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Magnetochemistry

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1. Diamagnetism and Paramagnetism

1.1 Introduction

This is a book concerning the magnetic properties of transition metal complexes. The subject has been of interest for a long time, for it was realized by Pauling as long ago as the 1930's that there was a diagnostic criterion between magnetic properties and the bonding of metal ions in complexes. Indeed, over the years, magnetic properties have continued to be used in this fashion. With time and the influence of physicists working in this field, the emphasis has shifted so that chemists are becoming more interested in the magnetic phenomena themselves. The subject is no longer a subsidiary one. One result of this new emphasis is that chemists have continued to decrease the working temperature of their experiments, with measurements at liquid helium temperatures now being common.

These notes are designed as a supplement to such current texts of inorganic chemistry as that by Huheey [1]. We go beyond the idea of counting the number of unpaired electrons in a compound from a magnetic measurement to the important temperature-dependent behavior. We emphasize the structural correlation with magnetic properties, which follows from a development of magnetic ordering phenomena. A more quantitative treatment of certain aspects of this field may be found in the book by Carlin and van Duijneveldt [2], and more details of the descriptive chemistry of the elements may be found in the text by Cotton and Wilkinson [3].

A magnetic susceptibility is merely the quantitative measure of the response of a material to an applied (i.e., external) magnetic field. Some substances, called diamagnets, are slightly repelled by such a field. Others, called paramagnets, are attracted into an applied field; they therefore weigh more in the field, and this provides one of the classical methods for the measurement of magnetic susceptibilities, the Gouy method. Diamagnetic susceptibilities are temperature independent, but paramagnetic susceptibilities depend on the temperature of the sample, often in a rather complex fashion. In addition, many paramagnetic materials have interactions which cause them to become antiferromagnets or ferromagnets, and their temperature-dependent properties become even more complex. These notes will outline these different behaviors in detail, and correlate the magnetic behavior with the chemical nature of the materials.

Since the question of the units of susceptibilities is often confusing, let us emphasize the point here. For the susceptibility χ , the definition is $M = \chi H$, where M is the magnetization (magnetic moment per unit of volume) and H is the magnetic field strength. This χ is dimensionless, but is expressed as emu/cm^3 . The dimension of emu is therefore cm^3 . The molar susceptibility χ_M is obtained by multiplying χ with the molar

volume, v (in cm^3/mol). So, the molar susceptibility leads to $M = H\chi_N/v$, or $Mv = \chi_N H$, where Mv is now the magnetic moment per mol. The dimension of molar susceptibility is thus emu/mol or cm^3/mol . We shall omit the subscript on χ in what follows.

Another physical quantity important for the understanding of magnetic systems is the specific heat. Indeed, no magnetic study, at least at low temperatures, is complete without the measurement of the specific heat. This point is emphasized in the text.

Finally, the magnetic properties of molecules, whether they interact with one another or not, depend on the local geometry and the chemical links between them. This means that a true understanding of a magnetic system requires a determination of the molecular geometry, which is usually carried out by means of an X-ray crystal structure determination. Chemists after all must be concerned about magneto-structural correlations, and this point is emphasized throughout.

1.2 Diamagnetism

Let us begin with diamagnetism, which of itself is not very interesting for transition metal chemistry. It is, nevertheless, something that cannot be ignored, for it is an underlying property of all matter.

Diamagnetism is especially important in the consideration of materials with completely filled electronic shells, that is, systems which do not contain any unpaired electrons. This cannot be taken as an operational definition of a diamagnet for, as we shall see, certain paramagnetic materials can become diamagnetic under certain conditions. So, we shall use the following definition [4,5].

If a sample is placed in a magnetic field H , the field within the material will generally differ from the free space value. The body has therefore become magnetized and, if the density of the magnetic lines of force within the sample is reduced, the substance is said to be *diamagnetic*. Since this is equivalent to the substance producing a flux opposed to the field causing it, it follows that the substance will tend to move to regions of lower field strength, or out of the field.

The molar susceptibility of a diamagnetic material is negative, and rather small, being of the order of -1 to $-100 \times 10^{-6} \text{ emu/mol}$. Diamagnetic susceptibilities do not depend on field strength and are independent of temperature. For our purposes, they serve only as a correction of a measured susceptibility in order to obtain the paramagnetic susceptibility.

Diamagnetism is a property of all matter and arises from the interaction of paired electrons with the magnetic field. Since transition metal substances with unpaired electrons also have a number of filled shells, they too have a diamagnetic contribution to their susceptibility. It is much smaller than the paramagnetic susceptibility, and can usually be separated out by the measurement of the temperature dependence of the susceptibility. Indeed, paramagnetic susceptibilities frequently become so large at low temperatures that it is scarcely necessary even to correct for them.

