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MAGNETIC CHEMISTRY

INTRODUCTION

All the magnetic properties of substances are determined by the electrical properties of the sub-atomic particles, electrons and neutron. Because the magnetic effects due to nucleons and nuclei are 10^3 times than those due to electron that is why mainly the magnetic property is due to the number of unpaired electrons present in an atom or ion.

(i) A **paramagnetic** substance is attracted into a magnetic field with a force proportional to the field strength times the field gradient. "Paramagnetism is generally caused by the presence in the substance of ions, atoms or molecules having unpaired electrons. Each of these has a definite paramagnetic moment that exists in the absence of any external magnetic field." A diamagnetic substance is repelled by a magnetic field." Diamagnetic behaviour is due to small magnetic moments that are induced by the magnetic field but donot exist in the absence of the field. Moments so induced are in opposition to the inducing field, thus causing repulsion.

✓ v) Even an atom with a permanent magnetic moment will have diamagnetic behaviour working in opposition to the paramagnetism when placed in a magnetic field, provided only that the atom has one or more closed shell of electrons. Thus the net paramagnetism measured is slightly less than the true paramagnetism because some of the

Diamagnetism Substance is not attracted by magnet because they have paired e (it) which cancel out each other effect.

paramagnetism Substance is attracted by magnetic field because they contain unpaired e (1)

[illegible faded lines at top] ... is cancelled out by the diamagnetism.

Since diamagnetism is usually several orders of magnitude weaker than paramagnetism, substances with unpaired electrons almost always have a net paramagnetism. Of course a very dilute solution of a paramagnetic ion in a diamagnetic solvent such as water may be diamagnetic because of the ratio of diamagnetic to paramagnetic species in it. Another important feature of diamagnetism is that its magnitude does not vary with temperature. This is because the moment induced depends only on the sizes and shapes of the orbitals in the closed shells, and these are not temperature dependent.

MAGNETIC SUSCEPTIBILITY

If a substance is placed in a magnetic field of magnitude H and if I is the intensity of magnetization induced, then there will be $4\pi I$ unit lines of force across the unit surface. In addition to this, there will be H lines of force of the applied magnetic field, superimposed on the induced magnetization. Therefore, the magnetic induction B, representing the total no. of lines of force across the unit surface, is given by:

$$B = 4\pi I + H$$

If there is a vacuum in place of magnetic material, one expects that $B = H$, because the magnetic permeability for vacuum is taken as 1. The magnetic permeability of the material is given by:

magnetic permeability is the ratio of the density of line of force within the substance to the density of line of force in same region in the absence of specimen.

If the Sub. is placed in a magnetic field H, the flux B unit C.... is given by $B = H + 4\pi I$

$$B/H = 4\pi I/H + 1$$

$$B/H = 4\pi K + 1$$

where K is constant of proportionality depending on the material of body. It is called the magnetic susceptibility per unit volume and may be defined as "the extent to which a material is susceptible to magnetization. The volume susceptibility of a vacuum by definition is "zero" since in a vacuum B/H must be "one". ($K = 0$ for vacuum)

MAGNETIC MOMENT - FROM MAGNETIC SUSCEPTIBILITY

Usually magnetic susceptibility is discussed on a weight basis than on a volume basis. If d is the density, then the susceptibility per gram of the material called the mass or specific susceptibility X is given by

$$X = K/d \qquad\qquad X = x_i (\delta l_i)$$

The atomic susceptibility X_A and the molar susceptibility X_m are simply defined as the susceptibility per gram atom and per gram mole respectively. Hence,

$$X_A = X \cdot \text{atomic weight}$$

$$X_m = X \cdot \text{molecular weight}$$

where a value of X_m is obtained from the measured volume susceptibility, K. It can be corrected for the diamagnetic contribution and for the temperature independent paramagnetism (TIP) to give a "corrected" molar susceptibility; X_m^{corr}, which is the most useful quantity in drawing conclusions about electronic structure.

The magnetic susceptibility for diamagnetic substance is -ve because the line of force of the induced dipole is cancell the lines of force of the applied field.

The magnetic susceptibility for paramagnetic substance +ve

As discussed above that paramagnetism is slightly less than the actual value when there are one more electron pair present. Therefore, diamagnetic correction is necessary.

