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VAPOR PRESSURE OSMOMETRY AS A MEANS OF DETERMINING POLYMER MOLECULAR WEIGHTS

I. J. GOLDFARB

AIR FORCE MATERIALS LABORATORY

A. C. MEEKS

UNIVERSITY OF DAYTON RESEARCH INSTITUTE

TECHNICAL REPORT AFML-TR-66-80

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FOREWORD

This report was prepared jointly by the Polymer Branch of the Nonmetallic Materials Division and the University of Dayton Research Institute. The work was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena," Task No. 734203, "Fundamental Principles Determining the Behavior of Macromolecules." It was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division. Dr. Ivan J. Goldfarb was the project engineer. The contractual portion of the work with the University of Dayton Research Institute (AF 33(657)-10683) was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734004, "New Organic and Inorganic Polymers" with Mr. E. R. Bartholomew, project engineer.

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This technical report has been reviewed and is approved.

William E. Gibbs

WILLIAM E. GIBBS
Chief, Polymer Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

The application of vapor pressure osmometry to the determination of molecular weights of polymers has been investigated. The principles of the theory and operation of a commercially available vapor pressure osmometer are described and the effects of reading time and drop size are analyzed.

It is shown that, for calibration with benzil in dihydroperfluorobutanol at 65°C, resistance readings reached a maximum after three to four minutes and then declined slowly. Extrapolation to zero time was essential.

It is further shown that drop size variations measurably effect the resistances making it desirable to account for this effect by using a standard drop size and correcting the results accordingly.

Some results obtained for the measurement of molecular weights of samples of polyhexamethylene sebacamide are quoted, and a discussion of potential errors and proper experimental procedures for minimum error is given.

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LIST OF SYMBOLS

SYMBOLS

DPFB	dihydroperfluorobutanol
VPO	vapor pressure osmometer
ΔR	any resistance increment
$\Delta R_{(\text{zero time})}$	resistance obtained by extrapolation to zero time
$\Delta R_{(\text{zero time})}$	resistance at zero time for a drop having a diameter 0.20 cm.
M	molarity of a solution
C	concentration of a solution in g. l ⁻¹ .
γ	activity coefficient or surface tension
a	thermodynamic activity
p	vapor pressure
T	absolute temperature
X	mole fraction of a component in a solution
n	number of moles
ρ	density
K	calibration constant
M	molecular weight

SECTION I

INTRODUCTION

At the present time considerable effort is being expended in the determination of mechanisms of polymer degradation of many types of polymers. For a complete description of what takes place when a polymer degrades, it is necessary to be able to detect, identify and measure small quantities of the degradation products and to measure other changes in physical and chemical properties. By no means the least important of the changes which occur is the change of molecular weight. Molecular weight changes, which are measures of the number of chemical bonds broken in the backbone of the polymer molecule, give a great deal of insight into the precise mechanism of the degradation reaction or reactions.

Therefore it is of utmost importance to be able to make precise measurements of the molecular weight of a polymer both before and after it has been subjected to the degradative environment. A wide range of techniques is available for the determination of both number average and weight average molecular weights but since the interest in this research lies in the number of molecules in the system before and after reaction, only the techniques listed below, which yield number average molecular weight, need be considered.

- (1) End Group Concentrations
- (2) Osmotic Pressure Measurements
- (3) Freezing Point Depression
- (4) Vapor Pressure Depression

Each of these colligative property measurements has its own peculiar advantages and disadvantages over the others. However, the object of this report is to consider only the last method. Measurements of vapor pressure depression as a means to the determination of polymer molecular weights has recently gained popularity (Reference 1) especially since the introduction of a compact, relatively simple instrument for measurement of small changes in vapor pressure. The "Mechrolab" Series 300 Vapor Pressure Osmometer (VPO) was used throughout this investigation. A description of the instrument is given in Section II.

SECTION II

DESCRIPTION OF THE VAPOR PRESSURE OSMOMETER

A sectional diagram of the VPO is shown in Figure 1. The instrument consists of a chamber which can be maintained accurately at a fixed temperature by means of an electrically heated aluminum block (A). The heating block is thermally insulated by polyurethane foam (B) and the whole is held in a steel case (C).

The temperature sensing probe (D) consisting of two matched thermistor beads in close proximity is held centrally in the chamber slightly above a cup of solvent. Six hypodermic syringes (E) in suitable holders enter the chamber through accurately machined holes and are aligned such that drops of solution may be discharged from the syringes directly on to the thermistor beads. A single syringe is aligned with one of the beads and the other five are aligned with the second bead.

The temperature inside the chamber may be controlled at one of several fixed temperatures (37, 65, 100 or 130°C) by means of a thermostat probe inserted into the heating block.

The principle of the method, which will be described in more detail later, consists of measuring the temperature difference between drops of solution and solvent deposited on the beads. This is done by measuring the resistance changes of the thermistors and since they have large temperature coefficients of resistance, a relatively simple Wheatstone Bridge circuit is sufficient to measure very small differences in temperature. Resistance changes may be measured down to 0.01 ohms which is equivalent to a temperature difference of about 10^{-4} of a degree. The two thermistors have carefully matched temperature coefficient of resistance and are connected in opposite arms of the bridge circuit such that the imbalance of the bridge is indicated on a null meter. The resistance difference may be measured by adding resistance to the dekastat to zero the null meter.

The essential circuitry is shown in Figure 2 but in practice it is slightly more refined to permit measurement of the resistance of a single bead to detect temperature equilibrium after initial warm-up.

SECTION III

PRINCIPLES OF OPERATION OF THE VPO

Figure 3 shows the theoretical interpretation of the VPO. The solvent vapor is in equilibrium with the liquid phase at a temperature T throughout the chamber. On one thermistor bead is placed a drop of the pure solvent identical with that in the reservoir and on the other bead is deposited a drop of a solution in the same solvent. If the vapor pressure of the liquid on the solvent bead is exactly the same as the equilibrium vapor pressure of solvent in the reservoir, no net condensation or evaporation of the liquid will take place. This drop will thus attain the temperature of the chamber T° . The vapor pressure of solvent in the solution on the other bead is reduced by the presence of the solute, the degree of reduction being determined by the mole fraction of the solute in the solution. Condensation of liquid from the vapor on to the solution drop will take place as the system attempts to achieve equilibrium of all liquids and vapor in the chamber. In condensing, vapor will deposit its latent heat of vaporization on the drop with consequent increase in the bead temperature and resistance.

