MAGNETIC PROPERTIES

OF

TRANSITION METAL COMPLEXES

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MAGNETIC PROPERTIES OF TRANSITION METALS

TRANSITION METALS

Paramagnetic

Diamagnetic

a) Attracted by magnetic field

b) arises due to unpaired electrons

a) Repelled by magnetic field

b) Arises due to paired electrons

- Most of the transition metals are **paramagnetic** in nature due to the presence of unpaired electrons in d – orbitals.

- Magnetic character is expressed in terms of **magnetic moment.**

- **Greater** the number of unpaired electrons , **greater** is the paramagnetic character and **greater** is the magnetic moment.

- The magnetic moment is expressed in **Bohr Magneton (B.M.)**

- **Bohr Magneton** is the magnetic moment of an atom due to the orbital motion of an electron in the first orbit of hydrogen atom.

- The magnetic moment is **only due to the spin of the electrons.**

ORIGIN OF PARAMAGNETIC MOMENT

- The magnetic property of a substance is due to both **electrons and nucleons.**

- Due to **large size** of the nucleons ,their contribution towards magnetic character is **very small** and can be **neglected.**

- *The magnetic moment of a substance is sum of*

i. *Spin magnetic moment:* arises due to spinning of electron about its axis.
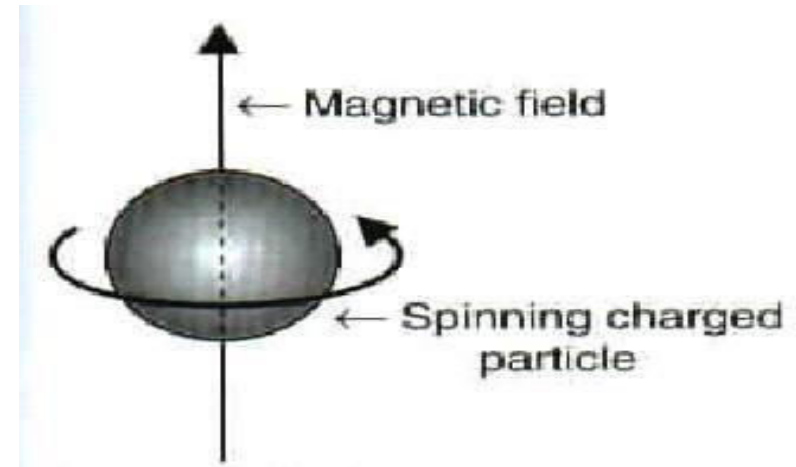
ii. *Orbital magnetic moment:* arises due to motion of electron around the nucleus.
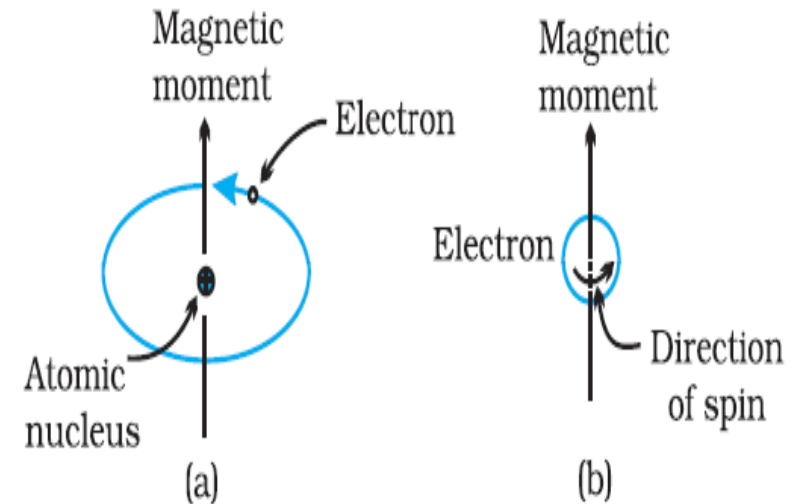
- The magnetic moment for an electron having mass 'm' and charge 'e' is given as

$$\mu_s = eh / 4\pi \, mc = 1 \text{ B.M.}$$

where **h** is Planck's constant and **c** is the velocity of light.

- The value of magnetic moment obtained from the above formula is **9.274×10^{-21} ergs gauss^{-1}**

- This value is taken as one unit of magnetic moment called **Bohr Magneton (B.M.)**

❖ The spin magnetic moment is given as

$$\mu_s = g \ \{S(S + 1)\}^{1/2}$$

where ,

    S is the spin quantum number and depends on the number of unpaired electrons

    g is the gyromagnetic ratio or the **'g' factor .**

❖ **'g' factor** is the ratio of the magnetic moment to the angular momentum.

❖ The value of **'g' factor** is 2.00023 and generally taken as 2.

❖ The spin magnetic moment can also be written as

$$\mu_s = g\ \{S(S + 1)\}^{1/2}\ = 2\{S(S + 1)\}^{1/2}$$

or

$$\mu_s = \{4S(S + 1)\}^{1/2}$$

EXAMPLES

❖ For **one unpaired electron**, S = 1/ 2

$$\mu_s = \{4S(S + 1)\}^{1/2}\ = \{4\times1/2(1/2 + 1)\}^{1/2}$$

$$= \sqrt{3}\ = 1.732\ \text{B.M.}$$

❖ For **two unpaired electron**, S = 1/2 + 1/2 = 1

$$\mu_s = \{4S(S + 1)\}^{1/2} = \{4 \times 1(1 + 1)\}^{1/2}$$

$$= \sqrt{8} = 2\sqrt{2} = 2 \times 1.414 = 2.828 \text{ B.M.}$$

❖ The spin magnetic moment can also be calculated from the relation

$$\mu_s = \{n(n + 2)\}^{1/2}$$

where **n** is the number of unpaired electrons

EXAMPLES

❖ For **one unpaired electron**, n = 1

$$\mu_s = \{n(n + 2)\}^{1/2} = \{1(1 + 2)\}^{1/2}$$

$$= \sqrt{3} = 1.732 \text{ B.M.}$$

❖ For **two unpaired electron**, n = 2

$$\mu_s = \{n(n + 2)\}^{1/2} = \{2(2 + 2)\}^{1/2}$$

$$= \sqrt{8} = 2\sqrt{2} = 2 \times 1.414 = 2.828 \text{ B.M.}$$

Table 1. Spin only magnetic moments for various number of unpaired electrons

No. of unpaired electrons	S	μ_s (B.M.)
1	$\frac{1}{2}$	1.73
2	1	2.84
3	$\frac{3}{2}$	3.87
4	2	4.90
5	$\frac{5}{2}$	5.92
6	3	6.93
7	$\frac{7}{2}$	7.94

- The experimentally calculated values of some transition metals were found to correlate with the spin only values.

- In many cases the experimentally calculated values were found to be larger than the spin only values.

- In such cases, the magnetic moment is dependent on both the spin and the orbital magnetic moment.

- The total magnetic moment is given as

$$\mu_{S+L} = \{4S(S+1) + L(L+1)\}^{1/2}$$

where,

S is the resultant spin angular momentum quantum no.

L is the resultant orbital angular momentum quantum no.

Ion	Configuration	Unpaired electron(s)	Magnetic moment	
			Calculated	Observed
Sc^{3+}	$3d^0$	0	0	0
Ti^{3+}	$3d^1$	1	1.73	1.75
Ti^{2+}	$3d^2$	2	2.84	2.76
V^{2+}	$3d^3$	3	3.87	3.86
Cr^{2+}	$3d^4$	4	4.90	4.80
Mn^{2+}	$3d^5$	5	5.92	5.96
Fe^{2+}	$3d^6$	4	4.90	5.3 – 5.5
Co^{2+}	$3d^7$	3	3.87	4.4 – 5.2
Ni^{2+}	$3d^8$	2	2.84	2.9 – 3, 4
Cu^{2+}	$3d^9$	1	1.73	1.8 – 2.2
Zn^{2+}	$3d^{10}$	0	0	

- As can be seen from the table that the experimentally calculated values of μ are greater than the μ_s values.

- The experimentally calculated values of μ are never greater than the μ_{s+L} values.

- This indicates that the **contribution** of orbital magnetic moment to the total magnetic moment is **very less.**

- This is because the electric field of the ligands which surround the central metal ion **hinder / restrict** the orbital motion of the electrons.

- So, the orbital magnetic moment gets **partially or completely quenched.**

- In case of **2nd and 3rd** transition series, especially in **lanthanides** the orbital magnetic moment **does not get quenched.**

- In these elements the **4f** orbitals **are shielded** by the outer **5s** and **5p** subshell.

- So, the electric field of the ligands surrounding the central metal ion **do not hinder** the orbital motion of the 4f electrons or inner d electrons.
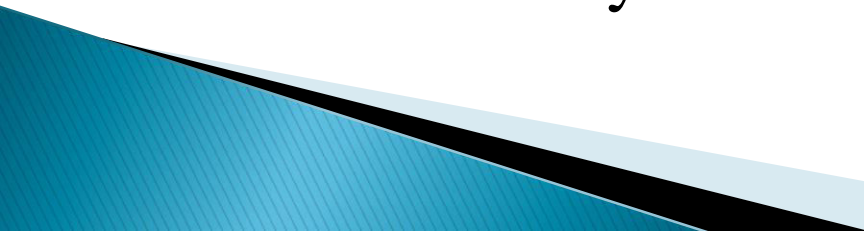
- The contribution of orbital magnetic moment to the total magnetic moment is not quenched.