Curie indicated that paramagnetic susceptibility depends inversely on temperature and often follows or closely approximates the behaviour required by the simple equation.

$$X_m^{corr.} = c/T \qquad \text{①}$$

where T is the absolute temperature, and c is a constant that is the characteristic of the substance known as its Curie constant and this equation is known as **Curie's Law.**

This equation shows that the molar susceptibility of a substance containing independent atoms, ions or molecules, each of magnetic moment u vary with temperature.

$$X_m^{corr} = \frac{N u^2/3K}{T} \qquad \text{②} \qquad X_M^{corr} = \frac{N u^2}{3KT}$$

u = magnetic moment

where N is Avogardro's number and K is Boltzmann constant. By comparing equation ① and ②, we can find out the value of c, i.e., Curie Constant.

$$c = \frac{N u^2}{3K}$$

and at any given temperature and by putting the value of c in equation ①, we get.

$$X_m^{corr} = \frac{N u^2/3K}{T}$$

$$u = \sqrt{3K/N} \cdot \sqrt{X_m^{corr} \, T}$$

where $\sqrt{3k/N}$ = 2.84

By putting the value of k and N in above equation, we get:

$$\mu = 2.84 \sqrt{X_m T} \quad\quad\quad ----(2)$$

First of all we calculate the volume susceptibility of a substance from which X_m is calculated, then the result is corrected for diamagnetism and temperature independent paramagnetism (TIP). From this corrected molar susceptibility and the temperature of the measurement, we can calculate the magnetic moment of the ion, atom or molecule responsible for the paramagnetism.

For a substance that **obeys** Curie's law, a plot of X_m^{corr} verses $1/T$ should give a straight line of slope c that interacts the origin as in line a. Although there are many substances that within the limits of experimental error obey the Curie law, there are also many others for which the line does not go through the origin but cut the T axis at a temperature below $0°K$ as in line b or above $0°K$ as in line c, such a line can be represented by a slight
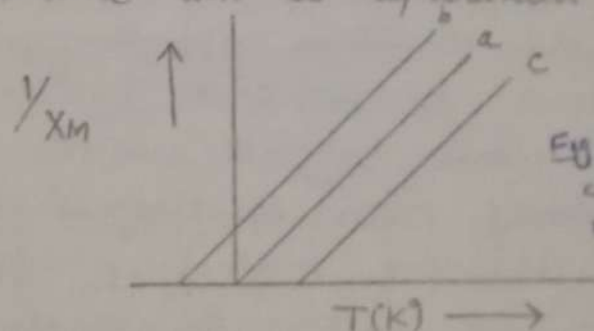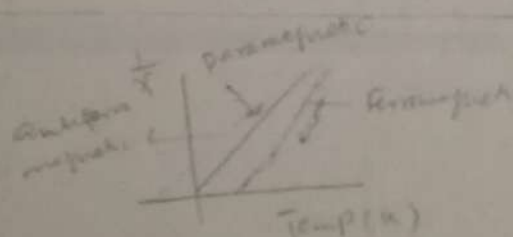

$1/X_M$ ↑

a

c

T(K) ⟶

E.g Some deviations from Curie law that may be fitted to the Curie-weiss law

modification of the Curie's equation.

$$\Delta X_M^{corr} = c/T - \theta \quad\quad\quad ----(3)$$

where $\Delta\theta$ = slight change.

antiferro magnetic

paramagnetic

ferromagnetic

Temp (K)

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and at any given temperature and by putting the value of C in equation ①, we get.

$$X_m^{corr} = \frac{N\mu^2/3K}{T}$$

$$\mu = \sqrt{3K/N} \cdot \sqrt{X_m^{corr}\, T}$$

If Θ is the temperature at which the line cuts the T axis, this equation is known as "Curie-Weiss law" and Θ is known as Weiss constant.

The Weiss constant may be due to the interionic or intermolecular interaction.

Now equation ③ becomes:

$$\mu = 2.84 \sqrt{X_m^{corr} (T - \Theta)} \qquad\text{⑤}$$

Usually when the Curie law does not, accurately fit the data or the Curie-Weiss law fit or does not fit the data, the best practice is to compute a magnetic moment at a given temperature using the Curie law and is called "effective magnetic moment" at the specified temperature.

$$\mu_{eff.} = 2.84 \sqrt{X_M^{corr} \cdot T} \qquad\text{⑥}$$

According to the wave mechanics, the magnetic moment (μs) of a single electron is given by:

$$\mu s = g \sqrt{S(S+1)} \qquad\text{⑦}$$

where,

g = gyramagnetic ratio called a g factor. g and S = Spin quantum number

For a free electron, g has a value of 2.00023 which may be taken as 2, for most purposes. From equation ⑦ we can calculate the spin magnetic moment of free electron by putting the value of g.

