Measurement of Magnetic Susceptibility (χ).

Magnetic Susceptibility is the physical quantity describing materials properties in the external magnetic field. It is defined as the ratio between magnetization M of the material in the magnetic field and the field. intensity H;

$$M = \chi_m H$$

All materials can be classified by value of magnetic susceptibility into 3-groups -

Diamagnetic $-1 < \chi_m < 0$

Paramagnetic $0 < \chi_m \ll 1$

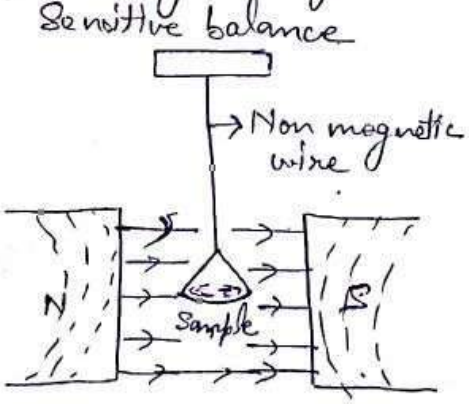
Ferromagnetic $\chi_m \gg 1$

Several methods are used for measuring the magnetic susceptibility -

1. Faraday' Method
2. Gouy's Method. (Gouy)
3. NMR- method.
4. VSM Method (Vibrating Sample magnetometer)
5. SQUID Method (Super quantum interface device).

Faraday's Scale - Faraday's scale is suitable for susceptibility measurement of a small specimen made from paramagnetic, diamagnetic or even ferromagnetic material.

Performed in any lab, but for room-temperature, gives accurate value Using a Faraday balance. - A Faraday balance is a device for measuring magnetic susceptibility. χ is related to the force experienced by a substance in a magnetic field. The force is measured as a weight change, using a torsion balance.



Here, the field is Homogeneous. The pole pieces of magnet are so shaped that there is a region in which the product of the field strength and field gradient in the z-direction is constant. The sample is placed in this region.

The force in this case is independent of the packing of the sample and depends only on the total mass of the material present. The method is sensitive and highly reproducible and can be applied to single crystals. The force is measured as a weight change, using a torsion change.

Use- electromagnetic field ⇒

Give electricity to produce magnetic field, & by varying electricity, magnetic field also varies.

In absence of magnetic field –

weight of Cup = x_1 mg.

weight of cup + sample = y_1 mg.

In presence of magnetic field. –

weight of Cup = x_2 mg.

weight of cup + sample = y_2 mg.

Hence,

In absence of magnetic field. the weight of ~~cup~~ sample = $(y_1 - x_1)$ mg
= w_1 mg.

In presence of magnetic field the weight of sample = $(y_2 - x_2)$ mg.
= w_2 mg.

So, change in weight of sample in the field = $(w_2 - w_1)$ mg
= Δw mg.

This change can be 0, +ve or -ve.

Case- I when $\Delta w = 0$, then substance is non-magnetic.

Case-II when Δw = +ve, then substance is paramagnetic

Case-III when Δw = -ve, then substance is diamagnetic.

Force acting on the sample, $F = \Delta w \cdot g$ ---------- (1) [Δw = mass]

g = acceleration due to gravity.

Force due to magnetic field ⇒ $F = HV(K_1 - K_2)\frac{dH}{dx}$ ---- (2)

Where; H = strength of mag. field.

V = Volume of the sample

K_1 & K_2 = volume susceptibility for sample and air, respectively.

$K_2 = (0.03 \times 10^{-6})$ CGS unit.