Diamagnetic susceptibilities of atoms in molecules are largely additive, and this provides a method for the estimation of the diamagnetic susceptibilities of ligand atoms and counter ions in a transition metal complex. The Pascal constants (Table 1.1)

Table 1.1. Pascal's constants^a
(susceptibilities per gram atom $\times 10^6$ emu)

Cations		Anions	
Li ⁺	- 1.0	F ⁻	- 9.1
Na ⁺	- 6.8	Cl ⁻	- 23.4
K ⁺	- 14.9	Br ⁻	- 34.6
Rb ⁺	- 22.5	I ⁻	- 50.6
Cs ⁺	- 35.0	NO ₃ ⁻	- 18.9
Tl ⁺	- 35.7	ClO ₃ ⁻	- 30.2
NH ₄ ⁺	- 13.3	ClO ₄ ⁻	- 32.0
Hg ²⁺	- 40.0	CN ⁻	- 13.0
Mg ²⁺	- 5.0	NCS ⁻	- 31.0
Zn ²⁺	- 15.0	OH ⁻	- 12.0
Pb ²⁺	- 32.0	SO ₄ ²⁻	- 40.1
Ca ²⁺	- 10.4	O ²⁻	- 12.0
<i>Neutral Atoms</i>			
H	- 2.93	As (III)	- 20.9
C	- 6.00	Sb (III)	- 74.0
N (ring)	- 4.61	F	- 6.3
N (open chain)	- 5.57	Cl	- 20.1
N (imide)	- 2.11	Br	- 30.6
O (ether or alcohol)	- 4.61	I	- 44.6
O (aldehyde or ketone)	- 1.73	S	- 15.0
P	- 26.3	Se	- 23.0
As (V)	- 43.0		
<i>Some Common Molecules</i>			
H ₂ O	- 13	C ₂ O ₄ ²⁻	- 25
NH ₃	- 18	acetylacetone	- 52
C ₂ H ₄	- 15	pyridine	- 49
CH ₃ COO ⁻	- 30	bipyridyl	- 105
H ₂ NCH ₂ CH ₂ NH ₂	- 46	o-phenanthroline	- 128
<i>Constitutive Corrections</i>			
C=C	5.5	N=N	1.8
C=C-C=C	10.6	C=N-R	8.2
C≡C	0.8	C-Cl	3.1
C in benzene ring	0.24	C-Br	4.1

^a From Ref. [5].

provide an empirical method for this procedure. One adds the atomic susceptibility of each atom, as well as the constitutive correction to take account of such factors as π -bonds in the ligands. For example, the diamagnetic contribution to the susceptibility of K₃Fe(CN)₆ is calculated as

$$\begin{aligned}
 \text{K}^+ \quad 3(-14.9 \times 10^{-6}) &= -44.7 \times 10^{-6} \\
 \text{CN}^- \quad 6(-13.0 \times 10^{-6}) &= -78.0 \times 10^{-6} \\
 \hline
 &= -122.7 \times 10^{-6} \text{ emu/mol}
 \end{aligned}$$

This procedure is only of moderate accuracy, and the values given could change from compound to compound. Greater accuracy can sometimes be obtained by the direct measurement of the susceptibility of a diamagnetic analog of the paramagnetic compound which is of interest. On the other hand, since a paramagnetic susceptibility is in the range $(10^2 - 10^4) \times 10^{-6}$ emu/mol at room temperature, and increases with decreasing temperature, the exact evaluation of the diamagnetic contribution is often not important.

1.3 Atomic Term Symbols

Each electron has associated with it four quantum numbers, n , ℓ , m , and m_s . They are restricted to the following values: $0 \leq \ell \leq n$, $|m| \leq \ell$, and $m_s = \pm \frac{1}{2}$. The iron series ions have $n = 3$ and $\ell = 2$; this means that m may take on the values 2, 1, 0, -1, and -2, and combining each of these states with $m_s = \pm \frac{1}{2}$, we see that there can be a maximum of 10 electrons in this shell. This result is consistent with the Pauli principle. The respective elements (Ti-Cu) are generally called the 3d or iron series. The naming of other shells, or states, is illustrated as follows:

$\ell =$	0	1	2	3
shell	s	p	d	f
orbital degeneracy	1	3	5	7
m	0	0, ± 1	0, ± 1 , ± 2	0, ± 1 , ± 2 , ± 3 .

