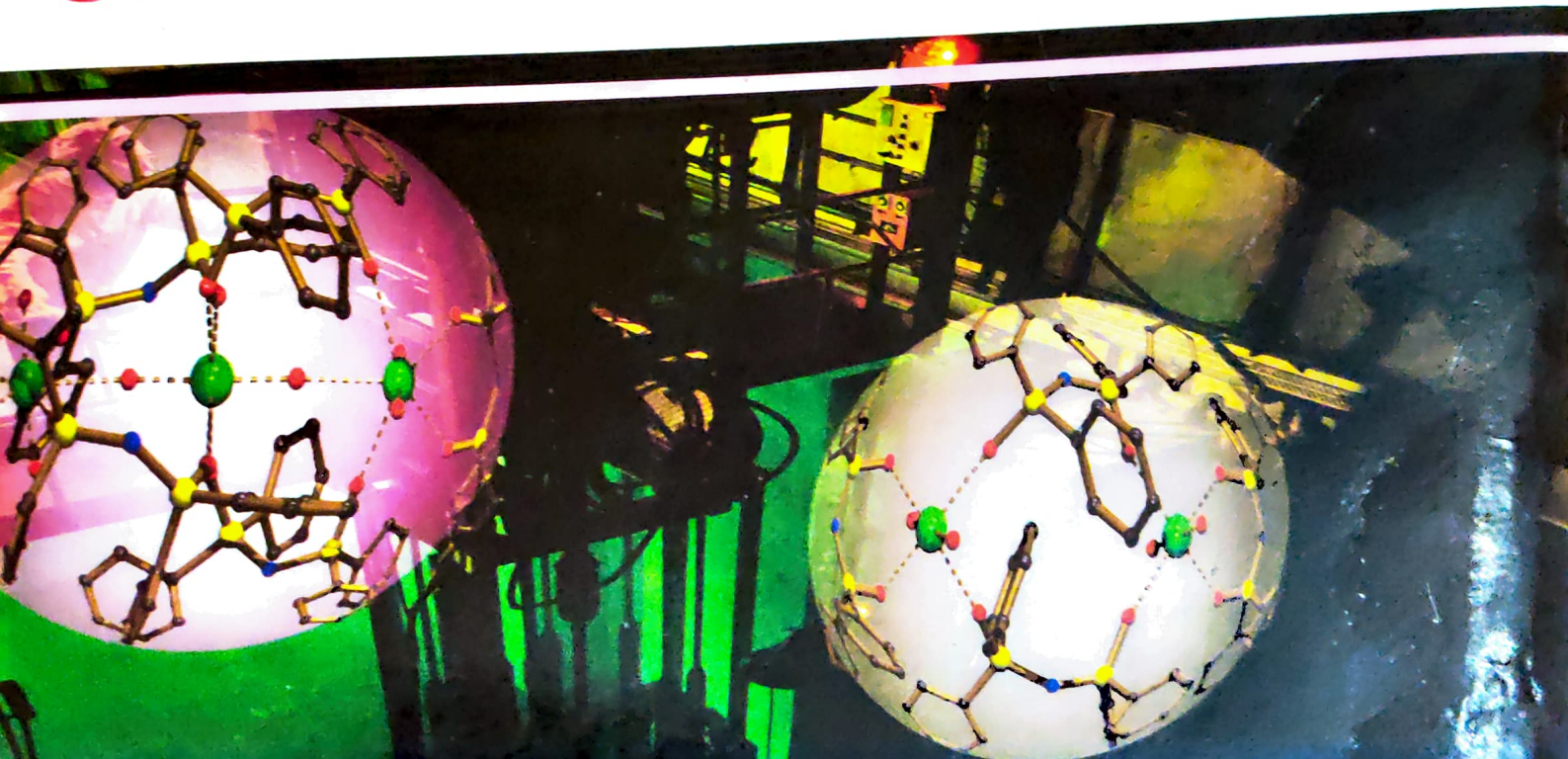


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COORDINATION CHEMISTRY



Colour and magnetic properties of a complex provides valuable informations about identification of stereochemistry of complexes.

MAGNETIC PROPERTIES

Definitions of some magnetic properties are listed below :

Pole strength : The strength of a magnet may be expressed in terms of unit pole. A unit pole may be defined as a pole that repels or attracts another unit pole placed 1 cm away with a force of 1 Dyne. Thus a unit intensity of magnetic field exists at the place where the unit pole experiences a force of 1 Dyne.

Lines of force : If a magnetic pole is placed at any point in a magnetic field, it will experience a force in the direction of the magnetic field and under the action of this force, it would move freely and follow a path, whose direction at every point is the direction of the field. Such a path is known as a line of force.

Pole strength and lines of force : A field of unit intensity is taken to give unit lines of force per square centimeter. If a pole of strength m is placed inside a sphere of radius one centimeter, then the surface area of the sphere is 4π and a total of $4\pi m$ lines of force will emerge from the pole. At the surface, the number of lines of force, per square centimeter will be given by $4\pi m/4\pi = m$ pole strength.

Magnetic field strength : Magnetic intensity at any point in a magnetic field can be defined as the force experienced by a unit pole placed at that point. This force is also known as strength of magnetic field.

$$F = \frac{m}{r^2}$$

The unit of magnetic intensity of field is oersted.

1 oersted = 1 dyne/unit pole.

Thus, if a unit pole placed at any point in the magnetic field experiences a force of H dynes, the strength of the magnetic field will be H oersted. A smaller unit of field strength is gamma (γ) 10^{-5} oersted = γ . If a pole of strength m is placed at the point in the field, the force experienced is given by $F = mH$ dynes.

Intensity of magnetisation : Intensity of magnetisation induced in a body by an applied field is expressed in terms of the pole strength induced per unit area of the body.

$$l = m/A \quad \dots (9.1)$$

m = pole strength induced over a total area A

For a magnetic dipole of length l and pole area A , we can write

$$l = \frac{m \times l}{A \times l} = \frac{\text{magnetic moment}}{\text{volume}} \quad \dots (9.2)$$

Thus, the intensity of magnetisation can be defined alternatively as magnetic moment per unit volume.

$$B = \frac{\text{Flux } \phi}{\text{Area } A}$$

Magnetic flux : The number of lines of force coming out from the pole of the magnet is called magnetic flux and is denoted by ϕ .

