The Dielectric Constant of Adsorbed Ethyl Chloride

A Thesis

by

Herbert W. Johnson, B.A., M.A.,

Submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

McGill University

April 1947

The Dielectric Constant of Adsorbed Ethyl Chloride

A Thesis

by

Herbert S. Johnson, B.A., M.A.,

Submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

McGill University

April 1947

Acknowledgments

The author wishes to express his sincere appreciation to the following:

Dr. R. L. McIntosh, who, acting at the request of Dr. O. Maass, suggested the problem and gave generously of encouragement and advice.

The National Research Council of Canada, for the award of a studentship in the 1946 - 1947 term.

The Directorate of Chemical Warfare for the purchase of apparatus used in this work.

Table of Contents

Page

Introduction

Apparatus

Bibliography

INTRODUCTION

General:

A very wide variety of techniques has been employed in the study of the physical adsorption of vapours on solids. Since the work to be described here concerns attempts to use yet another, practically untried, technique which must be evaluated in terms of those which have been more extensively tested, it seems appropriate to discuss briefly some of the more common experimental methods, the results obtained, and some of the views generally held about the significance of the results.

A theory of adsorption must attempt to describe the state of the adsorbed material on the surface of the adsorbent, and to discuss the forces involved in the attachment. It must consider the mechanism of adsorption processes and any specific effects attributable to the solid or vapour. Any hope of obtaining explanations of these phenomena depends on the extent to which they are reflected in observable quantities. Frequently this connection is quite remote, and complicated by the simultaneous operation of two or more factors, so that it is necessary to attempt to draw inferences from data which bear only indirectly on the question. Investigators are thus lead to the study of the way in which adsorption depends on the pressure of the vapor and the temperature at which adsorption occurs. In fact, the great bulk, both of data and of theory, comes from the adsorption isotherm, a curve which gives the relation at any one temperature, between the amount adsorbed and the equilibrium pressure of the vapor. Another very important reason for the intensive study of the adsorption isotherm is a practical one, since the isotherm is a convenient summary of the properties of an adsorbent-adsorbate system at any one temperature.

A number of mathematical isotherm equations have been derived and are in common use. The success with which these equations represent experimental data is taken to be a partial confirmation of the assumptions on which they were based. Further confirmation must come from comparison of values calculated from these equations of surface area and the like, with those obtained by other, and independent methods. When such confirmation is lacking, little confidence can be felt in the validity of the assumptions, however well the resulting equation may express experimental facts.

The study of the adsorption isotherm has lead to the belief that, in physical adsorption the adsorbed layer may be unimolecular or multimolecular, depending on the system, and frequently also on the relative pressure region considered. It is usually possible to decide whether the adsorbed film is unimolecular, and if so, over what range of pressure, from the form of the isotherm equation obeyed. The physical state of the adsorbate is usually considered to be that of a liquid or highly compressed gas. Calorimetric measurements have, in special cases, supported the conclusion that the adsorbed layers at least resemble the liquid quite closely. Such studies, again in special cases, have also pointed to the reality of two-dimensional phase changes in the adsorbed film. These will be discussed more fully in connection with the work of Bangham, and of Harkins and Jura.

The isotherm equations which have been of assistance in correlating data of this research are discussed in the next section.

The dielectric properties of an adsorbate are determined by its polarizability, and, if it is a polar substance, by the ability of the molecules to orient themselves in the field. Both of these quantities might conceivably be affected by the adsorptive forces holding the molecules to the solid, so that the dielectric constant of an adsorbed substance might be different from that of the free substance in the same physical state. Further, any changes which might occur in the adsorptive or cohesive forces as adsorption progresses would be expected to result in a changed dielectric constant of the adsorbate. Again, a study of the temperature variation of the dielectric constant may enable one to form an opinion concerning the mobility of the adsorbed molecules since these two properties are intimately related.

It was decided to use a bridge method for the determination of the change in capacity of a condenser packed with silica gel as ethyl chloride vapor was adsorbed. The problem may be stated thus:

1. to obtain a measure of the dielectric constant of adsorbed ethyl chloride, and thus to determine whether the dielectric constant varies with the amount adsorbed.

2. by making measurements at different temperatures, to obtain a measure of the temperature coefficient of the dielectric constant, and further to determine whether temperature affects the way in which the dielectric constant varies with the amount adsorbed.

3. to correlate the information obtained in 1. and 2. with information obtained by analysis of the adsorption isotherm.

THEORETICAL INTRODUCTION

1. Adsorption Theory:

We are concerned here to look for features of adsorption theory which can be correlated with information obtained from dielectric constant measurements. It would be of considerable value to determine for example whether adsorption is unimolecular over any part, or all of the isotherm. In reaching a conclusion on this matter, the Langmuir equation, based as it is on the assumption of unimolecularity, might be of value. In general, it will be important to know which of the isotherm equations are compatible with the experimental adsorption data over a reasonable pressure range, for then the assumptions underlying these equations can be regarded tentatively as applicable in this situation. It is therefore convenient to outline briefly the basic assumptions and the mathematical forms of equations which have been found useful, with this in view.

a. Langmuir Isotherm Equation:

This equation was derived by Langmuir (23) in connection with his work on chemisorption. Although the forces involved in chemisorption are similar to those involved in chemical reaction, and the phenomenon is characterized by unimolecular layers, the equation deals quite successfully with a considerable number of physical adsorptions, where the forces involved are of the van der Waals type. The kinetic arguments used in the development of the theory have, moreover, provided the basis for later adsorption isotherm equations which were more concerned with physical adsorption. In the derivation of the equation, it is assumed that:

(1) the molecules are adsorbed to definite points of attachment;

(2) there is only one molecule at each such point;

(3) there is no interaction between adsorbate molecules. This condition also implies a heat of adsorption that is uniform over the whole surface.

If v is the volume adsorbed at a pressure p, and v_m is the volume of adsorbate required to form a monolayer, the equation takes the form:

$$v = \frac{v_m bp}{1+bp} \qquad (1)$$

where b in Langmuir's kinetic derivation is given by the expression:

$$b = \frac{\alpha_o e^{q/kT}}{k_o(2\pi mkT)^{\frac{1}{2}}} \qquad (2)$$

In this equation, α_o is the condensation coefficient for the bare surface, q is the heat of adsorption, k is Boltzmann's constant, k_o is the evaporation coefficient, m is the mass of the molecule, and T is the absolute temperature. In the statistical derivation of Fowler, b is of a similar form, but involves the ratio of the partition functions of the adsorbed states and for the rotations and vibrations of the free gas molecules. In actual systems, this ratio, as well as the heat of adsorption may vary as adsorption progresses.

The isotherm equation, (1), is frequently used, for testing its applicability, in the form:

$$\frac{p}{v} = \frac{1}{v_m b} + \frac{p}{v_m} \qquad (3)$$

If the equation fits the experimental data, then a plot of $\frac{p}{v}$ vs. p should give a straight line.

This equation must be modified for a surface which is inhomogeneous with regard to adsorptive power, for in such cases the heat of adsorption will vary from the more to the less active points of the surface. This is frequently, if not always, the case in physical adsorption, as direct calorimetric investigations have shown. The surface area values calculated from v_m in some cases indicate, in comparison with values obtained by other methods, that only a part of the surface is active in adsorbing a particular substance. Langmuir has shown that the case of the inhomogeneous surface must be treated by an equation which is the sum of a number of equations (1)

$$v = \sum \frac{v_{mi} b_i p}{1 + b_i p} \qquad (4)$$

b. Williams-Henry Equation:

The kinetic derivation of this equation by Henry (19) starts from the Langmuir equation (1). On the assumption, however, that a molecule is held by more than one point on the surface, the equation assumes the modified form:

$$v = v_m bp\left(1 - \frac{v}{v_m}\right)^n \qquad (5)$$

where n represents the number of points of attachment, and the other symbols have the same meaning as before. By taking logarithms of both sides and using a series expansion of the term $\ln(1 - \frac{v}{m})$ valid for low values of $\frac{v}{v_m}$, the Williams-Henry equation,

$$\ln \frac{v}{p} = \ln v_m b - \frac{n}{v_m} v \qquad (6)$$

results. The limitations on this equation are the same as those on the Langmuir equation, and in addition, by the use of the series expansion approximation, it is limited to values of $\frac{v}{v_m}$ less than 0.3.

c. Potential Theory:

Polanyi (26) attacked the problem of adsorption in a quite different way. He considered the work required to bring a molecule from the free gas region to the adsorption region, and considered that the potential function thus established is independent of temperature, and of the distribution of other adsorbate molecules. The work is calculated from the basic relation

$$\epsilon_i = \int_{\delta}^{\delta_i} v\,dp \qquad (7)$$

where δ_i is the density of the adsorbed substance in the i^{th} potential region. This is evaluated by substituting for v from an assumed equation of state. When ϵ_i is plotted against ϕ_i , which may be regarded as the volume or area of the i^{th} potential level, the so-called "characteristic curve" results. This curve is then taken as a representation of the variation of potential with the distance from the region of maximum potential, and should be independent of the temperature. The temperature dependence of adsorption is then accounted for by the temperature dependence of the equations of state. The theory has had considerable success in accounting for the temperature dependence of adsorption.

It can be seen that the practical results of this theory depend only on the existence of a potential function which depends on only the one variable, ϕ , which in its applications is the volume of the adsorbed substance. Originally derived by considering thick, compressed multilayers, its basis has been changed by its author to bring it more in accord with modern ideas of the range of surface forces. The surface is covered by equipotential lines enclosing areas over which the potential is between the potentials of the bounding lines. According to this revised picture, adsorption of the first small amounts results in the formation of unimolecular "islands" covering the areas of highest potential. As the pressure is increased, these islands grow and finally coalesce.

The equations of state obeyed by the adsorbed phase show that at low temperatures it behaves like a liquid of low compressibility and at temperatures above the critical temperature it behaves like a highly compressed gas. It is an interesting feature of this theory that the adsorbate plays a quite passive part, except as it is involved in the work of compression. It was found empirically that the maximum adsorption potential, ϵ_o , is related to the van der Waals constant, a, of the gas by the relation $\epsilon_o = k\sqrt{a}$.

d. Multimolecular Adsorption Theory:

Brunauer, Emmett and Teller (5) derived this equation from a kinetic consideration of the rates of evaporation and condensation from each of a number of layers in an adsorption system at equilibrium. This theory, is capable of representing adsorption isotherms of the five types which occur in practice, over a relative pressure range from 0.05 to 0.35. For adsorption taking place on a free surface (where there is no limit to the number of layers which may be formed), without capillary condensation, the equation has the form

$$\frac{f}{v(1 - f)} = \frac{1}{v_m c} + \frac{c - 1}{v_m c} f \qquad (8)$$

Here f is the relative pressure p/p_o where p_o is the vapor pressure of the liquid at this temperature; v_m is the volume of the gas required to form a monolayer; v is the volume of gas adsorbed at pressure p, and c is a quantity related to the amount by which the energy of adsorption in the first layer exceeds the heat of liquefaction of the vapor in the following way:

$$c = \frac{a_1 b_2}{a_2 b_1} e^{(E_1 - E_L)/RT} \qquad (9)$$

Here, a_1 and b_1 are respectively the evaporation and condensation coefficients in the first layer, and a_2 and b_2 are the corresponding quantities for the second layer. The authors assumed that the term $\frac{a_1 b_2}{a_2 b_1}$ will be approximately unity. Recently Cassie (7), in deriving the Brunauer-Emmett-Teller equation by statistical thermodynamic methods concluded that this ratio was the ratio of the partition function of molecules in the first layer to that of molecules in higher layers, and that a value of about 0.02 was to be expected. Emmett (9) has shown that this ratio gives better agreement with experimental calorimetric data.

When the number of layers is limited, for example, by the sizes of the pores, to n layers, the equation takes the form:

$$v = \frac{v_m c f}{1 - f}\left[\frac{1 - (n+1)f^n + nf^{n+1}}{1 + (c-1)f - cf^{n+1}}\right] \qquad (10)$$

This equation has two limiting forms, when $n = 1$ and $n = \infty$. The first of these is

$$v = \frac{v_m \frac{c}{p_o} p}{1 + \frac{c}{p_o} p} \qquad (11)$$

which is formally identical with the Langmuir equation with b replaced by c/p_o. When $n = \infty$, (10) reduces to (8).

The most general form of the equation, which includes the other forms as special cases is the one which includes the possibility of capillary condensation. This possibility is included by considering the effect of the lowered vapor pressure on the rate of evaporation. This is equivalent to the requirement of a larger heat of liquefaction for the layer which completes the filling of the capillary. The resulting equation is, when (2n - 1) layers are required to fill the capillary:

$$v = \frac{v_m c f}{1 - f}\left[\frac{1 + (\frac{1}{2}ng - n)f^{n-1} - (ng - n + 1)f^n + \frac{1}{2}ngf^{n+1}}{1 + (c - 1)f + (\frac{1}{2}cg - c)f^n - \frac{1}{2}cgf^{n+1}}\right] \qquad (12)$$

The only new symbol in this equation is g, and this is define by the equation $g = e^{Q/RT}$, where Q is the excess heat of liquefaction of the last layer over that of the bulk liquid. If the maximum number of layers that can fit into the capillary is 2n in place of 2n - 1, a slightly different form is obtained (4).

e. Harkins-Jura Treatment:

Harkins and Jura have quite recently published a series of papers in which the essential similarity of adsorptions on liquid and solid surfaces is stressed. The relations between area and surface pressure have been worked out in considerable detail for liquid substrates in the work of Adam (1), Harkins (14), and others. The situation with insoluble films on liquid surfaces is less complicated than adsorption on solids because one can depend on the uniformity of the liquid surface and can study monomolecular films uncomplicated by formation of further layers, and capillary condensation. It is possible to study in considerable detail the phase changes which take place with changing surface pressure and temperature. It is clear from this work that five or six different phases can be recognized. In the nomenclature of Harkins (14), these are

(1) gaseous
(2) liquid expanded
(3) liquid intermediate
(4) liquid condensed
(5) liquid supercondensed
(6) solid or plastic

Designating the surface pressure by π and the area available to a single molecule by σ, the equations of state for the various phases are:

1. gaseous films at low compression:

$$\pi\sigma = kT, \qquad (13)$$

a two-dimensional analogue of the perfect gas law.

2. liquid expanded films:

$$K = -\frac{a}{\sigma + b} = -\frac{1}{\sigma}\left(\frac{\partial\sigma}{\partial\pi}\right)_T \qquad (14)$$

This is an empirical equation for the compressibility which is found to represent the isothermal behavior of such films very well. a and b are unknown functions of temperature only. Integration of this equation gives the desired relation between π and σ at constant temperature, i.e.

$$\pi = c + \frac{\sigma}{a} + \frac{b}{a}\ln\sigma \qquad (15)$$

Here, c, at a given temperature, is a constant of integration.

3. liquid intermediate films:

The empirical equation for the compressibility is

$$K = -\left(\frac{a}{\sigma} + b\right) = -\frac{1}{\sigma}\left(\frac{\partial\sigma}{\partial\pi}\right)_T \qquad (16)$$

On integration this gives:

$$\pi = c + \frac{1}{b}\ln(b\sigma + a) \qquad (17)$$

where again c is a constant of integration.

4. condensed films:

These exhibit a π-σ curve which is linear, and has a negative slope, so that they are represented by of state for the various phases are:

1. gaseous films at low compression:

$$\pi\sigma = kT, \qquad (13)$$

a two-dimensional analogue of the perfect gas law.

2. liquid expanded films:

$$\kappa = -\frac{a}{\sigma + b} = -\frac{1}{\sigma}\left(\frac{\partial \sigma}{\partial \pi}\right)_T \qquad (14)$$

This is an empirical equation for the compressibility which is found to represent the isothermal behavior of such films very well. a and b are unknown functions of temperature only. Integration of this equation gives the desired relation between π and σ at constant temperature, i.e.

$$\pi = c + \frac{\sigma}{a} + \frac{b}{a}\ln\sigma \qquad (15)$$

Here, c, at a given temperature, is a constant of integration.

3. liquid intermediate films:

The empirical equation for the compressibility is

$$\kappa = -\left(\frac{a}{\sigma} + b\right) = -\frac{1}{\sigma}\left(\frac{\partial \sigma}{\partial \pi}\right)_T \qquad (16)$$

On integration this gives:

$$\pi = c + \frac{1}{b}\ln(b\sigma + a) \qquad (17)$$

where again c is a constant of integration.

4. condensed films:

These exhibit a π-σ curve which is linear, and has a negative slope, so that they are represented by an equation of the form

$$\pi = b - a\sigma \qquad (18)$$

For the purpose of testing these relations in the adsorption of vapors by solids, two approaches are possible; first, one might calculate π and σ from the adsorption isotherm as indicated below; second, one might derive p - v relationships corresponding to the $\pi - \sigma$ relationships given above. Both of these methods are used by Harkins and Jura.

The surface pressure, π , is calculated from the adsorption isotherm by the integration of the Gibbs adsorption isotherm as suggested by Bangham (3). The equation is

$$\pi = \gamma_s - \gamma_{s_f} = \frac{TR}{V_M \Sigma} \int_0^f v \, d \ln f \qquad (19)$$

where γ_s is the surface free energy of the bare surface, γ_{s_f} is the surface free energy of the surface covered by the film, V_M is the molar volume of the gas, Σ is the specific surface of the adsorbent and must be known, T is the absolute temperature, R the gas constant, v the volume adsorbed, and f the fugacity of the vapor, usually taken to be equal to the pressure. This integral can be evaluated by plotting v/p vs. p and determining the area under the curve at various p values. This usually involves considerable uncertainty due to the shape of the curve and it is necessary to obtain numerous exact data at very low pressures in order to obtain the desired accuracy (see Harkins (15)). Sometimes a plot of v vs log p/v is preferable for the evaluation of this integral.

The value of σ can be obtained from a knowledge of the amount adsorbed and the specific surface of the adsorbent. When multimolecular layers are formed, however, it is necessary to remember that, for the purposes of this calculation the desired quantity is Σ/N where N is the number of molecules actually in contact with the surface of the solid.

The second method for investigating the phase relations of surface films on solids is to calculate the three dimensional p - v relations corresponding to the two dimensional equations of state between π and σ . This is accomplished by Harkins and Jura (16), starting with the identity

$$\left(\frac{\partial \ln f}{\partial v}\right)_T = \left(\frac{\partial \ln f}{\partial \pi}\right)_T \left(\frac{\partial \pi}{\partial v}\right)_T \qquad (20)$$

The two terms on the left are then evaluated in terms of v as follows:

$$\pi = \gamma_s - \gamma_{sf} \qquad \text{by definition} \qquad (21)$$

According to the Gibbs adsorption equation:

$$\Gamma = \frac{1}{RT}\left(\frac{\partial \gamma_{sf}}{\partial \ln f}\right)_{T,\Sigma} \qquad (22)$$

where $\Gamma = \frac{v}{V_M \Sigma}$ = moles adsorbed per unit area (23) if σ is in square cm. per molecule

$$\sigma = \frac{V_M \Sigma}{v\, N_o} \tag{24}$$

where N_o is Avogadro's number.

$$\left(\frac{\partial \pi}{\partial v}\right)_T = \left(\frac{\partial \pi}{\partial \sigma}\right)_T \left(\frac{\partial \sigma}{\partial v}\right)_T \tag{25}$$

$$= -\frac{V_M \Sigma}{v^2 N_o}\left(\frac{\partial \pi}{\partial \sigma}\right)_T \quad \text{using (24)} \tag{26}$$

from (21), (22), (23).

$$\frac{v}{V_M \Sigma} = -\frac{1}{RT}\left(\frac{\partial \pi}{\partial \ln f}\right)_{T,\Sigma} \tag{27}$$

or

$$\left(\frac{\partial \ln f}{\partial \pi}\right)_{T,\Sigma} = -\frac{V_M \Sigma}{RTv} \tag{28}$$

substituting (27), (28) in (20),

$$\left(\frac{\partial \ln f}{\partial v}\right)_T = \frac{(V_M \Sigma)^2}{RT N_o v^3}\left(\frac{\partial \pi}{\partial \sigma}\right)_T \tag{29}$$

Since, in general, π is a function, say ϕ of σ, the form of which is known for the various phases, we can write in place of (29),

$$\left(\frac{\partial \ln f}{\partial v}\right)_T = \frac{(V_M \Sigma)^2}{RT N_o v^3}\,\phi'\left(\frac{V_M \Sigma}{v\, N_o}\right) \tag{30}$$

where ϕ' is the derivative of ϕ with respect to σ, and the quantity $\frac{V_M \Sigma}{v N_o}$ has been substituted for σ in the functional relation.

