THE STEADY-STATE TEMPERATURE-DIFFERENCE

METHOD OF COMPARING VAPOR PRESSURES

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ii

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

INTRODUCTION

The steady-state temperature-difference method for measuring partial pressures was investigated as one phase of a U. S. Air Force-sponsored project at Oklahoma State University entitled, "Investigations of the Thermodynamic Properties of Inorganic Salts in Nonaqueous Salt Mixtures." The aim of the research described herein was to investigate the applicability of this less conventional method for measuring vapor pressures, and hence the solvent activity, in nonaqueous binary solutions involving one non-volatile component. From data so obtained it is then possible to calculate the solute activity.

The steady-state temperature-difference method is in essence one of wet-bulb thermometry. This method involves measuring the cooling effect produced by the evaporation of solvent in an atmosphere of a solution whose vapor pressure is to be determined. This temperature lowering continues until a non-equilibrium steady-state value is reached, and at this temperature the vapor pressure of the solvent may be approximately equal to that of the solution, which is maintained at a fixed temperature. A matched thermistor pair is employed as the temperature sensing element, and these thermistors form two arms of a Wheatstone bridge. One thermistor

contains a drop of the solvent, and will give a measure of the temperature change, while the other thermistor acts as a reference resistor. The steady-state temperature is the lowest temperature obtained in any measurement, and in this state the heat loss due to evaporation is equally balanced by the heat gains due to conduction, convection, and radiation from the surroundings. There results a constant resistance difference corresponding to the steady-state temperature.

Thermistors, or thermal resistors, are semiconductors, and as such possess high negative temperature coefficients of resistance. They are manufactured in various shapes, and those used in this research were all of the glass-coated bead type.

The results and reproducibility of the method are dependent on the thermistor cell design, hence calibration of the apparatus is necessary using solutions of known vapor pressures.

HISTORICAL

Semi-Conductor Background

The peculiar negative temperature coefficient of re-
sistance property of semi-conductors was first noticed by
Faraday in 1834. Because this property is so sensitive to
the composition, use, and treatment of the semi-conductors,
semi-conductors were used very little until comparatively
recently. Much research has been done in an effort to learn
how to control the peculiar properties of semi-conductors and
how to prepare them with reproducible properties (5). In the
1930's Bell Telephone Laboratories found an important use
for semi-conductors and in 1940 went into large scale pro-
duction of them (9). The uses and characteristics of therm-
istors (temperature sensitive semi-conductors) have been
discussed in a number of general articles, those by Bell
Telephone scientists being among the earlier works (6,10,
31, 37-39).

Applications of Thermistors as Temperature Sensing Devices

The literature dealing with the applications of therm-
istors as temperature sensing devices is by now rather ex-
tensive. The following references were chosen to provide the
reader with an idea of the comparative advantages of therm-
istors over mercury thermometers and thermocouples as well as
to familiarize him with pertinent applications.

3

Hutchinson (13) in a comparatively early chemical application used a thermistor to measure heats of wetting and adsorption. A change in temperature of 0.001°C was readily measured with considerably greater accuracy than could be obtained with a Beckmann thermometer. The thermistor also was found to have the advantage of a fast response and a much smaller thermal capacity by contrast with the Beckmann thermometer.

Greenhill and Whitehead (11) have developed an automatically balancing thermistor Wheatstone bridge which was capable of measuring temperatures of the order of 0.01°C with an accuracy of 0.0002°C. One thermistor served as an arm of the bridge which was automatically balanced by feeding back an alternating current proportional to the off-balance current to heat a second thermistor in the opposite arm of the bridge. The apparatus was used to measure heats of wetting and adsorption when fine-grained powders were immersed in various liquids and solutions.

Jehn (22) measured wet-bulb temperatures by dipping an electrically insulated bead-type thermistor into distilled water and exposing it to an airstream. A wick-covered rod-type thermistor had been used previously but was found to have certain disadvantages. Factors such as air-flow rate, optimum time of exposure, and lag coefficient were investigated, along with the degree of accuracy by comparison with

a standard psychrometer. The lag coefficient of a bead therm-
istor was found to be 10-15 times smaller than that of a
mercurial psychrometer.

A comparison of thermistors and thermocouples for temper-
ature measurement was made by Benedict (7). He stated that
although both are suitable for measuring temperatures to $\pm$
0.2°F, much greater care is necessary with the thermocouple
system. Both the thermistor and thermocouple are subject to
aging, but the thermistor stabilizes with age while the thermo-
couple becomes less stable. At temperatures below 580°F therm-
istors are superior to thermocouples for precise measurements,
but above this temperature thermistors deteriorate rapidly.
The thermistor, he found, is inherently more sensitive, has a
more rapid response to temperature changes, and is more de-
pendable than many other temperature measuring systems. The
thermocouples used in this comparison were iron-constantan,
and the thermistors used were Type 51A1 (10^5 ohms at 25°C)
obtained from the Victory Engineering Corporation.

Beck (4), in an article on the stability of thermistors,
stated that it is possible for thermistors to undergo sudden
changes which take place in a rather arbitrary manner. Ac-
cording to Beck, thermistors should not be subjected to
temperatures outside the range of temperature to be measured,
and he believed that it would be unwise to use two or more
thermistors to measure differences in temperature unless care-
ful calibrations of the thermistors were performed before and

after the experiment. He set the temperature accuracy at 0.02°C over a range of about 10°C under controlled conditions.

Müller (29) in discussing Beck's work on thermistor stability, stated that Beck did not say whether or not the thermistors he used were continuously excited, a point which Müller thinks is of great importance. Müller stated that work done by himself and Stolten (30) showed considerably greater reliability for thermistors than that of the workers cited by Beck. Müller and Stolten claimed short-term stability (30 minutes) of 0.0001°C and a reproducibility to within 0.02°C over a six month period. The sudden changes in characteristics observed by Beck were not observed by Müller and Stolten.

The Thermoelectric Method and the Measurement of Vapor Pressures

In the thermoelectric method for measuring vapor pressures a drop of solution is exposed to an atmosphere of solvent vapor in which the partial pressure is either greater or smaller than the vapor pressure of the solvent in the drop of solution. In all of the applications of the method described in the literature the partial pressure of solvent vapor in the atmosphere was kept greater than the vapor pressure of the solution studied. In such cases condensation on the drop occurs with the result that the heat of condensation raises the temperature of the drop until its vapor pressure at the higher temperature approaches the partial pressure of the solvent vapor in the surroundings. Because of heat

flow from the drop to the surroundings which are kept at a lower temperature, the vapor pressure of the drop never reaches that of the solvent vapor in the atmosphere surrounding the drop, but a state of approximately constant temperature of the drop is reached. This steady-state temperature can be made a function only of the relative difference in the vapor pressure of the solution drop and the partial pressure of the solvent vapor in the surroundings. Usually the atmosphere is saturated with solvent vapor at a carefully controlled temperature, and temperature difference between a drop of solution and another drop of solvent used as a reference is measured. Various experimental procedures have been used in an effort to achieve the best results with the method. These are reviewed in this section.

Hill (12) probably devised the first extremely sensitive thermal method for measuring vapor pressures of very dilute aqueous solutions. His method was a differential one in which a 71 junction thermopile was used. Two strips of filter paper, one moistened with solvent, and the other with a solution of unknown vapor pressure, were laid on each side of the thermopile, which was placed in a chamber whose walls were kept moist with a reference solution. The e.m.f. developed in the thermopile due to the temperature difference, which in turn was related to the vapor pressure difference, was measured. The apparatus was calibrated with solutions of known vapor pressure. The method is thus based on the principles of wet-bulb thermometry.

Baldes (1) pointed out that Hill's thermopile was inefficient (only about 6% efficiency was obtained) mainly because of heat losses due to the high thermal conductivity of the wire which Hill used in making the thermopile. Baldes described a differential thermocouple unit with insulated thermojunctions. He used manganin and constantan wires of 0.1 mm. diameter instead of the silver-plated constantan wire employed by Hill. By means of a micropipet his solution could be applied in the form of droplets directly to loops made in the wire at the thermojunctions.

Later Baldes (2) analyzed the thermoelectric method and derived a mathematical expression for the theoretical steady-state temperature difference. To simplify the mathematics he assumed two concentric spherical shells, the inner wall of the outer shell being moistened with solvent, and the outer wall of the inner shell being moistened with a solution. From Stefan's general theory of diffusion, taking into consideration heat transfer by conduction through the gas phase only, and by assuming the simple case of the pressure difference between an aqueous solution and water, Baldes derived the following expression for the temperature difference in the steady-state:

$$(T - T_o) = \frac{\alpha}{\beta + RT_o k/LDp_o} \tag{1}$$

where: $(T - T_o)$ = difference in temperature between the inner shell (T) and the outer shell (T_o).

α = coefficient of depression of the vapor pressure
of the solution.

β = the temperature coefficient of vapor pressure
of water.

D = the coefficient of diffusion of water vapor in air.

k = the thermal conductivity of air.

p_0 = the vapor pressure of solvent (water) at
temperature T_0.

On the basis of Baldes' theory if there are two spherical shells
(corresponding to the two thermojunctions), each moistened with
a solution of a different concentration, with the outer shell
temperature being held constant, the temperature difference be-
tween the inner shells will be determined by the above equation.
A simpler case arises when one of the inner shells (one thermo-
junction) contains the same solution as the outer shell (cell
wall). Baldes showed that when a solution containing one gram
of sodium chloride in 100 grams of water was placed on one ther-
mojunction with water on the other in a cell whose walls were
also wet with water, a temperature difference of 0.065°C was
measured. Using the above equation the temperature difference
was calculated to be 0.067°C for an efficiency of greater than
95%.

Baldes and Johnson (3) perfected a vapor pressure thermo-
couple which they called a thermoelectric osmometer. Like the
thermocouple discussed earlier by Baldes (1) this osmometer had
thermojunctions in the form of loops on which droplets of solution

were placed, and they completely eliminated the use of the
filter paper strips that were used by Hill (12). In the
construction of the thermoelectric osmometer it was found
to be of great importance to be able to reduce heat losses
by conduction to a minimum.

Roepke and Baldes (33) in a critical study of the thermo-
electric method state that since Hill's method is a dynamic
one, an error is introduced by having a solution on the wall
of the cell with a vapor pressure either higher or lower than
that of the reference solution which is on the thermocouple.
Other sources of error arising from the dynamic nature of
the method are: surface films, differences in diffusion rates
of water in the sample and in the reference solution, greater
non-solvent volume in sample (e.g., blood) compared with
reference solution, and differences in the shapes of drops.
Another important point in consideration of the method is the
difference in the heat of condensation of solvent in the
sample and reference solution. This is especially important in
concentrated solutions where the heat of solution of solvent is
appreciable. Without specifying conditions or specific systems
the authors then state that other conditions being equal, the
greater the heat of condensation, the greater the deflection
obtained on the galvanometer (see Page 72). The authors in-
vestigated the errors inherent in the dynamic method by com-
paring the pressure of a blood sample against that of a

reference solution, first under nearly static conditions (using an isosmotic reference solution on one junction and also on the cell walls), and then under dynamic conditions. By such a procedure it is possible to determine the errors and correct for them.

Roepke and Mason (34), using the Baldes modified thermoelectric method, measured the vapor pressures of bile salt solutions and compared them with sodium chloride reference solutions. Osmotic coefficients of the bile salts were calculated.

Later Roepke (32) in a discussion of the thermoelectric method pointed out that the vapor pressure lowering vs. solute concentration curve for the reference solute should be linear in the region used. It is more important that the relation between the galvanometer deflection and the vapor pressure be linear, since the vapor pressure of a solution is determined by the author from a single cali-bration measurement made by comparing a solution of known vapor pressure with water, with water on the walls and floor of the chamber. Because of the sensitivity of the method, pressure differences of the order of 0.001 mm. could be detected. Roepke stated that although an increase in drop size does increase the rate of evaporation, as shown by Stefan's general theory of diffusion used by Baldes (2), it also increases the heat transfer rate due to conduction, convection, and radiation. These factors

are also dependent on drop size. The resulting effect on the
temperature is not significant, and this was demonstrated by
comparing small drops of water with large ones on the thermo-
couple using a sodium chloride solution on the walls of the
container. The work of Baldes and Johnson (3) also indicated
that an increase in drop size had no appreciable effect on
their measured results.

The measured temperature difference was found to increase
with a decrease in atmospheric pressure because decreasing pres-
sure causes a decrease in the thermal conductivity of the gas
phase and an increase in the coefficient of diffusion of water
vapor through air. The effect of these changes on the temper-
ature difference is readily seen on examining equation (1).