Magnetic induction : The lines of force per unit area is called magnetic induction or flux density. The flux density is directly proportional to magnetic field. When a sample is kept in a magnetic field of strength H (i.e., H lines of force acting per unit area) then the total lines of force coming out of the sample will be given by the sum of H and that due to the induced magnetisation. Since I represents the pole strength induced per unit area, we can write

$$\text{Magnetic induction} \quad B = H + 4\pi I \quad \dots (9.3)$$

Magnetic permeability : It is denoted by P . The permeability of the sample measures the degree to which the lines of force can penetrate or permeate a magnetic field. For air $P = 1$.

$$P = B/H = 1 + 4\pi I/H \quad \dots (9.4)$$

Magnetic permeability is, therefore, the ratio of the density of lines of force within the body to that under vacuum.

Magnetic susceptibility : The ratio I/H is known as volume susceptibility (χ_v) of the sample. This property is characteristic for a particular compound. This may be expressed as a proportionately constant.

$$I \propto H \Rightarrow I = \chi_v H \quad \dots (9.5)$$

$$\Rightarrow \chi_v = I/H \quad \dots (9.6)$$

The susceptibility may be looked upon theoretically as the response of a given sample to induced magnetisation.

Permeability and susceptibility are both dimensionless quantities.

$$\text{Gram susceptibility} \quad \chi_g = \chi_v \times d \quad \dots (9.7)$$

$d = \text{density of the sample}$

In practice, susceptibility is usually expressed per unit mass, i.e., specific weight susceptibility rather than per unit volume.

$$\text{Molar susceptibility} : \chi_m = \chi_g \times m, m = \text{molecular weight} \quad \dots (9.8)$$

Magnetic moment μ : In discussion of magneto chemistry, the susceptibility χ is hardly used because of cumbersome figures. A more convenient property is the magnetic moment. If a magnet is suspended freely, it comes to rest with its north pole pointing towards north and south pole towards south due to earth field. Suppose H is the horizontal component of earth's field and m is the pole strength.

Moment = Force \times arm of the couple

Each pole of the magnet will experience a force equal to

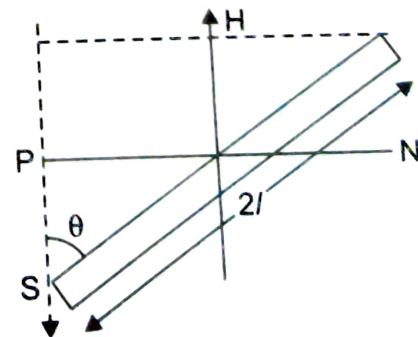


Fig. 9.1 : Turning effect on a magnetic dipole.

mH . Since two poles are opposite in nature, they will form a couple such that moment of the couple can be given as :

$$\begin{aligned} \text{Moment of the couple} &= \text{force} \times \text{distance} \\ &= mH \times PN \end{aligned} \quad \dots (9.9)$$

$$= mH / \sin \theta \quad \dots (9.10)$$

$$= \mu \cdot H \sin \theta \quad \dots (9.11)$$

If $\theta = 90^\circ$ then $\sin 90^\circ = 1$

$$H = 1 \text{ oersted}$$

Moment of the couple $= \mu$

Thus magnetic moment may be defined as the moment of the couple when a magnet is suspended freely in a field of 1 oersted such that it makes an angle of 90° with the field direction. The unit of magnetic moment is Bohr magneton

$$1 \text{ BM} = 5564 \text{ gauss cm mole}^{-1}$$

$$1 \text{ Weiss magneton} = 1123.5 \text{ gauss cm mole}^{-1}$$

The product ml gives the magnetic moment μ of the sample. Experimentally, it is the susceptibility of the sample that is determined. The susceptibility is then converted into magnetic moment with the help of the Curie equation. The susceptibility is additive in property while the square of the moment is additive in nature.

TYPES OF MAGNETIC MATERIALS

Magnetic materials can be classified into various ways which are described below :

1. On the basis of Gauss's Law : Gauss's Law predicts two types of magnetic materials :

(i) Paramagnetic substances : Paramagnetic substances when kept in a magnetic field are attracted towards the magnetic field. Paramagnetism of a substance is produced due to the presence of unpaired electrons and with the increase in number of unpaired electrons, paramagnetism also increases. Examples are : transition group elements such as Pt, Cr, Mn, free radicals (trimethyl phenyl radical), complex compounds.

Paramagnetic substances exhibit the following properties :

(1) Paramagnetic substances have small attraction towards the magnetic field as each unpaired electron produces equal magnetic moment because the magnetic field produced by these unpaired electrons are not mutually cancelled. Therefore these substances have some permanent and definite value of resultant magnetic moment *i.e.* a combination of spin and orbital magnetic moment. This resultant magnetic moment overcome the small magnetic field induced by the applied magnetic field with the result that the paramagnetic substances feel attraction in a magnetic field.

(2) When paramagnetic substances are placed in a magnetic field, they set in the direction of magnetic field. In a non uniform magnetic field, due to the force of attraction paramagnetic substances accumulate towards the stronger parts of the magnetic field.

(3) Paramagnetic substances allows more lines of magnetic force to pass through them, hence the permeability of a paramagnetic substances is slightly greater than one.

(4) The susceptibility of paramagnetic substances is high, value of susceptibility for paramagnetic substances is 1 to 100×10^{-6} .

(5) Paramagnetic susceptibility is independent of the applied magnetic field but show inverse relation to temperature.

(6) A paramagnetic liquid in U-tube when placed in a magnetic field shows a rise in a magnetic field.

(7) The intensity of magnetisation is greater in paramagnetic substances than that produced in a vacuum by the same magnetic field.

