Unit – 19 : Magnetic properties of complexes

Structure of Unit:

19.0 Objectives

At the end of the unit learner will be able to

- Learn about magnetic properties of complexes.
- Understand about paramagnetism, diamagnetism, ferromagnetism etc.
- Learn about Zeeman splitting and its effects.
- Quenching of orbital angular momentum.
- Understand the magnetic properties of A, E & T ground terms in complexes and spin equilibria.

19.1 Introduction

Magnetic properties can be determined by looking at a compound's electron configuration and the size of its atoms. Since Magnetism is created by the spin of electrons, we can look at how many unpaired electrons are present in a specific compound and determine how magnetic the compound is. For this purpose we will be evaluating the d-block elements or Transition Metals* (TMs) because they tend to have a large number of unpaired electrons. This unit deals with the applications of ligand field theory of complexes with special reference to magnetic properties of complexes. The unit explains fundamental of magnetism with mathematical back ground. The unit also describes the Zeeman splitting and its mathematical derivations alongwith these units explains the state of quenching of orbital angular momentum, groun state terms and their magnetic properties. And then lastly unit briefly describes about spin equilibria.

19.2 Magnetic Properties of Complexes- Paramagnetism

Magnetic properties can be determined by looking at a compound's electron configuration and the size of its atoms. Since Magnetism is created by the spin of electrons, we can look at how many unpaired electrons are present in a specific compound and determine how magnetic the compound is. For this purpose we will be evaluating the d-block elements or Transition Metals* (TMs) because they tend to have a large number of unpaired electrons.

The magnetism discussed in this chapter is paramagnetism, which occurs when there are one or more unpaired electrons in a compound. (The opposite, when all electrons are paired, is called diamagnetism). Di- and para-magnetism are often affected by the presence of coordination complexes, which the transition metals (d-block) readily form.

Singular electrons have a spin, denoted by the quantum number ms as +(1/2) or –(1/2). This spin is negated when the electron is paired with another, but creates a slight magnetic field when the electron is unpaired. The more unpaired electrons, the more likely paramagnetic a material is. The electron configuration of the transition metals (d-block) changes when in a compound. This is due to the repulsive forces between electrons in the ligands and electrons in the compound. Depending on the strength of the ligand, the compound may become paramagnetic or diamagnetic.

Some paramagnetic compounds are capable of becoming ferromagnetic. This means that the compound shows permanent magnetic properties rather than exhibiting them only in the presence of a magnetic field. In a ferromagnetic element, electrons of atoms are grouped into domains, where each domain has the same charge. In the presence of a magnetic field, these domains line up so that charges are parallel throughout the entire compound. Whether a compound can be ferromagnetic or not depends on how many unpaired electrons it has and on its atomic size.

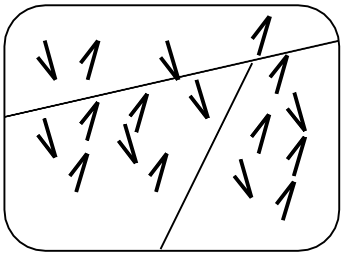

Figure 19.1 (a) The atom's electrons are organized into Domains (in absence of magnetic field)

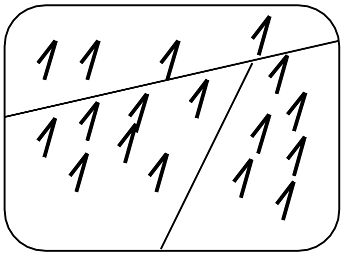

Figure 19.1 (b) The atom's electrons are align in the same direction (in presence of magnetic field) the atom is ferromagnetic

- Small atoms pair up too easily and their charges cancel.
- Large atoms are difficult to keep together, their charge interaction is too weak.

Therefore, only the right sized atoms will work together to group themselves into domains. Elements with the right size include: Fe, Co, Ni. That means that Fe, Co and Ni are paramagnetic with the capability of permanent magnetism; they are also ferromagnetic.