Kinsey (23), also employing thermocouples, modified and
improved the method described by Baldes for determining osmotic
pressures. The sensitive galvanometer normally used in this
type of measurement was eliminated by using a breaker-type
d.c.-a.c. amplifier. Kinsey also found that bath temperature
control to 0.001°C was unnecessary as long as the bath was
vigorously stirred. He also eliminated the double-pole re-
versing switch normally used which ordinarily produces high
contact potentials and substituted one which consisted of
copper blocks. This was believed to minimize contact poten-
tials.

Taylor and Hall (40) employing a single thermocouple
in a glass cell measured molecular weights in organic solvents.

Drops of solution were placed in tiny platinum cups welded on the thermojunctions. They stated that the experimentally-measured constants were lower than those calculated from theory because they are based on the assumption that in the steady-state the vapor pressures of the drops on the junctions are equal to the partial pressure of the solvent in the surrounding atmosphere.

Brady, Huff, and McBain (8) employed the thermoelectric method and a matched thermistor pair with an a.c. bridge to obtain a correlation between thermistor resistance change, arising from the steady-state difference in temperature of drops of solution and solvent in an atmosphere saturated with solvent vapor, and the solute concentration. From the experimental data the solute activities of colloidal electrolyte solutions in water were obtained. Drops of solvent and solution were applied in a special manipulation chamber and the thermistor pair was then lowered into the measuring chamber. Humidity in both chambers was maintained constant by wet blotting paper. When the steady-state resistance ΔR was plotted against osmotic concentration (the product of the molality and the osmotic coefficient) a single straight line was obtained for the two types of electrolyte solutions used. Observed thermal efficiencies were compared to theoretical values calculated from both humidity and evaporation theories.

Müller and Stolten (30) also used a thermistor pair to measure differences in temperature between solvent and solution

in an atmosphere saturated with solvent vapor. Instead of placing drops on the thermistor tips, they mounted the thermistor pair in small stainless steel cups containing mercury. The thermistor pair was placed in a glass chamber and the cups were kept in contact with a mercury pool to insure initial temperature equality. Small measured (0.15 ml.) samples of solvent and solution were placed in the cups, and the contact with the mercury was broken. The steady-state temperature was then measured. Thirty minutes were required to reach the steady-state temperature at the highest concentration. A correlation between resistance change and mole fraction of the solute, and hence the molecular weight, was derived. From the steady-state resistance difference the molecular weights of several organic compounds were determined in four solvents. Although the sensitivity of the method was greatly reduced because of the high thermal capacity of the mercury and the metal cups, the reproducibility of the method was good. Müller and Stolten found from the resistance-time studies that the thermistors exhibited long-range stability. They also stressed continued electrical excitation of the thermistors.

McGee and Iyengar (27) constructed a simple thermostat and thermistor bridge to measure small vapor pressure differences by the steady-state method. Their thermostat consisted of three concentric beakers, the innermost one housing the thermistor pair mounted in a cork top and containing 10-15 ml. of solvent. Solutions were placed on the thermistor tips by

means of a hypodermic syringe and needle through a hole in the cork top. The outer two beakers contained a thermometer, thermoregulator, and heater. The change in resistance of the thermistors was measured by means of an a.c. bridge using a frequency of 1000 c.p.s. Measurements were made with a drop of solution on one thermistor and a drop of solvent on the other. The initial resistance differential was obtained with solvent drops on both thermistors, a procedure which Brady, et al., (8) had also used.

In terms of the osmotic coefficient g and assuming the laws of dilute solutions, Iyengar showed that ΔR, the resistance change, was given by

$$\Delta R = KVgm \tag{2}$$

where K is a constant determined by calibration using solutions whose osmotic coefficients are known, V is the total number of moles of ions in one mole of the electrolyte, and m is the molality of the solution. Because of approximations made in its derivation, the above equation could be expected to hold only for dilute solutions and small ranges in temperature.

Using the apparatus described above (27), Iyengar and Kulkarni (21) determined osmotic coefficients of dilute aqueous solutions of soaps, certain dibasic acids, and aerosol M.A., calculating the values from the above equation after measuring the steady-state resistance differentials.

Iyengar (19) has also considered the problem of calculating the theoretical steady-state temperature difference, θ,

between a drop of a unit molal ideal solution and a drop of solvent in an atmosphere saturated with solvent vapor. He called attention to certain errors in a similar treatment given by Brady, et al (8). Based on Langmuir's theory of evaporation of droplets (25) he derived the following expression from which δ can be calculated from physical data*:

$$\delta = \Delta t/m = \frac{10^{-3}}{(L/RT^2 + k'RTx10^5/M^2p'DLx3.189)} \qquad (3)$$

where: k' = the thermal conductivity of the air.

D = diffusion coefficient of vapor in air.

L = latent heat of vaporization of the solvent.

p' = vapor pressure of the solvent at the steady-state temperature of the solution drop.

From thermodynamic considerations, δ_t, the maximum temperature difference attainable is given by:

$$\delta_t = \Delta t/m = \frac{RT^2}{10^3L} \qquad (4)$$

Calculations of the δ/δ_t ratio were made for a number of organic solvents by Iyengar, using the experimental data of Taylor and Hall (40), and for water at several temperatures. Similar ratios were calculated from an equation derived from humidity theory and from the experimental results of Brady,

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*This equation in a form applicable to the experimental measurements of this investigation can be found in a later section.

et al (8). Iyengar found errors in the ratios tabulated by Brady and coworkers and stated that their conclusion that heat exchange was almost entirely through the vapor phase was not justified.

After inclusion of a conduction correction to take into account the heat losses along the thermistor leads, the resulting equation based upon the theory of evaporation of droplets predicts that the steady-state temperature difference should be dependent on drop size. This theory, however, fails to agree with experiment, which shows that the temperature difference is independent of drop size as indicated by Baldes and Johnson (3). Iyengar further pointed out that as the solvent vapor pressure increases and approaches atmospheric pressure, the δ/δ_t ratio approaches unity, as calculated from the humidity theory.

In a later work Iyengar (20) stated that the agreement of the humidity theory and the theory of evaporation of droplets, which had been shown earlier (19) to give similar values of δ for water, was a numerical coincidence and proved that these two theories do not agree unless there is negligible convection.

Using a new thermistor cell and a precision thermistor bridge, Iyengar (18) measured the molal steady-state temperature difference, δ, for a number of solvents, and also determined molecular weights of solutes in these solvents. His new cell was designed so that the entire stem of the matched thermistor pair, mounted vertically in a wooden lid, remained below the liquid level of the thermostat at all times. One

lead wire from each thermistor was soldered together to form a common lead at the cell top. A 30 ml. sample of solvent was placed in the cell. Moistened absorbent paper helped to saturate the cell with solvent vapor. Drops of solvent and solution were applied to the thermistor tips, which could be viewed through a window cut in the absorbent paper. The steady state was reported to be reached within a minute or two after the drops were applied.

Iyengar has compared the experimental δ values with those calculated from the various equations for the maximum temperature difference, from humidity theory, and from evaporation theory. He draws from his own work as well as from that of two other groups of workers (30, 40). The δ values are tabulated for 13 organic solvents and for water along with the calculated values using each of the above methods wherever sufficient data were available. A comparison of the thermal efficiencies of the methods used by various investigators is also given.

EXPERIMENTAL

After a brief explanation of the purification of materials, discussion of the two major parts of the experimental work follows. One part of this discussion pertains to vapor pressure measurements on solutions used in the thermistor cell calibration and the other part pertains to an investigation of the steady-state method in general and the development of a technique and thermistor-cell design suitable for measuring partial pressures.

Materials

The di-n-butyl phthalate used was obtained from the Matheson Company and no further purification was made prior to the vapor pressure measurements. For some experiments, however, the phthalate was distilled under reduced pressure.

The diethyl ether used in the beginning of the work was anhydrous reagent grade ether, obtained from Mallinckrodt. It was stored over sodium and distilled when necessary. Later in the investigation a less highly refined grade of ether was used. This was distilled using a Steadman stainless steel-plate column and stored over sodium.

All other chemicals were of C. P. grade and were used without further purification.

Vapor Pressure Measurements

The steady-state temperature-difference method of measuring partial pressures is not an absolute method. It does not directly measure the vapor pressure of solutions, but does measure a property which is directly proportional to the vapor pressure; that is, the cooling effect produced by the evaporation of solvent into the atmosphere above a solution containing that solvent.

It was learned after searching the literature that vapor pressure data on binary systems involving organic solvents at a single temperature were extremely scarce. One system, KI in methanol (41), was given some early consideration, but the work had been carried out at 15°C and it was desired to work at 25°C if possible. Later it was decided to investigate the $MgBr_2$-diethyl ether system (35) on which there was found some limited vapor pressure data at 25°C in the literature. This system proved very difficult to work with, as $MgBr_2$ is very hygroscopic and had to be prepared directly in ether. After failure to prepare the salt in ether from metallic Mg and liquid Br_2, it was learned (36) that a displacement reaction using $HgBr_2$ and Mg in ether may be used. This reaction was found to work very well, but other serious difficulties were encountered with the system such as the formation of conjugate layer solutions upon dilution. At higher concentrations the solutions were even metastable, resulting in

large and unpredictable changes in the vapor pressure. For these reasons it was decided to abandon further work with this system for the purpose of obtaining vapor pressure calibration data.

Owing to the lack of suitable vapor pressure data in the literature it became necessary to measure the vapor pressures of a selected binary system over a wide range of concentrations. Since one of the aims of the project was to investigate systems of inorganic salts in organic solvents, it was decided to use diethyl ether as the organic liquid because of its ability to dissolve certain inorganic salts of interest. The binary system chosen was di-n-butyl phthalate in diethyl ether. Di-n-butyl phthalate is infinitely soluble in ether, and was found very suitable as a solute because of its nonvolatility.

The vapor pressure measurements were made employing the static method. A differential manometer was constructed of large (16 mm.) diameter pyrex-glass tubing. This tended to flatten the mercury meniscus and hence make readings easier and more accurate. The manometer is shown in Fig. 1. The columns of the manometer were joined together by means of a stopcock so that evacuation of the entire system could be carried out by means of a second stopcock placed on one side of the manometer. Ground-glass female joints (₮ 19/38) were sealed to the ends of the manometer at a slight angle to the parallel manometer tubes. The solvent and solution containers
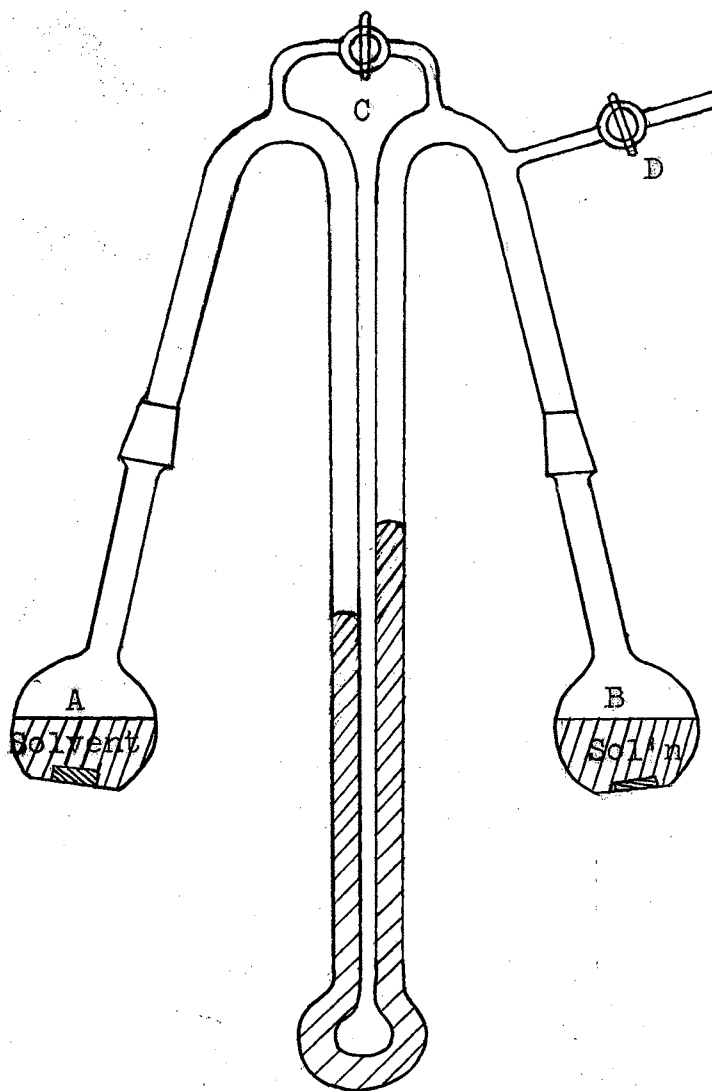
Figure 1. Differential Vapor Pressure Manometer

were made of 125 ml. Florence flasks fitted with male $\mathbb{F}$ 19/38 joints. Contamination of the solution and solvent was reduced by putting the male part of the joint on the flasks. A special ether-insoluble grease was made from glycerin, mannitol and dextrin (28) and was used on all joints and stopcocks which were in contact with ether vapor. The apparatus was fastened to a large ring-stand which could be conveniently moved in and out of a 24 inch-high cylindrical water bath. This bath contained copper cooling coils and its temperature was controlled by a mercury thermoregulator which rested on the bottom of the water bath and extended above the surface of the water. This thermoregulator was connected to an electronic relay. Efficient stirring of the bath was accomplished by means of a Little Giant No. 2 immersion pump. Temperature variations in the bath were read on a Beckmann thermometer. The control was $\pm$ 0.005°C.