The paramagnetic susceptibility can be as calculated as

$$\chi_M = \chi_P + \chi_{TIP} + \chi_{dia}$$

where χ_P = Normal paramagnetic susceptibility

χ_{TIP} = Temperature independent paramagnetic susceptibility

χ_{dia} = Diamagnetic susceptibility

As we do not generally know the value of χ_{TIP} , corrected molar susceptibility χ_M^{CORR} can be represented as

$$\chi_M^{CORR} = \chi_P - \chi_{dia}$$

Normal paramagnetic susceptibility is given by

$$\chi_P = N_A \mu^2 / 3kT \quad \dots (9.12)$$

where N_A = Avogadro's number

μ = Magnetic moment

k = Boltzmann constant = 1.38×10^{-16} erg/deg

T = Absolute temperature

The value of magnetic moment obtained by putting the corrected molar susceptibility instead of χ_P , is termed as effective magnetic moment μ_{eff} .

Hence
$$\chi_M^{CORR} = \frac{N_A \mu_{eff}^2}{3kT} \quad \dots (9.13)$$

$$\therefore \mu_{eff} = \sqrt{\frac{3kT \times \chi_M^{CORR}}{N_A^2}} \quad \dots (9.14)$$

Putting the values of k and N_A , we get

$$\mu_{eff} = 2.83 \sqrt{\chi_M^{CORR} \times T_{B.M.}} \quad \dots (9.15)$$

(ii) Diamagnetic substances : Diamagnetic substances are repelled away from the magnetic field, when placed in a magnetic field. Diamagnetism of a substance is produced due to the presence of paired electrons and with the increase in atomic number,

diamagnetic behavior increases. Examples are Bi, Sb, Au, H₂O, quartz, Zn, Ag, Au, N₂, H₂ etc. Diamagnetic substances show the following properties :

(1) Diamagnetic substances are repelled by magnetic field. Diamagnetism is caused by the presence of paired electrons as the magnetic field produced by one electron is counter balanced or neutralised by the magnetic field produced by the second electron because each of the two electrons has equal and opposite magnetic moment. Therefore, diamagnetic substances have zero resultant magnetic moment with the result they experiences repulsion in the magnetic field.

(2) Diamagnetic substances on placing in a magnetic field set themselves at right angles to the magnetic field. In a non-uniform magnetic field, they accumulate towards the lowest part of the magnetic field.

(3) Diamagnetic substances allows a smaller number of lines of magnetic force to pass through as compared to that in vacuum *i.e.* lines of magnetic force avoid diamagnetic substances hence the permeability of diamagnetic substances is less than unity.

(4) The susceptibility of diamagnetic substance is negative, value of susceptibility for diamagnetic substances are very small about -1×10^{-6} .

(5) Diamagnetic susceptibility is independent both of the applied magnetic field and temperature.

(6) A diamagnetic liquid placed in a U-tube shows a depression in a magnetic field.

(7) The intensity of induced magnetisation is less in diamagnetic substances than the applied magnetic field in vacuum.

(8) All the substances have diamagnetism even by paramagnetic substances because it is a universal property but it is much weaker than paramagnetism and both work opposite to each other, hence substance with unpaired electrons show a net paramagnetism.

The diamagnetic susceptibility is expressed as

$$\chi_A = \frac{N_A e^2}{6mc^2} \sum_{i=1}^{i=n} \bar{r}_1^2 \quad \dots (9.16)$$

where χ_A = atomic diamagnetic susceptibility

N_A = Avogadro's number

e = charge on electron

m = mass of electron

c = velocity of light,

n = number of electrons

\bar{r}_1^2 = mean square radius

2. On the basis of interaction between magnetic centres : On the basis of interaction between magnetic centres, magnetic materials can be divided into two types :

(i) Magnetically dilute substances : Magnetically dilute substances are the

magnetic materials in which the magnetic properties come entirely from the individual magnetic centres. The individual magnetic centres are sufficiently distant from near neighbouring magnetic centres to minimise further magnetic interaction. The possibility of secondary magnetic interaction between the neighbouring magnetic centre is ruled out in these substances.

The magnetically dilute substances are of two types :

- (a) Diamagnetic substances
- (b) Paramagnetic substances

(ii) Magnetically concentrated substances : Magnetically concentrated substances are the magnetic materials in which the individual magnetic centres are close enough to initiate magnetic interaction between neighbouring magnetic centres, hence secondary magnetic interaction exist between the neighbouring magnetic centres.

The magnetically concentrated substances can further be classified into three types :

(a) Ferromagnetic substances : In ferromagnetic substances strong magnetic interaction takes place between neighbouring paramagnetic centres when the paramagnetic centres are kept close enough with the result an increment or enhancement in magnetic moment is found. In these substances, infinite effective field called domains are formed. In these domains, the neighbouring spins are aligned parallel. The number of atoms in each domain ranges from 10^{17} to 10^{21} . Examples are Fe, Co, Ni, alloys of Fe, Co, Ni, magnetite (Fe_3O_4) etc. Ferromagnetic substances show the following properties :

- (1) Ferromagnetic substances exhibit greater force of attraction in a magnetic field.
- (2) The permeability of ferromagnetic substances is of the order 10^3 .
- (3) The susceptibility of ferromagnetic substances is positive and value is very high *i.e.*, $\sim 1 \times 10^2$.
- (4) In absence of magnetic field, effective magnetic moment is zero because of random arrangement of domains. In magnetic field, they align in parallel direction.
- (5) Ferromagnetism is quite magnetic field dependent which is described by the hysteresis curve *i.e.*, the curve between I or B and T at different field strength.
- (6) On heating ferromagnetic substances, start losing their magnetic property gradually.

After Curie temperature, ferromagnetism is converted into normal paramagnetism.

(7) Above Curie point, susceptibility show inverse relation with temperature but below Curie point it rises abruptly and show a dependence on magnetic field strength.

In these substances, the magnetic moments of all domains align parallel in the direction of magnetic field when kept in a magnetic field. As the strength of applied magnetic field is increased, parallel alignment of domains takes place in greater extent. At certain field strength, all domains present in the ferromagnetic substances are aligned parallel to the field. Above this optimum field strength, the magnetic susceptibility does

not rises with the applied field and therefore it depends on the magnetic field strength.

Thermal energy kT opposes the alignment of domains in the magnetic field, it tends to orient magnetic moments of domains randomly. If the magnetic field is removed, however the parallel alignment of domain restores to some extent hence, it is not possible to randomise, completely, it is termed as hysteresis.

