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The measurement of dipole moments

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THE MEASUREMENT OF DIPOLE MOMENTS

by

Anthony Martin DiCocco

A thesis presented to the Department
of Chemistry of Union College in partial
fulfillment of the requirements for the
degree of Bachelor of Science in Chemistry.

By Anthony M. DiCocco

Approved by Galen W. Ewing

Date June 6, 1949

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INTRODUCTION

It is the purpose of this thesis to present an outline of the determination of dipole moments according to the Heterodyne-Beat method, as a laboratory exercise in Physical Chemistry.

APPARATUS AND EXPERIMENTAL

The construction of the apparatus and its operation in the determination of dielectric constants is described with the aid of diagrams in a thesis by Czech (2). Essentially, it consists of two loosely coupled high frequency oscillators, one variable and the other fixed, operating on 115 volts A.C. The fixed oscillator, quartz crystal controlled, operates on a frequency of 2000 kilocycles and has a 6F6 electronic tube with a plate voltage of 200 volts. The variable oscillator containing a capacitance inductance circuit allows of an oscillation whose frequency is made variable by means of a variable condenser. In operation both high frequencies (fixed and variable) are electronically mixed and the result after amplification is detected as an audible frequency by earphones. By varying the capacitance of the variable condenser a frequency from the variable oscillator may be obtained which will give a dead silence or zero beat in the earphones. The zero

beat indicates a condition of constant capacitance in the measuring circuit and serves as a point of reference in the measurement of unknown capacitance. The unknown capacitance is added by means of a test cell to that of the variable condenser and the circuit restored by means of the variable condenser to the condition of constant capacitance. The difference in capacity of the variable condenser readings as interpolated from the calibration graph, Figure I, is the value of the unknown capacity.

The test cell provided and illustrated in Figure II is designed in such a way as to have large electric capacity, small internal volume and a minimum of temperature lag. It consists of two dewar sealed concentric glass cylinders (A). Two glass tubes having ground mouths, one connected at the top of the cell (B) and the other at the bottom (B^1) serve as inlet and outlet. The inner glass surfaces of the cell, with the exception of a centimeter or two at the top, have been silvered according to the Brashear method as described by Strong (6). Electrical connections within the cell are shown in the diagram. The cell is connected to a coaxial cable in such a way that it may readily be inserted into or removed from the oscillator circuit. The cell with copper leads and coaxial connector are held as a unit by a band of copper to a metal support. In use the cell is suspended in a water bath, care being taken not to cause water to enter the space in the center of the cell

in at least one of the several solvents listed.

The accuracy obtainable with the apparatus is limited by the inaccuracies involved in the calibration of the variable condenser and in the interpolation of condenser readings as capacitance values by means of the calibration graph. The maximum absolute error in graphical interpolations is given in the appendix.

THEORY

Dipole moment data afford a quantitative measure of the extent to which a molecule is electrically unsymmetrical. Thus, they provide information concerning molecular structure and are useful in the quantitative interpretation of the properties of solutions.

The theory and measurement of permanent dipole moments is dependent upon the classical theory of charges and the influence of a dielectric on an electric field. When two charges of equal size and of opposite sign are separated by a small distance they form an electric doublet or dipole having an electric moment. Charges within a molecule which are unsymmetrically distributed are resolvable into an electric dipole which gives the molecule a permanent dipole moment. The system of charges of which a molecule is formed whether symmetrically or unsymmetrically distributed may be distorted by an electric field to give an induced dipole moment to the molecule. In the presence of an

externally applied field, the molecules of a dielectric will tend to orient themselves by virtue of their permanent and induced dipole moments. This orientation or electric displacement is called the polarization. That part of the polarization due to the induced dipoles is called distortion polarization, while that due to the permanent dipoles is called permanent or orientation polarization.

A measure of the polarization or the force required to orient the molecule depends upon the magnitude of the dipole moment. Clausius and Mosotti have shown, according to the molecular theory of dielectrics (4) (5), that in the case of liquids and gases, the polarization per unit volume of dielectric is given by,

$$\frac{\epsilon-1}{\epsilon+2} = \frac{4\pi n}{3} \alpha_0 \quad 1$$

where (ϵ) is the dielectric constant which varies with temperature, (n) is the number of molecules per cubic cm. and (α_0) is the polarizability by distortion only of the molecule.

When the molecules of the dielectric contain a permanent dipole, Debye has shown that the polarizability by orientation $\left(\frac{u^2}{3kT}\right)$ must be added to (α_0). Thus the expression for the

total molar polarization of molecules in the liquid or gaseous state becomes with the interpretations of Debye (3),

$$P = \frac{4\pi}{3} N \left(\alpha_0 + \frac{u^2}{3kT} \right) \quad 2$$

where (u) is the permanent dipole moment, (k) the Boltzmann constant and (T) the absolute temperature. The polarization may be conveniently expressed in two parts:

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \left(\frac{4\pi}{3} N \right) \alpha_0 + \left(\frac{4\pi}{3} N \right) \frac{u^2}{3kT} \quad 3$$

the first part being the polarization due to distortion of the molecule by the field and the second that due to the orientation of the molecular permanent dipole in the field. When (P) for a liquid or gas is calculated from their measured dielectric constants at various temperatures by equation 3 and plotted against $\left(\frac{1}{T}\right)$, a straight line is obtained the slope of which will give the permanent dipole moment. In equation 3, (M) is the molecular weight and (d) the density of the substance whose dipole moment is being determined.