Stirring of the solution and solvent in the flasks was accomplished magnetically. The driver magnet was attached to a flexible shaft enclosed in a U-shaped piece of copper tubing to hold it rigid. The magnet was sealed in a large brass tube, the ends of which were made watertight by soldered copper discs. Another portion of flexible cable was attached above the copper-tube housing so that the assembly could be rotated when connected to a conventional stirring motor. Glass-sealed bar magnets were placed in each of the

flasks and driven from beneath by immersing the driver-magnet assembly in the bath under the flasks. This permitted very efficient stirring of the liquids during the measurements and helped to bring them to bath temperature rapidly.

A vapor pressure measurement was carried out by placing 60-70 ml. of anhydrous ether in the flask (A) on the left side of the manometer (Fig. 1), care being taken to cover the outside of the ground-glass joint with vaseline or silicone stopcock grease to prevent water from dissolving the glycerin-base grease with which the joint itself was greased. A similar volume of an ether-di-n-butyl phthalate solution was placed in the flask (B) on the right side of the manometer. With both stopcocks closed the flasks were immersed in liquid nitrogen, and the contents were allowed to freeze. The stopcock (C) connecting the mercury columns was opened, and the system was then evacuated from the stopcock (D) on the solution side of the apparatus to a pressure of less than 0.05 mm. Hg. The stopcock connecting the mercury columns was then closed and the system was warmed to allow the frozen liquids to melt. This procedure was repeated until no further change in the mercury levels could be observed when read with a cathetometer. The measurements were made at 25.00 ± 0.005°C, and pressures could be read to 0.1 mm. Hg with the cathetometer. Any ether condensed in the mercury columns was either returned to the flasks by gently heating the columns or if it was from the solution flask, it was sometimes allowed to distill back

when the apparatus was in the water bath. Five freezings and evacuations were usually necessary to produce a constant differential pressure. After each measurement was completed the contents of the solution flask were poured into a ground-glass stoppered Erlenmeyer flask and tightly stoppered until analysis could be made.

The solutions were analyzed by weighing out samples using either a Smith weighing buret or a Lunge pipet. The sample of solution taken for analysis was placed in 10 ml. tared beakers. The largest part of the ether was cautiously evaporated from the solution by placing the samples on a hot plate. They were then placed in an oven at 60-70°C for final heating until a constant weight was obtained. From the weight of di-n-butyl phthalate remaining the molality of the solution was determined. To minimize evaporation of ether from the solution in the process of sampling, each solution flask was cooled in an ice bath prior to withdrawing the sample for analysis.

The vapor pressures of 23 solutions were measured covering a concentration range of 0.08-2.85 molal in di-n-butyl phthalate and a differential pressure range of 2.8-76.8 mm. Hg. It was believed that these ranges of concentration and pressure were extensive enough to provide calibration data for systems of other nonvolatile solutes in ether which might be studied subsequently.

Investigation of the Steady State Method

A. Single Thermistor Measurements

Preliminary measurements were made using a single therm-istor mounted in a rubber stopper fitted into a 25 x 100 mm. test tube. All connections were made to the bridge with "banana" plugs. The first thermistor used was one of high resistance, 100KΩ, with a rated temperature coefficient of -4.6%/°C at 25°C and was obtained from the Victory Engineering Corporation. Temperature coefficients of resistance determined for a high resistance thermistor pair in the range 24-26°C compared favorably to the rated value above.

Resistance measurements were carried out using a modified Luder a.c. bridge (26) with about a 1.0 volt input and a fre-quency of 1200 cycles/sec. supplied by a Hewlett-Packard audio oscillator. The resistance components of the bridge were all obtained from the General Radio Company. They were G. R. Type 510 elements. The variable arm of the bridge covered a range of 0.1-211,110 ohms and had a tolerance of 0.05% with a temperature coefficient of 0.002%/°C. The standard arms in the a.c. bridge were 10KΩ resistors with the same specifica-tions. Two variable capacitors were placed in parallel with the variable and unknown resistors to balance out capacitance in the cell. Earphones were used as a null detector.

A small well-insulated 1X1X2' water bath containing an inner bath of kerosene provided a means of constant-tem-perature control. The entire thermostat was covered and the

inner bath had a removable cover. The inner bath held a circular metal disc containing holes for several sample tubes of solutions and a tube containing solvent. A Fahrenheit thermometer graduated in 0.05°F was compared with a Bureau of Standards thermometer (No. 73035) of 0.2°C divisions. This Fahrenheit thermometer was used as a reference for setting Beckmann thermometers and other thermometers used throughout the investigation. A mercury thermoregulator and an electronic relay controlled the temperature. Stirring was accomplished by means of a cone-drive motor and a large multi-bladed stirrer.

Sulfuric acid solutions of known vapor pressures (14) were used in the preliminary measurements. The change in resistance, ΔR, was taken as the difference between the resistance of the dry thermistor and the resistance value obtained by balancing the bridge several minutes after one drop of water was applied to the thermistor tip. In most of these measurements the resistance decreased steadily after having first risen to a maximum value immediately after the drop was applied, but no steady state or plateau was reached. An approximate relation was observed, however, between the resistance difference, which is proportional to the cooling effect, and the vapor pressure of the sulfuric acid solutions.

One of the difficulties encountered in working with these water solutions was the incomplete wetting of the thermistor tip by the water drop due to the high surface

tension of water. This problem was partially solved by etching the thermistor tip with a hydrofluoric acid solution. Another improvement in technique came from the use of a micropipet for delivering drops of more nearly constant size.

Troublesome variations in inner bath temperature appeared, probably due at least in part to the fact that the surrounding room temperature was not equal to the bath temperature. Opening the bath to load the thermistor tip with a water drop also resulted in temperature fluctuations. Efforts to overcome such temperature variations were made by using longer test tubes and by putting a thermoregulator in the inner bath, but they were in general unsuccessful.

In an effort to improve the method, differential thermistor measurements were tried. However, it was found that when two thermistors were employed, each serving as one arm of the bridge, no balance could be obtained. Changing the size of the capacitors and improving the shielding were tried in an effort to obtain a balance, but without success. It is believed that capacitance effects were responsible for the difficulties but they could not be overcome. It was then decided to convert the bridge to direct-current work. A diagram of the d.c. bridge designed for use with matched thermistors is shown in Fig. 2. One of the main objections to the use of a d.c. bridge lies in the requirement of a very delicate galvanometer for a null detector. A sensitive
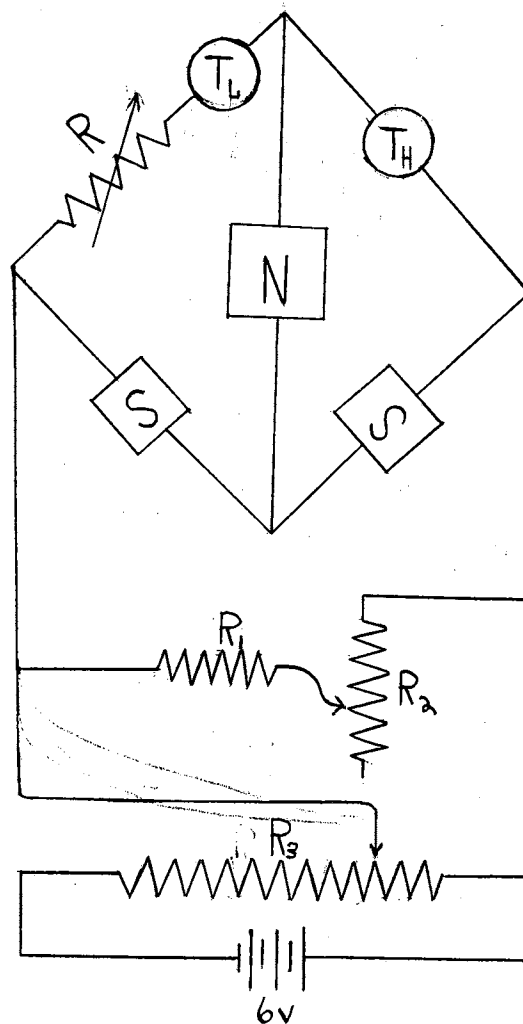
T_L - Low Resistance Thermistor
T_H - High Resistance Thermistor
S - Standard Resistors, $2K\Omega$ or $100K\Omega$
R - Variable Resistors, $0-211K\Omega$
R_1 - $1K\Omega$ Resistor
R_2 - $0-5K\Omega$ Resistor
R_3 - $0-0.5K\Omega$ Resistor
N - Null Indicator

Figure 2

Thermistor Wheatstone Bridge

electronic null-indicator was purchased from the Minneapolis-Honeywell Regulator Company, however, which was not affected by vibration and did not have to be leveled. But some difficulty was encountered with this instrument when it was first tried and a Rubicon galvanometer was temporarily substituted. This latter instrument was much slower in operation and also less sensitive (5×10^{-9} amps/div.) than the electronic null-indicator (1×10^{-9} amps/div.), and when the null-indicator began working satisfactorily, it was used throughout the rest of the experimental work.

B. Double Thermistor Measurements

The preliminary experiments employing an a.c. bridge with a single thermistor having indicated that in order to obtain any kind of steady-state, a double thermistor d.c. bridge would be necessary, attention was next directed toward designing a workable cell. Consideration was given to the following points: (1) simplicity (2) ease of manipulation (3) rate of attainment of temperature balance (4) sensitivity and reproducibility of measurements. A number of cells were built and modified in ways suggested by the experimental results.

A discussion of the various thermistor cells used throughout the investigation is given in the following sections, along with the different experimental techniques tried.

1. The Dipping Thermistor Tube Cell

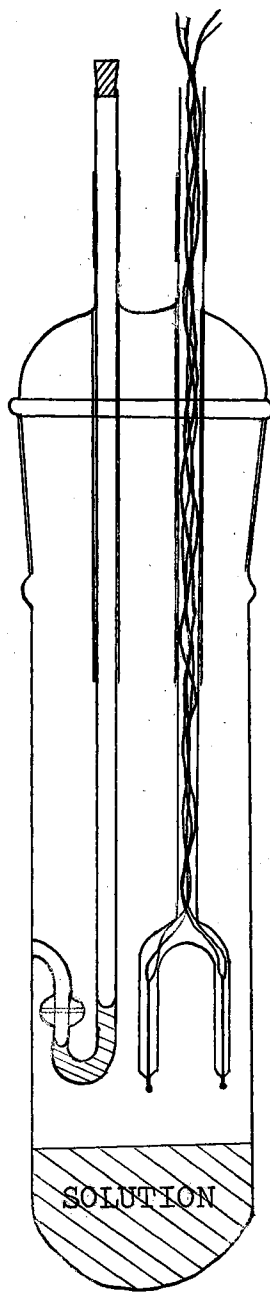A thermistor cell incorporating resistance-matched thermistors mounted in a forked tube was constructed (Fig. 3).

Figure 3. Dipping Thermistor Tube Cell

This cell consisted of a tube with a ground-glass top ($\mathbb{S}$ 45/50) having two openings. Through one opening the forked tube in which the thermistors were mounted was ground to pass smoothly through the cell top in order that the thermistors could be raised and lowered without excessive evaporation occurring. Through the other opening passed a glass tube bent into a U-shape and having sealed on its tip the female part of a ball joint. Pure solvent (ether) was placed in this U-tube. Both tubes had rubber tubing sleeves connected to the cell top to complete the seal; at the same time this also helped to hold the tubes rigidly in place. The solvent-containing U-tube could thus be closed off with the ball joint, the male part of which was sealed to the inner wall of the cell as shown in the figure. A sample of solution was placed in the bottom of the cell. To make a measurement the thermistors were wet simultaneously with solution and solvent by pushing the thermistor tube down and dipping the solvent thermistor (the one of higher resistance) into the U-tube and the solution thermistor (one of lower resistance) into the solution. The U-tube with the ball joint was then closed to prevent ether vapor from diluting the solution.