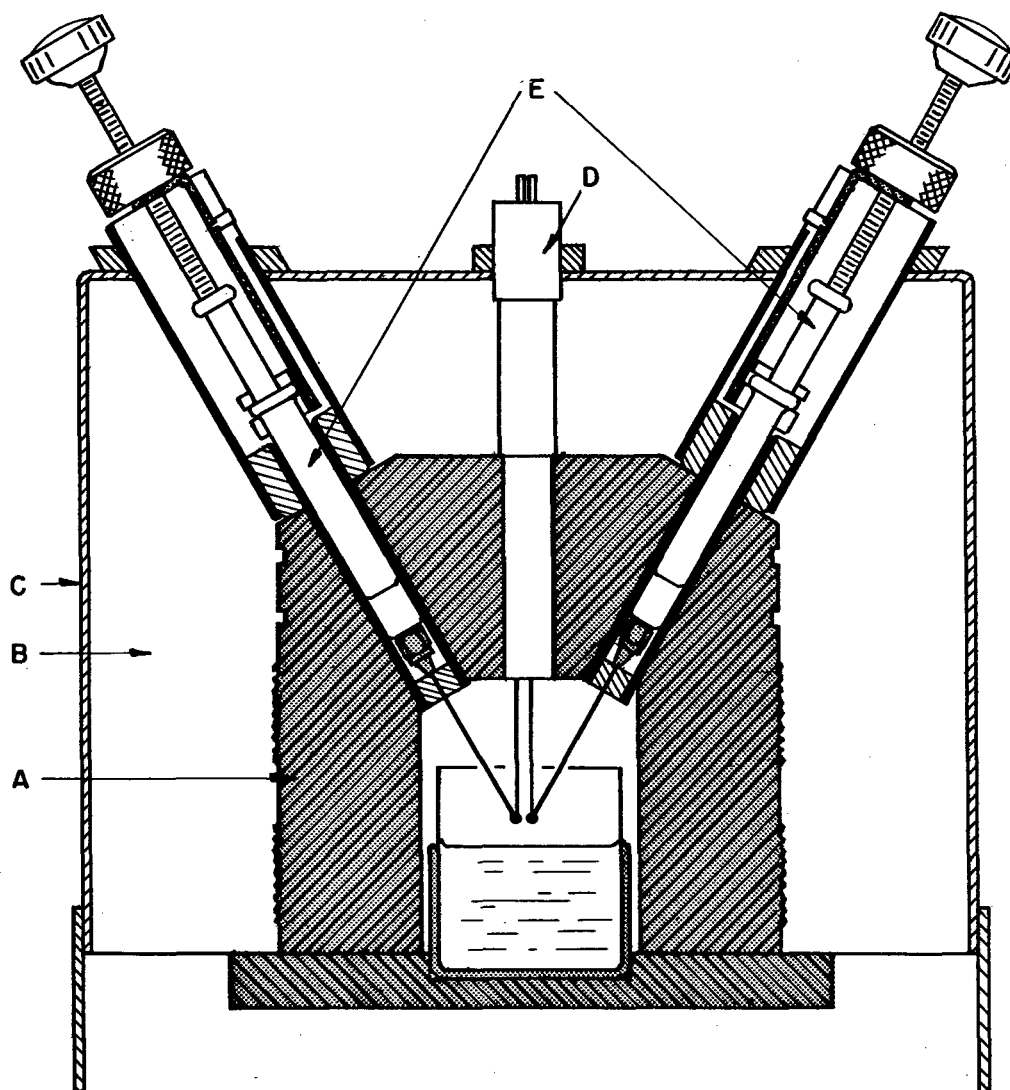


Figure 1. Sectional Diagram of VPO

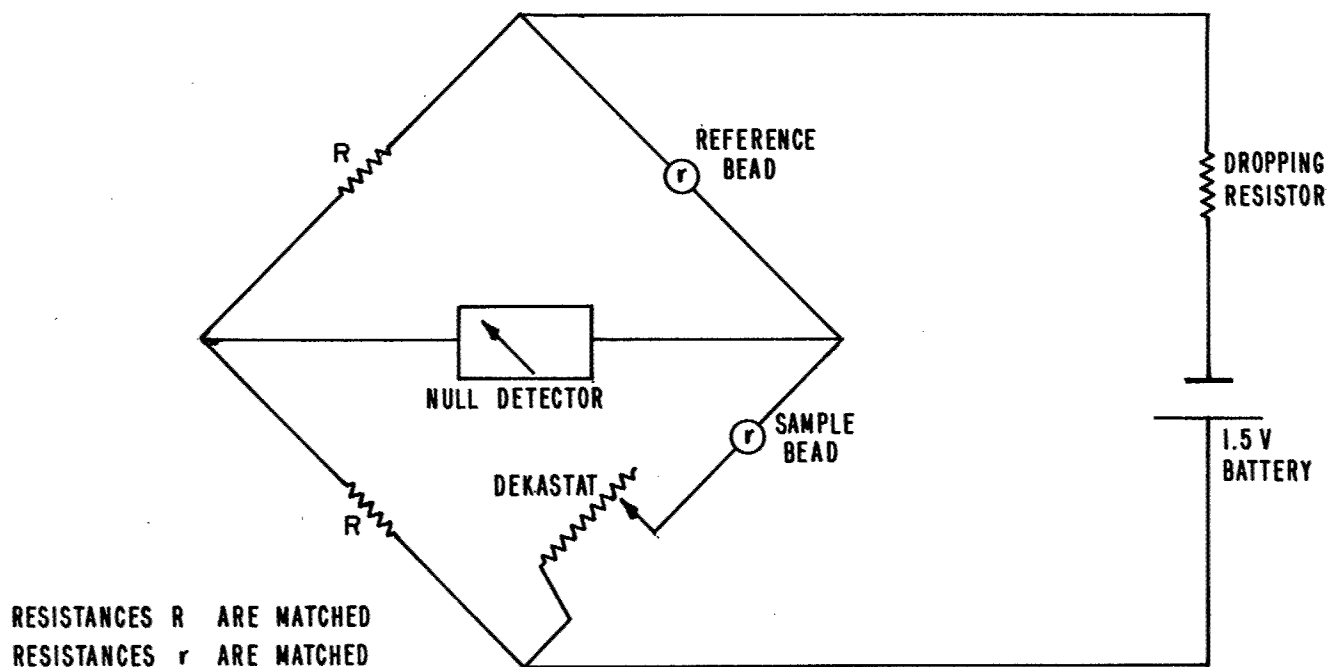


Figure 2. Wheatstone Bridge Circuit

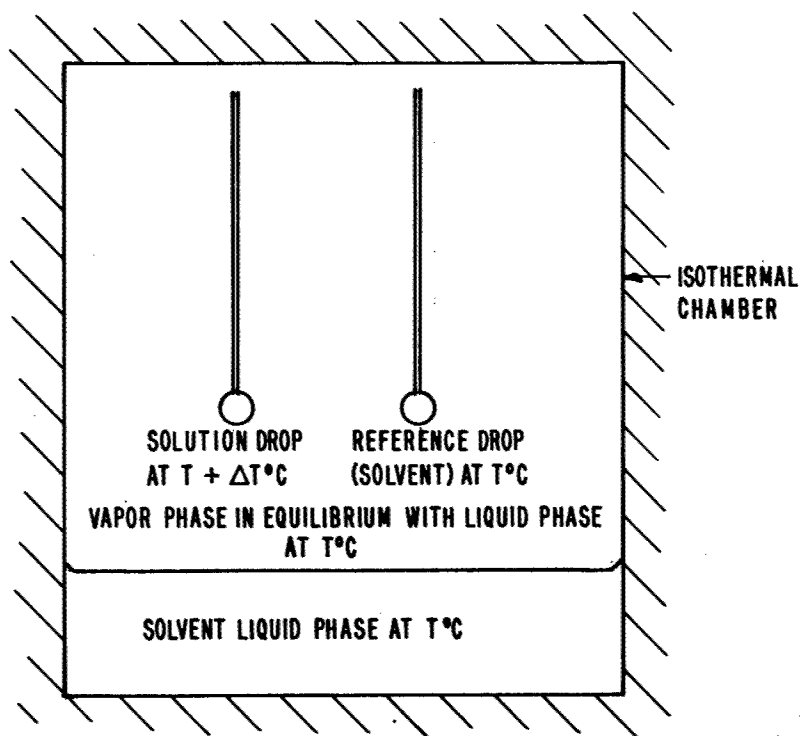
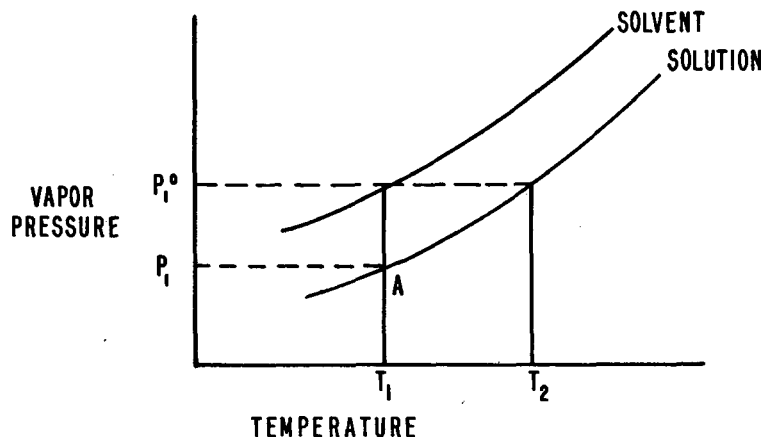


Figure 3. Theoretical Interpretation of VPO

SECTION IV

THEORETICAL ASPECTS OF VAPOR PRESSURE OSMOMETRY

The figure below shows the variation of vapor pressure with temperature for solvent and solution.



If a_1 = activity of solvent in solution at temperature T_1

P_1° = vapor pressure of pure solvent at temperature T_1

P_1 = vapor pressure of solvent in solution at temperature T_1

$$a_1 = P_1 / P_1^\circ$$

Raise the temperature of the solution corresponding to "A" to T_2 at which temperature its vapor pressure becomes equal to that of the pure solvent at temperature T_1 (that is, P_1°). Then the Clausius-Clapeyron equation may be applied to the solution.

$$\ln a_1 = \ln \frac{P_1}{P_1^\circ} = - \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) = - \frac{\Delta H}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

Let $T_2 - T_1 = \Delta T$ and for small ΔT , $T_1 T_2 \approx T_1^2$

$$\ln a_1 = - \frac{\Delta H}{R} \cdot \frac{\Delta T}{T_1^2}$$

or

$$\Delta T = - \frac{RT_1^2}{\Delta H} \ln a_1 \quad (1)$$

The activity of solvent in the solution may be defined by:

$$a_1 = \gamma_1 X_1$$

where γ_1 is the activity coefficient
and X_1 is the mole fraction of solvent
in the solution.

$$\ln a_1 = \ln \gamma_1 + \ln X_1 \quad (2)$$

Since the sum of the mole fractions of the components of a solution is equal to unity:

$$X_1 = 1 - X_2 \quad \text{where } X_2 \text{ is the mole fraction of solute} \\ \text{which is much smaller than } X_1$$

$\ln X_1$ may be expanded:

$$-\ln X_1 = X_2 + \frac{1}{2} X_2^2 + \frac{1}{3} X_2^3 + \dots \quad (3)$$

Assume a relationship between activity coefficient and mole fraction of solute of the following form:

$$-\ln \gamma_1 = AX_2 + BX_2^2 \quad (4)$$

where A and B are constants if temperature is approximately constant.

From Equations 2, 3, and 4

$$\begin{aligned} -\ln a_1 &= (A+1)X_2 + \left(B + \frac{1}{2}\right)X_2^2 + \dots \\ &= A'X_2 + B'X_2^2 + \dots \end{aligned}$$

Since X_2 is small, powers greater than 2 are neglected.

Also
$$X_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1} \quad \text{if } n_1 \gg n_2 \quad \text{where } n_1 \text{ and } n_2 \text{ are the} \\ \text{numbers of moles of solvent} \\ \text{and solute respectively.}$$

and
$$\frac{n_2}{n_1} = \frac{c}{M_2} \cdot \frac{M_1}{1000\rho}$$
 where M_1 and M_2 are the molecular weights of solvent and solute respectively, ρ is the density of solvent and c is in g.l.⁻¹

Finally from Equation 1

$$\begin{aligned} \Delta T &= \frac{RT^2}{\Delta H} \left[A'X_2 + B'X_2^2 + \dots \right] \\ &= \frac{RT^2}{\Delta H} \left[\frac{A'M_1}{1000\rho} \left(\frac{c}{M_2} \right) + B' \left(\frac{M'}{1000\rho} \right)^2 \frac{c^2}{M_2^2} + \dots \right] \end{aligned}$$

Combining constants and since $\Delta T = k \Delta R$

$$\frac{\Delta R}{c} = \frac{k_1}{M_2} + \frac{k_2}{M_2^2} c$$

Thus a plot of $\frac{\Delta R}{c}$ versus c for any solution should yield a straight line having an intercept of $\frac{k_1}{M_2}$ at zero concentration.

If a substance of known molecular weight is used and the results are plotted in the form $\Delta R/\text{molarity}$ against molarity, the intercept will yield the calibration constant K for the particular solvent-solute system. To determine an unknown molecular weight it is necessary to plot $\Delta R/c$ versus c and to divide the intercept into the calibration constant.

SECTION V

DISCUSSION OF THE SYSTEM UNDER INVESTIGATION

The overall objective of this investigation was the elucidation of the mechanism of degradation of polyhexamethylene sebacamide (nylon 6,10). This system raises difficulties with respect to the choice of the solvent that may be used.