<u>For one Electron</u>

$$S = \frac{1}{2}$$

$$\mu s = g \sqrt{S(S+1)}$$

$$\mu S = 2\sqrt{\tfrac{1}{2}(\tfrac{1}{2}+1)}$$
$$= 2\sqrt{\tfrac{3}{4}}$$
$$= \tfrac{2}{2}\sqrt{3} = \sqrt{3}$$

$$\mu S = 1.73 \; BM$$

<u>Magnetic moments for various numbers of unpaired electrons</u>

No. of unpaired electrons	Spin (S)	Magnetic moment μS (BM)
1	$\tfrac{1}{2}$	1.73
2	1	2.83
3	$\tfrac{3}{2}$	3.87
4	2	4.90
5	$\tfrac{5}{2}$	5.92
6	3	6.94
7		

Thus any atom, ion or molecule having one unpaired electron (i.e. Cu^{++}, Ag^+ etc) should have a magnetic moment of 1.73 BM from the electron spin alone.

PARAMAGNETISM :-

i) If the intensity of the induced magnetization is greater in a substance than the applied field in vacuum, the substance is called "paramagnetic" and the phenomenon of attraction of the substance towards the magnetic field is observed. ii) It is shown with a positive sign. iii) Paramagnetism occurs specially among the transition group elements. Such substances are called paramagnetics.

iv) All substances, even though paramagnetic, have an underlying diamagnetism, because such diamagnetism is a universal property; however, the magnitude of paramagnetism

that manifests itself as a force of attraction that is usually so great that it masks the feeble underlying and opposing diamagnetism.

v) Paramagnetic susceptibility is independent of the applied field, but often is inversely proportional to the temperature. Paramagnetism is of two types:

1) Normal temperature dependent paramagnetism

2) Temperature independent paramagnetism.

DIAMAGNETISM :-

i) If the intensity of magnetization induced in a body by an applied field is less than that produced in a vacuum by the same field, the substance is called "diamagnetic". ii) In practice, the net effect manifests itself as one of repulsion between the body and the applied field. iii) Hence, the susceptibilities are shown with a negative sign. Such substances are called 'diamagnetics'.

iv) Practically all organic and inorganic compounds with the exception of free radicals and compounds of elements of transition series are diamagnetic. Diamagnetic susceptibility is independent both of temperature and of the applied field. v) Any significant change in diamagnetic susceptibility with temperature in most cases may be attributed to a change in the physical or chemical structures of the material.

Ferromagnetism and Antiferromagnetism

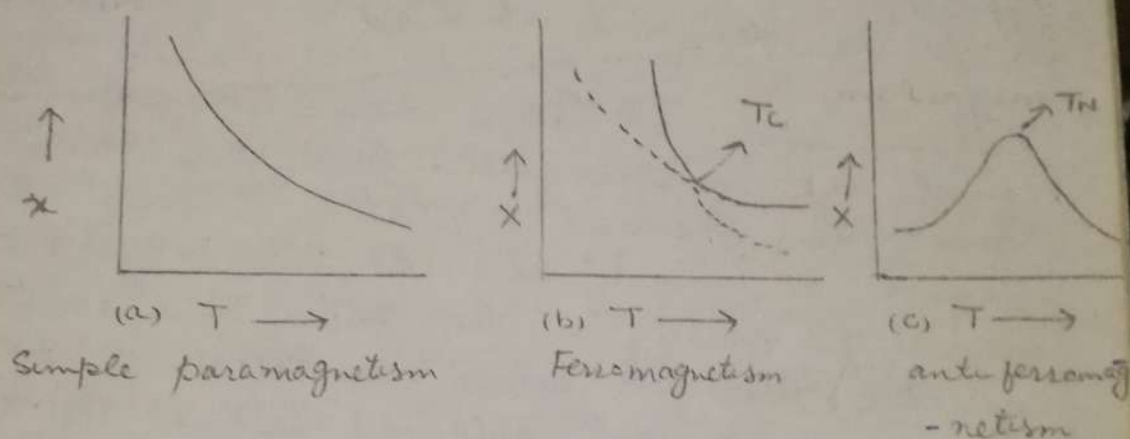In addition to simple paramagnetism, there are two other forms of paramagnetism in which dependence on

Curie or Neel points are due to intrinsic interactions which have magnitudes comparable to the thermal energies at the Curie or Neel temperature and thus become progressively greater than thermal energies as the temp is further decreased. In the case of antiferromagnetism, the moments of the ions in the lattice tend to align themselves so as to cancel one another out. Above the Neel temperature thermal agitation prevents very effective alignment, and the interactions are manifested only in the form of a Weiss constant. However, below the Neel temp, this antiparallel aligning becomes effective and the susceptibility is decreased.