With this apparatus ΔR values measured using a 1 molal solution of sulfuric acid in water could be reproduced to within about 5%. However, there was a large ΔR (_ca._ 23 ohms) for a small pressure lowering (_ca._ 1 mm. Hg), so that even with a 5% variation in the ΔR values the vapor pressures

could be reproduced to within several hundredths of a milli-
meter for that solution. These measurements did not represent
a steady-state condition, however, as the resistance was
observed to peak rapidly, and the first recorded measurement
(about two minutes after the initial wetting) was the one
used in the calculation of the ΔR. The low-resistance therm-
istor pair (about 2×10^3 ohms) was used in these measurements.

It was decided that the dipping technique used at this
time was at fault because apparently not enough liquid was
adhering to the thermistor tips. To correct this, small ab-
sorbent wicks about 3/16 in. long were fastened to the therm-
istor tips. While this seemed to help in obtaining a steady
state, which in most cases was reached in ten minutes, an
effort was made to achieve still better temperature control
by moving the apparatus into a much larger water bath whose
temperature was controlled to within about 0.002°C. Numerous
measurements on the same solution were made, many of which
exhibited well defined steady states. However, the repro-
ducibility achieved at this time was still poor. Both the
high and low-resistance thermistor pairs were used in these
studies.

A study of the effect of the voltage on the resistance
of the thermistors was also made. The power for the bridge
was furnished by a six-volt storage battery and the voltage
input was manually regulated by a potential divider (Fig. 2)
and measured on a Rubicon potentiometer (Serial No. 54864).
Five measurements were made of the resistance of each

thermistor and of the ΔR at five different input voltages ranging from 1,500-3,000 volts for both the high and low-resistance thermistors at 25°C. The resistance decreased as the voltage increased in all cases owing to the internal heating of the thermistors caused by increasing the current. Even the lowest voltage, 1,500, exceeded the maximum power input for no sensible heating for the low-resistance thermistor pair.

From time to time during the course of the work, electrical short circuits developed in the forked tube which contained the thermistor leads. When this occurred, another thermistor pair was often substituted while repairs were made. The thermistors were sealed into the end of the forked tube with a cement made from methyl methacrylate polymer dissolved in the monomer. Duco and Testor's cements were also used. Both of these cements had certain disadvantages, chiefly because of their solubility in ether, and their use was later discontinued.

In the early measurements the apparatus was partially removed from the temperature bath in order to carry out the dipping technique. Some measurements were made without lifting the thermistor cell, but there was always danger of impairing the thermistors. Some improvement was achieved by employing an unsilvered two-liter Dewar flask which was kept totally immersed except when the thermistors were being wetted. The apparatus was placed in the Dewar and the whole assembly could be raised out of the outer bath enabling one to see

the thermistors and thus carry out the dipping procedure
without appreciably changing the temperature.

The procedure generally, as discussed previously, con-
sisted of placing a drop of solvent in the atmosphere just
above a solution in that solvent. With this type of system
the initial ΔR reading between the two thermistors was usually
measured with no liquid on either thermistor. All other investi-
gators (8, 18, 30) apparently measured heating effects produced
by the condensation of solvent on a drop of solution kept in an
atmosphere of the pure solvent, and, furthermore, the initial ΔR
values measured by these workers were usually measured with
solvent on both thermistors. Several measurements were at-
tempted using this procedure with the initial ΔR values obtained
either with solution on both thermistors above a solution of the
same concentration or with dry thermistors above an atmosphere
of the solution to be studied. The latter seemed to give the
most reliable results.

2. The Modified Iyengar Thermistor Cell

Attention was turned next to the design of a new and
simpler thermistor cell. This cell was modeled after that
used by Iyengar (18) and consisted simply of an electrolytic
beaker covered with a cork-masonite stopper (Fig. 4). The
thermistors were encased in a short forked tube which ex-
tended through the top. In the cell top was a small hole,
normally covered with a cork, through which drops could be
applied to the thermistor tips by means of a micropipet.
The inner wall of the cell was lined with absorbent (filter)
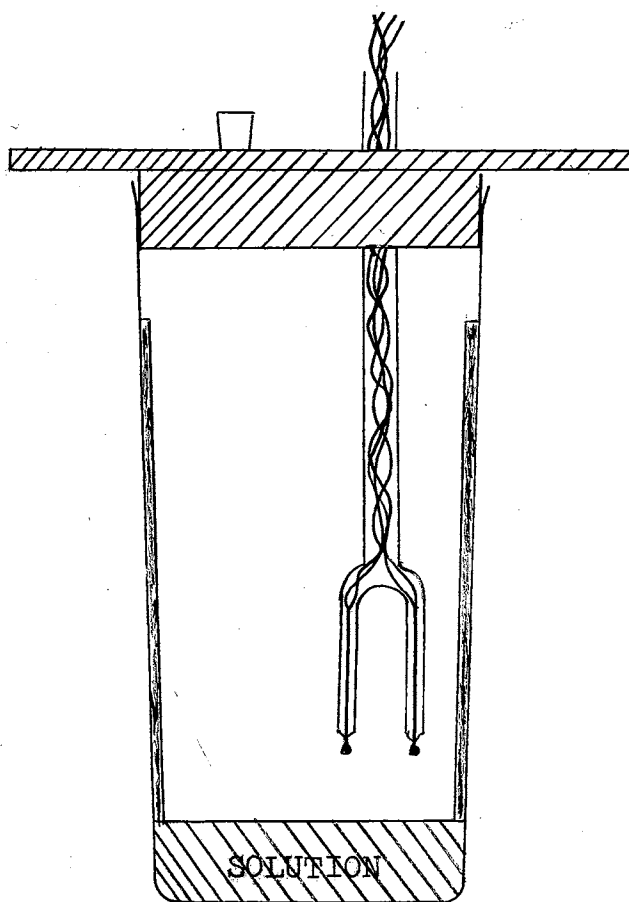paper as an aid in keeping a uniform atmosphere of vapor

Figure 4. The Modified Iyengar Thermistor Cell

in the cell. The new cell had the advantage of allowing several measurements to be carried out on the same sample of solution. After the steady state had been reached the excess ether was removed by means of some absorbent material; then after equilibrium had been again reached, new drops of solvent and solution were applied. The initial ΔR used with this cell was measured with the thermistors dry. A drop of solution was first placed on one thermistor tip, then a drop of solvent was placed on the other thermistor (the one of higher resistance). The solution drop was obtained from the solution in the bottom of the cell and the solvent drop was taken from a test tube of solvent kept in the water bath at all times. After experimenting with drops of different sizes, a drop size of about 7λ (0.007 ml.) was decided upon.

In order that the steady state might be studied in greater detail, a 0-10 millivolt-range Brown recorder was introduced in place of the null-indicator. This, it was hoped, would provide a graphical record of the attainment of the steady state by recording the unbalance in voltage brought about by the change in temperature, and hence change in the resistance of the solvent thermistor.

In order to translate the recorder deflection in terms of resistance changes in the bridge arms, a point-by-point calibration was carried out at six applied voltages in the range 0.250-1.500 volts using only the low-resistance thermistors because of an impedance matching requirement. The 10KΩ fixed-resistance arms of the bridge were replaced by

two decade boxes and the greatest sensitivity was obtained with standard-resistance arms of about 1000 ohms each. The calibration data were obtained by unbalancing the bridge in five ohm steps and observing the recorder deflections. Straight line (Ohm's law) plots of ohms of unbalance vs. recorder deflections were obtained. It was found that the sensitivity of the recorder was much less than that of the null-indicator and even more serious was the fact that the recorder seemed to be unable to follow the change in resistance or unbalance of the bridge. As a result the recorder graph would appear as a series of step-like lines instead of a plateau. In view of these disadvantages it was decided not to use the recorder further as a permanent instrument for measuring bridge unbalance as a function of time.

At this time consideration was given to the effect of relatively small voltage variations upon the thermistor resistance; however, a study of this factor showed that a variation of about 0.01 volt (at 1.500 volts) caused only a small change in resistance when the high resistance thermistors (100 KΩ) were used. The variation in input voltage was less than 0.001 volt during a measurement.

All measurements of the rise in temperature resulting when a drop of ether solution was placed on a thermistor tip in an atmosphere of solvent (ether) having proved unsuccessful, subsequent measurements with this cell were of the usual type; that is, the cooling effect produced by solvent evaporation in an atmosphere of solution was measured. The results were

discouragingly erratic and sometimes no steady-state at all
was reached. Even when a steady-state was obtained the measured
time of its appearance varied considerably.

The small absorbent wicks described earlier were again
tried, but there was no perceptible improvement in the re-
producibility. During the course of the measurements employing
wicks on the thermistor tips, however, several significant
observations were made. First, it appeared that a steady-state
could be reached a larger percentage of the time with wicks
than without wicks. Also it was found that if the excess ether
was removed from the wick after the steady-state was reached,
the next measurement of the ΔR at the steady-state for the same
solution sample was a little larger. If, however, the excess
ether was allowed to remain and completely evaporate, the
measurement immediately following resulted in a ΔR much closer
to that first obtained. This effect was believed to be due to
continuous evaporation of ether from the cell while it was kept
in the water bath. Thus when the excess ether on the therm-
istor tip was allowed to remain and evaporate, the resulting
dilution partially compensated for the evaporation of ether
from the solution. The result was that the vapor pressure and
the measured ΔR remained approximately constant. The continuous
evaporation of solvent from the cell was a serious problem and
restricted the use of the cell to only one measurement with
each sample of solution.

It was evident that some of the reasons for the erratic results obtained thus far could be traced to high volatility of the ether itself. To investigate a less volatile organic solvent a methanol solution of di-n-butyl phthalate was prepared and a series of measurements were made. Several interestering things were learned. First, it was discovered that each measurement took from 50-80 minutes compared to the 10-15 minutes required for the ether solutions. Second, in practically all of the measurements with the methanol solutions there occurred a very rapid initial increase in the values of ΔR after the drop was applied; then after about a minute ΔR decreased for about 10-15 minutes after which it slowly increased and finally leveled off at about 50 minutes. Third, a steady-state was obtained a greater percentage of the time than with the ether solutions. Fourth, the reproducibility was much greater, in many cases better than one percent.

Further detailed study was made of the peculiar behavior of the resistance change during the course of a measurement with the methanol solution. It was suspected that the resistance of the thermistor used for holding the drop of solution changed when a drop of solution was applied. This point had not been considered before as it was assumed that a drop of solution in an atmosphere of that same solution in the cell was in a state of equilibrium. However, it was discovered that the resistance of the solution thermistor increased considerably after a drop of solution was applied, while at the

same time the other (solvent) thermistor was kept dry. This was manifested by a decrease in the ΔR value since the solution thermistor was the one of lower resistance and an increase in its resistance would make the resistance difference, ΔR, smaller. This decrease in ΔR meant that the solution thermistor was being cooled and hence that methanol was evaporating from the solution drop, which, therefore, was not in equilibrium with the surrounding solution vapor. It seemed likely that a vapor concentration gradient existed above the solution. Drop size seemed to make no appreciable difference. Initial ΔR values obtained with solution on both thermistors were not reliable, and a final attempt to obtain reproducible initial ΔR values by using a long absorbent wick extending down from the solution thermistor into the solution also failed, again apparently because of evaporation of solvent from the solution.

In order to explore further this vapor concentration problem, a series of measurements were carried out with an ether solution in which the distance between the thermistor tip and the surface of the solution was varied. It was conclusively shown that the greater the distance between the thermistor tip and the ether solution surface, the greater was the increase in the resistance of the solution thermistor. This meant that the rate of evaporation was greatest when the thermistor was farthest removed from the solution surface. It was later believed, however, that some of the resistance change observed may have been due to the cooling of the solution thermistor by the drop since it was found that the thermistor was

internally heated by the 1.500v input voltage. A way to keep the
solution thermistor resistance constant was obviously necessary
if satisfactory measurements were to be made with the Iyengar-
type cell.