Formic acid (88 percent) readily dissolves nylon but also attacks the material of the VPO chamber. Meta-cresol was considered as a likely candidate for use in the VPO and some attempts were made to employ this solvent at 130°C. Considerable difficulties were experienced with drift and so forth and it was later found that the m-cresol vapor had diffused into the syringe guides and attacked the foam insulation around the chamber. Attempts will be made to seal the syringe guides but in the meantime a new solvent that is without effect on the insulation is being used.

Fluoroalcohols of the general formula $CF_3(CF_2)_xCH_2OH$ have been used as solvents for nylon (Reference 2). We had at our disposal a quantity of dihydroperfluorobutanol (DPFB) where $x = 2$, so this was tried as a solvent for nylon 6,10. DPFB would not dissolve appreciable amounts of the polymer at room temperature but would do so at about 70°. The solutions were quite stable at 65°C but on cooling to room temperature, solutions having a concentration greater than about 15 g.l⁻¹ precipitated out slowly. In order to overcome the precipitation difficulty all VPO measurements were carried out not at the usual 37° but at 65°. A bonus of increased sensitivity was provided by the higher temperature.

Before running the VPO with polymer solutions it was necessary to determine the calibration constant K (see later) for the system DPFB at 65°C. Standard solutions of several calibration substances in DPFB were prepared and run but, before discussing the results, it is worthwhile to describe in detail the procedure employed for the purification of reagents and the preparation of solutions.

SECTION VI

EXPERIMENTAL

A. PURIFICATION OF REAGENTS

1. Purification of Dihydroperfluorobutanol

The crude solvent was distilled at atmospheric pressure. Initially a mixture of water and the alcohol distilled over and separated into two distinct layers in the receiver. When approximately a third of the liquid had distilled over, the distillate was clear and was collected. Water was separated mechanically from the first distillate and the remaining alcohol dried with anhydrous magnesium sulphate before being redistilled. The distillate was added to the original pure fraction and the mixture further dried with anhydrous magnesium sulphate before being redistilled. The product (b p 95-96°C, lit. b p 96.5°) was stored in a single bottle to eliminate slight variations from batch to batch as this is said (Reference 4) to affect the molecular weight determination.

2. Preparation of Solutions in DPFb

In most cases only small quantities of polymer were available so small volumes of solution were prepared. Volumetric flasks of 1 or 2 ml capacity were weighed empty and then weighed containing the polymer or the calibration substance. Sample weights were usually only about 0.07 g so careful technique was required to insure precise concentrations. Solvent was added to the flasks and made up to the mark at room temperature.

a. Benzil, benzophenone and benzoic acid dissolved readily.

b. Polymers did not dissolve at room temperature so the flasks were stoppered tightly and heated to about 80°C in an oven until clear solutions were produced. The solutions were kept at about 65°C ready for use in the VPO at that temperature. Care was taken to prevent evaporation of solvent from the solutions but if any did take place the flask was cooled to room temperature, solvent added to bring the level up to the mark and the heating procedure repeated. It was appreciated that the concentrations of solutions changed due to the expansion of the solvent at higher than room temperature but since the same procedure was used for the calibration runs any errors due to this effect should cancel.

3. Purification of Solutes

Since pure compounds are required for good calibration, reagent grade solutes were used. Benzil was recrystallized from DPFb and dried in vacuo.

B. EXPERIMENTAL TECHNIQUES, RESULTS, AND DISCUSSION

1. Calibration

The first step in the determination of the number average molecular weight of an unknown sample is the establishment of a value for the calibration constant K by measuring the resistance increments for a series of solutions of a standard molecular weight material. Benzil was chosen for the initial experiments.

The technique recommended by the instrument manufacturer for obtaining ΔR values is to take the reading at the same fixed time, say 2 minutes, after deposition of the drop on the solution bead. If the reading at 2 minutes is reasonably stable the value of ΔR is recorded.

To establish the applicability of a 2 minute reading (or some other time) for the present system it was necessary to plot a ΔR versus time curve. The procedure adopted was as follows:

a. Drops of pure solvent were deposited on both beads and after three to four minutes the null detector was set to zero deflection by means of the zero potentiometer. This zero was periodically rechecked and adjusted if necessary. Often up to 30 minutes were required to establish an invariable zero point.

b. A drop of the solution having the lowest concentration was deposited on the solution bead displacing the solvent bead into the reservoir. Three or four more drops were deposited allowing each drop to remain in place for several seconds in order to effectively wash the bead. A stop watch was started immediately after the final drop was in place and ΔR readings were taken every 30 seconds for up to 15 minutes. Usually readings could not be taken for the first one to two minutes since the temperature of solution drops was below that of the solvent bead. As soon as the solution drop reached and exceeded the solvent drop temperature readings could be made. Some typical ΔR versus time curves are shown in Figure 4. Portion A-B of the curve represents the solvent drop increasing its temperature above the other drop and reaching a maximum at B. Condensation continues to take place but as the drop becomes diluted the rate of heat deposition declines. Since heat is continuously removed from the drop by conduction along the thermistor bead, the actual temperature falls slowly corresponding to B-C on the curve. The rate of decline is greater with the higher concentration solutions.

Obviously, it would not be satisfactory to take a two minute reading or any other time for that matter, since the position on the curve at any given time depends upon the concentration of the solution. Therefore it is most appropriate to extrapolate the linear part of the curve C-B back to the ΔR axis to obtain the ΔR (zero time) reading for each solution.

Graphs of the type shown in Figure 4 were obtained in all cases where ΔR values exceeded about 5 ohms so this technique was employed. When ΔR values were small the linear part of the curve (C-B) was usually parallel to the time axis so this maximum value of ΔR could be used.

After several solutions had been run using DPF as the solvent, it became clear that the reproducibility of the ΔR versus time plots was not satisfactory. Readings of three or more consecutive drops of the same solution often gave ΔR values differing by 10 - 30 percent. It was thought that insufficient washing of the beads was the cause so experiments were repeated taking care to use six or more drops of solution for washing even when replacing a drop by another of the same solution. It was realized that any liquid in the needle tip would undergo dilution in the same way as the sample drop; the use of many washing drops assured removal of this diluted solution.

The adoption of this procedure did improve the results but a disturbing irreproducibility was still evident. Variation in drop size seemed to have some effect on the ΔR values and this was looked into further. The question of drop size variation has been mentioned by the instrument manufacturer (Reference 3) in the following terms:

"drop size has no effect on readings except in extreme differences such as may be possible with a solvent with a very high surface tension" but it was suggested that drops be gauged by "approximately doubling the size of the dry thermistor bead."

In spite of this an experiment was conducted with a benzophenone solution, making deliberate variations in the sizes of drops.

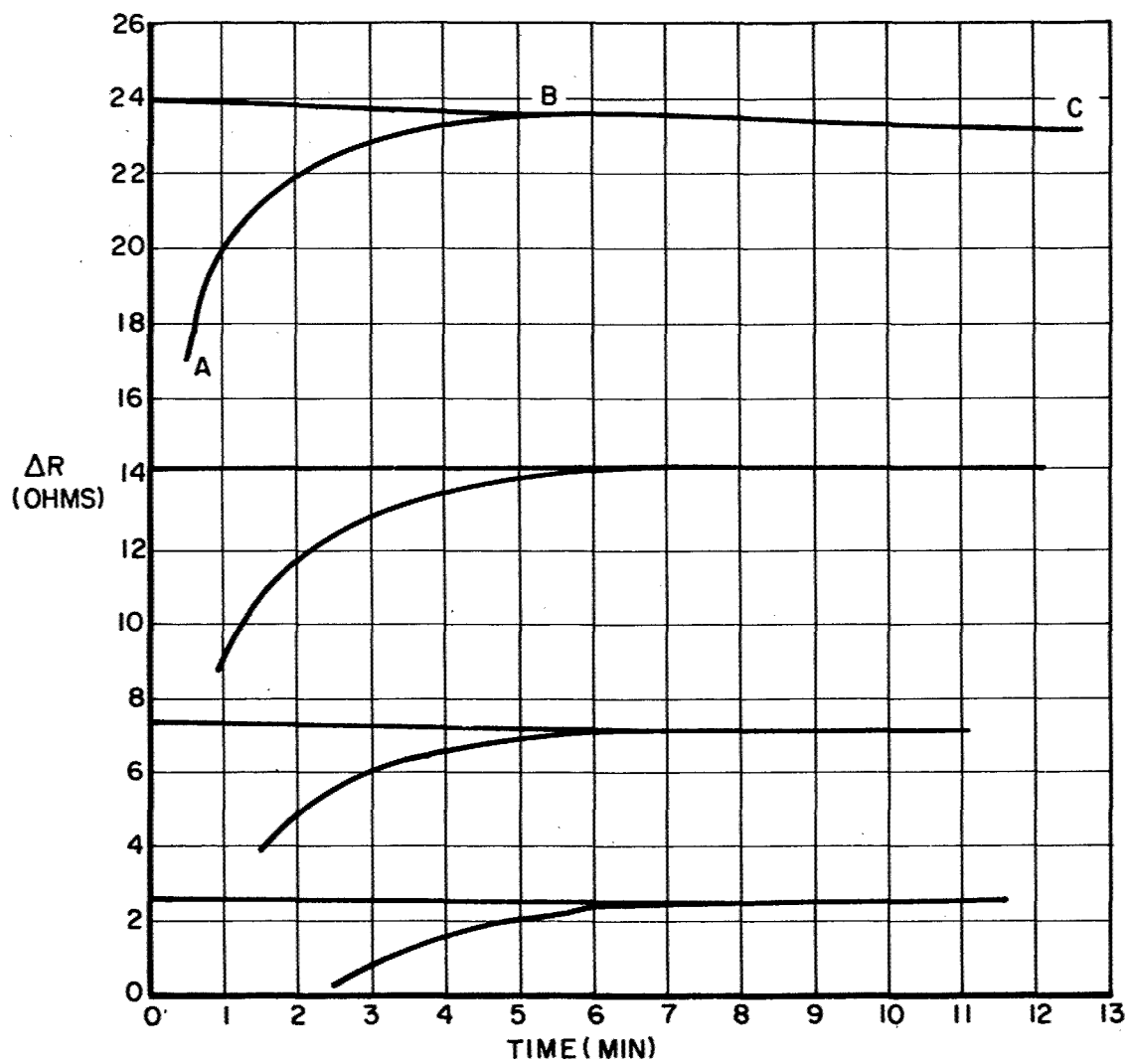


Figure 4. Representative Plots of ΔR versus Time

2. Drop Size Variations

The size of the drop placed on a bead could be varied between quite wide limits with the extreme cases being:

- a. A very large drop which was rather unstable and would readily fall from the bead.
- b. A very small drop which just wetted the surface of the thermistor (See Figure 5). With a little care it was possible to choose the size of the liquid drip deposited.

