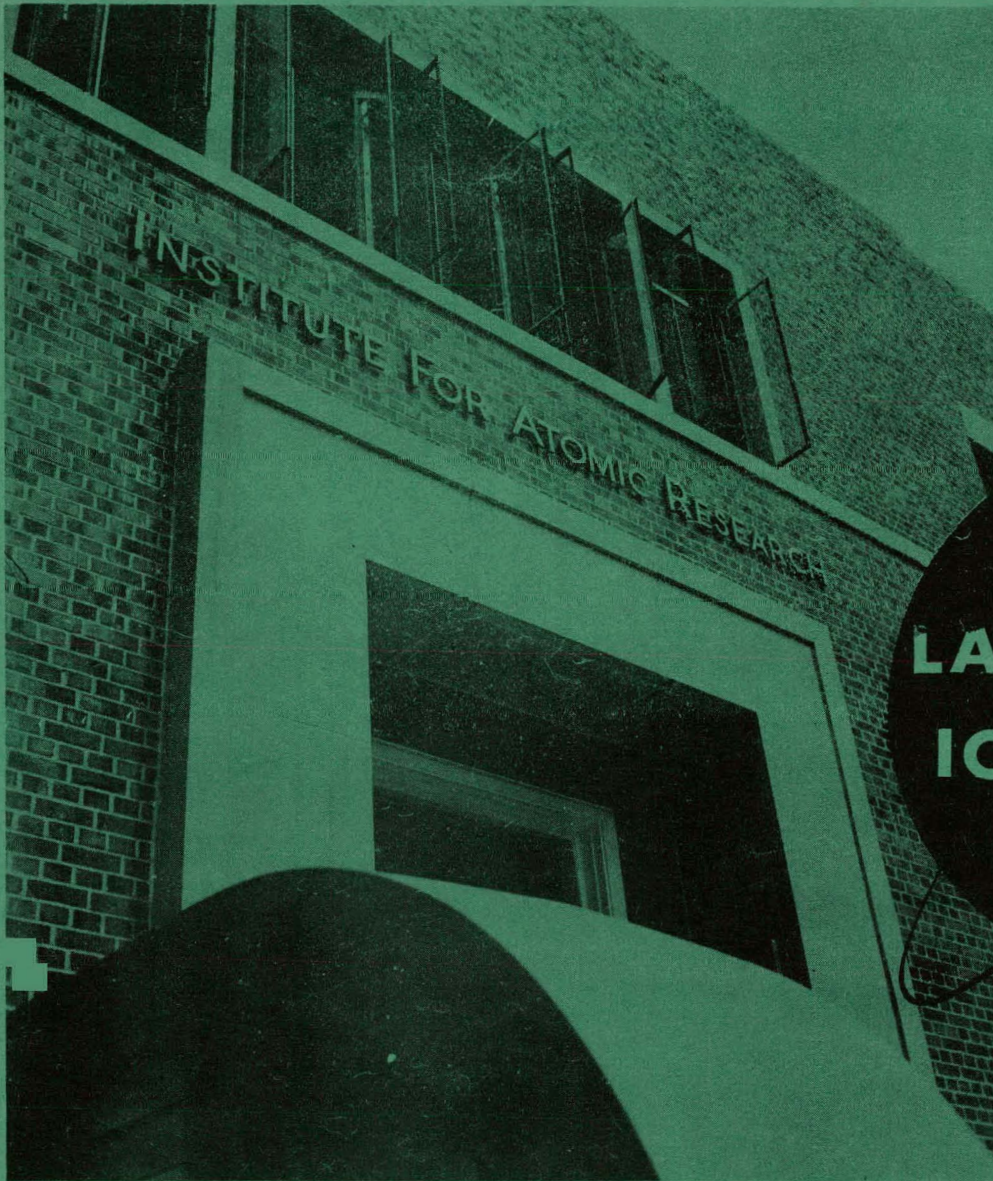


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THE USE OF THERMISTOR IN CRYOSCOPIC MEASUREMENT

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by

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The Use of Thermistors in Cryoscopic Measurements

Richard K. McMullan and John D. Corbett

Abstract

The applicability of thermistors to cryoscopic measurements has been examined. A simple Wheatstone bridge was used to measure the temperature-sensitive resistance of the thermistor. Theoretical equations directly relating thermistor resistance at the freezing point to the concentration of the solution have been developed. Data obtained in benzene or 1,4-dioxane with concentrations of phenanthrene or naphthalene up to a mole fraction of 0.008 fit the equations presented with a standard deviation corresponding to about one millidegree. Measurements in pyridine at -42° , where a Beckmann thermometer cannot be used, gave comparable results. Values calculated for the heats of fusion of the solvents employed agreed quite well with those reported in the literature. Simplified resistance-concentration equations that gave essentially the same results have also been suggested.