$\frac{dH}{dx}$ = magnetic field gradient in x-direction

From equation ① and ② we get -

$$\Rightarrow \quad \Delta W \cdot g = F = HV(K_1 - K_2)\frac{dH}{dx}$$

As K_2 is very very small, so neglecting K_2;

Then, $$\Delta W \cdot g = HVK_1 \cdot \frac{dH}{dx}$$

$$\Rightarrow \quad K_1 = \frac{\Delta W \cdot g}{HV\left(\frac{dH}{dx}\right)}$$

Mass or Specific susceptibility is. $$\frac{K_1}{\rho} = \frac{\Delta W \cdot g}{HV\rho\left(\frac{dH}{dx}\right)} = \frac{\Delta W \cdot g}{H \cdot W\left(\frac{dH}{dx}\right)}$$

Molar magnetic susceptibility,

$$\chi_M = \frac{K_1}{\rho} \times M \quad (\text{Molar mass})$$

$$= M \cdot \frac{\Delta W \cdot g}{HW\left(\frac{dH}{dx}\right)}$$

So, $$\boxed{\chi_M = M \cdot \frac{\Delta W \cdot g}{HW\left(\frac{dH}{dx}\right)}}$$

In practice, measurement of values done for reference also, which have standard values.

And we use, compounds having definite composition at r.t. such as -

(i) $NiCl_2 \cdot 6H_2O$ → Deep green solution.

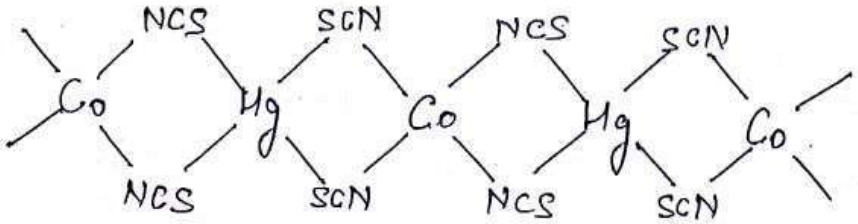
(ii) $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ ⇒ Light green solid.

(iii) $HgCo(NCS)_4$ ⇒ Deep blue colored solid. (Most frequently used)

Most common reference $HgCo(NCS)_4$ solution - also appear deep blue colored.

Co & Hg both in Td - form. polymeric complex.

Cobalt mercury tetrathiocyanate complex.



Polymeric Complex.

Due to Hard-Hard, Soft-soft combination.

Hg & S → Soft
Co & N → Hard
} HSAB- Principle.

Blue colour of complex comes due to Co^{2+} in tetrahedral.

Now for the reference material. (use R = reference).

The molar magnetic susceptibility $\chi_{M_R} = M_R \cdot \frac{\Delta W_R \cdot g}{H \cdot W_R \left(\frac{dH}{dx}\right)}$ — (3)

And the molar magnetic susceptibility for the sample- χ_{M_S}

$$\chi_{M_S} = M_S \cdot \frac{\Delta W_M \cdot g}{H \cdot W_M \left(\frac{dH}{dx}\right)} \quad \text{— (4)}$$

From the above two equations —

$$\frac{\chi_{M_S}}{\chi_{M_R}} = \frac{M_S}{M_R} \cdot \frac{\Delta W_S}{\Delta W_R} \cdot \frac{W_R}{W_S}$$

$$\chi_{M_S} = \left(\frac{\chi_{M_R}}{M_R}\right)\left(\frac{\Delta W_S}{W_S}\right)\left(\frac{W_R}{\Delta W_R}\right) \cdot M_S$$

$\Downarrow$

Constt. $\Rightarrow 16.44 \times 10^{-6}$ CGS.

$$\boxed{\chi_{M_S} = 16.44 \times 10^{-6} \left(\frac{\Delta W_S}{W_S}\right)\left(\frac{W_R}{\Delta W_R}\right) \cdot M_S}$$

Now, for correction for diamagnetic contribution by Pascal's constt:

$$\chi_{M_S}^{\text{correct}} = \chi_{M_S}^{P} - \chi_{M_S}^{D} - \chi^{TIP}$$

$\chi_{M_S}^{D}$ ↓ −ve value. less but increase the value of $\chi_{M_S}^{\text{correct}}$

χ^{TIP} ↓ +ve value, decrease the value of χ_{M_S} correct.