3. The Thermistor Cell with an Inner Chamber

It was thought advisable to construct a cell having an
inner cup in which the thermistors could be lowered (Fig. 5).
Ether solution was placed in both the inner cup and between
the inner cup and the cell wall. The purpose was to have
solution at two levels to provide an essentially saturated
blanket of vapor at the solution thermistor at all times. A
strip of absorbent paper connected the two separate bodies of
solution and the wall of the cell was also lined with absorbent
paper. The outside of the cell was covered with aluminum foil
to aid in establishing temperature uniformity throughout the
cell. A little improvement in the results was noticed, but the
decrease in ΔR due to the cooling of the solution thermistor
was still 15-18 ohms (for a ΔR of about 300). A long curved
capillary tube was used to apply the drops so that the therm-
istors could be loaded without moving them from the inner cup.
This resulted in no significant improvement in results, how-
ever. Measurements were also attempted with the solution therm-
istor immersed in the solution. This resulted in a permanent
cooling effect because of the loss of heat from the thermistor
to the solution. This also introduced new problems, since
the ether-phthalate solution dissolved the cement by which
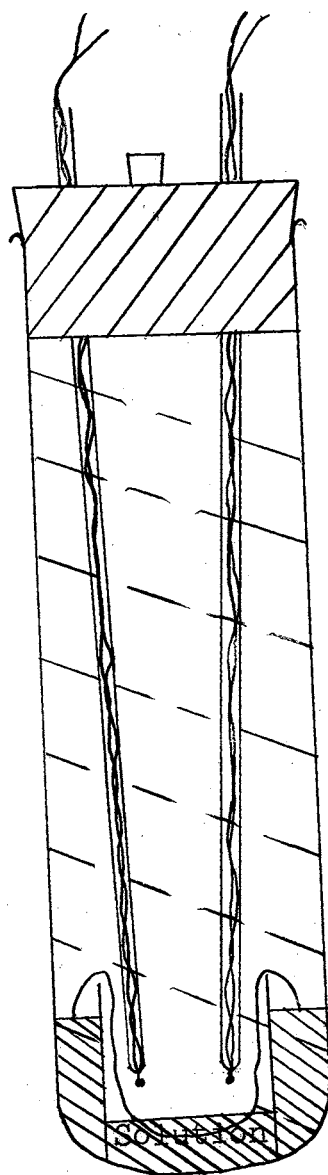the thermistors were sealed in their tubes. The cooling

Figure 5. Thermistor Cell with Inner Chamber

effect experienced when the solution thermistor was immersed
was especially noticeable with the low resistance thermistor
pair since this pair was known to be internally heated by the
1.500v input voltage.

A study was made of the effect of small variations in the
bath temperature upon the differential resistance of the low
resistance thermistor pair. Temperatures studied were within
a few hundredths of a degree of 25°C. The measurements were
made at an input voltage of 1.500v in the atmosphere above
a sample of pure ether with the thermistors either suspended
dry, with ether drops on them, or totally immersed in the
ether. The results were as expected, with the ΔR values in-
creasing with decreasing temperature when the thermistors
were immersed or when suspended dry; however, the ΔR value
showed less variation when the thermistors were suspended with
drops on them.

In order to eliminate some of the difficulties introduced
by internal heating of the thermistors, lower input voltages
were employed. Measurements were made at 0.5, 0.4, 0.3, and
finally at 0.25 volts. At the lower voltages the change in
ΔR when a drop of solution was applied was reduced considerably
until it was only a few ohms. This confirmed the belief,
stated previously, that some of the solution thermistor
resistance change was due to cooling of the tip by the drop
because it had been internally heated at the higher input
voltage. Some measurements were made by applying the solution
drop first and allowing the resistance to level off, using
the resulting constant, though lower, value as an initial ΔR

before the solvent drop was applied. Although not much improvement in precision was noticed, good steady-state values could be obtained; this, perhaps, was due in part to the improved design of the cell which had a tight-fitting rubber stopper in which the thermistor tubes were held. Further improvements in the measuring technique resulted from connecting a new ground lead and shortening the leads between the thermistors and the bridge. At 0.25v the sensitivity of the null-indicator was found sufficient to enable accurate resistance measurements to be made, and it was decided to continue work at this voltage.

4. The Immersible Side-Arm Thermistor Cell

All of the thermistor cells described thus far were not completely immersed in the constant-temperature bath. It was thought that if all of the vapor space above a solution sample could be kept also at a constant temperature, better resistance control and perhaps better reproducibility would result. A cell to accomplish this was designed and constructed (Fig. 6). Both ends of a ground-glass joint ($ 34/45), to be used as a cell top, were sealed, and two tubes were ring-sealed through the top. Only those short portions of the tubes containing the thermistor leads remained above the bath surface. The thermistors were loaded with their drops of solvent and solution through a side-arm opening, at the end of which was a ground-glass male-joint ($ 14/35). Through this side arm a micropipet, delivering 7-10λ of liquid, could be inserted to apply a drop of solution or solvent to the thermistor tips.
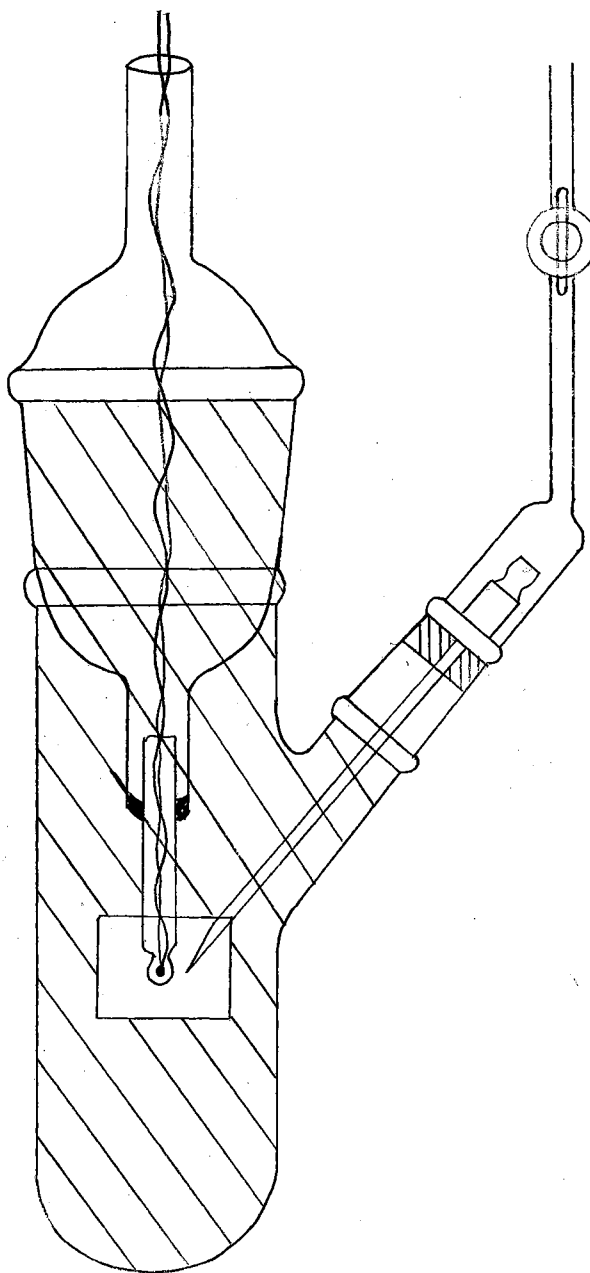
Figure 6. The Single Thermistor Cell

The cell top could be rotated so as to maneuver the therm-
istors into position for drop application. The side arm was
enclosed in the female part of the ground-glass joint having
sealed to its end a capillary-tube vent with a stopcock for
release of gas pressure.

With this new cell it was found possible to reproduce
the initial ΔR very well. The necessity for a side-arm vent
containing a stopcock illustrates an important characteristic
of thermistor operation. It was found that large changes in
resistance resulted if the side arm was removed without first
opening to the atmosphere. Since the ether solution had been
cooled prior to its having been placed in the cell and sealed
soon thereafter, a pressure greater than atmospheric resulted
when the solution came to bath temperature. This change in
resistance was due to ether vapor streaming past the therm-
istors when the cell was opened and is called the "flow-meter"
characteristic of the thermistors. Since the cell was normally
open to the atmosphere only through a small capillary, evapo-
ration was greatly reduced and several measurements could be
made with the same sample.

Although the results obtained with a 0.6 molal solution
of di-n-butyl phthalate in ether showed considerable improve-
ment over the previous measurements, the resistance of the
solution thermistor was still found to increase when a drop
of solution was applied. Measurements were made by first
applying the solution drop, and after the resistance leveled
off, applying the solvent drop. However, this procedure had

a disadvantage in that more time was required for the solution drop to come to equilibrium with the solution vapor in the cell than for the steady state to be reached with the solvent ether drop. An increase of several percent in the resistance change was noticed, however, when an absorbent filter paper lining was used. The combined mean deviation of these measurements (with and without filter paper lining) was slightly more than one percent.

An experiment designed to compare the sensitivity of the method with water and with ether as solvents was next performed. A sulfuric acid solution of known vapor pressure was prepared, and the ΔR measured when a drop of water was placed on the thermistor tip, the initial ΔR having been determined with dry thermistors. Next, ΔR was measured on an ether solution of di-n-butyl phthalate possessing the same ΔP (pressure difference between solvent and solution, 5.6 mm. Hg) as the sulfuric acid solution. Since the value of ΔR was measured in the same way, the results could be compared with the results obtained with the aqueous acid solution. However, the values obtained for the acid solution were not very precise, probably because of poor wetting of the thermistor tip by water and the acid solution. Two of the three measurements on the acid solution were made using a long curved capillary tube to apply the solution drop. This drop was obtained from solution in the bottom of the cell, while the initial ΔR was taken with solution on one thermistor. Only a rough comparison could be

made of the results obtained with the water and ether solutions. The comparison simply showed that the water solution, in qualitative agreement with theory, produced a ΔR of 6-7 times larger than that obtained with the ether solution for the same absolute lowering of the vapor pressure.

As with earlier cell designs a few experiments were carried out in which measurements were made of the heating effect produced by condensation of solvent at the vapor pressure of the pure solvent on a solution drop. For the first time a steady state ΔR value could be reached. Using the low-resistance thermistor pair the resistance leveled off in about 1.5-2.0 minutes after the drop was applied. Although good precision was not achieved, the measurements did show that the ΔR was smaller (ca. 25%) than that which was obtained by measuring the reverse effect, i.e., the cooling of the solvent thermistor by evaporation at the vapor pressure of the solution.

At this time it was discovered that a vapor pressure gradient apparently existed in this cell also. When a larger sample of solution (25 ml. instead of 20 ml.) was used, the measured ΔR was observed to be smaller. This agreed with earlier measurements whereby the existence of a vapor concentration gradient was established. Thus as more solution was used the thermistors were brought closer to the liquid surface and hence were in a region richer in ether vapor; correspondingly, a smaller cooling effect was produced by solvent evaporation. Stirring

the solution in the cell was one of several things done to solve the vapor gradient problem, but this like the others was unsuccessful.

During the course of these experiments it was found that removing the aluminum foil covering from the outside of the cell seemed to affect the time required for the appearance of the steady-state. The cell was therefore silver-plated on the outside, leaving a small clear window for viewing the thermistors.

Among the variations in technique tried in effort to improve the precision and usefulness of the method was the provision of a strip of aluminum (and later silver) foil in the cell. The foil was designed to act as a thermal short-circuit when the thermistor position was changed by rotating the cell top until contact was made with the foil. This aided in speeding the return of the thermistor to room temperature. The usefulness of such a short-circuit had been shown by some experiments with methanol solutions of potassium iodide where excessive periods of time were required for the resistance values to return to the initial values. Although fairly good results were obtained ($\pm$ 0.6%) with a 0.45 molal solution, the peculiar resistance effects which had been observed earlier with methanol were still present, and the measurements were still found to require a much longer time to complete than those using ether.

5. The Mercury Cup Thermistor Cell

The earlier thermistor cells all had the thermistors mounted vertically, and their use had involved the placing of

drops of solvent and solution on the thermistor tips. A new
cell, suggested by one described in a paper by Müller and Stolten
(30), was now constructed. It involved the use of thermally in-
sulated glass cups into which the thermistors were sealed so
that they could be covered, or partially covered, with mercury.
This cell is shown in Fig. 7. In this cell the cups are posi-
tioned mouth upward from the bottom and are vacuum jacketed.
The lower part is a silver-plated vacuum jacket through which
a "Y" tube is ring-sealed at its lower end. This divided
tube in the evacuated jacket enclosed the thermistor leads
and the lower part of the glass stems of the thermistors. A
pair of new low-resistance thermistors having a -3.9%/°C temper-
ature coefficient completed the new cell.

It was realized that the use of a relatively large mass
of mercury would cause the cell to be inherently less sensi-
tive than the other cells because of its large heat capacity,
but it was hoped that the cell would possess the advantages
of stability and reproducibility reported by Müller and Stolten
for their cell.