In the application of equation 3 to solids and liquids, the limitations in the derivation of the equation must be borne in mind. The values of dielectric constants of a solid used in equation 3 must be those obtained for the molecules of the solid acting as in an ideal liquid or gaseous state where the molecules are so far apart that they do not induce electric charges in each other and are able, except for the effects of thermal motion, to freely orient themselves when a field is applied. In practice, these values are obtained by determining the contributions to the dielectric constants of a non-polar solvent by the solute in dilute solutions at various temperatures and extrapolating to

infinite dilution.

The measurement of the capacity of a cell empty, then filled with the solvent and then with the solution enables the determination of the contribution of the solute to the dielectric constant of the solvent.

The theory of the heterodyne beat method is described in some detail by Smyth (5) (8). The method depends on the beat effect of the frequencies between two loosely coupled oscillators and takes advantage of the dependency of the frequency of an electron tube oscillator upon the resistance, inductance and capacity of its circuits.

In the measurement of dielectric constant conductance effects introduce errors. If the material in the cell has much conductance, the energy absorbed may be great enough to cause the tube to stop oscillating. An appreciable conductance may affect the frequency so that the difference between condenser readings with the material in and then out of the cell will not be measuring the effect of pure capacity but of capacity and inductance. These points are important in the selection of solvents for the determination of dielectric constants of solids. A favorable solvent is one whose ionizing power and association tendency are small. The ionizing power of a solvent is greater the larger its dielectric constant and hence to minimize conductance effects a solvent of low dielectric constant is desirable. A general discussion of other factors which influence the value of (ϵ) is given by Taylor (7).

PROCEDURE

Connect the apparatus to a 115 volt A.C. outlet and turn the power switch located on the right side of the crystal or fixed oscillator chasis. After allowing the electronic elements of the circuit to warm up, vary the control on the lower left side of the chasis until the circuit of the fixed oscillator is in resonance. This is obtained when the neon bulb on the top of the chasis glows with a maximum brightness.

Maintain a temperature of 40°C in a water bath using a 50°C thermometer graduated in tenths of degrees. Place the test cell in the water bath, the cell being kept in place by clamping its metal support to an iron ring stand.

Next, using an appropriate non-polar solvent prepare at least three solutions of 100 ml. each, of varying concentration, of the solid whose dipole moment is to be determined. For best results prepare solutions in which the mole fractions of the solute lie between 0.01 and 0.02.

When ready to proceed with the measurements, check the fixed oscillator for resonance. Plug the earphones in the jack provided. Disconnect the coaxial cable leading to the test cell from the variable condenser. Adjust the variable condenser until zero beat or silence is obtained in the phones and record the condenser dial reading. Replace the coaxial cable and connect the clean, dry cell in parallel to the variable condenser by means

of the cable. Adjust the variable condenser again until zero beat is obtained as before and again record the reading of the condenser dial. The difference in capacities corresponding to the two condenser readings interpolated from the graph of Figure I gives the capacity of the cell filled with air.

The solvent is now introduced into the cell, the space between the silvered walls being completely filled, and the condenser reading at zero beat is recorded. The cell is then emptied and dried with a current of air by suction. The cell is now filled in a like manner with one of the solutions and condenser readings from 40°C to 25°C are taken at 5° intervals, each reading being made at the condition of constant capacitance indicated by the zero beat note. This procedure is repeated with the other two solutions. Solution is added to the cell whenever necessary to keep the silvered surfaces completely bathed as the temperature is lowered. When the measurements are completed, the power switch is snapped to the off position.

CALCULATIONS OF DIPOLE MOMENTS OF SOLIDS

The capacitance of the cell with solvent will not vary appreciably with temperature but it will vary when filled with the solutions.

With the aid of the calibration graph determine the capacitance of the cell with solvent and with each of the solutions at the various temperatures by the method of differences.

Calculate the dielectric constants of the solvent and of each solution at the various temperatures by means of the relation:

$$\epsilon_x^t = \frac{C_x - C_o}{C_{air} - C_o}$$

where (C_{air}) is the capacitance of the cell with air, (C_x) the capacitance of the cell filled with substance (x) and (C_o) the sum of the capacitance of the coaxial cable connecting the cell to the condenser and the lead wires in the cell unit. C_o for the apparatus is approximately 93.5 m.m.f.

In the case of a binary mixture, the polarization at any one temperature is:

$$P_{1,2} = n_1 P_1 + n_2 P_2 = \frac{(E_{1,2} - 1)}{(E_{1,2} + 2)} \cdot \frac{n_1 M_1 + n_2 M_2}{d_{1,2}}$$

where, the subscripts (1) and (2) refer to solvent and solute respectively,

n = mole fraction

P = molar polarization

M = molecular weight

$E_{1,2}$ = dielectric constant of solution

$d_{1,2}$ = density of solution.

Making use of the dielectric constant and the density of each solution at each temperature, N_1 , N_2 , M_1 , and M_2 calculate the polarization of each solution ($P_{1,2}$) for each temperature.