Hence, calculated magnetic moment—

$$\boxed{\mu_{eff} = 2.828 \sqrt{\chi_{M_S}^{\text{correct}} \cdot T}}$$

where $\chi_{M_S}^{\text{correct}}$ in CGS

$$\boxed{\mu_{eff} = 797.5 \sqrt{\chi_{M_S}^{\text{correct}} \cdot T}}$$

$\chi_{M_S}^{\text{correct}}$ in MKS System.

eg. For a sample, Mol. weight, $M_s = 493.2$
At temp., $T = 302K$.
$W_R = 12.24$ mg $\quad W_2 = 22.44$ mg
$\Delta W_R = 1.20$ mg $\quad \Delta W_s = 0.90$ mg.
Calculate $\chi_{M_s} = ?$ and $\mu_{eff} = ?$

Ans-

$$\chi_{M_s} = 16.44 \times 10^{-6} \times \left(\frac{\Delta W_s}{W_s}\right) \cdot \left(\frac{W_R}{\Delta W_R}\right) \cdot M_s$$

$$\chi_{M_s} = 16.44 \times 10^{-6} \times \frac{0.90}{22.44} \times \frac{12.24}{1.20} \times 493.2$$

$$\chi_{M_s} = 33.17 \times 10^{-4} \text{ CGS unit.}$$

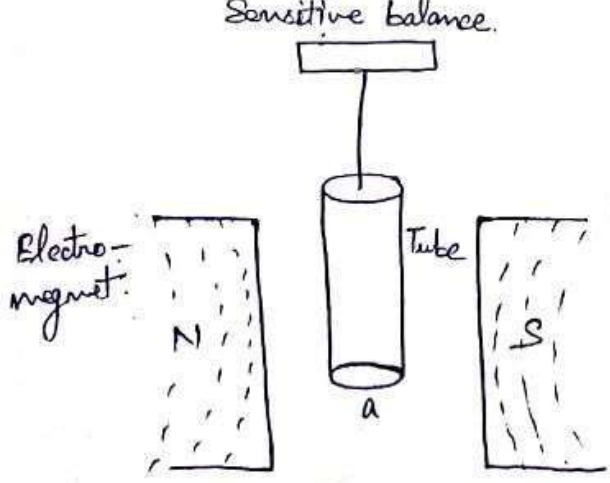
$$\mu_{eff} = 2.828 \sqrt{\chi_{M_s}^{corrected} \cdot T}$$

$$\mu_{eff} = 2.828 \sqrt{33.17 \times 10^{-4} \times 302}$$

$$\boxed{\mu_{eff} = 2.83 \text{ BM.}}$$

Sample given was Ni^{2+}
Octahedral (sp^3d^2) complex.
d^8, 2.8 - 3.2 BM

(2) Gouy Method- An alternative method, for measuring magnetic susceptibility. In this, there is an inhomogeneous field in the central region between two flat poles of a permanent magnet or electromagnet. Sample is filled in form of a cylindrical tube which is suspended in such a way that one end lies in centre of the field and other is effectively outside the magnetic field.



In absence of field weight of sample = w_1 gram
In presence of field weight of sample = w_2 gram.
Change in weight of sample = $w_2 - w_1$
$= \Delta w$ gram.

Force acting on sample = $\Delta w \cdot g$ — (1)

Force due to mag. field = $\frac{1}{2}(K_1 - K_2) H^2 a d_0$

K_1 = volume susceptibility of sample
K_2 = volume susceptibility of air, as large sized tube, it can't be neglected here.

reason of Errors } H = magnetic field strength.
a = cross-sectional area.

$\mu_0 = 1$ Permeability. (air)

From equations ① & ② –

$$\Delta w \cdot g = \frac{1}{2}(K_1 - K_2) H^2 a$$

$$\frac{2 \cdot \Delta w g}{H^2 a} = K_1 - K_2$$

$$K_1 = K_2 + \frac{2 \Delta w g}{H^2 a}$$

Gram/~~Molar~~ Specific susceptibility $\frac{K_1}{\rho} = \frac{1}{\rho}\left[K_2 + \frac{2 \Delta w g}{H^2 a}\right]$

Molar magnetic susceptibility

$$\chi_M = \frac{K_1 \cdot M}{\rho} = \frac{M}{\rho}\left[K_2 + \frac{2 \Delta w g}{H^2 a}\right]$$

Measurement is done w.r.t. reference comp. $Hg[Co(SCN)_4]$
Deep blue color solid.