In order to describe the states of an atom or ion, it is necessary to combine the quantum numbers of the electrons into what are called Russell-Saunders (R-S) term symbols; these are valid when spin-orbit coupling is relatively small. A general representation of a R-S term symbol is ^{2S+1}L , where $L = S, P, D, F, \dots$ as $\mathcal{L} = 0, 1, 2, 3, \dots$. An atom with filled shells has $\mathcal{S} = 0$ and $\mathcal{L} = 0$ and is therefore said to be in a 1S state.

The derivation of term symbols is easily described with reference to the $(2p)^2$ configuration of the carbon atom. Each electron has $n = 2$ and $\ell = 1$, so one can construct a list (Table 1.2) of the values of m and m_s which are allowed by the Pauli principle. The quantum number m will take on the values of 0, +1 and -1, and m_s will be $+\frac{1}{2}$ or $-\frac{1}{2}$; no two electrons can be assigned the same set of quantum numbers. As Table 1.2 illustrates, there are 15 such allowed combinations, or microstates. The value of \mathcal{L} is $(M_L)_{\max}$ and the first value found is 2. Five micro-states are assigned to this state ($M_S = 2, 1, 0, -1, -2$) and it is found that these micro-states all have $\mathcal{S} = (M_S)_{\max} = 0$. The fivefold degenerate state is called 1D .

After excluding the above micro-states from the table, one finds that there remains a set of nine micro-states belonging to the 3P state. These correspond to $M_S = +1, M_S = 0, \pm 1$; $M_S = 0, M_S = 0, \pm 1$; and $M_S = -1, M_S = 0, \pm 1$. Then $(M_L)_{\max} = \mathcal{L} = 1$, and the term is a P state; $2\mathcal{S} + 1 = 3$, and so a 3P state is ninefold degenerate. There is but one micro-state remaining, corresponding to a 1S state. Hund's rule places the 3P state as the ground state.

The degeneracies of some of the atomic states are partially resolved by weak crystalline fields, since the maximum orbital degeneracy allowed in this situation is

Table 1.2. Terms for $(2p)^2: {}^1D, {}^3P, {}^1S$ Quantum nos.: $nlmm_s = 2lmm_s$; $m = \pm 1, 0$; $m_s = \pm \frac{1}{2}$.

$(mm_s)_1$	$(mm_s)_2$	M_L	M_S	
1 $\frac{1}{2}$	1 $-\frac{1}{2}$	2	0	} 1D
1 $\frac{1}{2}$	0 $-\frac{1}{2}$	1	0	
1 $-\frac{1}{2}$	-1 $-\frac{1}{2}$	0	0	
0 $\frac{1}{2}$	-1 $-\frac{1}{2}$	-1	0	
-1 $\frac{1}{2}$	-1 $-\frac{1}{2}$	-2	0	
1 $\frac{1}{2}$	0 $\frac{1}{2}$	1	1	} 3P
1 $-\frac{1}{2}$	0 $\frac{1}{2}$	1	0	
1 $-\frac{1}{2}$	0 $-\frac{1}{2}$	1	-1	
1 $\frac{1}{2}$	-1 $\frac{1}{2}$	0	1	
1 $-\frac{1}{2}$	-1 $\frac{1}{2}$	0	0	
1 $-\frac{1}{2}$	-1 $-\frac{1}{2}$	0	-1	} 3P
0 $\frac{1}{2}$	-1 $\frac{1}{2}$	-1	1	
0 $-\frac{1}{2}$	-1 $\frac{1}{2}$	-1	0	
0 $-\frac{1}{2}$	-1 $-\frac{1}{2}$	-1	-1	
0 $\frac{1}{2}$	0 $-\frac{1}{2}$	0	0	
				1S

$\mathcal{L} = (M_L)_{\max}$	$\mathcal{S} = (M_S)_{\max}$
$(M_L)_{\max} = 2, M_S = 0$	${}^1D (M_S = 0, \pm 1, \pm 2; M_S = 0)$
$(M_L)_{\max} = 1, M_S = 1$	${}^3P (M_S = 0, \pm 1; M_S = 0, \pm 1)$
$(M_L)_{\max} = 0, M_S = 0$	${}^1S (M_S = 0; M_S = 0)$

three. Neither S nor P states are affected, but they are frequently renamed as A_1 (or A_2) or T_1 , respectively. A D state is resolved into $E + T_2$, and an F state to $A_2 + T_1 + T_2$.

1.4 Paramagnetism

These notes are primarily about paramagnets and the interactions they undergo. As has been indicated above, paramagnetism is a property exhibited by substances containing unpaired electrons. This includes the oxygen molecule, nitric oxide and a large number of organic free radicals, but we shall restrict our concerns to the transition metal and rare earth ions and their compounds.