- The magnetic moment of lanthanide ions is due to both electron spin and orbital motion of electrons.

- The magnetic moment is calculated as

$$\mu_{S+L} = \{4S(S+1) + L(L+1)\}^{1/2}$$

where,
S is the resultant spin angular momentum quantum no.
L is the resultant orbital angular momentum quantum no.

- In few cases , it was observed that **coupling** occurs between the **spin and the orbital** contribution.

- This coupling /interactions can be of three types:
i.   Spin – spin interaction
ii. Orbital – orbital interaction
iii. Spin – orbital interaction

- In case of lanthanide metal ions all three types of couplings play an important role.

- The resultant magnetic moment in these cases is calculated by means of **Russell Saunders coupling**.

- Russell Saunders coupling is also known as **L – S coupling.**

- It is given as

$$\mu_s = g\{J(J + 1)\}^{1/2}$$

where,
      J is the total angular momentum.

- **J is the vector sum of total orbital angular momentum (L) and total spin angular momentum (S).**

- **'g'** is called the **Lande splitting factor** and is given as

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

- The theoretical and calculated magnetic moment values for trivalent lanthanide ions have been found to be **in agreement**.

- If **L and S are not coupled**, then both **L** and **S** will align separately with the external magnetic field.

MEASUREMENT OF MAGNETIC PROPERTIES

- Magnetic moments cannot be measured directly.

- Magnetic moment can be measured from a parameter called **magnetic susceptibility (χ)**.

- The magnetic susceptibility (χ) is a property which determines how easily a substance can be magnetised.

- **It is defined as the capacity of a substance to get magnetised when placed in an applied magnetic field.**

When a substance is placed in an external magnetic field of strength **H**, the total magnetic induction or magnetic flux density **(B)** within the substance is given as

$$B = H + 4\pi\,I$$
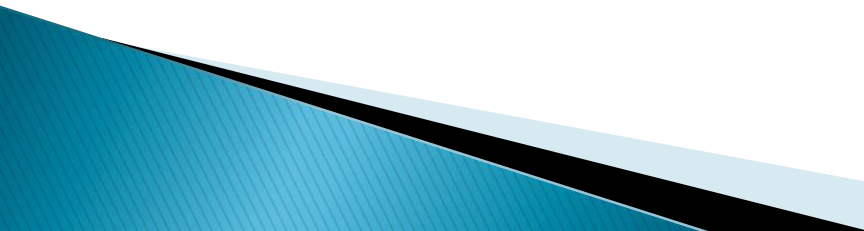
where I is the intensity of magnetisation.

Dividing the above equation by H

$$B/\,H \;=\; 1 + 4\pi\,I\,/H \;=\; 1 + 4\pi\,\kappa$$

The ratio **B / H** is called **magnetic permeability**

- The ratio **I /H** is called the **magnetic susceptibility per unit volume or volume susceptibility.**

- **Magnetic permeability** is the ability of a material to permit the passage of magnetic lines of force through it.

- The magnetic permeability (**B / H**) of a substance **is the ratio of the density of magnetic lines of force within a substance in a magnetic field to the density of magnetic lines of force in the magnetic field in the absence of the substance**.

EXPERIMENTAL MEASUREMENT OF MAGNETIC MOMENT

1. GOUY'S METHOD

- It is used to measure **paramagnetism.**

- Finely powdered substance is filled to a certain height in a pyrex tube called **Gouy's tube.**

- The tube is suspended from the arms of an analytical balance in a magnetic field.

- An electromagnet providing a constant magnetic field in the range 5000 – 20,000 gauss is used

- The lower part of the sample is in the stronger part of the magnetic field.

- The top part of the tube is in a zero magnetic field.

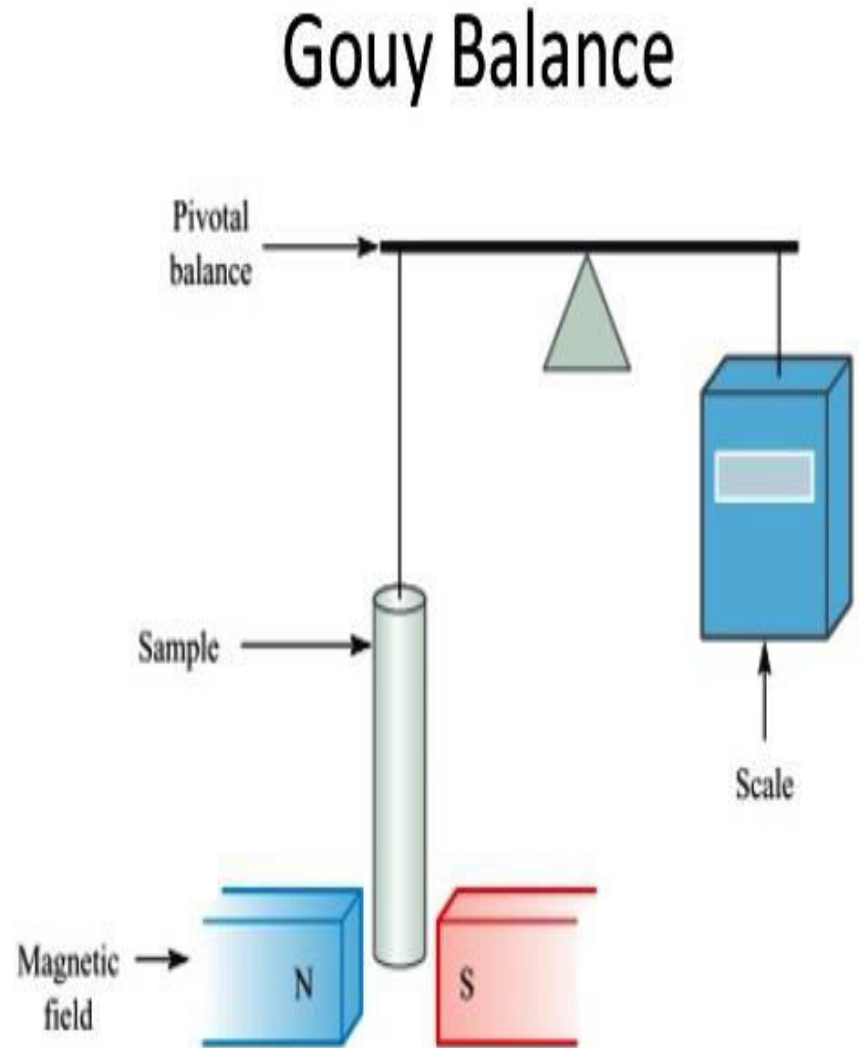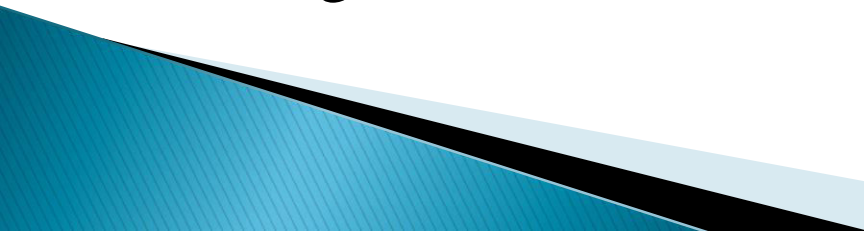- The weighing assembly is enclosed in order to avoid vibrations of the suspended samples.

Gouy Balance

Pivotal balance

Sample

Scale

Magnetic field

N

S

Fig. 20.21 Schematic representation of a Gouy balance.

- The powdered substance in the Gouy's tube is first weighed in the absence of magnetic field.

- Later it is weighed in the presence of magnetic field.

- In case of **paramagnetic substances**, the substance will be strongly attracted by the magnetic field.

- The weight of the substance will be **more in magnetic field** as compared to in the absence of magnetic field.

- This increase in weight is a measure of the paramagnetism of a substance **caused by the unpaired electrons.**

- **More** the number of unpaired electrons in a substance, **more** will be the weight of substance in the magnetic field.

- The **difference in weight** of the sample in the presence and absence of magnetic field gives the magnetic susceptibility of a substance.

- In case of **diamagnetic substances**, a decrease in the weight of a substance is seen in the magnetic field.

The sample is suspended in a non homogenous magnetic field.

The force acting on the sample is given by

$$F = \tfrac{1}{2} A \kappa H^2$$

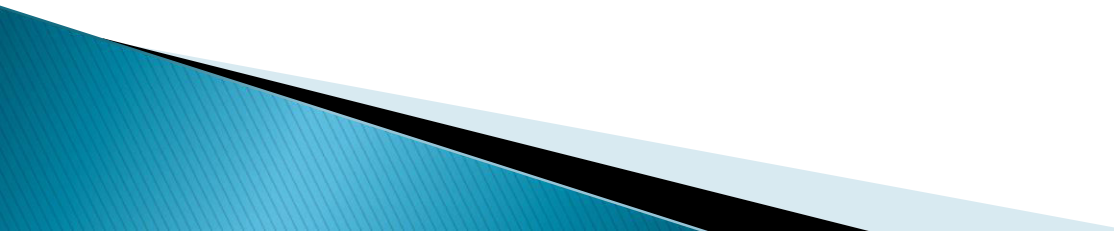where,

A = cross sectional area of the cyclinder

H = intensity of the central homogenous part of the magnetic field

κ = magnetic or volume susceptibility

- The above equation is only valid if the measurement is done in vacuum.