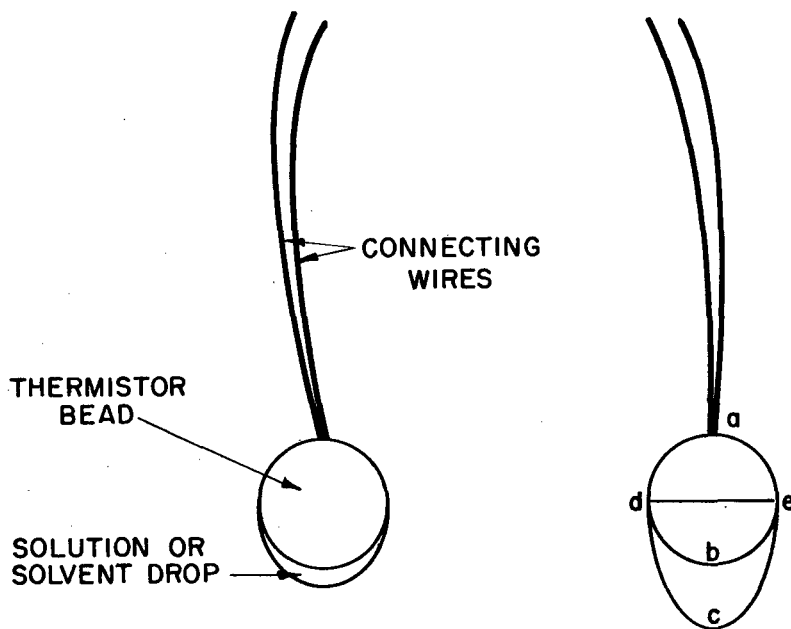


Figure 5. Thermistor Beads

In this drop size experiment ΔR versus time plots were determined for each of seven sizes of drops the sizes being estimated by the eye as large, medium, small, and so forth. The results obtained are shown in Figure 6. It is immediately apparent that drop size has a profound influence on the ΔR versus time relationship and on the ΔR (zero time) value. It should be noted that the largest and smallest drops used here were extreme sizes and would never have been used for other determinations. However, most of the drops represented on this graph might have been considered acceptable for use before drop sizes were considered.

In order to obtain more precise data it is necessary to measure the sizes of drops used in further experiments and to correct for their influence in some way. The drop size could be measured in several ways but the most meaningful measurement seems to be the total height of the bead plus the drop. Figure 5 shows an enlarged view of two beads; one retaining a large drop and the other, a small one.

The width of the drop d-e is very close to a-b which is constant and equal to the diameter of the thermistor itself. However, the length b-c is very dependent upon the quantity of liquid in the drop. Since the position of b is difficult to locate the drop size is conveniently measured by the length a-c.

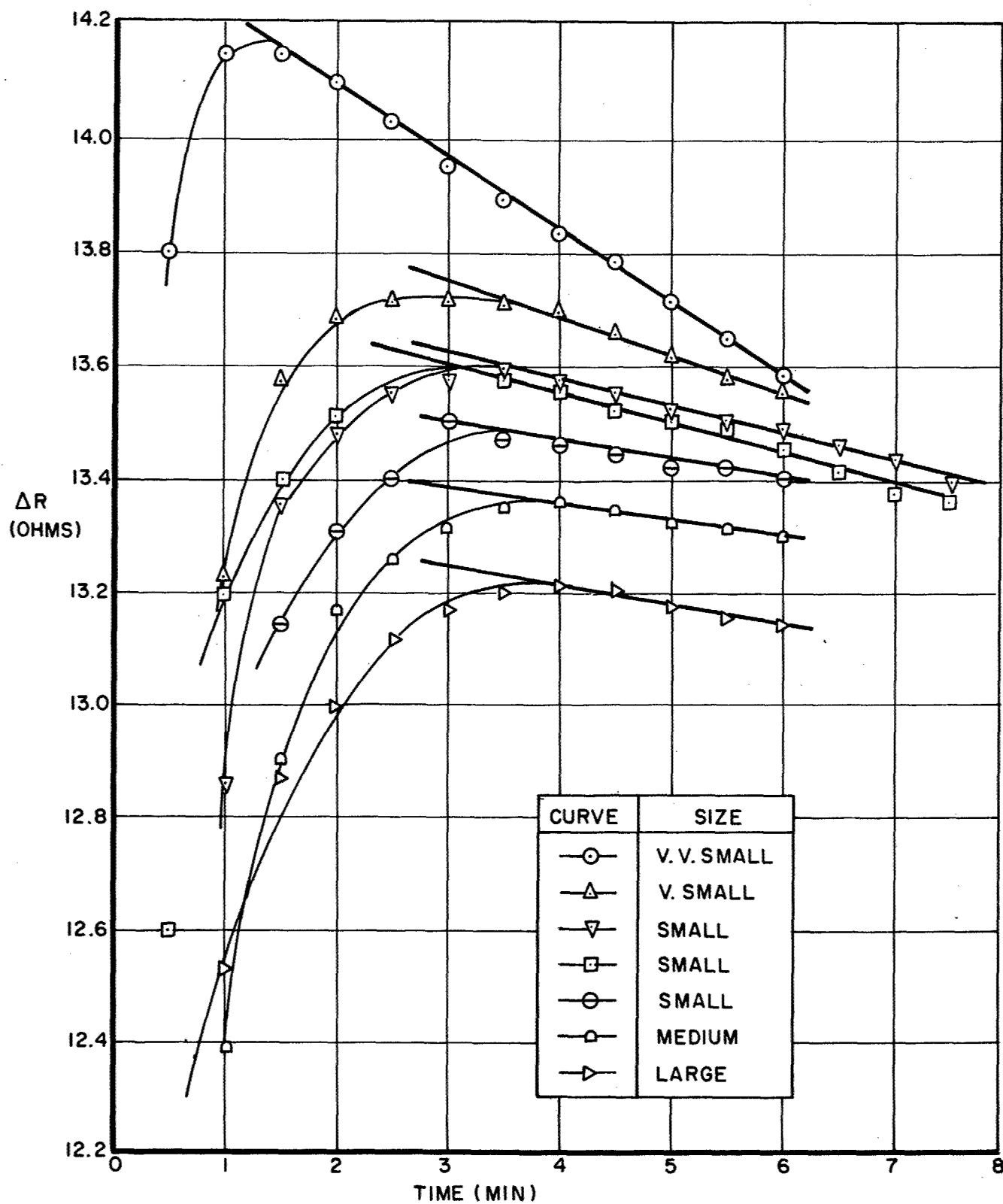


Figure 6. ΔR, versus Time for Several Drop Sizes

Figure 7 shows the set-up used to measure ΔR by means of a cathetometer. At one stage a lens system was designed to display the drops magnified on a screen but the light source sufficient for an adequately illuminated image had an adverse heating effect on the beads and had to be abandoned.

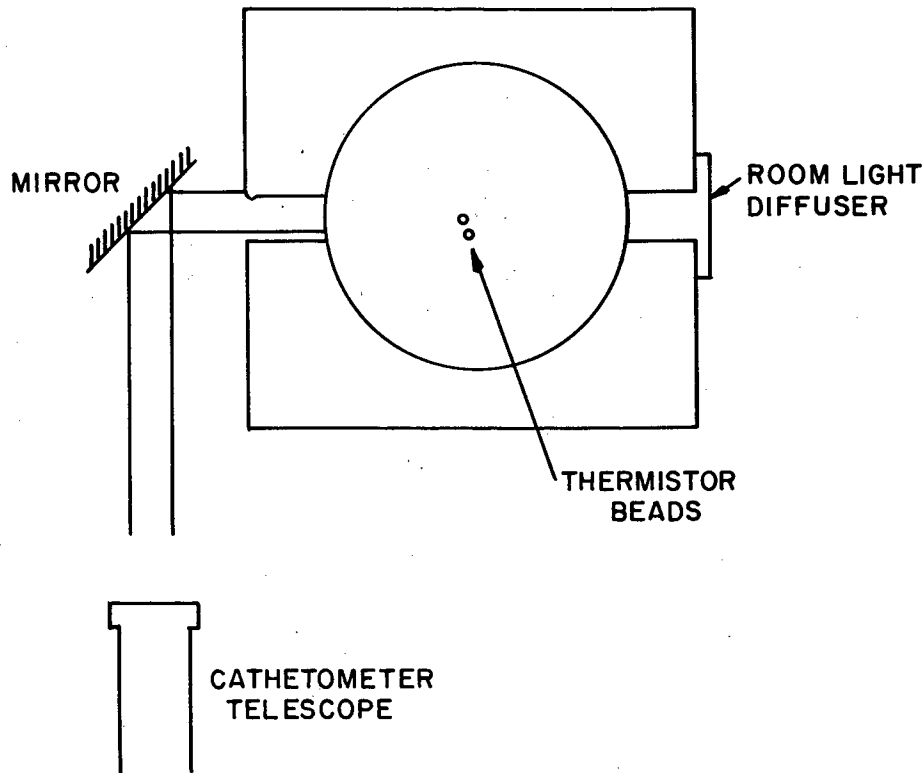


Figure 7. Drop Size Measurement Arrangement

Sizes usually ranged from 0.18-0.28 cm (diameter of the thermistor, dry = 0.15 cm) and were measured to the nearest 0.005 cm.