A paramagnet concentrates the lines of force provided by an applied magnet and thereby moves into regions of higher field strength. This results in a measurable gain in weight. A paramagnetic susceptibility is generally independent of the field strength, but this is true only under the particular conditions which are discussed below.

Paramagnetic susceptibilities are temperature dependent, however. To a first (high-temperature) approximation, the susceptibility χ varies inversely with temperature, which is the Curie Law:

$$\chi = C/T. \quad (1.1)$$

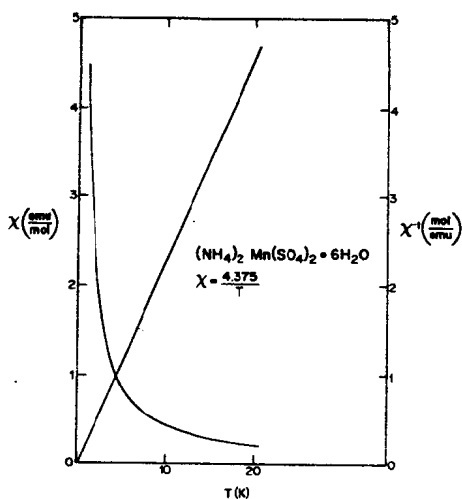


Fig. 1.1. Curie and inverse Curie plots for a salt containing manganese(II), for which $C = 4.375$ emu-K/mol.

Here, χ is the measured susceptibility (from now on, we assume that the proper diamagnetic correction is either unnecessary or else has been made), C is called the Curie constant, and T is the absolute temperature. We plot in Fig. 1.1 the Curie law and the inverse of χ for a representative ion. Since $\chi^{-1} = C^{-1}T$, a plot of χ^{-1} vs. T is a convenient procedure for the determination of the Curie constant; note that the line goes through the origin.

Since the magnitude of χ at room temperature is an inconvenient number, it is common among chemists to report the effective magnetic moment, μ_{eff} , which is defined as

$$\begin{aligned}\mu_{\text{eff}} &= (3k/N)^{1/2} (\chi T)^{1/2} \\ &= [g^2 s(s+1)]^{1/2} \mu_B.\end{aligned}\quad (12)$$

Here, k is the Boltzmann constant, $1.38 \times 10^{-23} \text{ JK}^{-1}$, N is Avogadro's number, $6.022 \times 10^{23} \text{ mol}^{-1}$ and

$$\mu_B = |e\hbar/2mc| = 9.27 \times 10^{-24} \text{ JT}^{-1}$$

is the Bohr magneton. Planck's constant h , divided by 2π , is denoted by \hbar . That is, the units of μ_{eff} is μ_B .

Compounds containing such ions as Cr^{3+} and Mn^{2+} have magnetic moments due to unpaired electron spins outside filled shells. The orbital motion is usually quenched by the ligand field, resulting in spin-only magnetism. Consider an isolated ion, acted on only by its diamagnetic ligands and an external magnetic field H (the Zeeman perturbation). The field will resolve the degeneracy of the various states according to the magnetic quantum number m_s , which varies from $-\mathcal{S}$ to \mathcal{S} in steps of unity. Thus, the ground state of a free manganese(II) ion, which has $\mathcal{S} = 0$, has $\mathcal{S} = 5/2$, and yields six states with $m_s = \pm 1/2, \pm 3/2$, and $\pm 5/2$. These states are degenerate (of equal energy) in the absence of a field, but the magnetic field H resolves this degeneracy. The

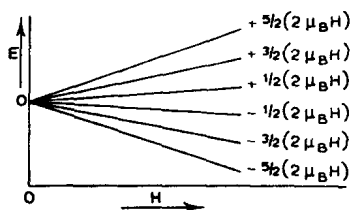


Fig. 1.2. Splitting of the lowest energy level of manganese(II) by a magnetic field into six separate energy levels

energy of each of the sublevels in a field becomes

$$E = m_s g \mu_B H, \quad (1.3)$$

where g is a (Landé) constant, characteristic of each system, which is equal to 2.0023 when $\mathcal{L}=0$, but frequently differs from this value. The convention used here in applying Eq. (1.3) is that the 6S ground state of the manganese ion at zero-field is taken as the zero of energy.

The situation is illustrated in Fig. 1.2. The separation between adjacent levels, ΔE , varies with field, and is easily calculated as $\Delta E = g \mu_B H = 2 \mu_B H$. In a small field of 0.1 T

$$\Delta E = 2 \mu_B H = 2 \times 9.27 \times 10^{-24} \times 0.1 = 1.85 \times 10^{-24} \text{ J}$$

while at a temperature of 1 K, $kT = 1.38 \times 10^{-23} \times 1 = 1.38 \times 10^{-23} \text{ J}$. Thus, at $H=0.1 \text{ T}$ and $T=1 \text{ K}$, $\Delta E < kT$, and the resulting levels have almost the same population, as may be found by calculating the distribution of magnetic ions among the various states from the Boltzmann relation,

$$N_i/N_j \propto \exp(-\Delta E_{ij}/kT),$$

ΔE_{ij} being the energy level separation between the levels i and the ground state j .