- In Gouy's method the sample is placed in air.

- So, the susceptibility due to air has to subtracted from the measured susceptibility.

- The equation now is

$$F = ½\,A\,H^2\,(\kappa - \kappa')$$

where , **κ'** is the magnetic/ volume susceptibility of air.

- **Another correc**tion is that the Gouy's tube is in the form of a hollow cylinder.

- It exerts / develops a force which is always present.

- This force has to be subtracted from the measured force.

- The force on the Gouy's tube is taken as **δ** and is **always negative** as the tube is made up of diamagnetic material.

- Applying the correction , the equation now is

$$F = \tfrac{1}{2} A H^2 (\kappa - \kappa') + \delta$$

where , δ = force developed due to Gouy's tube.

- The factor $\tfrac{1}{2} A H^2$ is **constant** for a specimen of constant length and cross sectional area.

- Taking the density of the sample in consideration, the equation can be rewritten as

$$10^6 \chi = \alpha + \beta F' / w$$

where
α = constant for displaced air = 0.029 x volume of the sample.

β = tube calibration constant
w = weight of the sample in gms.
F'= Force on the sample = **F – δ,** where F and **δ** are in gms

- The calibration of the tube is done by filling the tube with a substance whose susceptibility is accurately known.

- The most commonly used substance **is mercury tetrathiocyanatocobaltate (II), Hg[Co(CNS)$_4$].** Its susceptibility is 1.644 x 10^{-7} at 20^{0}C.

- β can be calculated by making measurements with the standard substance.

- Knowing the value of **α , β, F and δ** the magnetic susceptibility **χ** can be calculated.

DIAMAGNETIC CORRECTION

- The calculated magnetic susceptibility is due to both **paramagnetic and diamagnetic susceptibilities.**

- Diamagnetic substances have no unpaired electrons and have zero magnetic moment.

- When a diamagnetic substance is placed in a magnetic field, the internal magnetic field induces a small magnetic field which is in opposition to the external field.

- Diamagnetic substances repel the lines of force and show a decrease in weight in Gouy's method.

- Every molecule of the substance has **large number of paired electrons.**

- These paired electrons do not contribute to magnetic moment but affect the magnitude of χ_M.

- The contribution from paired electrons oppose that from unpaired electrons.

- The measured magnetic susceptibility is due to both **paramagnetic and diamagnetic susceptibilities.**

$$\chi_M \text{ (measured)} = \chi_{PM} + \chi_{DM}$$

- The correct paramagnetic susceptibility of a substance is obtained as

$$\chi_M{}^{Corr} = \chi_{PM} = \chi_M \text{ (measured)} - \chi_{DM}$$
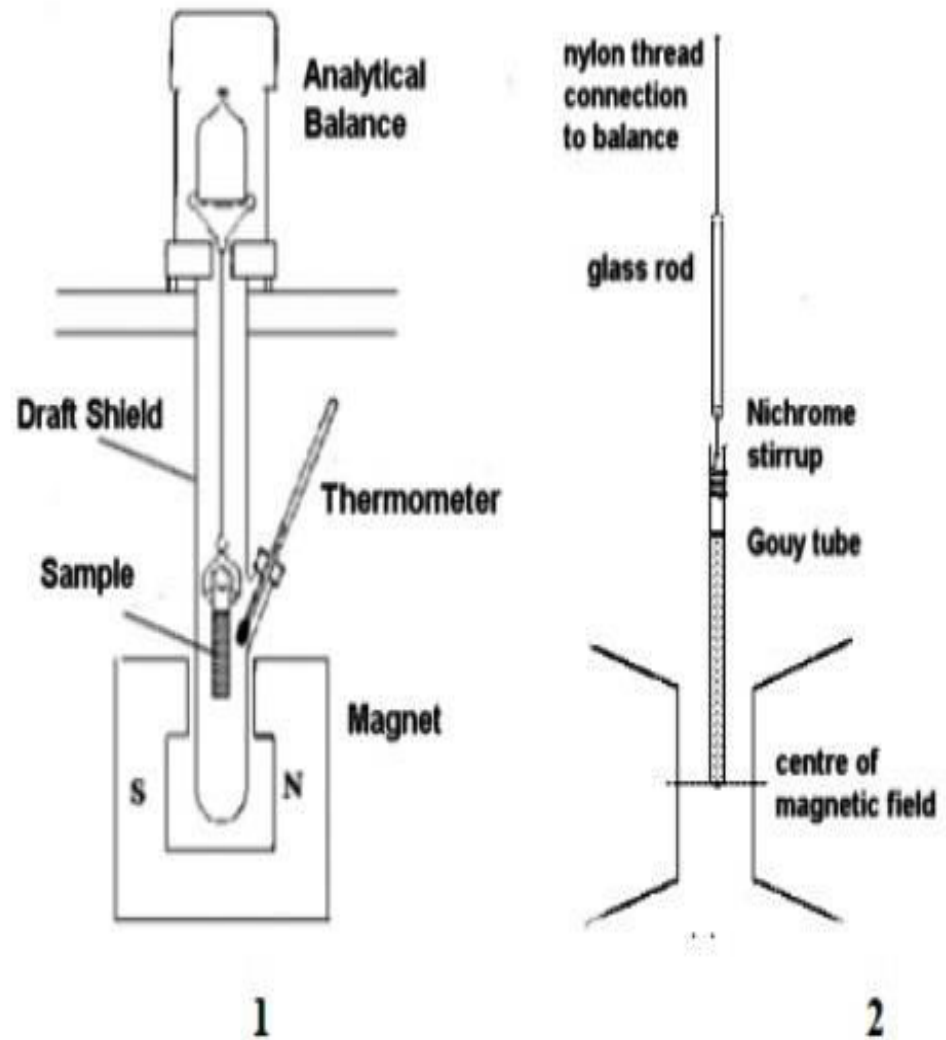
ADVANTAGES OF GOUY'S METHOD

- Very simple and easy to assemble apparatus.
- Easy to handle and use
- Requires large amount of sample. So, an ordinary balance can be used to measure the change in mass.

DISADVANTAGES OF GOUY'S METHOD

- Requires large amount of sample.
- Requires perfect uniform packing of the sample. It is tedious and time consuming.
- Correct results are not obtained if the packing is not uniform.

FARADAY'S METHOD

- Faraday's method gives the magnetic susceptibility directly.

- It requires a very small amount of the sample.

- The sample packed in a quartz ampule is suspended between magnet poles from a sensitive balance

Analytical Balance

Draft Shield

Thermometer

Sample

Magnet

S   N

nylon thread connection to balance

glass rod

Nichrome stirrup

Gouy tube

centre of magnetic field

1

2

- The sample is suspended between the magnetic poles so that the value of the product **H(dH/dx)** is constant over the region occupied by the sample.

- **dH/dx** is the gradient of the field.

- The whole system is enclosed and can be flushed with inert gases like nitrogen or helium.

- A sample weighing (0.1 – 10 mg) is taken in an ampule of internal diameter ~ 1mm is placed in a magnetic field of constant gradient **dH/dx.**

- The force acting on the sample is measured directly using a quartz fibre torsion balance and is given as

$$f = m \chi H(dH/dx)$$

where
m = mass of the sample
χ = susceptibility of the sample
H = intensity of the central homogenous part of the field
dH/dx = gradient of the field in x direction

- The force f can be measured by weighing the sample both in the field and out of the field. The difference of the two weights gives the value of force.

- This method is based on comparison of unknown substance and the standard **[mercury tetrathiocyanatocobaltate (II)].**

- As the magnetic field H and the field gradient dH/dx are the **same in both case**, the force acting on the standard and the unknown sample can be rewritten as

$$\textbf{H (dH/dx)} = f_u / m_u \, \chi_u \quad \text{(for unknown sample)}$$

$$\textbf{H (dH/dx)} = f_s / m_s \, \chi_s \quad \text{(for standard)}$$

Equating the above equations, we get

$$f_u / m_u \, \chi_u = f_s / m_s \, \chi_s$$

On rearranging ,

$$\chi_u = f_u \, m_s \, \chi_s / m_u \cdot f_s$$

where,
χ_u and χ_s are the susceptibilities of the sample & standard
m_u and m_s are the masses   and
f_u and f_s are the respective forces at constant H(dH/dx)

ADVANTAGES OF FARADAY'S METHOD

- Requires very small quantity of the sample and it need not be homogenous.
- Gives the magnetic/specific susceptibility directly.

DISADVANTAGES OF FARADAY'S METHOD

- Equipment is very delicate and require great skill.
- As small amount of sample is used, reactions occurring at the surface of the sample will lead to large errors.

