

Magnetic susceptibility measurements of transition metal containing compounds

Introduction:

Measurements of magnetic properties have been used to characterize a wide range of systems from oxygen, metallic alloys, solid state materials, and coordination complexes containing metals. Most organic and main group element compounds have all the electrons paired and these are diamagnetic molecules with very small magnetic moments. All of the transition metals have at least one oxidation state with an incomplete d subshell. Magnetic measurements, particularly for the first row transition elements, give information about the number of unpaired electrons. The number of unpaired electrons provides information about the oxidation state and electron configuration. The determination of the magnetic properties of the second and third row transition elements is more complex.

The magnetic moment is calculated from the magnetic susceptibility, since the magnetic moment is not measured directly. There are several ways to express the degree to which a material acquires a magnetic moment in a field. The magnetic susceptibility per unit volume is defined by:

$$\kappa = \frac{I}{H}$$

where I is the intensity of the magnetization induced in the sample by the external magnetic field, H . The extent of the magnetic induction (I) depends on the sample. The induction may be visualized as an alignment of dipoles and/or by the formation of charge polarization in the sample. H is the strength of the external magnetic field in units of oersteds (Oe). The κ is unitless.

Generally, it is more convenient to use mass units, therefore the mass or gram susceptibility is defined as:

$$\chi_g = \frac{\kappa}{d}$$

where d is the density of the solid. The molar susceptibility is the mass susceptibility multiplied by the formula weight.

$$\chi_m = \chi_g (\text{F.W. in g mol}^{-1})$$

The terms κ , χ_g , and χ_m are all measures of the magnetic moment of a substance in a magnetic field.

Relating susceptibility to unpaired electrons:

The relationship between the applied magnetic field and the moments resulting in the diamagnetic and paramagnetic susceptibilities, combined with the contribution for other effects including Van Vleck paramagnetism, can be described in terms of the effective magnetic moment μ_{eff} , where k = Boltzmann's constant, T = absolute temperature, β = Bohr Magneton, N is Avogadro's number, and χ_A is the susceptibility per gram of the paramagnetic ion.

$$\mu_{\text{eff}} = \sqrt{\frac{3k\chi_A T}{N\beta^2}} = 2.84\sqrt{\chi_A T} \text{ B.M.}$$

The units are in B.M. (Bohr Magnetons), which is a unit of magnetic moment and equal to $eh/4\pi mc = 9.27 \times 10^{-21}$ erg/gauss. The χ_a is the atomic susceptibility corrected for the diamagnetic components of the ligands and associated ions. The diamagnetic corrections for cations, anions, and individual atoms and are given in units of $\times 10^{-5}$ /g atom.

Table 1 (left) Diamagnetic corrections and (right) Pascal's Constants in $\times 10^{-5}$ /g atom or $\times 10^{-6}$ erg*G⁻² mol⁻¹.

Cations		Anions		Molecules	
Li ⁺	1.0	F ⁻	9.1	H ₂ O	13
Na ⁺	6.8	Cl ⁻	23.4	NH ₃	16
K ⁺	14.9	Br ⁻	34.6	en	47
Rb ⁺	22.5	I ⁻	50.6	py	49
Cs ⁺	35.0	CH ₃ CO ₂ ⁻	29	PPh ₃	167
Tl ⁺	35.7	C ₆ H ₅ CO ₂ ⁻	71		
NH ₄ ⁺	13.3	CN ⁻	13		
Hg ²⁺	38	CNO ⁻	23		
Mg ²⁺	5	CNS ⁻	34		
Zn ²⁺	15	ClO ₄ ⁻	34		
Pb ²⁺	32	CO ₃ ²⁻	28		
Ca ²⁺	10.4	C ₂ O ₄ ²⁻	28		
Si ²⁺	16	HCO ₂ ⁻	17		
Ba ²⁺	26	NO ₃ ⁻	19		
Fe ²⁺	12.8	O ²⁻	6		
Cu ²⁺	12.8	OH ⁻	11		
Co ²⁺	12.8	S ²⁻	28		
Ni ²⁺	12.8	SO ₄ ²⁻	38		
Cu ¹⁺	15	S ₂ O ₃ ²⁻	46		
Ag ¹⁺	27	acac ⁻	55		
Cd ²⁺	20				
Other First Row Transition Metals	13				

Pascal's Constants	
H	2.93
C	6.00
N (ring)	4.61
N (open chain)	5.57
N (mono amide)	1.54
N (diamide imide)	2.11
O (ether alcohol)	4.61
O (ketone aldehyde)	-1.73
O (carboxyl)	3.36
F	6.3
Cl	20.1
Br	30.6
I	44.6
S	15.0
Sr	23
Te	37.3
P	26.3
As(V)	43.0
As(III)	20.9
Sb(III)	74.0
Li	4.2
Na	9.2
K	18.5
Si	20
Pb	46
Sb(IV)	30
Mg	10.0
Ca	15.9
Al	13
Zn	13.5
Hg(II)	33

Measurement of magnetic susceptibility:

The Guoy method, Faraday method, and determination of magnetic susceptibility by nuclear magnetic resonance (NMR) are all experimental techniques to determine the magnetic susceptibility of transition metal containing coordination compounds. The Evans balance, developed by Professor D.F. Evans of Imperial College London, is a compact and self contained experimental apparatus. The digital readout provides rapid and accurate readings and the sensitivity rivals that of traditional methods. The instrument also has the advantage that samples as small as 50 mg may be measured.