Since each state corresponds to a different orientation with regard to the external magnetic field, the net magnetic polarization or magnetization M of the substance would then be very small. Or, the field tends to align the spins with itself, but this is opposed by thermal agitation.

On the other hand, in a larger field of 2 T, $\Delta E = 4 \times 10^{-23} \text{ J}$, and at 1 K, $\Delta E > kT$. Then, only the state of lowest energy, $-5/2 g \mu_B H$, will be appreciably populated, having about 95% of the total. This corresponds to the moments lining up parallel to the external field, and the magnetization would almost have its largest or saturation value, M_{sat} . Real crystals that have been shown to exhibit behavior of this sort include potassium chrome alum, $\text{KCr}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$, and manganese ammonium Tutton salt, $(\text{NH}_4)_2\text{Mn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. Each of the magnetic ions in these salts is well-separated from the other magnetic ions, so it is said to be magnetically dilute. The behavior then is analogous to that of ideal gases in the weakness of the interactions. The statistical mechanics of weakly interacting, distinguishable particles is therefore applicable. This means that most properties can be calculated by means of the Boltzmann distribution, as already suggested.

At low temperatures, the vibrational energy and heat capacity of everything but the magnetic ions may be largely ignored. The spins and lattice do interact through the

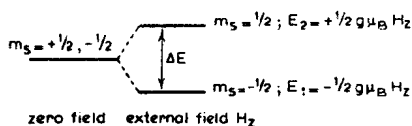


Fig. 1.3. Energy levels of an electron spin in an external magnetic field

time-dependent phenomenon of spin-lattice relaxation, a subject which will be described later. The magnetic ions form a subsystem with which there is associated a temperature which may or may not be the same as that of the rest of the crystal. The magnetization or total magnetic moment M is not correlated with the rest of the crystal, and even the external magnetic field has no effect on the rest of the crystal. Thus, the working hypothesis, which has been amply justified, is that the magnetic ions form a subsystem with its own identity, describable by the coordinates H , M , and T , independent of everything else in the system.

This model provides a basis for a simple derivation of the Curie law, which states that a magnetic susceptibility varies inversely with temperature. Although the same result will be obtained later by a more general procedure, it is useful to illustrate this calculation now. Consider a mol of $\mathcal{N} = 1/2$ particles. In zero field, the two levels $m_s = \pm 1/2$ are degenerate, but split as illustrated in Fig. 1.3 when a field $H = H_z$ is applied. The energy of each level is $m_s g \mu_B H_z$, which becomes $-g \mu_B H/2$ for the lower level, and $+g \mu_B H/2$ for the upper level; the separation between them is $\Delta E = g \mu_B H_z$, which for a g of 2, corresponds to about 1 cm^{-1} at 1 T.

Now, the magnetic moment of an ion in the level m_s is given as $\mu_n = -\partial E_n / \partial H = -m_s g \mu_B$; the molar macroscopic magnetic moment M is therefore obtained as the sum over magnetic moments weighted according to the Boltzmann factor.

$$M = N \sum_n \mu_n P_n = N \frac{\sum_{m_s = -1/2}^{1/2} (-m_s g \mu_B) \exp(-m_s g \mu_B H_z / kT)}{\sum_{m_s = -1/2}^{1/2} \exp(-m_s g \mu_B H_z / kT)}, \quad (1.4)$$

where the summation in this case extends over only the two states, $m_s = -1/2$ and $+1/2$. Then,

$$\begin{aligned} M &= \frac{1}{2} N g \mu_B \left[\frac{\exp(g \mu_B H_z / 2kT) - \exp(-g \mu_B H_z / 2kT)}{\exp(g \mu_B H_z / 2kT) + \exp(-g \mu_B H_z / 2kT)} \right] \\ &= \frac{1}{2} N g \mu_B \tanh(g \mu_B H_z / 2kT), \end{aligned} \quad (1.5)$$

since the hyperbolic tangent (see the Appendix to this chapter) is defined as

$$\tanh y = (e^y - e^{-y}) / (e^y + e^{-y}). \quad (1.6)$$

One of the properties of the hyperbolic tangent is that, for $y \ll 1$, $\tanh y = y$, as may be seen by expanding the exponentials:

$$\tanh y \simeq \frac{(1 + y + \dots) - (1 - y + \dots)}{(1 + y + \dots) + (1 - y + \dots)} \simeq y.$$

