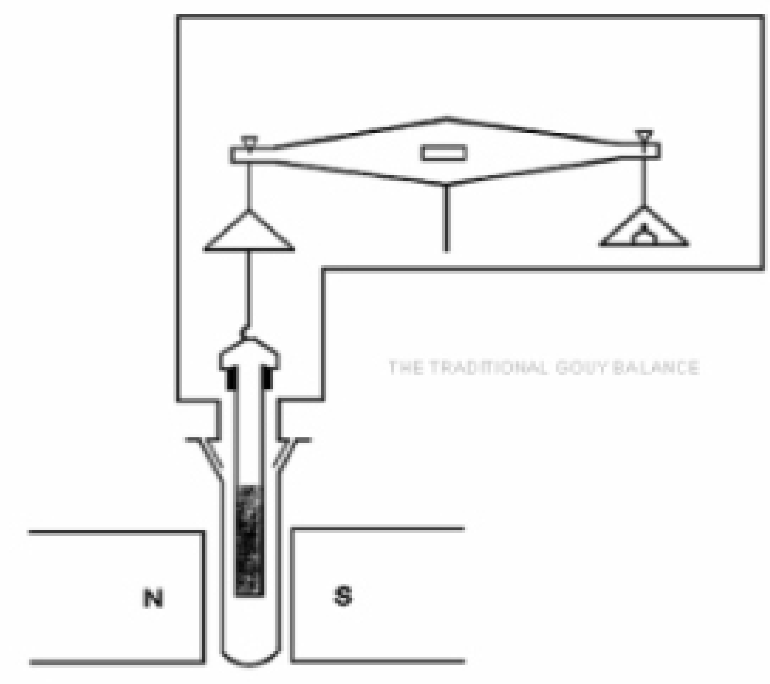
Microscale Determination of Magnetic Susceptibility

- Electrons have a magnetic moment that can be aligned either ***parallel*** or ***anti-parallel*** to an applied magnetic field, depending on whether the spin magnetic quantum number (m_s) is +½ or –½.

- If the sample is suspended between the poles of the magnet and is connected to the pan of an analytical balance. This is the experimental arrangement of a ***Gouy balance***.



Diamagnetic Repulsion

- For an atom or ion with only paired electrons, the individual electron contributions to the overall spin magnetic quantum number (M_s) cancel one another, giving a zero net value of the overall spin quantum number; i.e., $S = 0$.
- Such a species is said to be ***diamagnetic***.
- If a diamagnetic material is placed between the poles of a strong magnet it will experience a repulsion for the applied field.
- The ***repulsion arises from circulation of the electrons caused by the applied field***, resulting in an induced magnetic field in opposition.
- As a result of the induced diamagnetic repulsion, the ***sample will appear to weigh less in the magnetic field***, compared to its true weight outside the field. When removed from the applied field, the sample has no residual magnetic moment, and its apparent weight will be its true weight.

Paramagnetic Attraction

- If the sample contains one or more unpaired electrons, the overall spin quantum number will be greater than zero; i.e., $S > 0$. Such a species is said to be ***paramagnetic***.
- If a paramagnetic species is placed between the poles of a strong magnet it will experience an attraction for the field, due to the ***alignment of the permanent paramagnetic moment with the applied field***.
- If the sample is weighed with a Gouy balance, ***it will appear to be heavier in the magnetic field***, compared to its true weight outside the field.
- With the exception of monatomic hydrogen, all atoms or ions with unpaired electrons also have paired electrons. In an applied field, these paired electrons and their associated induced diamagnetic moment slightly mitigate the paramagnetic attraction for the applied field.
- Nonetheless, ***the paramagnetic moment is always stronger than the opposing diamagnetic moment***, so the net effect is an attraction for the field.
- However, whenever we refer to a substance as paramagnetic, owing to an electronic configuration having unpaired electrons, we must realize that there is also a subtractive diamagnetic contribution to the overall magnetic moment of the sample.

The Magnetic Moment *(μ)*

- Transition metals, by definition, have at least one oxidation state with an incompletely filled *d* or *f* subshell and are consequently paramagnetic in such states.
- The *magnetic moment* ***(μ) results from both the spin (m_s) and orbital (m_l) contributions*** of these unpaired electrons.
- The presence of coordinated ligands around the metal ion quenches the orbital contribution to greater or lesser degree, making the spin contribution most important.
- As an approximation, the expected magnetic moment for an ion with a certain number of unpaired electrons can be estimated from the ***spin-only magnetic moment (μ_s)*** which disregards orbital contributions:

$$\mu_s = g\sqrt{\{S(S+1)\}} \qquad \textbf{(eqn. 1)}$$

- In equation (1), g is the electron gyromagnetic ratio ($g = 2.00023$) and $S = n(½)$, where n is the number of unpaired electrons in the configuration.