Using the equations of state relating π and σ for the various types of films in (30), the p-v relations result, as follows:

(1) gaseous films

$$p = K v \tag{31}$$

(2) liquid expanded films

$$\ln p = K + \frac{C}{2aDv^2} + \frac{b}{aDv} \tag{32}$$

(3) liquid intermediate films

$$\ln p = K - \frac{1}{bDv} + \frac{a}{b^2DC} \ln \frac{bC + av}{v} \tag{33}$$

(4) condensed films

$$\ln p = K - \frac{(V_M \Sigma)^2 a}{2RTN_0 v^2} \tag{34}$$

where $C = V_M/N_0$

$$D = \frac{RT}{V_M \Sigma} \tag{35}$$

The equation for condensed films given above has been applied successfully in a number of cases, especially by Harkins and Jura, and is the basis of a new method (17) for determining surface areas without the necessity for any assumptions concerning the cross-sectional area of the adsorbed molecules.

Harkins and his co-workers have calculated force-area curves for a number of gas-solid adsorption systems (16), and have obtained curves which reproduce the behavior of insoluble films on water very closely. The effect of temperature here is also similar to its effect on films on a liquid, and to the corresponding phenomena associated with the critical temperature region in three-dimensional systems. Evidence for the reality of phase changes in certain adsorption systems has also been presented.

Most of the possible phase transitions in two-dimensional systems are different from those of three-dimensional systems in that they do not have heats of transition. Such phase changes are said to be of second or higher order.

Harkins and Boyd (18) have discussed the criteria for phase changes in films on liquids. Harkins and Jura have carried over these criteria to films on solids. In order to demonstrate a phase change it is necessary to show that a discontinuity exists in the compressibility K, where

$$K = \frac{V_M \Sigma p}{RTv^2} \left(\frac{\partial V}{\partial p}\right)_T \qquad (36)$$

This amounts to the demonstration of a discontinuity in the derivative $\frac{\partial V}{\partial p}$. If $\left(\frac{\partial V}{\partial p}\right)_T$ becomes infinite the change is a so-called "first order" phase change. If $\left(\frac{\partial V}{\partial p}\right)_T$ shows a finite discontinuity, the phase change is of the second order, such as that occurring between liquid expanded and liquid condensed films.

It is pointed out, that, in order to detect phase changes, more accurate and detailed data are needed than are available in most adsorption studies, and in particular, numerous data are required for the low pressure region.

It is felt that the Harkins-Jura concept is of considerable importance in work of the type discussed here, for it is not unreasonable to expect that such phase changes would be accompanied by changes in the dielectric constant of the adsorbed substance.

2. Dielectric Constant Theory:

The dielectric constant, e , of a substance is defined as the ratio of the capacity (C) of a condenser filled with the substance to the capacity of the same condenser when empty (C_o), i. e.,

$$e = \frac{C}{C_o} \qquad (37)$$

In the electrostatic system of units, the dimensions of C are those of length, and the unit in this system is known as the centimeter or statfarad. In the m.k.s. system, unit capacity is 1 coulomb/volt and is given the name 1 farad. Since this is an extremely large unit, the microfarad, 10^{-6} farad, and the micro microfarad, 10^{-12} farad, are more commonly used. These are commonly abbreviated μf and $\mu\mu$f respectively.

The dielectric constant of a substance is related to the structure of the molecules in a way that is now quite well understood. The ability of a substance to reduce the intensity of the electric field between the plates is due to two factors,the induced dipole of the molecules, and the permanent dipole possessed by certain molecules. The induced dipole results from the separation of the centres of positive and negative electricity in the molecule, and is proportional to the strength of the internal field, F. The proportionality constant, α_0, is called the polarizability of the molecule.

For the intensity of the internal field, Clausius and Mosotti used the expression:

$$F = E + \frac{4\pi}{3} I \qquad (38)$$

where E is the electric intensity, and I is the electric moment per unit volume. On this assumption, they derived the expression relating the dielectric constant of a non-polar substance to its polarizability. This expression is

$$\frac{e - 1}{e + 2} \cdot \frac{M}{d} = \frac{4\pi N}{3} \alpha_0 = P \qquad (39)$$

where M is the molecular weight, d is the density, N is the Avogadro number and P is called the molar polarization. The dimensions of P and α_0 are those of volume.

The effect of a permanent dipole, μ, in the molecule is to introduce a temperature dependent term into this equation as first shown by Debye (8). The equation which includes this effect is

$$P = \frac{e-1}{e+2} \cdot \frac{M}{d} = \frac{4\pi N}{3}\left(\alpha_o + \frac{\mu^2}{3kT}\right) \qquad (40)$$

where k is Boltzmann's constant. The inverse dependence on temperature results from the effect of thermal agitation in opposing the tendency of the dipoles to orient in the field.

Representing the molar polarization due to the induced dipole by $(P_A + P_E)$, and that due to the permanent dipole by P_M, equation (40) can be written:

$$P = (P_A + P_E) + P_M \qquad (41)$$

The induced polarization is made up of polarization resulting from displacement of electrons (P_E) and that resulting from displacement of atoms (P_A) within the molecule from their equilibrium positions. This last type of polarization occurs only when the applied electromagnetic field has a frequency comparable to, or lower than, the natural vibrational frequencies of the atoms. The electronic polarization, on the other hand, occurs even for very high light frequencies, and is, in fact, responsible for the refraction of light. Maxwell's well-known relationship equating the dielectric constant and the square of the refractive index ($e = n^2$) is valid when only electronic polarization is involved. Indeed, this equation makes it possible to evaluate P_E from refractive index measurements, and thus to obtain independent checks on the values of P_E obtained from equation (40) for polar molecules.

In order to obtain P_M, it is necessary to determine P at a number of different temperatures and to plot the values so obtained vs. 1/T. The slope of the curve then gives P_M and the intercept gives $(P_E + P_A)$. P_A is commonly small, so that the value of $(P_E + P_A)$ should check the value of P_E determined from refractive index measurements quite closely.

The polarization due to the orientation of permanent dipoles in the electromagnetic field might be expected to decrease and approach zero as the frequency is increased to a high value. This is related to the fact that a finite time, the "relaxation time", must elapse before oriented molecules can revert to a random orientation after the removal of the field. This decrease of the dielectric constant with increasing frequency is called "anomalous dispersion", and occurs quite generally with polar substances, usually in the radio frequency range for gases and liquids.

The Debye equation (40) is valid for polar molecules in the gas phase and in dilute solutions in non-polar solvents. For the treatment of liquids, it was suggested by Onsager (25) that the assumption of the Lorentz inner field must be abandoned, and he proposed that the field acting on a molecule should be considered as the resultant of two fields, the reaction field $\overline{R}$, and the cavity field $\overline{G}$, where the lines over the letters indicate their vector nature. The reaction field arises from polarization of the surrounding medium by the field of the dipole. It acts in a direction parallel to the instantaneous dipole moment $\overline{m}$, and exists even in the absence of an applied field. He derived the expression:

$$\overline{R} = \frac{2(e - 1)}{2e + 1} \cdot \frac{\overline{m}}{a^3} \qquad (42)$$

where a is the radius of the molecule. The field $\overline{G}$ is caused by, and acts parallel to the applied field:

$$\overline{G} = \frac{3e}{2e + 1} \cdot \overline{E} \qquad (43)$$

The essential difference between this and the field assumed in the Clausius-Mosotti derivation is that in the latter, the polarization of the molecule was assumed to have its average value, whereas in the Onsager derivation, its instantaneous value is considered. A treatment similar in the main to that used by Debye then yields the equation:

$$\frac{M}{d} \frac{(e - n^2)(2e + n^2)}{e(n^2 + 2)^2} = \frac{4\pi N}{3} \frac{\mu^2}{3kT} \qquad (44)$$

This is the Onsager equation and it has been used with considerable success in the study of the dielectric constants of liquids.

A molecule adsorbed on the surface of a solid is situated at a discontinuity or singularity in the electrical field. It is therefore not valid to apply equations derived for a homogeneous dielectric to this situation. While the mathematical treatment of such a situation would be very complicated, it seems reasonable that a reaction field should exist due to the presence of the highly polarizable silica. It will, however, differ in some respects from that existing in a pure liquid.

In the first place, the field of the dipole will be distorted because of the presence, on one side, of the silica. The reaction field will also be distorted, because on the other side is the less polarizable gas phase. In any event, there should be a reaction field which will, in turn, polarize the adsorbed molecule.

If the molecule is stationary, the reaction field will alternately aid and oppose the alternating applied field, but if the molecule is free to orient with the field, the reaction field will aid the applied field, and increase the polarization of the molecule. Thus, if the rotational mobility of the molecule were not affected by adsorption, it might be expected on this basis that the effective dielectric constant of the adsorbed ethyl chloride would be higher than that of the bulk liquid. This effect would decrease when further adsorption occurs on those molecules already adsorbed, and as saturation is approached the "differential" dielectric constant should approach that of the bulk liquid.

If increasing temperature has the same effect on the adsorbed molecules as it has on the molecules of a gas or liquid, then the dielectric constant should fall as the temperature increases for a given amount adsorbed. It appears possible however, that this effect will be complicated by others. For example, a molecule might be freed sufficiently from the restrictive forces of the adsorbent or of its neighbors to acquire an orientability which it lacked at a lower temperature. It is required only that the number of molecules thus acquiring orientability should be proportional to temperature in order to reduce the temperature coefficient to a value which might escape detection.

In the present problem it is necessary to consider the possibility of obtaining the true dielectric constant of silica from that of silica gel which may be considered as a mixture of silica and a gas phase or vacuum. We have further to consider the possibility of calculating the dielectric constant of adsorbed ethyl chloride from the experimental value for the dielectric constant of the silica gel with the ethyl chloride adsorbed on it.

The theoretical basis for determining the dielectric constants of pure solids from those of powders was reviewed and extended by Bruggeman (6). Wiener had previously derived equations which took account of the strong dependence on crystal form and arrangement. He first derived two limiting relationships for the dependence of the dielectric constant of a mixture on the dielectric constants and volume fractions of the two constituents. For crystals of a lamellar shape arranged parallel to the plates of the condenser he derived the relation:

$$E_p = f_1e_1 + f_2e_2 \qquad (45)$$

where E_p is the dielectric constant of the mixture, e_1 and e_2 the dielectric constants of the individual components, f_1 and f_2 their respective volume fractions. This represents a straight line joining e_1 and e_2 when E_p is plotted against the ratio f_1/f_2. For lamellar crystals arranged perpendicularly to the plates, he derived the relation:

$$E_s = \frac{1}{\frac{f_1}{e_1} + \frac{f_2}{e_2}} = \frac{e_1e_2}{f_1e_2 + f_2e_1} \qquad (46)$$

This relation corresponds to an effective dielectric constant which is always below the one obtained from the previous relation, except, of course, at the end points. He then showed that these relations were the upper and lower limits between which actual dielectric constants of mixtures of different crystal forms and arrangements must lie.

Wiener later proposed a more general formula, incorporating a "form number", u, which was dependent on the crystal form. This formula is:

$$E = \frac{E_p u + e_1 e_2}{E_p{}^1 + u} \qquad (47)$$

where

$$E_p^1 = f_1 e_2 + f_2 e_1 = \frac{e_1 e_2}{E_s} \qquad (48)$$

Bruggeman, starting from four assumptions which are quite generally valid about the particles and their arrangements, derived limiting equations which considerably narrow the gap between the E_p and E_s values of Wiener. The assumptions which he made were such as to ensure a quasi-homogeneous mixture and, in consequence, a quasi-homogeneous field.

For mixtures of solid substances designated as 1 and 2, and so distributed that $(f_1 + f_2)$ approaches unity, he derived two equations, the first for disordered aggregates of lamellar crystals:

$$E_1 = \tfrac{1}{2}\left[-E_s + \sqrt{E_s(8E_p + E_s)}\right] \qquad (49)$$

the second for aggregates of spheres:

$$E_s = \tfrac{1}{4}\left[2E_p - E_p^1 + \sqrt{(2E_p - E_p^1)^2 + 8e_1 e_2}\right] \qquad (50)$$

These curves intersect near the middle of their range. The Wiener form number is evaluated at this point and has the value $u_w = \sqrt{e_1 e_2}$. The general Wiener formula with this form number then has a course that lies at all points between E_1 and E_s, and can be used as a quite good approximation for actual mixtures. It has the form:

$$E_w = \sqrt{e_1 e_2} \cdot \frac{2E_p + \sqrt{e_1 e_2}}{E_p^1 + 2\sqrt{e_1 e_2}} \qquad (51)$$

Bruggeman then deals with mixtures which he calls "porphyritic", implying that small particles are embedded in a homogeneous, isotropic matrix. These are therefore akin to powders in an otherwise evacuated space. For lamellar crystals imbedded in the matrix he obtains:

$$E_{el} = e_1 \frac{e_2 + 2E_p}{2e_1 + E_p^1} \qquad (52)$$

and for spheres, the value E_{ek} may be obtained from the relation:

$$1 - f_1 = \frac{e_1 - E_{ek}}{e_1 - e_2} \sqrt[3]{\frac{e_2}{E_{ek}}} \qquad (53)$$

A value of the Wiener form number u_{ew} is then obtained which makes the general Wiener curve lie between these two extremes. He shows that the resulting Wiener equation gives values quite close to those obtained by the use of (51) when the ratio e_1/e_2 is not too large, so that the use of equation (51) is frequently justified when dealing with powders. Formula (51) was tested on data for KCl powders obtained by Sanger, Stocker and Errera and very good agreement was obtained.

The system with which we are dealing, consisting of adsorbent, adsorbate and vapour phase, is considerably more complicated than those considered in the Bruggeman theory. Still, it seems likely that the effective dielectric constant of such a system would, for a given volume ratio of the phases, lie below the line connecting the dielectric constants of adsorbent and adsorbate. If the behaviour were similar to that considered by Bruggeman, the apparent dielectric constant of the adsorbate would tend to decrease as its volume fraction increased. Any such effect would be small, and continuous with respect to the volume ratio.

In the preceding discussion we have encountered a number of effects which could cause real or apparent changes in the dielectric constant of an adsorbate as the amount adsorbed increases. These may be summarized as follows:

1. Restricted rotation -

   This would cause the dielectric constant to be lower than the bulk value. It could arise if the molecule were held rigidly by the adsorbent or, if the surface film were a condensed phase, by the close proximity of other adsorbed molecules. Only if the molecules were entirely prevented from orienting would the dielectric constant of the adsorbate be independent of temperature, and it would seem most improbable that this condition would obtain for the higher relative pressures.

2. Phase changes -

   If, as adsorption progressed, the surface films were to undergo a change to a denser phase, it is probable that the adsorbed material would exhibit a change in dielectric constant. It is difficult, on account of the complexity of such a change, to predict the magnitude, or even the sign of the change.

3. Surface inhomogeneity -

It seems likely, since both orientability and polarizability may be affected by adsorptive forces, that any variation in these forces over the surface will result in a variation of apparent dielectric constant as adsorption proceeds.

4. Changes in the nature of the adsorption -

In most physical adsorption systems involving a highly porous adsorbent, formation of second and higher adsorption layers begins when, or even before, the first adsorption layer is complete. It is generally agreed that the adsorption forces in the first layer are considerably stronger than in the higher layers. On this view, then, a change in apparent dielectric constant toward that of the bulk liquid should occur at the stage when higher layers begin to form. It has been pointed out that at this stage, the polarizability of the environment of the molecule will be changed from that of silica to that of adsorbed ethyl chloride. This would result in a changed reaction field.

5. In a sense, the specific inductive capacity of the silica gel itself will be increased because of the increased reaction field resulting from the presence, on one side, of the adsorbate.

PREVIOUS WORK

Argue and Maass (2) studied the dielectric constant of water adsorbed on cellulose. They found that the "differential" dielectric constant of the adsorbed water increased from the low value of 15.8 to a value only slightly below that of the bulk liquid. The dielectric constant of the adsorbed water was calculated from the experimental data by means of the formula:

$$E = f_1e_1 + f_2e_2 + f_3e_3$$

which is an extension of equation (45) given previously. The symbols have the same significance as in the previous equation, the additional term corresponding to the contribution of the adsorbate.

A report on a study of the dielectric constants of various vapours adsorbed on silica gel has been made by Zhilenkov, Perskii and Fedotova (32). It has not been possible to obtain a copy of this paper, so that only the limited information given by the abstract is available. The statement is made, however, that the dielectric constants of the adsorbed vapors were the same as those of the corresponding liquids. The frequencies used in this work are not given in the abstract. The vapors used were those of water, acetone, chloroform and benzene. The density of the silica gel is reported to be 2.095 and the dielectric constant 6.47. These are of some interest in connection with values reported in the present work.

A very interesting report has been published by Higuti (20) on the dielectric constant of n-propyl alcohol adsorbed on titania gel. The temperature range from -60° C. to 60° C. is covered in temperature intervals of 20°. Four wave lengths all in the radio frequency range, were used, namely; 100, 200, 345 and 804 meters. The heterodyne beat method was employed in the measurements.

The method used was to permit the adsorption of a certain amount of vapor on the adsorbent between the plates of a condenser. The "dead space", containing free vapor, was kept small in order to obviate the necessity for considering the small amount of vapor desorbed as the temperature of the closed cell was raised. Measurements were then made at seven temperatures ranging from -60°C. to 60°C. This was repeated after each increment of vapor. Additions of vapor were made in this way until the saturated vapor pressure was reached, so that free liquid was present in some of the tests.

Pressure measurements are not reported, so that it is not possible to study the data thoroughly in the light of adsorption theory. However, it is quite clear from several isotherm plots given in the paper that capillary condensation occurs in the upper region of the isotherm.

From the dielectric properties of the adsorbate, Higuti distinguishes four regions on each adsorption isotherm. The first and second adsorption regions do not involve capillary condensation. The other two regions he identifies as the capillary condensation region and the free liquid region. In the first adsorption region the plot of capacity change vs. amount adsorbed is linear at the lower temperatures but curves upward at higher temperatures. The temperature coefficient in this region is positive. A peculiar "ageing" effect was noticed on the third addition (65 mg. per gm. of adsorbent). The capacity, after rising, fell slowly to an equilibrium value.

In the second region, the author states that the plot is linear for all values of temperature and pressure. A few of his data were replotted on a larger scale graph and it was found that the linearity was only approximate. The deviations however, appeared to be quite random and are probably due to inaccuracies in the measurements. This observation does not reflect in any way on the general conclusions reached by the author, for the changes in slope on which these are based are, in most cases, quite definite.

