ELECTROKINETIC TRANSDUCERS

Technical Report No. 3

PROPERTIES OF ELECTROKINETIC TRANSDUCERS

Technical Report No. 3

Prepared for the Office of Naval Research under:

Contract Nonr-617(00)
Project NR 385 407

THE BETA CORPORATION
Post Office Box 8625
Richmond 26, Virginia

By: E.V. Hardway Jr.
E. V. Hardway, Jr.
President

July 1, 1953

TABLE OF CONTENTS

LIST OF FIGURES

PROPERTIES OF ELECTROKINETIC TRANSDUCERS

1. INTRODUCTION

This report is a sequel to Technical Report No. 2 which contained summarized information relating to properties of certain types of electrokinetic cells and emphasized factors which might influence their selection or design for various applications.

In this report theoretical derivations will be given and test methods and results will be presented. An attempt will be made to define and isolate the various parameters which affect the conversion of energy in electrokinetic cells and to illustrate how their magnitude is affected by temperature and other factors.

Insofar as is known the data presented in this report are the first in which streaming potential measurements at alternating pressures are used to study variations of the electrokinetic parameters with temperature under fully stabilized conditions, all prior work of this type having been done under conditions of steady flow. The advantages of this method of investigation are discussed.

An objective of the tasks performed was to study various combinations of materials and techniques which would lead to greater energy conversion efficiency. Inasmuch as the factors which govern the magnitude of the electric moment at a solid-liquid interface are not well known or understood, an experimental approach was necessary. As an almost unlimited number of liquid-solid combinations are possible it was necessary to limit the number of combinations attempted by a rule-of-thumb method for the liquids and to choose porous solids from those available from the commercial sources. Various coatings and addition agents were selected on a more or less intuitive basis and a few of these showed definite promise.

Another objective was to obtain sufficient information on the best available tested material combinations to enable predictions to be made in advance as to the probable performance of an underwater microphone or hydrophone with regard to sensitivity, stability, impedance and frequency response insofar as it is affected by the electrokinetic cell. To a large extent it is believed that this phase of the work has been successfully accomplished.

Should the importance of certain applications of electrokinetic transducers at some future date dictate, it would appear that additional detailed analytical and experimental studies should be carried out with regard to maximizing the electric moment and increasing the porosity-permeability ratio of the porous materials. Such studies might best be carried out by organizations with the required specialized facilities and personnel. Suggested future studies are discussed in this report.

The investigations of electrokinetic phenomena on which this report is based were sponsored by the Acoustics Division of the Office of Naval Research under Contract Nonr-617(00), Project NR 385 407.

Future reports will relate largely to the development of experimental electrokinetic hydrophones.

2. HISTORICAL BACKGROUND

An excellent historical review of the important discoveries relating to electrokinetic phenomena is given in Abramson's Electrokinetic Phenomena. (1).

The phenomena of electro-osmosis and electrophoresis were discovered by Reuss (2) in 1808, his discoveries having since led to many important applications in biochemical research and in industry.

The streaming potential phenomenon was discovered by Quincke (3) in 1859. He first observed that a "streaming potential" would develop across a porous diaphragm through which a liquid was forced under a pressure differential. He further observed that the voltage was independent of the dimensions of the diaphragm or the amount of liquid but was proportional to the applied pressure. His later experiments included measurements with a large variety of materials of streaming potential and electro-osmotic pressure.

In later publications theories were developed by Helmholtz (4), Smoluchowski (5), Gouy (6), Briggs (7) and many others to explain the origin of streaming potential.

Commercial applications of the streaming potential phenomena have been very limited. Schlumberger (8) recognized that the pressure of drilling fluid in open oil wells in driving it into porous formations traversed by the bore hole would produce a self-potential useful as a means of locating porous and possibly oil or gas bearing formations. Doll (9) developed a logging tool with a means provided to produce alternating pressures and thus alternating electrokinetic potentials in the vicinity of porous formations.

Insofar as is known, Williams (10), (11), was the first to recognize that the streaming potential phenomena might be applied to a self-contained pressure measuring instrument or transducer. His experimental transducers for measuring "hammer" in high pressure oil lines are described in the references.

The alternating streaming potential phenomena and its possible applications have also been recognized by Japanese investigators at Kyoto University and are discussed in Reference (12). Most of their experiments, however, were with electro-capillary instruments employing mercury acid interfaces.

The results of work carried out by this Corporation have been reviewed in Technical Report No. 2 or will appear in this report. Experimentation in this field was carried out as early as 1950. Military and commercial applications have included pressure gages, blast gages, physiological instruments, accelerometers, and will in the near future include both experimental Naval and geophysical hydrophones.

A modified classical form of the streaming potential equation developed by Helmholtz (4), but containing the dielectric constant, (assumed by Helmholtz to be unity.) is given below:

$$H = \frac{\zeta \varepsilon}{4 \pi \eta K} P$$

where:

H is the streaming potential

ζ is the zeta potential across the double-layer

ε is the dilectric constant

η is the fluid viscosity

K is the fluid conductivity

and P is the applied pressure

This equation which applies to porous plugs or single capillaries indicates a linear relation between voltage and pressure independent of area, length, or pore size. Experimental evidence has been obtained to verify the independence of voltage-pressure sensitivity on pore size in certain ranges (13). For very small pore radii the sensitivity is affected and equations predicting this effect have been developed, (14), (15). This reduction of sensitivity has been found to be important in transducers designed for low frequency operation, i.e. below 10 c.p.s. and using microporous plugs.

Conflicting data may be found with regard to linearity in various published papers but it is believed that most departures from linearity observed in the past have been the result of the techniques employed rather than anything inherent in the phenomena particularly in apparatus employing rigid porous plugs of glass or ceramics. Tests conducted in ranges from a few microbars to up to 95 psi by this organization have shown no measureable departures from linearity. The latter measurements were made with sealed and stabilized transducers and were not subject to noticeable errors due to polarization or unstabilized adsorbtion of foreign matter.

It is anticipated that the streaming potential phenomena will receive renewed interest among physical chemists and others as more applications develop.

3. GENERAL THEORY OF OPERATION OF ELECTROKINETIC TRANSDUCERS

3.1 Single Capillary Transducer

The general theory of energy conversion in a porous plug can best be understood by first considering the case of a single capillary since a porous plug is in effect a bundle of capillaries of irregular size and shape.

First consider a round liquid filled capillary such as is shown in a broken away section in Figure 3-1. It is assumed that a layer of liquid a distance "d" from the capillary wall is charged with a charge "e" per unit area and that the capillary wall is equally and oppositely charged. The product of the distance and the charge "de" is defined as the electric moment "β" of the electrokinetic double layer assumed to exist at the interface.

It is now assumed that a voltage gradient E exists in the capillary along its axis and that, as a result, a force F is produced on the unit area which is equal to the product of the charge e and the gradient E or:

$$F = Ee \tag{1}$$

If the unit area or shell of liquid is moving, a viscous force will act due to the shearing of the double layer, this force being equal to:

$$F' = -\eta \frac{v_d}{d} \tag{2}$$

where vd is the velocity of the unit element of the inner layer.

If no longitudinal pressure gradient exists, it is evident that the forces will balance and that:

$$Ee = \eta \frac{v_d}{d} \tag{3}$$

From the definition of β :

$$v_d = \frac{E\beta}{\eta} \tag{4}$$

The above relation relates the inner shell velocity to the applied voltage gradient when no differential pressure exists across the capillary. It is evident that the bulk velocity in this instance