Measurement of magnetism in a compound

The Gouy balance is used to measure paramagnetism by suspending the complex in question against an equivalent weight with access to a magnetic field. We first weigh the complex without a magnetic field in its presence, then, we weigh it again in the presence of a magnetic field. If the compound is paramagnetic, it will be pulled visibly towards the electromagnet, which is the distance proportional to the magnitude of the compound's paramagnetism. If the compound, however, is diamagnetic, it will not be pulled towards the electromagnet, instead, it might even slightly be repelled by it. This will be proven by the decreased weight or the no change in weight. The change in weight directly corresponds to the amount of unpaired electrons in the compound.

Magnetic Properties relate to the "Real World"

Ferromagnetism, the permanent magnetism associated with nickel, cobalt, and iron, appears throughout everyday life, Einstein declared that electricity and magnetism are inextricably linked in his theory of "special relativity." He also showed examples that a magnet can be disturbed by electricity.

Paramagnetism and diamagnetism explain and describe some of the properties of certain elements and complexes, which we work with on a regular basis. In the early days of complex-compound chemistry, paramagnetism was often used to help identify the shape of complexes. A technique known as electron paramagnetic resonance has been used in systems with certain para- and dia- magnetic properties to distinguish

Magnetic Properties of Complexes

Types of Magnetic Behaviour Fundamentals

If a magnetic field, H, is applied to a substance the value of the field inside it, B, in general differs from that external to it. We write

$$B = H + I \qquad (1)$$

where I is the intensity of magnetization of the substance. For many substances I is colinear with H and proportional to it. Then B/H is a constant and may be expressed in the SI system as

$$\begin{aligned} B/H &= 1 + I/H \\ &= 1 + \chi \end{aligned} \qquad (2)$$

χ, the ‘volume susceptibility’, is also a constant, usually of rather small value. It measures how susceptible the substance is to magnetization by the applied field. If χ is negative the substance is said to be diamagnetic; if positive, paramagnetic or perhaps ferro- or antiferro-magnetic.

For some purposes, an alternative but equivalent definition of χ is preferable. In general, the energy of the substance is altered by the presence of the field. If, for unit volume, the energy is W, we write

$$\chi = \frac{-\langle\mu\rangle}{H} \quad \frac{dW}{dH} \qquad (3)$$

where $\langle\mu\rangle$ is the ‘magnetic moment’. In most cases the change in W is proportional to H^2, and again χ is a constant.

The interaction of an electron, as charged particle, with an applied magnetic field causes a precession of its orbital motion which acts to cancel the field so that I, and hence x in equation is negative. The effect is small but universal. The spin and angular momentum of an electron confer upon it the properties of a magnetic dipole, which tends to be oriented by the applied field, lowering the energy and making *x* positive (equation 3). This effect is larger than that due to electron charge, so the paramagnetism of an atom is larger than its diamagnetism. Net spin and angular momenta appear only for partly filled electron shells, and so paramagnetism is essentially a phenomenon of the transition, lanthanide and actinide elements. The charge-magnetic field interaction is independent of temperature, so that diamagnetism is essentially independent of temperature. The energy of orientation of the atomic dipole by the magnetic field is usually less than the thermal energy available to the substance, so that its effects

are temperature dependent. Paramagnetism is usually a temperature-dependent phenomenon. An ideal paramagnet obeys the *Curie law*

$$\chi = \frac{C}{T} \qquad (4)$$

where C is the Curie constant. Since diamagnetism is omnipresent, this equation, in practice, must be modified to

$$\chi = \frac{C}{T} + \chi_{\text{diam}} \qquad (5)$$

Few substances behave as ideal paramagnetics, even with allowance for the diamagnetic contribution of the second term in equation (5). It is found that a more practical expression for dealing with most: paramagnets is a variation of the Curie-Weiss Law

$$\chi = \frac{C}{T-\theta} + \chi_{\text{TIP}} + \chi_{\text{diam}} \qquad (6)$$