In ferromagnetic substances, the moments of the separate ions tend to align themselves parallel and thus to reinforce one another. Above the Curie temp, thermal energies are more or less able to randomise the orientations; below, T_c, however, the tendency to alignment becomes controlling, and the susceptibility increases much more rapidly with decreasing temp (than it would if the ion moments behaved independently of one another!

Presumably, in those substances we can ordinarily regard as simple paramagnetics, there are some interionic interactions, however, weak and therefore there must be some temperature, however, low below which they will show ferromagnetic and antiferromagnetic behaviour depending on the

both field strength and temperature is complicated. Two of the most important of these are:

(1) Ferromagnetism

(2) Anti-ferromagnetism

(a) T →
Simple paramagnetism

(b) T →
Ferromagnetism

(c) T →
anti ferromag
- netism

<u>Diagrams indicating the qualitative temperature
dependence of magnetic suscebtibility</u>

Fig. (a) is just a rough graph of Curie's law. In figure (b) there is a discontinuity at some temperature, T_c, called the Curie temperature. Above the Curie temperature the substance follows the Curie or Curie - Weiss law; i.e. it is a simple para-magnetic. Below the Curie temperature, however, it varries in a different way with temperature, and is also field - strength dependent.

For <u>anti-ferromagnetism</u>, there is again a characteristic temperature, T_N, called the Neel temperature. Above T_N the substance has the behaviour of a simple paramagnetic, but below the Neel temperature, the susceptibility drops with decreasing temperature.

This behaviour of <u>ferromagnetic</u> and <u>antiferromagnetic</u> substances below their

And if the field doesnot become negligible at the other end of the sample, then above equation becomes,

$$f = \frac{1}{2}(K - K_0)(H^2 - H_0^2) A$$

where H_0 is the field strength at the other end of the sample.

In practice H_0 may be considered negligible by using hydrogen and nitrogen for the surrounding atmosphere, K_0 may also be negligible. It is convenient to measure F by suspending a sample from a balance in which case one may have

$$f = \frac{1}{2} K H^2 A = g \Delta w$$

where g is gravitational constant and Δw is the apparent change in the weight of sample on the application of magnetic field. From this, K can be obtained. By putting the value of K and density of the compound in gms, molar susceptibility, the X_m^{corr} and the μ_{eff} can be calculated.

$$\mu_{eff} = 2.84 \sqrt{X_m^{corr} \cdot T}$$

where T is absolute temperature.

Several modifications of this balance have appeared in the literature, for example, the sample may be suspended from a spring, the extention of which on application of the field may be observed with microscope.
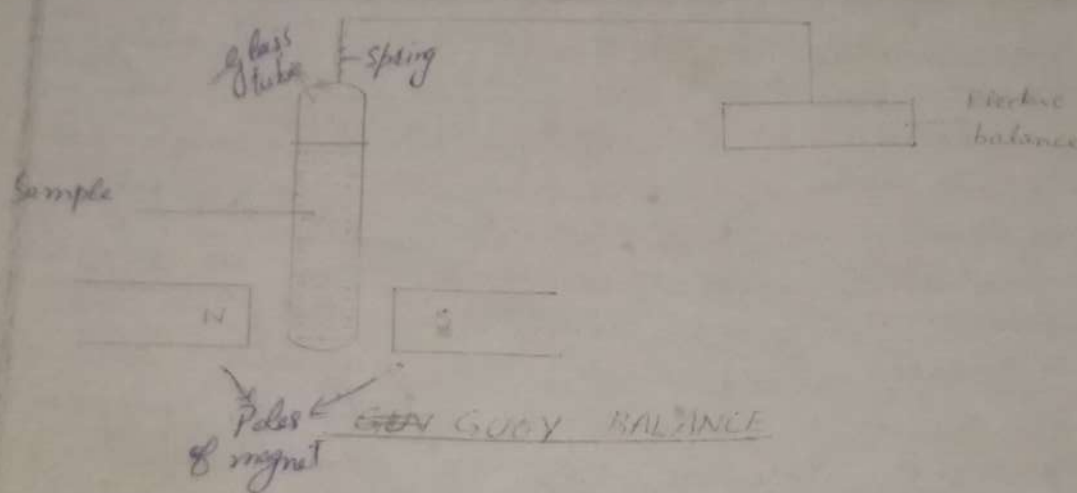
Measurements of metal or alloy are very simple by the Guoy method. The accuracy of the magnetic measurement will generally be increased by reproducibility by the Guoy method

① The Gouy method is particularly suitable for the measurement of the pure and diamagnetic susceptibilities of samples obtainable in the form of powdered solids, liquids and solutions. Powdered samples may be made by packing them into a cylindrical glass sample tube. Correction must be done for the susceptibility of the glass which is generally diamagnetic. The accuracy of the measurement on powdered sample is limited by the uniformity and reproducibility of the packing.