Results obtained simultaneously with a thermistor and a Beckmann thermometer indicated that the method gave results with about one-third the uncertainty of the usual Beckmann technique. Observations on the stability of thermistors are presented.

Introduction

Several articles in the literature have reported the application of thermistors to the measurement of temperature and small temperature differences (1-4). However, the adaptability of these semiconductors to accurate measurement of freezing point depression and concentration without the use of elaborate or expensive equipment does not seem to have been emphasized. The purpose of this article is to point out the practicability of cryoscopic measurement of concentration by means of a thermistor with an uncertainty less than that obtainable with the conventional Beckmann thermometer, and with a measuring circuit available in any undergraduate physical chemistry laboratory. In addition, at temperatures below -39° , the freezing point of mercury, the thermistor appears unexcelled for such measurements.

The usefulness of thermistors as temperature-sensing devices results from their relatively large negative temperature coefficient of resistance. This changes from 1% per degree at 300° to 4% at 25° and 6 to 8% at -50° , in contrast to about 0.35% for platinum at all temperatures. Commercial varieties composed of sintered transition metal oxides are available from 0.1×0.05 to 1.0×0.24 inches in size, and from 10 to 10^5 ohms in resistance (5). The temperature-resistance relationship of the individual element must be obtained by calibration. Although at elevated temperatures thermistors slowly increase in resistance with time, this change at room temperature and below is usually very minor, and its effect on the results can be eliminated.

APPARATUS

For the measurements described herein a simple Wheatstone bridge was used to follow the resistance of the element. The thermistor used was a Carbaloy type D-102 (5) (about \$3.00), with resistances of 1010, 2300 and 22,000 ohms at 25, 5 and -40°C , respectively. For measurements in the range of 0 to 10°C the bridge included two 1000 ohm standard resistors for the fixed arms, a Leeds and Northrup 2420-d galvanometer for the detector, and a 1.5 volt dry cell with a 500 ohm resistor in series as the current source. For the variable resistance, two decade boxes (1, 10, 100, 1000 ohm steps) were used in parallel so as to increase the sensitivity of the bridge without the use of decades with smaller resistance increments. The thermistor, connected to the bridge with #22 copper wire, was positioned in the bottom of a thin-walled glass tube projecting into the solution from above. The bottom inch of this tube was filled with petroleum ether for better thermal contact with the system. Use of water-miscible liquids here gave erratic results, apparently due to conduction between the lead wires. The thermistor could, of course, be immersed directly in the solution if it were not conducting or reactive.

Since the apparatus was to be used for the study of complexing reactions in non-aqueous solvents, the cryometric cell employed was of all-glass construction. Evacuation of the intervening space in the double wall of the cell gave much more satisfactory results. With a cooling bath five degrees below the melting point of the solvent, a constant resistance plateau was obtained for several minutes following a supercooling of a

few tenths of a degree. Balance was achieved in a closed circuit so that the effect of thermistor heating by the bridge current (about one milliwatt) would reach a steady state. The solution was stirred magnetically with a Teflon-covered stirring bar.

The reagent grade or EK White Label benzene, pyridine and 1,4-dioxane solvents used were distilled from CaH_2 or LiAlH_4 into the cell in vacuo in most experiments and the cell and solvent weighed on a solution balance. The dioxane, as obtained from Mr. Wilfred Borduin, had been treated with HCl , NaOH , refluxed over sodium metal, and fractionated in a 30 plate Oldershaw column. "Nonaq" stopcock grease (Fisher Scientific Co.) was used for ground joint lubrication in the presence of these solvents.

Over a temperature interval of several degrees, the resistance of a thermistor can be expressed quite accurately as

$$\ln r/r_0 = B(1/T - 1/T_0) \quad (1)$$

where B is a constant of the thermistor (5). At the freezing point of benzene the sensitivity of the galvanometer enabled balancing to the nearest 0.03 ohms in r , so that a temperature difference of about 3.5×10^{-4} degrees could be detected with this circuit. Use of different relative resistance settings on the parallel decades, or only a single decade, does not affect the sensitivity of the measurement provided the variable is equipped with sufficiently small resistance increments so that the full sensitivity of the galvanometer can be utilized.

