

Magnetic Properties of Complexes

It should be quite clear that electronic spectroscopy is a powerful method for investigating transition metal complexes. Additional and complementary information can be provided by magnetic measurements. Because complexes generally have partially filled metal d or f orbitals, a range of magnetic properties can be expected, depending on the oxidation state, electron configuration, and coordination number of the central metal.

**** Magnetism** is the force of attraction or repulsion of a magnetic material due to the arrangement of its atoms, particularly its electrons.

**** Magnetic field** is the space surrounding the magnet up to which its influence felt.

**** Origin of magnetic moment**

- 1- Orbital motion - Orbital magnetic moment
- 2- Spin motion – Spin magnetic moment

When any substance is placed in an external magnetic field, there is an induced circulation of electrons producing a net magnetic moment aligned in opposition to the applied field. This is the diamagnetic effect and it arises from paired electrons within a sample. Since all compounds contain some paired electrons, diamagnetism is a universal property of matter if a substance has only paired electrons, this effect will dominate, the material will be classified as diamagnetic, and it will be slightly repelled by a magnetic field.

Paramagnetism is produced by unpaired electrons in a sample. The spins and orbital motions of these electrons give rise to permanent molecular magnetic moments that tend to align themselves with an applied field. Because it is much larger than the diamagnetic effect, the paramagnetic effect cancels any repulsion between an applied field and paired electrons in a sample. Thus even substances having only one unpaired electron per molecule will show a net attraction into a magnetic field.

The paramagnetic effect is observed only in the presence of an external field. When a field is present, there is competition between the thermal tendency toward randomness and the field's capacity to force alignment. Consequently, paramagnetic effects decrease in magnitude as the temperature is increased.

The quantity that is most frequently obtained from experimental measurements of magnetism is the specific (or mass) susceptibility, χ . It is related to the volume susceptibility through the density, d : $\chi = \frac{\chi_v}{d}$

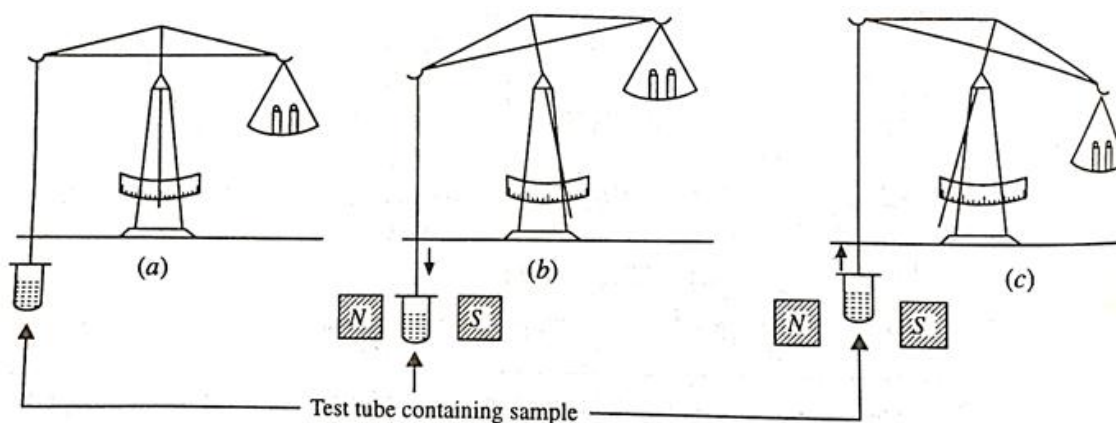
By multiplying the specific susceptibility of a compound by its molecular weight, we can obtain the molar susceptibility, X_M :

$$X_M = X \cdot MW$$

A number of methods exist for laboratory measurement of magnetic susceptibilities . Two that are very common and quite similar to each other are Gouy and Faraday methods. Both technique are based on the determination of the force exerted on a sample by an inhomogeneous magnetic field and both of them involve measuring the weight of a substance in the presence and absence of the field.