The Evans balance has the same basic configuration as found in the Guoy method. The sample is suspended between two poles of a magnet. The balance measures the apparent change in the mass of the sample. The sample is repelled or attracted to the magnetic field for diamagnetic and paramagnetic substances, respectively. The Evans balance doesn't measure mass directly or the force the magnet exerts on the sample. It measures the force the stationary sample exerts on the suspended permanent magnets, which is accomplished by measuring the change in current required to keep a set of permanent magnets in balance after the magnetic fields interact with the sample. The two pairs of magnets are located on one end of a balance beam. When the sample is placed between the poles of one pair of magnets, the beam is deflected and changes position. The change is detected by a coil or photodiode on opposite side of the equilibrium position of the balance beam. A current is passed through a coil to exactly cancel the interaction force. The current needed is proportional to the force exerted by the sample and is used to measure the magnetic susceptibility. The current is measured with a digital voltmeter connected across a precision resistor, in series with the coil, and displayed on the digital display.

The general mass magnetic susceptibility, χ_g , by the use of an Evans balance is:

$$\chi_g = \frac{L}{m} \{C(R - R_0) + \chi_v' A\}$$

L = sample height in centimeters

m = sample mass in grams

C = balance calibration constant (printed on back of balance)

R = reading from the digital display when the sample and tube is in place in the instrument

R_0 = reading from the digital display when the empty sample tube is in the instrument

χ_v' = volume susceptibility of air ($0.029 \times 10^{-6} \text{ erg G}^{-2} \text{ cm}^{-3}$)

A = cross-sectional area of the sample

Calibration of the Evans balance is typically done with $\text{Hg}[\text{Co}(\text{SCN})_4]$ or $[\text{Ni}(\text{en})_3]\text{S}_2\text{O}_3$, which have values of $1.644 \times 10^{-5} \text{ erg G}^{-2} \text{ cm}^{-3}$ and $1.104 \times 10^{-5} \text{ erg G}^{-2} \text{ cm}^{-3}$, respectively. The volume susceptibility contribution from air is relatively small and can usually be neglected for the measurement of the magnetic susceptibility of solid samples.

The mass magnetic susceptibility can be rewritten as:

$$\chi_g = CL(R - R_0) / [1 \times 10^9 (m)]$$

and has units of $\text{erg G}^{-2} \text{ g}^{-1}$. Use this equation to calculate the χ_g .

The molar susceptibility, χ_m , is calculated by:

$$\chi_m = \chi_g (\text{F.W. in g mol}^{-1})$$

and has c.g.s. units of $\text{erg}\cdot\text{G}^{-2} \text{ mol}^{-1}$.

Diamagnetic corrections to the molar susceptibility are made to account for the inner core electrons, ligands, atoms, and ions in the compound or material, which make the apparent molar susceptibility smaller than it really is from the contribution from the unpaired electrons. The diamagnetic contributions are added to the value of χ_m to obtain the χ_A , the molar susceptibility of the paramagnetic atom. Select diamagnetic corrections are given in table 1 and more extensive tables are found in the literature.[1, 2] The diamagnetic correction for ligands or other groups not found in the table can be obtained by summing the Pascal's constants for each atom or type of atom in the group as found in the table 1 or primary literature.

$$\chi_A = \chi_m + \text{sum of all diamagnetic corrections}$$

The measured χ_A can be related to the effective magnetic moment in Bohr Magnetons by:

$$\mu_{\text{eff}} = \left[\frac{3kT \chi_A}{N \beta^2} \right]^{1/2}$$

where k is the Boltzmann constant, N is Avogadro's number, and β is the Bohr magneton. Thus, the equation simplifies to:

$$\mu_{\text{eff}} = 2.828(\chi_A T)^{1/2}$$

The measured μ_{eff} can be compared to the calculated value, μ_s , from the spin-only formula, where the orbital angular momentum is assumed to be quenched by the ligand field.

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

where S is the total spin of the paramagnetic center with n unpaired electrons.

n	μ_s (B.M.)
1	1.73
2	2.83
3	3.87
4	4.90
5	5.92

The measured value of μ_{eff} varies slightly from one compound or material to another, as shown in tables 2 and 3 for transition metals in an octahedral and tetrahedral geometry, respectively. The number of unpaired electrons for other coordination geometries can be predicted by considering the splitting of the d-orbitals, and crystal field stabilization energy.[3]

Table 2 Measured magnetic moments, *d*-configuration, and number of unpaired electrons for transition metal ions with an octahedral geometry.