CALIBRATION

As will be shown later, a differential calibration of the thermistor that may be adequate for some purposes can be obtained by comparison with a Beckmann thermometer. Direct calibration of the element could also be obtained by comparison with a standard resistance thermometer, if available. However, for molecular weight studies, the simplest and most convenient method of calibration was taken to be the direct measurement of the resistance to the thermistor at the freezing point of solutions of known concentration, using systems in which the solvent presumably behaved ideally. Phenanthrene or naphthalene (EK White Label, vacuum sublimed) were used as solutes in benzene, dioxane and pyridine, and C.P. urea or dextrose in water. Concentrations were calculated directly from the weights of the components.

For a dilute solution in which the solvent obeys Raoult's Law, the classical expression for the variation of the freezing point depression ΔT with concentration is

$$-\ln N_1 = \Delta H^\circ \Delta T / RTT_0 \quad (2)$$

where N_1 is the mole fraction solvent, and the other symbols have the usual significance. When allowance is made for the change in the heat of fusion with temperature, the expression

$$-\ln N_1 = \frac{\Delta H^\circ \Delta T}{RTT_0} - \frac{\Delta C_p \Delta T^2}{2RTT_0} - \frac{\Delta C_p \Delta T^3}{6RTT_0^2} - \dots \quad (3)$$

can be derived (6), where ΔC_p , the difference in heat capacity of the liquid and solid solvent at T_0 , is assumed constant over the temperature range involved. For this work terms higher than

T^2 in the power series are insignificant and can be dropped.

Substitution for ΔT in terms of the thermistor resistance (equation 1), with $TT_0 = T_0^2$ in the ΔC_p term, gives

$$-\log N_1 + \frac{2.303 \Delta C_p T_0^2 (\log r/r_0)^2}{2RB^2} = \frac{\Delta H^\circ (\log r/r_0)}{RB} \quad (4)$$

A test of the suitability of this equation was made employing measured values of r at the freezing points of thirteen known solutions of phenanthrene in benzene. A measured value of B , obtained as described below, and a ΔC_p of $1.82 \text{ cal. mole}^{-1}$ (7) were used in evaluation of the coefficient of the $(\log r/r_0)^2$ term (7.67×10^{-3}). In practice, an estimated B (5) would be sufficient. Within the concentration range where the solvent behaves ideally, the accuracy of the measurement varies directly with ΔT , or N_2 . Accordingly, a value of 0.3612_2 for the constant $\Delta H^\circ/RB$ was obtained from a weighted average of the ratio of the left hand side of equation 4 to $\log r/r_0$, using N_2 as the weight for each measurement. The fit of the data to the expression so obtained is shown in Table 1. The freezing point depression for the largest concentration shown would be 0.54° . The last column expresses the difference between the known and calculated values of N_2 in terms of the equivalent error in measurement of ΔT . The average and standard deviations of 0.96×10^{-3} and 1.24×10^{-3} degrees in ΔT , respectively, or a confidence range of $\pm 0.74 \times 10^{-3}$ degrees for a 95% confidence level, are indicative of both the accuracy of the measurements, and the suitability of equation 4 as a description of the relationship between resistance and concentration. The deviation obtained here are one-half to one-fourth of those reported in the

Table 1

The Suitability of the Equation $-\log N_1 + 7.67 \times 10^{-3} (\log r/r_0)^2 = 0.36122 \log r/r_0$ As A Description of the Calibration Data in Benzene

r_0 ohms	r ohms	$\log r/r_0$ $\times 10^3$	N_2 $\times 10^3$	N_2 calc. $\times 10^3$	ΔN_2 $\times 10^5$	$\Delta(\Delta T)$ $\times 10^3$
2299.09	2305.39	1.1883	1.024	0.988	+3.6	+2.39
	2311.52	2.3415	1.950	1.946	+0.4	+0.32
	2317.24	3.4148	2.823	2.836	-1.3	-0.85
	2321.86	4.2801	3.554	3.553	+0.1	+0.08
	2327.18	5.2740	4.386	4.377	+0.9	+0.62
	2334.02	6.5486	5.435	5.431	+0.4	+0.23
	2348.63	9.2588	7.689	7.670	+1.9	+1.28
2288.92	2296.45	1.4265	1.194	1.186	+0.8	+0.51
	2303.81	2.8160	2.324	2.339	-1.5	-0.97
	2314.16	4.7628	3.920	3.953	-3.3	-2.22
	2321.80	6.1942	5.114	5.138	-2.4	-1.57
	2332.06	8.1090	6.710	6.721	-1.1	-0.71
	2341.75	9.9100	8.219	8.207	+1.2	+0.78
					1.5	0.96
					1.24	St'd dev.

literature for other similar measurements with thermistors (1,2).