Gouy magnetic balance

The paramagnetic / diamagnetic nature of a given substance can be determined by weighing the substance in a Gouy magnetic balance in the absence and presence of magnetic field as shown in the figure below. The substance is taken in a small test tube and weighted in air (in the absence of magnetic field) and then weighted between the poles of a magnet. If the substance shows an increase in its weight, this implies that the substance is attracted by the magnetic field and hence is paramagnetic. On the other hand , if the substance shows a decrease in its weight, it implies that the substance is repelled by the magnetic field and hence is diamagnetic.

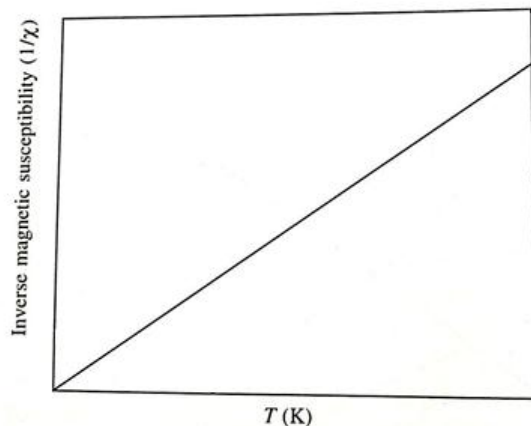


Pierre Curie established in 1895 that paramagnetic susceptibility is inversely proportional to the absolute temperature

$$X_M = \frac{C}{T}$$

This expression is known as Curie's law.

The Curie law is obeyed fairly well by paramagnetic substances that are magnetically dilute (those in which the paramagnetic centers are well separated from each other by diamagnetic atoms).



The magnetic materials are classified into five groups depending on their response to the magnetic field

- 1- Diamagnetic Materials
- 2- Paramagnetic Materials
- 3- Ferromagnetic Materials
- 4- Antiferromagnetic Materials
- 5- Ferrimagnetic Materials

1- Diamagnetism

When an external field is applied, the motion of electrons in their orbits changes resulting in induced magnetic moment in a direction opposite to the direction of applied field.

** When the magnitude of susceptibility is small and negative, it is independent of temperature.

** The magnetic susceptibility is independent of applied magnetic field strength.

2- Paramagnetism

When an external magnetic field is applied, there is tendency for the dipoles to align with the field giving rise to an induced positive dipole moment.

- ** Paramagnetic susceptibility is small and positive and is independent of applied field strength.
- ** Spin alignment is random.
- ** If the magnitude of susceptibility is small and positive it is independent of temperature.

3- Ferromagnetism

Even in the absence of external applied field, some substances exhibit strong magnetization.

- ** Magnitude of susceptibility very large and positive and temperature dependence.
- ** Each ferromagnetic material has a characteristic temperature called the ferromagnetic Curie temperature θ_f below this temperature the spontaneous magnetization exists.
- ** Spin alignment is parallel.

4- Anti-ferromagnetism

In certain materials when the distance between the interacting atoms is small the exchange forces produce a tendency for antiparallel alignment of electron spins of neighboring atoms.