Determination was practiced earlier – $CuSO_4 \cdot 5H_2O$
(while showing orbital contribution).

Faraday & Gouy methods are very common.

Advantage and Disadvantage of Faraday's Method –

Advantage:

(a) It requires very less amount of sample. (0.10 mg)
(b) Preparation (packing) of sample is easy.
(c) It can be used for measuring magnetic properties of precious samples i.e. very-very less amount of sample. eg. for La and Ac. (Trace samples)
(d) Anisotropy can be measured.
If we change the direction of field, we can know the magnetic value in that direction.

Disadvantage

(1) Frequent Calibration for equipment required. (First for known, Second for unknown)
(2) Sample with surface tension, can not be measured exactly, b/c surface tension, also possesses forces.

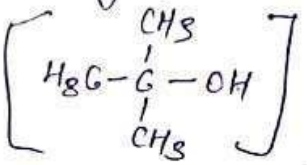
Advantages and Disadvantages of Gouy's Method.

Advantage: ⓐ Fabrication of equipment is easy.
ⓑ Large sample is used so, measurement of balance is easy.

Disadvantage: ⓐ Packing of sample in tube is not uniform. Some error come due to air. (not much)
ⓑ Anisotropy can not be measured because sample is large, Magnetic field direction is not affected because bulk is independent of the field.

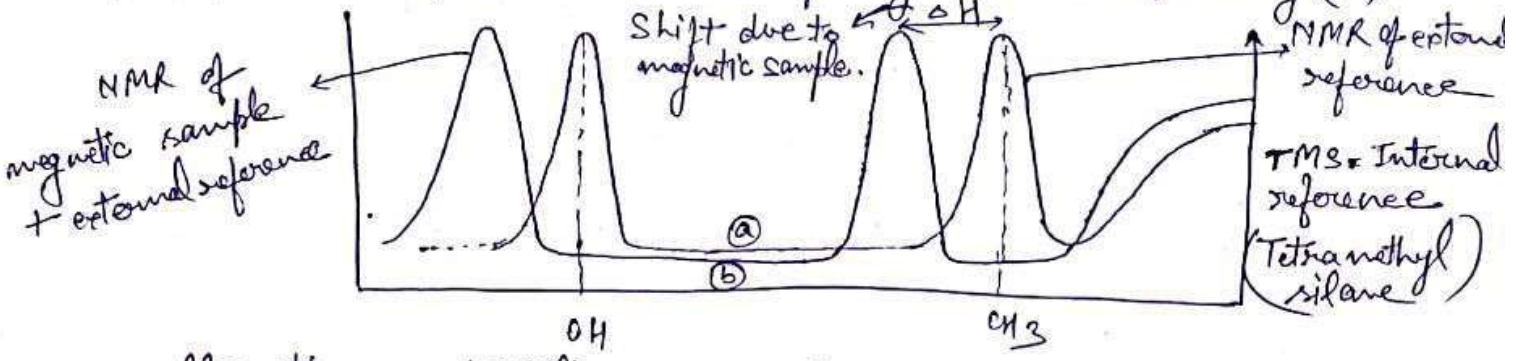
NMR-Method - Basic requirement : Nuclear spin.
It describes that there are how many types and relative no. of proton.

ⓐ Take NMR of t-Butanol.



used as a Reference material.

ⓑ After that, take NMR of the magnetic sample + 2% t-Butanol.
There will be shifting of the spectrum in case of ⓑ than case ⓐ, then take the corresponding shift of magnetic field ΔH.
$\frac{\Delta H}{H}$ is used for measurement of magnetic susceptibility (χ)



Magnetic susceptibility for sample –

$$\chi_s = \frac{3}{2\pi C} \cdot \frac{\Delta H}{H} + \chi_0 + \frac{(\rho_0 - \rho_s)}{C} \chi_0$$

Where: C = concentration of magnetic sample (g/mL)
χ_0 = volume susceptibility of solvent.
ρ_0 = Density of solvent.
ρ_s = Density of sample
Since $\frac{(\rho_0 - \rho_s)}{C} \chi_0$ is very small, so neglected –

Then $\chi_s = \frac{3}{2\pi C} \frac{\Delta H}{H} + \chi_0 \Rightarrow \frac{\Delta H}{H} = \left(\frac{2}{3}\pi C.\chi_s - \chi_0\right)$

Further, $\frac{\Delta H}{H} = \frac{2}{3}\pi \Delta K$ ΔK = Change in susceptibility.