The first major change in slope occurs at the beginning of the capillary condensation region. Here, the dielectric constant of the adsorbate is considerably higher,

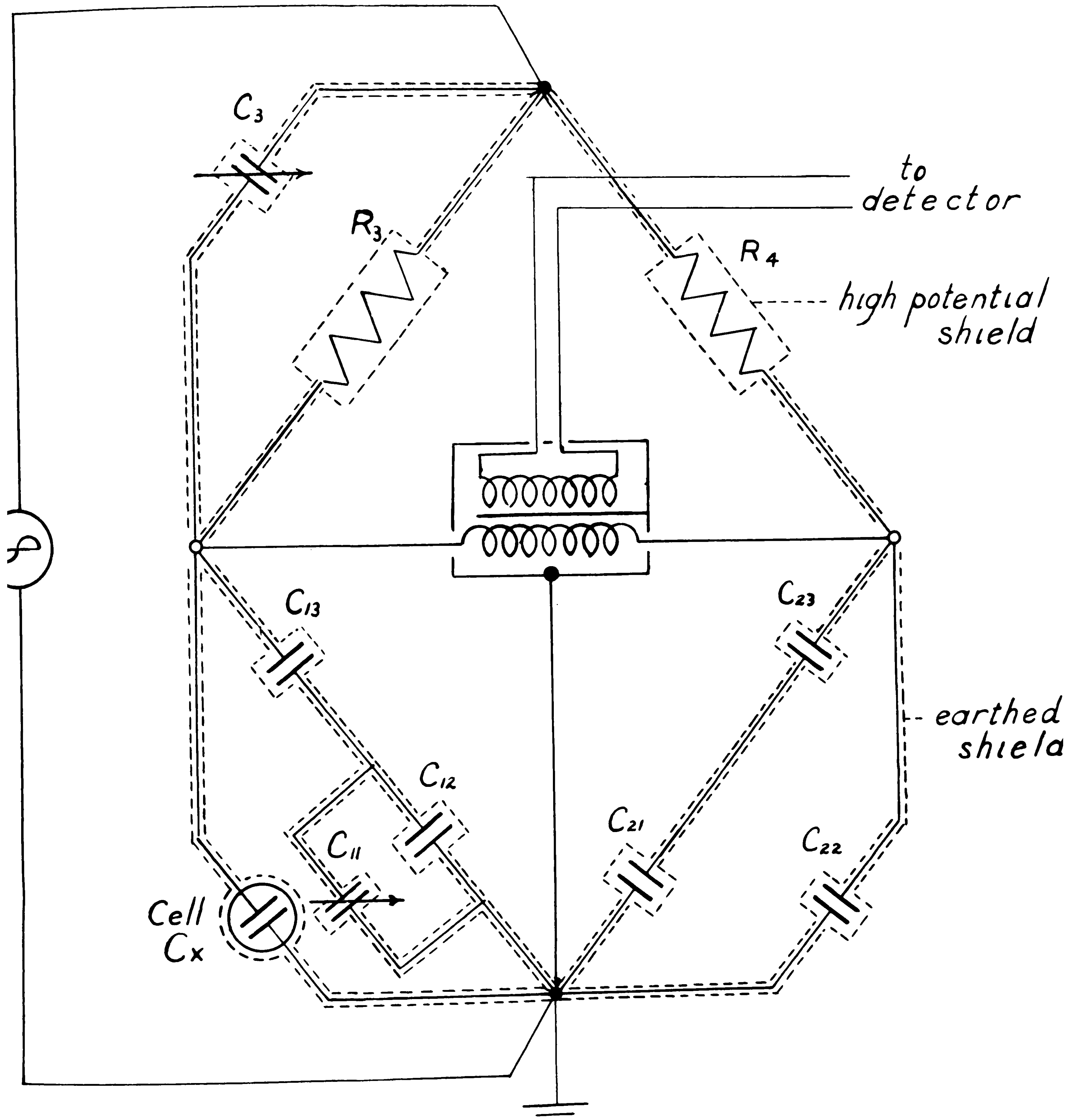


FIG. 2-BRIDGE CIRCUIT DIAGRAM

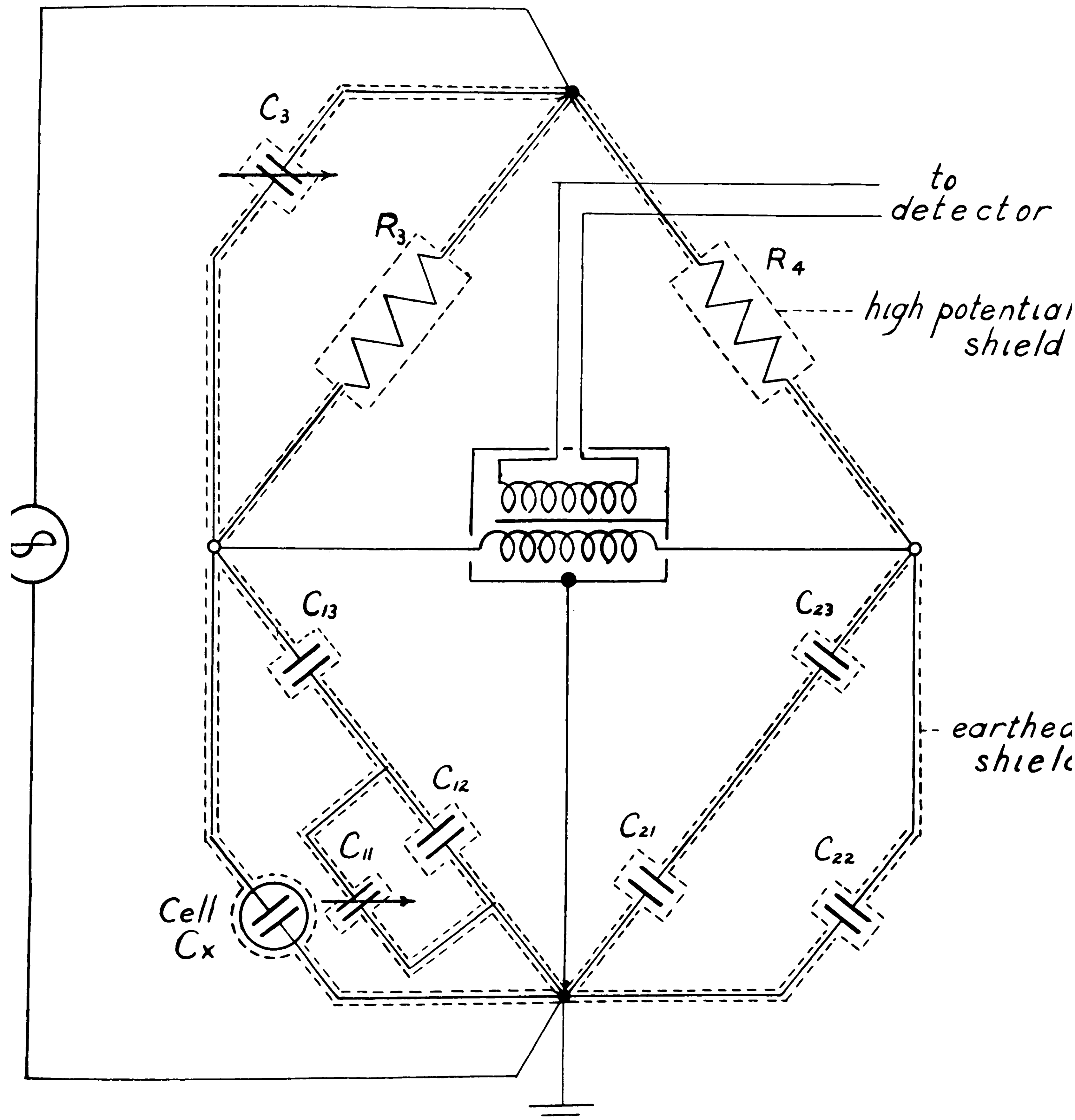


FIG. 2-BRIDGE CIRCUIT DIAGRAM

and, like the pure liquid, has a negative temperature coefficient. The temperature coefficient is somewhat lower than for the pure liquid.

After the appearance of the free liquid, the dielectric constant calculated for each increment of liquid is quite close to that for the pure liquid. This is a quite good indication that the method used for calculating the dielectric constant of the adsorbate is not greatly in error. This method is essentially that used by Argue and Maass, mentioned previously.

The author concludes that the orientation polarization is very small in the first and second adsorption regions, and that the positive temperature coefficient is a consequence of an increased mobility as the temperature rises. In capillary condensation, the dipoles have a much greater mobility. In this region, also, there was evidence of anomalous dispersion.

APPARATUS

Electrical Apparatus

The so-called "Schering Bridge" was used throughout for measurement of capacity and power factor, though in a modified form for later work. For purposes of reference, the general form of the bridge together with its balance conditions will be given here.

In Fig. I is shown the usual form of the Schering bridge. C_1 represents the condenser whose capacity and associated series resistance are to be determined. It will be assumed for the moment that C_2, a high quality standard condenser, presents a purely capacitive reactance to the e.m.f., in other words, its associated series resistance, r_2 is negligibly small.

Of the two decade resistance boxes R_3 and R_4, one (R_3) is normally left fixed at a convenient value while R_4 and C_4 are changed to balance the bridge.

Balance Conditions:

The bridge is balanced when:

$$C_1 = \frac{R_4}{R_3} C_2 \qquad \text{(a)}$$

$$r_1 = \frac{C_4}{C_2} R_3 \qquad \text{(b)}$$

It is seen that these conditions are independent of the frequency of the alternating current supplied by the generator. To quite a good approximation this is true, but when C_2 is not a perfect condenser, so that $r_2 \neq 0$, the following conditions must obtain for balance:

$$R_4C_2(1+\omega^2 r_1C_1R_3C_3) = R_3C_1(1+\omega^2 r_2C_2R_4C_4) \qquad (c)$$

$$R_4C_2(r_1C_1+R_3C_3) = R_3C_1(r_2C_2+R_4C_4) \qquad (d)$$

In these expressions, ω is the frequency in radians per second, C_3 refers to the capacity of a condenser in parallel with R_3, and takes account of the fact that there will be earth capacitances across R_3. These are compensated by the condenser C_4 in the opposite arm.

Balance conditions (c) and (d) are evidently slightly frequency-dependent. Conditions (a) and (b) derive from (c) and (d) respectively if C_3 and r_2 are taken equal to zero in (c) and (d).

Generator:

Alternating potential was supplied to the bridge by a phase-shift oscillator-amplifier run by a power pack. These pieces of apparatus were constructed, and are described by N. R. S. Hollies (21). The power pack consists of a transformer operating a full-wave rectifier. The output of the rectifier tube is put through a two-section smoothing filter and finally two voltage regulating tubes.

The output of the oscillator is put through two stages of voltage amplification, and a push-pull power amplification stage. The frequency range was from 455 to 5580 cycles per second. In most of the work under discussion, frequencies of 3530 and 3350 c.p.s. were used. The output wave, examined on the oscilloscope, had a good sine wave form.

Bridge:

It was originally planned to use a Schering bridge constructed by N. R. S. Hollies (21), and used by him in measurement of the dielectric constant of certain vapors. The various components of the terminal board were reassembled incorporating several minor mechanical improvements. At the same time, it was decided to employ a standard device for the elimination of the effect of earth admittances. This device is variously known as the "Butterworth Earthing Mechanism" (13) or the method is referred to as the "Double Balance Method". The device was employed in the form of a rheostat connecting the detector points and having an intermediate tap connected to a grounded point.

The connections were all enclosed in a metal chassis while the small sockets or "jacks" protruded, and were conveniently available for connecting the various circuit elements. Some such method of making the connections is necessary in order to ensure that the leads occupy the same positions for different determinations. Whenever possible the leads were made very short in order to reduce the capacity between the two wires.

The standard condenser C_2 was a 1000 μμf General Radio Company standard, type 505 which plugged in to the two jacks on the surface of the chassis. The condenser C_4 was constructed from five mica condensers and an air condenser having a maximum capacity of about 600 μμf. By the use of a two-gang, 10-position switch, the capacity could be varied from zero to 10,000 μμf in steps of 1,000 μμf. A mica condenser of 500 μμf capacity which could be placed in parallel with the air condenser served, with the air condenser, to give continuous variation of capacity between successive 1,000 μμf steps. All these condensers were mounted in a metal chassis and the leads terminated in plugs so spaced as to fit into the jacks on the terminal board. This variable condenser was later calibrated by plugging it into the C_1 position and determining the capacity for various settings. The terminal board carried a switch by means of which the condenser designated as C_4 could be placed in parallel either with R_4 or R_3 as required.

Originally, all leads consisted of two strands of wire insulated with rubber, both surrounded by a flexible metal sheath to serve as a shield. No small part of the difficulty encountered with the bridge in this form is believed to be due to the use of this type of lead, since the capacity between the leads, and between the leads and shield is very high, and there are good indications that the loss factor is also high. In the early work the flexible shield was grounded on all the leads, introducing small systematic errors, as will be seen in the section on shielding.

The Butterworth earthing mechanism consisted here of a 1 megohm rheostat of the radio volume-control type. In operation, R_3 and R_4 were first disconnected and a balance was obtained using the rheostat in their stead. Then R_3 and R_4 were connected again and R_4 and C_4 were adjusted to restore balance. The theory of this mechanism (13) shows that when balance is first obtained with small admittances (the two sections of the rheostat) in the ratio arms, and a second balance obtained by placing much larger admittances (R_3 and R_4) across these arms, then R_3 and R_4 give the true values of the resistive ratio, i.e. the error due to earth admittances has been eliminated. If C_4 and C_4' are the first and second values of the capacity shunting R_4, then the true value is $C_4' - C_4$. This mechanism is generally used in preference to the Wagner earth in a Schering bridge of the type shown.

The bridge in the form described above was tested very thoroughly and many minor changes were made to improve the constancy of the capacity readings. When, however, the last of these minor improvements had been made, the reliability of the bridge was still something less than was desired. Since it was necessary to measure capacity changes resulting from a convenient increment of adsorbed ethyl chloride vapor, a change amounting to only 1 - 3 μμf in some cases, it was clearly desirable and in all probability, necessary, to be able to measure 0.01 or 0.02 μμf reliably. Now, although with this bridge it was possible to set the bridge with this degree of precision, the value changed with time by perhaps 0.5 μμf in the course of a few hours. This was, for a long time, accepted as an inevitable limitation on the method.

In time, it was established that fluctuations in the temperature of the bridge itself, or at any rate, some part of it, were responsible for these drifts in apparent capacity values.

Modified Schering Bridge:

It was at first thought that this difficulty might be overcome without the necessity of thermostatting the entire apparatus, by using a bridge having a greater degree of symmetry. The Hartshorn modification (29) of the Schering bridge satisfied this requirement very well and it was decided to construct a bridge of this type. The

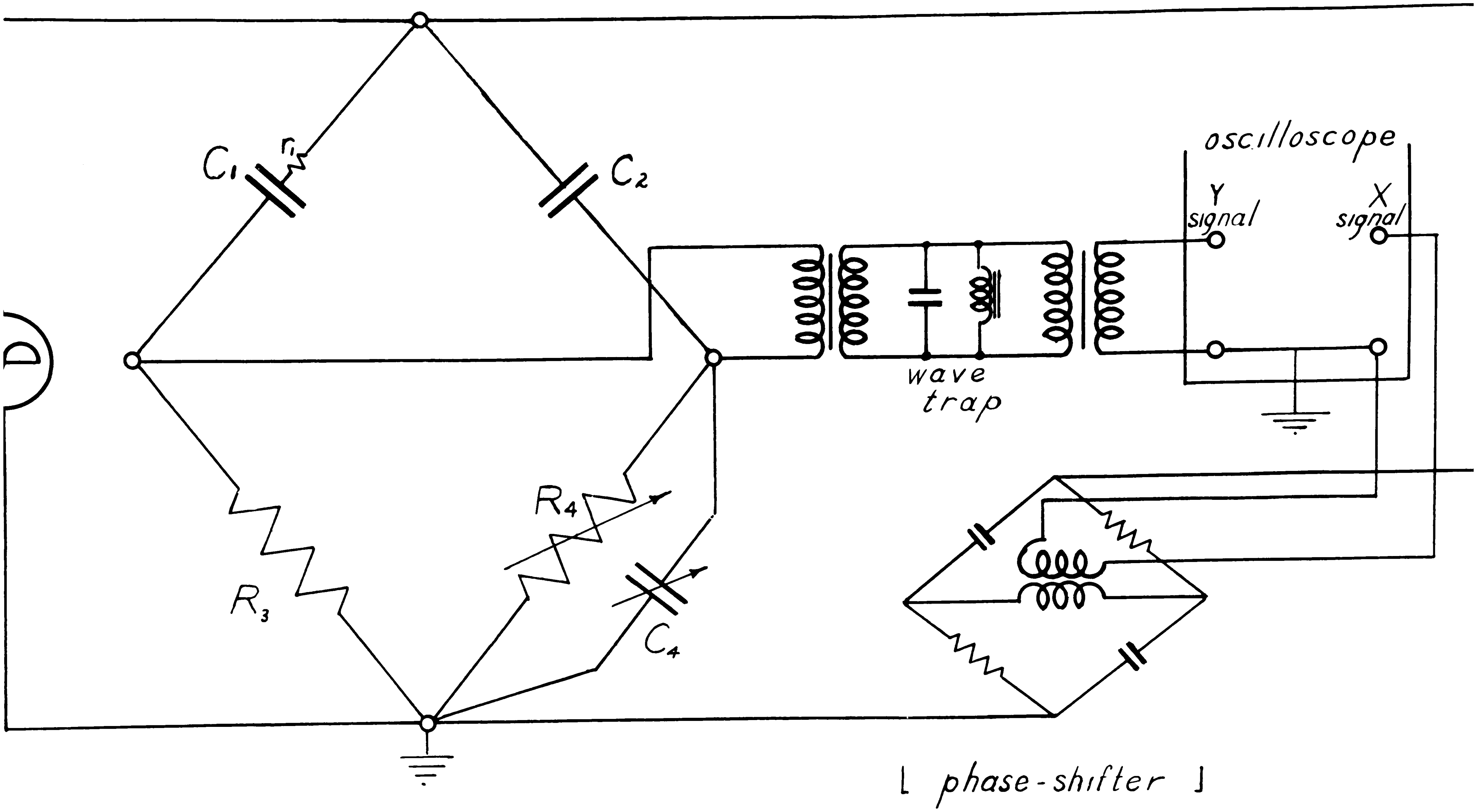


FIG. I – SCHERING BRIDGE

advantages of this type of bridge from the point of view of the present study may be summarized as follows:

1. Symmetry: in the original Hartshorn modification, the opposite arms are identical and the effect of temperature might well be minimized.
2. As an equal arm bridge it satisfies the conditions for optimum sensitivity.
3. Since it is essentially a substitution method, errors due to earth admittances and other stray effects are eliminated or minimized directly.
4. Since only changes in capacity are being measured, it is not necessary to disconnect the leads to the cell for the purpose of measuring their capacity.

One rather important disadvantage of this bridge is that its range is very small, and when constructed to measure 0.01 μμf, it will probably not be capable of measuring a change of more than 15 μμf in the arm containing the condenser under investigation. For this reason, it cannot be used to obtain the total capacity of the condenser. This, however, can be accomplished to a sufficient degree of accuracy by an expedient described in connection with the form of bridge finally adopted.

The perfect symmetry of the Hartshorn modification is destroyed here by the necessity of placing the relatively large test condenser across the C_1 arm (Fig. 2). This was matched in the C_2 arm by a variable air condenser of about 500 $\mu\mu$f maximum capacity. The condenser corresponding to C_{11} was eliminated because it was thought that the dissymmetry introduced with C_x and C_{22} removed the justification for the retention of this element of symmetry.

The resistors R_3 and R_4 were 1000 ohm elements from a good quality decade resistance box. The condenser C_{11} was a General Radio Precision Model of 1500 $\mu\mu$f capacity. C_{23} was the General Radio standard 1000 $\mu\mu$f condenser previously mentioned. C_{13} was a 1000 $\mu\mu$f mica condenser while C_{12} and C_{21} were 10,000 $\mu\mu$f mica condensers enclosed in shields and plugged into the top of the chassis.

Regarding the whole C_1 arm as a single condenser C_1, and the C_2 arm as a single condenser C_2, balance condition (d) becomes:

$$R_4C_2R_3C_3 = R_3C_1(r_2C_2 + R_4C_4) \qquad \text{(e)}$$

assuming $r_1 = 0$ (i.e. that C_1 is a perfect condenser). If now the capacity of the condenser C_1 is increased and this increase is considered as a small condenser C with an associated series resistance r placed in parallel with C_1, then C_1 itself will have to be reduced by an amount C, so that the total capacity of this arm will remain unaltered, and C_4, will have to be altered to, say, C_4' in order to maintain balance. For this second balance, from (d):

$$R_4C_2(rC_1 + R_3C_3) = R_3C_1(r_2C_2 + R_4C_4') \quad \text{(f)}$$

Subtracting (e) from (f)

$$rC_2 = R_3(C_4' - C_4)$$
$$= R_4(C_4' - C_4) \text{ since } R_3 = R_4 \quad \text{(g)}$$

The power factor $rC\omega$ of the small added condenser = $R_4(C_4' - C_4)\frac{C_1}{C}$. Detailed derivations of these balance conditions may be obtained from standard books on the subject (29). Thus the change in the capacity of the cell is equal, but opposite in sign, to the change which must be made in the C_1 arm to restore balance, and the power factor is given by the above expression.

The arrangement of condensers in the C_1 arm is the "magnifying" arrangement due to Hartshorn, and its effect in the arrangement of Fig. 2 is to make necessary a change of about 1500 μμf in C_{11} in order to change the effective capacity of the C_1 arm by 15 μμf. That is, the 50.00 scale divisions on the precision condenser C_{11} are made by this arrangement to correspond to 15 μμf instead of 1500 μμf (which is the actual capacity of this condenser). Thus readings can be made much more accurately; in fact, to about $\frac{0.01}{50}(15) = 0.003$ μμf.