(b) Antiferromagnetic substances : In antiferromagnetic substances secondary magnetic interaction between neighbouring paramagnetic centres takes place with the result a decrement or lowering of magnetic moment is found. In antiferromagnetic substances, the neighbouring spins (domains) are opposed to each other. Examples are titanium sesquioxide, MnO_2 , FeO , copper acetate, oxovanadium (IV) etc.

In antiferromagnetic substances, the induced magnetism increases with temperature upto a critical point *i.e.* Neel point or antiferromagnetic Curie temperature. Beyond this temperature, antiferromagnetic substances behave as normal paramagnetic substances. The susceptibility above Neel point varies inversely with temperature but below Neel point it decreases. The susceptibility of antiferromagnetic substances may depend on magnetic field strength.

(iii) Ferrimagnetic substances : In these substances, the magnetic centres are close enough to produce interaction between them and the neighbouring spins are aligned in opposite directions but the number of opposite spin are less with the result the resultant magnetic moment of these substances are not zero but have some positive value. Examples include Fe_3O_4 .

The magnetic susceptibility of these substances depends upon temperature. Above Curie temperature, they behave as paramagnetic substances.

(3) On the basis of magnetic behaviour : When a substance which act as a magnet due to orbital and spin motion of its electrons is kept in a magnetic field, the magnetic field produced by the orbital and spin motion of electrons interacts with the applied magnetic field. The substances do not behave in similar manner and show different behaviour which is called magnetic behaviour. The various magnetic behaviour show difference with respect to (i) sign and values of susceptibilities (ii) temperature dependence of susceptibilities (iii) magnetic field strength dependence of susceptibilities.

On the basis of magnetic behaviour, substances are classified as described below :

(i) Diamagnetic substances : These substances have negative susceptibility and the numerical values are very small of the order -1×10^{-6} cgs units. Susceptibility is both temperature and magnetic field independent.

(ii) Paramagnetic substances : These substances have positive susceptibility and numerical values are small of the order $10 - 100 \times 10^{-6}$ cgs units. The susceptibility shows an inverse relation with temperature *i.e.* varies inversely with temperature but is independent of magnetic field strength.

(iii) Ferromagnetic substances : The susceptibility of ferromagnetic substances is positive and numerical values are quite very large of the order 10^{-2} to $10^4 \times 10^{-6}$ cgs

units. Above Curie temperature, susceptibility varies inversely with temperature but below Curie temperature it rises abruptly and it is dependent on magnetic field strength also. In these compounds, the magnetic susceptibility can be taken as sum of individual paramagnetic susceptibilities. The spin interaction energy $\Delta E = 2J(S)_i(S)_k$

where J = exchange coupling constant.

$(S)_i$ = total electron spin of i ion

$(S)_k$ = total electron spin of k ion

(Orbital contribution is negative)

In ferromagnetic substances, J value is positive.

(iv) Antiferromagnetic substances : The susceptibility of antiferromagnetic substances is positive but numerical value is very small of the order of ~ 0.1 to 10×10^{-6} cgs units. Above Neel point susceptibility varies inversely with temperature but below Neel point, it decreases. It may depend on magnetic field strength.

The spin interaction energy $\Delta E = 2J(S)_i(S)_k$

In antiferromagnetic substances J value is negative. so the total electron spin tends to get paired and magnetic susceptibility value is very low.

SOME IMPORTANT LAWS

1. Coulomb's law : The force between two magnetic poles is directly proportional to product of their pole strength and inversely proportional to the square of the distance between them. This can be expressed mathematically as

$$F \propto \frac{m_1 m_2}{r^2} \quad \dots (9.17)$$

$$F = \frac{1}{\mu} \cdot \frac{m_1 m_2}{r^2} \quad \dots (9.18)$$

where m_1 and m_2 = pole strength of two magnetic poles

r = distance between the two magnetic poles

μ = a constant called permeability of the medium (for air $\mu = 1$)

2. Gauss' law : When a substance is kept in a magnetic field, total magnetic induction or magnetic flux induced in the substance is equal to the sum of strength of magnetic field and 4π times of pole strength induced per unit area. This can be expressed mathematically as

$$B = H + 4\pi I \quad \dots (9.19)$$

where H = strength of magnetic field

B = total magnetic induction or magnetic flux which can be defined as total number of lines of magnetic force per unit area

I = pole strength induced per unit area

Table 9.1 : Types of Magnetic Materials

Type	Reason	x_g	Temperature and magnetic field dependence of x_g	Examples
Diamagnetic	Pairing of electrons	negative, small -1×10^{-6} cgs units	Independent of temperature T and magnetic strength H	H_2 , N_2 , $NaCl$, KCl , $MgCl_2$, $K_4[Fe(CN)_6]$, $[Co(NH_3)_6]Cl_3$
Paramagnetic	Presence of unpaired electrons	positive, small $10 - 100 \times 10^{-6}$ cgs units	Varies inversely with temperature but independent of magnetic strength	O_2 , $NiCl_2 \cdot 6H_2O$, $[CoCl_4]$
Ferromagnetic	Assemblage of particles with unpaired electrons	positive, very large, 10^{-2} to $10^4 \times 10^{-6}$ cgs units	Above Curie point, x_g varies inversely with temperature but below Curie point x_g rises abruptly and dependent on magnetic field strength	Metallic iron, Mn-Cu alloys
Antiferromagnetic	Two lattice of particles with spins of one lattice opposite to the spins of the other lattice with the result to reduce magnetism	positive, very small, ~ 0.1 to 10×10^{-6} cgs units	Above Neel Point x_g varies inversely with temperature but below Neel point x_g decreases, it may depend on magnetic field strength	Copper acetate monohydrate, oxovanadium (IV)
Ferrimagnetic	Due to exchange of spins	positive, small, $10^{-3} - 10^{-4}$	depend on temperature and may depend on magnetic field	Fe_3O_4