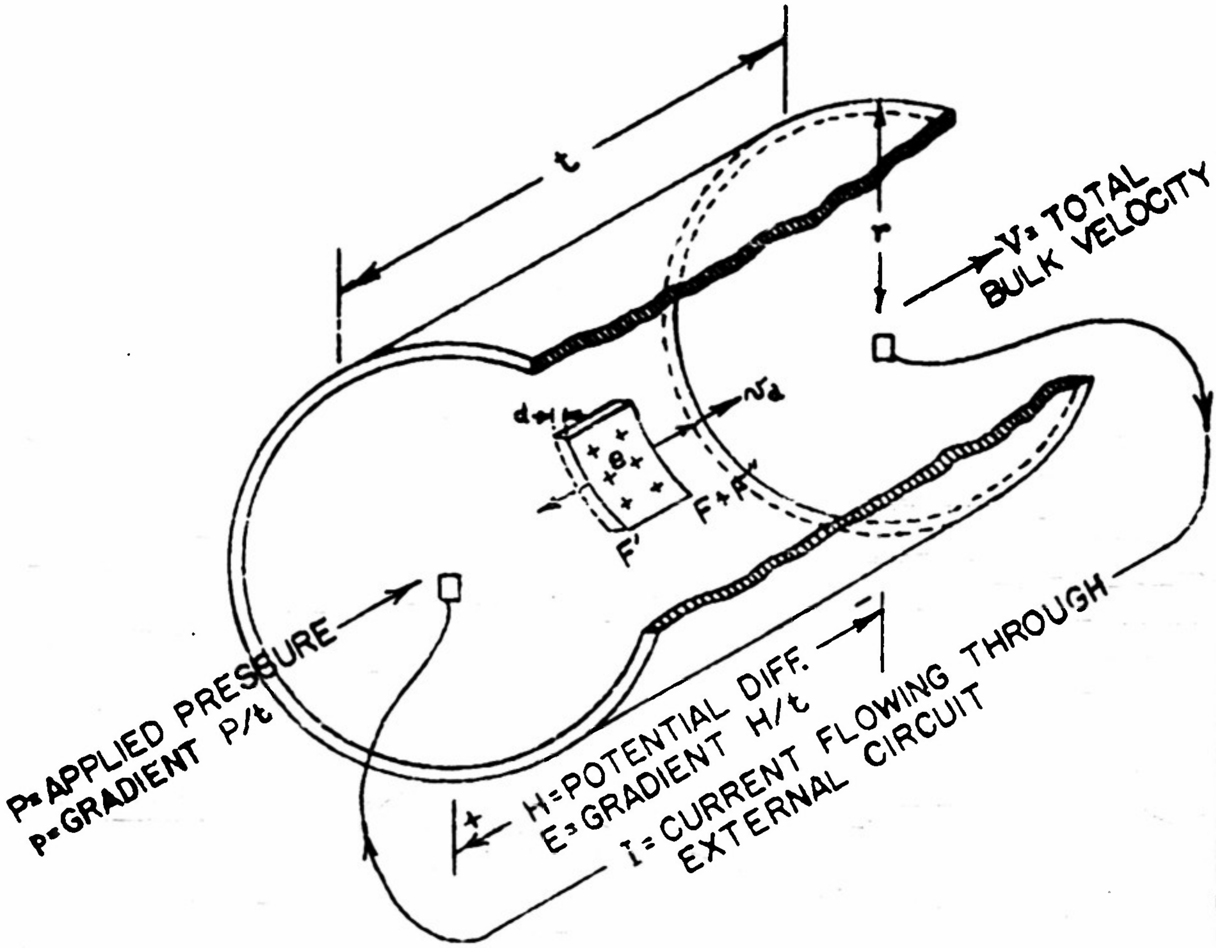


FIGURE 3-1

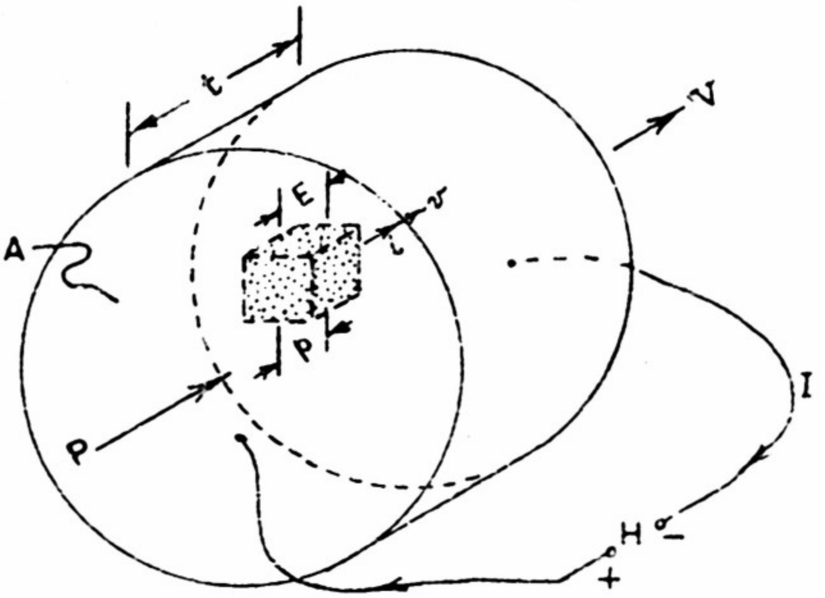


FIGURE 3-2

would be simply:

$$V = \pi r^2 v_d = \pi r^2 \frac{E\beta}{\eta} \tag{5}$$

where r is the radius of the capillary.

To obtain the <u>layer</u> current we simply relate the charge per unit length to the velocity of transportation of the charge:

$$I_l = 2\pi r v_d e \tag{6}$$

When a differential pressure "P" is applied to the capillary giving rise to a longitudinal pressure gradient "p" an additional force acts on the unit element of area. It is simply the pressure gradient multiplied by the cross sectional area and divided by the circumference.

$$F'' = p\frac{r}{2} \tag{7}$$

In this instance the balance of forces becomes:

$$Ee - \eta\frac{v_d}{d} + p\frac{r}{2} = 0 \tag{8}$$

In this instance the total volumetric flow will be equal to the shear velocity multiplied by the area plus the flow in the center of the capillary in accordance with Poiseuille's formula:

$$V = \pi r^2 v_d + \frac{\pi r^4}{8\eta} p \tag{9}$$

Solving Equation 8 for vd:

$$v_d = \frac{rd}{2\eta} p + \frac{\beta}{\eta} E \tag{10}$$

and substituting from Equation 9:

$$V = \frac{\pi r^4}{8\eta}\left[1 + \frac{4d}{r}\right] p + \pi r^2 \frac{\beta}{\eta} E \tag{11}$$

The assumption is now made that $r/4 \gg d$, the thickness of the double layer permitting the equation to be rewritten as:

$$p = -\frac{8\beta}{r^2}E + \frac{8\eta}{\pi r^4}V \qquad (12)$$

Equation 12 is one of the fundamental electrokinetic equations for a single round capillary.

The total current under a given voltage gradient and condition of volumetric flow is simply the current transported in the charged layer plus the current flowing as a result of the bulk conductivity of the liquid:

$$I = 2\pi r e v_d + K_B \pi r^2 E \qquad (13)$$

Again substituting for vd and using the relation $\beta \simeq ed$ we obtain:

$$I = \pi r^2 \frac{\beta}{\eta} p + \left[\frac{2\pi r}{\eta d}\beta^2 + K_B \pi r^2\right]E \qquad (14)$$

In all instances for small capillaries where the flow is laminar we may write:

$$p = \frac{8\eta}{\pi r^4}V \qquad (15)$$

And substituting Equation 15 into 14:

$$I = \frac{8\beta}{r^2}V + \left[\frac{2\pi\beta^2}{\eta}\left(\frac{r}{d}\right) + K_B \pi r^2\right]E \qquad (16)$$

This equation is a second fundamental equation which in combination with Equation 12 describes the electrokinetic phenomena taking place in a single capillary.

The first term of Equation 12 is the electroosmotic pressure term, significant only when the capillary is connected to an energy source, and being negligible when the ends of the capillary are connected through electrodes to a passive load. The second term of Equation 12 is merely the pressure gradient due to viscous shearing in the body of the liquid.

In Equation 16 the first term represents that component of double-layer current which is effective in transducing external mechanical and electrical energy. The first bracketed term relates to that component of layer current associated with the internal viscous dissipation of energy due to the shearing of the double layer as a result of an existing potential gradient. The last bracket term is simply the conductance per unit length due to the bulk conductivity of the fluid.

The "surface conductance" term, or the first bracketed term of Equation 16 corresponds with the one derived by Smoluchowski (5) in terms of the "zeta potential" where:

$$\zeta \varepsilon = 4\pi d e \tag{17}$$

and in which ζ is the potential across the double layer and ε is the dielectric constant.

More complete relations for "surface conductance" including the changes in concentration and mobilities of ions produced by the presence of a charge surface have been developed by others including Bickerman (16), and presumably should be considered for high values of zeta potential. Such considerations are not, however, treated in this report, as an experimentally determined overall conductivity parameter is employed in the final equations.

3.2 Energy Conversion in a Porous Plug

In Figure 3-2 a liquid filled porous plug is shown in which the pressure and voltage gradients are perpendicular to the parallel faces of area "A". It is assumed that the faces are good conductors, as they would be if covered with a thin deposited metal film, and that the gradients are uniform.