The magnetic susceptibility χ_M is related to magnetic moment μ as

$$\chi_M^{Corr} = N_0\, \mu^2 / 3kT$$

where k is the Boltzmann constant

N_0 is the Avogadro number

T is the absolute temperature

χ_M^{Corr} is the corrected magnetic moment

Rearranging the equation,

$$\mu^2 = 3k \cdot \chi_M^{Corr} \cdot T / N_0$$

$$\mu = (3k / N_0)^{1/2} (\chi_M^{Corr} \cdot T)^{1/2}$$

where $(3k / N_0)^{1/2}$ = constant = 2.828

Thus the magnetic moment μ can be calculated from magnetic susceptibility χ_M by

$$\mu = 2.828 (\chi_M^{Corr} \cdot T)^{1/2} \text{ B.M.}$$

A Gouy tube having $\alpha = 0.0106$ mg, $\beta = 607.98$ and $\delta = -2.0$ mg was filled with 418.85 mg of a complex (mol.wt. = 487). The force on the sample was observed to be 7.0 mg when the measurements were done at 27°C. Calculate χ^{Corr} and μ_{eff} when diamagnetic correction for the sample was -172.7×10^{-6}/g atom.

Solution. Volume susceptibility can be calculated as :

$$10^6 \chi = \frac{\alpha + \beta F}{w}$$

$$\alpha = 0.0106, \ \beta = 607.98, \ F = 7.0 \text{ mg}, \ \delta = -2.0 \text{ mg}$$
$$F' = F - \delta = 7.0 - (-2.0) = 9.0$$
$$w = 418.85 \text{ mg}$$

$$10^6 \times \chi = \frac{0.0106 + 607.98 \times 9.0}{418.85}$$

$$\chi = 13.06 \times 10^{-6}$$

Now
$$\chi^M = 13.06 \times 10^{-6} \times 487$$
$$= 6360.22 \times 10^{-6}$$

$$\chi^{Corr} = \chi_M - \text{Diamagnetic correction}$$
$$= 6360.22 \times 10^{-6} - (-172.7 \times 10^{-6})$$
$$= 6532.92 \times 10^{-6}$$

$$\mu_{eff} = 2.828 \sqrt{\chi_M^{corr} \times T} \qquad \text{where } T = 273 + 27 = 300 \text{ K}$$

$$= 2.828 \sqrt{6532.92 \times 10^{-6} \times 300}$$

$$= 3.96 \text{ B.M.}$$

$$\therefore \qquad \mu_{eff} = 3.96 \text{ B.M.}$$

VARIATIONOF MAGNETIC SUSCEPTIBILITY WITH TEMPERATURE

❖ Magnetic susceptibility of a substance varies with temperature.

❖ According to Pierre Curie, paramagnetic susceptibilities vary inversely with temperature.

$$\chi_M^{Corr} \propto 1/T$$
$$\chi_M^{Corr} = C/T$$

where
C = constant, characteristic of the substance known as Curie's constant, **T =** absolute temperature

- Curie's law state that the paramagnetic susceptibilities vary inversely with temperature.

- A plot of graph between χ_M^{Corr} and absolute temperature T (K) is parabolic in nature.

- If χ_M^{Corr} of a substance is measured at different temperatures and the reciprocal of those values (1/ χ_M^{Corr}) plotted against absolute temperature T, a straight line with slope C is obtained which intersects the origin


χ

$\chi = C/T$

T

$1/\chi$

slope = 1/C

T

Curie Law Plots

slope = $\frac{1}{C}$
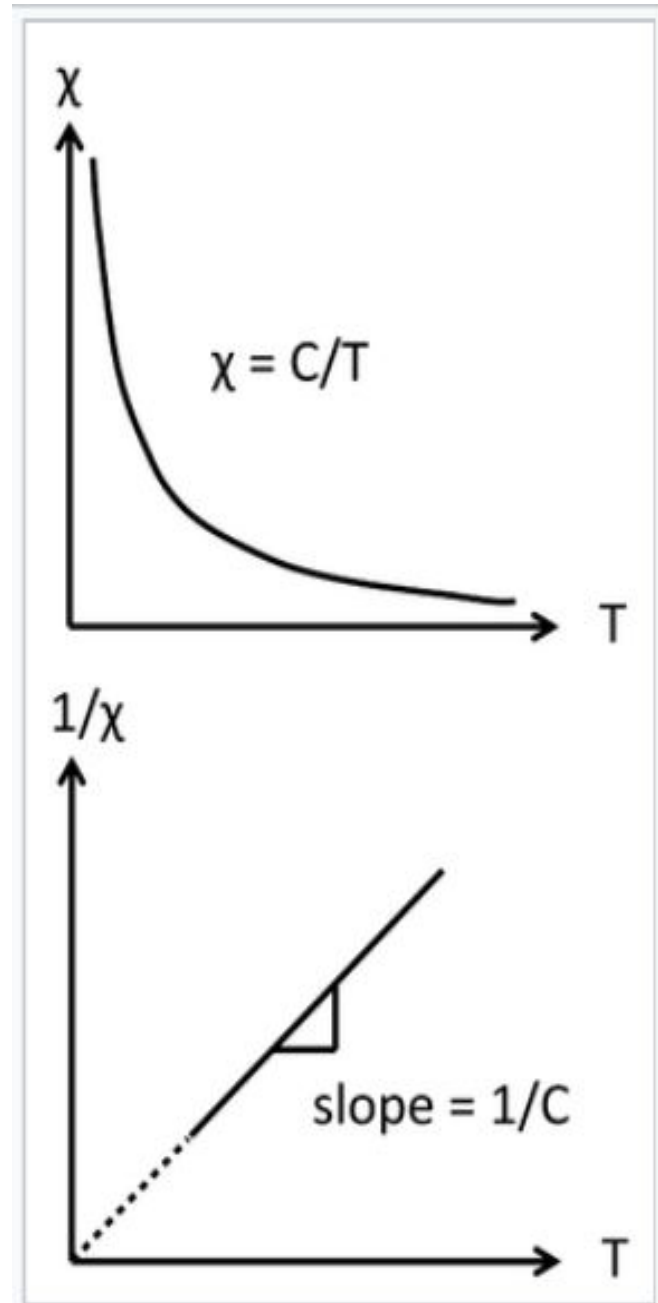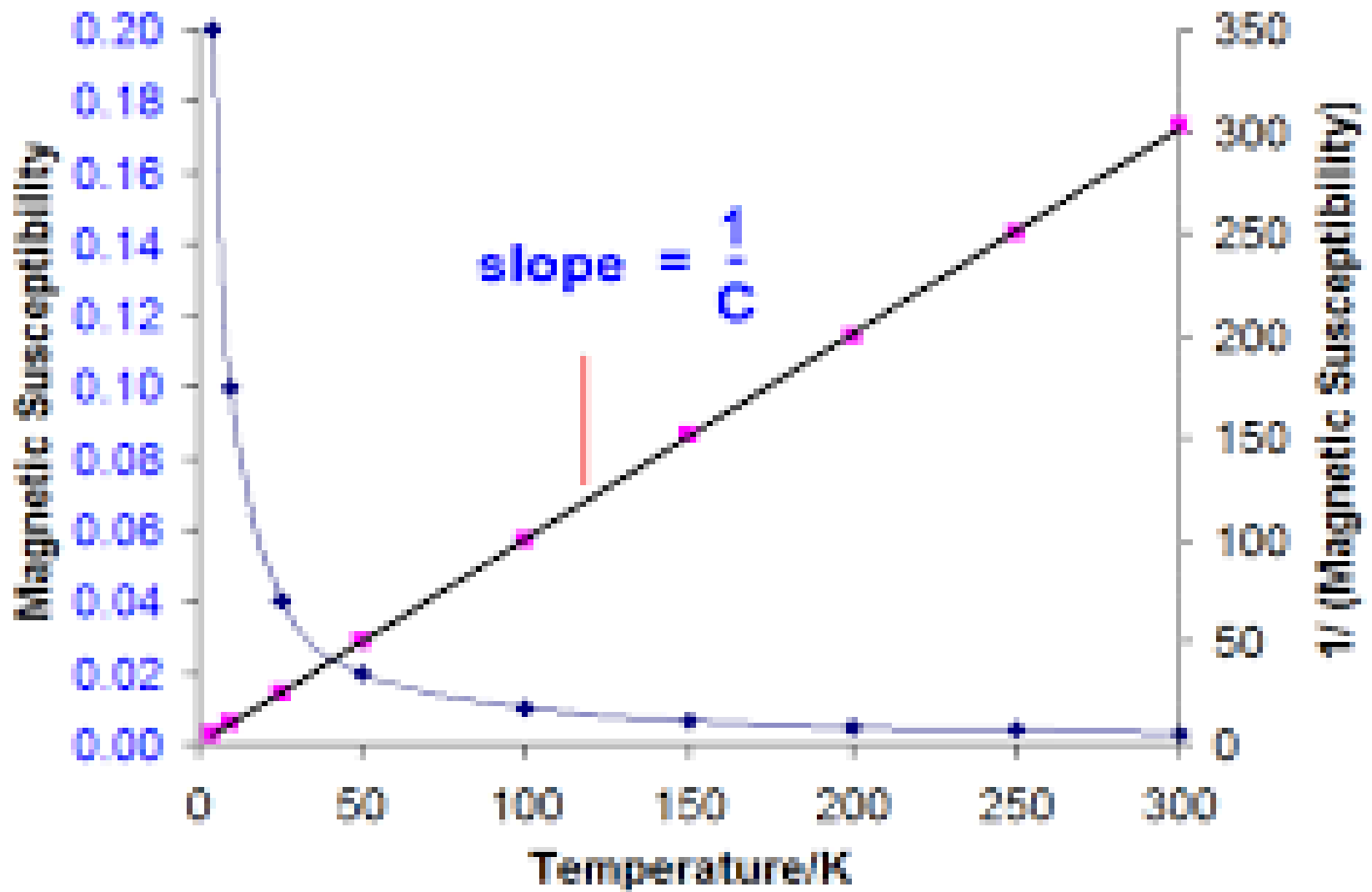
- Curie's law is followed by substances in whom there is no spontaneous interaction between adjacent unpaired electrons i.e. paramagnetic substances.