The source of the apparently systematic trend in the deviations shown in Table 1 is not completely understood. Non-ideal behavior of the solvent would be expected to have an opposite effect. Possibly either small weighing errors, uncompensated lead resistances, or the need for additional small terms in the description of the resistance of the thermistor by equation 1 (8) are responsible. Since these deviations show a regular trend, they could be reduced by curve fitting, although the desirability of having a theoretical expression to express the relationship may be considered more important.

A value of 2345 calories for the molar heat of fusion of benzene was calculated from the constant $\Delta H^\circ/RB$ obtained in the calibration, and a measured value of B. This compared to 2351 cal. mole⁻¹ reported from calorimetric measurements (7). A heat of fusion of 2344 cal. mole⁻¹ was obtained from the same data without the use of the ΔC_p term, and the data fit the resulting equation with the same accuracy.

The thermistor so calibrated was also used to determine the molecular weights of a number of substances in benzene. For example, from measurements on ten concentrations of naphthalene in benzene, an average molecular weight of 128.08 ± 0.66 average deviation (0.87 st'd. deviation) was calculated, as compared to 128.16 for the accepted value. From the change in resistance observed when benzene was saturated with SbI_3 , the solubility at 5.5° was calculated to be 6.00 ± 0.06 grams per 1000 grams of solvent.

ALTERNATE EXPRESSIONS

The use of equation 4 for the calibration and subsequent evaluation of molecular weights may for many purposes be found to be somewhat lengthy, since evaluation of $\log N_1$ and antilog N_1 for N_1 close to unity requires use of the first two or three terms of the equivalent power series expansion. A more facile expression can be derived from equation 4 with only minor approximations. Taking $-\ln N_1 = mM_1/1000$, where m is the molality and M_1 , the molecular weight of the solvent, and noting that r/r_0 is equal to $1 + \Delta r/r_0$, expansion of $\ln(1 + \Delta r/r_0)$ in a power series gives

$$m = \frac{1000 \Delta H^\circ}{RBM_1} \left[\frac{\Delta r}{r_0} - \frac{1}{2} \left(1 + \frac{\Delta C_p T_0^2}{B \Delta H^\circ} \right) \left(\frac{\Delta r}{r_0} \right)^2 \right]. \quad (5)$$

A calibration can then be obtained by fitting the data to this quadratic in $\Delta r/r_0$. Actually the ΔC_p term for benzene is so small that it can be dropped, giving the simple expression

$$m = \frac{1000 \Delta H^\circ}{RBM_1} \left[\frac{\Delta r}{r_0} - \frac{1}{2} \left(\frac{\Delta r}{r_0} \right)^2 \right]. \quad (6)$$

Fitting the same benzene calibration data to this one-constant equation gave average and standard deviations of 1.11×10^{-3} and 1.43×10^{-3} degrees in ΔT and a ΔH° of $2349 \text{ cal. mole}^{-1}$, values not significantly different from those obtained with equation 4. Equation 6 is the resistance-concentration relation that has been found most convenient for subsequent applications of the thermistor in this laboratory.

If the coefficients of the first and second powers of $\Delta r/r_0$ are allowed to vary independently, the error in the approximation of molality for $\log N_1$, as well as any systematic errors, can be partially eliminated. A general quadratic in $\Delta r/r_0$ was fit to the same data with average and standard deviations in ΔT of 0.83×10^{-3} and 0.95×10^{-3} degrees, respectively.

Actually for student use a large graph of $\Delta r/r_0$ vs. m or N_2 is probably the most convenient procedure as the result is very nearly linear. Slightly better results can be obtained if a curve for the deviations of the data from the straight line $m = a(\Delta r/r_0)$ is obtained analytically, and this applied to the concentrations calculated from the linear relationship.