We now consider a unit cubical element in the plug with one face perpendicular to the direction of flow. The cube is assumed to be porous, the pores being irregular in shape and following tortuous paths through the cube. This concept is then replaced by considering only the multiplicity of active pores effectively parallel to the direction of flow, again of irregular shape but with average flow resistance and area equivalent to the average of the actual pores.

It is then necessary to define the following new terms:

N is the number of pores per unit area.

F is the average total pore area per unit area.

F/N is the average pore area.

k_v is the flow conductivity of the porous material.

P is the perimeter of an average pore (averaged with respect to perimeter).

r_v' is the flow resistance of an average pore per unit length and is equal to

i is the current per unit area.

v is the effective velocity per unit area or the bulk velocity divided by the unit area. (It is not the average pore velocity.)

It is evident that because of the complicated nature of the flow in a pore of irregular shape that it would not be possible to derive an expression for flow resistance. On the other hand from dimensional considerations it should be recalled that for a typical shape the flow resistance would decrease with the fourth power of the effective pore radius, and that the flow conductivity of the element would vary with the number of pores per unit area.

The first term in Equation 12 was obtained from the last term of Equation 11 being related simply to the shell velocity of the inner layer resulting from the gradient E. It is evident therefore that since shell velocity is independent of the pore shape:

$$p = -F\frac{\beta}{N}\frac{r_v'}{N}E + \frac{r_v'}{N}v \qquad (18)$$

$$p = -F\frac{\beta}{\eta k_v}E + \frac{1}{k_v}v \qquad (19)$$

Similar methods may be applied to modifying Equation 16 to apply to the unit element of porous material. Again the first term relates to shell velocity. The first bracketed term is dependent on the pore perimeter rather than the radius. For a round pore:

$$r = \frac{p}{2\pi} \qquad (20)$$

permitting a substitution.

The last term is dependent merely on the average effective pore area per unit area. Equation 16 can then for the porous material be rewritten as:

$$i = \frac{F\beta}{\eta k_v} + \left[\frac{\beta^2}{\eta}\left(\frac{p}{d}\right) + K_B F\right]E \qquad (21)$$

In determining the property of the solid material related to the flow conductivity it is convenient to define a permeability factor "B" which will be independent of viscosity. This factor is defined as follows for a porous plug:

$$V = \frac{BA}{\eta t} P \qquad (22)$$

where V is the total bulk velocity, A is the area perpendicular to the flow, η is the viscosity, t is the thickness, P is the applied pressure and B is the permeability characteristic of the solid, (only), and has the dimensions of length squared.

For a unit cube of material:

$$\frac{v}{p} = \frac{B}{\eta} = k_v \qquad (23)$$

where v is the effective velocity and p is the pressure gradient.

For the second term in Equation 21, it is convenient to introduce the experimental parameter K_o the overall electrical conductivity of the liquid filled solid where:

$$K_o = \left[\frac{\beta^2}{\eta}\left(\frac{p}{d}\right) + K_B F\right] \qquad (24)$$

Equations 19 and 21 may then be rewritten as follows:

$$p = -\frac{F\beta}{B} E + \frac{1}{k_v} v \qquad (25)$$

$$i = \frac{F\beta}{B} + K_o E \qquad (26)$$

It should be noted that the first terms on the right of both equations contain the coupling constant $F\beta/B$ and that certain generalizations may be noted since it will be later evident that it is desirable to maximize this coupling constant:

(1.) The electric moment "β" and the porosity factor "F" appear as a product. It is therefore equally important to maximize porosity as to maximize the electric moment.

(2.) The electric moment β is unique to a given liquid-solid material interface.

(3.) The terms forming the ratio F/B are both characteristic to the structure of the solid material. The appearance of this ratio illustrates the importance of securing a material with the largest ratio of porosity to permeability.

It is now convenient to define the coupling constant M:

$$M \triangleq \frac{F\beta}{B} \tag{27}$$

The Equations 25 and 26 are then rewritten as:

$$p = -ME + \frac{1}{k_v} v \tag{28}$$

$$i = Mv + K_o E \tag{29}$$

The above equations contain three parameters, M, the coupling constant, k_v the flow conductivity, and K_o the overall electrical conductivity, all subject to measurement, and together completely describe the electrokinetic properties of a given liquid filled porous solid. These three parameters are used throughout this report.

By including the area "A" and length "l" of the equations may be rewritten in terms of pressure, P, bulk velocity, V, the potential difference, H, and the total current I in an external circuit as follows:

$$P = -MH + \frac{1}{k_v} \frac{t}{A} V \tag{30}$$

$$I = MV + K_o \frac{A}{t} H \tag{31}$$

The above relations may be used by substituting the values plotted in Section 4 to determine the performance of a porous plug in converting energy under any circumstances. It is important to recognize that the value of "H" was derived from the actual gradient and corresponds to terminal voltage only when polarization effects are negligible at the electrodes.

The electrokinetic relations may also be written in terms of the current pressure sensitivity with the voltage equal to zero as was done in Technical Report No. 2. This sensitivity is convenient as an index of various liquids in the same solid or when a transducer is operated into a low impedance load.

Here by definition:

$$\mathcal{R}_{(ip)h} \triangleq \mathcal{S}_{(IP)H}\frac{t}{A} \triangleq \frac{\beta F}{\eta} \quad (32)$$

$$G_o \triangleq K_o \frac{A}{t} \triangleq \frac{1}{R_o} \quad (33)$$

$$g_v \triangleq k_v \frac{A}{t} \triangleq \frac{1}{r_v} \quad (34)$$

where G_o and gv are the electrical conductance and the fluid flow conductance of the plug.

With the above substitutions Equations 30 and 31 become:

$$P = -\frac{S_{(IP)H}}{g_v} + \frac{1}{g_v} V \quad (35)$$

$$I = \frac{\mathcal{S}_{(IP)H}}{g_v} + G_o H \quad (36)$$

3.3 Important Relations Obtained from Electrokinetic Equations

3.3.1 Streaming Potential:

The streaming potential of an electrokinetic cell operating open circuit may be derived from Equations 30 and 31. When no external voltage source is present the first term on the right of Equation 30 may be neglected and the equations may be rewritten as:

$$P = \frac{1}{k_v}\frac{t}{A} V \quad (37)$$

$$0 = MV + K_o \frac{A}{t} H \quad (38)$$

From which we obtain:

$$\left(\frac{H}{P}\right)_{I=0} = \frac{M k_v}{K_o} \quad (39)$$

Using Equations 23 and 27:

$$\left(\frac{H}{P}\right)_{I=0} = -\frac{F\beta}{\eta K_0} \qquad (40)$$

From the above it is evident that since F is a fixed property of the solid, if β were constant with temperature and the ηK_0 product were constant or with the deviations cancelling, the sensitivity H/P would be independent of temperature. This has been found to be the case for certain material combinations, but not for others.

3.3.2 Osmosis with no Pressure Differential

By assuming P as zero and neglecting the first term on the right hand side of Equation 31 to be zero when no external mechanical work is involved:

$$\left(\frac{V}{I}\right)_{P=0} = \frac{M k_v}{K_0} \qquad (41)$$

Inasmuch as the voltage does not appear in this relation it is evident from comparison with Equation 40 that the sensitivity H/P may be determined from measuring the volume rate of flow for a known current.

3.3.3. Osmostic Pressure:

If a porous plug were inserted with electrodes in the bottom of a "U" tube filled with electrokinetic liquid and a potential applied between two non-polarizing electrodes a difference of level would be observed as first discovered by Reuss (2). Since the net volume flow would be zero the difference in pressure across the plug from Equation 30 would be:

$$P_{(V=0)} = -MH \qquad (42)$$

From energy considerations it is evident that some electrical energy must be dissipated other than that converted to heat in the bulk of the liquid, since the electrokinetic forces act at the pore walls only. Actually a circulation takes place in the pores with the liquid moving in one direction near the walls and flowing back through the center. A circulation of this type will always be present when both the pressure and voltage are finite, but its effects are negligible when the external circuit is passive.