Assuming that, (P_1) the polarization of the solvent is identical in value with that of the pure solvent and unaffected

by the solute, calculate P_1 for each temperature by means of the relation:

$$P_1 = \frac{(E_1 - 1)}{(E_1 + 2)} \cdot \frac{M_1}{d_1}$$

where E_1 = dielectric constant of pure solvent

d_1 = density of pure solvent

M_1 = molecular weight of pure solvent.

Substitution of the relation $n_2 = 1 - n_1$ in $P_{1,2} = n_1 P_1 + n_2 P_2$ gives:

$$P_2 = P_1 + \frac{P_{1,2} - P_1}{n_2}$$

from which (P_2) the molar polarization of the solute for each solution at each temperature is calculated. Plot the values of P_2 corresponding to each temperature against n_2 as abscissas. From these isotherms, obtain the extrapolated values P_2 at $n_2 = 0$. The extrapolated values represent (P_∞), the molar polarization values of the solute at infinite dilution for each temperature. These limiting values contain two terms: a polarization due to deformation of the molecule's electrons and a polarization, affected inversely by temperature, due to the molecule's orientation or permanent dipole. Hence,

$$P_\infty = P_{2(\text{deformation})} + P_{2(\text{orientation})}$$

$$= a + b/T$$

$$\text{where } b = \frac{4\pi N}{3} \frac{u^2}{3k}$$

Plot P_{∞} against reciprocal absolute temperatures as abscissas.
From this graph determine the slope and calculate the permanent
dipole moment of the solute (μ).

APPENDIX

Dipole Moment Data and Calculations of
P-Nitro Toluene

A. Composition of Solutions

Solu.	C Cl ₄ (Tech)	P.N.T. (Tech)	°/o Solu (wt/vol)
I	220 c.c.	4.0002 g	1.82
II	220 c.c.	6.0004 g	2.73
III	220 c.c.	8.0001 g	3.64

M.P. of P.N.T. = 53.9°C (uncor.)

B. Condenser Readings and Capacitance Values for Solutions

I, II, III at Various Temperatures.

Solu.	t°C	R _{no cell}	R _{air}	R _{C Cl₄}	R _{Solu.}	C _{air}	C _{C Cl₄}	C _{Solu.}
I	25	16.39	15.50	14.67	14.43	19.5	37.7	43.0
	30	"	"	"	14.46	"	"	42.4
	35	"	"	"	14.48	"	"	41.9
	40	"	"	"	14.50	"	"	41.5
	45	"	"	"	14.53	"	"	40.9
II	25	16.39	15.50	14.67	14.33	19.5	37.7	45.3
	30	"	"	"	14.35	"	"	44.9
	35	"	"	"	14.37	"	"	44.4
	40	"	"	"	14.39	"	"	43.9
	45	"	"	"	14.40	"	"	43.6
III	25	16.36	15.44	14.60	14.13	19.5	37.7	49.7
	30	"	"	"	14.15	"	"	49.2
	35	"	"	"	14.18	"	"	48.6
	40	"	"	"	14.21	"	"	47.9
	45	"	"	"	14.24	"	"	47.2

Note: The subscripts in Table B refer to condenser readings and oscillator circuit capacitance values without the test cell in the circuit, then with the cell in the circuit containing the dielectrics indicated.

These condenser readings are those of a condenser which has now been replaced by a new condenser. The calibration curves (Figure I) appearing in this appendix are those of the new condenser.

C. Densities and Calculated Dielectric Constants

Solu.	n_1	n_2	$d_{1,2}^{25^\circ}$	$d_{1,2}^{30^\circ}$	$d_{1,2}^{35^\circ}$	$d_{1,2}^{40^\circ}$
I	0.988	0.012	1.580	1.572	1.562	1.554
II	0.982	0.018	1.576	1.566	1.556	1.548
III	0.977	0.023	1.576	1.566	1.556	1.546

Solu.	$E_{1,2}^{25^\circ}$	$E_{1,2}^{30^\circ}$	$E_{1,2}^{35^\circ}$	$E_{1,2}^{40^\circ}$	$E_{1,2}^{45^\circ}$
I	2.72	2.68	2.65	2.62	2.58
II	2.90	2.87	2.83	2.79	2.77
III	3.22	3.18	3.14	3.09	3.04

n_1 = mole fraction of solvent

n_2 = mole fraction of solute

$d_{1,2}^t$ = density of solution at temp. ($t^\circ\text{C}$).

$E_{1,2}^t$ = dielectric constant of the solution
at temp. ($t^\circ\text{C}$).