3. Curie Law : The equation of magnetic susceptibility

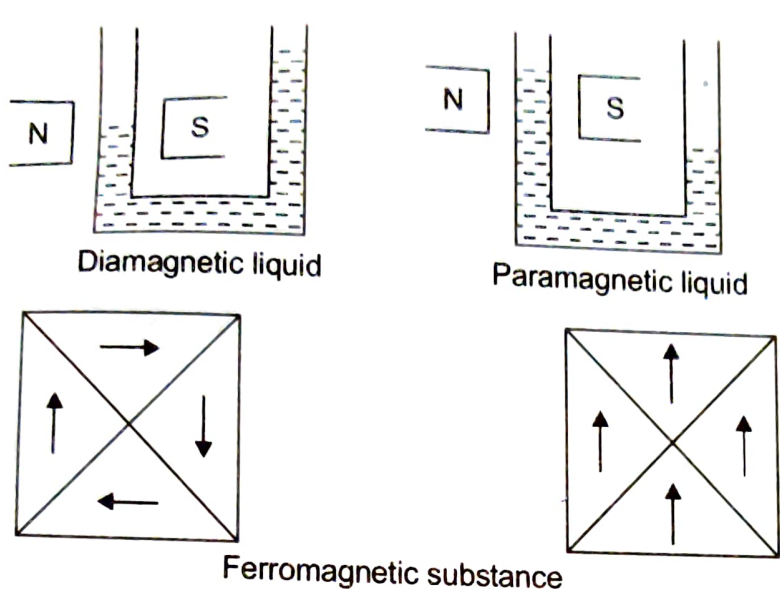
$$\chi_M^{Corr} = \frac{N A \mu_{eff}^2}{3kT} \quad \dots (9.20)$$

indicates that χ_M^{Corr} is in inverse relation to temperature.

Hence

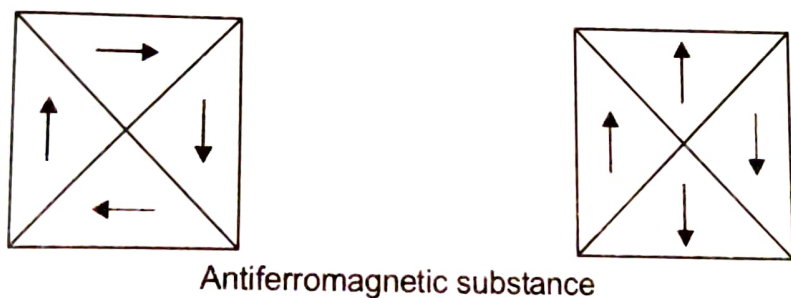
$$\chi_M^{Corr} \propto \frac{1}{T} \Rightarrow \chi_M^{Corr} = \frac{C}{\theta} \text{ (Curie law)} \quad \dots (9.21)$$

where $C = (\text{a constant}) = \frac{N_A \mu_{eff}^2}{3k}$ and is characteristic of the substance under study. The



(a) in absence of magnetic field

(b) in presence of magnetic field



(a) in absence of magnetic field

(b) in presence of magnetic field

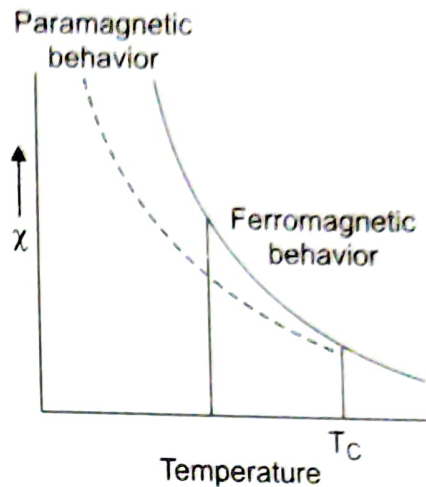
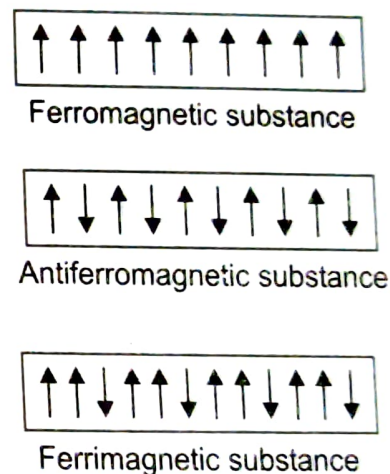


Fig. 9.2 : Plot of temperature vs. susceptibility



plot of χ_M^{Corr} values against $1/T$ will yield a straight line with slope C which intercepts the origin. This constant is called Curie constant.

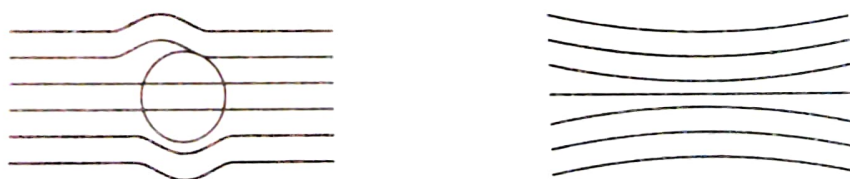


Fig. 9.3 : Diamagnetic and paramagnetic samples in a magnetic field.

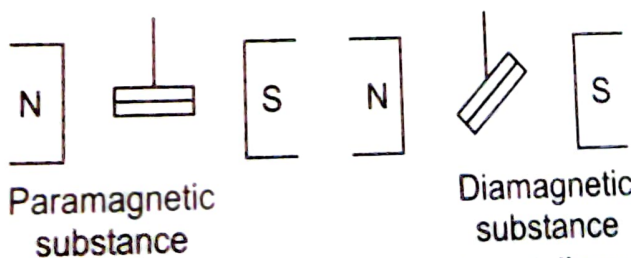


Fig. 9.4 : Effect of magnetic field on paramagnetic and diamagnetic samples.

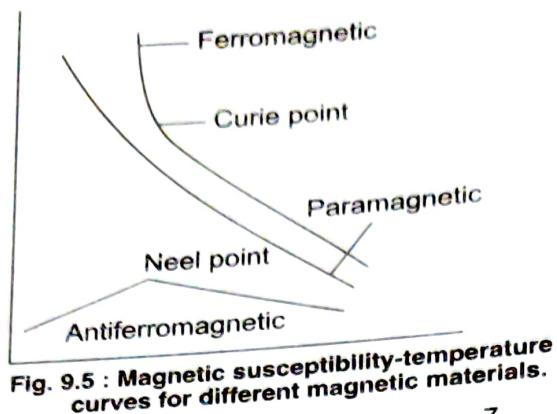


Fig. 9.5 : Magnetic susceptibility-temperature curves for different magnetic materials.