Therefore, $\chi_s = \frac{3}{2\pi C} \times \frac{2}{3}\pi \Delta K + \chi_0$

$$\boxed{\chi_s = \frac{\Delta K}{C} + \chi_0}$$

Then $$\boxed{\mu_{eff} = 2.828 \sqrt{\chi_{m_0} \cdot T}}$$ B.M.

The Applications of magnetic measurements. (μ_{eff} from χ)

(1.) Oxidation State. (Information)

Diamagnetic (all electrons are paired), magnetic moment (μ) = 0

Paramagnetic (No. of unpaired electrons), magnetic moment (μ) $\neq$ 0.

(a) Cu - Complex.

If $\mu_{eff} = 0$, Diamagnetic

Hence, d^{10} - configuration, i.e. oxidation state = +1 (Cu^+)

If $\mu_{eff} = 1.73$ - Paramagnetic with 1 unpaired electron.

$= 1.79$, Hence, d^9 - Configuration.

i.e. oxidation state = +2 (Cu^{2+})

If $\mu_{eff} = 1.93$, i.e. Cu^{2+}, d^9 in $CuSO_4.5H_2O$.

(b.) Iron - Compounds -

Diamagnetic: $Fe^{2+}(d^6)$, eg. $K_4[Fe(CN)_6]$, $\mu_{eff} = 0$

Paramagnetic: $Fe^{2+}(d^6)$, eg. $[Fe(H_2O)_6]SO_4$, $\mu_{eff} = 4.90$ BM.

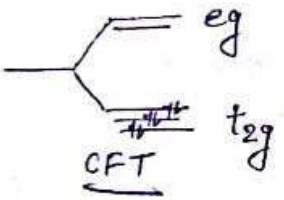
$Fe^{3+}(d^5)$, eg. $[FeF_6]^{3-}$, $\mu_{eff} = 5.92$ BM.

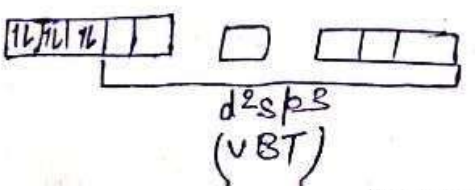
$Fe^{3+}(d^5)$, eg $[Fe(CN)_6]^{3-}$, $\mu_{eff} = 2.1$ B.M.

(experimental value)

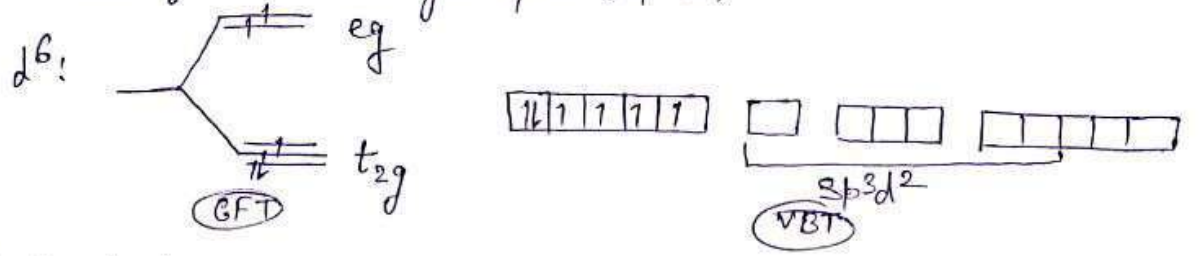
CN^- strong field case -

d^6:





(5) H_2O- Weak field Case- High spin (sp^3d^2)



Very Important:

$Na_2[Fe^{II}(CN)_5NO] \xrightarrow{H_2S} Na_4[Fe^{III}(CN)_5NOS]$

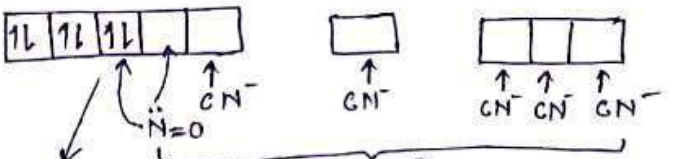
Sod. nitroprusside (Light Colour) → Sod. thionitroprusside. (Deep purple colour)

In $Na_2[Fe(CN)_5NO] \rightarrow Fe^{2+} \rightarrow$ Diamagnetic, $\mu_{eff} = 0$. (experimental.)