Thus, for moderate fields and temperatures, with $g\mu_B H_z/2kT \ll 1$,

$$\tanh(g\mu_B H_z/2kT) \simeq g\mu_B H_z/2kT$$

and

$$M = Ng^2 \mu_B^2 H_z / 4kT. \quad (1.7)$$

Since the static molar magnetic susceptibility is defined as $\chi = M/H$, in this case

$$\chi = M/H_z = \frac{Ng^2 \mu_B^2}{4kT} = C/T \quad (1.8)$$

which is in the form of the Curie law where the Curie constant

$$C = Ng^2 \mu_B^2 / 4k.$$

This is a special case of the more general and more familiar spin-only formula,

$$\chi = \frac{Ng^2 \mu_B^2 \mathcal{S}(\mathcal{S} + 1)}{3kT} \quad (1.9)$$

$$= N\mu_{\text{eff}}^2 / 3kT, \quad (1.10)$$

where $\mu_{\text{eff}}^2 = g^2 \mathcal{S}(\mathcal{S} + 1) \mu_B^2$ is the square of the "magnetic moment" traditionally reported by inorganic chemists. This quantity is of less fundamental significance than the static susceptibility itself, particularly in those cases where μ_{eff} is not independent of temperature. Other definitions of the susceptibility will be introduced later, since in practice one often measures the differential susceptibility, dM/dH , which is not always identical to the static one.

It is also of interest to examine the behavior of Eq. (1.5) in the other limit, of large fields and very low temperatures. In Eq. (1.6), if $y \gg 1$, one may neglect e^{-y} compared to e^y , and

$$\tanh y = 1. \quad (1.11)$$

Then,

$$M_{\text{sat}} = Ng\mu_B/2, \quad (1.12)$$

where the magnetization becomes independent of field and temperature, and, as discussed earlier, becomes the maximum or saturation magnetization M_{sat} which the spin system can exhibit. This situation corresponds to the complete alignment of magnetic dipoles by the field. The more general, spin-only version of (1.12) reads as

$$M_{\text{sat}} = Ng\mu_B \mathcal{S}. \quad (1.13)$$

1.5 Some Curie Law Magnets

The Curie constant

$$C = Ng^2 \mu_B^2 \mathcal{S}(\mathcal{S} + 1)/3k \quad (1.14)$$

takes the following form

$$C = \frac{[6.02 \times 10^{23} \text{ mol}^{-1}][9.27 \times 10^{-24} \text{ JT}^{-1}]^2 g^2 \mathcal{S}(\mathcal{S} + 1)}{3[1.38 \times 10^{-23} \text{ JK}^{-1}]}$$

which, since it can be shown that the unit T^2 is equivalent to J/cm^3 , becomes

$$C = 0.125 g^2 \mathcal{S}(\mathcal{S} + 1) \text{cm}^3 \cdot \text{K/mol}$$

or dividing this expression by T in K, one has the volume susceptibility χ in units of cm^3/mol .

It should be apparent that a good Curie law magnet will be found only when there are no thermally accessible states whose populations change with changing temperature. Four salts which offer good Curie-law behavior are listed in Table 1.3. Each is assumed to have $g = 2.0$, which is consistent with a lack of mixing of the ground state with nearby states with non-zero orbital angular momentum. A plot of inverse susceptibility vs. temperature for chrome alum in Fig. 1.4 illustrates how well the Curie law holds over a wide region of temperature for this substance.

Table 1.3. Several Curie law magnets.

	\mathcal{S}	$\mathcal{S}(\mathcal{S} + 1)$	C (expt)	C (calc)
			emu-K/mol	
KCr(SO ₄) ₂ · 12 H ₂ O	$\frac{3}{2}$	3.75	1.84	1.88
(NH ₄) ₂ Mn(SO ₄) ₂ · 6 H ₂ O	$\frac{5}{2}$	8.75	4.38	4.38
(NH ₄)Fe(SO ₄) ₂ · 12 H ₂ O	$\frac{5}{2}$	8.75	4.39	4.38
Gd ₂ (SO ₄) ₃ · 8 H ₂ O	$\frac{7}{2}$	15.75	7.80	7.87

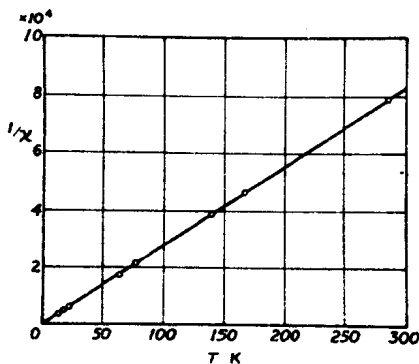


Fig. 1.4. The inverse susceptibility per g of chromium potassium alum as a function of temperature showing the very good agreement with Curie's law (after de Haas and Gorter, 1930)

1.6 Curie-Weiss Law

The Curie law is really just the magnetic analog of the ideal gas law, which is expressed in terms of the variables pVT (pressure, volume, temperature). For magnetic systems, one uses HMT (magnetic field, magnetization, temperature) and the thermodynamic relations derived for a perfect gas can be translated to a magnetic system by replacing p by H and V by $-M$.