OTHER SOLVENTS

Cryoscopic measurements in dioxane and in water utilizing the thermistor gave similar results. In dioxane, five concentrations of naphthalene up to $N_2 = 0.009$ fit equation 4 with an average deviation in ΔT of 0.82×10^{-3} degrees, using a ΔC_p of 1 cal. mole⁻¹ (9). An estimated B gave 3021 cal. mole⁻¹ for the heat of fusion, as compared to 3070 and 3017 cal. mole⁻¹ reported in the literature (9,10). The heat of fusion of water similarly obtained differed from the accepted value by 3 calories.

Since measurements in low melting solvents with Beckmann thermometers are limited by the freezing point of mercury (-39°), the thermistor appears particularly useful for investigations at lower temperatures. To confirm this, the element was calibrated in pyridine at -42°, using naphthalene as the solute. Since r_0

at this temperature was 22,250 ohms, the bridge was modified by substitution of higher resistance components in the fixed arms and a single decade for the variable resistance. The considerable supercooling observed with a -80° cooling bath was overcome by starting the freezing process with a few crystals of the solvent already present. Under these conditions, the resistance of the thermistor was reproducible to one to two ohms, the larger value corresponding to 1.6×10^{-3} degrees. With $\Delta C_p = 0$, the three concentrations used fit equation 4 with an average deviation of 2.8×10^{-3} degrees in ΔT for N_2 up to 0.0063. A heat of fusion for pyridine of 1880 ± 8 cal. mole $^{-1}$ was calculated from the slope and an estimated B. A literature value for this constant was not found.

DETERMINATION OF B AND COMPARATIVE BECKMANN MEASUREMENTS

In order to obtain the values of B employed in the above heat of fusion calculations, as well as to estimate the comparative accuracy of Beckmann thermometer readings in cryoscopic measurements, several series of experiments were made in which both a Beckmann thermometer and a thermistor were used. The thermometer readings were corrected for emergent stem, and for the setting factor. The latter allowed for the difference in the mass of mercury in the bulb at temperatures other than that at which it was calibrated, usually 20° (11). In three separate runs, seventeen solutions of phenanthrene in benzene gave a weighted average B of 3.267×10^3 degrees (equation 1). Similarly, eleven solutions of urea in water gave a B of 3.233×10^3 degrees. From these values, it can be seen that, although the "constant" B for the thermistor does change slightly with temperature, the change

would result in an error of only 0.2×10^{-3} degrees for a 0.5 degree interval. The values of B used in the ΔH° calculations with dioxane and pyridine were estimated from the rate of change observed with benzene and water, together with data provided by the manufacturer (5), and are probably accurate to 0.5%.

The differences between the observed and calculated values of ΔT (equation 1) are shown in Figure 1 for both solvents. The average and standard deviations in ΔT for benzene are 2.6×10^{-3} and 3.4×10^{-3} degrees, and for water, 2.7×10^{-3} and 3.5×10^{-3} degrees, respectively. It will be noted that the deviations found here are about three times as large as those found for a similar temperature interval in the resistance calibration with equation 4 (Table 1). Moreover, all systems studied with the thermistor showed about the same trend in the deviations, whereas with the Beckmann these show quite different behaviors in the solvents water and benzene. Accordingly, the deviations shown in Figure 1 are interpreted to be essentially a calibration curve for the Beckmann in the (different) scale ranges employed, with a scatter indicative of the reproducibility of such a measurement, and with the smaller trend observed in the use of equation 4 superimposed. The effect of the deviations from the resistance-concentration expression found for benzene is to reduce the largest differences shown and to increase slightly those in the intermediate range; the over-all average is not affected significantly. Since all the benzene solutions used were of known concentration, comparison of the observed depressions with those calculated from concentration (equation 2) confirms the effect of the thermistor deviations.