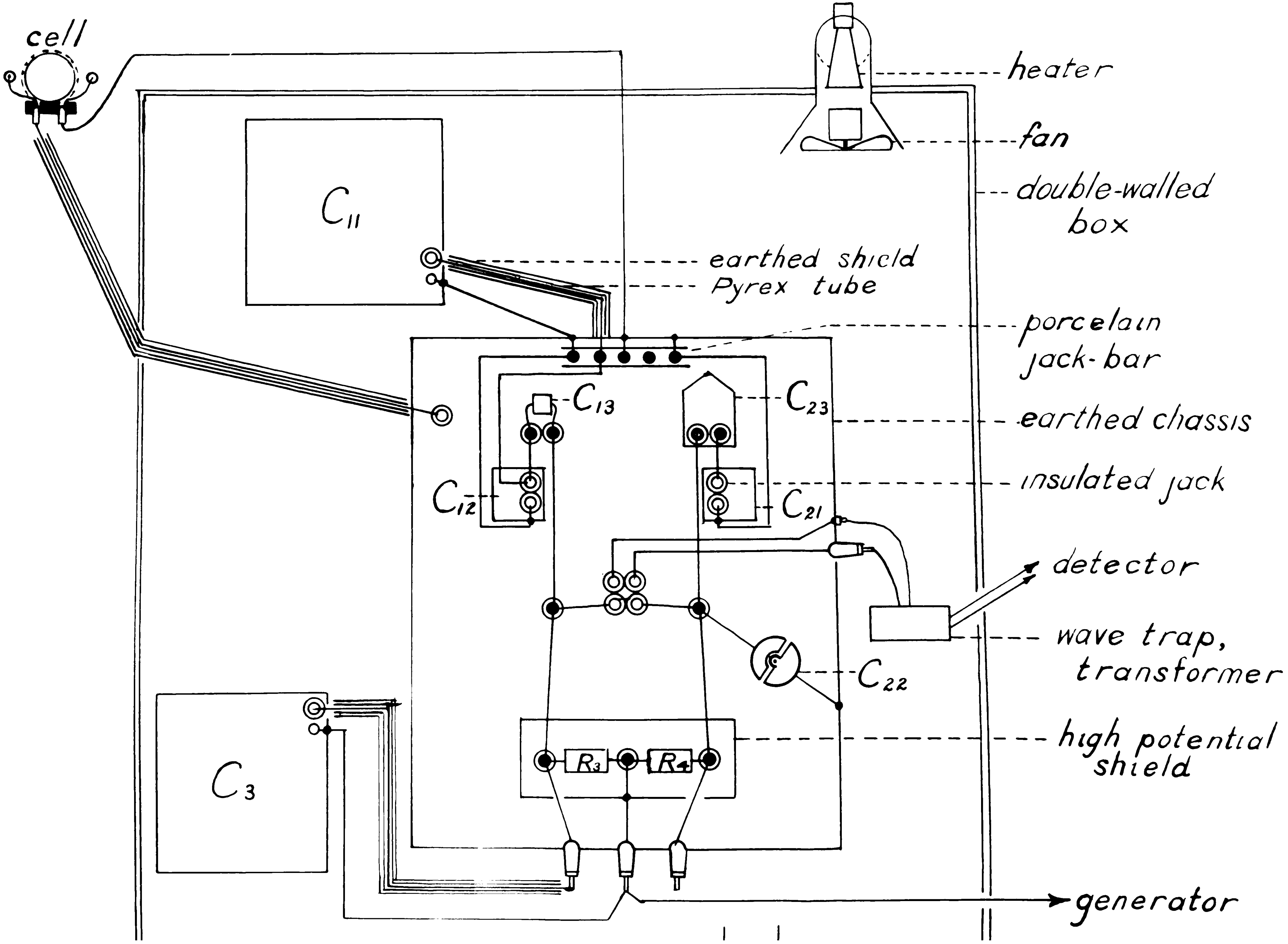
The actual arrangement of the bridge components is shown in Fig. 3. The chassis is a metal box 24 in. x

18 in. x 4 in. Porcelain insulators are used throughout to support the wiring, the condensers and the high tension shield surrounding the two resistors. Porcelain insulated jacks as shown are used for transformer plugs, the plug-in condensers C_{12} and C_{21} and some of the leads, and a porcelain jack-bar is used for other leads. The design is symmetrical as far as possible, and the wiring is rigid and such as to minimize dielectric loss.

In order to measure the total capacity of the first condenser used, a 100 $\mu\mu$f variable air condenser, C_{14}, was mounted in a metal box and provided with a dial marked off in 100 divisions. When this is placed across the C_1 arm, the bridge can be balanced when the test cell is connected, and again with the test cell disconnected, by changing C_{14}. The difference between the dial readings of C_{14} then gives a measure of the capacity of the test cell. The capacity of the second condenser was measured by disconnecting the 1500 $\mu\mu$f precision condenser, connecting it across the whole C_1 arm and repeating the procedure just described. The use of the large precision condenser was made possible by the relatively large capacity of the second test condenser.

Electrostatic shielding of this bridge was done, as far as possible, in strict conformity to the principles of shielding as given, for example, by Fergusson (11). The shields are shown by broken lines in Fig. 2. The high tension shield surrounding the two resistances consisted of a metal box 8 in. x 4 in. x 2 in. mounted on porcelain insulators inside the large chassis. All external leads which were not either at the high potential or at ground potential were shielded by insertion in a metal tube from which it was insulated by Pyrex glass, or paper. This shield was then given the proper potential as indicated by the shield connections in Fig. 2. The transformer was of the type having a shield between the primary and secondary, and this shield was inseparably connected to the external shield surrounding the transformer. This does not conform exactly to best shielding practice, but is a considerable improvement over an unshielded transformer.

It will be observed that, in contrast to the original Schering bridge, the condenser side of the bridge is grounded, thus making it possible to use a grounded shield on the precision condenser C_{11} and on the test condenser C_x. This arrangement which would be inadvisable if headphones were being used as the detector, is made possible by the use of an oscilloscope as the detector. The lead to the test condenser is necessarily quite long, about three feet, so that it is necessary to ensure low dielectric loss. Moreover its position must remain absolutely unchanged since


cell
heater
fan
double-walled box
C_{11}
earthed shield
Pyrex tube
porcelain jack-bar
C_{13}
C_{23}
earthed chassis
insulated jack
C_{12}
C_{21}
detector
wave trap, transformer
C_{22}
high potential shield
R_3
R_4
C_3
generator

even small changes of position can produce changes in the balance point considerably greater than those under investigation. In order to satisfy these requirements, the heavy copper wire which served as the lead to the higher potential plate was enclosed in a Pyrex glass tube. This was then enclosed in BX cable which could be clamped securely in position.

Detector:

A Sylvania oscilloscope, type 112, was used as a balance detector. The alternating potential from the detector points was put through an isolating transformer, through a wave trap designed to remove such higher harmonics as were present, through another transformer chosen to improve the match between the bridge impedance and the oscilloscope impedance, and was applied through an amplifier to the "Y Signal Input" of the oscilloscope. The amplifier referred to was actually the Y signal amplifier of another Sylvania oscilloscope. This voltage causes a rapid vertical oscillation of the spot at which the electron beam impinges on the end of the cathode ray tube.

The horizontal deflection of the spot was produced by the application of the oscillator potential to the "X - Signal Input" of the oscilloscope. When the bridge is unbalanced, therefore, there will be simultaneous horizontal and vertical deflections of the spot, producing a figure on the screen, in general an ellipse, the shape and inclination of which will depend on the relative magnitudes and phase of the X and Y signals. When the bridge is balanced, that is, when the two detector points have the same instantaneous potential, there will be no Y signal and the pattern degenerates into a horizontal straight line.

The task of balancing the bridge is considerably simplified if, of the two components C_{11} and C_3, which are variable, one affects only the inclination of the major axis of the ellipse, the other only the size of the minor axis. This can be achieved by the use of a phase shifting network in the X signal input. Following the suggestion of Lamson (22) in this connection the bridge type of phase shifter due to Turner and McNamara (28) was used, followed by an isolating transformer. This is indicated in Fig. 1.

Cell:

The design of a suitable condenser and its incorporation in a glass vacuum apparatus has presented considerable difficulty. The requirements on such a cell are listed below:

1. The condenser must have a capacity large enough so that the changes in dielectric constant produced by adsorption of ethyl chloride will give changes in capacity which the apparatus is capable of measuring with a sufficient degree of accuracy.

2. Since it is desirable to obtain a measure of the capacity of the condenser when empty, and when filled with silica gel, the cell should be constructed in such a way that the process of filling the cell will not involve indeterminate changes in lead capacities and so on.
3. It must be possible to heat the cell in order to free the silica gel of adsorbed material.
4. The design must be such as to minimize stray electrical effects.

The first satisfactory condenser is shown in Fig. 4. It was made of Duralumin in the form of two concentric cylinders with the following dimensions:

	Outer Cylinder	Inner Cylinder
Length (cm.)	13	12.3
Inside radius (cm.)	0.94	0.48
Outside radius (cm.)	1.27	0.69

Volume - 15.3 cc. between plates.

The condenser is fitted, at its base, with plugs which fit into a standard receptable at the bottom of the glass envelope. The condenser can be removed without altering the positions of the leads in any way, so that the capacity of the condenser can be obtained by difference without any error due to the lead wires except for the very small

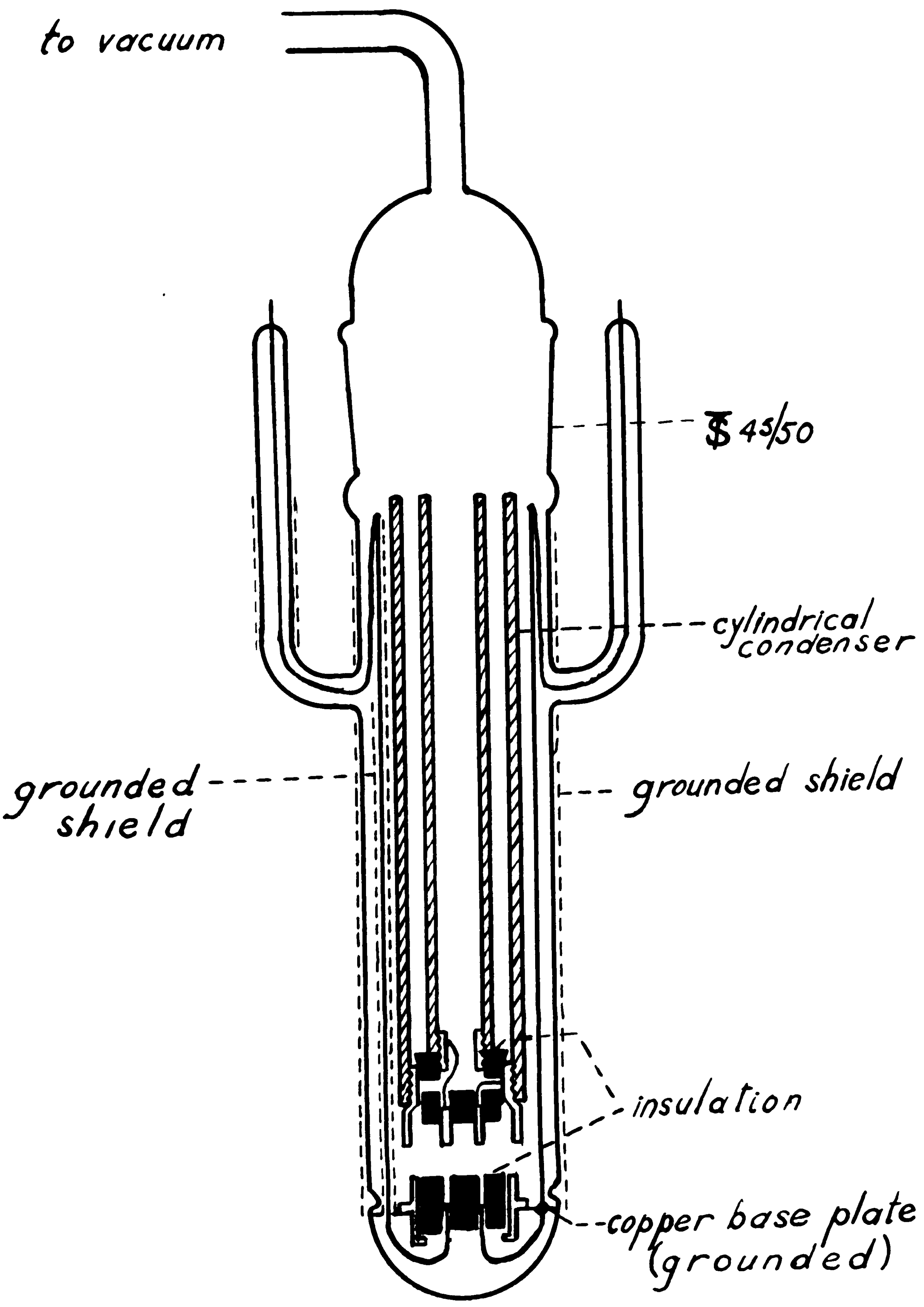
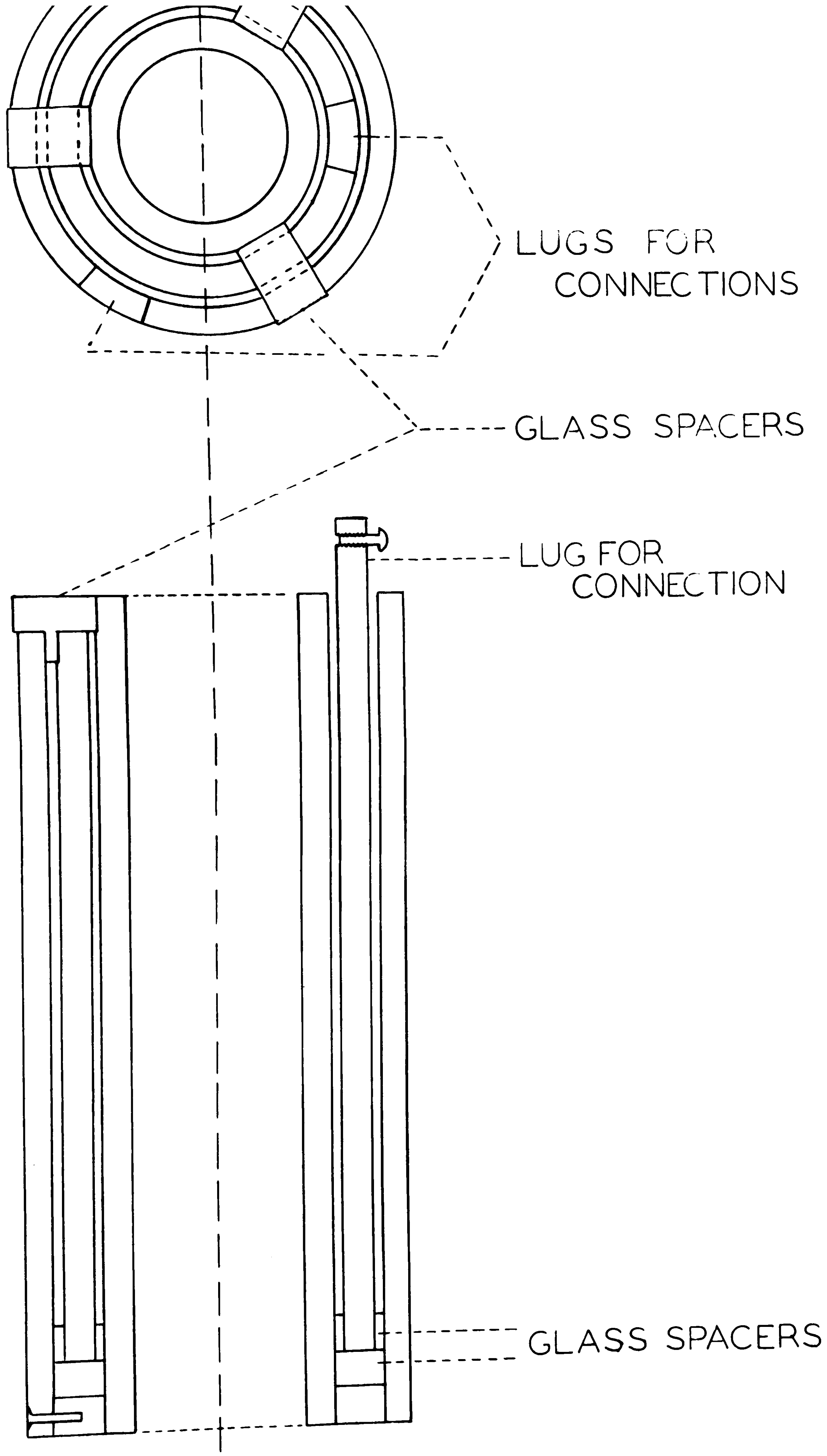


FIG. 4-CROSS-SECTION OF FIRST CELL

capacity between the two plugs. The higher potential lead (Fig. 4) is shielded by a metal tube, so that the capacity between this lead and the condenser is negligible.

The second condenser (Fig. 5) was designed by R. L. McIntosh and L. A. McLeod and made by the National Research Council. It is made of "Invar" in the form of three concentric cylinders of which the innermost and outer are at ground potential. It has two important advantages over the first condenser. It has a larger electrical capacity (three or four times as great), and the three cylinders are retained at the proper relative positions by a very effective set of Pyrex glass spacers, accurately ground to fit. These ensure that the necessary handling of the condenser will not alter its capacity appreciably, and thus makes possible an accurate estimation of the dielectric constant of the material between the plates. The leads to this condenser enter from the top of the cell and are held in fixed positions by sleeves of narrow Pyrex tubing joined by a glass cross-arm.

Originally a sample of silica gel which had been quite finely ground was used. Considerable difficulty was encountered in freeing this silica gel of adsorbed material because the evolved gases would accumulate within the silica gel until the excess pressure was sufficient to blow



TOP VIEW AND CROSS-SECTION OF
INVAR CONDENSER

FIG 5

the obstructing gel out of the condenser. This difficulty was avoided in later work by using coarser silica gel which had been carefully sieved to remove undersize.

Another difficulty was the melting of the grease on the ground glass joint on the envelope during the initial desorption heating of the silica. At one time, the ground glass joint was dispensed with for this reason even though it made the condenser completely inaccessible once in position. In later work, the ground glass joint was again used, and overheating was prevented by playing a stream of air over the joint from a U-shaped glass tube perforated on the sides facing the ground glass joint.

The leads from the bridge to the cell were plugged into two standard jacks mounted in a Lucite platform which was clamped onto the body of the cell. This receptable must be situated several inches above the level of the water in the water bath in order that the capacity readings should not be affected by the level of the water. Further, in order to protect any unshielded portion of the higher potential lead such as that in the glass arm of the first cell from the effect of the bath water, the whole cell was wrapped with tin foil to a point an inch or two above water level, and this tin foil was grounded. This was found to be unnecessary with the second condenser because the leads do not come close to the water.

Temperature Control:

Trial of the Hartshorn-type bridge described in detail above soon disclosed that it would be necessary to control the temperature of the bridge components. Consequently, several air baths were constructed and tried out. Only the one at present in use will be described.

The air bath consists of a double walled box of masonite construction on a frame of 1½" x 1½" lumber. A table top forms the bottom of the box, and the top of the box is removable. The outside dimensions of the box are 40 in. x 30 in. and it is 16 in. in depth. All of the bridge components with the exception of the cell and part of its lead are contained in this bath. The top of the box has three hand-holes with closely fitted covers. After trying simple stirring of the air in conjunction with a thermostatically controlled heater, it was decided that a closed circulation system would have to be adopted in order to eliminate the effect of variations in room temperature. This necessitates the use of both a cooling and a heating system. The latter is thermostatically operated. As an example of the unsatisfactory operation of earlier air baths, it may be mentioned that in one rather inefficient bath, in which the temperature varied periodically over about 0.8°C., the capacity readings parallelled the temperature changes very closely, the variations being about 0.02 μμf.

At another time, when a satisfactory air bath was in operation, the temperature coefficient of the capacity readings was evaluated roughly and found to be about 0.3 μμf per degree. This is extraordinarily large, and is now thought to be attributable to the 500 μμf variable air condenser in which the plates are quite close together and no attempt made in the design to minimize the effect of temperature on plate separation.

The present air bath has a high speed fan with a four inch blade driving air out of the bath into a 3½ inch pipe of thin sheet iron which leads the air outside of the bath back to the opposite side. In one section of this pipe is a copper coil through which cold water circulates so that the air is cooled somewhat. A thermostatically controlled 200-watt heater is placed directly in front of the fan. By this arrangement a continuous flow of air takes place across the bath. The thermoregulator was especially designed to meet the requirements of an air bath. It consists of a hollow, thin walled cylinder, open at both ends to allow free access of air. It was made by blowing out the walls of two Pyrex tubes in order to reduce the wall thickness by about one half. It has the desirable characteristic of a large surface-to-mercury volume ratio.

The temperature of the cell is maintained by an ordinary water bath containing a heater and, when necessary, a copper cooling coil.