D. Calculated Polarization Values

Solu.	$P_{1,2}^{25^\circ}$	$P_{1,2}^{30^\circ}$	$P_{1,2}^{35^\circ}$	$P_{1,2}^{40^\circ}$	$P_{1,2}^{45^\circ}$	$P_1^{25^\circ}$	$P_1^{30^\circ}$	$P_1^{35^\circ}$	$P_1^{40^\circ}$	$P_1^{45^\circ}$
I	35.4	35.1	34.9	34.7	34.3	29.9	30.1	30.3	30.5	30.7
II	37.8	37.6	37.5	37.1	37.0	"	"	"	"	"
III	41.4	41.4	41.2	40.8	40.4	"	"	"	"	"

Solu.	$P_2^{25^\circ}$	$P_2^{30^\circ}$	$P_2^{35^\circ}$	$P_2^{40^\circ}$	$P_2^{45^\circ}$	$P_\infty^{25^\circ}$	$P_\infty^{35^\circ}$	$P_\infty^{40^\circ}$
I	483	446	412	379	325			
II	502	444	428	397	381	447	376	343
III	531	522	505	478	452			

$P_{1,2}^t$ = molar polarization of solution at temp. ($t^\circ\text{C}$)

P_1^t = molar polarization of solvent " " "

P_2^t = molar polarization of solute " " "

P_∞^t = molar polarization of solute in infinitely
dilute solution by extrapolation

E. Dipole Moment of P.N.T. (Tech.) as Calculated by Means of the Slope of the P vs. $1/T$ Curve (Figure A)

$$u = \sqrt{\frac{9k}{4\pi N}} \sqrt{\text{slope}}$$

$$u = (0.0127 \times 10^{-18}) (401.9) = 5.11 \times 10^{-18} \text{ e.s. units}$$

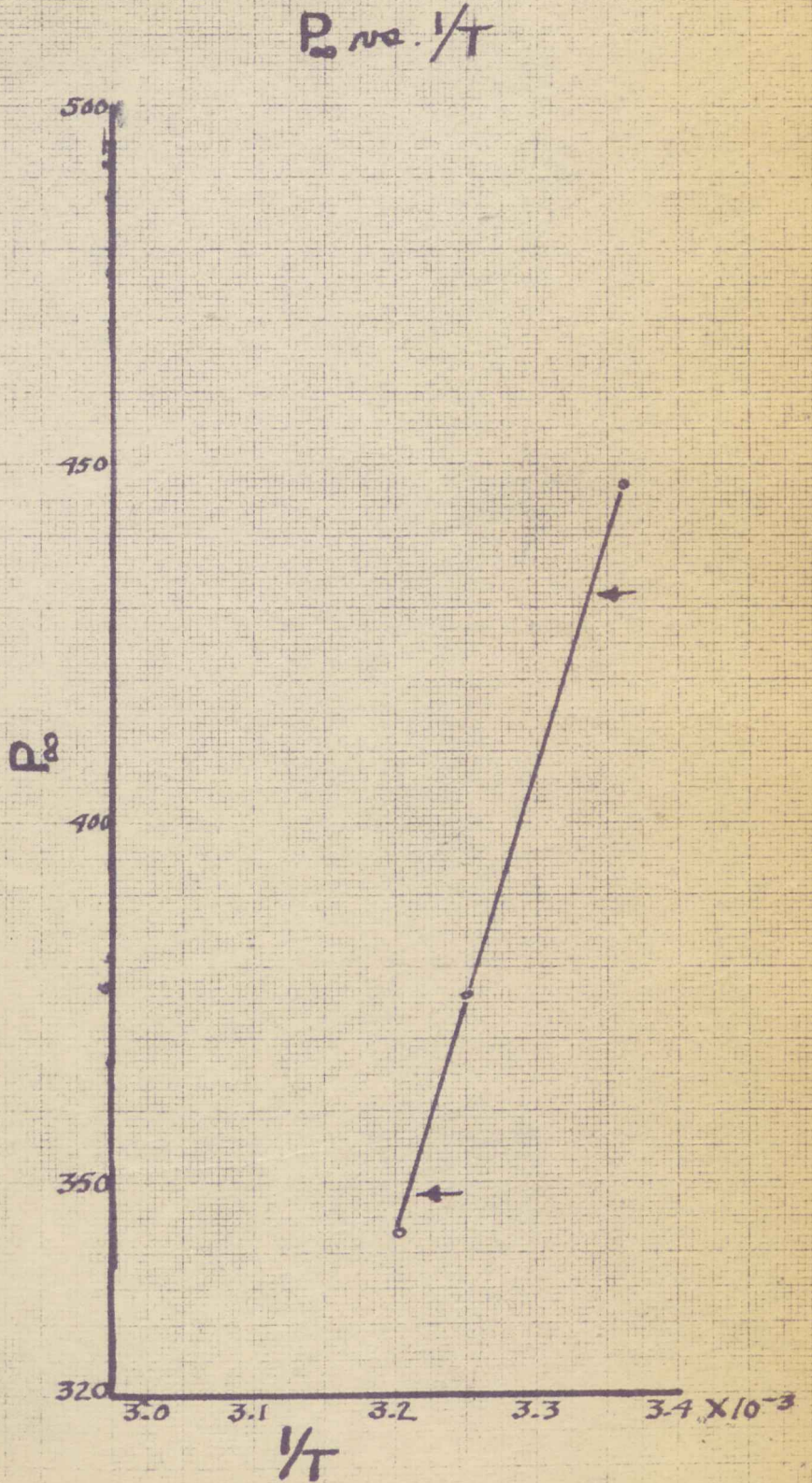
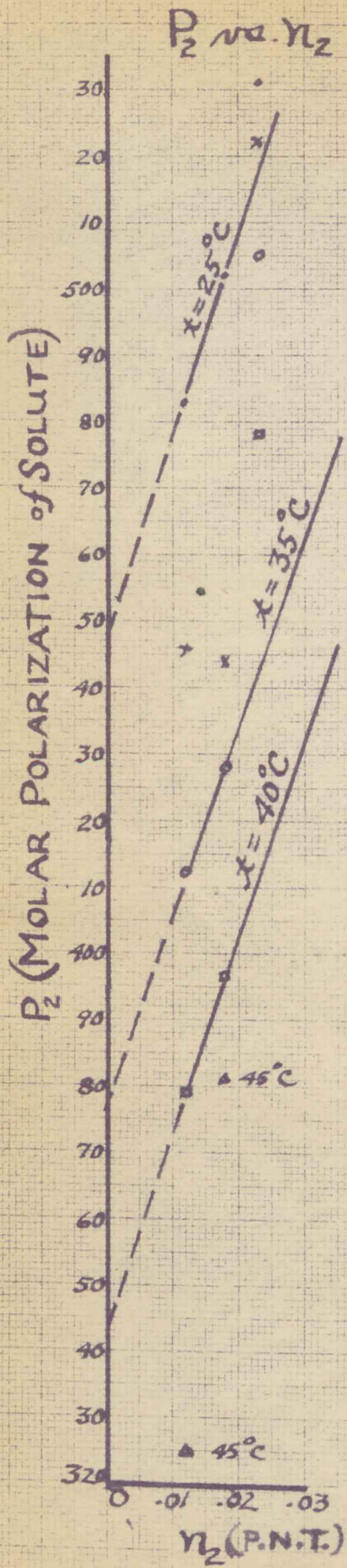
RESULTS