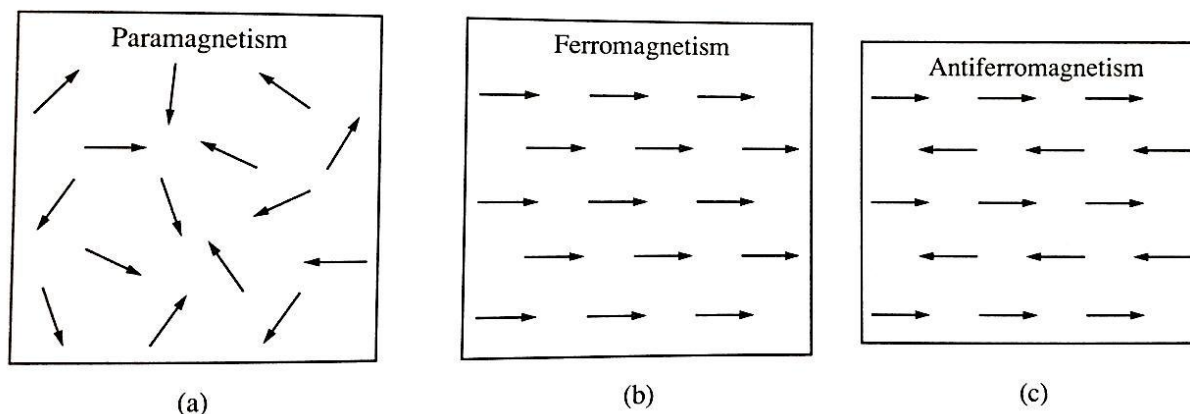
- ** The magnetic susceptibility increases with the increase of temperature and reaches maximum at a certain temperature, this temperature is known as Neel temperature (T_N), above this temperature the susceptibility again decreases.
- ** Spins are aligned antiparallel.
- ** Magnitude of susceptibility small and positive and temperature dependence.

5- Ferrimagnetism

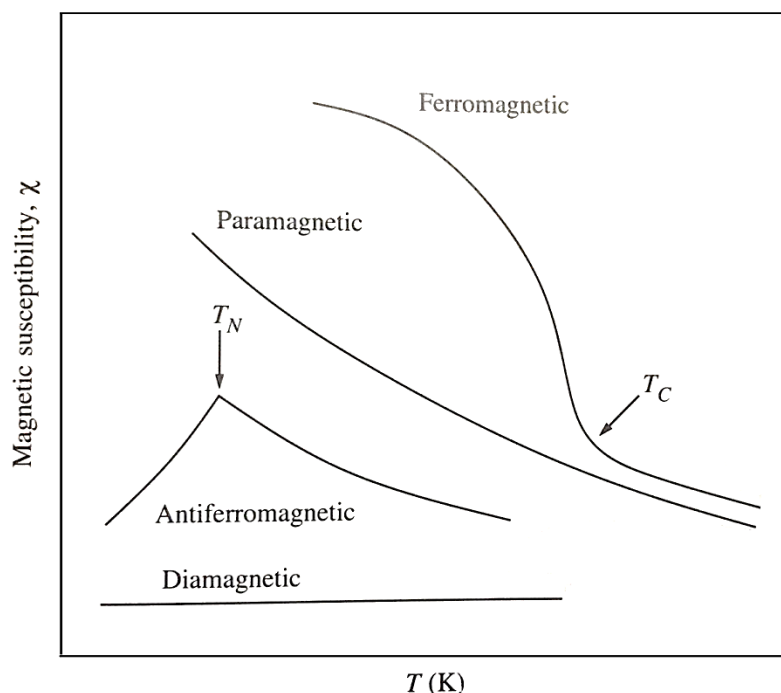
It is a special case of anti-ferromagnetism.

- ** Hence ferrimagnetic materials possess a net moment, this moment disappears above a Curie temperature analogous to the Neel temperature.
- ** Spin alignment is antiparallel of different magnitudes.
- ** Magnitude of susceptibility very large and positive and temperature dependence.

If the interacting magnetic dipoles on neighboring atoms tend to assume a parallel alignment, the substance is said to be ferromagnetic. If, on the other hand, the tendency is for an antiparallel arrangement of the coupled spins, the substance is antiferromagnetic.



In any material that exhibits magnetic exchange, the tendency towards spin alignment will compete with the thermal tendency favoring spin randomness. In all cases, there will be some temperature below which magnetic exchange dominates. This temperature is called the Curie temperature (T_C) if the type of exchange displayed is ferromagnetic and the Neel temperature (T_N) if it is antiferromagnetic. The change in susceptibility as the temperature is decreased below either T_C or T_N is shown in Figure below:



Variation of magnetic susceptibility with temperature for diamagnetic, paramagnetic, ferromagnetic, and antiferromagnetic substances. Transitions to paramagnetic behavior for ferromagnetic and antiferromagnetic substances occur at the Curie (T_C) and Neel (T_N) temperatures, respectively.