3.3.4 Other Relations:

A number of relations and equalities may be derived from Equations 30 and 31 without approximating assumptions other than that the pore radius is assumed to be much greater than the double layer thickness, this relation being implicit in the equations. Some are important in that they suggest measurement techniques and methods of checking in the laboratory:

$$\left(\frac{H}{P}\right)_{I=0} = \left(\frac{E}{p}\right)_{i=0} = -\left(\frac{V}{I}\right)_{P=0} = -\left(\frac{v}{i}\right)_{p=0} = -\frac{k_v M/K_0}{1 + k_v M^2/K_0} \qquad (37)$$

$$\left(\frac{P}{H}\right)_{V=0} = \left(\frac{I}{V}\right)_{H=0} = \left(\frac{p}{E}\right)_{v=0} = \left(\frac{i}{v}\right)_{p=0} = M \qquad (38)$$

$$\left(\frac{V}{P}\right)_{H=0} = \left(\frac{V}{P}\right)_{I=0} = \frac{k_v A}{t} \qquad (39)$$

$$\left(\frac{v}{p}\right)_{E=0} = \left(\frac{v}{p}\right)_{i=0} = k_v \qquad (40)$$

$$\left(\frac{V}{H}\right)_{P=0} = \left(\frac{I}{P}\right)_{H=0} = M k_v \frac{A}{t} \qquad (41)$$

$$\left(\frac{v}{E}\right)_{p=0} = \left(\frac{i}{p}\right)_{E=0} = M k_v \qquad (42)$$

$$\left(\frac{I}{H}\right)_{V=0} = \left(\frac{I}{H}\right)_{P=0} = K_0 \frac{A}{t} \qquad (43)$$

$$\left(\frac{P}{I}\right)_{V=0} = \left(\frac{H}{V}\right)_{I=0} = -\frac{M}{K_0}\frac{t}{A} \qquad (44)$$

$$\left(\frac{p}{i}\right)_{v=0} = \left(\frac{E}{v}\right)_{i=0} = -\frac{M}{K_0} \qquad (45)$$

4. ELECTROKINETIC PROPERTIES OF CERTAIN LIQUIDS AND SOLIDS

4.1 TEST METHODS

4.1.1 Measurements of Streaming Potential, Cell Resistance, Pressure and Temperature for the Determination of E/P, H, and K_0 as Functions of Temperature.

For satisfactory determinations of the effects of temperature on the sensitivity, the electromechanical coupling constant, and the overall conductivity of the liquid filled porous solid, it was necessary to employ an enclosed and sealed cell mounted in a transducer such as is shown in Figure 3-2 of Technical Report No. 2 and to use alternating pressures. In addition to the fact that it made linearity and frequency response measurements possible on the same transducer, this method has the following advantages:

First, the method lends itself to rapid pressure measurements using an accurately calibrated strain-gage transducer operating safely within its useful frequency range. Second, the streaming potentials may be readily amplified with an A.C. vacuum tube voltmeter with negligible polarization effects and using the same amplifier and scale to read pressure for comparison. Last and of greatest importance is the fact that the transducers may be stored with a fixed sealed off body of liquid to allow complete stabilization to take place internally.

In some instances it was found that several days storage were required to obtain repeatable measurements. This is understandable as some time would be required to achieve complete uniformity of the liquid with regard to contaminants which go into solution during assembly or which are adsorbed on the surfaces of the solid components. In each instance, however, the sensitivity approached an equilibrium level in an almost exponential fashion by either increasing or decreasing with time. This is illustrated in Figure 4-1.

In Figure 4-2 a plot is shown which illustrates the extent to which data may be in error prior to approaching stabilization. The arrows indicate the sequence of the measurements during temperature cycling. Here deviations from the final curve are noted during temperature cycling indicating temperature differences between the measuring point and the porous disc in the transducer. These may be averaged for increasing and decreasing temperatures. The initial points are far removed from the final curve. For the reasons stated above the majority of the data was taken using alternating techniques with apparatus later described.

Figure 4-3 shows a sectional view of the steady flow cell used in certain measurements where it was desirable to run a variety of liquids through the cell in a reasonably short time (for comparisons) and further where it was advantageous to know as nearly as possible the bulk conductivity of the liquid. It was not possible

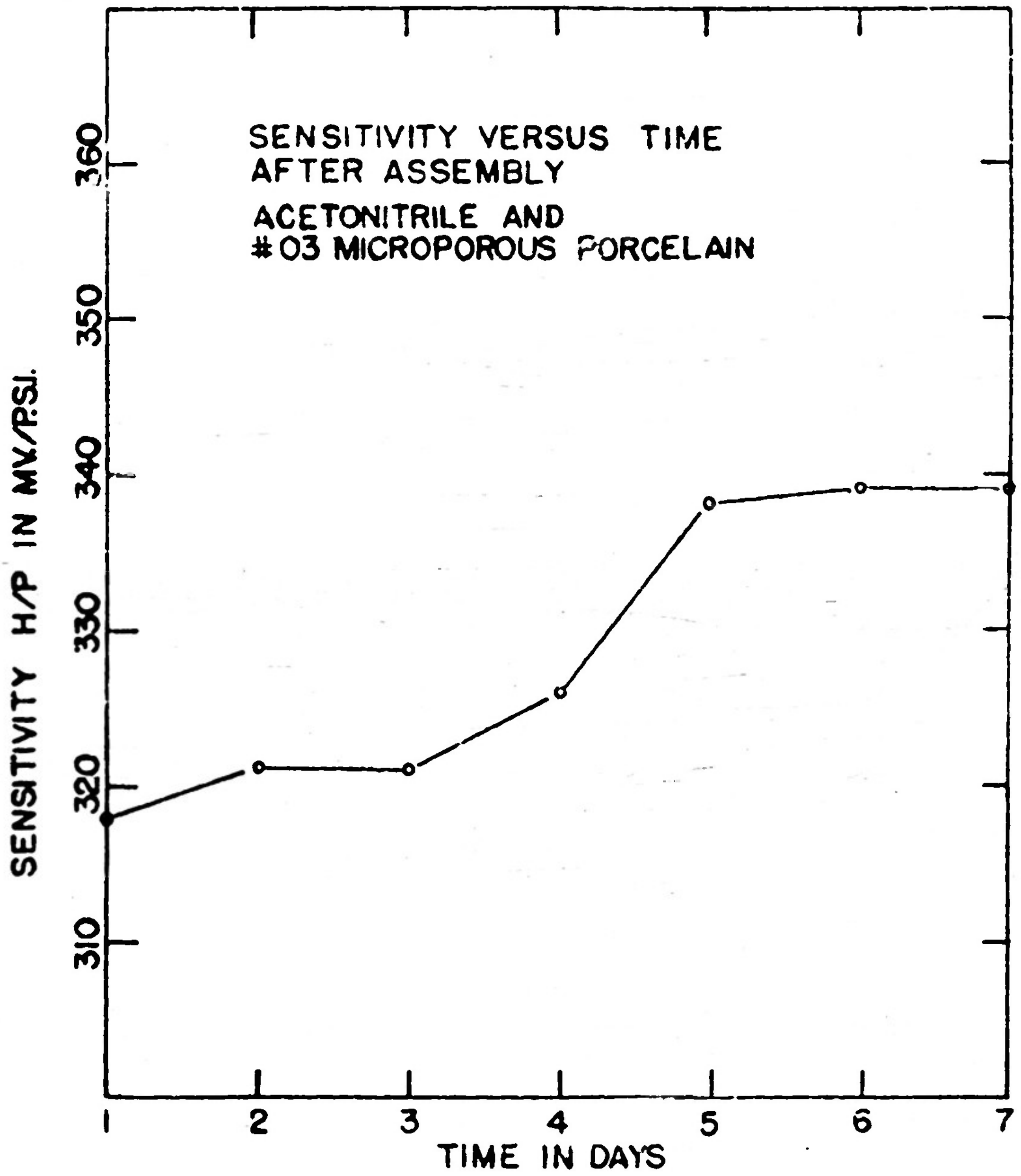

SENSITIVITY VERSUS TIME
AFTER ASSEMBLY
ACETONITRILE AND
#03 MICROPOROUS PORCELAIN
SENSITIVITY H/P IN MV./P.S.I.
310
320
330
340
350
360
1
2
3
4
5
6
7
TIME IN DAYS