As low spin complex, so, one can expect Fe in Fe^{II} form. But Mass Bauer. Spectral study shows it is actually Fe^{III}.

Then How its diamagnetic character is explained?

Ans. Here, NO ligand acts as a $3e^-$ donor.



Diamagnetic $\mu_{eff} = 0$

d^2sp^3

Then it becomes diamagnetic.

(2) Bond Type- To know what type of Hybrid-orbitals are involved in metal ligand bonding. i.e. sp^3/dsp^2, sp^3d/dsp^3, d^2sp^3/sp^3d^2.

eg. d^1, d^2, d^3 — d^8, d^9 (d^8 → only for octahedral, not sq. planar Ni^{2+})

Whether strong field or weak field ligand, no change in magnetic moment.

e.g. d^4 — Cr^{2+}

$[Cr^{II}(H_2O)_6]Cl_2$

$\mu_{eff} = 4.90$ B.M.

μ_{exp} (exact) $= 4.96$ B.M.

4 unpaired e^-

sp^3d^2

High spin Complex.

$[Cr^{II}(CN)_6]^{4-}$

$\mu_{eff} = 2.83$ B.M.

2 unpaired e^-

d^2sp^3

low spin Complex.

d^5

Fe^{3+}, Mn^{2+}

$[Fe^{III}(H_2O)_6]^{3+}$, $[Fe(Fe)]^{3-}$, $[Mn^{II}(H_2O)_6]^{2+}$

μ_{eff} = 5.92 BM.

5- Unpaired electron.

sp^3d^2

High-spin Complex.

$t_{2g}^3 eg^2$

$[Fe^{III}(CN)_6]^{3-}$, $[Mn^{II}(CN)_6]^{4-}$

μ_{eff} = 2.1 BM, μ_{eff} = 1.73 BM.

One unpaired electron.

d^2sp^3

Low spin complex.

$t_{2g}^5 eg^0$.

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d^6

Fe^{2+}, Co^{3+}

$[Fe^{II}(en)_3]Cl_2$, $[Co^{III}F_6]^{3-}$

μ_{eff} = 4.90 BM.

4 Unpaired e^-.

sp^3d^2.

High Spin Complex

$t_{2g}^4 eg^2$

$[Fe^{II}(CN)_6]^{4-}$, $[Co^{III}(CN)_6]^{3-}$

$[Co^{III}(NO_2)_6]^{3-}$, $[Co^{III}(NH_3)_6]^{3+}$

μ_{eff} = 0 BM.

d^2sp^3.

Low spin Complex.

$t_{2g}^6 eg^0$

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d^7

Co^{2+}

$[Co^{II}(H_2O)_6]Cl_2$

μ_{eff} = 3.87 BM

3- Unpaired e^-

sp^3d^2

High-spin Complex

$t_{2g}^5 eg^2$

$[Co^{II}(CN)_5H_2O]^{3-}$

μ_{eff} = 1.73 BM.

d^2sp^3

Low spin Complex

One unpaired e^- goes to 4d and magnetic moment corresponds for one e^-.

→ Due to strong Jahn Teller distortion.

$[Co(CN)_6]^{4-}$ → Unstable.

$t_{2g}^6 eg^1$

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(3) Geometry, (Stereochemistry)

If μ_{eff} = 4.2 – 4.8 BM (Tetrahedral)

(less orbital contribution)

μ_{eff} = 4.8 – 5.2 BM (Octahedral)

(more orbital contribution.)

Co^{3+}: d^6

In both cases, there are 4 Unpaired electrons —

From above one can distinguish whether complex is tetrahedral or octahedral from measured magnetic moment.