The paramagnetic character increases with the increase in the number of unpaired electrons. The paramagnetism of a substance is expressed in terms of its magnetic moment (μ). The larger is the number of unpaired electrons in the central atom/ion of a given complex compound, the greater is its paramagnetic character and hence larger is the value of the magnetic moment of that complex compound.

The magnetic moment is expressed in **Bohr Magnetons (B.M.)**. Paramagnetic substances have some value of magnetic moment while diamagnetic substances have zero value of their magnetic moment.

$$\text{Bohr Magnetron (B.M.)} = \frac{eh}{4\pi mc}$$

One B.M. is equal to 9.27×10^{-21} erg/gauss. Here e = charge on the electron, h = Plank's quantum number, m = mass of the electron and c = velocity of light.

In case of transition metal ions of 3d-series, the crystal fields (the ligands surrounding the metal ions) restrict the movement of the electron round the nucleus in orbitals and hence the magnetic moment due to the orbital motion of the electron (μ_l) is quenched and hence $\sqrt{l(l+1)} = 0$. Thus the magnetic moment of an unpaired electron residing in 3d-orbital of the ions of 3d-series element is given by:

$$\mu = 2\sqrt{S(S+1)} \text{ B.M.}$$

Since the value of s for one electron = $\frac{1}{2}$, μ is given by:

$$\mu = 2 \sqrt{\frac{1}{2} \left(\frac{1}{2} + 1 \right)} \text{ B.M.}$$

If a metal ion of 3d-series elements has two, three, four,..... n unpaired electrons in its 3d orbitals, the value of magnetic moment for n unpaired electrons (called effective magnetic moment, μ_{eff}) will be obtained by putting the sum of the spin quantum numbers of n unpaired electrons.

Since $s = \frac{1}{2}$ for one electron, the sum of s for two, three, four, n unpaired electrons is equal to $2 \times \frac{1}{2}$, $3 \times \frac{1}{2}$, $4 \times \frac{1}{2}$... , $n \times \frac{1}{2}$ respectively. Thus the value of μ_{eff} for n unpaired electrons is given by:

$$\begin{aligned} \mu_{\text{eff}} &= 2 \sqrt{\frac{n}{2} \left(\frac{n}{2} + 1 \right)} \text{ B.M.} \\ &= \sqrt{n(n+2)} \text{ B.M.} \end{aligned}$$

Since the value of μ_{eff} is only due to the spin motion of n unpaired electrons, it is also called Spin-only magnetic moment and is represented as μ_s . Thus:

$$\mu_{\text{eff}} = \mu_s = \sqrt{n(n+2)} \text{ B.M.}$$

For $n = 0$ $\mu_{\text{eff}} = \sqrt{0(0+2)} = 0.0 \text{ B.M.}$

For $n = 1$ $\mu_{\text{eff}} = \sqrt{1(1+2)} = \sqrt{3} = 1.73 \text{ B.M.}$

For $n = 2$ $\mu_{\text{eff}} = \sqrt{2(2+2)} = \sqrt{8} = 2.83 \text{ B.M.}$

For $n = 3$ $\mu_{\text{eff}} = 3.87 \text{ B.M.}$

For $n = 4$ $\mu_{\text{eff}} = 4.90 \text{ B.M.}$

For $n = 5$ $\mu_{\text{eff}} = 5.92 \text{ B.M.}$

Thus we see that greater is the number of unpaired electrons, greater is the value of μ_{eff} . The value of μ_{eff} of a given complex ion whose central metal atom is from 3d-transition series depends on the number of unpaired electrons present in 3d orbitals of the central metal atom. Greater is the number of unpaired electrons present in 3d orbitals of central metal atom, greater is the value of μ_{eff} . The complex ions which have a definite value of μ_{eff} are paramagnetic.