FIGURE 4-1

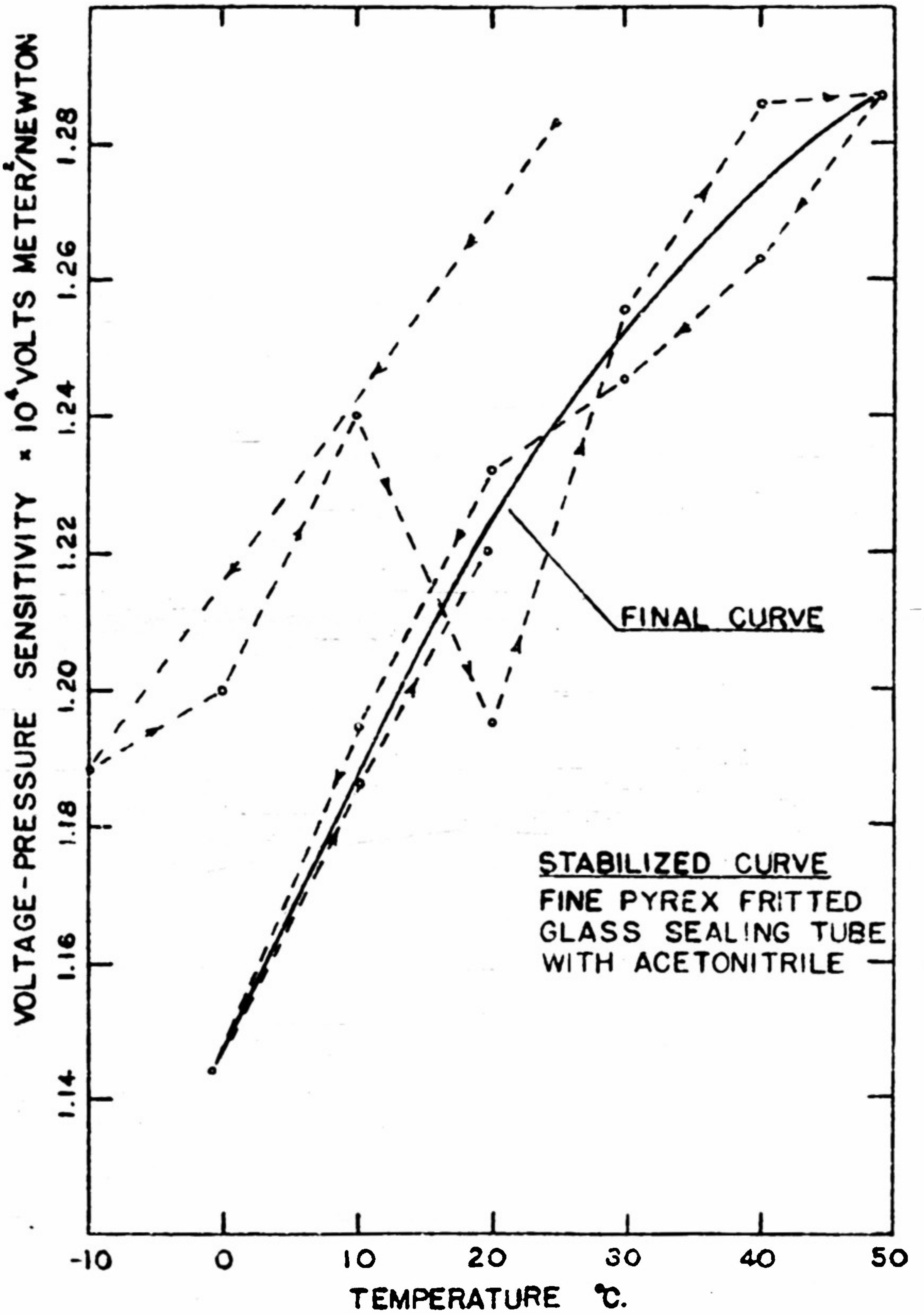
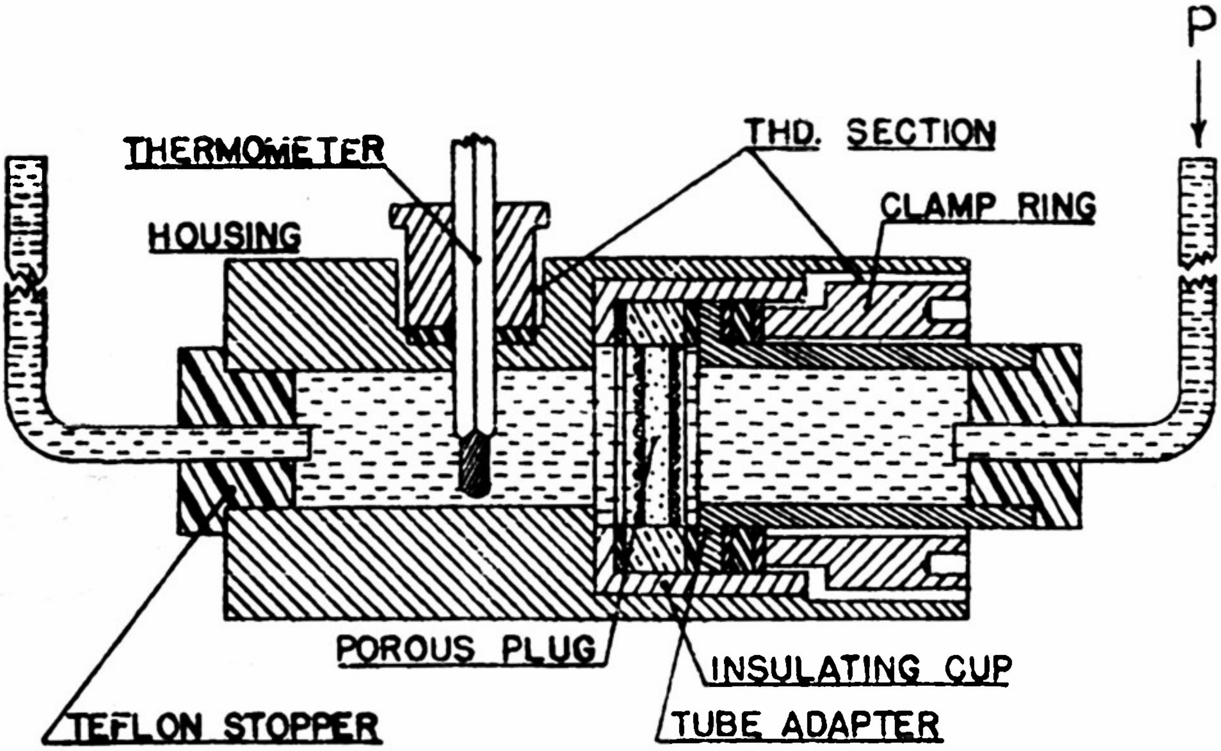

VOLTAGE-PRESSURE SENSITIVITY × 10⁴ VOLTS METER²/NEWTON
1.28
1.26
1.24
1.22
1.20
1.18
1.16
1.14
-10
0
10
20
30
40
50
TEMPERATURE °C.
FINAL CURVE
STABILIZED CURVE
FINE PYREX FRITTED
GLASS SEALING TUBE
WITH ACETONITRILE

FIGURE 4-2



STEADY FLOW CELL

FIGURE 4-3

to measure the latter in the sealed transducers employed in other tests. In the apparatus shown in Figure 4-3 a porous disc glazed into a solid ring is clamped, using insulating materials, in the path of the liquid flowing under a known pressure. Electrical circuits to the wire mesh electrodes on each side of the plug are established by foils and wires not shown.

A few steady flow and alternating pressure measurements were made using sealing tubes (Corning #39580) modified as illustrated in Fig. 4-4. This apparatus was only used for certain comparative experiments in early phases of the work.

In determining H/P from the alternating pressure test data the measured voltage was merely divided by the measured pressure and the ratio converted to the MKS system of units for plotting.

The cell resistance was measured at each temperature either using a bridge or by measuring the drop in cell output with a known shunt resistance. Inasmuch as the porous disc dimensions were known and most of the impedance was in the disc pores, the overall conductivity of the liquid filled porous solid material, K_o, could be readily computed.

The flow conductivity of the material for the given liquid is computed from the material's permeability and the liquid's viscosity, the measurements of which are later discussed.

