

KCl in the same electrolyte mixture. We have defined the selectivity ratio ( $K_s$ ) by the equation (3)

$$E = E^\circ + \frac{RT}{F} \ln [(m_2\gamma_{21}^2 + K_s m_1\gamma_{12}^2)(m_1 + m_2)] \quad (2)$$

where  $m_1$  is the molal concentration of NaCl,  $m_2$  is the molal concentration of KCl, and the other symbols are as defined above. The values obtained for  $K_s$  are listed in Table II for solutions where the Na/K ratio is greater than 5. For solutions consisting mostly of KCl, the uncertainties in the mean activity coefficient are much greater than the effects of selectivity.

Note that the selectivity ratio is relatively independent of total ionic strength, but depends in a consistent way on the Na/K ratio. Extrapolation of  $K_s$  to zero KCl concentration is shown in Figure 2. Values between  $5 \times 10^{-4}$  and  $4 \times 10^{-3}$  are consistent with the data. Although this is slightly higher than the published value (4), a slightly lower extrapolated value might be obtained if fresh exchanger were used for each measurement and correction were made for residual  $K^+$  in the NaCl.

Because the total ionic strength is held constant for each set of measurements, the gradient of chloride concentration across the ion exchange membrane is also constant, and thus deviations from Nernstian behavior due to chloride transport should contribute negligibly to these measurements. The fact that systematic deviations from the calculated potentials are observed (or alternatively, that the selectivity ratio is composition dependent) indicates that the transport mechanism is more complicated than might be supposed on the basis of a simple ion exchange model.

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## CORRESPONDENCE

### Calibration of Methanol Nuclear Magnetic Resonance Thermometer at Low Temperature

SIR: In high resolution proton magnetic resonance, the temperature of a sample is commonly obtained by measuring the chemical shift of methanol. At low temperature, more hydrogen bonding occurs, and the OH peak shifts downfield. The temperature dependence has been determined with a thermocouple by Varian Associates (1), and more accurately by Van Geet (2,3) using a static thermistor probe, in which the sample container can spin around the static probe. A cylindrical weight of polyperfluoroethylene (4) prevents lifting of the sample tube by the nitrogen flow which cools the sample. The static thermistor is more accurate than the spinning thermistor (5) which has a delicate coaxial electrical contact.

#### CHEMICAL SHIFT OF METHANOL

We have measured the chemical shift  $\Delta\nu$  (in Hz) between the  $\text{CH}_3$  and OH groups down to the melting point of methanol, and have also repeated previous measurements (2). Part of the new results have been reported (3). A quadratic equation fits the data with an error (RMS) of 0.8 °K over the entire temperature range from 175 to 330 °K (convenient graphs are available from the author):

$$T = 403.0 - 0.491 |\Delta\nu| - 66.2 (10^{-2}\Delta\nu)^2 \quad (1)$$

The coefficient of the quadratic term is small, and over a temperature range of 50 °K, the data can be fitted to a straight line:

$$175\text{--}225 \text{ °K: } T = 537.4 - 2.380 |\Delta\nu| \quad (2)$$

$$220\text{--}270 \text{ °K: } T = 498.4 - 2.083 |\Delta\nu| \quad (3)$$

$$265\text{--}313 \text{ °K: } T = 468.1 - 1.810 |\Delta\nu| \quad (4)$$

At the limits of these ranges, the straight line approximations still agree with Equation 1 within 0.7 °K.

Shoup (6) used a thermocouple to measure the shift of methanol from 210 to 310 °K, and her results are in excellent agreement with Equation 1.

Above 255 °K, Equation 1 is in excellent agreement with the previously reported result (2), but at 220 °K, the deviation has risen to 4 °K. The deviation results from the cooling of the sweep coil of the Varian A60 by the cold nitrogen gas, which causes the sweep width to drift (6).

If one fits a straight line to the data of Equation 1 over the entire temperature range, one obtains very nearly Varian's calibration chart (1), but the fit is not good. Varian's line intersects the curve of Equation 1 at 221 and at 312 °K. Near the extremes, at 190 and 325 °K, Varian's chart gives a temperature higher by, respectively, 5.5 and 3.2 °K, while near the center of the range, at 270 °K, it gives 3.6 °K lower. At room temperature, the slope of the Varian line for methanol is 7% lower, leading to activation energies 7% lower.

Above room temperature, ethylene glycol is frequently used to measure temperatures. We have also repeated (3) our

(1) Varian Associates, Palo Alto, Calif. 94303, Publication Number 1481.

(2) A. L. Van Geet, *ANAL. CHEM.*, **40**, 2227 (1968).

(3) A. L. Van Geet, Paper presented at the 10th Experimental NMR Conference, Mellon Institute, Pittsburgh, Pa., February 1969.

(4) A. L. Van Geet, *ANAL. CHEM.*, **40**, 1914 (1968).

(5) A. L. Van Geet, *Rev. Sci. Instrum.* **40**, 177 (1969).

(6) R. R. Shoup, National Institutes of Health, Bethesda, Md. 20014, private communication, 1968.

previous measurements (2) of its chemical shift, and obtain the same results within 0.6 °K.