***** If there is a possibility for contribution from the orbital angular momentum,**

$$\mu = \sqrt{L(L + 1) + 4S(S + 1)}$$

If L is greater than zero, it is possible of orbital contribution like $3d^7$ of oh complexes of cobalt (II).

Now let us consider a complex of 3d series elements whose central metal atom/ion contains all the electrons in the paired state in its 3d orbitals (the central atom/ion contains no unpaired electrons in its 3d orbitals) (e.g., Cu^+ , $\text{Zn}^{2+} = 3d^{10}$, $n = 0$). Since the two electrons residing in the same orbital have opposite spins, the magnetic field produced by one electron is neutralized by that produced by the other electron which has opposite spin and consequently the resultant magnetic moment is zero ($\mu_{\text{eff}} = 0$). The substances having $\mu_{\text{eff}} = 0$ are diamagnetic.

The value of μ_{eff} for the complex compounds whose central ion contains no electron at all in its 3d-orbitals or has vacant 3d orbitals (e.g., Sc^{3+} , $\text{Ti}^{4+} = 3d^0$, $n = 0$) is also equal to zero and hence such complex compounds are also diamagnetic.

Ion	Valence-shell configuration	n	Complex compounds	Shape and hybridisation	Calculated value of μ (μ_{cal})	Experimental value of μ (μ_{exp})
Ti ³⁺	3d ¹	1	K ₃ [Ti ³⁺ F ₆]	Octahedral (d ² sp ³)	1.73	1.70
V ⁴⁺	3d ¹	1	[V ⁴⁺ O(acac) ₂]	Square pyramidal (d ² sp ²)	1.73	1.70
V ³⁺	3d ²	2	NH ₄ [V ³⁺ (SO ₄) ₂].12H ₂ O	Octahedral (d ² sp ³)	2.84	2.80
Cr ³⁺	3d ³	3	[Cr ³⁺ (NH ₃) ₆]Br ₃	Octahedral (d ² sp ³)	3.87	3.77
Cr ²⁺	3d ⁴	4	[Cr ²⁺ (H ₂ O) ₆]SO ₄	Octahedral (sp ³ d ²)	4.90	4.80
Fe ³⁺	3d ⁵	5	[Na ₃ [Fe ³⁺ F ₆]	Octahedral (sp ³ d ²)	5.92	5.85
Fe ²⁺	3d ⁶	4	(Et ₄ N) ₂ [Fe ²⁺ Cl ₄]	Tetrahedral (sp ³)	4.90	5.40
Co ²⁺	3d ⁷	3	Cs ₂ [Co ²⁺ F ₄]	Tetrahedral (sp ³)	3.87	4.60
Ni ²⁺	3d ⁸	2	[Ni ²⁺ (NH ₃) ₆]Cl ₂	Octahedral (sp ³ d ²)	2.84	3.32
Cu ²⁺	3d ⁹	1	[Cu ²⁺ (bigH) ₂]Cl ₂	Square planar (dsp ²)	1.73	1.79
Zn ²⁺	3d ¹⁰	0	[Zn ²⁺ (NH ₃) ₄] ²⁺	Tetrahedral (sp ³)	0.00	0.00
Sc ³⁺	3d ⁰	0	[Sc ³⁺ F ₆] ³⁻	Octahedral (d ² sp ³)	0.00	0.00

Uses of magnetic moment value

The experimental magnetic moment value of a given complex compound can be used to determine the number of unpaired electrons occupying the d-orbitals of the central metal ion of a given complex compound. The number of unpaired electrons determined in this way can be used to predict :

- 1- Whether a given 4-coordinated complex compound is square planar (dsp² hybridization) or tetrahedral (sp³ hybridization).
- 2- Whether a given 6-coordinated complex compound (octahedral) results from d²sp³ hybridization (inner orbital octahedral complex) or sp³d² hybridization (outer orbital octahedral complex).