1. In (u) determinations of solids with high dipole moments the upper limit of the concentration range with this apparatus is approximately $n_2 = 0.02$. As seen from Figure III, each value of P_2 corresponding to $n_2 = 0.023$ for P.N.T. departs greatly from the straight line P_2 vs. n_2 isotherms. This is probably due to appreciable self-inductive and solvent effects at concentrations greater than $n_2 = 0.02$.

2. With the condenser used in this work, the lower limit of the concentration range is approximately $n_2 = 0.01$. This is due to the insensitiveness of the condenser at lower concentrations as indicated by the closeness of condenser readings tabulated in Table B, Solu. I under "Dipole Moment Data and Calculations".

3. As published by Smyth (5), (u) for P.N.T. (C.P.) = 4.4×10^{-18} e.s. units. The value of (u) for P.N.T. (Tech.) as determined in this work is in error by 16.1% with respect to the value published by Smyth.

FIGURE A
P.N.T.



CALIBRATION DATA VARIABLE CONDENSER

FIGURE I

<u>Dial Readings</u>	<u>Cap.(m.m.f.)</u>	<u>Dial Readings</u>	<u>Cap.(m.m.f.)</u>
9	87.0	24	92.0
10	87.8	25	90.8
11	88.6	26	89.7
12	89.4	27	88.8
13	90.4	28	87.9
14	91.3	29	87.0
15	92.2	30	86.1
16	93.1	31	85.4
17	94.0	32	84.7
18	95.2	33	83.9
19	96.9	34	83.0
20	96.6	35	82.3
21	95.5	36	81.2
22	94.3	37	81.0
23	93.0		