Knowing the sensitivity, H/P, the electrical conductivity, K_o, and the flow conductivity, k_v, for the liquid-solid combination from direct measurements, the electro-mechanical coupling constant, M, was computed from the relation:

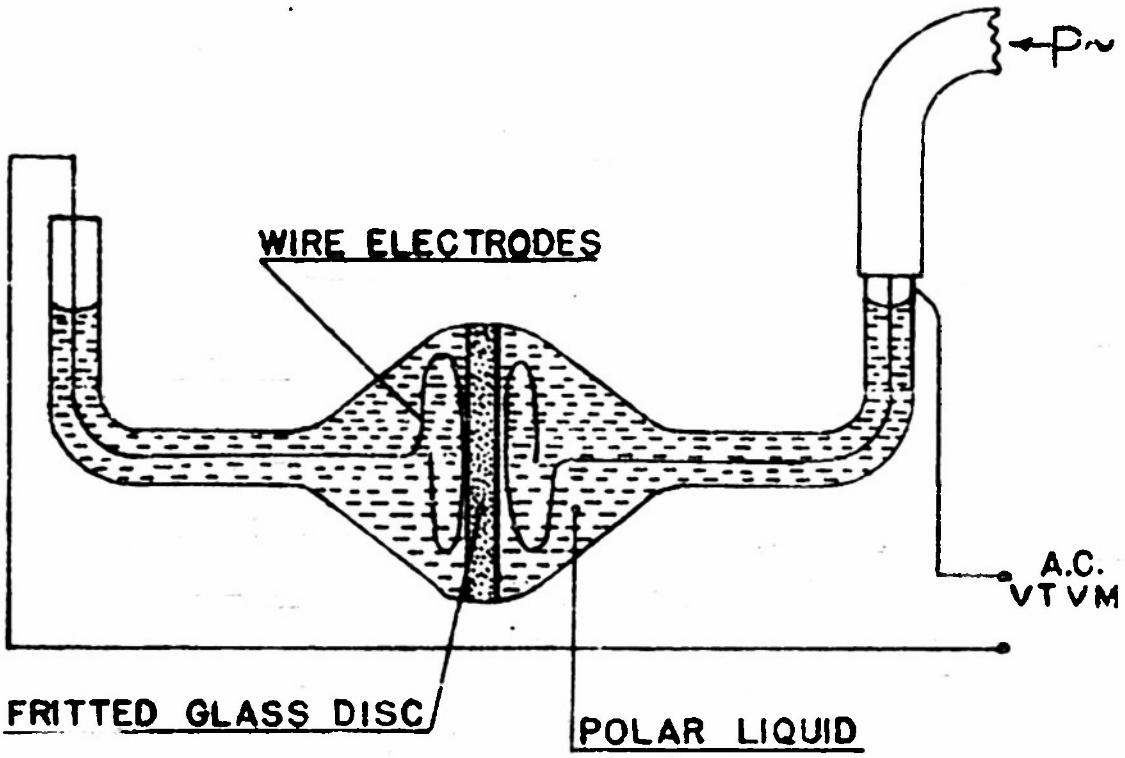
$$M = \left(\frac{H}{P}\right)_{I=0} \frac{K_o}{k_v}$$

The above methods were employed using apparatus illustrated in Figures 4-5 and 4-6 to obtain the data plotted in Figures 4-13 through 4-23.

4.1.2 Apparatus Employed in Measuring Alternating Streaming Potential.

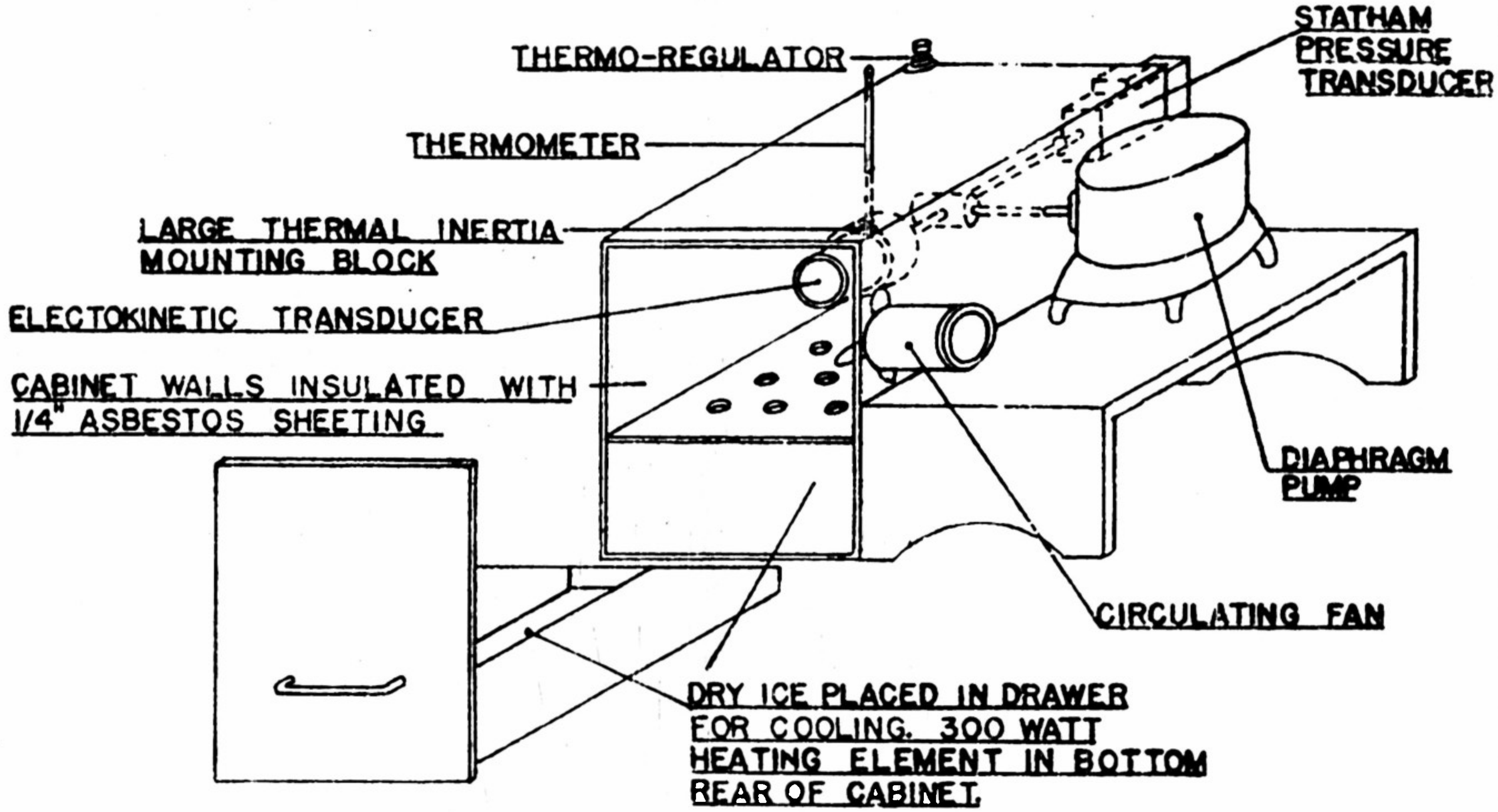
The apparatus used to obtain data plotted in Figures 4-13 through 4-23 is illustrated in Figure 4-5. A diaphragm pump with the valves removed was used to produce a near sinusoidal alternating pressure of about 1.5 psi. and at a frequency of 30 cps., the latter being well within the midband range of the transducers tested and the reference transducer. The line from the pump was connected through a small orifice, (for wave shaping), into a T fitting with one short line connecting with an external standard transducer and the other to the electrokinetic unit under test.

The electrokinetic transducer in each instance was screwed to



SEALING TUBE CELL

FIGURE 4-4



CALIBRATION CABINET

FIGURE 4-5

a large adapter block into which a thermometer was inserted, and which provided substantial thermal inertia. The alternate use of dry ice and a 300 watt lamp provided for the required temperature cycling, a fan being used for air circulation.

The alternating pressure apparatus was wired as shown in Figure 4-6. Here the reference transducer was a Statham P21-100-300, temperature compensated and calibrated to within 1%. The switches shown provided for reading the output of the transducer under test, the output of the reference gage, and the cell resistance in rapid sequence.

4.1.3 Apparatus for Obtaining Response to a Step Function.

A simple device which was used largely for comparative purposes is illustrated in Figure 4-7. Here the transducer was clamped against an open port in a block having an internal cavity with a fragile cellophane diaphragm opposite. A vacuum line and gage made it possible to set a predetermined pressure difference relieved in a few milliseconds with a violent transient upon bursting the diaphragm. A Sanborn direct writing recorder unresponsive to the transient oscillation recorded the transducer output thus providing an approxiamte means of calibration and an accurate means of determining the time constant and low frequency 3db "break point".

4.1.4 Apparatus for Determining Frequency Response.

Frequency response studies were conducted in a test tank as shown in Figure 4-8. This apparatus which was designed for measuring diaphragm rather than free field response was subject to some uncertainty in making measurements but provided a means of making comparative calibrations in relatively short time and with sufficient accuracy to show deviations of 1 to 2 db.

In practice, frequencies were selected to set up longitudinal standing waves in the tank as indicated by peak readings of the test transducer at the end of the tank. The region near the tank wall was then explored for the first or second pressure antinode with the head of the Brush microphone. It was assumed that the pressure at the end of the tank was the same as that at the first or second antinode. A switching arrangement made possible comparative DB readings (on the scale of a vacuum tube voltmeter) which were used in combination with the Brush Calibration curves, corrected for the preamplifier response, to plot the various frequency response curves given and discussed in Technical Report No. 2.