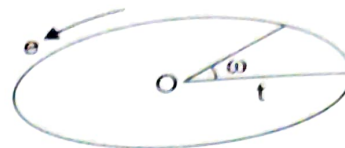


Fig. 9.6 : An electron orbit.

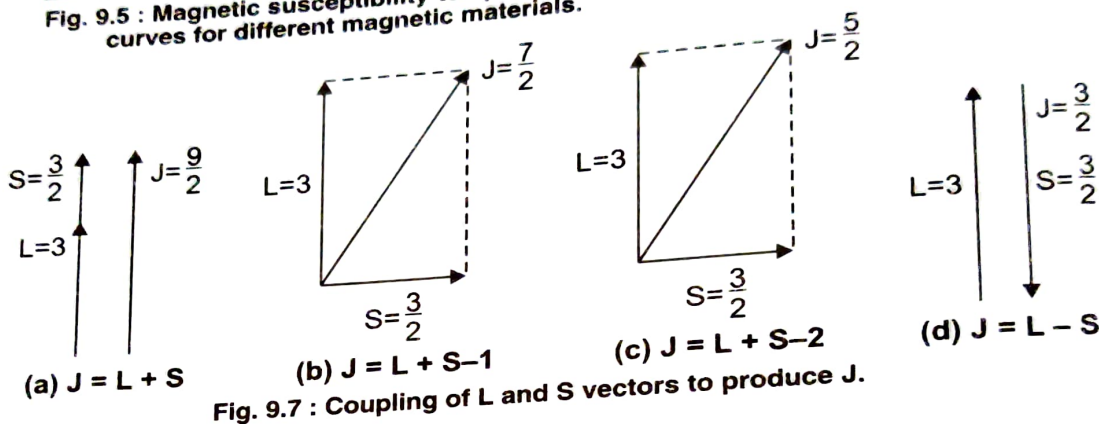


Fig. 9.7 : Coupling of L and S vectors to produce J.

On substituting the value of k and N_A in above equation

$$\mu_{eff} = 2.83 \sqrt{\chi_M^{COIT} \times T} \text{ B.M.}$$

(1 BM = Bohr magneton. $eh/4\pi m c = 9.27 \times 10^{-21}$ erg/gauss)

(One BM is magnetic moment of single electron.)

Many paramagnetic substances follow Curie's law but there are many paramagnetic substances which do not follow Curie's law. For such paramagnetic substances, modified form of Curie's law also known as Curie-Weiss law is given

$$\chi_M^{Corr} = C/(T - \theta) \quad \dots (9.22)$$

θ = Temperature at which the straight line cuts the temperature axis called Curie temperature or Weiss constant.

Due to presence of molecular field, the magnetic susceptibility varies inversely as the excess of the temperature over a certain critical value θ of the temperature.

If the value of θ is positive, i.e., above OK, corresponds to the point at which ferromagnetism becomes paramagnetism. For paramagnetic substances, θ is usually small and may be positive or negative depending upon experimental temperature. Below Curie point θ when $T < \theta$ the paramagnetic substance is converted into diamagnetic substances. But it is rarely found as Curie temperature for most of the paramagnetic substances is so small that Curie law is followed the substance is called ferromagnetic and

if θ is negative i.e., below OK, the substance is called antiferromagnetic.

The value of μ_{eff} for the substances which follow Curie-Weiss law is given by

$$\mu_{eff} = 2.83 \sqrt{\chi_M^{Corr} \times (T - \theta)} \text{ B.M.} \quad \dots (9.23)$$

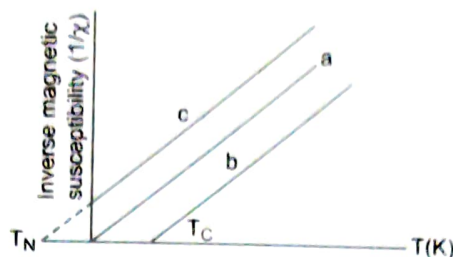


Fig. 9.8 : Plot of the reciprocal of magnetic susceptibility Vs temperature for three magnetic behaviour
(a) Curie law (b) Curie-Weiss law for ferromagnetic substance.
(c) Curie-Weiss law for antiferromagnetic substances.

Bohr magnetons : For a molecule or atom

$$1 \text{ Bohr magneton} = \frac{eh}{4\pi mc} \quad \dots (9.24)$$

Putting the values of e, h, π, m and c , we get

$$1 \text{ Bohr magneton (B.M.)} = 9.17 \times 10^{-21} \text{ gauss cm per molecule}$$

The unit $\frac{h}{2\pi} \cdot \frac{e}{2mc}$ is termed as Bohr magneton as the quantum unit of magnetic

moment and thus has the same significance as that of $h/2\pi$. the quantum unit of mechanical momentum.

The numerical value 9.17×10^{-21} gauss cm per molecule, on multiplying the Avogadro's number gives the magnetic moment for a mole. Thus

$$\begin{aligned} \mu_B &= 9.17 \times 10^{-21} \times 6.00625 \times 10^{23} \\ &= 5564 \text{ gauss cm per mole} \end{aligned}$$

Weiss magneton : Weiss (1911) noticed that iron and nickel have 12360 gauss cm per atom and 3370 gauss cm per atom saturation moments respectively, with a factor of 1123.5 gauss cm. per atom common. The two atoms have their saturation moments in the ratio 11 : 3. Other ferromagnetic substances also have saturation moments per gram the factor 1123.5 common. This common factor is called the Weiss magneton. Thus

$$\begin{aligned} \text{Weiss magneton } \mu_w &= 1123.5 \text{ gauss cm per mole} \\ &\quad \text{(magnetic moment per gram molecule)} \end{aligned}$$

The value per molecule is obtained by dividing the gram molecular moment by Avogadro's number N_A

$$\begin{aligned} \mu_w &= \frac{1123.5}{6.0625 \times 10^{23}} \\ &= 1.85 \times 10^{-21} \text{ gauss cm per molecule} \end{aligned}$$

p-values : p-Weiss Magnetron : p-value is the factor which when multiplied by the

Weiss magneton 1123.5 gauss cm/mole gives the saturation moment per gram molecule. Thus,

$$p = \frac{\sigma_0}{1123.5} = \frac{\sqrt{3}R.C}{1123.5} \quad \dots (9.25)$$

$$= 14.06\sqrt{C}$$

The p -value can be determined by calculating the paramagnetic susceptibility at three or more temperatures and a plot is made between $1/\chi_M$ and T which would be a straight line. If the curve passes through the origin, Curie's law is followed and the determination of Curie's constant can be made from $\chi_M = C/T$ and from this p , the Weiss magneton number can be deduced from the relation $p = 14.06\sqrt{C}$.

