

Utilizing the Evans Method with a Superconducting NMR Spectrometer in the Undergraduate Laboratory

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In his publication in 1959, D. F. Evans outlined a new method for determining the paramagnetic susceptibility of a substance in solution utilizing a relatively young instrumental technique, nuclear magnetic resonance (NMR) spectroscopy.² Evans correlated the observed difference in chemical shift of a signal from an inert reference material in the presence and absence of a paramagnetic solute (accomplished easily using a coaxial NMR sample tube) with the following equation:²

$$\chi_g = \frac{3\Delta f}{2\pi f m} + \chi_o + \frac{\chi_o(d_o - d_s)}{m} \quad (1)$$

where:

- χ_g = mass susceptibility of the solute (cm³/g)
- Δf = observed frequency shift of reference resonance (Hz)
- f = spectrometer frequency (Hz)
- χ_o = mass susceptibility of solvent (cm³/g)
- m = mass of substance per cm³ of solution
- d_o = density of solvent (g/cm³)
- d_s = density of solution (g/cm³)

With the introduction of high-field NMR spectrometers, Live and Chan noted a major difference in the chemical shift of a reference signal in the presence of a paramagnetic solute — “[it was] . . . *twice* in magnitude (in ppm) and of the *opposite* sign from that expected in the case of conventional spectrometers”.³ High-field NMR spectrometers utilize superconducting solenoids to generate an applied magnetic field. These solenoids produce a magnetic field parallel to the long axis of the sample in contrast to the field generated by conventional NMR spectrometers; these spectrometers use permanent magnets or electromagnets that create a field perpendicular to this axis. The result is a “ . . . difference in the effective magnetic field experienced by a molecule in the sample . . . ”.⁴ To compensate for this difference, eq 1 should be corrected as follows:⁵

$$\chi_g = \frac{-3\Delta f}{4\pi f m} + \chi_o + \frac{\chi_o(d_o - d_s)}{m} \quad (2)$$

Using the Evans method has become a standard experiment in many physical chemistry laboratory texts. Yet, these texts make no mention of this inherent difference be-

tween conventional and high-field NMR instruments. One text acknowledges that the “. . . principal magnetic field [may be] provided by a permanent magnet (~1.5T), an electromagnet (2.5 to 5.0T), or a superconducting electromagnet (5.0 to 7.5T),”⁶ but does not provide the corrections needed when the latter is used. With superconducting magnets becoming more and more commonplace, this difference should be brought to the attention of chemical educators as well as to their students. A powerful way to drive the concept home is to perform the experiment on both types of NMR instruments (in departments where this luxury is available) and observe the difference firsthand. At UWF, these experiments were performed on a Varian EM360A (¹H at 60MHz) and a General Electric QE-Plus (¹H at 300MHz).

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The Effect of Temperature on the Solubility of Gases in Liquids

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It seems to be thought that increasing the temperature decreases the solubility of a gas in a liquid. Some texts indicate that this is *always* true. At least two texts offer explanations for why the solubility of gases in liquids *always* decreases with increasing temperature. The fact that there are many exceptions to this generalization was pointed out in 1955 in the *Textbook Error* column.¹ However, the error persists. Of 13 current-edition general chemistry texts designed for a full-year course, 11 made errors regarding this topic.

It is accurate to indicate that the water solubility of *most* gases decrease with increasing temperature. However, in solvents other than water, the solubility of *many*, if not *most*, gases increase with increasing temperature as indicated by data obtained from compilations of solubilities.^{2,3} Because this error continues to be widespread, it seems appropriate to point this out to teachers and authors.

¹Mysels, K. J. *J. Chem. Educ.* **1955**, *32*, 399.

²Seidell, A. *Solubilities of Organic Compounds*, 3rd Ed.; D. Van Nostrand: New York, 1941; Vol 2.

³Linke, W. F. *Solubilities of Inorganic and Metal-Organic Compounds*, 4th Ed.; D. Van Nostrand: New York, 1958; Vol 1.

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²Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

³Live, D. H.; Chan, S. I. *Anal. Chem.* **1970**, *42*, 791.

⁴See footnote 3 for a more comprehensive discussion of the underlying arguments that cause this difference.

⁵Phillips, W. D.; Poe, M. *Meth. Enzymol.* **1972**, *24*, 304.

⁶Shoemaker, D. P.; Garland, C. W.; Nibler, J. W. *Experiments in Physical Chemistry*; 5th ed.; McGraw-Hill: New York, 1989; p 434.