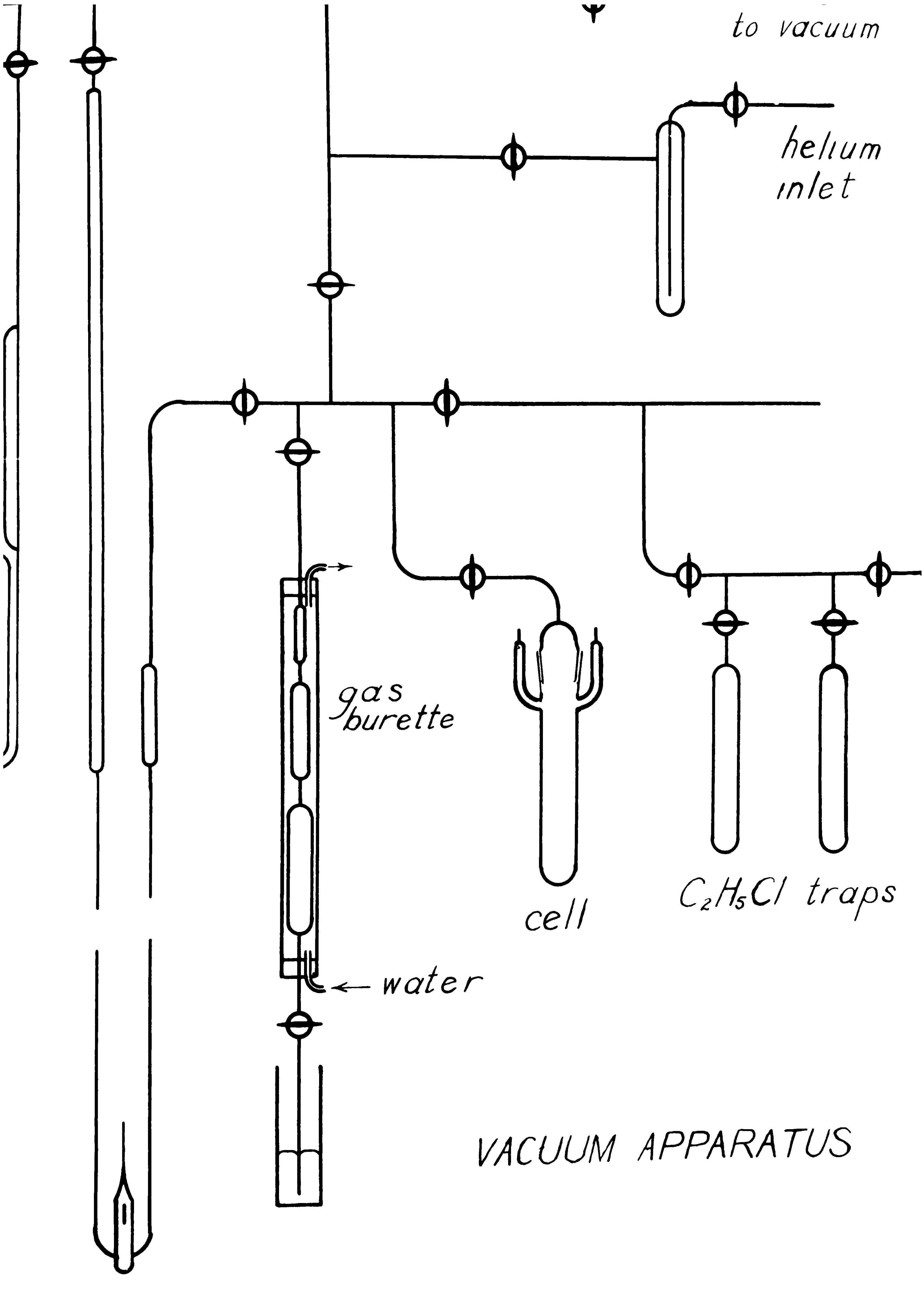
Voltage Stabilization:

The line voltage supplying the power pack and two oscilloscopes was stabilized by a 250-watt Sola constant voltage transformer.

Vacuum Apparatus:

The vacuum apparatus in its present form is shown in Fig. 6 which is largely self-explanatory. Provision is made for admitting and storing ethyl chloride and for purifying it by distillation from a dry ice-acetone bath to a liquid air bath. The amount of vapor is measured by admitting the vapor to the calibrated gas burette, through which circulates water from the constant temperature water bath. The pressure is measured on the constant volume manometer which is read with the aid of a cathetometer to 0.01 cm. of mercury.

Helium, for volume determinations, was first purified by passing it through a charcoal trap (Fig. 6) at liquid air temperature.



VACUUM APPARATUS

FIG. 6

Materials:

The silica gel used was a commercial product made by the Davison Chemical Corporation, Baltimore, Md. It carried the number 6956-160. A sample of this silica gel was ground and the fraction passing a 40-mesh screen but retained by a 60-mesh screen was used in the first two runs. In the last two runs, 45-80 mesh silica gel was used. The manufacturers have kindly supplied the following information on this product:

1. Surface area about 700 square meters per gram measured by nitrogen adsorption.
2. Dehydration under vacuum at 200°C. gives a product with about 5 per cent water. This water cannot be removed without partial collapse of the gel structure.
3. The analysis is:

SiO_2 - 99.6 per cent minimum on dry basis

Na as Na_2O - 0.03 per cent average

Fe as Fe_2O_3 - 0.03 per cent average

Al as Al_2O_3 - 0.10 per cent average

The ethyl chloride was a product of the Ohio Chemical and Manufacturing Company. The cylinder was attached to the vacuum apparatus by a short length of pressure tubing and when required, a small volume of the liquid was collected in a trap immersed in dry-ice acetone. Some of this liquid was then permitted to distil into an adjacent trap cooled in liquid air. The sample thus obtained was isolated and stored until needed at the temperature of a dry ice-acetone mixture. Before use, the ethyl chloride was frozen by immersing the trap in liquid air. The space above the ethyl chloride was then thoroughly evacuated, and the ethyl chloride was allowed to melt. This was repeated several times in order to free the ethyl chloride of entrapped gases.

EXPERIMENTAL RESULTS

The duralumin condenser was used in the first two series of experiments at 20°C. and 10°C. Because of the smaller electrical capacity of this condenser, the accuracy of the electrical measurements was less than when the Invar condenser was used. Nevertheless, the essential features of the later work are apparent in the results of the first two runs.

It was necessary to determine the volume of the cell before and after packing the condenser with silica gel in order to determine the volume of the silica. This was accomplished by expanding helium from a known volume into the cell. The known volume was that of the gas burette (Fig. 6) which was calibrated by weighing the mercury delivered between successive calibration marks. The volume of the constant volume manometer and tubing connected to the gas burette was determined by expanding helium from the burette into this part of the apparatus. The volume of the cell was then determined by expanding helium from the burette and connecting tubing into the cell.

The results of the volume determinations are given in Table I. In the interests of conciseness, the necessary volume data for all runs are included here, those for the 40°C. and 25°C. runs being identical. The volume of the manometer and line section was changed from its value in the first two runs by the introduction of a section making possible the removal of the cell in the last two runs.

Table I

Determinations of volumes of cell and other sections of vacuum apparatus as described in the text.

Section	Volume, cc.
1. gas burette	
top bulb	4.07
middle bulb	16.80
lowest bulb	50.83
Total	71.70

Section	20°C.	10°C.	40° and 25°C.
2. manometer	38.61		
and line	38.64		66.21
	38.61		66.16
mean	38.62	same	66.18
3. cell (condenser empty)	262.2	——	210.83
	262.7		210.85
mean	262.5		210.84
4. cell (condenser filled)		258.7	208.52
	258.4	258.5	208.33
mean	258.4	258.6	208.42
5. volume of silica gel (difference)	4.1	——	2.42
6. weight of silica gel (gm.)	9.89	9.70	5.713
7. density	2.41	——	2.36

of the manometer and line section was changed from its value in the first two runs by the introduction of a section making possible the removal of the cell in the last two runs.

Table I

Determinations of volumes of cell and other sections of vacuum apparatus as described in the text.

Section	Volume, cc.					
1. gas burette						
top bulb			4.07			
middle bulb			16.80			
lowest bulb			50.83			
Total			71.70			
	20°C.		10°C.		40° and 25°C.	
2. manometer	38.61					
and line	38.64				66.21	
	38.61				66.16	
mean		38.62	same			66.18
3. cell (condenser						
empty)	262.2		——		210.83	
	262.7				210.85	
mean		262.5				210.84
4. cell (condenser						
filled)			258.7		208.52	
	258.4		258.5		208.33	
mean		258.4		258.6		208.42
5. volume of silica gel (difference)	4.1		——		2.42	
6. weight of silica gel (gm.)	9.89		9.70		5.713	
7. density	2.41		——		2.36	

In all experiments involving the first condenser, the weight of the silica was obtained from the difference in weight of a weighing bulb containing the silica, before and after filling the condenser. The silica in the weighing bulb was freed from adsorbed substances before and after removal of the silica, by attaching it to the vacuum apparatus and heating at about 200°C. for several hours under the fullest vacuum obtainable with the diffusion pump about 10^{-4} mm. After cooling in air for half an hour, the bulb was weighed to the nearest 0.01 gm. The silica in the condenser was then subjected to a repetition of the heating under vacuum for a period of six hours, the cell was closed off, ready for admission of ethyl chloride.

The second cell could be detached from the vacuum system and weighed before and after filling it with silica gel. This cell was not heated above 120° because of the danger of cracking the glass spacers. The cell was heated under full vacuum for three days, after which another day was required for the cell to come to equilibrium, as evidenced by constancy of the capacity readings. In order to assure that the contents of the cell actually underwent the same temperature changes as the exterior, the cell was filled with helium during the heating and cooling processes.

A calibration of the bridge was carried out in order to relate the change in the reading of C_{11}

directly to the change in capacity of the cell. This was done by placing the precision air condenser having a range of 1500 $\mu\mu$f across the cell and determining by how much its capacity must be altered to compensate a full scale change (988 $\mu\mu$f) on another variable condenser connected in the C_{11} position. A number of trials showing good agreement gave a value of 10.8 $\mu\mu$f for the change in the precision condenser. The magnification of the arrangement is therefore 988/10.8 = 91.5, in quite good agreement with the calculated value of 100 (considering the allowable variations in the mica condensers used and the effect of shield capacities).

When the precision condenser is put back in the C_{11} position, the magnification is unchanged, and a change of 1 division (30 $\mu\mu$f) on C_{11} will correspond to a change of 30/91.5 $\mu\mu$f = 0.328 $\mu\mu$f in the cell. The total range of 50 divisions on C_{11} will then correspond to a change of 16.4 $\mu\mu$f in the cell. When accurate values for the capacities of C_{12} and C_{13} are available, an accurate value for the effective capacity change, ΔK, can be calculated from the equation:

$$\Delta K = \frac{(C_{13})^2 \cdot \Delta(C_{11})}{(C_{12}+C_{13})(C_{12}+C_{13}+C_{11})}$$

It can be seen that when ΔC_{11} is negligible by comparison with C_{12} (10,000 μμf), the factor, by which ΔC_{11} should be multiplied to give ΔK, is a constant. Since, with the arrangement described above, this factor changes by more than ten percent, the effective capacities of the C_1 arm were calculated for different settings of C_{11}, assuming the nominal values of the condensers to be correct. The changes in capacity for changes of 6.67 (200 μμf) in the dial reading of C_{11} were computed by subtraction. The ratio of the changes was calculated, assigning a value of unity to the dial change from 46.67 to 40.00. The value of unity was then assigned to the dial reading 43.33 (average value) and the corresponding numbers to other positions of the dial. These were then plotted, and the value obtained in each run was multiplied by the factor corresponding to the region of the C_{11} dial actually used. This procedure eliminates most of the error which would result from assuming ΔK to be linear in ΔC_{11}, and is satisfactory for our purpose. If absolute values were required with the same degree of accuracy as that of the relative values used here, the equation given above would be used with exact values of C_{12} and C_{13}.

In the 20°C. series, 9.89 gm. of silica gel were used in packing the condenser. Using the figure 4.1 cc.

for the volume of this silica gel from Table I, the density is 2.41 gms. per cc. This value, within the limits of its accuracy, gives the "true" density, assuming that all the pores and interstices are penetrated by the helium.

The electrical capacity of the condenser was determined during the 10°C. series. Since, for reasons already mentioned, the values obtained with the Invar condenser are more reliable and are the only ones used in subsequent calculations, the values given below are only of interest for comparison.

The dial readings on the 100 μμf condenser are given below:

cell leads out	89.1
cell leads in	75.7
capacity of leads	13.4 μμf
empty condenser out	75.7
empty condenser in	36.3
capacity of empty condenser	39.4 μμf
packed condenser out	89.1
packed condenser in	12.2
capacity of packed condenser	76.9 μμf

$$\text{dielectric constant of silica gel} = \frac{76.9}{39.4}$$

$$= 1.95$$

Before starting a determination, the temperature of the water bath was adjusted to the desired value. In order to ensure that the condenser was in temperature equilibrium with the bath, helium was introduced to a pressure just below one atmosphere and the cell was then left in the bath for several hours. The helium was then removed and the cell stopcock closed.

Ethyl chloride vapor was admitted to the burette system and the pressure was measured. It was found that when initial pressures of about 50 cm. of mercury and higher were used, the pressure fell very slowly, probably due to solution of the ethyl chloride in the stopcock grease. Except in the higher pressure region of the adsorption, therefore, initial pressures below 50 cm.were used. When it was necessary to employ initial pressures of about 70 cm. the practice was adopted of reading the pressure as quickly as possible and opening the stopcock to the cell and thus reducing the pressure before appreciable solution of ethyl chloride could occur.

The cell stopcock was then opened slightly and the pressure quickly fell to within a millimeter of the equilibrium value. The capacity of the precision condenser C_{11} was then reduced to restore the bridge balance. Readings of pressure and C_{11} were taken at intervals of fifteen minutes or so until no further change could be detected. All readings, together with room temperature and the temperatures of the air and water baths were recorded.

In the first series, at 20°C., a period of from six hours to a day or more was allowed for attainment of adsorption equilibrium. Certain difficulties, due principally to inadequate temperature control of the air bath and improperly shielded leads were encountered during the early runs. A number of improvements were made during the course of this series, and the apparatus was checked frequently for constancy of the equilibrium readings. By the seventeenth addition of ethyl chloride, the air bath had been modified to substantially its present form, and no further trouble was encountered with the bridge itself.

It had been planned to continue additions of ethyl chloride up to an equilibrium pressure of 50 or 60 cm. of Hg, and then to follow the desorption process. After the 26th addition of ethyl chloride, however, the pressure and capacity readings failed to reach equilibrium values within a day. After another day, the bridge was found to be very far off balance. The most striking change was in the resistive component of the cell impedance as measured on the condenser C_3. It was impossible to balance this component, indicating the presence of some conducting material between the plates of the condenser. At this point it was noticed that the silica gel, formerly white in color, had acquired a brownish tinge. This series was abandoned, and desorption of the adsorbed material was begun. At low pressures, the C_3 balance values began to return to normal. A brown material collected in the grease of the stopcocks. The cell was heated in order to complete the removal of adsorbed products but this resulted in the evolution of larger amounts of the brown material and was discontinued. The cell was removed from the vacuum system and opened. The odor of HCl was noticed in the cell, and the condenser itself, and the wall of the cell, were coated with a brown tarry material.

The various possible explanations which were considered for the appearance of the brown substance will not be detailed here. It was finally decided that it was due to a chemical reaction between the Bakelite insulators and the ethyl chloride. The Invar condenser was ordered, and while awaiting delivery, it was decided to replace the Bakelite by inorganic material. The Bakelite mountings for the small plugs and receptables were replaced by Insa-lute cement mountings. The Bakelite ring on which the inner cylinder of the condenser rested was replaced by a short section of Pyrex tubing. This condenser was used for the series at 10^oC.

without encountering any of the difficulties which had terminated the previous series.

Calculations of the volume of vapor adsorbed, expressed in terms of cc. at 0°C., 760 mm. were made according to the formula:

$$V = \left[(p_1 - p)\frac{V_b}{T_b} - (p - p_2)\frac{V_c}{T_c} \right] \frac{273}{76}$$

where

p_1 is the initial pressure in the burette system before opening the cell;

p is the equilibrium pressure after adsorption is complete;

p_2 is the pressure of ethyl chloride in the cell before the addition, i.e. the equilibrium pressure of the preceding addition;

V_b is the volume of the burette system used;

T_b is the temperature of the burette system. This must take into account the fact that the manometer and connecting tubing is at room temperature while the burette is at the temperature of the water bath.

V_c is the volume of the cell. At higher pressures this must be decreased by the volume occupied by the adsorbate, assuming normal liquid density;

T_c is the temperature of the cell. This must take account of the fact that the part of the cell above water is at room temperature.

No correction has been made for deviations from the ideal gas laws.

Sample calculation:

Addition number 20 at 20°C.

Room temperature 26°C.

$T_b = 296°K$ $\qquad p_1 = 47.04$ cm.

$T_c = 297°K$ $\qquad p = 14.24$ cm.

$V_b = 110.3$ cc. $\qquad p_2 = 12.28$ cm.

$V_c = 258.4 - 2.3 = 256.1$ cc.

$$\frac{V}{m} = \left[32.80\ \frac{110.3}{296} - 1.89\ \frac{256.1}{297}\right]\frac{273}{76}\cdot\frac{1}{9.89}$$

$= 3.87$ cc. per gm.

The capacity change was calculated from the formula:

$\triangle C =$ (change in dial reading)(0.328)(f)

Here f is the factor referred to on page 68 taking account of the non-linearity of capacity change with respect to dial reading.

Sample calculation:

Addition number 20 at 20°C.

$$\triangle C = (27.54 - 24.83)(0.328)(1.106)$$

$$= 0.98 \text{ uuf}$$

$$\frac{\triangle C}{\triangle V} = \frac{0.98}{3.87} = 0.254$$

The results of the 20°C. series are summarized in Table IIa. Results derived from these are given in Table IIb of a later section. The symbol $\triangle V/m$ used in this table and in other sections means the amount of ethyl chloride adsorbed, expressed as cc. of the vapour at 0°C. and 76 cm. pressure per gram of silica gel.

Table IIa

Effect of adsorbed ethyl chloride on capacity of a condenser with silica gel dielectric. Temperature 20°C. Duralumin condenser.

Addition Number	p(cm.)	$\Delta V/m$ cc./gm.	Total $\Delta V/m$	ΔC μμf	Total ΔC μμf	$\frac{\Delta C}{\Delta V/m}$
1	0.01	1.71	1.71	1.12	1.12	0.65
2	0.04	2.81	4.52	0.63	1.75	0.337
3	0.09	2.42	6.94	0.94	2.69	0.385
4	0.18	3.93	10.87	1.30	3.99	0.330
5	0.45	3.70	14.57	1.22	5.21	0.325
6	0.71	4.53	19.10	1.54	6.75	0.330
7	1.06	4.77	23.87	1.61	8.36	0.337
8	1.41	4.16	28.03	1.37	9.73	0.328
9	1.90	4.35	32.38	1.45	11.18	0.330
10	2.48	4.41	36.79	1.44	12.62	0.325
11	3.19	4.09	40.88	1.27	13.89	0.309
12	3.97	4.04	44.92	1.31	15.20	0.317
13	4.70	3.19	48.11	1.04	16.24	0.325
14	5.46	3.24	51.35	0.96	17.20	0.292
15	6.49	3.10	54.45	0.94	18.14	0.300
16	7.78	3.63	58.08	1.23	19.37	0.340
17	9.16	3.57	61.65	0.99	20.36	0.272
18	10.53	3.38	65.03	0.90	21.26	0.264
19	12.28	3.85	68.88	1.03	22.29	0.266
20	14.24	3.87	72.75	0.98	23.27	0.254
21	18.00	6.80	79.55	1.83	25.10	0.267
22	22.24	6.56	86.11	1.68	26.78	0.257
23	26.25	6.00	92.11	1.53	28.31	0.256
24	30.37	5.55	97.66	1.51	29.82	0.270
25	34.04	4.78	102.44	1.17	30.99	0.246
26	37.61	4.04	106.48	1.04	32.03	0.256

The 20°C. series was in progress for a total of two months. There was by this time abundant evidence that no appreciable error would be caused by assuming equilibrium after about two hours, at least for the earlier additions.

Two false starts were made on the 10°C. series, the first due to a short circuit in the cell, the second due to a leak. The silica gel, which had been subjected to a thorough heating and evacuation before the run was started, was evacuated for one day at room temperature before making the third start. The work went well until the eighth addition when the pattern on the oscilloscope became unstable. Since this behaviour was faintly reminiscent of the trouble experienced in the 20°C. series, it was decided to desorb some of the adsorbed material.

The distortion of the oscilloscope pattern was finally traced to a loose contact in the phase-shifting network. A number of additions and some desorptions were carried out after this had been remedied. Subsequent calculations showed, however, that these later points did not fit the isotherm as established by the first eight additions, and they have been omitted. This run was completed in five days. The results of the first eight additions are given in Table IIIa.