Metal Ion	d configuration	Number of Unpaired Electrons	Magnetic moment¹ (B.M.)
Ti ⁴⁺ , V ⁵⁺	d ⁰	0	0
Ti ³⁺ , V ⁴⁺	d ¹	1	1.7-1.8
V ³⁺	d ²	2	2.7-2.9
Cr ³⁺ , Mn ⁴⁺	d ³	3	3.7-3.9
Cr ²⁺ , Mn ³⁺	d ⁴	4 (high spin) 2 (low spin)	4.8-5.0 3.0-3.3
Fe ³⁺ , Mn ²⁺	d ⁵	5 (high spin) 1 (low spin)	5.7-6.0 2.0-2.5
Fe ²⁺ , Co ³⁺	d ⁶	4 (high spin) 0 (low spin)	5.6-5.9 0
Co ²⁺	d ⁷	3 (high spin) 1 (low spin)	4.3-5.2 2.0-2.7
Ni ²⁺	d ⁸	2	2.9-3.3
Cu ²⁺	d ⁹	1	1.8-2.1
Cu ⁺	d ¹⁰	0	0

Table 3 Measured magnetic moments, *d*-configuration, and number of unpaired electrons for transition metal ions with a tetrahedral geometry.

Metal Ion	d configuration	Number of Unpaired Electrons	Magnetic moment (B.M.)
Ti ⁴⁺ , V ⁵⁺	d ⁰	0	0
Cr ⁵⁺	d ¹	1	1.7-1.8
Cr ⁴⁺	d ²	2	2.6-2.8
Fe ⁵⁺	d ³	3	3.6-3.7
-	d ⁴	-	-
Mn ²⁺	d ⁵	5 (high spin)	5.9-6.2
Fe ²⁺	d ⁶	4 (high spin)	5.3-5.5
Co ²⁺	d ⁷	3 (high spin)	4.2-4.8
Ni ²⁺	d ⁸	2	3.7-4.0
Cu ²⁺	d ⁹	1	-
Cu ⁺	d ¹⁰	0	0

¹ Data taken from Magnetic Susceptibility Balance Instruction Manual, Johnson Matthey, Issue 3, 10th March 2004, ECN 306

Instructions for operation of the Evans Balance by Johnson Matthey:

1. Place the balance on a flat surface and level using the bubble. Plug in/turn on. *Note: the balance is sensitive to breakage and should not be moved.*
2. Turn the RANGE dial to $\times 1$ and allow the balance to warm up for 10-30 minutes.
3. Adjust the ZERO dial until the display reads 000. The zero should be readjusted if the range is changed. *Note: The zero dial has a range of about 5 turns and works best in the middle of the range. If needed, adjust the dial 5 turns from one end and adjust the back legs of the balance until the display reads near zero. All further adjustments should be done from the front of the Evans balance.*
4. Weigh an empty tube and place into the tube guide. Record the reading R_0 . The instrument can drift over time, therefore it should be rezeroed before each measurement. The digital display should fluctuate by no more than ± 1 on the $\times 1$ setting. Note a range of readings if there is significant fluctuation.
5. Fill the sample tube with the sample of interest. Gently tap the bottom of the tube on a hard surface to increase the packing density. The height of the sample in the tube should be at least 1.5 cm, ideally between 2.50 and 3.50 cm. Measure and record the mass of the tube and sample using an analytical balance. Measure the height of the level sample contained in the tube.
6. Rezero the empty balance and place the tube containing the sample into the tube guide. Record the reading R .
 - a. If the reading of off-scale, adjust the RANGE dial to $\times 10$, rezero, and take an additional reading and multiply the reading by 10.
7. Gently tap the tube containing the sample on a hard surface again to further pack the sample, and then take another reading of R . Repeat until several readings are within ± 1 .
8. Determine the temperature (T) to $0.1\text{ }^\circ\text{C}$ with a thermometer clamped near the balance.
9. The sample may be removed from the tube by gently tapping the tube upside down on a piece of weighing paper. Avoid breaking the glass lip on the tube.
10. After removing most of the cotton from a cotton swab, scrub the inside of the tube to remove any remaining loose powder.
11. Rinse the empty tube with ethanol and then acetone with a fine-tip disposable pipette, drying between each step. Ensure the tube is dry before using again.
12. Tabulate the data R , R_0 , L , M , and T with proper units and significant figures.
13. Calculate the μ_{eff} and compare to predicted values from μ_s calculated by assuming a spin-only contribution.

References

- 1 Figgis, B. N.; Lewis, J. In Lewis, J., Wilkins, R. G., Eds.; *Modern Coordination Chemistry*; Interscience Publishers Inc.: New York, 1960; pp 400-454
- 2 Angelici, R. J. In *Synthesis and technique in inorganic chemistry*. W.B. Saunders: 1977;
- 3 Housecroft, C. E.; Sharpe, A. G. In *Inorganic Chemistry*; Pearson Education Limited: 2008; Vol. 3