Chemistry 332 2003
Assignment #2 and TM Magnetism Handout

Determination of Unpaired Electrons in TM Complexes

The first portion of this handout outlines three methods for the determination of the number of unpaired electrons in TM compounds. It is <u>your responsibility</u> to learn how to apply these techniques to data and understand the advantages and disadvantages of each of these techniques. **THIS MATERIAL WILL NOT BE COVERED *EXPLICITLY* IN CLASS.**

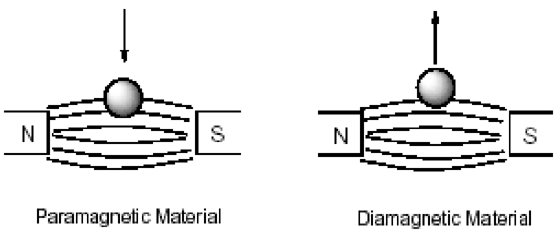
When determining the magnetic susceptibility (χ) we do so at a particular temperature (T in units of Kelvin). Numerous experimental methods for measuring χ exist, each with their own advantages and disadvantages. Below we will outline four methods: the Gouy, Faraday, and Evans NMR methods.

A very important point to remember is the measured magnetic susceptibility, $\chi_{measured}$, is the sum of the diamagnetic (χ_{dia}) and paramagnetic (χ_{para}) susceptibilities:

$$\chi_{measured} = \chi_{dia} + \chi_{para}$$

While you can calculate the value for χ_{dia} using a series of Pascal constants for the purposes of our work we will assume that χ_{dia} is negligible. We can make this assumption given that the diamagnetic susceptibility is usually (10^{-4} to 10^{-6} emu) two to three orders of magnitude smaller than the paramagnetic susceptibility (10^{-2} to 10^{-3} emu). **NOTE. In a molecule with a large "organic" component, the contribution from χ_{dia} towards $\chi_{measured}$ may <u>not</u> be negligible.**

Two of the methods described here (Gouy and Faraday) may be considered as force methods. Each involves the measurement of a compounds interaction with a magnetic field by monitoring the change in its weight as a function of applied magnetic field. When a substance is placed near a magnet two possible events will occur. If the material is **paramagnetic**, it will be **drawn into the area of greatest magnetic field** in the magnet. If the material is **diamagnetic** then it will be **repelled from the area of greatest magnetic field**.



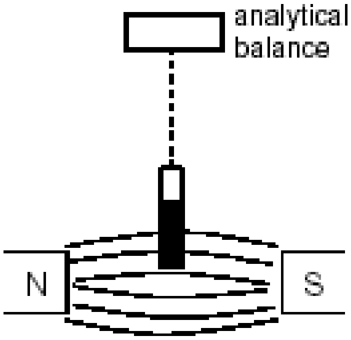
The Gouy and Faraday methods measure the force exerted on the material as it is attracted to for repelled from the magnet. It is important to realize that the material has to be placed in an area of magnetic field, which is less than the maximum field generated by the magnet. If a paramagnetic material is already in the area of greatest field, then there will be no more attractive force. The mathematical description of this force is:

$$F = M\frac{\partial H}{\partial z}$$

where M is the magnetization of the material, and $\frac{\partial H}{\partial z}$ is the field gradient along an axis (for example the z axis). In general the field is greatest in the area centered between the poles of the magnet and drops off radially. The force exerted on the sample is measured with a sensitive analytical balance.

The Gouy Method

The schematic design of a Gouy magnetometer (or balance) is shown to the below. The sample is placed in a cylindrical tube and suspended on a thread (or non-magnetic wire such as a silver chain) from an analytical balance. The sample tube is hung such that some of the material is exposed to the region of homogeneous magnetic field (supplied by an electromagnet) and some of the sample is out of the field. This guarantees that there will be a force acting on the sample to draw it into the area of strongest magnetic field.



The force acting on this sample is:

$$F = M\frac{\partial H}{\partial z} = \chi_v\ V\ H\frac{\partial H}{\partial z}$$

Where χ_v is the volume susceptibility of the sample, V is the volume of the sample, and H is the field strength of the magnet. By integrating this equation along the entire length of the sample, we find:

$$F = \frac{1}{2}\chi_v H^2 A$$

where A is the cross-sectional area of the sample.

The force is measured by weighing the sample very accurately with the magnetic field turned on and with the field off. To determine the volume susceptibility experimentally, we must know the exact **cross-sectional area (A)** and the **magnetic field strength (H)**. This is far from practical and we typically use a calibration standard (like water). This may be viewed as a baseline measurement and provides values for H and A.

Note that when using the Gouy Method you determine χ_g and measure the mass of a given compound in and out of a strong magnetic field.