Figure 8 shows a representative plot of drop size versus ΔR (zero time) and it is noted that the relationship between the two may be adequately represented by a straight line. To standardize measurements from one solution to the next, a standard drop size had to be decided upon. Many of the drops measured had sizes close to 0.20 cm so this was used as the standard size throughout the measurements.

3. Summary of Measurements Required to Determine ΔR for a Solution

- a. Plot ΔR versus time for each of several drops of measured size.
- b. Extrapolate the linear part of the curve to the ΔR axis to determine ΔR (zero time)
- c. Plot ΔR (zero time) against drop size.
- d. Read off from this graph a value of ΔR at a predetermined drop size (usually ΔR (0.20)).

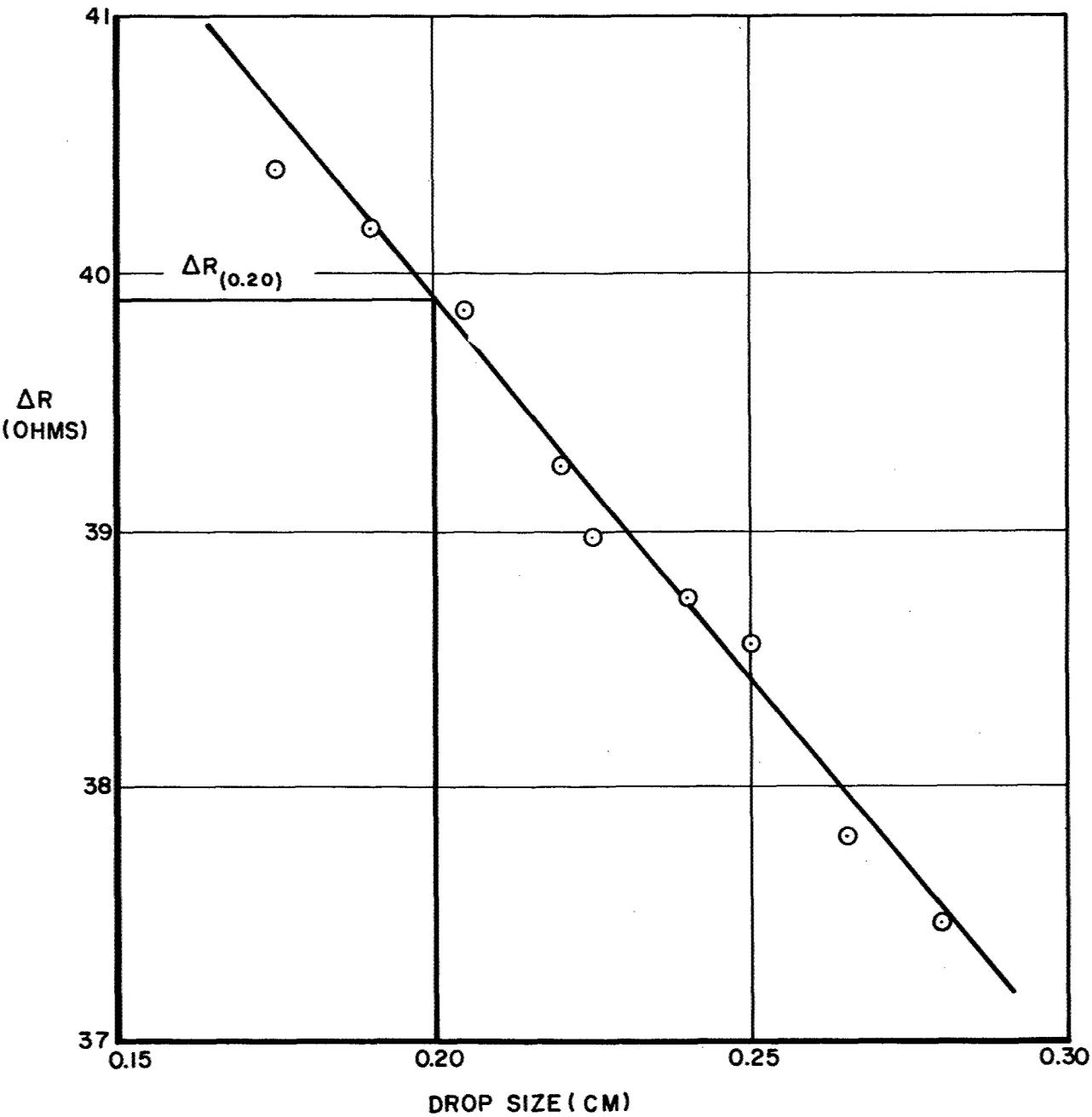


Figure 8. Plot of ΔR (zero time) versus Drop Size

Using these techniques, three calibration substances (benzil, benzophenone and benzoic acid) were run and the results obtained with the first two compounds are shown in Figure 9. With benzil and a drop size of 0.200 cm K was found to be 395 and with benzophenone (0.230 cm drop size) it was 393. Benzoic acid yielded the anomalously low value of 290. This we attribute to association of benzoic acid to the extent of 15 percent in dihydroperfluorobutanol at 65°C.

Table I shows the values of K obtained from different drop sizes using benzil as the standard solute. The calibration constant varies about 4 percent for extreme drop sizes from 0.200 to 0.280 cm.

4. Discussion of Drop Size Variation

It might be reasonable to suppose that drop size variations would be without effect on the vapor pressure of a solution.

It has been shown, however, that when a liquid drop is very small, the vapor pressure rises above the equilibrium vapor pressure of the bulk liquid. Kelvin has derived a theoretical equation (Reference 4) which relates vapor pressure to the radius of curvature of a liquid surface.

The equation may be written:

$$\Delta p = \frac{2\gamma}{r} \frac{\rho'}{\rho - \rho'}$$

where Δp = change in vapor pressure

γ = surface tension of the liquid vapor interface

ρ' = density of vapor

ρ = liquid density

Since the density term is quite small, Δp will only become appreciable when r is very small, for example, for a drop of radius 10^{-4} cm the increase in vapor pressure is of the order of 0.1 percent. Drops used here had radii of about 0.1 cm so the increase in vapor pressure is correspondingly less. Even minute vapor pressure changes may bring about measurable temperature changes of the beads and calculations are now being made to determine whether this is so. If it is assumed, however, that these drop sizes do not appreciably alter the vapor pressure some other explanation must be put forward for the drop size effects.

Consider the simplified case of a drop of liquid in the form of a sphere of radius r .

$$\text{The surface area is } 4\pi r^2 \quad (a)$$

$$\text{The volume is } \frac{4}{3}\pi r^3 \quad (b)$$

The total rate at which vapor condenses on the drop will be proportional to the surface area hence the rate of deposition of heat will also be proportional to the surface area.

From (a) rate of heat deposition = $k_1 r^2$ where k_1 is a constant.

If this heat is dissipated only in heating the entire mass of the drop and none is lost by conduction and so forth, the temperature rise will be proportional to H/volume where H is the rate of heat deposition.

$$\text{That is, } \text{temperature rise} = \frac{H}{k_2 r^3} = \frac{k_1 r^2}{k_2 r^3} = \frac{\text{surface area}}{\text{volume}} = \frac{k_3}{r}$$