If the straight line makes an intercept on the Y-axis, Curie-Weiss law is followed and $\chi_M = \frac{C}{T - \theta}$ determines the p value if the Curie point θ is experimentally available. The value of θ gives useful information about the magnitude of the internal molecular field.

The p values provides useful information regarding the effect of temperature, solvent and presence of water molecules, on the magnetic properties of most of the single and double salts.

Table 9.2 : Single electron spin-orbit coupling constants (cm^{-1}) for different oxidation states of the first and second transition series elements.

Element	0	+ 1	+ 2	+ 3	+ 4	+ 5	+ 6
Ti	70	90	120	155			
V	(95)	135	170	210	250		
Cr	(135)	(190)	230	275	325	380	
Mn	(190)	(255)	(300)	355	415	475	540
Fe	255	345	400	(460)	515	555	665
Co	390	455	515	(580)	(650)	715	790
Ni	–	605	630	(715)	(790)	(865)	950
Cu	–	–	830	(875)	(960)	(1030)	(1130)
Zr	270	340	425	500	–	–	–
Nb	(365)	490	555	670	750	–	–
Mo	(450)	(630)	(695)	820	850	1030	–
Tc	(550)	740	(850)	(990)	(1150)	(1260)	1450
Ru	745	900	1000	(1180)	(1350)	(1500)	(1700)
Rh	940	1060	1220	(1360)	(1570)	(1730)	(1950)
Pd	–	1420	1460	(1640)	(1830)	(2000)	(2230)
Ag	–	–	1840	(1930)	(2100)	2300	2500

Table 9.3 : Single electron spin-orbit coupling constants for trivalent lanthanides.

<i>f</i> -electrons	Ion	δ (cm ⁻¹)
1	Ce ³⁺	
2	Pr ³⁺	640
3	Nd ³⁺	711
4	Sm ³⁺	810
5	Eu ³⁺	1180
6	Gd ³⁺	1360
7	Tb ³⁺	-
8	Dy ³⁺	1720
9	Ho ³⁺	1920
10	Er ³⁺	2080
11	Tm ³⁺	
12	Yb ³⁺	
13		

Table 9.4 : Spin-orbit coupling constants for first transition series element ions (in cm⁻¹)

Ion	δ	<i>d</i> -electron	Weak octahedral ground term	λ	Strong octahedral ground term	λ	Weak tetrahedral ground term	λ
Ti ³⁺	155	1	² T _{2g}	+ 155	² T _{2g}	+ 155	² E	+ 155
V ³⁺	210	2	³ T _{1g}	+ 105	³ T _{1g}	+ 105	³ A ₂	+ 105
V ²⁺	170	3	⁴ A _{2g}	+ 57	⁴ A _{2g}	+ 57	⁴ T ₁	+ 57
Cr ³⁺	275	3	⁴ A _{2g}	+ 92	⁴ A _{2g}	+ 92	⁴ T ₁	+ 92
Cr ²⁺	230	4	⁵ E _g	+ 58	³ T _{1g}	- 115	⁵ T ₂	+ 58
Mn ³⁺	355	4	⁵ E _g	+ 89	³ T _{1g}	- 178	⁵ T ₂	+ 89
Mn ²⁺	300	5	⁶ A _{1g}	-	² T _{2g}	- 300	⁶ A ₁	-
Fe ³⁺	460	5	⁶ A _{1g}	-	² T _{2g}	- 460	⁶ A ₁	-

Fe ²⁺	400	6	⁵ T _{2g}	-100	¹ A _{1g}	-	⁵ E	-100
Co ³⁺	580	6	⁵ T _{2g}	-145	¹ A _{1g}	-	⁵ E	-145
Co ²⁺	515	7	⁴ T _{1g}	-172	² E _g	-515	⁴ A ₂	-172
Ni ³⁺	715	7	⁴ T _{1g}	-238	² E _g	-715	⁴ A ₂	-238
Ni ²⁺	630	8	³ A _{2g}	-315	³ A _{2g}	-315	³ T ₁	-315
Cu ²⁺	830	9	² E _g	-830	² E _g	-830	² T ₂	-830

Table 9.5 : Magnetic Properties of first transition series

Ion	S	L	Ground State	μ_J (BM)	μ_{L+S} (BM)	μ_S (BM)	Experimental value (BM)
3d ¹ (V ⁴⁺)	1/2	2	² D _{3/2}	1.55	3.0	1.73	1.7 – 1.8
3d ² (V ³⁺)	1	3	³ F ₂	1.63	4.47	2.83	2.7 – 2.9
3d ³ (Cr ³⁺)	3/2	3	⁴ F _{3/2}	0.70	5.20	3.87	3.7 – 3.8
3d ⁴ (Cr ²⁺)	2	2	⁵ D ₀	0	5.48	4.90	4.9 – 5.3
3d ⁵ (Mn ²⁺)	5/2	0	⁶ S _{5/2}	5.92	5.92	5.92	5.9
3d ⁶ (Fe ²⁺)	2	2	⁵ D ₄	6.70	5.48	4.90	5.1 – 5.5
3d ⁷ (Co ²⁺)	3/2	3	⁴ F _{9/2}	6.64	5.20	3.87	4.3 – 5.2
3d ⁸ (Ni ²⁺)	1	3	³ F ₄	5.59	5.83	4.47	2.8 – 4.0
3d ⁹ (Cu ²⁺)	1/2	2	² D _{5/2}	3.55	3.00	1.73	1.7 – 2.2