A 0.15 ml. sample of solvent and an equal amount of solu-
tion were placed in the cups from long capillary tubes that
had been previously calibrated. The large ground-glass top
(₮ 60/50) was fastened with rubber bands. The mercury
was carefully weighed and an equal amount was placed in
each cup prior to a measurement. The thermistors were
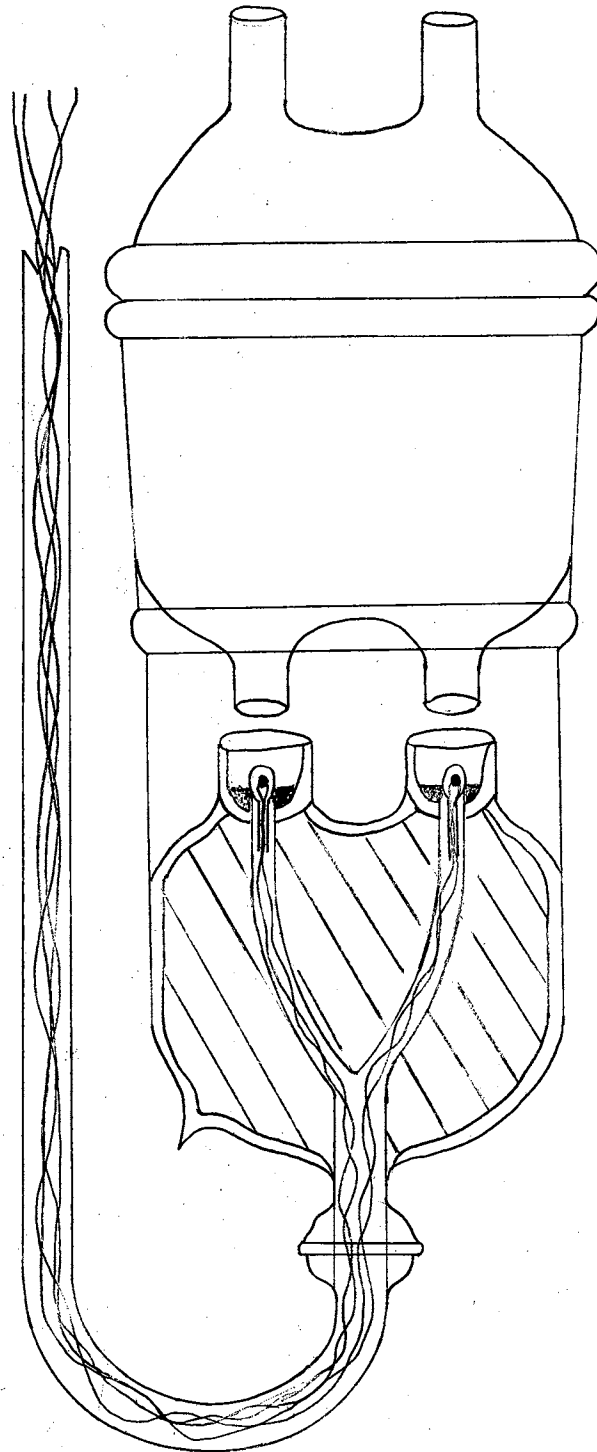sealed in the cups. Duco cement was first used, then Fisher

Figure 7. The Mercury Cup Thermistor Cell

"Sealit" was tried, and finally a still more satisfactory cement, sodium silicate solution, was used.

In order to follow the measurements graphically, a Sargent Model XII Polarograph was modified and used in conjunction with the null-indicator. Photographic records of the resistance change as a function of time were made in this way. A fast period galvanometer was used in the Sargent instrument, and other modifications were made so that one could detect a 0.1 ohm bridge unbalance.

The photographs obtained showed the same peculiar effect noticed with ether solutions in the other thermistor cells. For example, a peak in resistance occurred within a few seconds after the solvent was applied (the initial ΔR being taken with solution already in the cup), and this was then followed by a decrease in resistance. After the resistance reached a minimum, it again increased to the steady-state value. Since all of this usually occurred within the first minute, it could not be observed in detail with manual recording of the data. A drawing of this rapid peaking is shown in Fig. 8, occurring in this case in about ten seconds after solvent had been placed in the cup. An ether solution of phthalate at a concentration of about 0.6 molal was used in this experiment. The straight lines at the top of the drawing show the plateau or steady state.

Most of the investigations with the mercury cup cell were concerned with (1) a study of the effect of different weights

Figure 8

Drawing of a photographically recorded Resistance-Time Thermistor Measurement
Using a Solution of Di-n-Butyl Phthalate in Diethyl Ether
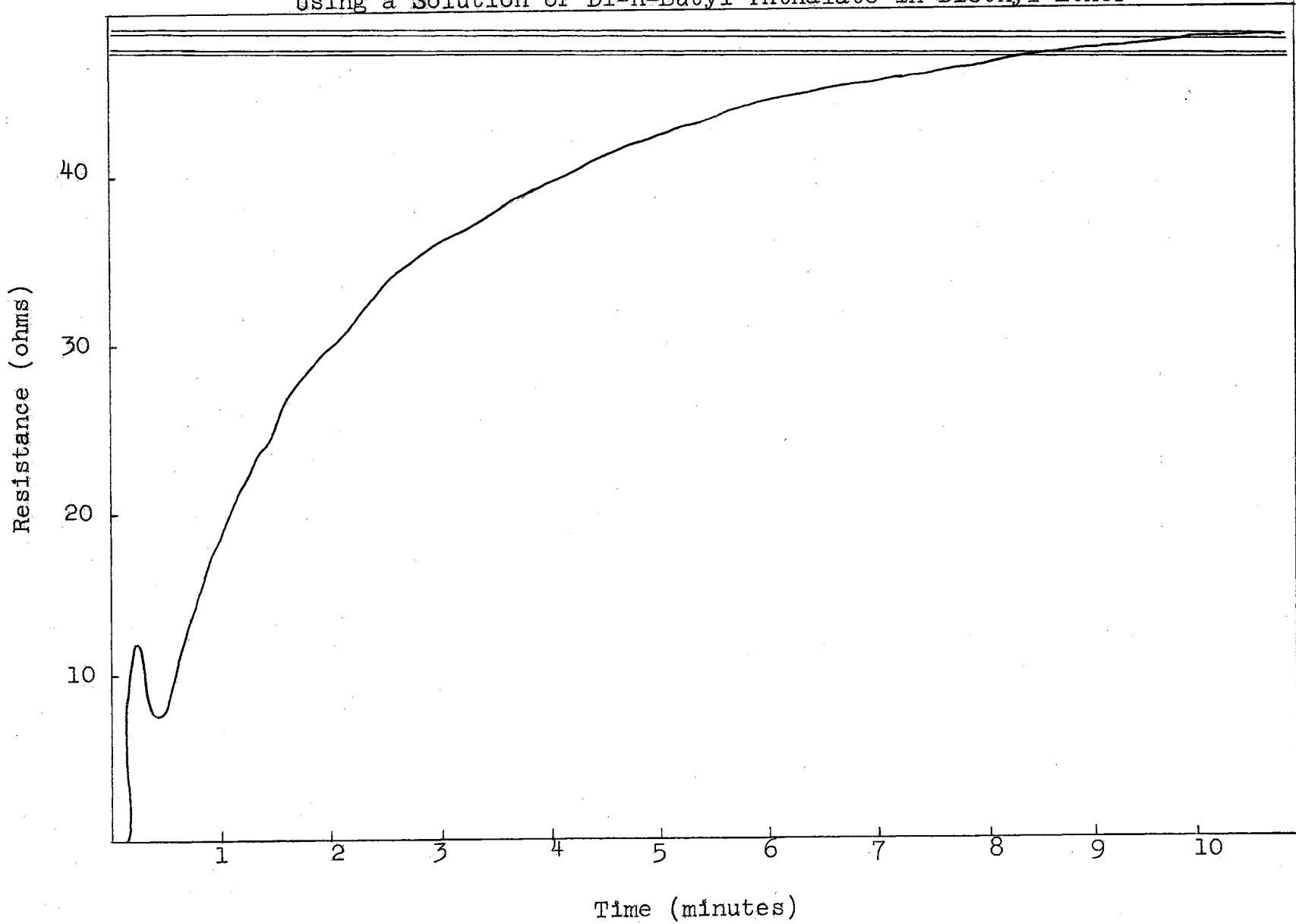
of mercury in the cups on the sensitivity, (2) the effect of changing the temperature of the solvent applied, and (3) the reproducibility of the resistance change. In general it was found that there was no trend in the ΔR sensitivity with the weight of mercury over the range of 1.5 to 2.0 grams. Also no appreciable differences resulted in the ΔR values with a given solution when the temperature of the solvent applied was varied from 24° to 26°.

In general the precision of the measurements made with the mercury-cup cell were in the range 1-2%. Although very stable steady states often resulted using this cell, it was found that the cell was much less sensitive and a much longer time was required for each measurement than with the cells studied earlier.

Because the above disadvantages seemed to outweigh the advantages, it was decided to discontinue work with the mer-cury-cup cell in favor of the side-arm cell previously used. Since this cell appeared to be the best of the cells studied, being simple in construction and manipulation, a careful ex-amination of the suitability of the method for the determin-ation of the activity of a volatile solvent such as ether was now undertaken using the side-arm cell. The side-arm was first modified slightly in that a small tight-fitting cork was placed in the end of the side arm tube, and through this cork a long hypodermic needle was inserted. Each measurement was made by removing the side arm cover and placing the tip of a micropipet into the end of the hypodermic needle. The ether

was thereby transferred first to the hypodermic and finally to
the thermistor tip. The amount of ether needed to produce a
drop of constant size was approximated visually each time.

The modified side-arm cell was tested for reproducibility
with the same 0.2 molal solution that had been used with the
mercury-cup cell. Twelve measurements using the new low-
resistance thermistors showed a mean deviation of less than one
percent. These measurements were made taking the initial ΔR
with both thermistors dry, and making the measurement with the
reference (solution) thermistor also dry. The cell was always
kept at atmospheric pressure by means of the capillary tube
vent on the side arm. Use of the needle for applying the drops
also eliminated the possibility of any displacement of vapor
from the cell, such as may have occurred previously when the
micropipet itself was inserted. These measurements were made
using a silver-plated cell with two small unsilvered windows
(front and back) for viewing the thermistors. A 20 ml. sample
of solution was placed in the cell. The cell walls were lined
with thick absorbent paper.

It was decided to begin the actual calibration measure-
ments, that is, a study of ΔR vs. solute concentration,
beginning with a solution of about 0.08 molal with respect to
phthalate as the most dilute solution. The precision obtained
with this solution was not very good, however, for the ΔR values
were in the range 11-15 ohms and were measured to only 0.1 ohm.

It was suspected at this time that one thermistor might thermally interact with the other because of their temperature difference. This was shown to be the case by measurement of the resistance of the reference (dry) thermistor during the course of the evaporation of a drop of solvent. It was found, for example, that the cooling increased the resistance in some cases by as much as two ohms. Efforts to eliminate this cooling included the construction of various forms of baffles. For example, a semi-circular silvered-glass sleeve was inserted around the reference thermistor in one such attempt, while in another an aluminum foil was placed between the thermistors. None of these modifications were entirely satisfactory, however, the best solution seemed to be to isolate the reference thermistor completely, or, in effect, to eliminate it. This was accomplished by mounting it in a long glass tube and positioning it in another part of the bath where it served merely to compensate for temperature fluctuations.

The next more concentrated solution was 0.2 molal, and it was with this solution that a new technique was devised which was ultimately adopted for the remainder of the investigation. First a drop of solvent was placed on the solvent thermistor and the steady-state plateau recorded. Then a second drop was placed on the thermistor and again the plateau observed. After three to four such repeated applications the plateaus seemed to be reproducible. In this manner the concentration range from 0.08 molal to 2.48 molal phthalate in ether was covered.

Each solution was analyzed by the evaporation method and its concentration determined. The vapor pressures were obtained from the vapor pressure-composition curve obtained earlier in the investigation. The differential vapor pressure range covered was from 3.2 to 68.7 mm. Hg and corresponded to ΔR values from 15.1 to 304.8 ohms.

RESULTS AND DISCUSSION

Vapor Pressure Measurements

As described under the Experimental section the vapor pressure of ether in the di-n-butyl phthalate-diethyl ether system was measured over a concentration range from 0 to 2.85 molal with respect to the phthalate ester at 25°C, using the conventional static vapor-pressure technique. These data are presented in Table 1, and a plot of vapor pressure lowering vs. molality is shown in Fig. 9. A gently sloping curve showing negative deviations from Raoult's law is obtained. By the method of least squares, empirical equations expressing the vapor pressure and pressure lowering in terms of the solute molality were found; these are:

$$P = 536.6 - 33.64m + 2.478m^2 \qquad (5)$$

and,

$$\Delta P = 0.43 + 33.64m - 2.478m^2 \qquad (6)$$

From the above equation, vapor pressures and solvent activities were calculated at convenient concentrations over the experimental range. The Gibbs-Duhem equation was also graphically integrated, as outlined by Klotz (24), to give the solute activity and activity coefficient. The activity data for the system are given in Table 2.

TABLE 1

Vapor Pressures of Ether in the Di-n-Butyl Phthalate-
Diethyl Ether System at 25°C

[Vapor Pressure of ether at 25°C = 537.0 mm. Hg (I.C.T.)]