TABLE I
DROP SIZE STANDARD VERSUS K

DROP SIZE (CM)	CALIBRATION CONSTANT K
0.20	395.0
0.22	391.3
0.24	387.7
0.26	384.2
0.28	380.8

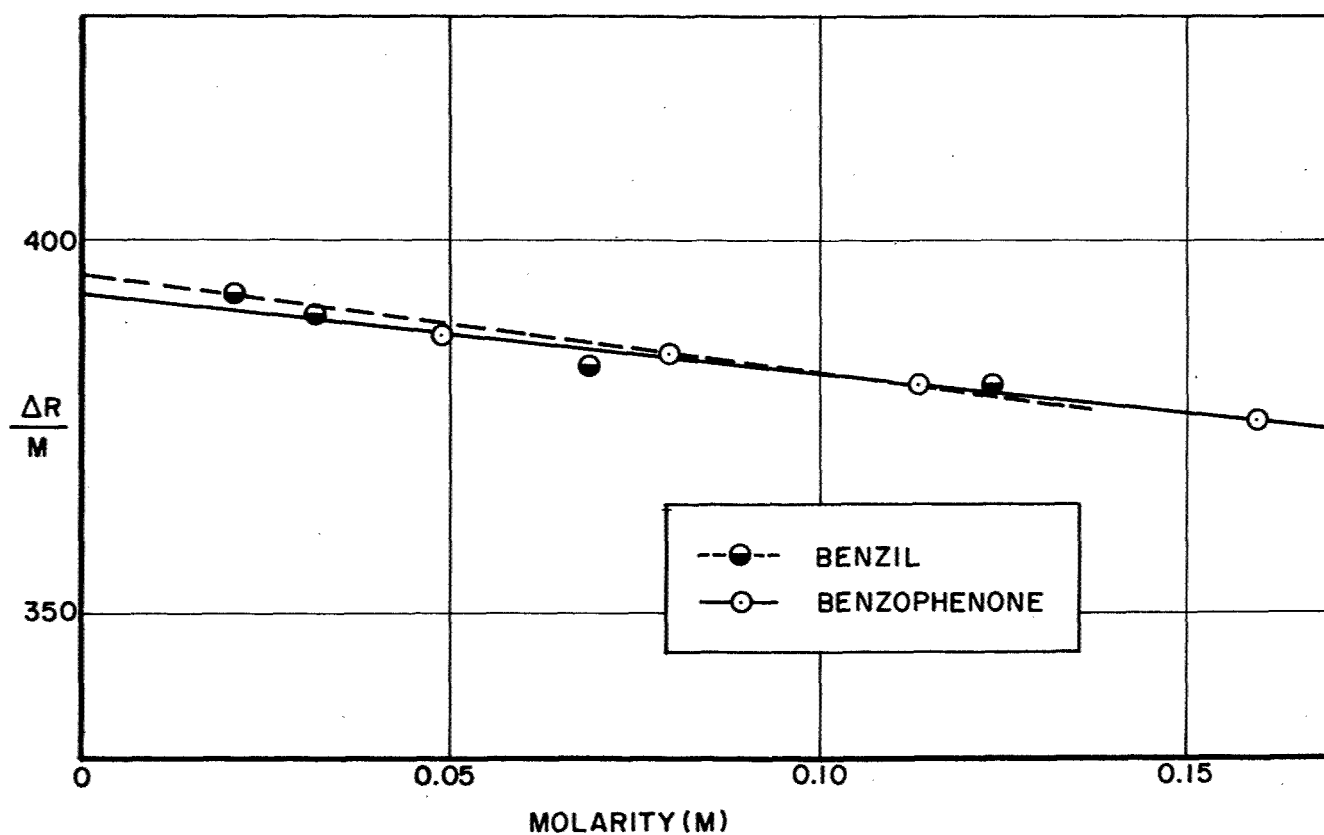


Figure 9. Final Plot $\Delta R/M$ versus M for Different Solutes

Temperature rise is equivalent to resistance increase, therefore it is predicted that the resistance measured will increase as the radius of the drop is decreased. This conclusion is in qualitative accord with the experimental findings for some of the solutions measured. Reference to Figure 6 shows, however, that as the solution concentration is decreased the slopes of the drop size versus ΔR plots change from large negative values to small positive values passing through zero slope. This may be explained if it is assumed that the temperature of the drops is always greater than the temperature of the vapor in the chamber. If this is true, slight evaporation will take place from both the solution drop and the solvent drop. In the case of the solution drop this evaporation may or may not be balanced by the condensation of solvent on to the drop. If the heating effect due to condensation outweighs the cooling effect of the drop evaporation, that is, when solution concentration is sufficiently high, the resistance measured by the bridge circuit will increase as the drop size decreases as explained previously. When lower concentration solutions are employed condensation is not sufficient to balance evaporation and the sign of the slope of ΔR versus drop size changes. Thus there will be a unique condition under which these two effects cancel and there is no size effect. For the present system this occurs with a 2×10^{-2} M solution drop.

Each thermistor bead has a small but finite current flowing through it, the resistance to the passage of this current being a measure of the temperature of the bead. This current flow increases the temperature of the bead and thus of the drop. Therefore the initial postulate that the beads are at a higher temperature than the vapor in the chamber is not unreasonable.

The actual situation existing here is, of course, somewhat more complicated since the sample drops are not spheres but coatings on an inert bead. Also heat will be dissipated from the drops by conduction through the beads to the thermistor wires. For these reasons it is possible only to give this qualitative picture of the drop size effects.

It is evident from an inspection of Figure 10 that the slopes of the drop size curves increase as the concentration (and thus the $\Delta R_{(0.20)}$ value) increases. Figure 11 shows the variation of the slope with changes in $\Delta R_{(0.20)}$. The following points should be noticed on this graph.

- a. The plot is characteristic of the solvent alone and not of the solute. Points obtained with several solutes all fall approximately on the same straight line.
- b. The straight line does not pass through the origin but cuts the $\Delta R_{(0.20)}$ axis at about 4 ohms. Thus it may be predicted that the slope of the $\Delta R_{(0.20)}$ versus drop size curve will be zero for solutions which give a $\Delta R_{(0.20)}$ value close to 4 ohms. Also when $\Delta R_{(0.20)} = \text{zero}$, that is, when both drops are pure solvent the slope of the plot of ΔR versus drop size will have a small but finite value. This value should be about 4 ohms per cm.

The next experiment performed was designed to test the effects of drop sizes on the zero point of the instrument. The procedure for zeroing as recommended by the manufacturer had already been described but that employed here is described in the following section.

5. Zero Point Measurements

The following technique was devised. Drops of pure solvent of approximately equal size were placed on both beads and allowed to equilibrate thermally for about 15 minutes. The dekastat was set to 10.00 ohms and the balance control operated to null the meter reading. Next a new drop was placed on one of the beads and after equilibrium the ΔR value was determined and the two drop sizes measured. This was repeated several times changing both