FIGURE I

CALIBRATION GRAPH VARIABLE CONDENSER

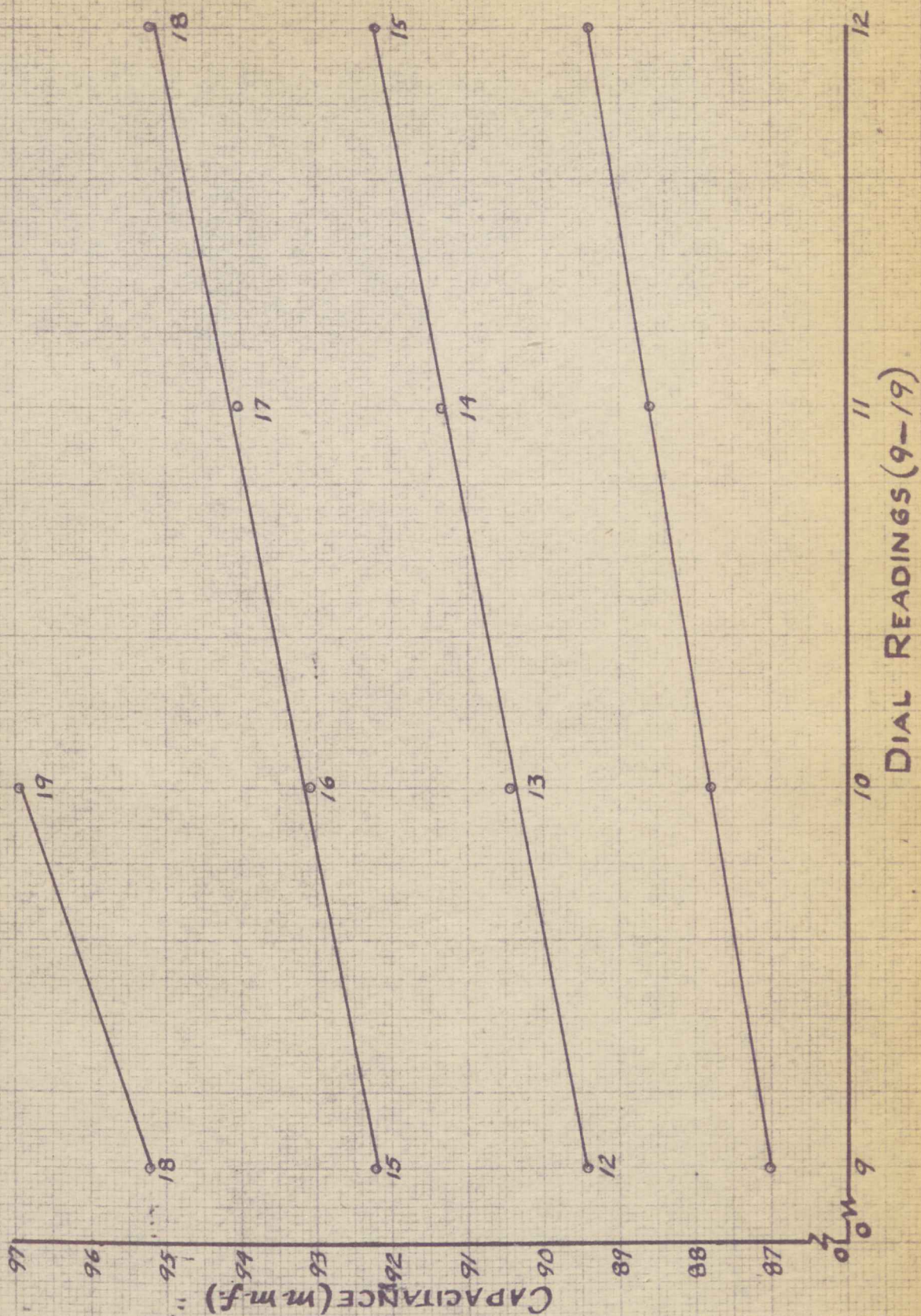


FIGURE I

CALIBRATION GRAPH
VARIABLE CONDENSER

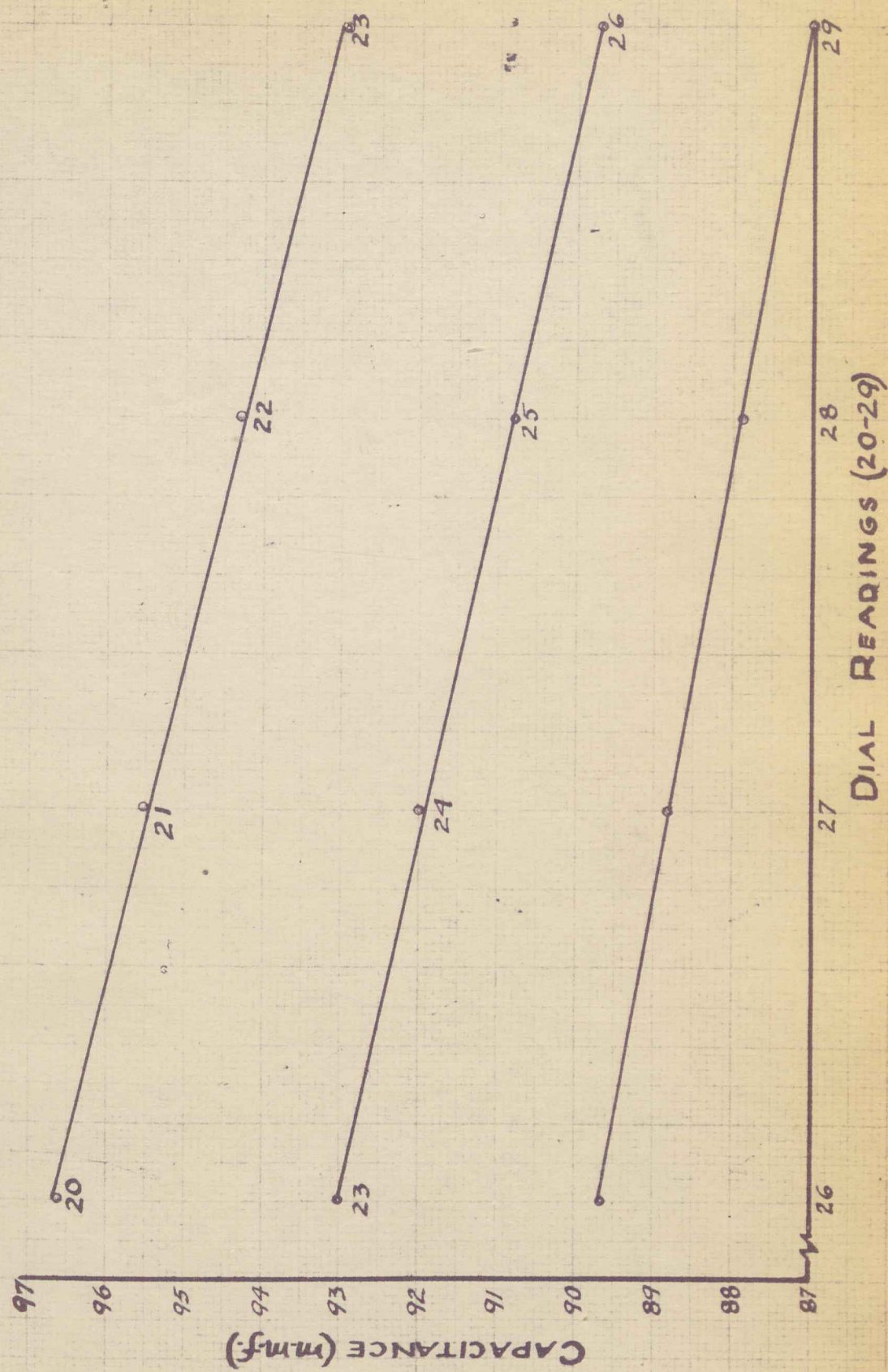
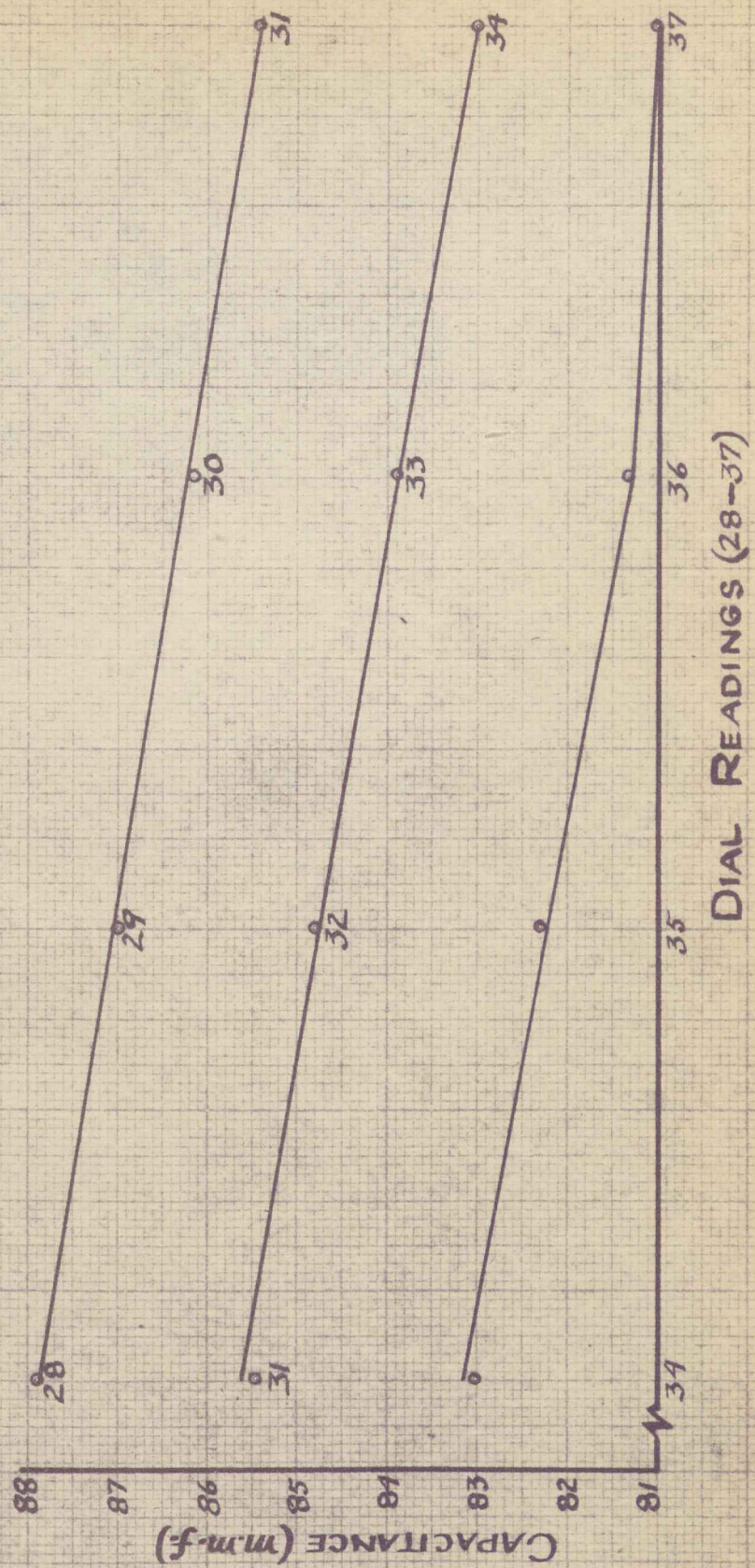


FIGURE I

CALIBRATION GRAPH
VARIABLE CONDENSER



MAXIMUM ABSOLUTE ERROR IN GRAPHICAL INTERPOLATIONS

FIGURE I

1. The error equation for a straight line graph
($y = mx + b$),

$$(\Delta y_x)^2 = S_1^2 \left(\frac{\partial y}{\partial x} \right)^2 + S_2^2 \left(\frac{\partial y}{\partial m} \right)^2 + S_3^2 \left(\frac{\partial y}{\partial b} \right)^2$$

where

$$\Delta y = \Delta y_x + \Delta y_y$$

S_1 = error in x

S_2 = error in m

S_3 = error in b

Δy_x = error in y due to abscissa error

Δy_y = error in y due to ordinate error

Δy = error in y, the max. absolute error.