- In other words, there is no secondary magnetic interactions between the neighbouring magnetic centres.

- Such substances are called **magnetically dilute.**

- Many substances give straight lines which do not pass through the origin.

- The straight lines intersect the temperature axis either a little above the 0K or little below 0K.

- Such compounds are said to obey modified Curie equation
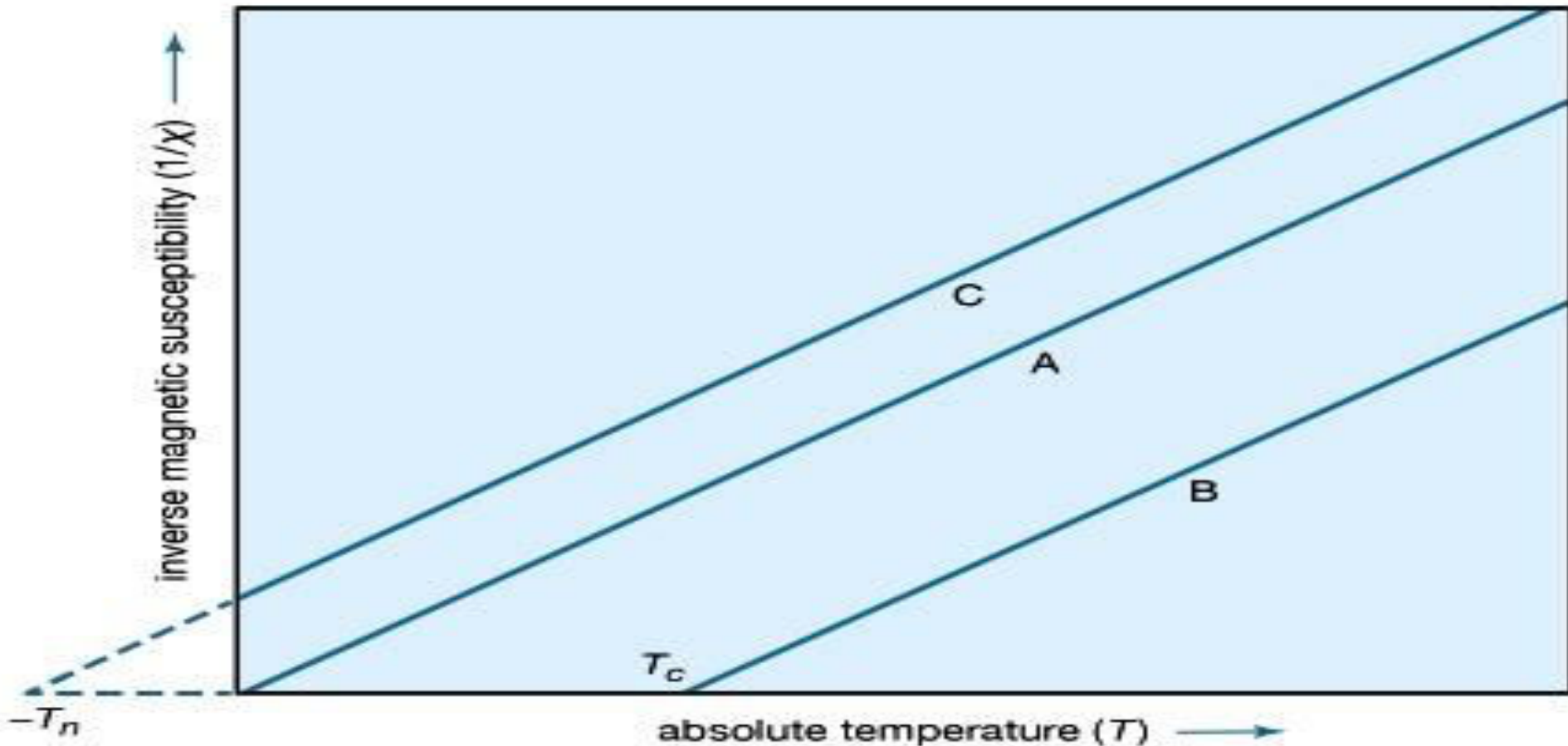
- The modified Curie's equation is

$$\chi_M{}^{Corr} = C / T - \theta$$

where θ is the temperature at which the straight line cuts the absolute temperature axis.

- The modified equation is called **Curie – Weiss law** and the θ is called Weiss constant.

- The Weiss constant takes into account interionic/ intermolecular interactions and eliminate them.

- So, Magnetic moment $\mu = 2.828 \left[\chi_M{}^{Corr} (T - \theta) \right]^{1/2}$

MAGNETISM

There are many kinds of magnetic substances and the magnetic properties exhibited by them are of the following types

Paramagnetism
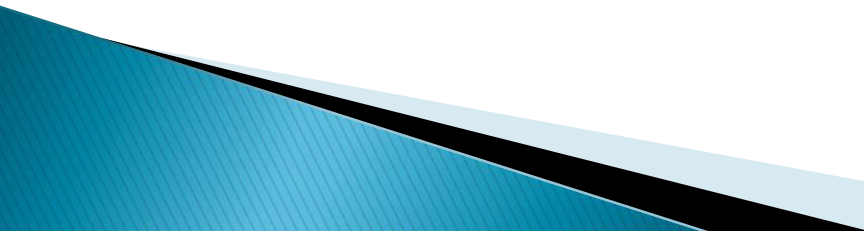
Diamagnetism

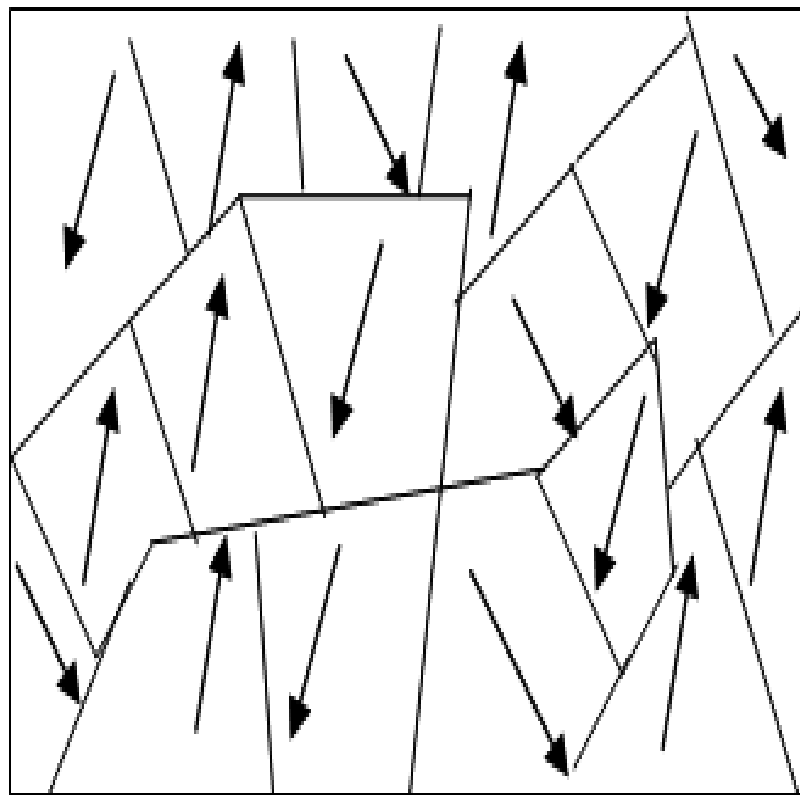Ferromagnetism

Anti – Ferromagnetism

A. *FERROMAGNETIC SUBSTANCES*

- In some materials, the **permanent atomic magnetic moments** have a strong tendency to **align themselves** even without any external field.

- These materials are said to be **Ferromagnetic materials.**

- The **ferromagnetic materials** are those substances which exhibit strong magnetism in the same direction of the field, when a magnetic field is applied to it.

- In solid state , the metal ions of ferromagnetic substances are **grouped together** into small regions called **Domains.**

- They get their **strong magnetic properties** due to the presence of magnetic domains.

- In these domains, large numbers of atom's moments (10^{12} to 10^{15}) are **aligned parallel** so that the magnetic force within the domain is strong.

- When a ferromagnetic material is in the **unmagnetized state**, the domains are nearly randomly organized and the net magnetic moments get cancelled.

- When a magnetizing field is applied, the domains become aligned in the direction of the magnetic field.

- They are able to **retain their magnetic properties** after the external field has been removed.

- It means it becomes **permanently magnetized** even after the removal of the external magnetic field.