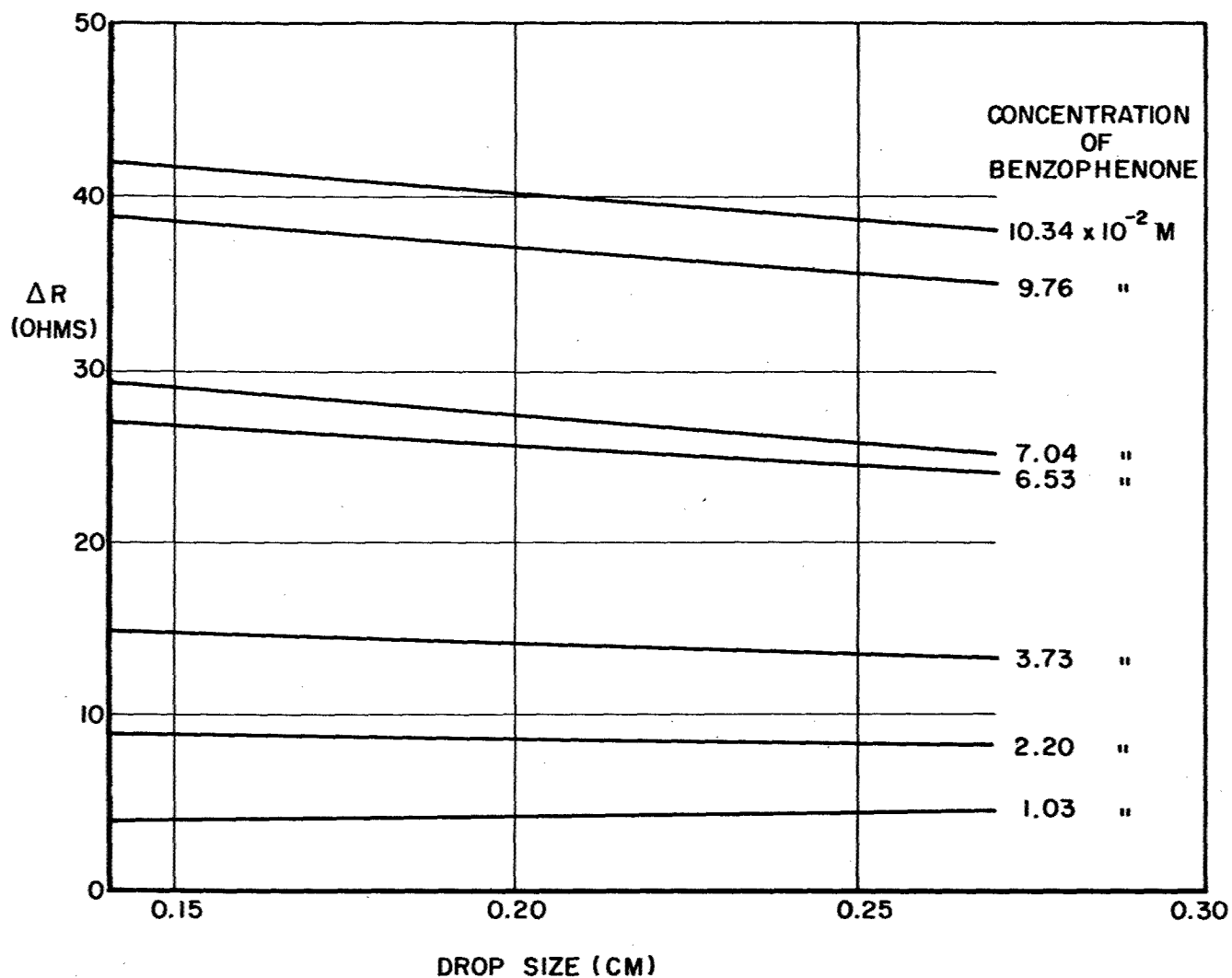


Figure 10. Drop Size Curves for Several Concentrations

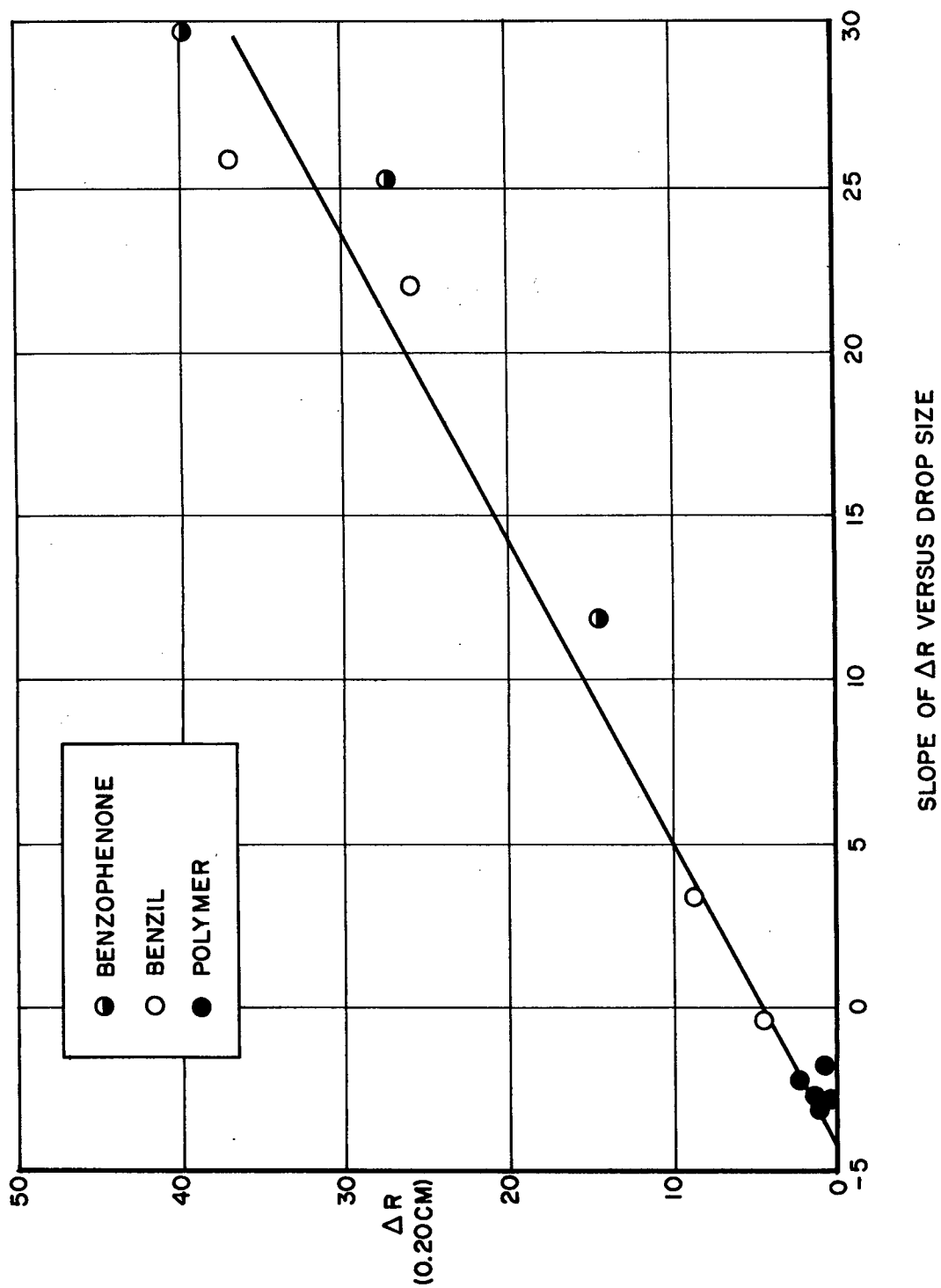


Figure 11. Plot of $\Delta R_{(0.20)}$ versus Slope of Drop Size Curve

drops and corresponding drop sizes and ΔR values recorded. Results are plotted in Figure 12 in the form ΔR versus the difference in drop size. This graph shows beyond doubt that the variation in solvent drop sizes even affects the zero point. The slope of the line is $2.4 \Omega \cdot \text{cm}^{-1}$; therefore if the drops differ in size by as little as 0.01 cm, the zero will be off by about 0.02Ω . The value of the slope is in quite good agreement with the predicted value of $4 \Omega \cdot \text{cm}^{-1}$.

6. Use of Other Solvents

Dihydroperfluorobutanol might be considered to be an "exotic" solvent so it is desirable to investigate the applicability of these conclusions with other solvents. Perhaps the widest use is made of benzene so this solvent was looked into.

It is not necessary to repeat the procedures used, suffice it to say that exactly the same measurements were made with benzene and all of the effects evident with DPFB were found to apply to benzene run at 37°C in a second VPO chamber.

The slope of the graph corresponding to Figure 12 was approximately half in the case of benzene ($1.25 \Omega \cdot \text{cm}^{-1}$) so the equivalence of drop sizes when zeroing with this solvent is less important. It is not possible to give definitive reasons for the difference but it may be due to either or both of the following causes:

- a. Differences in surface tension between DPFB and benzene.
- b. Differences in temperature and/or the latent heat of vaporization both of which change the sensitivity $T^2/\Delta H$.

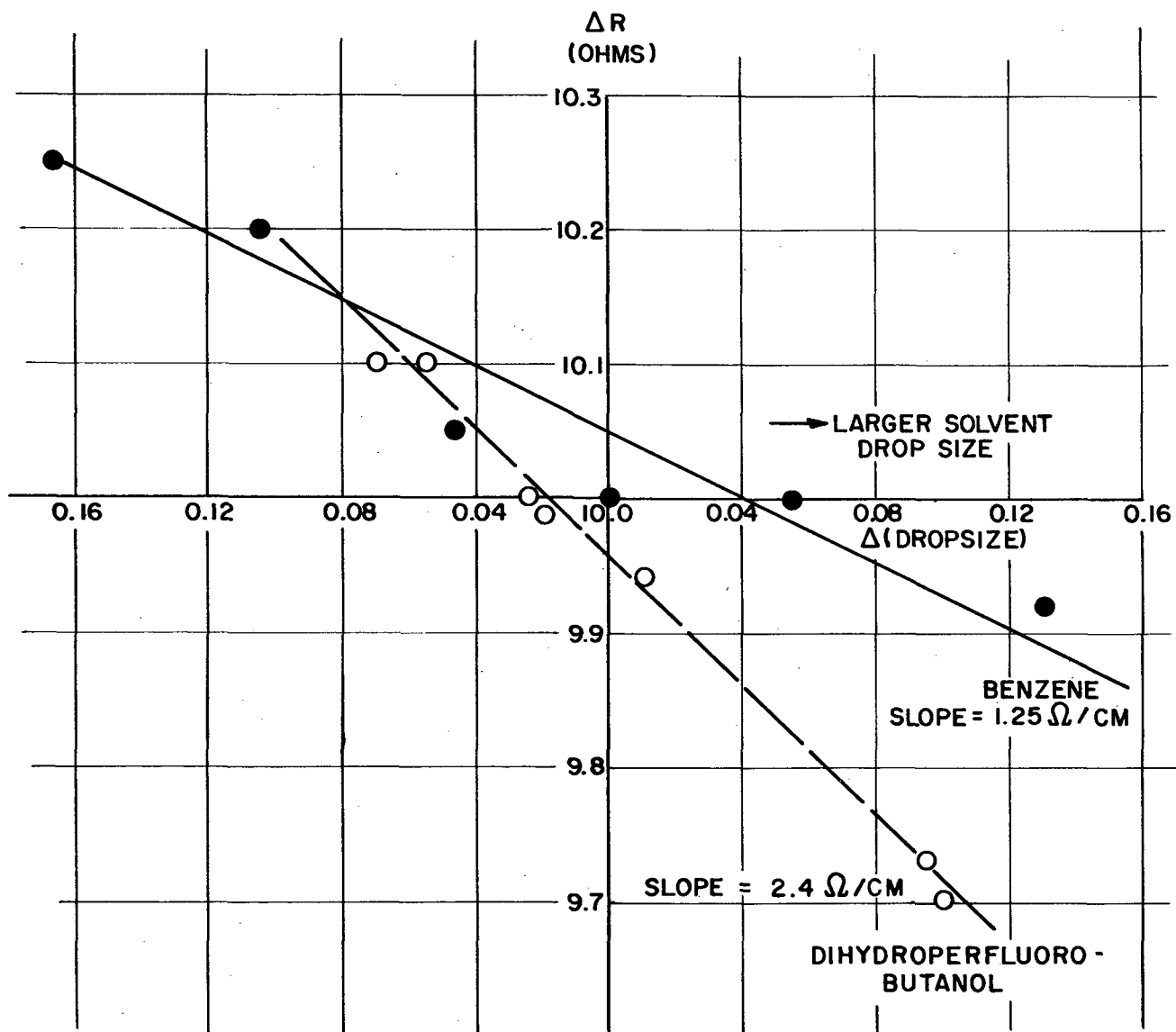
There is every reason to expect that this is a general phenomenon which occurs in all solvents to a lesser or greater degree. It may be possible to extend this work to other systems. All the previous lengthy discussion has been limited to the initial calibration of the instrument. Once a value had been assigned to K it was possible to go ahead with polymer molecular weight determinations.

7. Measurement of Polymer Molecular Weights

The preparation of solutions of nylon 6,10 in DPFB has already been described. For these determinations three or four solutions of approximate concentrations 4, 8, 12 and 16 g.l⁻¹ were prepared. In order to lessen disturbance of the thermal equilibrium in the chamber when a syringe was put in the block, a syringe preheater was constructed.

Syringe Preheaters

An aluminum block 15 cm in diameter and 14 cm high was drilled with 7 holes to accept syringes in their holders. See Figure 13. The exterior of the block was covered with a layer of asbestos moulded into place. A heating element of about 15 feet of 20 gauge nichrome wire was wound around the insulation and then covered with a final layer of asbestos. The power input to the heating coil was varied by a rheostat and temperature control was effected by means of a "Therm-o-Watch" controller. Syringes were placed empty in the heater block and warmed to about 67°C. Then they were filled with the hot polymer solutions and returned to the block for about 15 minutes prior to being placed in the VPO. In this way it was possible to prevent both cooling of the VPO and precipitation of polymer in the syringes.