Here, θ is the Weiss constant and χ_{TIP} is a temperature-independent paramagnetic contribution, often neglected as it may be even smaller than χ_{diarn}. For some purposes it is more convenient to deal with magnetic properties per unit mass rather than per unit volume. We define

$$\chi_{\text{m}} = \chi/\rho$$

where ρ is the density. Equations (3)-(6) all may be written replacing χ by χ_{m}. The units of χ and χ_{m} in the SI system are respectively m^3 and $\text{m}^3\ \text{kg-}^1$. In the c.g.s. system the quantities are related to the SI values by

$$\chi(\text{c.g.s.}) = (4\pi)^{-1} \times 10^6 \chi \quad (\text{c.g.s.}) \text{ unit cm}^3$$
$$\chi_{\text{m}}(\text{c.g.s.}) = (4\pi)^{-1} \times 10^3 \chi_{\text{m}} \quad (\text{c.g.s.}) \text{ unit cm}^3\ \text{g}^{-1}$$

Diamagnetic susceptibilities are approximately $\chi_{\text{mdiam}} = -0.5 \times 10^{-8}\ \text{m}^3\ \text{kg-}^1$; paramagnetic susceptibilities vary from zero to the order of $\text{l0}^{-5}\ \text{m}^3\ \text{kg-}^1$

19.3 1st & 2nd Ordered Zeeman effect

Zeeman effect

Zeeman effect, the splitting of the lines in a spectrum into a group of closely spaced lines when the substance producing the single line is subjected to a uniform magnetic field. The effect was discovered in 1896 by the Dutch physicist Pieter Zeeman. In the so-called normal Zeeman effect, the spectral line corresponding to the original frequency of the light (in the absence of the magnetic field) appears with two other lines arranged symmetrically on either side of the original line. In the anomalous Zeeman effect (which is actually more common than the normal effect), several lines appear, forming a complex pattern. The normal Zeeman effect was successfully explained by H. A. Lorentz using the laws of classical physics (Zeeman and Lorentz shared the 1902 Nobel Prize in Physics). The anomalous Zeeman effect could not be explained using classical physics; the development of the quantum theory and the discovery of the electron's intrinsic spin led to a satisfactory explanation. According to the quantum theory all spectral lines arise from transitions of electrons between different allowed energy levels within the atom, the frequency of the spectral line being proportional to the energy difference between the initial and final levels. Because of its intrinsic spin, the electron has a magnetic field associated with it. When an external magnetic field is applied, the electron's magnetic field may assume only certain alignments. Slight differences in energy are associated with these different orientations, so that what was once a single energy level becomes three or more. Practical applications based on the Zeeman effect include spectral analysis and measurement of magnetic field strength. Since the separation of the components of the spectral line is proportional to the field strength, the Zeeman effect is particularly useful where the magnetic field cannot be measured by more direct methods.

High magnetic fields(1st order and 2nd order Zeeman effect)

The linearity of I in equation *(2)* with H, which gives χ as constant in the case of paramagnetics, only holds so long as the orienting effects of the magnetic field on the atomic dipoles is very much less than the disordering effects of temperature. If the magnetic field is strong enough, or the temperature low enough, χ becomes field dependent. The relationship $g\beta H >> kT$ is necessary for linearity in equation *(2),* where β is the Bohr magneton and k the Boltzmann constant; *g* is a number defined in Figure 19.2. If magnetic exchange is present its orienting effects must also be considered. For g = 2, a common situation, and H = 1 T, $g\beta H \underline{=} 1.44$ K. For an ideal paramagnet which obeys the Curie law at low magnetic field strengths the solution of the problem at $g\beta H \sim kT$ available in closed form. It is convenient to formulate the situation in terms of the magnetization, $M = \chi_m H$, rather than of χ. Then