#### METHOD

A spectrometer with an internal lock was used to obtain the present results. With the spectrometer locked to the CH<sub>3</sub> protons, the recorder is centered on the OH resonance, and the frequency difference  $\Delta\nu$  is read directly on a counter.

A trace (0.03% by volume) of concentrated aqueous hydrochloric acid was added to the air-saturated methanol or glycol samples (Fisher reagent grade). This caused a complete collapse of the multiplet structure, and sharp lines were obtained at all temperatures. Most likely, even smaller amounts of HCl would be adequate. The addition of HCl does not affect the chemical shift at any temperature, and the sharp lines are a great convenience. The esterification reaction of the HCl with the methanol is not noticeable over a period of half a year, and the lines remain sharp.

Oxygen or nitrogen gas was bubbled through some methanol samples. Within the accuracy of 0.5 Hz, the chemical shift is not affected, at least not at 300 °K. Also, the chemical shift of the air-free methanol and glycol standards supplied by Varian Associates is identical to our air-saturated samples at all temperatures. Moisture has a small effect.

Temperatures were measured with a static thermistor sensor (2) in a spinning sample tube. Its resistance was measured with a bridge (Electroscentific Industries 250 DE, Portland, Ore.). Using an external bridge resistor of 100  $\Omega$ , resistances up to 100 M $\Omega$  could be measured to better than 0.5%. At the

melting point of methanol (175.4 °K), the resistance was 22.4 M $\Omega$ .

The thermistor was calibrated by comparison with a vibrating quartz thermometer (Dymec 2801 A, Hewlett-Packard), and the calibration agreed with the melting point of methanol (observed 175.3 °K, lit. 175.4 °K) and with the sublimation point of carbon dioxide (obsd 194.5  $\pm$  0.2 °K, lit. 194.7 °K).

The temperature at the coil is affected only slightly by spinning, and then only at low temperature. When the spinning was stopped at 230 °K, the temperature fell only 0.4 °K. At 390 °K, no change could be observed (reproducibility 0.2 °K). The bottom of the sample tube was 10 mm below the receiver coil.

In our experience, temperature measurement with the thermistor thermometer is faster and more accurate and reliable than measurement of the methanol shift. For most purposes, it is not necessary to spin the tube. The thermistor thermometer should be inserted to the right depth, since a temperature gradient occurs (0.5 °K/cm at 233 °K). It should be remembered that the probe constitutes a heat leak. At 233 °K, the probe raises the temperature by 1.0 °K.

ANTHONY L. VAN GEET

Department of Chemistry  
Oakland University  
Rochester, Mich. 48063

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## Simultaneous Spectrophotometric Determination of Hydrogen Peroxide and Peroxyacids of Sulfur

SIR: A few years ago (1, 2) a cerimetric macro scale method was described for the simultaneous determination of hydrogen peroxide, peroxymono- and peroxydisulfuric acids. The method was based on the selective removal of peroxymonosulfate by arsenious acid. There were some attempts, too, (3, 4) to use this procedure for the estimation of minute quantities. We have to say, however, that we were not satisfied with the accuracy offered by our method in micro scale; therefore we tried to find a more appropriate way of analysis. In the following we describe a micro method successfully applied for studying the X-ray radiolysis of sulfuric acid solutions as well as that of sulfuric acid glasses (5).

The estimation of hydrogen peroxide can be carried out directly by measuring the absorbance of the peroxo-titanium(IV) complex at 410 m $\mu$ , which is not interfered by any substances present. Unfortunately, the absorbance of the peroxo complex is not high enough (the molar absorptivity is 718 l. mole<sup>-1</sup>cm<sup>-1</sup> in 0.5M sulfuric acid); consequently, only solutions having [H<sub>2</sub>O<sub>2</sub>]  $\geq$  10<sup>-5</sup>M can be determined with sufficient accuracy.

The next step of the analysis is the estimation of the sum of hydrogen peroxide and peroxymonosulfuric acid. To this end the sample is added to a mixture of arsenious acid and osmic acid catalyst and after the quantitative reduction of the peroxo titanium(IV) complex and peroxymonosulfuric acid (about 10 min) the excess of arsenic(III) is determined spectrophotometrically by cerium(IV) sulfate reagent at 320 m $\mu$ .

Finally, the total oxidizing capacity is estimated by using ferrous sulfate reagent, measuring the absorbance of ferric ions formed at 304 m $\mu$ .

#### EXPERIMENTAL

**Apparatus.** The absorbance of solutions was measured by Unicam SP 500 spectrophotometer supplied with a thermostated cell housing. The temperature was kept at 25  $\pm$  0.15 °C.

**Reagents.** Ordinary distilled water was purified by two successive redistillations. The first redistillation was from an alkaline permanganate medium, the second from a slightly acidic peroxydisulfate medium (0.05M in sulfuric acid containing 2 g of potassium peroxydisulfate per liter). Peroxydisulfate stock solution was always freshly prepared by dissolving K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> N-free Merck reagent of G.R. grade in triple-distilled water. Peroxymonosulfuric acid solution was prepared from KHSO<sub>5</sub> c.p. reagent supplied by Laporte Chemicals Ltd., by dissolving it in 0.01M sulfuric acid. Hydrogen peroxide solution was prepared from Merck Per-

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