Table 9.6 : Magnetic Properties of Lanthanides

n (4f ⁿ)	M ³⁺	L	Number of unpaired electrons	S	J	Ground state	g	Calculated $\mu = g \sqrt{J(J+1)}$ (BM)	$\mu_S = \sqrt{4S(S+1)}$ (BM)	Experimental μ (BM)
0	La	0	0	0	0	¹ S ₀	-	0	0	Dia
1	Ce	3	1	1/2	5/2	² F _{5/2}	6/7	2.54	1.7	2.3 – 2.5
2	Pr	5	2	1	4	³ H ₄	4/5	3.58	2.8	3.4 – 3.6
3	Nd	6	3	3/2	9/2	⁴ I _{9/2}	8/11	3.62	3.9	3.5 – 3.6
4	Pm	6	4	2	4	⁵ I ₄	3/5	2.68	4.9	-

5	Sm	5	5	5/2	5/2	${}^6H_{5/2}$	2/7	0.84	5.9	1.5 - 1.6
6	Eu	3	6	3	0	7F_0	-	0	6.9	3.4 - 3.6
7	Gd	0	7	7/2	7/2	${}^8S_{7/2}$	2	7.94	7.94	7.8 - 8.0
8	Tb	3	6	3	6	7F_6	3/2	9.72	6.9	9.4 - 9.6
9	Dy	5	5	5/2	15/2	${}^6I_{15/2}$	4/3	10.63	5.9	10.4 - 10.5
10	Ho	6	4	2	8	5I_8	5/4	10.60	4.9	10.3 - 10.5
11	Er	6	3	3/2	15/2	${}^4F_{15/2}$	6/5	9.57	3.9	9.4 - 9.6
12	Tm	5	2	1	6	3H_6	7/6	7.63	2.9	7.1 - 7.4
13	Yb	3	1	1/2	7/2	${}^2F_{7/2}$	8/7	4.50	1.7	4.4 - 4.9
14	Lu	0	0	0	0	1S_0	-	0	0	Dia

Cause of Paramagnetism : Orbital effect and spin effect : Paramagnetism of a substance is caused by the presence of unpaired electrons. An electron has associated with it two motions (i) Orbital motion (ii) Spin motion.

(1) Orbital motion : Motion of electrons around the nucleus in an orbit which produces magnetic field perpendicular to the plane of the orbit. The resultant magnetic moment is called orbital magnetic moment.

(2) Spin motion : Motion is caused by the spinning of the electrons about its axis which generates a magnetic field or magnetic moment referred to as spin magnetic moment.

The orbital magnetic moment : Assume a single electron of charge e and mass m is moving around a nucleus O with an average angular velocity ω . Then the number of revolutions made by the electron in one second = $\frac{\omega}{2\pi}$ and

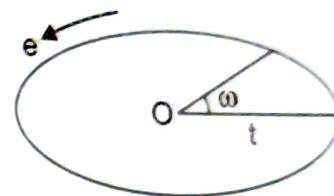


Fig. 9.9 : An electron orbit.

Orbital magnetic moment = (strength of the current) \times (area of the orbit)

$$= \frac{\omega}{2\pi c} \times \pi r^2 \quad \dots (9.26)$$

where c = velocity of light,

r^2 = mean square radius of the orbit

The electron has a characteristic angular momentum which can be expressed in terms of orbital angular momentum quantum number (l). We know

$$\text{Angular momentum} = m\omega r^2 = \sqrt{l(l+1)}h/2\pi \quad \dots (9.27)$$

$$\therefore \text{Therefore orbital magnetic moment } \mu_L = \frac{e\omega r^2}{2c} = \sqrt{l(l+1)} \frac{eh}{4\pi mc} \quad \dots (9.28)$$

$$\mu_L = \sqrt{l(l+1)} \beta \quad \dots (9.29)$$

β -unit of magnetic moment known as Bohr magneton

$$1 \text{ BM} = \frac{eh}{4\pi mc} = 9.27 \times 10^{-21} \text{ ergs/gauss}$$

where h = Planck's constant and the charge on electron is measured in electrostatic units. If charge on electron is measured in electromagnetic units, then

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

Spin magnetic moment : The ratio of orbital magnetic moment ($e\omega r^2/2c$) to orbital angular momentum ($m\omega r^{-2}$) is given by $e/2mc$. In the case of spin motion, the correct ratio is given by e/mc . Thus,

spin magnetic moment = spin angular momentum $\times e/mc$

$$\mu_S = \sqrt{s(s+1)} h/2\pi \times e/mc \quad \dots (9.30)$$

$$\mu_S = 2\sqrt{s(s+1)} eh/4\pi mc \quad \dots (9.31)$$

$$\mu_S = 2\sqrt{s(s+1)} \beta \quad \dots (9.32)$$

The orbital equation and spin equation are often written as

$$\mu_L = g \sqrt{l(l+1)} \beta \quad (g = 1) \text{ and} \quad \dots (9.33)$$

$$\mu_S = g \sqrt{s(s+1)} \beta \quad (g = 2) \quad \dots (9.34)$$

g is called the gyromagnetic ratio *i.e.*, the ratio of the magnetic moment to the corresponding angular momentum.

Spin-orbit interaction : In Russell-Saunders coupling the interaction of orbital and spin angular momentum takes place and give resultant inner quantum number or total angular momentum quantum number J . The spin-orbit interaction strength is usually expressed in terms of spin-orbit coupling constant.

The spin-orbit interaction energy for a single electron may be written as proportional to $ls \cos(l, s)$ where l and s represent the respective angular momentum and spin vector. The spin-orbit coupling constant ζ is thus given as a proportionality constant. On the vector model, the spin angular momentum S is added to the orbital angular momentum L to give the resultant momentum J . where

$$S = \sqrt{s(s+1)} h/2\pi \quad \dots (9.35)$$

$$L = \sqrt{l(l+1)} h/2\pi \quad \dots (9.36)$$

$$J = \sqrt{J(J+1)} h/2\pi \quad \dots (9.37)$$

The L and S may combine to give several values of J 's such that they vary integrally between $|L + S|$ to $|L - S|$ as $(L + S), (L + S - 1), (L + S - 2) \dots, 0 \dots (L - S + 1), (L - S)$. These different values suggest that the respective l and s vectors are at different angles so that in the interaction energy terms, it is the $\cos(l, s)$ that changes although the spin-orbit coupling constant remains the same.