The results of the second run confirm those of the first run quite well. In Fig. 7, the data of Tables IIa and IIIa are plotted. This plot of ΔC vs. V/m (the total amount adsorbed) has several interesting features. In the first place, each curve appears to consist of three linear sections. Moreover, the slopes in all three sections are very nearly, if not exactly, identical for the two different temperatures. The position of the first break is the same, within the limits of experimental error, at the two temperatures. It occurs at about 30 cc. per gm. adsorbed. The positions of the second breaks differ by about 5 cc. in terms of amount adsorbed. These breaks occur at about 52.5 and 57.5 cc. adsorbed. Later, more accurate results indicate that the second of these is in error.

Table IIIa

Effect of adsorbed ethyl chloride on capacity of condenser containing silica gel as dielectric. Temperature 10°C. Duralumin condenser.

Addition Number	p(cm.)	ΔV/m cc. per gm.	Total ΔV/m	ΔC $\mu\mu$f	Total ΔC $\mu\mu$f	$\frac{\Delta C}{\Delta V/m}$
1	0.12	8.4	8.4	3.05	3.05	0.363
2	0.32	8.4	16.8	2.97	6.02	0.354
3	1.24	16.2	33.0	5.30	11.32	0.327
4	3.23	15.6	48.6	4.82	16.14	0.309
5	6.44	14.3	62.9	3.90	20.04	0.275
6	13.27	19.2	82.1	4.86	24.90	0.253
7	20.98	17.0	99.1	4.44	29.34	0.261
8	29.75	14.3	113.4	3.82	33.16	0.267

The capacity changes in the first run ranged from 0.63 to 1.68 μμf. In view of the smallness of these changes it is felt that the results show good consistency. The results will be discussed more fully after the results of the last two runs are presented.

The Invar condenser was placed in the modified cell and the cell was evacuated. With the precision condenser C_{11} in parallel with the cell, readings of C_{11} were taken, with the cell in and out of the circuit. The capacity difference is the capacity of the empty cell plus that of the leads. When, at a later time, the condenser was removed from the cell to be filled with silica gel, the capacity of the leads was determined in a similar manner. The condenser was then replaced, and the silica gel was subjected to a temperature of 120°C. under full vacuum for three days. The cell was then filled with helium and allowed to come to the temperature of the water bath (40°C.). When the capacity of the cell had reached a constant value, the capacity of the filled condenser and leads was determined by the substitution method as above. The temperature of the bath was then changed to 25°C. and, after the condenser had reached temperature equilibrium, the determination was repeated. It was found in the above determinations that by standardizing the positions of the lead which had to be disconnected, results could be duplicated to about ± 0.05 μμf. The results of these measurements are given in Table IV. The dial readings are converted to capacity values by multiplying them by 30. Subtracting the capacity of the cell leads, we obtain the capacities of the filled condenser at 25°C. and 40°C. as 232.2 and 230.4 μμf respectively. The corresponding dielectric constants are, for 25°, 1.957 and for 40°, 1.942.

Table IV

Determination of dielectric constant of silica gel.

Temp. °C.	Element	Dial Reading Element in	Dial Reading Element out	Capacity (μμf)
	Cell with empty condenser	5.936	10.059	123.7
40	Cell with filled condenser	7.131	14.972	235.23
25	Cell with filled condenser	7.079	14.981	237.06
	Cell leads	14.816	14.978	4.86

$$\text{Temperature coefficient} = \frac{235.23 - 237.06}{15}$$

$$= -0.122 \text{ μμf per degree.}$$

The weight of the silica was obtained by weighing the thoroughly evacuated cell before and after filling the condenser with silica gel. The value so obtained was 5.713 ± 0.003 gm.

The volume of the silica obtained as previously described was 2.42 ± 0.1 cc. This gives a density of 2.36 gm. per cc. The calculated volume of the condenser up to the top of the intermediate electrode is 8.56 cc. The "apparent" density of the silica gel is thus $\frac{5.71}{8.56} = 0.667$ gm. per cc.

The results of the 40°C. series are summarized in Table Va.

Table Va

Effect of adsorbed ethyl chloride on capacity of condenser containing silica gel as dielectric. $\Delta \epsilon' = \text{Total } \Delta C/118.8$ Temperature 40°C. Invar condenser. Dielectric constant of silica gel before adsorption = 1.942.

No.	p(cm.)	$\Delta V/m$ cc. per gm.	Total $\Delta V/m$	ΔC μμf	Total ΔC μμf	$\frac{\Delta C}{\Delta V/m}$	$\Delta \epsilon'$	$\frac{\Delta \epsilon'}{1.942}$
1	0.06	1.05	1.05	2.39	2.39	2.28	0.020	0.0103
2	0.24	4.01	5.06	6.10	8.49	1.52	0.071	0.0366
3	0.30	0.74	5.80	1.10	9.59	1.49	0.080	0.0412
4	0.52	3.04	8.84	4.45	14.04	1.46	0.118	0.0609
5	1.15	5.77	14.61	8.59	22.63	1.49	0.190	0.0981
6	2.03	5.39	20.00	7.77	30.40	1.44	0.255	0.132
7	3.69	6.98	26.98	10.05	40.45	1.44	0.340	0.175
8	5.20	4.87	31.85	6.79	47.24	1.39	0.397	0.205
9	6.76	4.13	35.98	5.60	52.84	1.36	0.444	0.229
10	9.87	6.60	42.58	9.24	62.08	1.40	0.522	0.270
11	14.84	8.06	50.64	10.20	72.28	1.26	0.608	0.314
12	20.80	7.34	57.98	9.28	81.56	1.26	0.686	0.354
13	30.28	9.47	67.45	11.30	92.86	1.19	0.781	0.403
14	45.0	11.87	79.32	13.44	106.30	1.13	0.894	0.461
Desorptions								
1	29.92	-12.13	67.19	-13.77	92.53	1.13		
2	12.49	-20.75	46.44	-25.10	67.43	1.21		
3	7.93	- 8.63	37.81	-11.03	56.40	1.28		
4	4.68	- 8.44	29.37	-11.32	45.08	1.34		
5	2.29	- 8.66	20.71	-12.50	32.58	1.44		
6	0.89	---	---	-12.78	19.80	--		
7	0.15	---	---	-12.90	6.90	--		
				- 7.56	-0.66	--		

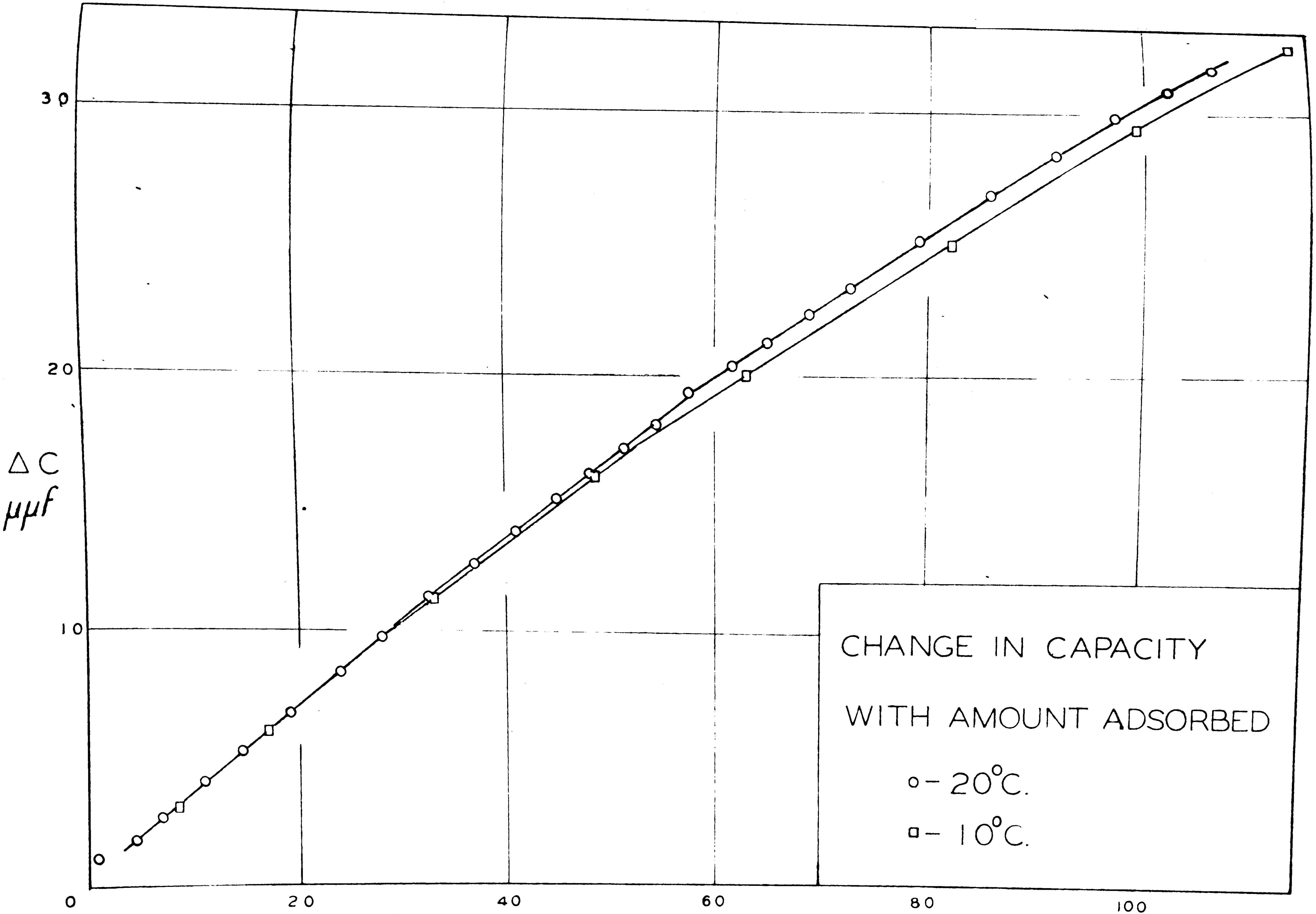


Fig. 7 - V/M - CC. AT S.T.P PER GM.

The maximum cumulative capacity change in this run was 106.3 μμf compared to 32 μμf in the 20°C. run. Since the maximum range of the precision condenser is about 16 μμf and the working range was about 12 μμf, this involved a change corresponding to about 9 times the capacity change of the working range of the dial. In order to make possible the measurement of a total change of this magnitude, the 100 μμf condenser C_{14}, set to maximum capacity was connected across the cell. As ethyl chloride was added, the capacity of the precision condenser C_{11} had to be decreased from an initial high value to a value near the lower limit of the working range. After equilibrium had been established and no further change in capacity could be observed, the capacity of C_{11} was increased to a value near the top of the working range. Balance was then restored by decreasing C_{14} sufficiently to compensate exactly for the increase in C_{11}. The bridge was then in condition to measure another change of, say, 12 μμf in the test condenser. When it is considered that the bridge has been required to measure capacity changes from 1 μμf to several hundred μμf with a precision approaching 0.01 μμf in all cases, it is clear that the versatility of this type of bridge in this respect is one of its great assets.

The desorption was carried out by closing the cell stopcock, evacuating the burette system, and then opening the cell stopcock. This causes a decrease in the capacity of the cell and must be compensated by an increase in the condenser C_{11}. The equilibrium readings of the manometer and C_{11} were noted, and the volume desorbed and the corresponding capacity decrease were calculated. The results are given in Table Va. When the pressure in the desorption process reached a low value, it became impracticable to measure the amount of vapor removed. In this region therefore, the vapor was pumped off slowly but continuously until a desired capacity change had resulted. Pumping was then interrupted and the adsorption system was allowed to come to equilibrium. The pressure and the final reading on C_{11} were then read, C_{11} was adjusted to a low value, compensating for this change by increasing C_{14}. The desorption was then continued. In this way it was possible to determine the total capacity decrease on desorption. The amounts desorbed in this low range might have been estimated by interpolating the equilibrium pressures on the adsorption isotherm. The amounts thus estimated will, however, be rather inaccurate and they are omitted from Table Va. It may be noticed that the total decrease in capacity during desorption exceeds the total increase during adsorption by about 0.6 $\mu\mu$f. This is only 0.6 per cent of the total change, but it is possible that the net decrease is real.

After the completion of the 40°C. run, the water bath was cooled to 25°C. After the cell had reached temperature equilibrium and the initial value of C_{11} had become steady, additions of ethyl chloride were made as before. The results of this series are summarized in Table VIa.

Table VIa

Effect of adsorbed ethyl chloride on capacity of condenser containing silica gel as dielectric. Temperature 25°C. Invar condenser. Initial dielectric constant of silica gel = 1.957.

No.	p(cm.)	$\Delta V/m$ cc. per gm.	Total $\Delta V/m$	ΔC $\mu\mu f$	Total ΔC $\mu\mu f$	$\frac{\Delta C}{\Delta V/m}$	Total $\Delta\epsilon'$	$\frac{\text{Total } \Delta\epsilon'}{1.957}$
1	0.02	1.14	1.14	1.91	1.91	1.68	0.016	0.0082
2	0.09	3.94	5.08	6.08	7.99	1.54	0.067	0.0342
3	0.19	3.31	8.39	5.10	13.09	1.54	0.110	0.0563
4	0.50	6.93	15.32	10.40	23.49	1.50	0.197	0.101
5	1.07	7.20	22.52	10.69	34.18	1.49	0.287	0.147
6	1.91	6.90	29.42	9.99	44.17	1.45	0.372	0.191
7	3.05	6.82	36.24	9.54	53.71	1.40	0.452	0.232
8	4.71	7.00	43.24	9.64	63.35	1.38	0.533	0.273
9	6.98	7.27	50.51	9.53	72.88	1.31	0.613	0.314
10	10.88	9.18	59.69	11.07	83.95	1.21	0.706	0.362
11	15.79	8.89	68.58	10.59	94.54	1.19	0.796	0.408
12	21.80	9.04	77.62	10.53	105.07	1.17	0.883	0.452
13	28.31	8.35	85.97	9.84	114.91	1.18	0.967	0.495
14	37.26	10.57	96.54	12.53	127.44	1.19	1.072	0.549
15	47.23	9.75	106.29	12.00	139.44	1.23	1.173	0.600
16	55.31	6.47	112.76	7.84	147.28	1.21	1.239	0.634
Desorptions								
1	45.04	8.64	105.6	10.13	137.15	1.17		
2	37.73	7.79	97.8	8.94	128.21	1.15		
3	31.74	(6.5)	(91.3)	(7.35)	120.86	(1.13)		
4	27.29	6.0	(85.3)	6.68	114.18	1.11		
5	17.74	13.6	(71.7)	15.06	99.12	1.11		
6	6.44	12.2	(59.5)	14.45	84.67	1.19		
7	4.54	11.8	(47.7)	14.53	70.14	1.23		
8	3.35	--	--	15.10	55.04	--		
9	1.59	--	--	14.65	40.39	--		
10	0.60	--	--	14.82	25.57	--		
11	0.17	--	--	11.83	13.74	--		
12	0.00	--	--	14.88	-1.14	--		

No correction has been applied to the capacity data for the capacity increase caused by the ethyl chloride vapor. The effect of such a correction proves to be quite small, and may be neglected without serious error. Any error is in a direction which will accentuate the downward tendency of the ΔC vs. $\Delta V/m$ curves. For example, taking the value for the dielectric constant of the vapor given by Fuchs (11a) of 1.00773 at 25°C. and a pressure of 45.47 cm., the change in the capacity of the condenser caused by an increase in the pressure of ethyl chloride can be calculated from equation (45) in the extended form used by Argue and Maass (2). For a pressure increase of 5 cm., this amounts to about 0.07 μμf. The error would thus approach one per cent only in the last few determinations of each series.

The results of the adsorption parts of the 25°C. and 40°C. series are presented graphically in Fig. 8. The data are plotted somewhat differently from those of previous runs. The "effective" dielectric constant has been calculated at each stage of the adsorption. The cumulative change, $\Delta \epsilon'$, caused by addition of ethyl chloride is divided by the initial dielectric constant, ϵ, of the pure silica gel at the corresponding temperature. The quotient $\frac{\Delta \epsilon'}{\epsilon}$ is plotted vs. $\frac{V}{m}$, the amount adsorbed per gram of silica gel. This procedure corrects for the small displacement which would occur in the ΔC vs. $\frac{V}{m}$ curve due to different initial dielectric constant.

No correction has been applied to the capacity data for the capacity increase caused by the ethyl chloride vapor. The effect of such a correction proves to be quite small, and may be neglected without serious error. Any error is in a direction which will accentuate the downward tendency of the ΔC vs. $\Delta V/m$ curves. For example, taking the value for the dielectric constant of the vapor given by Fuchs (11a) of 1.00773 at 25°C. and a pressure of 45.47 cm., the change in the capacity of the condenser caused by an increase in the pressure of ethyl chloride can be calculated from equation (45) in the extended form used by Argue and Maass (2). For a pressure increase of 5 cm., this amounts to about 0.07 $\mu\mu$f. The error would thus approach one per cent only in the last few determinations of each series.

The results of the adsorption parts of the 25°C. and 40°C. series are presented graphically in Fig. 8. The data are plotted somewhat differently from those of previous runs. The "effective" dielectric constant has been calculated at each stage of the adsorption. The cumulative change, $\Delta\epsilon'$, caused by addition of ethyl chloride is divided by the initial dielectric constant, ϵ, of the pure silica gel at the corresponding temperature. The quotient $\frac{\Delta\epsilon'}{\epsilon}$ is plotted vs. $\frac{V}{m}$, the amount adsorbed per gram of silica gel. This procedure corrects for the small displacement which would occur in the ΔC vs. $\frac{V}{m}$ curve due to different initial dielectric constant.

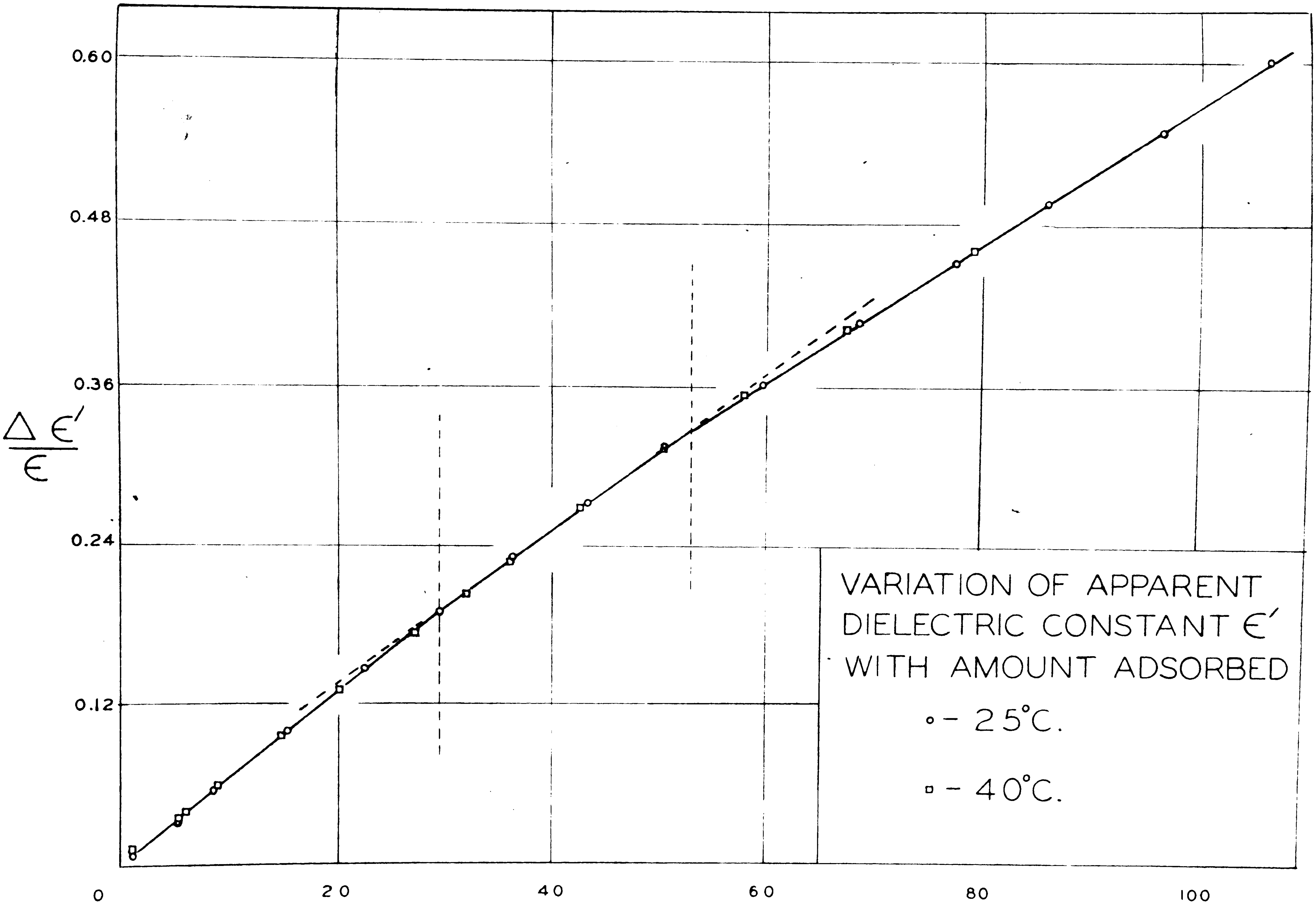


Fig. 8 - V/M- CC. AT S.T.P. PER GM.