- Some of the examples of ferromagnetic materials are **cobalt, iron, nickel, gadolinium, dysprosium.**


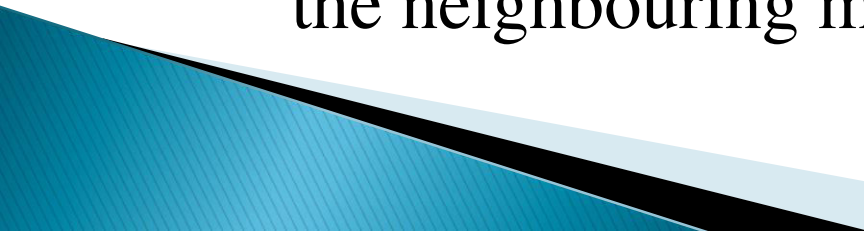A. Random domain orientation
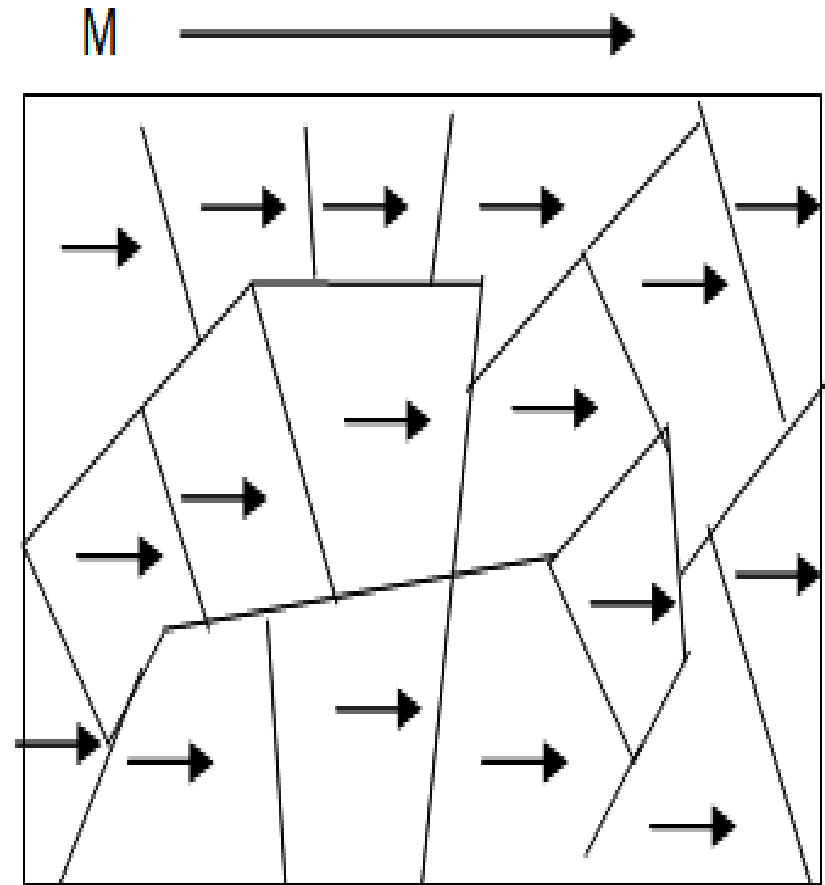
B. After magnetization
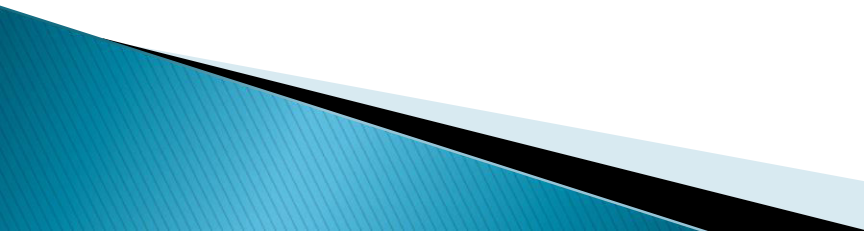
B. ANTI FERROMAGNETIC SUBSTANCES

- In this the adjacent ions / domains that behave as tiny magnets spontaneously align themselves into opposite or antiparallel arrangement throughout the material

- The magnetism from magnetic atoms or ions oriented in one direction is canceled out by the set of magnetic atoms or ions that are aligned in the reverse direction.

- So that the compound exhibits almost no gross external magnetism.

- This type of behaviour is observed at low temperatures.

Examples of anti ferromagnetic substances are MnO, FeO, NiO, MnO_2, V_2O_3.
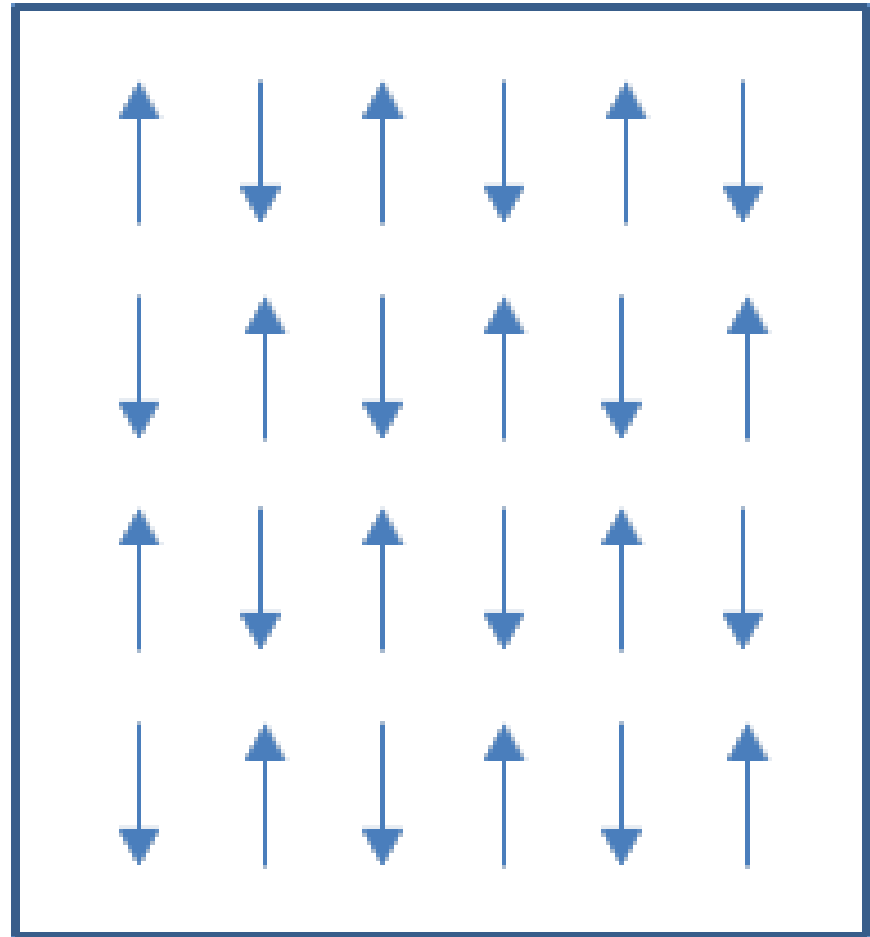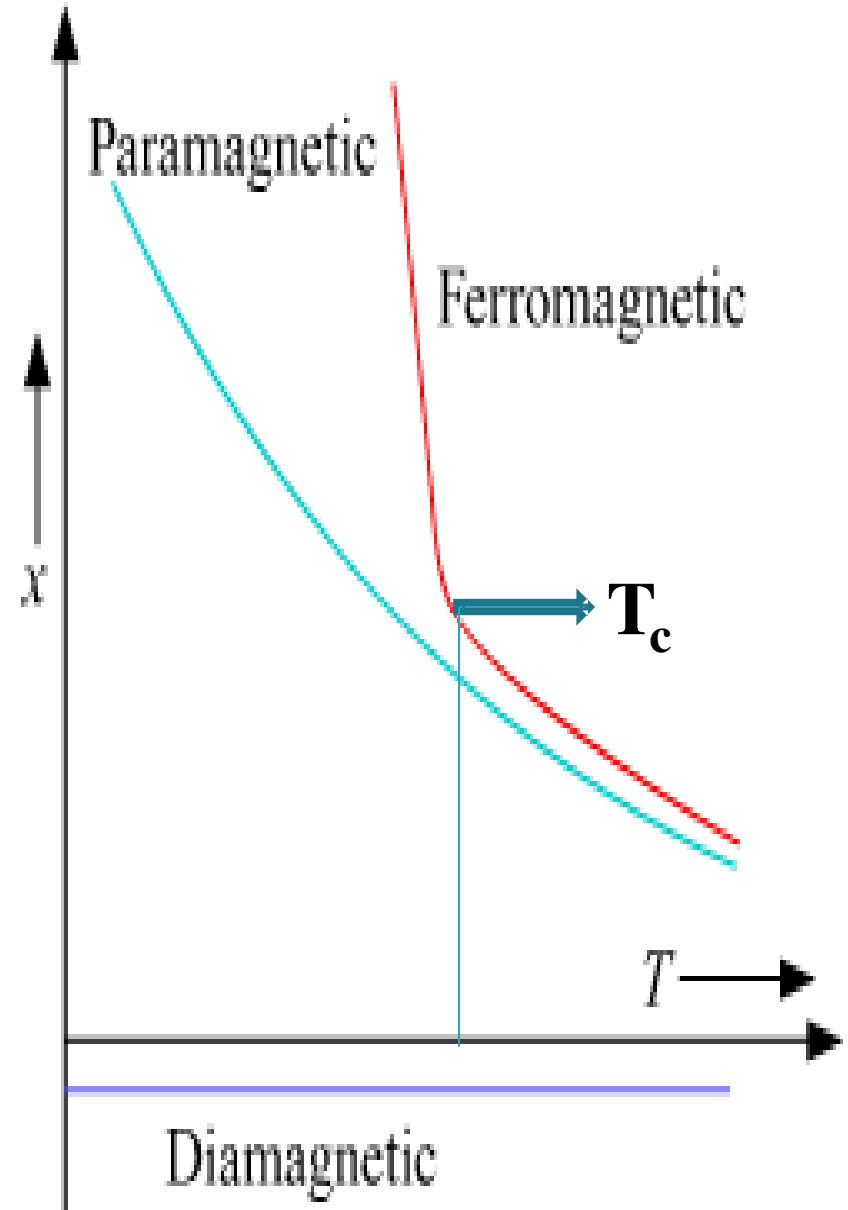

Antiferromagnetic ordering

- In paramagnetic substances, the magnetic moment results entirely from the individual magnetic centres.