The gram susceptibility (χ_g) for a sample is given by:

$$\chi_g = \beta \frac{\left(\Delta_{mass}^{sample} - \Delta_{mass}^{tube}\right) + \chi_v^{air} V}{mass\ sample}$$

where β is a calibration constant, and Δ_{mass}^{sample}, and Δ_{mass}^{tube} are the changes seen in mass of the sample and empty sample tube respectively when the magnetic field on and off. χ_v volume susceptibility for air, and V is the volume of the sample in the tube.

Why do we set up the equation this way?

The χ_v^{air} compensates for the susceptibility of the air displaced from the sample tube by the sample. Given the measurements of Δ_{mass}^{sample} and Δ_{mass}^{tube} are performed in a room full of air, the displaced air leads to magnetic buoyancy.

Why would air result in such and effect? What paramagnetic compound is in air?

The value of χ_v for air is 1.7×10^{-4}.

Δ_{mass}^{tube} is included to compensate for the magnetic behavior of the empty sample tube.

This is basically a blank.

The calibration constant (β) can be calculated for the specific magnetometer by using a sample with known gram susceptibility and working the relationship backwards.

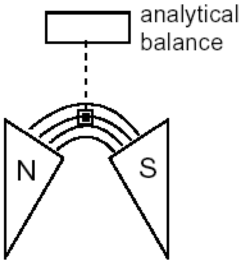
The Good, Bad and the Ugly of the Gouy Approach.

The Good: very sensitive, and can be used at reasonable temperatures.
The Bad: Requires a lot of sample, large uncertainty, the sample must be packed evenly.
The Ugly; The sample must be packed VERY EVENLY…..this is VERY TIME

CONSUMING.

The Faraday Method.

This technique is very similar to the Gouy method. However, it is not plagued with a sensitivity to the cross sectional area of the sample in the sample tube. The Faraday method uses a specially designed magnet to create an area of constant magnetic field. A schematic illustration of the magnetometer is shown below.



The specially designed magnet produces a field such that a relatively large portion of it has a constant $H\frac{\partial H}{\partial z}$. If the sample is placed into this region then the force acting on the sample is independent of the density of the sample and only dependent upon its mass.

$$F = M\frac{\partial H}{\partial z} = \chi_m\ (Mass)\ H\frac{\partial H}{\partial z}$$

As is the case with the Gouy approach although the field is constant, we still do not know its value. It is practical to use a calibration standard.

The gram susceptibility in the Faraday method is given by:

$$\chi_g = \beta\frac{\Delta_{mass}^{sample} - \Delta_{mass}^{tube}}{mass\ sample}$$

as with the relationship we use with the Gouy data β is the calibration constant calculated for the specific Faraday magnetometer. One difference from the previous expression you will notice is we neglect the magnetic buoyancy caused by the air displaced. This is because the experiment is typically carried out with a small quartz boat and its volume is negligible.

The Good, Bad and the Ugly of the Faraday Approach.

The Good: very sensitive, and can be used at reasonable temperatures, small amount of sample, uniform packing is not an issue, error is reduced by the direct measurement of χ_g.

The Bad: Requires a specialized magnet. $$$$$

The Ugly: NO UGLY

The biggest advantage of the Faraday method over the Gouy approach is the small amount of sample that is needed.

Evans NMR Method

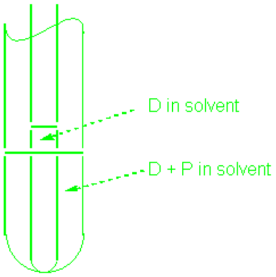
The chemical shift of a NMR active nucleus is dependent upon the bulk magnetic susceptibility of its surroundings. We can measure the susceptibility of a sample by observing the change in the NMR shift of a probe molecule in the same solution as the sample. This is the basis of the Evans NMR method.

A hydrogen nucleus in a molecule gives rise to an NMR signal because it has spin (analogous to electron spin). The value of the spin for H is 1/2, and this spin may align itself in one of two ways with respect to an applied magnetic field: parallel or antiparallel. These are called spin states. These two states are of different energies, and we may cause a transition from one state to the other by providing a photon whose energy matches the energy difference between the two spin states. The absorption of energy accompanying the transition is what we measure in NMR, and it is thus analogous to any other spectroscopic technique. The energy difference between spin states depends upon the environment of the hydrogen nucleus. The more highly shielded a proton is, the larger the magnetic field at which it resonates (absorbs). This is the basis of the standard NMR experiment.