ΔP in mm. Hg	m	N_2
2.8	0.0798	0.00588
6.2	0.190	0.01389
7.8	0.236	0.01719
11.4	0.319	0.02310
14.9	0.429	0.03082
18.7	0.558	0.03972
21.7	0.665	0.04697
25.7	0.761	0.05339
27.1	0.831	0.05802
30.1	0.952	0.06591
33.3	1.06	0.07284
35.0	1.13	0.07728
39.2	1.26	0.08541
40.8	1.33	0.08973
43.5	1.44	0.09644
47.4	1.59	0.1054
51.5	1.74	0.1142
54.9	1.90	0.1234
59.1	2.07	0.1330
62.6	2.22	0.1413
65.2	2.32	0.1467
70.0	2.55	0.1590
76.8	2.85	0.1744

Figure 9

Vapor Pressure Lowering vs. Molality for the Di-n-Butyl Phthalate.
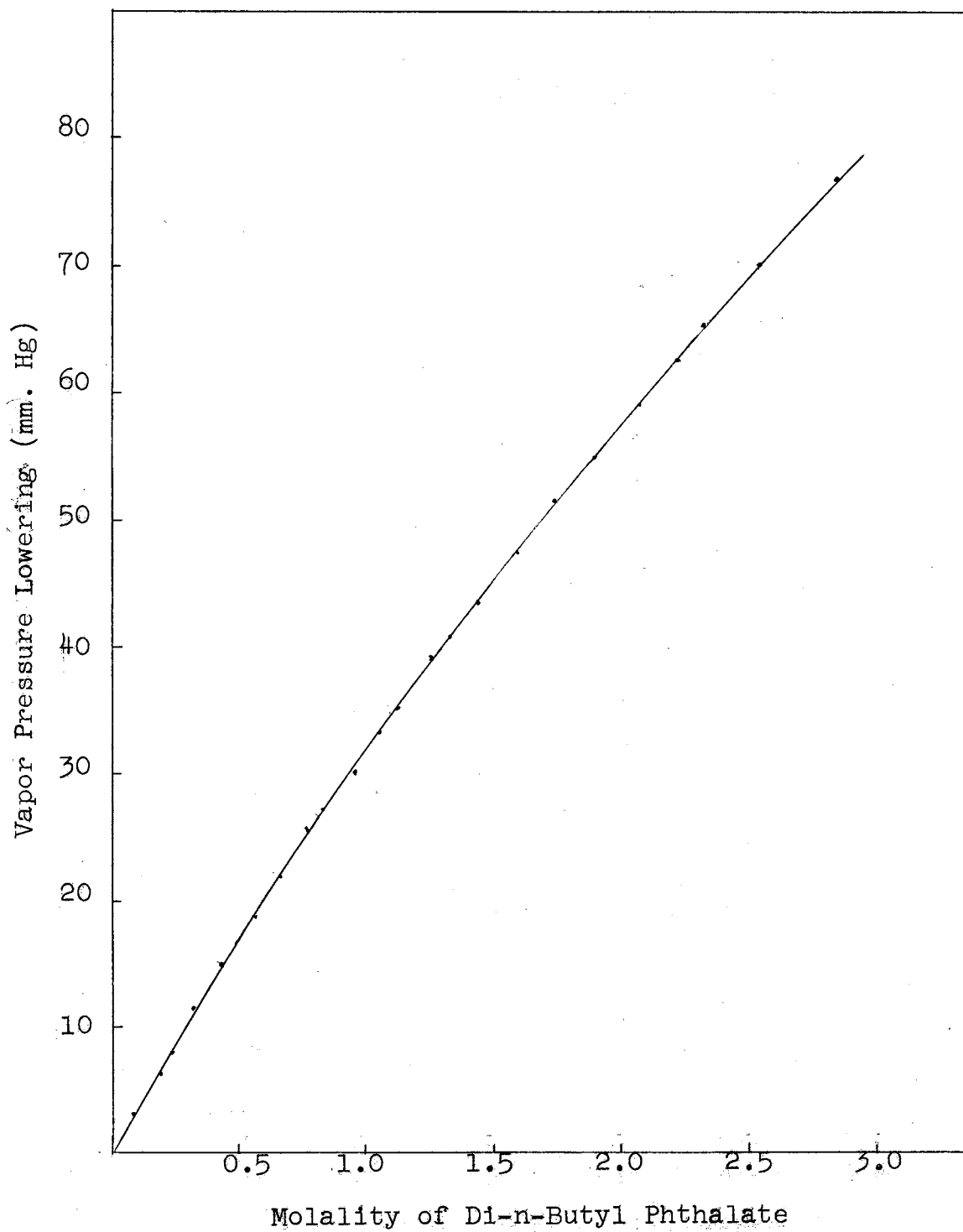Diethyl Ether System at 25°C

TABLE 2

Activity Data for the Di-n-Butyl Phthalate-Diethyl Ether
System at 25°C

N_1	a_1	γ_1	N_2	a_2	γ_2
0.9854	0.9868	1.0014	0.01461	0.01393	0.9535
0.9712	0.9749	1.0038	0.02879	0.02625	0.9118
0.9574	0.9633	1.0062	0.04258	0.03636	0.8539
0.9396	0.9484	1.0094	0.0604	0.04874	0.8070
0.9274	0.9382	1.0116	0.0726	0.05682	0.7826
0.9158	0.9287	1.0141	0.0842	0.06402	0.7603
0.9049	0.9197	1.0164	0.0951	0.07064	0.7428
0.8947	0.9114	1.0187	0.1053	0.07661	0.7275
0.8850	0.9035	1.0209	0.1150	0.08212	0.7141
0.8755	0.8959	1.0233	0.1245	0.08741	0.7021
0.8670	0.8894	1.0258	0.1330	0.09194	0.6913
0.8589	0.8831	1.0282	0.1411	0.09613	0.6813
0.8513	0.8771	1.0303	0.1487	0.09994	0.6721
0.8442	0.8719	1.0328	0.1558	0.1034	0.6637
0.8373	0.8667	1.0351	0.1627	0.0067	0.6558
0.8296	0.8611	1.0380	0.1704	0.1102	0.6467

Steady-State Measurements

The method for comparing vapor pressures investigated in this research depends on the attainment of a steady state, that is, a non-equilibrium stationary state. In this investigation, however, a drop of solvent was allowed to evaporate in an atmosphere controlled by the vapor pressure of the solution, and the consequent cooling effect was detected by an increase in thermistor resistance. As pointed out in an earlier section, other investigators have employed a solvent atmosphere for their measurements. In such cases solvent condenses on the solution drop affecting its concentration unless the solution is very dilute, and for measurements over a wide range of concentrations the heat of condensation of solvent cannot be considered as remaining constant. Aside from these theoretical drawbacks this procedure does have the advantage of maintaining a constant partial pressure in the surroundings and requires very little of the solution. For the purpose of studying activities, however, it seemed better to measure the temperature decrease arising from the evaporation of a drop of solvent in an atmosphere of solvent vapor whose partial pressure was determined by the solution vapor pressure.

The data on the steady-state resistance change for the di-n-butyl phthalate-diethyl ether system over the range of concentrations from 0 to 2.483 molal with respect to di-n-butyl phthalate are presented in Table 3. Values of ΔR for solutions at eight concentrations are shown. The corresponding

TABLE 3

Resistance Changes and Vapor Pressure Lowerings at Various Experimental Concentrations of Di-n-Butyl Phthalate in Diethyl Ether at 25°C

m	ΔP^* (mm. Hg)	Ave. ΔR (ohms)	Ave. % Deviation
0.0827	3.2	15.1	4.0
0.2057	7.3	32.4	0.93
0.5052	16.8	75.2	0.53
0.8034	25.9	114.4	0.44
1.019	32.1	141.1	0.21
1.481	44.8	196.8	0.05
2.031	58.5	259.4	0.11
2.483	68.7	308.4	0.78

ΔP^* - vapor pressure lowerings calculated from least squares equation.

vapor pressure lowerings calculated by equation (6) are also
given in Table 3, along with the average percent deviation of
each value. It will be noticed that the most dilute solution
has the greatest deviation. Great difficulty was encountered
in getting a reproducible value of ΔR at this concentration.
A plot of ΔR against vapor pressure lowering (Fig. 10) shows
a straight line with a slope of 4.38 ohms per mm. Hg. The
curve tends to deviate slightly from linearity at the highest
concentrations.

It was found that whereas the curve giving the resistance
change with time reached a plateau at the steady state for the
more dilute solutions, with the more concentrated solutions only
a maximum resulted. This probably can be largely attributed to
the extremely rapid evaporation of the drop owing to the large
difference in the vapor pressures of the solution and solvent
at the higher concentrations.

Ideally, at the steady-state temperature of the solvent
drop, the vapor pressure of a thermally-isolated solvent drop
equals that of the solution in the thermostat. Although the
temperature in the steady state is constant, as shown by the
plateau in the resistance-time measurements, it falls short
of the ideal value due to heat losses arising from the thermal
conductivity of the medium (2). From the properties of the
solvent and the solution the theoretical maximum temperature
lowering can be calculated, and hence the thermal efficiency.

Figure 10

Steady-State Resistance Difference vs. Vapor Pressure Lowering
for the Di-n-Butyl Phthalate-Diethyl Ether System
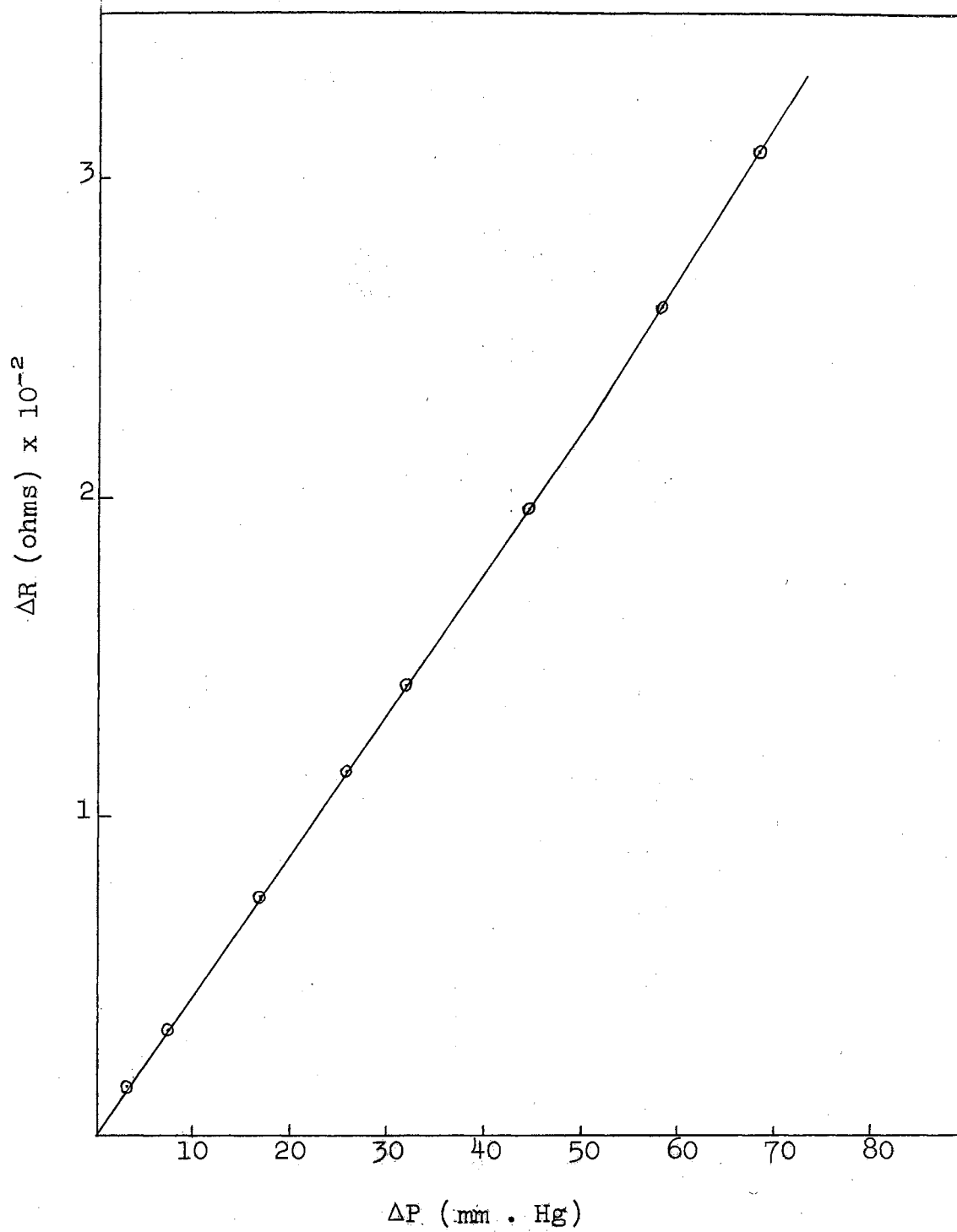
Using the experimental steady-state resistances, thermal efficiencies for the thermistor and cell were calculated as follows. From the measured resistance of the solvent thermistor at 25° (2290.6 ohms) and the empirical equation found for its resistance as a function of temperature

$$R = 2290.6 \, e^{+3480} \, (1/T - 1/298.16) \qquad (7)$$

the experimental temperature lowerings were computed. These calculated temperature differences were converted to pressure differences from the literature values of the vapor pressure of the solvent (ether) at various temperatures (15). Assuming the vapor pressure-temperature curve to be linear in the region 21-25°C· (range of experimentally measured changes), the change in vapor pressure with temperature was found to be 18.96 mm./°C. Using this value, in conjunction with the temperatures calculated from equation (7), the vapor pressures of the solutions were calculated. The ratio (η) of the calculated vapor pressure lowering (Δp_c) to the manometrically measured or maximum vapor pressure lowering (ΔP_{exp}) read from a large-scale plot gives a measure of the efficiency of the method, and the values (100η) are listed in Table 4. Neglecting the first value, it is seen that the efficiency decreases slightly with an approximately 30-fold increase in concentration. The ΔR value for the lowest concentration is the least accurate and the abnormally high efficiency for this solution (greater than 100%) is obviously due to experimental error.