- In other words, there is **no secondary magnetic interactions** between the neighbouring magnetic centres.

- Such substances are called **magnetically dilute.**

- But, there are some paramagnetic substances in which **secondary interactions exist** between the neighbouring magnetic centres.

- Such substances are called **magnetically concentrated substances.**

- In such substances the magnetic susceptibility shows dependence on both field strength and temperature.

- These substances are **Ferromagnetic and Anti ferromagnetic substances.**

- The main features of the curves of these substances can be understood in terms of **Curie – Weiss law.**

The curve for ferromagnetic substances shows some discontinuity at temperature T_c. This is called **Curie temperature.**

Above T_c the ferromagnetic substances follow **Curie or Curie – Weiss law** and behave as **simple paramagnetic substances.**
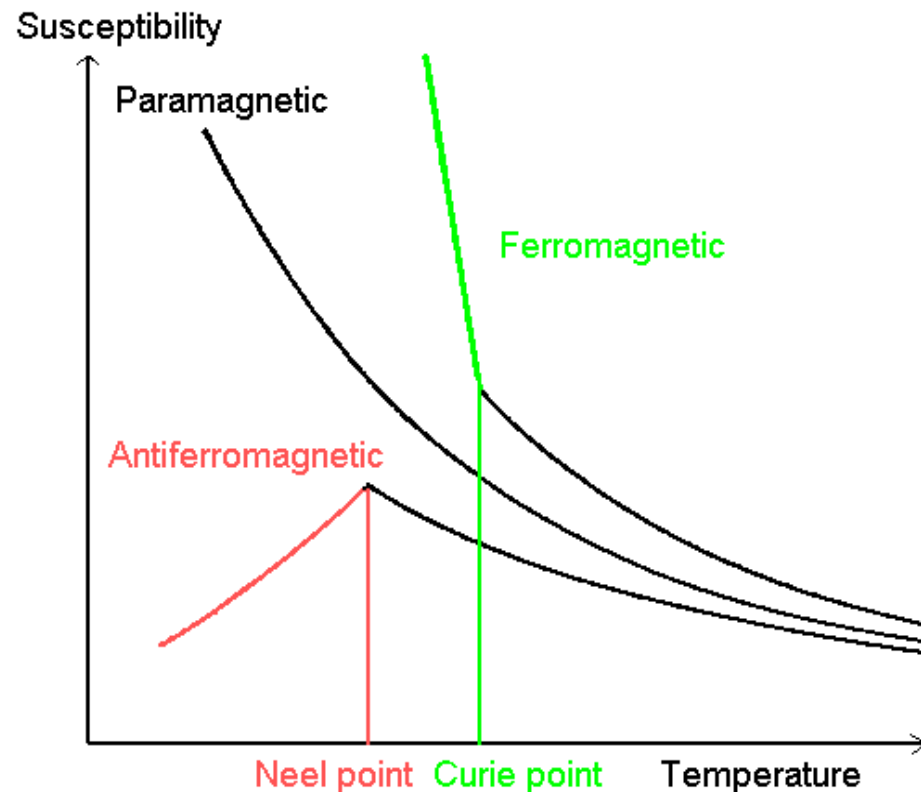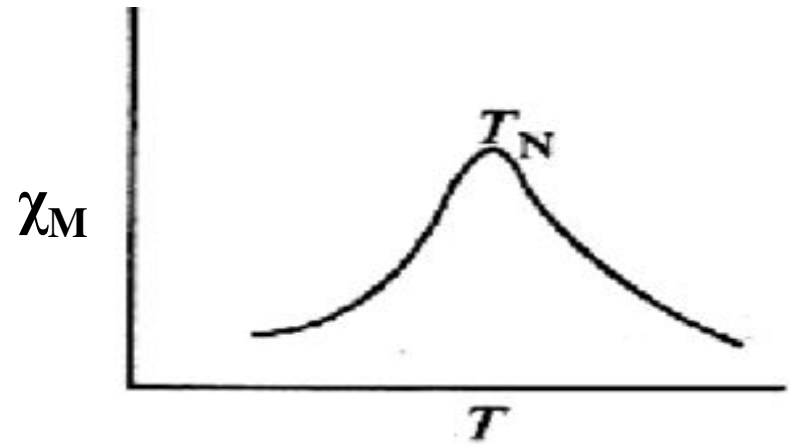
Below T_c the magnetic susceptibility behaviour is **different** and it depends on **field strength** of the magnetic field.

In case of **anti ferromagnetic substances**, a characteristic temperature T_N called the **Neel's temperature** can be observed.

Above T_N, all anti ferromagnetic substances follow **Curie or Curie Weiss law** and show **paramagnetic behaviour.**

Below T_N , the magnetic susceptibility **decreases** with decrease in temperature.

- The **abnormal behaviour** in ferromagnetic and anti- ferromagnetic substances is due to **interionic interactions.**

- **Above T$_c$** thermal energies are able to **randomize the orientations**, resulting in **decrease in magnetic susceptibility with increase in temperature**.

- **Above Neels temperature**, the magnetic moments are **not aligned in antiparallel** directions due to large thermal energy.

ALIGNMENT OF MAGNETIC MOMENTS

Ferromagnetic ↑ ↑ ↑ ↑ ↑ ↑ ↑	Below T_C, spins are aligned parallel in magnetic domains
Antiferromagnetic ↑ ↓ ↑ ↓ ↑ ↓ ↑	Below T_N, spins are aligned antiparallel in magnetic domains
Ferrimagnetic ↑ ↓ ↑ ↓ ↑ ↓ ↑	Below T_C, spins are aligned antiparallel but do not cancel
Paramagnetic ↑ ↓ ↑ ↑ ↓ ↑ ↓	Spins are randomly oriented (any of the others above T_C or T_N)

ORBITAL CONTRIBUTION TO MAGNETIC MOMENT

- The total magnetic moment of a substance is due to both **spin and orbital contribution.**

- Both these contributions occur because of **unpaired electrons.**

- In many cases, the unpaired electrons are the **outermost electrons** under consideration and these are **not screened** by other electrons.

- In such cases, magnetic moment depends on only the spin contribution, the orbital contribution can be neglected.

- In cases like **lanthanides and actinides**, the unpaired electrons are **inside** (lie within the shell) and are **shielded** by the outer electrons (from the electric field of the in coming ligands), **orbital contribution cannot be neglected.**

- Thus in these the total magnetic moment is due to both **spin and orbital magnetic moment**.

- The spin angular momentum of an electron does not depend on its surrounding (chemical environment).

- The orbital angular momentum of an electron depend on its surrounding (chemical environment).

- The orbital contribution can be **reduced or quenched** in the substance.

- Qualitatively, **quenching of orbital angular** momentum can be explained on the basis of crystal field theory.

- In case of first transition series, the unpaired electrons are present in **3d orbitals**.

- A transition metal ion has **five** 3d orbitals of **same energy (degenerate).**

- The orbital angular momentum arises due to **rotation** of electron about the nucleus **via these 3d orbitals**.

- Generation of orbital angular momentum occurs only if the **following conditions are satisfied:**

i. The orbitals should have the **same energy** (degenerate).
ii. The orbitals should have **similar size and shape**, so that they may be **transformed** into one another by **rotation about some axis**.
iii. The orbitals **should not have** electrons of **same / identical spin.**

- The orbital angular momentum of an electron along an axis is **equal to the number of times** the orbital gets transformed into equivalent orbitals during a rotation of $\pi / 2$ (or 90^0) around that axis.

- Consider a **free metal ion** in which all d – orbitals are degenerate.

- An electron in $d_{x^2-y^2}$ orbital will contribute **2 units of angular momentum ($h / 2\pi$)** along z – axis towards orbital angular momentum **as rotation of $d_{x^2-y^2}$ orbital by 45^0 around the z – axis will transform it into equivalent d_{xy} orbital.**

- In other words, a rotation of $d_{x^2-y^2}$ orbital by 90^0 around the z – axis will carry the $d_{x^2-y^2}$ orbital into d_{xy} orbital twice.

- Similarly, an electron in d_{xy} orbital will contribute **2 units of angular momentum ($h/2\pi$)** along z – axis towards orbital angular momentum.

