The Evans method

Measuring magnetic susceptibility by NMR—application

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Magnetic Susceptibility

- Magnetic susceptibility is the ratio between magnetization M of the material in a magnetic field and the field intensity H:
- $M = \chi \cdot H$.
- Diamagnetic materials have $\chi < 0$
- Paramagnetic and ferromagnetic materials have $\chi >$ or $>> 0$

Magnetic Field in an NMR

- H” is the component of applied field due to given concentration of paramagnetic ions in solution
- $H'' = H_1 + H_2$
- H_1 = Lorentz or cavity field of induced magnetization in a sphere around the paramagnet = $(4\pi/3)M$
- H_2 is demagnetizing field, opposing applied field; $H_2 = -\alpha M$ (α depends on sample geometry and relative orientation of sample tube and external field)
- $H'' = [(4\pi/3)-\alpha]M$
- But $M = \chi H$
- So $H''/H = [(4\pi/3)-\alpha]\,\chi$

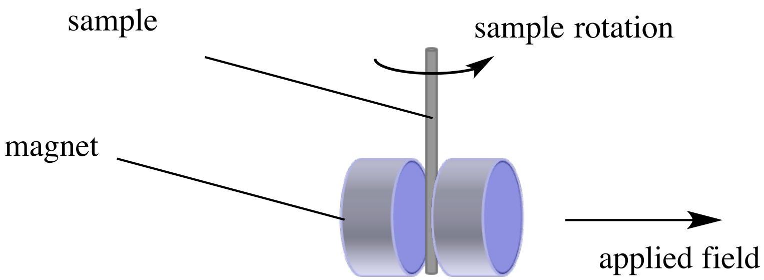
- Given: $H''/H = [(4\pi/3)-\alpha]\chi$
- But $\Delta H''/H = \Delta f/f$
- $\Delta f/f = [(4\pi/3)-\alpha]\chi$

- Finally, add a correction term for the magnetic susceptibility of the solvent and for the change in density of solution vs. solvent. This was all derived using mass susceptibilities (χ_m)

$$\chi_m = \frac{\Delta f}{\left(\frac{4\pi}{3} - \alpha\right) fm} + \chi_o + \frac{\chi_0 (d_o - d_s)}{m}$$

History

- Originally developed for permanent magnet application
- Applied field perpendicular to sample



$$\alpha = 2\pi$$

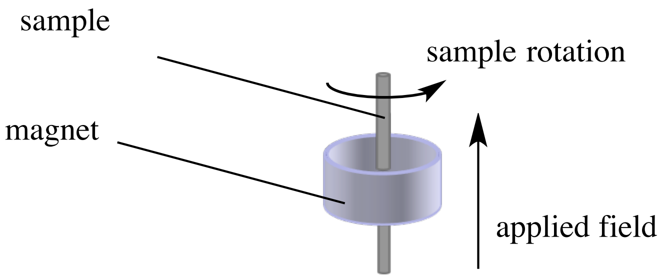
$$\chi_m = \frac{-3\Delta f}{2\pi f m} + \chi_o + \frac{\chi_0 (d_o - d_s)}{m}$$

$$\chi_m = \frac{3|\Delta f|}{2\pi f m} + \chi_o + \frac{\chi_0 (d_o - d_s)}{m}$$

Δf = peak separation (Hz)
f = NMR frequency (Hz)
m = mass per cm^3
χ_m = mass susceptibility

History

- Modern instrumentation: coaxial superconducting magnet
- Applied field parallel to sample



$$\alpha = 0$$

$$\chi_m = \frac{3\Delta f}{4\pi f m} + \chi_o + \frac{\chi_0 (d_o - d_s)}{m}$$

Δf = peak separation (Hz)
f = NMR frequency (Hz)
m = mass per cm^3
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Relationship to number of unpaired electrons