Figure 12. Drop Size Difference versus ΔR for Zero Point

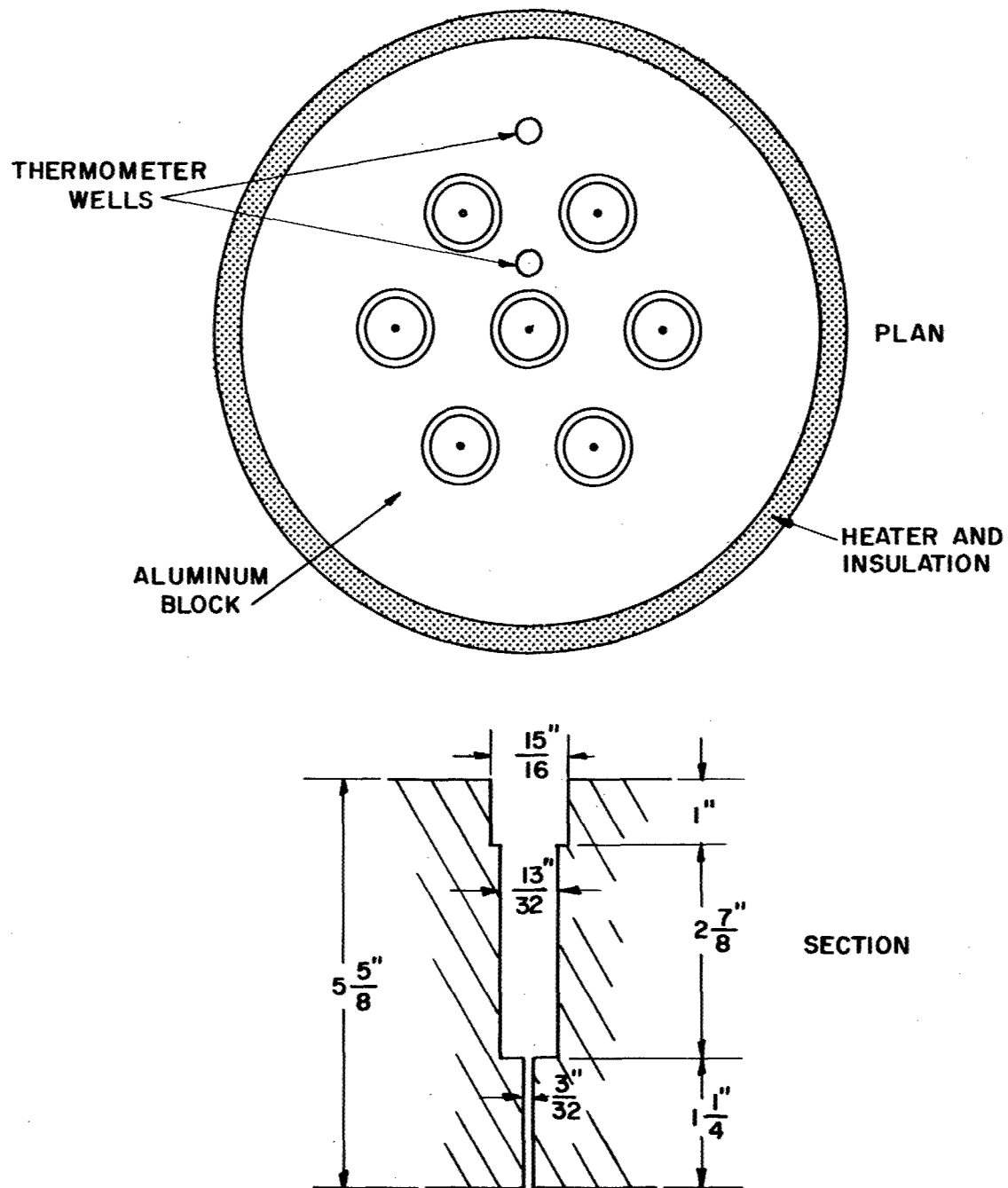


Figure 13. Syringe Preheater

Method

The instrument was zeroed using equal sized drops of solvent on the beads then measurements were made on three or four different sized drops of each solution. The usual graphs of ΔR versus time and $\Delta R_{(\text{zero time})}$ versus drop size were plotted. A typical set of results is shown in Table II and the corresponding $\Delta R/C$ versus C plot is shown in Figure 14. The number average molecular weights of the samples represented a range from 5.3 to 15.5×10^3 .

8. Errors Involved in Non-Consideration of Drop Sizes

Many of the effects described in this report may be considered to be small so it is worthwhile to consider how important correction of these effects is to the final molecular weight.

a. Calibration

Since the calibration is the starting point for the determination of all molecular weights it is obviously desirable to determine the value of the constant K as precisely as possible by removing or accounting for as many of the variables which affect the system as possible. It has been established that ΔR values may differ up to 4 percent using slightly different sized drops (for the dihydroperfluorobutanol system) so correction of this is essential. The real test is the difference between the $\Delta R/M$ versus M plots obtained considering and neglecting drop sizes. In the former case the points all fall closely near the best straight line (mean deviation not greater than $1/2$ percent of the $\Delta R/M$ value). However, the points obtained when drop sizes are neglected usually give a much poorer line, the mean deviation being 1 percent or more. The K values for a typical set of results differed by 2 percent.

b. Sample Measurement

With high molecular weight materials very low ΔR values are obtained and the variation with drop size can be as much as 15-20 percent. Therefore correction for this effect is quite important.

It may not be necessary to measure drop sizes in order to correct for variations, all that is really necessary is to fix the size as accurately as possible. Since no satisfactory method has been devised to do this and it is very difficult to hang equal sized drops successively on the beads we consider it highly desirable to measure drop sizes of at least three different drops (large, medium and small) and to follow the procedure previously outlined.

TABLE II
TYPICAL RESULTS

ΔR Zero Time	Drop Size (cm)	ΔR At 0.20 cm Drop Size	Molarity of Solution M	$\frac{\Delta R}{M}$
8.00 8.06 7.91 7.86 7.78 7.70	0.195 0.215 0.235 0.250 0.285 0.285	8.04	0.02048	392.6
12.44 12.11 12.02	0.200 0.215 0.225	12.35	0.03168	389.8
25.97 25.71 25.36 25.11	0.215 0.240 0.260 0.270	26.29	0.06862	383.1
46.67 45.68 46.00 46.08 45.86 44.38	0.200 0.215 0.220 0.220 0.225 0.275	46.87	0.1232	380.4

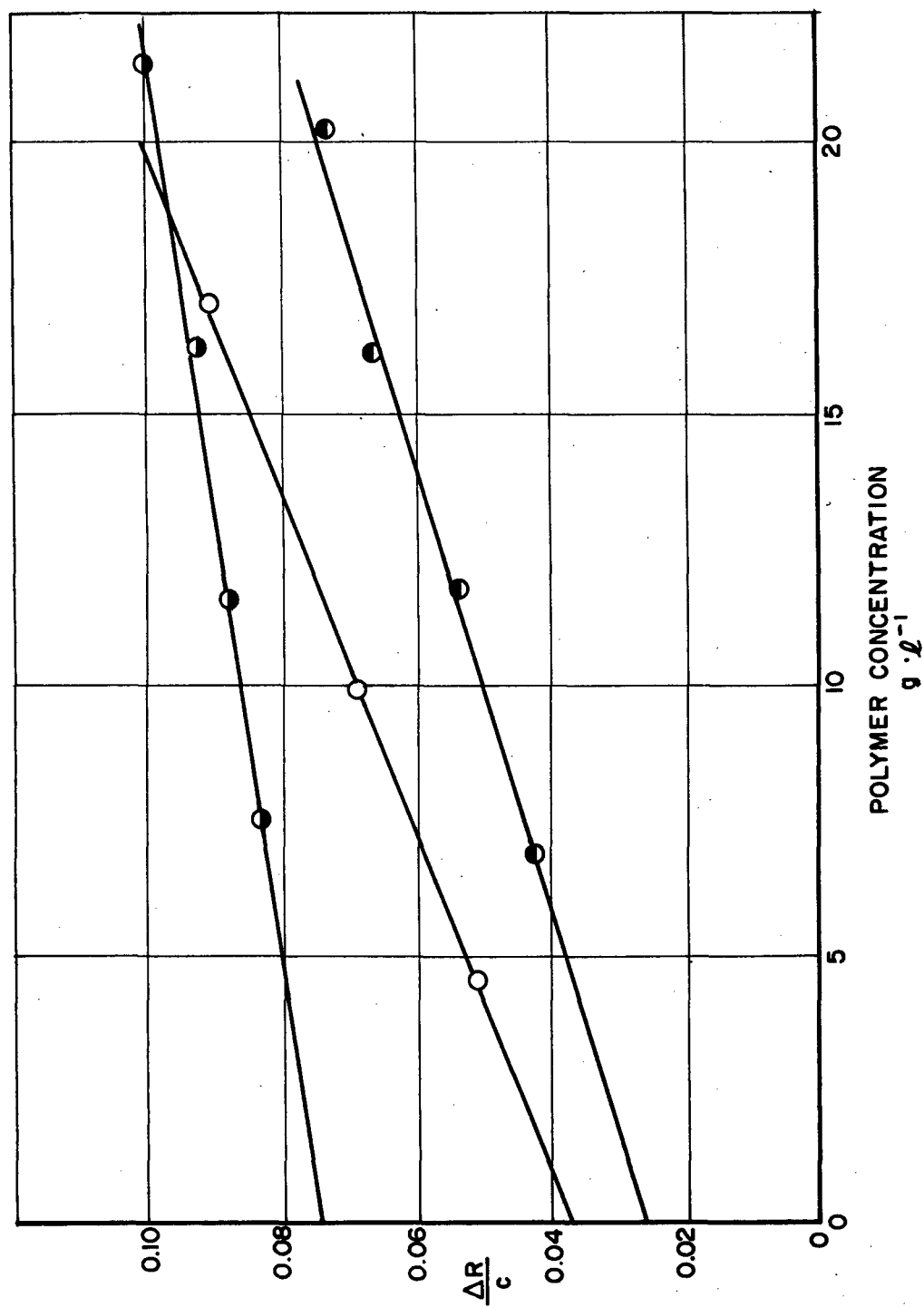


Figure 14. Representative $\Delta R/C$ versus C Plots for Polymers

SECTION VII

CONCLUSIONS

In light of the previous discussion it is contended that consideration should always be given to the drop size question whenever a new solvent is employed in the VPO. Indeed, since there has been little previous discussion of this effect, it might be worthwhile for VPO users to repeat some of these measurements to check its importance in their systems.

It may well be claimed by analytical service VPO operators that all these measurements are laborious and time consuming. This is true, but it must be stated that the use to which the molecular weight data is to be put must be considered to decide whether these measurements are worthwhile in a particular case. If $\bar{M}_n$ is needed solely as a polymer screening method to determine degree of polymerization, it is reasonable to neglect size effects.

On the other hand $\bar{M}_n$ values which are to be used for kinetic measurements and, of course molecular weights of non-polymeric materials for the confirmation of structure should always be measured as precisely as possible within the bounds of reason. In these cases drop sizes ought to be measured or at least closely controlled in order to give the best results.

For the initial calibration of the VPO with a low molecular weight material we consider it important to establish the constant K as accurately as possible since errors in its magnitude will show in all other molecular weights derived from it. A precision of ± 1 percent should be attainable with the calibration solute.

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13. ABSTRACT The application of vapor pressure osmometry to the determination of molecular weights of polymers has been investigated. The principles of the theory and operation of a commercially available vapor pressure osmometer are described and the effects of reading time and drop size are analyzed. It is shown that, for calibration with benzil in dihydroperfluorobutanol at 65°C, resistance readings reached a maximum after three to four minutes and then declined slowly. Extrapolation to zero time was essential. It is further shown that drop size variations measurably effect the resistances making it desirable to account for this effect by using a standard drop size and correcting the results accordingly. Some results obtained for the measurement of molecular weights of samples of polyhexamethylene sebacamide are quoted, and a discussion of potential errors and proper experimental procedures for minimum error is given.		

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