- An electron in d_{xz} orbital will contribute **1 unit of angular momentum ($h/2\pi$) along z – axis** towards orbital angular momentum, because d_{xz} orbital will transform into d_{yz} orbital once on rotating around x – axis by 90^0.
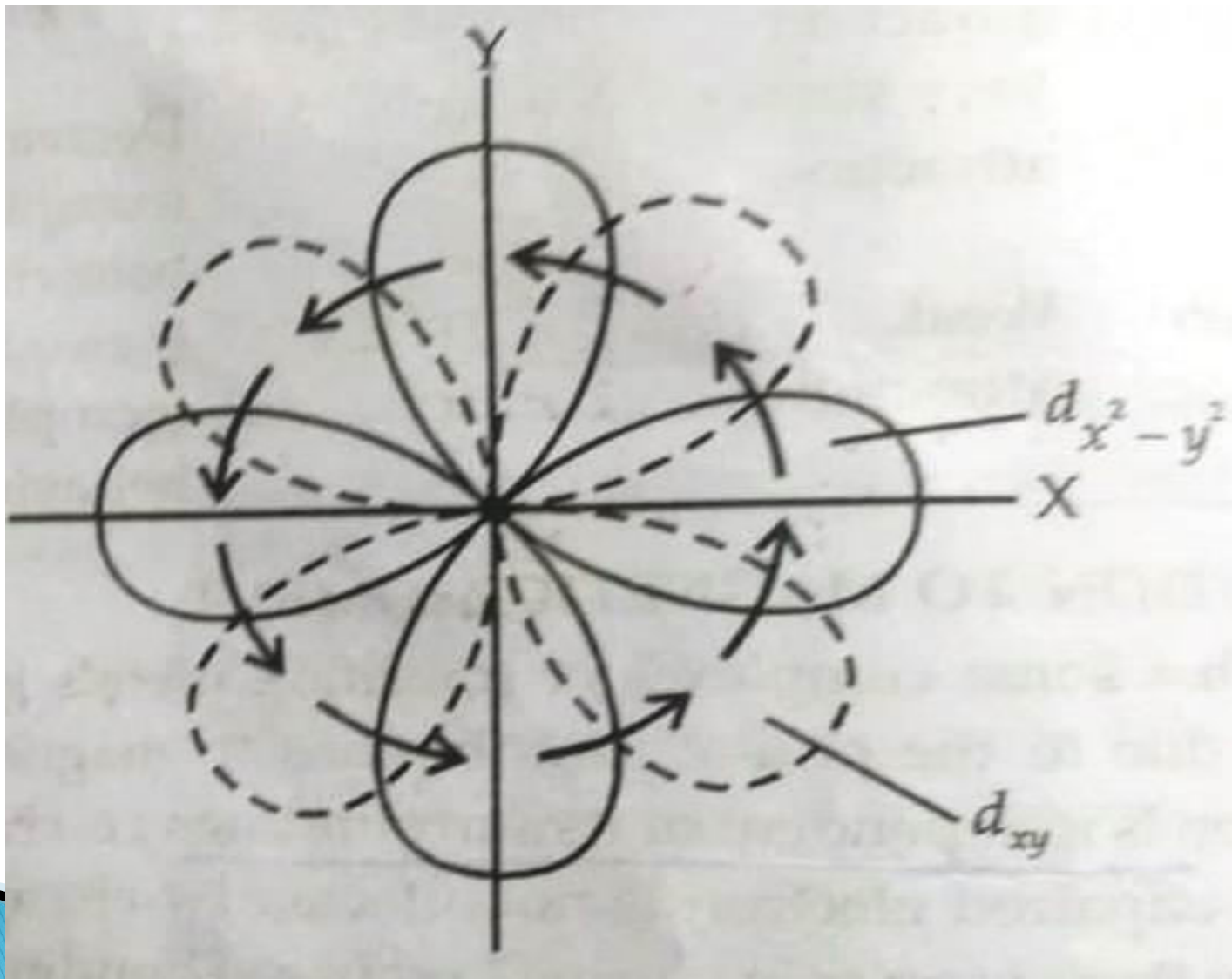
- Only d_z^2 orbital **cannot be transformed** into any other d – orbital due to their different shape.

- So, d_z^2 orbital has **zero orbital angular momentum** along z – axis.

- **When the metal ion gets surrounded by ligands, the degeneracy of d – orbitals gets splitted.**

- The $d_{x^2-y^2}$ **(e set)** and d_{xy} **(t_2 set)** orbitals are **no longer equivalent** as they now **have different energies** and cannot be transformed into each other by rotation along z – axis.

QUENCHING OF ORBITAL ANGULAR MOMENTUM IN OCTAHEDRAL COMPLEXES

- In octahedral complexes, the five d – orbitals are split into two sets :

i) t_{2g} (d_{xy} , d_{xz} and d_{yz})   ii) e_g ($d_{x^2-y^2}$ and d_{z^2})

- Due to splitting the $d_{x^2-y^2}$ and d_{xy} orbitals are no longer equivalent and cannot transform into each other.

- So, their orbital angular momentum gets quenched.

- However, the two t_{2g} orbitals d_{xz} **and** d_{yz} are still equivalent in size and are degenerate .

- They will **show some contribution** towards orbital angular momentum on rotation about z – axis.

- Thus in octahedral complexes, the metal ion having unpaired electrons in t_{2g} orbital will make some contribution along z – axis to the **overall magnetic moment (μ_{eff}) of the complex.**

- **But if t_{2g} and e_g orbitals are half filled or fully filled, their transformation into each other becomes impossible.**

Table 3. Orbital contribution in octahedral complexes

No. of electrons d^n	High spin octahedral		Low spin octahedral	
	Electronic configuration	Orbital contribution	Electronic configuration	Orbital contribution
d^1	t_{2g}^1	Expected	t_{2g}^1	Expected
d^2	t_{2g}^2	Expected	t_{2g}^2	Expected
d^3	t_{2g}^3	Not Expected	t_{2g}^3	Not Expected
d^4	$t_{2g}^3 e_g^1$	Not Expected	t_{2g}^4	Expected
d^5	$t_{2g}^3 e_g^2$	Not Expected	t_{2g}^5	Expected
d^6	$t_{2g}^4 e_g^2$	Expected	t_{2g}^6	Not Expected
d^7	$t_{2g}^5 e_g^2$	Expected	$t_{2g}^6 e_g^1$	Not Expected
d^8	$t_{2g}^6 e_g^2$	Not Expected	$t_{2g}^6 e_g^2$	Not Expected
d^9	$t_{2g}^6 e_g^3$	Not Expected	$t_{2g}^6 e_g^3$	Not Expected

ORBITAL CONTRIBUTION IN TETRAHEDRAL COMPLEXES

- In tetrahedral complexes, the five d – orbitals are split into two sets :

i) $\mathbf{t_2}$ ($\mathbf{d_{xy}}$, $\mathbf{d_{xz}}$ and $\mathbf{d_{yz}}$)   ii) $\mathbf{e}$ ($\mathbf{d_{x^2-y^2}}$ and $\mathbf{d_{z^2}}$)

- The energies of t_2 (d_{xy} , d_{xz} and d_{yz}) orbital **are higher than that of** e ($d_{x^2-y^2}$ and d_{z^2}) orbital.

- So, the metal ions as shown in the table will not have orbital contribution.

ORBITAL CONTRIBUTION IN TETRAHEDRAL COMPLEXES

Table 4. Orbital contributions in tetrahedral complexes.

n d^m	Electronic configuration	Orbital contribution
d^1	e^1	Not expected
d^2	e^2	Not expected
d^3	$e^2 t_2^1$	Expected
d^4	$e^2 t_2^2$	Expected
d^5	$e^2 t_2^3$	Not expected
d^6	$e^3 t_2^3$	Not expected
d^7	$e^4 t_2^3$	Not expected
d^8	$e^4 t_2^4$	Expected
d^9	$e^4 t_2^5$	Expected

- The tetrahedral complexes of Co(II) (d^7) have magnetic moment values vey close to the spin only values.

- However the magnetic moment values for tetrahedral complexes of Ni(II) (d^8) are more than the spin only values.

- This is because in some cases there may be contribution from **spin orbital coupling**.

- In such cases the magnetic moment is calculated as:

$$\mu_{eff} = \mu_0 \left(1 - \alpha \lambda / \Delta \right)$$

where,

μ_0 is the spin only magnetic moment

α is a constant depending on spectroscopic terms.

λ is the spin orbital coupling constant. It depends on the total number of electrons. It has a **+ve** value for d^n configuration with **n < 5** and a **−ve** value for d^n configuration with **n > 5**

and

Δ is the difference in energy level between the ground state and the higher state.

TEMPERATURE   INDEPENDENT   PARAMAGNETISM

- Certain compounds show weak paramagnetism or paramagnetic behaviour despite having no unpaired electrons in their ground state.

- This paramagnetism is independent of temperature and is called temperature independent paramagnetism (TIP).

- Complex ions such as MnO_4^-, CrO_4^{2-}, $[Co(NH_3)_6]^{3+}$ etc. show TIP.

- This paramagnetism arises due to **coupling of the ground state of the system with excited states of higher energy** under the influence of the magnetic field.

- This coupling leads to complexes having some orbital magnetic moment.

- This paramagnetism does not depend on thermal population of levels, so it is called TIP.

- This TIP gets induced only when the complex is placed in a magnetic field.