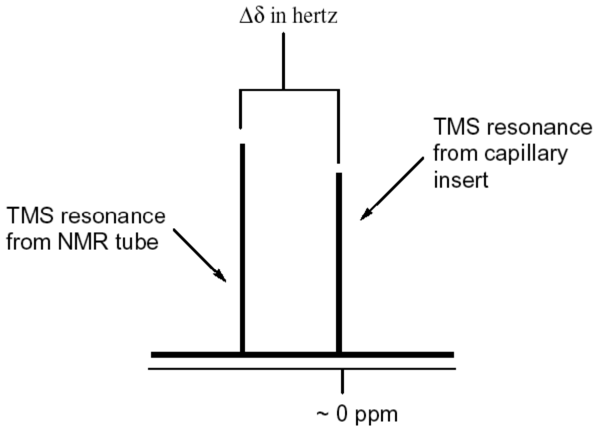
It is possible to exploit influence of shielding on chemical shift resonances and effectively measure the magnetic susceptibility of a paramagnetic species. If we consider a solution containing two solutes (one paramagnetic (P) and one diamagnetic (D)), the magnetic moment (μ) of P deshields the protons of D. As a result a smaller applied magnetic field will be required to cause resonance of the protons in D than if P was absent. The difference, in frequency units, between the resonance position of D with and without P is related to the mass magnetic susceptibility (χ_g) of P by the equation below.

$$\chi_g = \frac{3}{4\pi}\frac{\Delta\delta}{(SF)(conc)}$$

Where $\Delta\delta$ ιis the chemical shift difference in Hz, SF is the frequency of the NMR spectrometer (in Hz), and (conc) is the concentration of P. To measure $\Delta\delta$ experimentally, we must observe the resonances of D in the presence and absence of P simultaneously. This is done using a double (concentric) NMR tube (see the figure below). The inner tube contains D in a suitable solvent. The outer tube contains D and P in the same solvent. Very often, D is TMS or t- butanol. Both of these compounds have well-defined, large proton signals resonance signals, and they addition do not interact to a significant extent with metal ions.



The proton spectrum will show two signals for the probe molecule (TMS or t-butanol). A "cartoon example is shown below.



Just as in the Gouy and Faraday methods outlined above, the value for χ_g is the measured susceptibility. To find the contribution from χ_{para}, you must subtract away the contribution from χ_{dia} (using the Pascal constants). In the Evans NMR method, account for χ_{dia} arising from the solvent used to dissolve your sample. The solvent contributes to the measured susceptibility because the volume of solvent in the NMR sample tube is much greater than the volume in the capillary insert.

The Good, Bad and the Ugly of the Evans Approach.

The Good. high sensitivity, minimal sample requirements, fast

The Bad. high uncertainty, limited temperature range

Questions.

1. Using the following data obtained at 25°C with a Gouy balance and given relationships determine the electron configuration (i.e., $t_{2g}^{x}e_{g}^{y}$) and the number of unpaired electrons in $TiCl_3$. You may also find it useful to know that $[Fe(OH_2)_6]Cl_3$ has a measured paramagnetic moment of 5.3B.M. **Show all your work.**

   mass of the empty tube (magnet on) = 5.1377g mass of the empty tube (magnet off) = 5.1377g

mass of the $TiCl_3$ filled tube (magnet on) = 16.2451g
mass of the $TiCl_3$ filled tube (magnet off) = 16.2412g

mass of the $[Fe(OH_2)_6]Cl_3$ filled tube (magnet on) = 8.6674g
mass of the $[Fe(OH_2)_6]Cl_3$ filled tube (magnet off) = 8.6608g

mass of the tube filled with distilled water (magnet off) = 5.6377g
density of water = 1.000g ml^{-1}

2. Using the following data obtained from a Faraday balance and given relationships determine the electron configuration (i.e., $t_{2g}^{x}e_g^{y}$) and the number of unpaired electrons in $CrCl_3\cdot 6H_2O$. You may also find it useful to know that $[Fe(OH_2)_6]Cl_3$ has a measured paramagnetic moment of 5.3B.M. **Show all your work.**

   mass of the empty tube (magnet on) =
   mass of the empty tube (magnet off) =

   mass of the $CrCl_3\cdot 6H_2O$ filled tube (magnet on) =
   mass of the $CrCl_3\cdot 6H_2O$ filled tube (magnet off) =

   mass of the $[Fe(OH_2)_6]Cl_3$ filled tube (magnet on) =
   mass of the $[Fe(OH_2)_6]Cl_3$ filled tube (magnet off) =

3. The following data was obtained using a 400MHz NMR spectrometer for the proton spectrum of trimethylsilane (TMS).

   TMS signal = 0 ppm
   TMS signal exposed to $[Co(en)_3]Cl_3$ =
   Mass of $[Co(en)_3]Cl_3$ =
   Volume of $[Co(en)_3]Cl_3$ solution =

   Use this data and the Evans approach to determine the electron configuration (i.e., $t_{2g}^{x}e_g^{y}$) of Co in $[Co(en)_3]Cl_3$.

4. For the potassium salt of $[Fe(CN)_6]^{3-}$ has a magnetic moment of 2.3B.M. This value lies between the values for one (1.7B.M.) and two (2.8B.M.). Suggest an explanation for this observation.

5. The magnetic moment for the $[Mn(NCS)_6]^{4-}$ ion is 6.06B.M.. What is the electron configuration of the Mn (i.e., $t_{2g}^{x}e_g^{y}$).