Tests from about 100 cps. to 20 KC were conducted in air using various loudspeakers for sources. Tests from about 10KC to 100KC were conducted with the tank filled with water using a Brush BM-102 transducer as a sound source.

Any important resonant effects in the transducers were clearly measurable by this method.

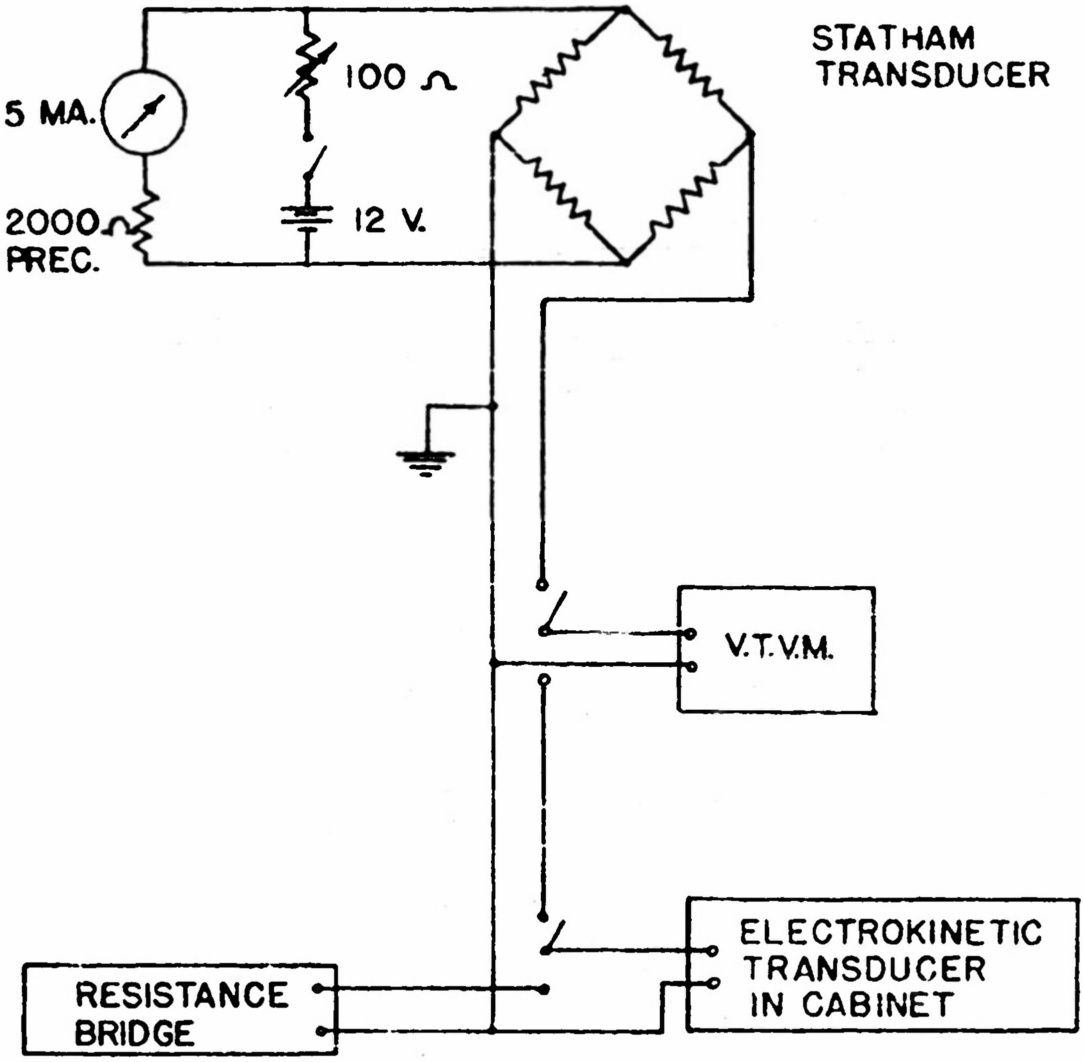

STATHAM TRANSDUCER
5 MA.
100 Ω
2000 Ω PREC.
12 V.
V.T.V.M.
ELECTROKINETIC TRANSDUCER IN CABINET
RESISTANCE BRIDGE

FIGURE 4-6

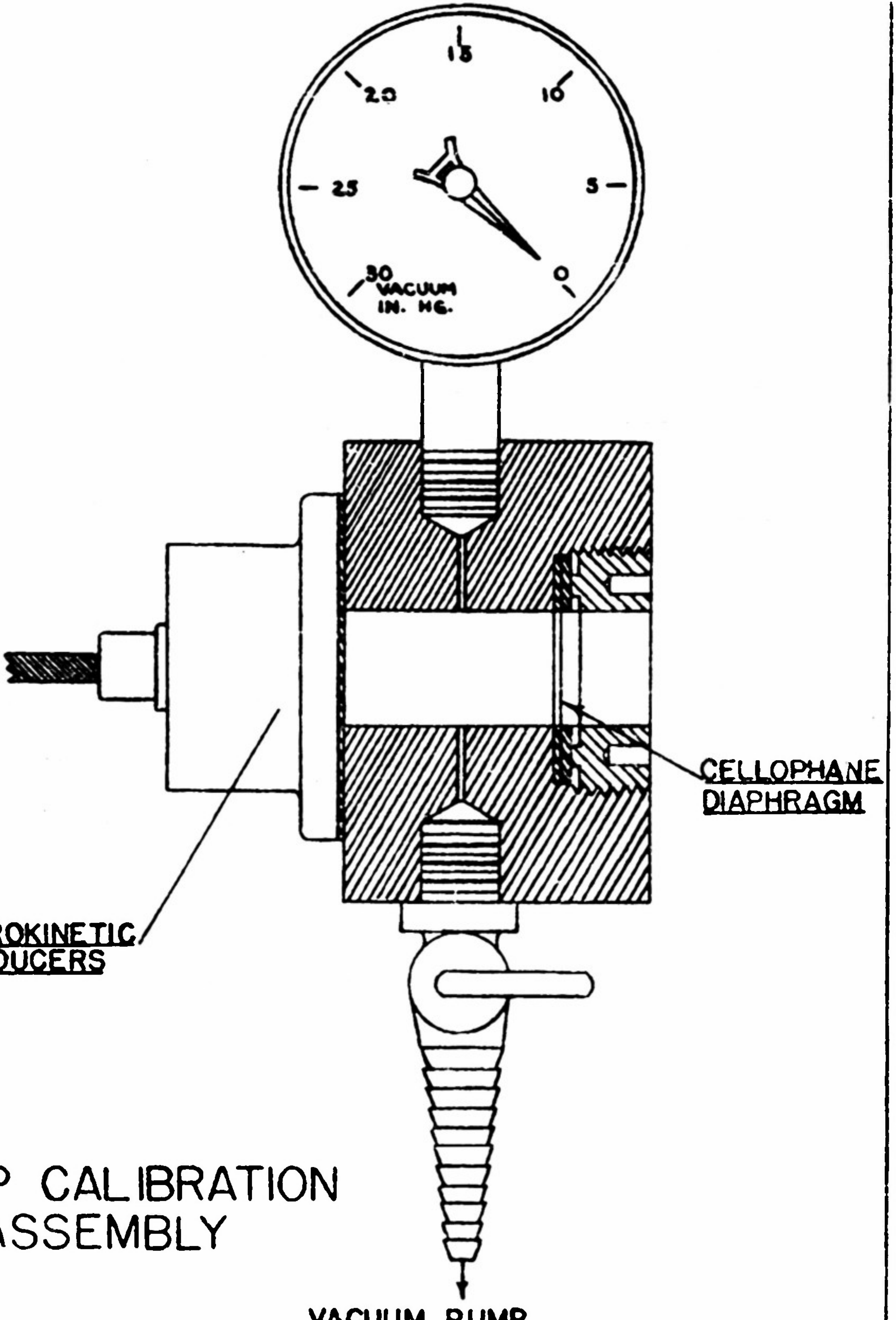
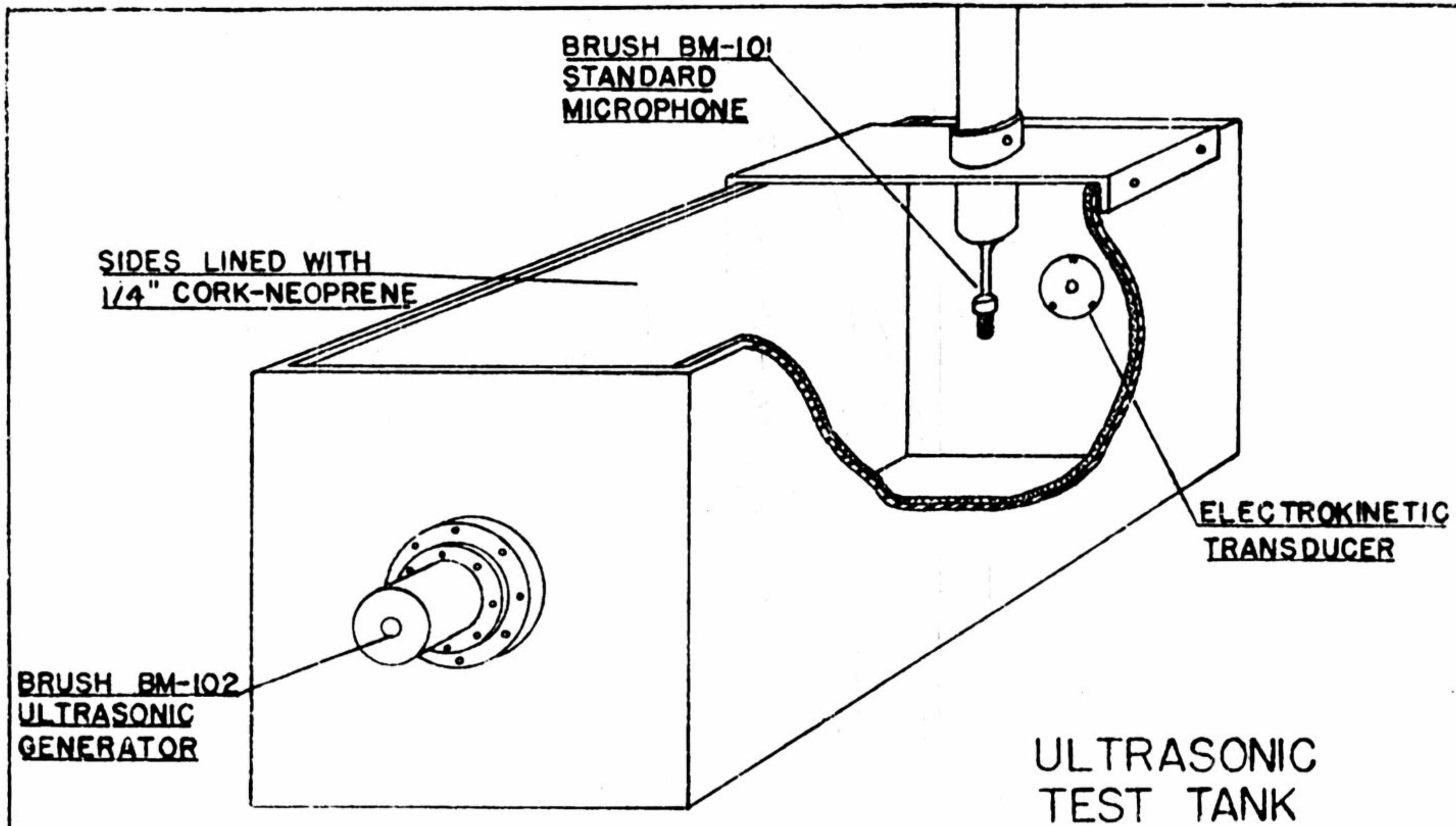