χ_pT = constant for simple paramagnets (Curie Law)

$$\chi_P T = \frac{N_A g^2 \beta^2}{3k_B}[S(S+1)] = 0.50157[S(S+1)] \approx \frac{1}{2}[S(S+1)]$$

$$\chi_P T \approx \frac{1}{8} n(n+2)$$

$$8\chi_P T \approx n(n+2)$$

χ_P = paramagnetic susceptibility
T = absolute temperature (K)
N_A = Avogadro's number
g = magnetogyric constant for electron
β = Bohr magneton
k_B = Boltzmann constant
S = Total spin Quantum number
n = number of unpaired electrons

Must include Russell-Saunders coupling for 2nd or 3rd row
And also spin-orbit coupling for f block

(CGS units)

Effective magnetic moment[†]

$$\mu_{eff} = \sqrt{\frac{3k_B}{N_A\beta^2}(\chi_P T)} \approx \sqrt{7.9933(\chi_P T)} \approx 2.827\sqrt{\chi_P T}$$

$$\mu_{eff} = \sqrt{\frac{3k_B}{N_A\beta^2}(\chi_P T)} = \sqrt{\frac{3k_B}{N_A\beta^2}(\frac{N_A g^2\beta^2}{3k_B}[S(S+1)])} \approx \sqrt{4S(S+1)}$$

$$\mu_{eff} \approx 2\sqrt{S(S+1)} = \sqrt{n(n+2)}$$

μ_{eff} is *independent of temperature* and *unitless* but is usually reported in units of Bohr magneton: μ_B

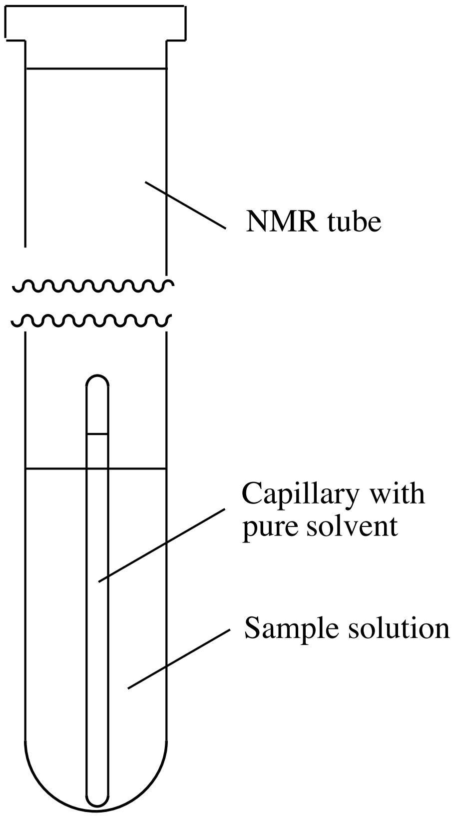
χ_P can be measured at any T and related to n or S

[†]The Chemist's magnetic unit

(CGS units)

Evans' method

- Using ^{1}H NMR to determine magnetic susceptibility
  - NMR tube
    - Sample solution
    - Capillary with pure solvent
  - NMR spectrum collected
    - NMR solvent in capillary (shifted peak)
    - NMR solvent in tube (reference peak)
  - Use peak shift to calculate unpaired electrons



Commonly published equation

- Use c for concentration (mol·L^{-1} = M)
- Ignore solvent diamagnetism
- Ignore density correction
- Combine constants
- Ignore sign of Δf; take positive value

$$\chi_m = \left| \frac{-3\Delta f}{4\pi f m} \cdot \frac{1000 cm^3}{L} \cdot \frac{m'}{n} \right| = \left| \frac{-3000\Delta f}{4\pi f c} \right| = \frac{477\Delta f}{2fc}$$

Δf = peak separation (Hz)
f = NMR frequency (Hz)
m = mass concentration (g/mL)
m’ = mass

n = moles
c = molar concentration
χ_m = molar susceptibility

Diamagnetic correction

- One unpaired electron can be detected even in a large molecule because the magnitude is ~1000 times greater
- For careful work with large molecules, correct observed susceptibility for presence of paired e^-
- χ_D tabulated
- χ_D opposite sign to χ_P!

$$\chi_{meas} = \chi_P + \chi_D$$

$$\chi_P = \chi_{meas} - \chi_D$$