When the pressure of a gas becomes too high or molecular interactions occur, deviations from ideal gas behavior occur. Then, one turns to the van der Waals equation to describe the situation, or perhaps an even more elaborate correction is required. In the same fashion, there are many situations in which the Curie law is not strictly obeyed; much of this book is devoted to those cases. One source of the deviations can be the presence of an energy level whose population changes appreciably over the measured temperature interval; another source is the magnetic interactions which can occur between paramagnetic ions. These interactions will be discussed in later chapters, but we can assume their existence for now. To the simplest approximation, this behavior is expressed by a small modification of the Curie law, to the Curie-Weiss law,

$$\chi = C/(T - \theta), \quad (1.15)$$

where the correction term, θ , has the units of temperature. Negative values of θ are common, but this should not be confused with unphysical negative temperatures. The θ is obtained empirically from a plot of χ^{-1} vs. T , as for the Curie law, but now the intercept with the abscissa is not at the origin. When θ is negative it is called *antiferromagnetic* in sign; when θ is positive, it is called *ferromagnetic*. These terms will be explained in later chapters. The constant, θ , characteristic of any particular sample, is best evaluated when $T \geq 10\theta$, as curvature of χ^{-1} usually becomes apparent at smaller values of T .

The Curie and Curie-Weiss laws are compared for a hypothetical situation in Fig. 1.5.

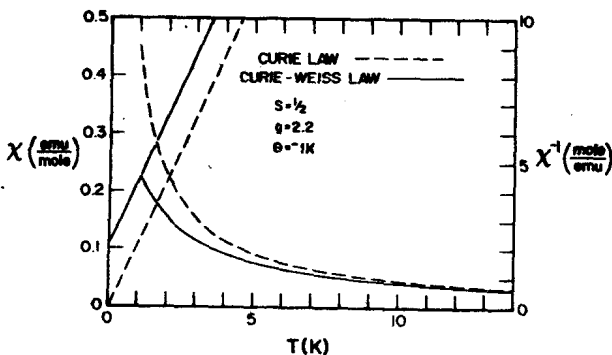


Fig. 1.5. The Curie and Curie-Weiss laws. The Curie constant $C = 0.454 \text{ emu-K/mol}$ ($S = \frac{1}{2}$, $g = 2.2$) has been used for both curves, while $\theta = -1 \text{ K}$ has been used

1.7 Temperature Independent Paramagnetism

It sometimes happens that systems with a spin singlet ground state, which from the development presented above would be expected to be diamagnetic, in fact exhibit a weak paramagnetic behavior. This paramagnetism is found to be temperature independent and, since it is only of the order of 10^{-4} emu/mol, is generally more important when considering measurements made at 80 K and above. This temperature independent paramagnetism (TIP) arises from a mixing into the ground state wave function the wave function of the excited states that are *not* thermally populated. They may be connected with an orbital operator to the ground state, however; a spin operator will not suffice, for the problem assumes that $S = 0$ for the ground state, and all spin matrix elements will therefore be zero.

An ion such as octahedral cobalt(III), with a 1A_1 ground state, is typical of those which exhibits a TIP. The first excited singlet state (1T_1) usually lies some $16\,000$ – $21\,000\text{ cm}^{-1}$ above this, varying with the particular compound, and it can be shown [2] that

$$\chi_{\text{TIP}} \simeq 4/\Delta(T_1),$$

where $\Delta(T_1)$ is the energy of the 1T_1 state, in wave numbers, above the ground state. For $[\text{Co}(\text{NH}_3)_6]^{3+}$, the 1T_1 state is at $21\,000\text{ cm}^{-1}$, so one calculates

$$\chi_{\text{TIP}} = 1.95 \times 10^{-4} \text{ emu/mol},$$

which is the order of magnitude of the experimental result.

Temperature independent paramagnetism has been observed in such other systems as chromate and permanganate ions and with such paramagnetic systems as octahedral cobalt(II) complexes which have low-lying orbital states.