TABLE 4

Experimental and Theoretical Efficiency Data for the Thermo-
electric Measurement of the Vapor Pressure of Diethyl Ether
in the Di-n-Butyl Phthalate-Ether System at 25°C.

m	ave. ΔR	ΔPc	ΔP_{exp}	100η	Δt	Δt_{theo}	100ρ
0.0827	15.1	3.03	2.8	-	0.16	0.14	-
0.2057	32.4	6.64	7.1	93.5	0.35	0.35	100
0.5052	75.2	15.4	16.9	91.1	0.81	0.85	95.3
0.8034	114.4	23.5	26.1	90.0	1.24	1.32	93.9
1.019	141.1	28.8	32.3	89.2	1.52	1.64	92.7
1.481	196.8	39.8	44.6	89.2	2.10	2.29	91.7
2.031	259.4	52.0	58.4	89.0	2.74	3.04	90.1
2.483	308.4	60.3	68.7	87.8	3.18	3.62	87.8

---

m   — molality of di-n-butyl phthalate in ether.

ΔPc — pressure lowering calculated from Δt value and vapor
            pressure of ether.

ΔP_{exp} — experimental vapor pressure lowering as read from
            large-scale plot of experimental data from manometric
            measurements.

η — ratio of ΔPc to ΔP_{exp}.

Δt_{theo} — theoretical temperature lowering calculated from
            modified Iyengar equation.

Δt — actual temperature lowering as calculated from therm-
            istor specifications.

ρ — ratio of Δt to Δt_{theo}.

Reference has already been made to an attempt by Iyengar (19) to calculate the theoretical thermal efficiency of the thermoelectric method. A modified form of this same equation (3) was used to estimate the theoretical efficiency for the ether system studied. Before discussing the results of this calculation, however, a derivation of Iyengar's equation seems appropriate. The following symbols are used throughout the derivation:

p_{11} = solvent vapor pressure at temperature T_1, the steady-state temperature of the drop

p_{12} = solvent vapor pressure at temperature T_2, the steady-state temperature of the solution drop = temperature of thermostat in this case or 25°C

p_{22} = solution vapor pressure at T_2

M_1 = molecular weight of solvent (ether)

m_2 = molality of solute (di-n-butyl phthalate)

a_2 = activity of solute

L_1 = heat of vaporization of solvent per gram

k = thermal conductivity

From the Clausius-Clapeyron equation for the solvent (in its restricted form)

$$\frac{d \ln p_1}{dT} = L_1 M_1/RT^2 \tag{8}$$

and the Gibbs-Duhem equation

$$\frac{1000}{M_1} d \ln p_1 + m_2 d \ln a_2 = 0 \tag{9}$$

one has upon integration and combination

$$(\ln p_{22} - \ln p_{12}) - (\ln p_{11} - \ln p_{12}) = \frac{L_1 M_1 (1/T_1 - 1/T_2)}{R} -$$

$$\frac{M_1}{10^3} \int_0^{m_2} m_2 \, d \ln a_2 \qquad (10)$$

Now let $p_{11} = p_{22} + \Delta p$ and the left member becomes $- \ln (1 + \Delta p/p_{22})$ or upon expanding the logarithm and dropping terms of order higher than the first, $-\Delta p/p_{22}$. On the basis of Langmuir's theory of the evaporation of drops (25), one has

$$\Delta p = k \, R\overline{T} \, (T_2 - T_1)/(M_1 L_1 D_1 \cdot 3.189 \times 10^{-5}) \qquad (11)$$

where $\overline{T}$ is the mean of T_1 and T_2, and D_1 is the coefficient of diffusion of the solvent vapor. Substitution of equation (11) into equation (10) gives finally

$$(T_2 - T_1) = \int_0^{m_2} \frac{m_2 d \ln a_2 \times 10^{-3}}{[L_1/R\overline{T}^2 + kR\overline{T}/(M_1^2 D_1 L_1 p_{22} \times 3.189 \times 10^{-5})]} \qquad (12)$$

The numerical factor comes into equation (11) as a conversion factor for the gas constant R from cc.-mm./°K to cal./°K. From the Gibbs-Duhem equation the numerator in (12) is equal to $1/M_1 \, (\ln p_{12}/p_{22})$, and setting k equal to K (thermal conductivity of air-ether mixture) we have:

$$(T_2 - T_1) = \frac{\frac{1}{M_1} (\ln p_{12}/p_{22})}{[L_1/R\overline{T}^2 + KR\overline{T}/(3.189 \times 10^{-5} M_1^2 D_1 L_1 p_{22})]} \qquad (13)$$

To simplify the calculations the mean temperature was arbitrarily taken to be 25°C. The value of K (equation (13)),

the thermal conductivity of ether vapor in air (17), was cal-
culated on a weighted basis from the ratio of the partial
pressures of the solutions (p_{22}) and air assuming a constant
total pressure of 745 mm. Hg. Values of D_1, the coefficient
of diffusion of ether vapor in air (16), were also computed
for each solution pressure. The second term in the denominator
varies very little over the experimental range and an average
value can be used and combined with the first term. With
these simplifications, equation (13) becomes:

$$\Delta t = 60.8 \log(p_{12}/p_{22}) \tag{14}$$

Using the experimental pressures (read from a large-
scale plot) at the molalities of the solutions used in the
measurements, the theoretical maximum temperature lowerings
were calculated. A comparison of the Δt values calculated
from the thermistor measurements with those obtained from the
modified Iyengar equation showed that the ratio (ρ) varied
from 0.953 to 0.878 (see Table 4). The first two values are
not consistent with the rest and are not included in the
range mentioned above. It is seen that these ratios vary a
little more than the experimental efficiency ratios calculated
on a pressure basis, and also show a decrease with increase in
concentration.

If the thermal conductivity of the vapor space above
the solution were zero, the temperature lowering of the
solvent required to equalize the solvent and solution vapor
pressures calculated from equation (13) with $\underline{K}$ equal zero
is 0.37°C for the 0.206 molal solution compared to the
value of 0.35°C listed in the table and calculated from the

same equation, but taking the thermal conductivity of the vapor
into account. From the experimental vapor pressure of this solu-
tion and the vapor pressure lowering per degree (18.96 mm. Hg) of
the solvent, the calculated temperature lowering of the solvent
required to equalize the vapor pressures is also found to be
0.37°C, comparing favorably with the value calculated assuming
the thermal conductivity is zero. For the most concentrated
solution, the lowering calculated from the equation assuming K
is zero is 3.78°C compared to 3.62°C calculated from the vapor
pressure data on ether and also from equation (13). This larger
discrepancy at the higher concentration may be partially due
to an error in the assumption of a linear vapor pressure-temper-
ature relationship over this temperature range, but probably also
due to the neglect of the terms taking into account the various
ways that heat can be transferred in the system.

Both the modified Iyengar equation (12) for small values of
k and the equation for maximum temperature difference in the
steady state (4) predict that the steady-state temperature lower-
ing decreases as the heat of vaporization of the solvent increases.
However, from the Clausius-Clapeyron equation one has approxi-
mately

$$\Delta t \cong \frac{RT^2 \Delta p}{p \Delta H} \tag{15}$$

and for equal values of Δp and T, one sees that the temperature
lowering of a particular solvent will be inversely proportional
to the product of its heat of vaporization and its vapor pres-
sure. Thus, although water has a molar heat of vaporization
which is roughly 1.7 times that of ether, the much larger

vapor pressure of ether will result in a Δt value which is about 14 times greater for water than for ether. This is in qualitative agreement with experiments involving both aqueous and ether solutions having the same vapor pressure lowerings. The use of the thermoelectric method with solvents of high vapor pressures thus apparently compares unfavorably in sensitivity with its use with solvents of lower vapor pressures, if comparisons are made on solutions of the same vapor pressure lowering; however, a 1 mm. lowering of an ether solution corresponds to a much more dilute solution than does a 1 mm. lowering of an aqueous solution.

SUMMARY AND CONCLUSIONS

The steady-state temperature-differential or "wet-bulb thermometry", method for comparing vapor pressures has been investigated with respect to its suitability for the measurement of solvent activities in solutions of nonvolatile solutes in volatile organic solvents; e.g., diethyl ether. Factors receiving consideration and study have been (1) apparatus and technique, (2) measurement time, (3) precision and accuracy, (4) sensitivity and thermal efficiency.

Five types of cells were studied. The best design was found to be a simple all-glass single-thermistor cell. Solution was placed in the bottom to provide a definite partial pressure of solvent, and solvent was allowed to evaporate from a drop of solvent applied to the thermistor tip through a hypodermic syringe. The drop could be introduced without the necessity of opening the cell which was held at constant temperature throughout the measurement.

It was found that the steady state was reached within approximately 7 minutes after introducing the solvent drop for many of the solutions investigated, but varied considerably from that time for other solutions. The duration of the steady state was a function of the difference in the vapor pressures of the solution and solvent, varying from

ca. 30 minutes for a vapor pressure difference of about 3 mm.
Hg to less than 0.5 minutes for a vapor pressure difference of
about 69 mm. Hg. With a drop size of ca. 0.007 ml. of ether
the duration of the steady state appeared to determine the
highest concentration of solute which could be studied.

A study of double thermistor differential resistance-time
curves showed that the approach to the steady state apparently
depended upon several factors including the proximity of the
other thermistor, and the positioning of the thermistors in
the cell. The single-thermistor design proved most satis-
factory in giving reproducible resistance values for succes-
sively repeated measurements with the same solution sample in
the cell.

In order to provide calibration reference data, the vapor
pressure of ether in the system di-n-butyl phthalate-diethyl
ether was measured at 23 concentrations over the range of
phthalate mole fractions from 0.006 to 0.17 at 25°C. Measure-
ments were made by the conventional manometric vapor-pressure
method, employing alternate freezing and thawing with vacuum
degassing. Solvent and solute activities were calculated for
the measured concentration range. Di-n-butyl phthalate was
found to show negative deviations from Raoult's law in ether.
The vapor pressure is empirically given in terms of the phthal-
ate molality by:

$$P = 536.6 - 33.64m + 2.478m^2$$

The method was evaluated at eight concentrations of di-n-
butyl phthalate in the range of concentrations from 0.08 to

2.48 molal corresponding to vapor pressure lowerings of from 3 to 69 mm. Hg at 25°C. With the exception of the most dilute solution the average of the average deviations in the differential resistance between the solvent and reference thermistors at each concentration was 0.4% or about 0.1 mm. The data were found to be represented by a line of slope 4.38 ohms per mm., except at the highest concentrations where the points lay slightly above the line.

The experimental thermal efficiency of the cell was calculated and found to decrease slightly with increase in concentration over a 30-fold concentration range. The values found were between 93.5 and 87.8%, which are somewhat higher than the 79% value reported in the literature for ether. On the assumption that heat transfer occurs only by conduction through the vapor phase, the theoretical efficiency was also calculated and compared with the experimental values. The ratio was also found to decrease with increasing concentration, the values lying between 0.953 and 0.878 (omitting the first two). Since heat transfer by radiation, convection, and conduction through the leads and the cell wall was neglected, the agreement with theory appears reasonably good. These results show, furthermore, that the single thermistor cell can be operated with a drop of solvent evaporating into a solution-controlled atmosphere whose solvent partial pressure may vary over a comparatively wide range without significant loss of thermal efficiency.

It is concluded that while many of the difficulties encountered with the method have their origin in the extreme volatility of the solvent selected for study (ether), the

method is still subject to a great many unpredictable and uncontrollable experimental variations which affect the precision. The method, therefore, does not seem to have any very great advantage over other methods for the measurement of activities, except possibly in highly dilute solutions.

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