2. Calculation of Δy for Figure I.

According to the method of least squares(1) for a straight line graph,

$$(\Delta y_x)^2 = S_1^2 \left(\frac{\partial y}{\partial x} \right)^2, \quad S_2 = S_3 = 0.$$

For figure I,

$S_1 = 0.03$ the error in each dial reading or the abscissa plot.

$\frac{\partial y}{\partial x} = m = 0.948$ as determined by the method of least squares.

$$\Delta y_x = \sqrt{(.03)^2 (.948)^2} = \pm .03 \text{ m.m.f.}$$

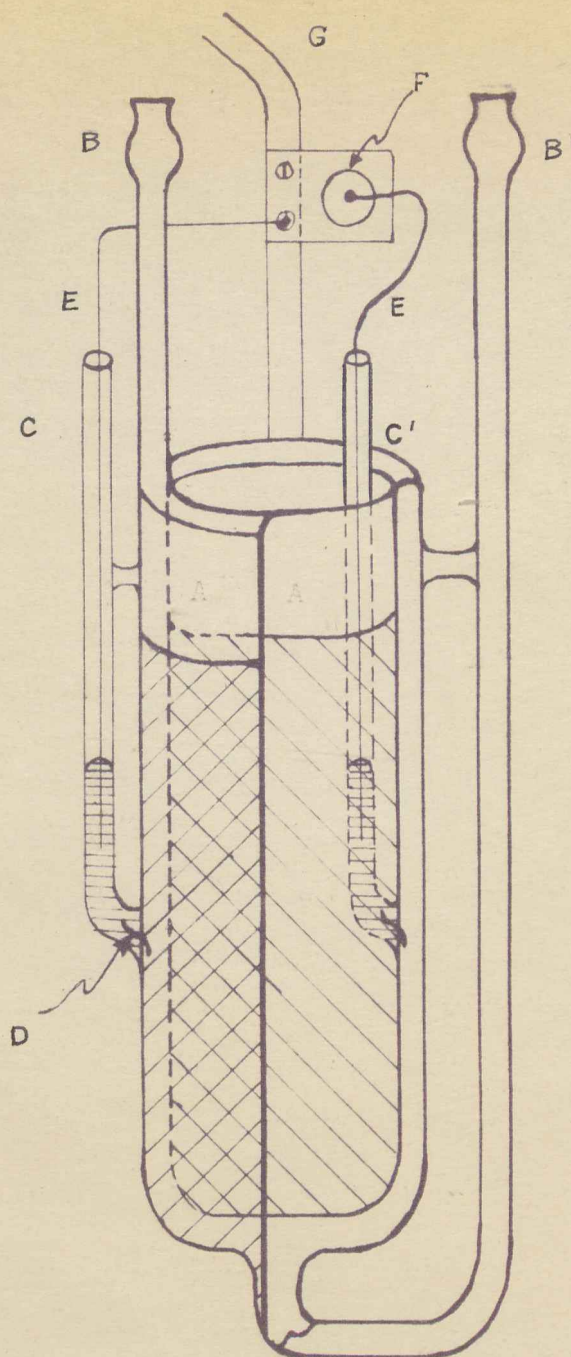
$\Delta y_y = \pm 1 \text{ m.m.f.}$ due to the limit of accuracy in the
capacitance values of the calibrating
instrument.




$$\therefore \Delta y = \pm 1.03 \text{ m.m.f.}$$

Fig. I

Figure II

TEST CELL



- A - Dewar sealed concentric glass cylinders.
- B, B' - Inlet and outlet arms.
- C - Glass tubing attached to outer glass cylinder.
- C' - Glass tubing attached to inner glass cylinder.
-  - Silvered outside surface area of inner glass cylinder.
-  - Silvered inside surface area of outer glass cylinder.
-  - Mercury pool.
- D - Pt. wire making electrical contact between silvered surface and outside.
- E - Copper lead wire dipping in mercury pool.
- F - Coaxial connector.
- G - Metal support for cell.

SUGGESTED COMPOUNDS AND SOLVENTS

Compounds

<u>Formula</u>	<u>Name</u>	<u>$U \times 10^{-18}$</u>
CH_3NO_2	Nitromethane	3.0
$\text{C}_2\text{H}_5\text{NO}_2$	Nitroethane	4.0
$\text{C}_6\text{H}_5\text{NO}_2$	Nitrobenzene	3.9
$\text{C}_6\text{H}_5\text{NO}_3$	m-Nitrophenol	3.9
	p-Nitrophenol	5.0
$\text{C}_6\text{H}_6\text{N}_2\text{O}_2$	O-Nitroaniline	4.4
	m-Nitroaniline	4.7
$\text{C}_7\text{H}_5\text{NO}_4$	p-Nitrobenzoic Acid	3.5
$\text{C}_{13}\text{H}_{10}\text{O}$	Benzophenone	2.95
$\text{C}_{10}\text{H}_{18}\text{O}$	Camphor	2.95
$\text{C}_5\text{H}_4\text{O}_2$	Furfural	3.57
$\text{C}_8\text{H}_8\text{O}_2$	Acetophenone	2.9

Solvents

<u>Formula</u>	<u>Name</u>
C Cl_4	Carbon Tetrachloride
C_6H_6	Benzene
C_6H_{12}	Cyclohexane
$\text{C}_4\text{H}_8\text{O}_2$	Dioxane

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