The data are given in Tables Va and VIa.

In the third desorption of the 25°C. series, quite inadvertently, the C_{11} dial was initially set too high so that the capacity change could not be determined. The pressure was read after about half an hour, and the next desorption was begun. In order to obtain values for total capacity change and total amount adsorbed in subsequent desorptions, it was necessary to make an estimate of the amount desorbed in the third removal. This was done by reference to the adsorption isotherm. The capacity change was estimated by multiplying this value for the amount desorbed by a reasonable value of $\Delta C/\frac{\Delta V}{m}$. All values after the second total capacity change and total amount adsorbed are accordingly enclosed in brackets to indicate this. With the assumed value of 7.35 $\mu\mu$f for the third capacity decrement, the total capacity decrease in desorption exceeds the total increase during adsorption by about 1 $\mu\mu$f. In view of the assumptions made, no great significance can be attached to this result.

The four adsorption isotherms are shown graphically in Fig. 9. Desorption points are shown for the 40°C. and 25°C. series. A number of the low pressure points are omitted.

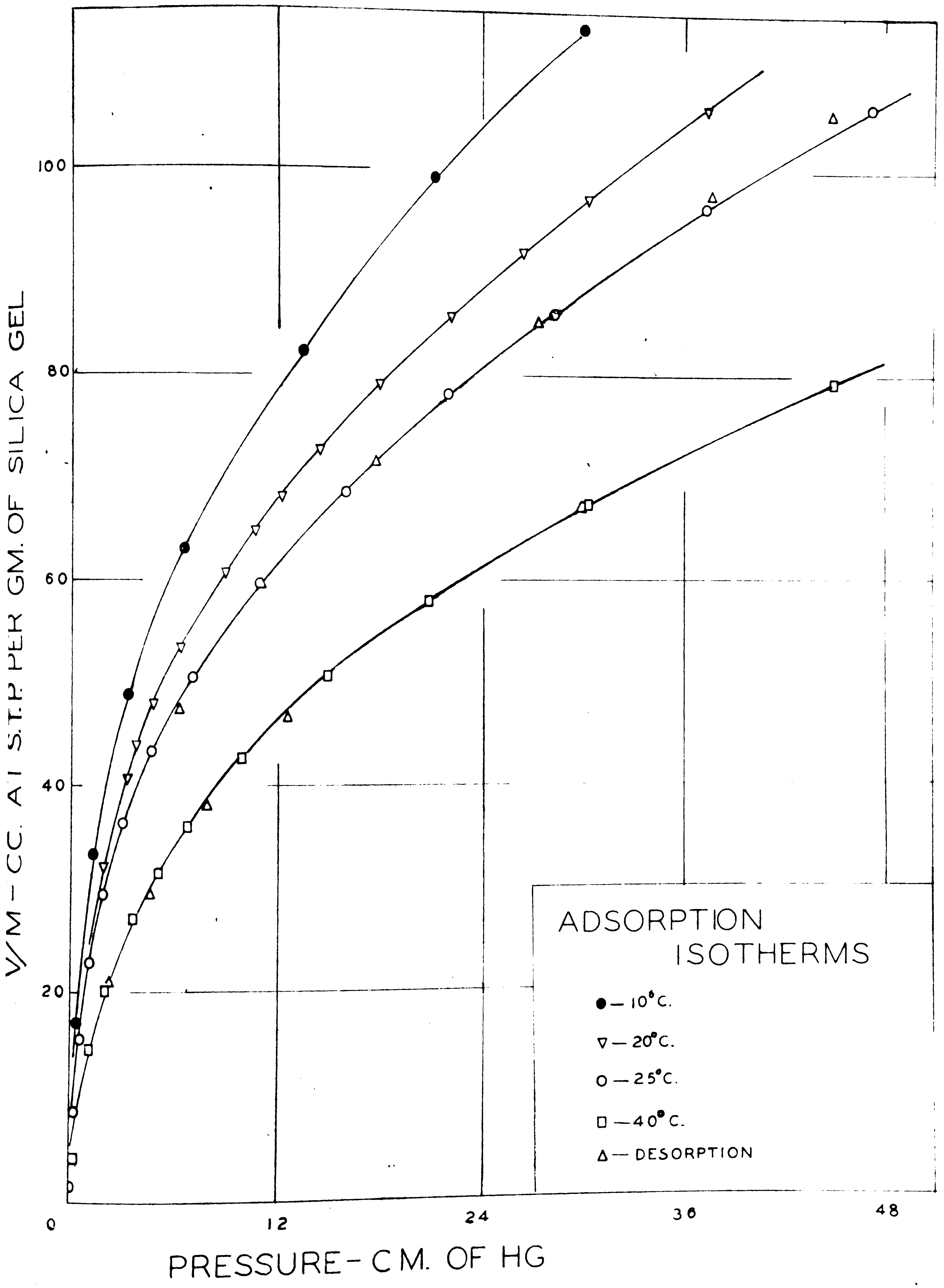

V/M - CC. AT S.T.P. PER GM. OF SILICA GEL
100
80
60
40
20
0
12
24
36
48
PRESSURE - CM. OF HG
ADSORPTION ISOTHERMS
● — 10°C.
▽ — 20°C.
○ — 25°C.
□ — 40°C.
△ — DESORPTION

Fig. 9

DISCUSSION OF RESULTS

All of the foregoing results indicate that the relationship between capacity increase and amount adsorbed is not accurately linear over the whole range. It appears, rather, that there are three distinct linear regions in the range covered, each of which corresponds to a quite definite rate of change with respect to amount adsorbed. In order to demonstrate that the relationship is not to be represented by a smooth curve, it is only necessary to study the values of $\Delta C/\frac{\Delta V}{m}$ given in the preceding tables. The mean values of $\Delta C/\frac{\Delta V}{m}$ for each range are given in Table VII. The average deviation in each range, without regard of course to the sign of the deviation, is also given. Detailed examination of the tabulated values of this rate of change quantity affords quite convincing evidence of the linearity of the relationship in each range. For example, to choose some of the more favourable cases, additions no. 10 and no. 16 of Table VIa give the same value of $\Delta C/\frac{\Delta V}{m}$ although $\frac{\Delta V}{m}$ has changed by about 63 cc. per gm. Between additions no. 3 and no. 4 of Table IIIa there is a change of 0.018 for 16 cc. adsorbed, between no. 4 and no. 5 there is a change of 0.034 for 14 cc. adsorbed, while between no. 5 and no. 8 for about 50 cc. adsorbed, there is change of only 0.008.

Table VII

Calculated average slopes of the curves of ΔC vs. $\Delta V/m$ for each of the three linear sections.

First Linear Section

	$\Delta C/\frac{\Delta V}{m}$ Mean	Average Deviation	No. of Values
10°C.	0.359	0.005	2
20°C.	0.338	0.012	7
25°C.	1.50	0.03	5
40°C.	1.47	0.03	6

Second Linear Section

	$\Delta C/\frac{\Delta V}{m}$ Mean	Average Deviation	No. of Values
10°C.	0.318	0.009	2
20°C.	0.317	0.011	7
25°C.	1.36	0.04	3
40°C.	1.35	0.04	4

Third Linear Section

	$\Delta C/\frac{\Delta V}{m}$ Mean	Average Deviation	No. of Values
10°C.	0.264	0.007	4
20°C.	0.261	0.006	10
25°C.	1.20	0.02	7
40°C.	1.19	0.04	3

Unquestionably, in each "linear" range there is a slight systematic tendency toward curvature, but this is much smaller than the breaks occurring at the end of each range.

It is also quite apparent that the points at which the changes of slope occur are determined only by the amount adsorbed. Examination of Fig. 8 shows that the breaks occur at 29.5 and 53 cc. adsorbed, both at 25°C. and 40°C. Comparison with Fig. 7 shows that here too the lower break occurs close to 29.5 cc. adsorbed and the upper break for the 10°C. run occurs close to 53 cc. The upper break for the 20°C. run occurs at 57.5 cc., but in view of the consistency of the results at 10°C., 25°C., and 40°C. this can probably be regarded as an error. An important result of this agreement between the first two and last two runs is to confirm that the dimensions and capacity of the condenser are without effect.

Examination of Figs. 7 and 8 shows that the slopes of the two curves corresponding to the two different temperatures are very nearly, when not exactly, the same. This indicates that the dielectric constant of the adsorbate has a very small, or zero, temperature coefficient. The lack of temperature dependence is particularly surprising in view of the polar nature of the adsorbate. The dielectric constant of pure ethyl chloride vapor has a negative temperature coefficient in accordance with the ideas outlined in connection with dielectric constant theory. The results of Eversheim (10) indicate that this is also true of the liquid at temperatures in the range 170° - 185°C. Nevertheless, ethyl bromide shows no temperature coefficient in the liquid state (27), due to association effects in the liquid. As far as is known, no data on the dielectric constant of ethyl chloride are available for the room temperature range. Eversheim points out that the capacity measurements in this range were made difficult by the relatively high conductivity of the ethyl chloride liquid.

The possibility of association occurring between adsorbed molecules may be considered to be quite remote in the low pressure region, where the molecules are likely to be quite widely separated. There is no evidence of a negative temperature coefficient, except perhaps in the lowest range studied. Association of this type might be considered more probable if the film were of the condensed type. For this reason it is of interest that Harkins - Jura condensed film plot of log p/p_0 vs. $\frac{1}{V^2}$ does not give a straight line relationship with the adsorption system studied here.

The nature of the relationship encountered in the present work between capacity and amount adsorbed is different from any reported by Zhilenkov with silica gel, by Higuti with titania gel, or by Argue and Maass with cellulose. The results of these workers have been briefly discussed in an earlier section. Before attempting to interpret the experimental capacity data presented in the previous section in terms of nature of the adsorption process, it is necessary to consider what information can be derived from the adsorption data alone. In the following tables are presented certain data derived from Tables IIa, IIIa, Va, VIa necessary for plotting the Brunauer-Emmett-Teller and Williams-Henry isotherm equations.

A plot of p/V vs. p according to the Langmuir equation gave a smooth curve containing no linear section. This indicates that the assumptions underlying the derivation of this equation are not valid in the present instance. Since, in the low pressure range, the adsorption is probably unimolecular, it is customary in cases of this kind to suggest that the invalidity of the Langmuir equation is due to a varying heat of adsorption.

The Williams-Henry isotherm equation is applied in Fig. 10, where log $\frac{V/m}{p}$ is plotted against V/m. The data from which these curves are plotted are given in Tables IIb, IIIb, Vb and VIb. The shape of these curves is of interest in view of the nature of the curve of capacity change vs. amount adsorbed, for the former curves also consist of three quite distinct sections. At low $\frac{V}{m}$ values the curves are straight lines except at the lowest extremities where the percentage error in the pressure readings is, in any case, high. The 25°C. and 40°C. curves exhibit another linear section in the $\frac{V}{m}$ range between 29 and 53 cc. per gm. which is precisely the range of the middle linear section of the ΔC vs. $\frac{V}{m}$ curves. Beyond this, the curves deviate upward.

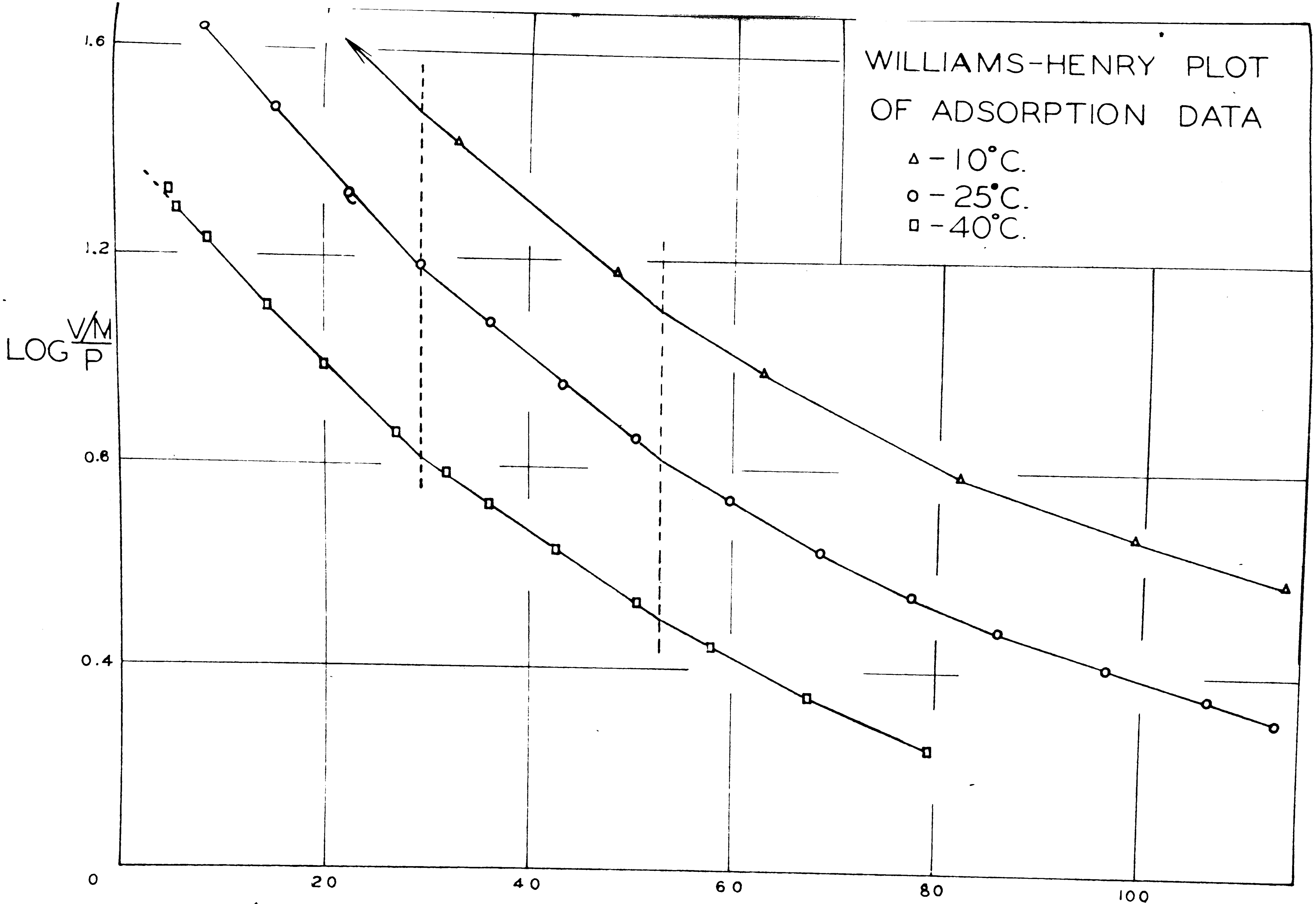


Fig. 10 - V/M-CC. AT S.T.P. PER GM.

Table IIb

Data derived from Table IIa for use in Williams-Henry and Brunauer-Emmett-Teller plots. Temperature 20° C. Saturated vapor pressure P_o of ethyl chloride 100 cm. Relative pressure $f = P/P_o$. In this table, V means the volume of vapor adsorbed per gm. of silica gel.

Addition Number	V	V/p	log V/p	f	$\frac{10^3 f}{V(1 - f)}$
1	1.71	171	2.23	0.0001	negl.
2	4.52	113	2.05	0.0004	"
3	6.94	77	1.89	0.0009	"
4	10.87	60.3	1.78	0.0018	"
5	14.57	32.4	1.51	0.0045	"
6	19.10	26.9	1.43	0.0071	"
7	23.87	22.6	1.35	0.0105	"
8	28.03	19.9	1.30	0.0140	"
9	32.38	17.0	1.23	0.0188	"
10	36.79	14.8	1.17	0.0246	"
11	40.88	12.8	1.11	0.0316	0.8
12	44.92	11.3	1.05	0.0393	0.9
13	48.11	10.2	1.01	0.0465	1.0
14	51.35	9.41	0.97	0.0540	1.1
15	54.45	8.40	0.92	0.0642	1.26
16	58.08	7.47	0.87	0.0770	1.44
17	61.65	6.74	0.83	0.0906	1.61
18	65.03	6.17	0.79	0.104	1.79
19	68.88	5.61	0.75	0.121	2.01
20	72.75	5.10	0.71	0.141	2.26
21	79.55	4.41	0.64	0.178	2.73
22	86.11	3.87	0.59	0.220	3.29
23	92.11	3.50	0.54	0.260	3.83
24	97.66	3.22	0.51	0.300	4.40
25	102.44	3.02	0.48	0.337	4.98
26	106.48	2.83	0.45	0.372	5.59

Table IIIb

Data derived from Table IIIa for use in Williams-Henry and Brunauer-Emmett-Teller plots. Temperature 10°C. Saturated vapor pressure P_0 of ethyl chloride 67.7 cm. Relative pressure $f = P/P_0$. In this table, V refers to the volume of vapor adsorbed per gm. of silica gel.

Addition Number	V	V/p	log V/p	f	$\frac{10^3 f}{V(1-f)}$
1	8.4	70.0	1.84	0.0018	0.21
2	16.8	52.5	1.72	0.0047	0.28
3	33.0	26.6	1.42	0.0183	0.56
4	48.6	15.0	1.18	0.0476	1.03
5	62.9	9.78	0.99	0.0950	1.67
6	82.1	6.19	0.79	0.196	2.97
7	99.1	4.71	0.67	0.310	4.54
8	113.4	3.84	0.58	0.439	6.90

Table Vb

Data derived from Table Va for use in Williams-Henry and Brunauer-Emmett-Teller plots. Temperature 40°C. Saturated vapor pressure P_0 of ethyl chloride 194.0 cm. Relative pressure $f = P/P_0$.

Addition Number	V	V/p	log V/p	f	$\frac{10^3 f}{V(1-f)}$
1	1.05	17.5	1.24	0.0004	0.4
2	5.06	21.1	1.32	0.0017	0.3
3	5.80	19.3	1.29	0.0021	0.4
4	8.84	17:0	1:23	0.0036	0.4
5	14.61	12.7	1.10	0.0080	0.6
6	20.00	9.86	0.99	0.0141	0.7
7	26.98	7.32	0.86	0.0256	1.00
8	31.85	6.13	0.79	0.0360	1.17
9	35.98	5.32	0.73	0.0470	1.37
10	42.58	4.21	0.63	0.0685	1.72
11	50.64	3.41	0.53	0.103	2.27
12	57.98	2.79	0.45	0.144	2.90
13	67.45	2.22	0.35	0.210	3.94
14	79.32	1.76	0.25	0.322	5.99

Table VIb

Data derived from Table VIa for use in Williams-Henry and Brunauer-Emmett-Teller plots. Temperature 25°C. Saturated vapor pressure, P_o, of ethyl chloride 123.0 cm. Relative pressure $f = P/P_o$.

Addition Number	V	V/p	log V/p	f	$\frac{10^3 f}{V(1 - f)}$
1	1.14	57.0	1.75	0.00016	negl.
2	5.08	56.5	1.75	0.00073	"
3	8.39	44.1	1.64	0.0015	"
4	15.32	30.6	1.49	0.0041	"
5	22.52	21.0	1.32	0.0087	"
6	29.42	15.4	1.19	0.0155	0.54
7	36.24	12.1	1.08	0.0248	0.70
8	43.24	9.18	0.96	0.0382	0.92
9	50.51	7.25	0.86	0.0567	1.19
10	59.69	5.49	0.74	0.0885	1.62
11	68.58	4.34	0.64	0.128	2.14
12	77.62	3.56	0.55	0.177	2.77
13	85.97	3.04	0.48	0.230	3.47
14	96.54	2.59	0.41	0.303	4.51
15	106.29	2.25	0.35	0.384	5.86
16	112.76	2.04	0.31	0.450	7.26

The 20° curve is not shown in Fig. 10 for reasons which will now be discussed. When the 20° data are plotted in this form, the fifth point (V/m = 14.57) is considerably off the curve established by the first four points, and as a result the remainder of the curve has a somewhat different slope from the curves shown. A large scale plot of the p vs. V/m data likewise shows a discontinuity here. Because none of the other curves exhibits this behaviour, the only alternative is to assume that it is due to an error in the determination of the pressure reading such as might have been caused by a jar to the cathetometer. An error of 0.15 cm. would account for the deviation. This plot is much more critical in this respect than any other used in this work.