- Substituting $g = 2$ and $S = n/2$ into equation (1), we can calculate the spin-only moment in terms of the number of unpaired electrons from the expression

$$\boxed{\mu_s = \sqrt{\{n(n+2)\}}} \qquad \textbf{(eqn. 2)}$$

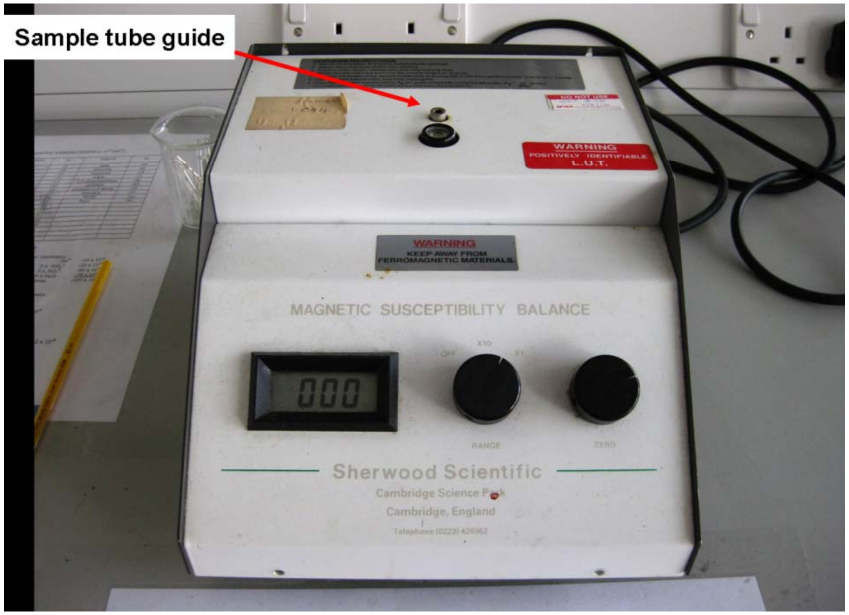
- Thus, for a d^1 configuration, such as Ti^{3+}, we obtain $\mu_s = [1(1 + 2)]^{½} = \sqrt{3} = 1.73$.
- The units of the magnetic moment are Bohr magnetons (BM).
- Actual magnetic moments tend to be somewhat larger than the spin-only values obtained from either equation (1) or (2), owing to incomplete quenching of the orbital contribution.

Nonetheless, the experimentally obtained value of the *effective magnetic moment*, μ_{eff}, taken as approximately the spin-only value, often serves as a practical means of determining the number of unpaired electrons on the transition metal in a complex. This, in turn, gives information about the spin state of the metal and can suggest its oxidation state or mode of bonding.

Experimental Determination of Magnetic Moments

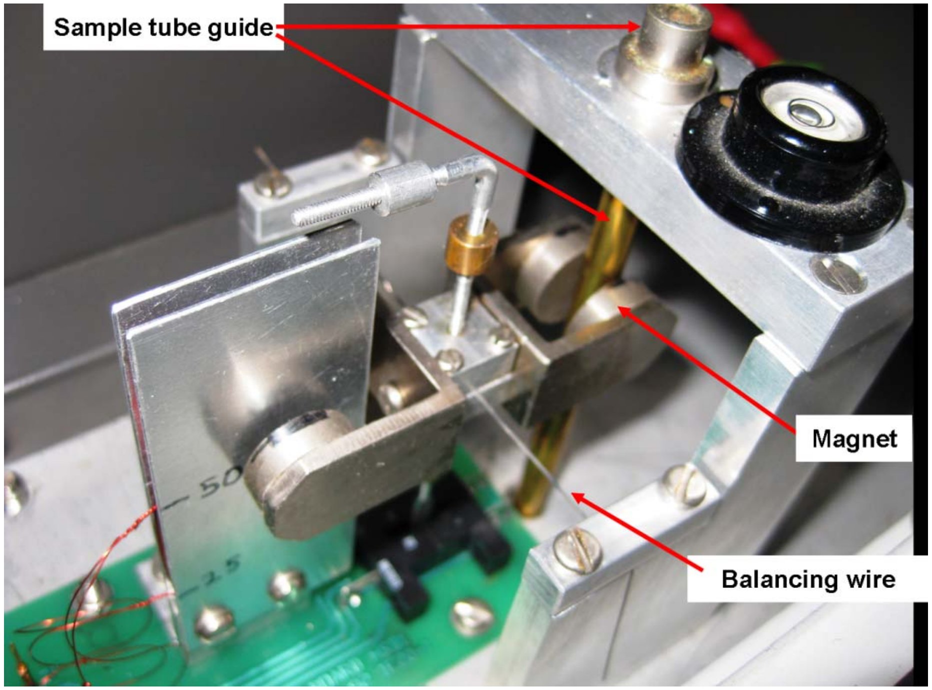
- Magnetic moments are not measured directly.
- Instead, they are calculated from the measured *magnetic susceptibility*, χ.
- In 1974, D. F. Evans of Imperial College, London, developed a new type of magnetic susceptibility balance suitable for semi-microscale samples, which is commercially available from Johnson Matthey.
- The Evans balance employs the Gouy method in a device that is compact, lightweight, and self-contained.
- It does not require a separate magnet or power supply, and is therefore portable.
- The instrument has a digital readout that provides quick and accurate readings, with sensitivity matching traditional apparatus.
- It can be used with solids, liquids, and solutions. As such, the Evans balance is ideal for our purposes.
- In this experiment you will determine the magnetic susceptibility, and from it the magnetic moment, of your previously prepared $Mn(acac)_3$.