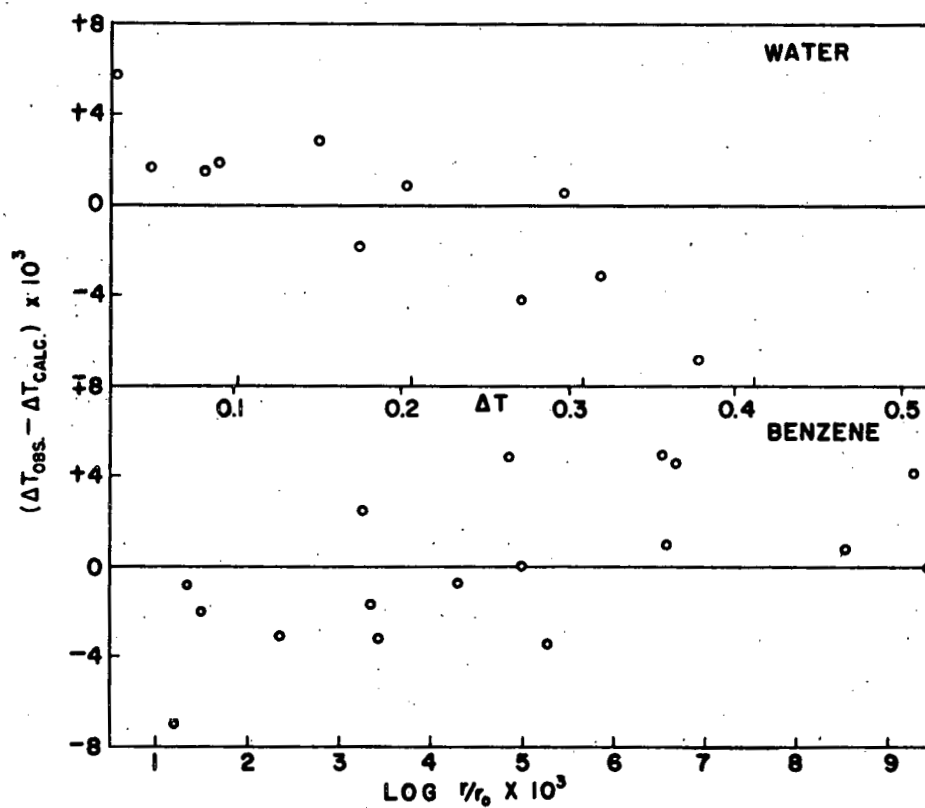


FIGURE 1: DEVIATIONS OF TEMPERATURE DIFFERENCES OBSERVED WITH A BECKMAN THERMOMETER FROM THOSE CALCULATED FROM $\Delta T = \frac{2.211}{5} \text{ LOG } \frac{\%}{100}$

THERMISTOR STABILITY

One difficulty often mentioned in the application of thermistors to temperature measurement is that they tend to undergo slow changes in resistance over a period of time (5), and at a rate that varies with the individual element. However, for the type of work described herein, this factor has been substantially eliminated by the use of expressions relating the temperature change to the ratio of the resistance r at the freezing point of a given solution to the resistance r_0 for the pure solvent at the start of the measurement. This then requires only that the thermistor resistance not change during the run, a condition which from experience has been found to be quite practical. The two series of measurements shown in Table 1 were purposely chosen to test this concept. The runs were carried out seven weeks apart, during which time, as a result of various treatments, r_0 had changed by several tenths of a per cent. Moreover, the first group was obtained with undried benzene at one atmosphere pressure (not the usual procedure), while the second set under the vapor pressure of the solution used dry vacuum-distilled benzene. Although in the former the 0.003° depression of the freezing point reported for one atmosphere of air (12) affected r_0 only slightly, an unknown but apparently small concentration of water condensed from the air also served to increase r_0 . Much smaller differences were found between separate sets of data obtained under similar conditions only a few days apart.

When the resistance of a thermistor is first measured at a new and somewhat different temperature, a slow drift is sometimes

noted. However, if the element is allowed to age at that temperature for a short time, the values become quite constant. Thermal shock, such as cooling to -190° , will change the resistance observed at a reference temperature, although again, after a few hours, the element will settle down to a constant value. Cooling to -80°C was observed to have little effect on the resistance at 0° . Johnson and Kraus (3) observed that, over a period of 15 days, the variations in the apparent temperature of the ice point as measured with a thermistor showed a standard deviation of only 1.1×10^{-3} degrees.

CONCLUSION

The application of thermistors to cryoscopy, or what is actually cryometry, using a simple expression directly relating concentration and thermistor resistance, has been shown to give better results than those obtained by the usual Beckmann technique. In addition, once the element has been calibrated, the ease of the measurements is somewhat greater. The method has been used for the determination of the molecular weights of gallium(II) halides in anhydrous solvents, and to determine the stoichiometry of various acid-base and disproportionation reactions of these compounds. The results of this work will be reported elsewhere.

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