There are scarcely enough points on the 10° curve to establish its form in any detail. Purely for the sake of comparison with the 25° and 40° curves, however, a straight line is drawn through the two points in the range between $V/m = 29$ and $V/m = 53$. The slope of the curve over its entire range then corresponds quite well with those of the other two curves. The arrow on the upper end of the 10°C. curve indicates that it is directed toward a point beyond the range covered in Fig. 10.

An interesting feature of the Williams-Henry plot is the occurrence of the middle linear section in spite of the fact that the theoretical limit of $V/V_m = 0.3$ occurs when V/m is about 20 cc. per gram. This suggests either that the equation is more fundamental than its derivation, or that the V_m values commonly used are greatly in error. In the present instance, the presumption of an extended range of validity is based, not alone on the existence of a linear range considerably above the theoretical limit, but also on the supporting evidence supplied by the capacity measurements.

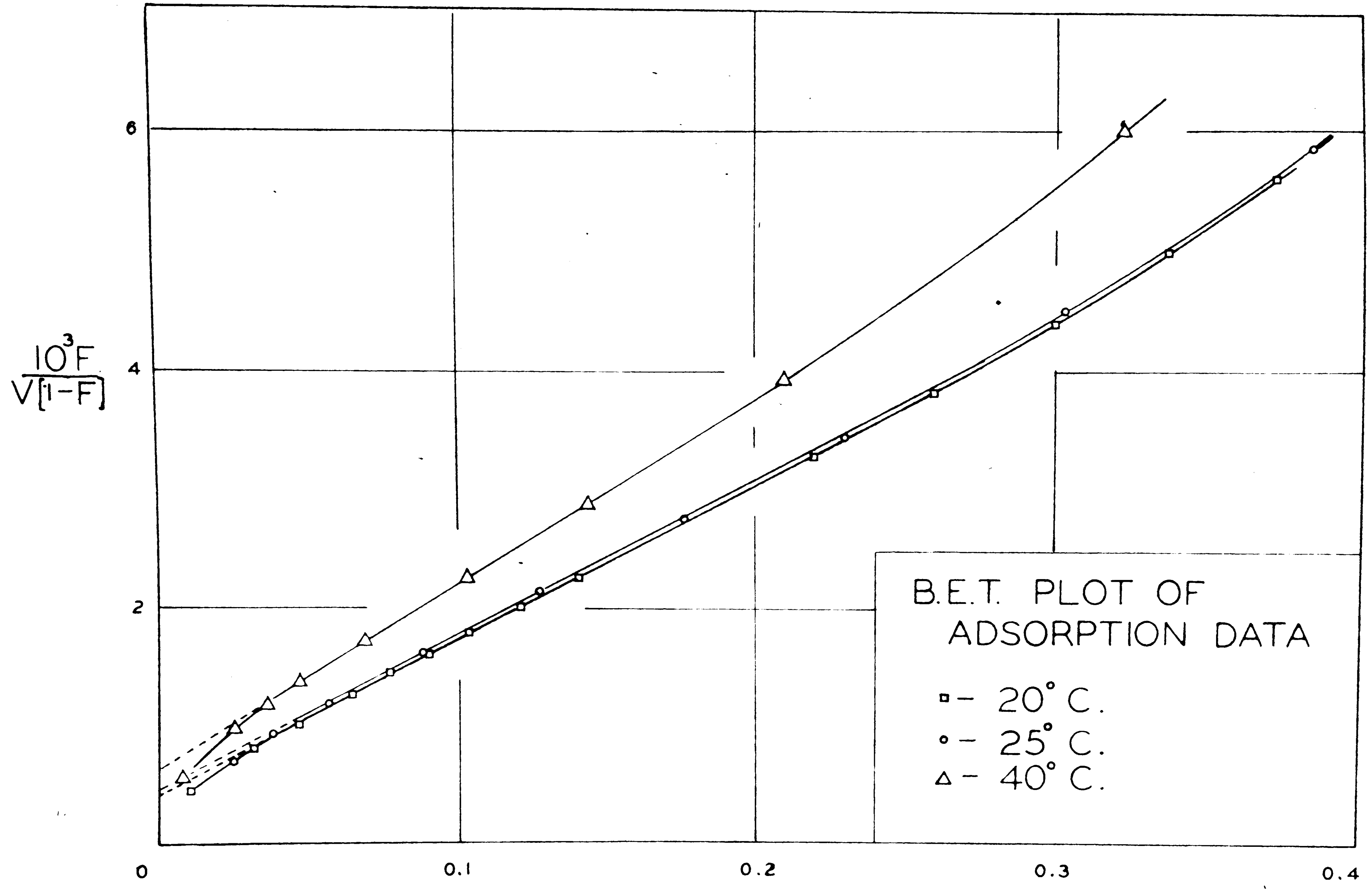


Fig. 11 - RELATIVE PRESSURE-F

There is good reason to believe that the interpretation of the curves of Fig. 10 would be critical for the interpretation of the capacity data. However, the theoretical basis for the equation can scarcely be employed in a range beyond that imposed in the derivation.

The adsorption data for 20°, 25° and 40°C. are plotted according to the Brunauer-Emmett-Teller relation in Fig. 11. The data from which this graph is plotted, are given in Tables IIb, IIIb, Vb, and VIb. In the relative pressure range from 0.05 to 0.24 the data fall on quite good straight lines. From the slopes and intercepts, values for c and V_m can be calculated. Using the relation:

$$\sigma = (4)(0.866)\left(\frac{M}{4\sqrt{2}\ \rho N}\right)^{2/3} \qquad (1)$$

where σ is the area per molecule, ρ is the density, M the molecular weight and N is Avogadro's number, values of σ can be obtained, and hence of the surface area of the adsorbent. The values calculated from Fig. 11 are given in Table VIII.

The values of S are between 25 and 35 per cent lower than the values quoted by the manufacturer, 700 $m.^2$ per gm. In order to give a value close to this, a value of about 35 $A.^2$ per molecule would have to be assumed for the area per molecule. In view of the uncertainty which prevails (17) concerning the proper choice of cross-sectional area, the disagreement is not too serious.

Table VIII

Values of V_m, c, σ, and specific surface, S, calculated from Fig. 11. The units of σ are Angstrom units squared = 10^{-16} $cm.^2$

	20°C.	25°C.	40°C.
V_m	74.7 cc.	74.2 cc.	61.4 cc.
c	33.5	30.0	25.5
σ	26.6 $A.^2$	26.7 $A.^2$	27.2 $A.^2$
S	532 $m.^2$/gm.	530 $m.^2$/gm.	447 $m.^2$/gm.

Fig. 11 perhaps gives an erroneous impression of the way in which the experimental data fit the Brunauer-Emmett-Teller equation. It should be noted, for example, that of the 26 experimental points at 20°C., only about 6 or 7 fall accurately on the straight line. Only enough of the low pressure points are plotted to show the nature of the deviation in this region.

It is proposed now to discuss attempts to derive values for the dielectric constant of the adsorbed ethyl chloride from the experimental capacity measurements. It is first necessary, for purposes of comparison, to calculate the dielectric constant of ethyl chloride liquid at the temperatures used in the experimental work. Two methods are available. The empirical relation due to Wyman (31) relating an "ideal" polarization per cc., p, to the dielectric constant may be used. The relation is:

$$p = (e - 1)/8.5 \qquad (2)$$

and has been found to hold quite well for a large number of liquids. Values of p can be calculated if the refractive index and dipole moment are known. The only data of which the author is aware for the refractive index of liquid ethyl chloride are those of Grosse (12) for low temperatures. At -20°C. the refractive index is 1.3913. The molar refractivity is therefore:

$$R = \frac{n^2 - 1}{n^2 + 2}\frac{M}{d} \qquad (3)$$

where M is the molecular weight and d the density of the liquid. The density values were obtained either directly, or by extrapolation, from the International Critical Tables. The molar refractivity has the value 16.1 cc. Taking the value for μ, the dipole moment, as 2 Debye units, the polarization due to orientation is $\frac{4\pi N\mu^2}{9kT} = 1.16$, where N is the calculated number of molecules per cc. The value of 16.1 cc. for molar induced polarization gives a value of 0.223 for the induced polarization per cc. The total polarization, p, is therefore 1.38. Using Wyman's relation, the calculated dielectric constant is 11.8.

For the calculation of e from Onsager's equation, values of n^2 were obtained by using the value of 16.1 cc. for the molar polarization. The results, as well as the data used, are given below.

Table IX

Calculation of dielectric constant of ethyl chloride according to the Onsager equation.

Temp. ^{o}C.	n^2	d	$N \cdot 10^{-21}$	e calc.
0	1.90	0.924	8.60	10.35
20	1.86	0.894	8.31	9.70
40	1.83	0.863	8.03	8.78

Attempts to check these figures by extrapolation of the Eversheim data to a temperature of 20^{o}C. gave unsatisfactory results for a number of reasons. In the first place, Eversheim's data are not very self-consistent. Further, no experimental refractive index data are available. Finally, his data are for the critical temperature region, and extrapolation from this region is likely to be unsatisfactory. In any event, the results obtained were about 60 per cent in error, assuming the values of Table IX to be correct.

The values given in Table IX also fall quite well in line with the dielectric constants of ethyl iodide and ethyl bromide, which, for 20^{o}C. have the values 7.82 and 9.41 respectively. For the purposes of the following discussion, therefore, it will be assumed that these values are correct.

The dielectric constant of silica can be calculated, from the data for the 25^{o}C. series, according to the Bruggeman formula (51) given in the introduction. The volume fraction of the silica gel, f_1, is $\frac{2.42}{8.56} = 0.282$. With the symbols of the earlier section,

$$E_p^1 = 0.282 + 0.718e_1$$

$$E_p = 0.282e_1 + 0.718$$

$$E_s = \frac{e_1}{0.282 + 0.718e_1}$$

$$E_w = 1.957 = \sqrt{e_1}\,\frac{0.564e_1 + 1.436 + \sqrt{e_1}}{0.282 + 0.718e_1 + 2\sqrt{e_1}}$$

$$e_1 = 6.6$$

This may be compared with the value of 6.47 obtained by Zhilenkov and co-workers (32).

The values for the dielectric constant of the adsorbed ethyl chloride have been calculated from the relation:

$$E = f_1e_1 + f_2e_2 + f_3e_3$$

If we assume provisionally that the dielectric constant of the silica gel, designated as component 1, remains unchanged, and consider the effect on E of an increment of adsorbed ethyl chloride (component 2), we have the relation:

$$\Delta E = \Delta f_2e_2 + \Delta f_3e_3$$

where component 3 is the ethyl chloride vapor. The value of e_3 proves to be substantially unity. Since the adsorbate diminishes the volume available to the vapor, $\Delta f_2 = -\Delta f_3$. We may therefore use the relation in the form employed by Higuti (20):

$$\Delta E = \Delta f_2(e_2 - 1) \qquad (4)$$

In order to make use of the calculated average slopes of the ΔC vs. $\Delta V/m$ curves (Table VII), both sides of this equation are divided by $\Delta V/m$:

$$\frac{\Delta E}{\Delta V/m} = \frac{\Delta C}{C_0 \, \Delta V/m} = \frac{\Delta f_2}{\Delta V/m}\left(e_2 - 1\right) \qquad (5)$$

The values of $\Delta f_2 / \frac{\Delta V}{m}$ can be calculated for each temperature. This amounts to the change in the volume fraction of the adsorbate for a change of 1 cc. per gm. in the amount of adsorbate. In order to determine the dielectric constant for an adsorbate having, at all temperatures, the same number of molecules per cc., it is necessary to employ the same density throughout. The density of the bulk liquid at 25°C., 0.886 gm. per cc., will therefore be used. For the 25°C. series, using the Invar condenser, therefore,

$$\Delta f_2 \Big/ \frac{\Delta V}{m} = \frac{1}{22,400} \times \frac{64.5}{0.886} \times \frac{5.713}{8.56} = 0.00217 \text{ per cc. per gm.}$$

In this calculation, 64.5 is the molecular weight of ethyl chloride, 5.713 is the weight in gm. of the silica gel, 8.56 is the total volume between the plates, in cc. The capacity of the empty condenser, C_0, is 118.8 uuf. From Table VII, the average value of $\Delta C / \frac{\Delta V}{m}$ for the first linear section is 1.50. Therefore, by (5):

$$\frac{1.50}{118.8} = 0.00217\ (e_2 - 1)$$

$$e_2 = 6.81$$

The values calculated in this way are collected in

Table X. The values from the first two series at 10°C. and 20°C. are also given. The absolute values are much less accurate than those obtained from the 25°C. and 40°C. series for reasons given earlier, but the temperature coefficients should be comparable.

Table X

Dielectric constant of adsorbed ethyl chloride calculated for a constant density of 0.886 gm. per cc.

	Dielectric Constant		
Temp.	First Section	Second Section	Third Section
25°C.	6.81	6.27	5.61
40°C.	6.70	6.23	5.61
(10°C.	5.34	4.84	4.19)
(20°C.	5.08	4.83	4.15)

The first linear section shows a slight negative temperature coefficient, about 1.6 per cent. This would appear to be somewhat greater than could be accounted for by experimental error, particularly in view of the agreement of the second and third linear sections at all four temperatures. The values of the temperature coefficient obtained from the less accurate 10°C. and 20°C. series confirm those obtained from the 25°C. and 40°C. series quite well.

The temperature coefficient in the first linear section is lower than that of the bulk liquid as given in Table IX, even when the latter are calculated for a constant density as was done in Table X. When this is done, the temperature coefficient of the bulk liquid is about 3.5 per cent.

It appears therefore, that, to within experimental error, the dielectric constant of the adsorbate in the first linear range has a negative temperature coefficient which is smaller than that of the bulk liquid. Over the other two ranges, the temperature coefficient is zero, or very nearly zero.

The values of the dielectric constant calculated for all of the three linear sections are lower than the corresponding values for the bulk liquid calculated according to the Onsager equation. Because of the lack of experimental data on liquid ethyl chloride, there is perhaps little to be gained by comparison of absolute values. However it seems safe to suggest that the ethyl chloride in the adsorbed state has considerable orientational mobility. This is corroborated by a comparison of the calculated values for the dielectric constant with the corresponding value of n^2, about 1.9, which would approximate to the dielectric constant in the absence of a permanent dipole contribution. Moreover, the existence of a negative temperature coefficient in the first linear region indicates a contribution by the permanent moment.

Association between adsorbate molecules might conceivably be responsible for one of the two breaks. There is little justification for attempting to account for both breaks on this basis. Recent work by McIntosh (24) on the dielectric constant of adsorbed butane, carried out with apparatus very similar to that described in this report, is of interest in this connection. Association would not be expected to occur between the non-polar butane molecules. Moreover, a zero temperature coefficient would be expected of the dielectric constant of adsorbed butane. It has been found experimentally that one break does occur in the ΔC vs. ΔV plot, at a value of ΔV close to that obtained for the upper of the two breaks with ethyl chloride. A small temperature coefficient, the same as that found for ethyl chloride, was also found, and is probably attributable to the temperature dependence of the dielectric constant of the silica gel itself.

These results appear to suggest that the upper break, which occurs with both ethyl chloride and butane, is to be attributed to some property of the silica gel surface, such as might be responsible for a change in the nature of the adsorption.

A brief reference will now be made to another feature of the ΔC vs. $\Delta V/m$ relationship not discussed previously.

The values of $\Delta C/\frac{\Delta V}{m}$ for the first very small increment of vapor have been found to be considerably higher than any of the succeeding values. These values have been omitted in the calculations of the average slope of the first linear section. Lacking more detailed information on the magnitude and temperature dependence of this initial capacity change, little can be said of its significance. A consideration of equation (4) from which the dielectric constant of the adsorbate has been calculated shows that, to within the limitations of this equation, it must be attributed either to a high dielectric constant or to a low density.

SUMMARY, CONCLUSIONS AND CLAIMS TO ORIGINAL WORK

The dielectric constant of ethyl chloride adsorbed on silica gel has been studied at temperatures of 10°, 20°, 25° and 40°C. The results obtained differ in essential ways from any previously reported in the literature for other adsorption systems.

A bridge method, based on the Schering bridge, has been developed for the measurement of the very small capacity changes. The bridge, with proper temperature control of the bridge components, is capable of measuring capacity changes of 0.01 micro-microfarad. It has been used to measure capacity changes ranging from one to several hundred micro-microfarads. A frequency of 3530 cycles per second was used in all measurements.

It has been found that the relationship between the capacity change and the amount adsorbed is not accurately linear over the whole range. Rather, there are three adsorption ranges, over each of which the relationship is very nearly linear. For each of these ranges, a value for the dielectric constant of the adsorbate has been calculated. The first adsorption range gives the highest value for the dielectric constant of the adsorbate. In each of the other two ranges, the calculated value for the dielectric constant is lower than that calculated for the preceding range.

The results further indicate that the dielectric constant for the first adsorption range has a small negative temperature coefficient, while, for the other two ranges, the dielectric constant appears to be nearly independent of temperature.

On the basis of these results, the conclusion is reached that the adsorbed molecules retain a large part of the rotational mobility possessed by molecules of the bulk liquid. In an attempt to account for the disappearance of the temperature coefficient, it is tentatively suggested that association occurs between the adsorbed molecules, beginning at the end of the first adsorption range.

An attempt has been made to correlate the information obtained from the capacity measurements with that obtained by the application of adsorption theory to the adsorption data.

Bibliography

1. Adam, N. K., Physics and Chemistry of Surfaces, second edition, Oxford (1938).

2. Argue, G. H. and Maass, O., Can. J. Research, B, 13:155 (1935).

3. Bangham, D. H., Trans. Faraday Soc., 33, 805 (1937).

4. Brunauer, S., The Adsorption of Gases and Vapors: Vol. I: Physical Adsorption: Princeton (1945).

5. Brunauer, S., Emmett, P. H. and Teller, E., J. Am. Chem. Soc., 60, 309 (1938).

6. Bruggeman, D. A. G., Ann. d. Phys., 24, 636 (1935).

7. Cassie, A. B. D., Trans. Faraday Soc., 41, 450 (1945).

8. Debye, P., Polar Molecules, Chemical Catalog Co., New York (1929).

9. Emmett, P. H., J. Am. Chem. Soc., 68, 1784 (1946).

10. Eversheim, P., Ann. d. Phys., 8, 539 (1902).

11. Fergusson, J. G., Bell System Tech. J., 8, 560 (1929).

11a. Fuchs, O., Z. Physik, 63, 824 (1930).

12. Grosse, A. V., J. Am. Chem. Soc., 59, 2739 (1937).

13. Hague, B., Alternating Current Bridge Methods, fourth edition, Pitman (1938).

14. Harkins, W. D., in Surface Chemistry, edited by F. R. Moulton, American Association for the Advancement of Science, Washington (1943).

15. Jura, G., and Harkins, W. D., J. Am. Chem. Soc., 66, 1356 (1944).

16. Jura, G. and Harkins, W. D., J. Am. Chem. Soc., 68, 1941 (1946).

17. Harkins, W. D., and Jura, G., J. Am. Chem. Soc., 66, 1366 (1944).

18. Harkins, W. D. and Boyd, G. E., J. Chem. Phys., 45, 20 (1941).

19. Henry, D. C., Phil. Mag., 44, 689 (1922).

20. Higuti, I., Bull. Inst. Phys. Chem. Research, (Tokyo) 20, 8, 489 (1941).

21. Hollies, N. R. S., Thesis presented to Faculty of Graduate Studies and Research, McGill University, (1947).

22. Lamson, H. W., Rev. Sci. Inst., 9, 272 (1938).

23. Langmuir, I., J. Am. Chem. Soc., 40, 1361 (1918).

24. McIntosh, R. L., Private Communication.

25. Onsager, L., J. Am. Chem. Soc., 58, 1486 (1936).

26. Polanyi, M., Verh. deut. physik. Ges., 16, 1012 (1914).

27. Smyth, C. P., Dielectric Constant and Molecular Structure, Chemical Catalog Co., Inc., New York, (1931).

28. Turner, H. and McNamara, P., Proc. Inst. Radio Eng., 18, 1743 (1930).

29. Vigoureux, P. and Webb, C. E., Principles of Electric and Magnetic Measurements, Blackie and Sons Ltd., London and Glasgow (1936).

30. Williams, A. M., Proc. Royal Soc., (London), A, 96, 287, 298 (1919).

31. Wyman, J., J. Am. Chem. Soc., 58, 1482 (1936).

32. Zhilenkov, I., Perskii, I. and Fedotova, L., Colloid J. (U.S.S.R.), 3, 537 (1937). Abstract in Chemical Abstracts, 32, 6117 (1938).