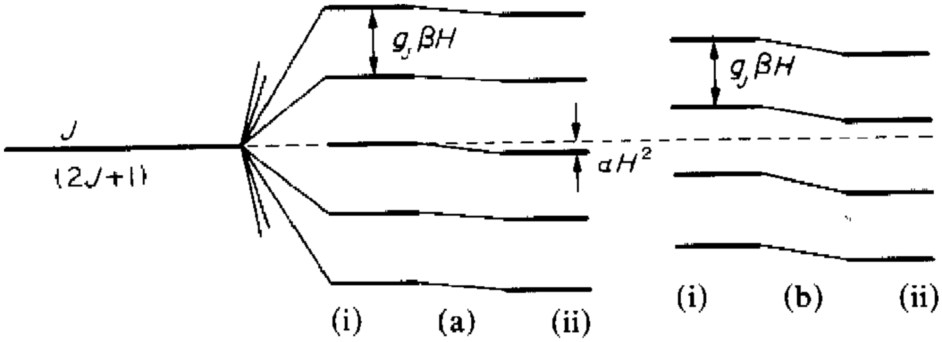

Figure 19.2 Splitting of a free-ion state into 2J+1 components by a magnetic field (a) for J even, (b) for J odd: (i) for the first-order Zeeman effect; (ii) including the second-order Zeeman effect

$$\begin{aligned} M &= g\beta S B(S,a) \\ &= g\beta S\left[\frac{2S+1}{2S}\coth\left(\frac{2S+1}{2S}a\right) + \frac{1}{2S}\coth\left(\frac{a}{2S}\right)\right] \end{aligned} \quad (7)$$

with S the spin quantum number from the paramagnetic atom, a = gPSH/kT and B(S,a) is the Briliouin function.

Quantities for chemical applications

The measurement χ or χm or perhaps M, is the one usually carried out. For chemical applications it is usual to relate these to more relevant quantities. The molar susceptibility, χ_M, is

$$\chi_{\mathrm{M}} = \chi(MV) = \chi_{\mathrm{m}}(MW)$$

where *MV* and *MW* are the molecular volume and mass respectively. Further, in most applications only the paramagnetism of a single atom amongst many diamagnetic atoms is of interest. A correction for the diamagnetism of other atoms is made to give the atomic paramagnetism of the transition metal, lanthanide or actinide atom:

$$\chi_{\mathrm{A}} = \chi_{\mathrm{M}} - \sum_{i = \text{other atoms}}^{\text{molecule}} \chi_{\mathrm{A}_i} \qquad (8)$$

where , $\chi_{Ai}$is the atomic diamagnetism, including covalent bonding contributions, of the ligands and counterions, if present. Atomic diamagnetic susceptibilities are of the order of 2 x 10^{-10} m^3 mol^{-1}; atomic paramagnetic susceptibilities, at ambient temperature, range up to 3 x 10^{-7} m^3 mol^{-1}.

If the Curie law is obeyed, μ_{eff} is not dependent on the temperature. If , χ_A is expressed in c.g.s. units the number in equation (8) is 2.84 rather than 797.5. Mostly, of course, the Curie law is not obeyed accurately. A form of equation (6) is usually sufficient to describe magnetic behaviour except at the lowest of temperatures or if the magnetic exchange is strong

In such a case μ_{eff} does depend upon temperature although the change is small unless θ is large, usually indicating strong magnetic exchange, or χ_A (TIP) is large, a rare situation. If it is known that θ arises mainly from magnetic exchange it may be useful to derive, ignoring the χ_A (TIP):

$$\mu'_{\mathrm{eff}} = 797.5\,[\chi_{\mathrm{A}}(T-\theta)]^{1/2} \qquad (9)$$

which will be less dependent on temperature and may be properly related to the value of μ_{eff} for the system in the absence of magnetic exchange. However, if θ arises from causes other than magnetic exchange, this procedure will be misleading and will obscure important facets of magnetic behavior.

2g