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1.10 Appendix

1.10.1 Physical Constants and Units

Molar gas constant $R = 8.3144 \text{ J mol}^{-1} \text{ K}^{-1}$

Avogadro constant $N = 6.0220 \times 10^{23} \text{ mol}^{-1}$

Boltzmann constant $k = 1.3807 \times 10^{-23} \text{ J K}^{-1}$

Bohr magneton $\mu_B = 9.274 \times 10^{-24} \text{ J T}^{-1}$

Easy to remember

$$N\mu_B^2/k = 0.375 \text{ emu-K/mol}$$

and for the translation of energy 'units'

$$1 \text{ cm}^{-1} \simeq 30 \text{ GHz} \simeq 1.44 \text{ K} \simeq 1.24 \times 10^{-4} \text{ eV} \simeq 1.99 \times 10^{-23} \text{ J}.$$

At 1 K, $(kT/hc) = 0.695 \text{ cm}^{-1}$. We do not distinguish magnetic field from magnetic induction, and take 1 Tesla (T) as 1 kOe.

1.10.2 Hyperbolic Functions

The hyperbolic functions occur repeatedly in the theory of magnetism. Though they are described in most elementary calculus texts, some properties are summarized here.

The two basic hyperbolic functions are defined in terms of exponentials as follows

$$\sinh x = \frac{1}{2} [\exp(x) - \exp(-x)],$$

$$\cosh x = \frac{1}{2} [\exp(x) + \exp(-x)]$$

and, by analogy to the common trigonometric functions, there are four more hyperbolic functions defined in terms of $\sinh x$ and $\cosh x$, as follows:

$$\tanh x = \sinh x / \cosh x$$

$$\operatorname{sech} x = 1 / \cosh x$$

$$\operatorname{coth} x = \cosh x / \sinh x$$

$$\operatorname{csch} x = 1 / \sinh x.$$

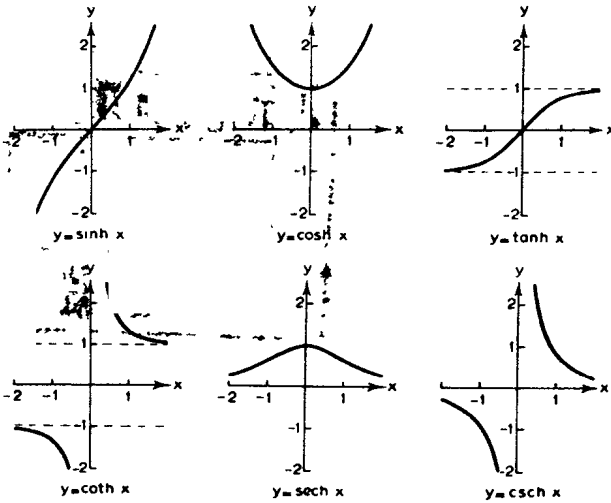


Fig. A.1.
The hyperbolic functions

These functions are sketched in Fig. A.1. It is evident that, unlike the trigonometric functions, none of the hyperbolic functions is periodic. $\sinh x$, $\tanh x$, $\coth x$, and $\operatorname{csch} x$ are odd functions, while $\cosh x$ and $\operatorname{sech} x$ are even.

Lastly, the derivatives of the hyperbolic functions may be shown to be:

$$\begin{aligned} d(\sinh x) &= (\cosh x)dx \\ d(\cosh x) &= (\sinh x)dx \\ d(\tanh x) &= (\operatorname{sech}^2 x)dx \\ d(\coth x) &= -(\operatorname{csch}^2 x)dx \\ d(\operatorname{sech} x) &= -(\operatorname{sech} x)(\tanh x)dx \\ d(\operatorname{csch} x) &= -(\operatorname{csch} x)(\coth x)dx. \end{aligned}$$

1.10.3 Magnetic Moment of a Magnetic Ion Subsystem

It is illuminating to calculate the magnetic moment of a magnetic system with arbitrary spin-quantum number. In order to allow an orbital contribution, we use the total quantum number J , where $J = L + S$. With \hbar the total angular momentum, the energy is $E = -\mu \cdot H$, where $\mu = g\mu_B J$ and $E_m = mg\mu_B H_z$. The Boltzmann factor is

$$P_m = \exp(-mg\mu_B H_z/kT) / \sum_m \exp(-mg\mu_B H_z/kT)$$

so that $\langle \mu_z \rangle$, the average magnetic moment of one atom is

$$\langle \mu_z \rangle = \frac{\sum_{m=-J}^J (-mg\mu_B) \exp(-mg\mu_B H_z/kT)}{\sum_{m=-J}^J \exp(-mg\mu_B H_z/kT)}.$$