D. F. Evans, *J. Phys. E; Sci. Instr.*, **1974**, *7*, 247.



The Evans balance (or Johnson-Matthey balance) is a variation of the Gouy system. In a Gouy balance the sample is pulled into (or repelled from) the field of a large, fixed magnet. In the Evans balance the sample stays still and a small magnet is attracted (or repelled) by the sample.

The magnet is balanced on a fine wire (actually a flat tape) which twists in response to the force acting on the magnet. This is what makes the instrument sensitive and fragile despite its chunky appearance - please treat it gently.



- The sample's magnetic susceptibility per gram is called the ***mass magnetic susceptibility* (χ_g)**.
- For the Evans balance, the general expression for the mass magnetic susceptibility is

$$\chi_g = (L/m)[C(R\text{-}R_0) + (\chi_v{}'A)] \qquad \textbf{(eqn. 3)}$$

where χ_g = mass magnetic susceptibility (erg.$G^{-2}cm^{-3}$)

L = sample length (cm)

m = sample mass (g)

C = balance calibration constant (different for each balance; printed on the back of the instrument - Calculated in this experiment using a calibration standard.)

R = reading from the digital display when the sample (in the sample tube) is in place in the balance

R_o = reading from the digital display when the empty sample tube is in place in the balance

$\chi_v{}'$ = volume susceptibility of air (0.029×10^{-6} erg·$G^{-2}cm^{-3}$)

A = cross-sectional area of the sample

- The volume susceptibility of air is usually ignored with solid samples, so equation (3) can be rewritten as

$$\boxed{\chi_g = [LC(R\text{-}R_0)]/(m \times 10^9)} \qquad \textbf{(eqn. 4)}$$

$$\boxed{\chi_g = [LC(R-R_0)]/(m \times 10^9)} \qquad \textbf{(eqn. 4)}$$

- Equation (4) gives the mass magnetic susceptibility χ_g in the cgs-units of erg.$G^{-2}cm^{-3}$ (where G is Gauss).
- The calibration standards usually employed in magnetic susceptibility measurements are $Hg[Co(SCN)_4]$ or $[Ni(en)_3]S_2O_3$, which have χ_g values of 1.644×10^{-5} and 1.104×10^{-5} erg.$G^{-2}cm^{-3}$, respectively.
- A preferred method to evaluate the balance calibration constant C is to perform the experiment with one of these calibration standards employing the appropriate value of χ_g.
- In order to avoid the use of a mercury compound we will use the $[Ni(en)_3]S_2O_3$.

Calculation of Magnetic Moment

- The ***molar magnetic susceptibility (χ_M)*** is obtained from the mass magnetic susceptibility by multiplying by the molecular weight of the sample in units of g/mol; i.e.,

$$\boxed{\chi_M = M.\chi_g} \qquad \textbf{(eqn. 5)}$$

- The units of χ_M are erg·G^{-2}.
- This experimentally obtained value of χ_M includes both paramagnetic and diamagnetic contributions, which we may identify as χ_A and χ_α, respectively.
- All sources of paired electrons (e.g., ligands, counter ions, core electrons on the paramagnetic species) contribute to the diamagnetic portion of the overall susceptibility.
- In 1910, Pascal observed that these contributions were approximately additive and consistent from sample to sample.
- Consequently, the diamagnetic contribution to the observed molar susceptibility can be estimated as the sum of constants (called Pascal's constants) for each diamagnetic species in the sample.

- We are interested in the ***paramagnetic molar susceptibility***, which can be obtained by removing the diamagnetic contributions (χ_α) from χ_M. Thus we may write

$$\boxed{\chi_A = \chi_M - \sum \chi_\alpha} \qquad \textbf{(eqn. 6)}$$

- Values of χ_A (sometimes called the corrected magnetic susceptibility, χ_M^{corr}) are inherently positive, while those of χ_α are inherently negative.
- Thus, for a paramagnetic substance, it must be that $\chi_A > \chi_M$.
- The value of the ***effective magnetic moment (μ_{eff})*** can be determined from χ_A by the *Curie Law* equation where k is the Boltzmann constant, T is the absolute temperature (K), N is Avogadro's number, and β is the Bohr magneton. If the appropriate constants are substituted, equation (7) becomes equation (8)

$$\mu_{\text{eff}} = \sqrt{\frac{3kT\chi_A}{N\beta^2}} \qquad \textbf{(eqn. 7)}$$

$$\boxed{\mu_{eff} = 2.828\sqrt{\chi_A T}} \qquad \textbf{(eqn. 8)}$$

A table of Pascal's constants can be found in the Appendix. Other values may be found in P. F. Selwood, *Magnetochemistry*, 2nd ed., Wiley (Interscience), N.Y., 1956. **An updated tabulation of values has been given by G. A. Bain and J. F. Berry, *J. Chem. Educ.*, 2008, *85*, 532.**