② The susceptibility of the pure liquid is conventionally measured in glass sample tube. As the difficulty of packing does not arise with liquid, the accuracy may be considerabely greater.

③ Most magnetic measurements require a range of temperature and often a very accurate control of temperature.

④ During measurement of solution using microbalance it is often necessary to control the temperature within 0.1°C. High temperature is easily obtained by surrounding the sample tubes within electric furnace. The only precautions necessary are to protect the sample and balance from current of air and the magnet pole pieces from extremes of temperature. Low temperature may be achieved by surrounding the sample tube with a Dewar flask of appropriate design to go between the pole pieces. Various low boiling liquids

Precautions

glass tube | spring

Sample

Electric balance

N | S

Poles of magnet GEN GUOY BALANCE

where K is the volume susceptibility.
V is volume
H is field strength
and S is the direction

Integrating the equation ①.

$$f \int dS = KV \int H \, dH$$

$$f . S = KV \, H^2/2$$

$$f = \frac{1}{2} K \, V/s \, H^2$$

Since $V/s = A$, area of cross section of sample

$$f = \frac{1}{2} K A H^2$$

If atmospheric surrounding of the sample does not have a negligible susceptibility, then above equation becomes:

$$f = \frac{1}{2} (K - K_0) H^2 A$$

where K_0 is the volume susceptibility of the atmosphere.

sign of interactions. We still do not know why such interactions are so large in some substances that they have Curie or Neel temperature near and even above room temperature.

In general, ferro and antiferromagnetic interactions are decreased when the magnetic species are separated from one another physically. Thus, when the magnetic behaviour of a solid shows the effects of interionic coupling, solutions of the same substance will be free from such interactions. This includes solid solutions, for example, when K_2OsCl_6, which has μ_{eff} per Os atom at 300°K of 1.44 BM, is diluted with diamagnetic and isomorphous K_2PtCl_6, its μ_{eff} value at the same temperature rises to 1.94 BM due to the elimination of antiferromagnetic coupling between the Os^{IV} ions.

<u>Experimental Methods for determining the magnetic moments</u>

<u>GOYS Method</u> (Guoy's method) Gouy

This method is also known as uniform field method and it was developed by the French physicist Guoy. In this method, a long cylindrical sample is suspended such that one end lies in a region of strong uniform field and other end lies in a region of negligible field.

The force acting on the sample is given by the following expression.

$$f = KVH \, dH/dS \qquad\qquad ①$$

F

THE QUINCKE METHOD

This method is familiar in principle to the Gouy method except that the force on the liquid sample is measured in terms of the hydrostatic pressure developed when the liquid is placed in a capillary tube t, so that the meniscus stands in a strong magnetic field.

On application of the field, the meniscus rises if the liquid is paramagnetic or will fall if the liquid is diamagnetic.

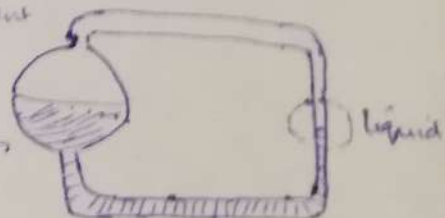For a diamagnetic liquid such as water, the change in height of the meniscus may be several millimeters. When the Reservoir R of large diameter compared with capillary, and when the susceptibility of vapor above the meniscus is negligible, the mass susceptibility of the sample is given by.

$$ \chi = \frac{2 \Delta h g}{H^2} $$

where Δh = change in vertical height of meniscus

Advantages

① It has advantage that independent measurement of the density is not necessary.

② Sometimes rise or fall of the meniscus is observed directly.

③ More frequently the meniscus is returned to its original position by changing the height of reservoir.

④ Accuracy of the readings may be increased

(Quincke magnetic balance)   liquid

For liquids, the Quincke method is well adopted for the measurement of liquid unfortunately, arrangements for changing the temp over a wide range are not convenient. For measurement at room temp, it is possible to control the temp. with high degree accuracy.

For Gases the Quincke method may also be used for gases. If susceptibility of the vapor over the meniscus is not negligible, the hydrostatic pressure developed on application of the field is

$$ P = \frac{1}{2}(k - k_0) H^2 $$

k, k_0 vol. susceptibility of liquid & vapour