15
20
10
25
5
30
VACUUM
IN. HG.
0
CELLOPHANE DIAPHRAGM
ELECTROKINETIC TRANSDUCERS
STEP CALIBRATION ASSEMBLY
VACUUM PUMP

FIGURE 4-7



ULTRASONIC
TEST TANK

FIGURE 4-8

4.1.5 Impedance Measurements.

Wiring diagrams of circuits used for measuring the internal impedance and the internal shunt capacity of the electrokinetic cells are illustrated in Figures 4-9 and 4-10.

In Figure 4-9 two 10 meghhm resistors provide current sources of equal value. The transducer to be tested is placed across one source and the circuit shown was wired in series with the other, an oscilloscope being wired to both as shown. The dummy transducer circuit provides for the internal resistance of the porous plug and for the capacity and resistance of the electrodes. The parameters were adjusted until equal and in phase voltages appeared on the oscilloscope from 20 cps. to 1000 cps. The equivalent values for the transducer were then obtained from known or measured values in the dummy circuit.

In Figure 4-10 a shunt choke was used to produce a resonance dependent on the total shunt capacity of the circuit. Here the resonant frequency was first obtained without the transducer connected to determine the total effective circuit capacity. The transducer was then connected and the two frequencies noted. Knowing these two frequencies and the inductance of the choke the shunt capacity of the transducer was computed.

4.1.6 Permeability Measurements.

Rough values of the permeability of the various materials are contained in the manufacturers' literature. These were verified on sample discs by measuring the elapsed time required to pass a given quantity of fluid at a measured temperature. The permeability was obtained using the relation:

$$B = \frac{t\eta}{A}\left(\frac{Q}{\Delta T}\right)P$$

where B is the permeability, (as here defined), t is the plug thickness, A is the plug area, η is the viscosity at the known temperature, Q is the volumetric quantity of liquid, ΔT is the elapsed time, and P is the pressure differential.

4.1.7 Conductivity.

Inasmuch as the majority of tests were conducted with acetonitrile and very frequent conductivity measurements were necessary, special apparatus was made up and calibrated for conductivity measurements. (Noble metal conductivity cells are unsatisfactory for use with nitriles because of the formation of complex ions.) The cells used are illustrated in Figures 4-11 and 4-12. In the apparatus in 4-11 the liquids could be readily streamed into the cell by means of a pipette and emptied by revolving the cell about the bearing hole in the upright insulating stand. An impedance bridge was used to measure the cell resistance with a variable capacitor

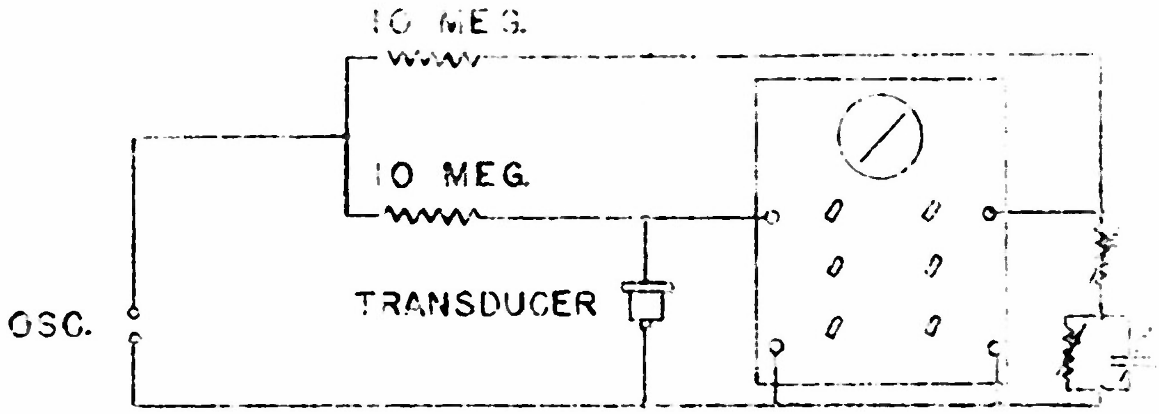


FIGURE 4-9

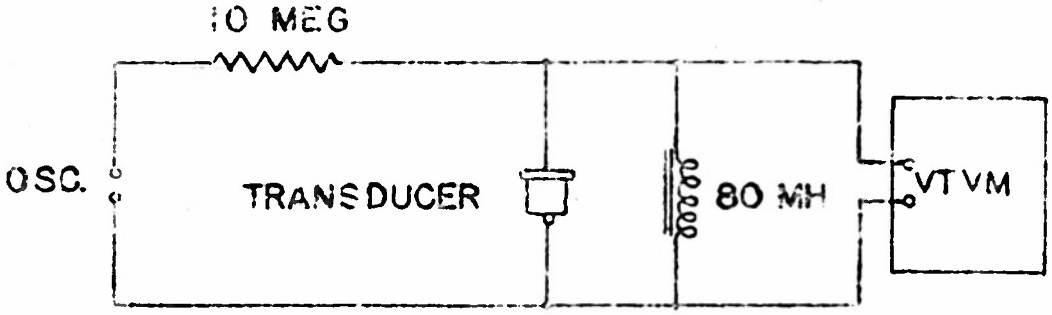
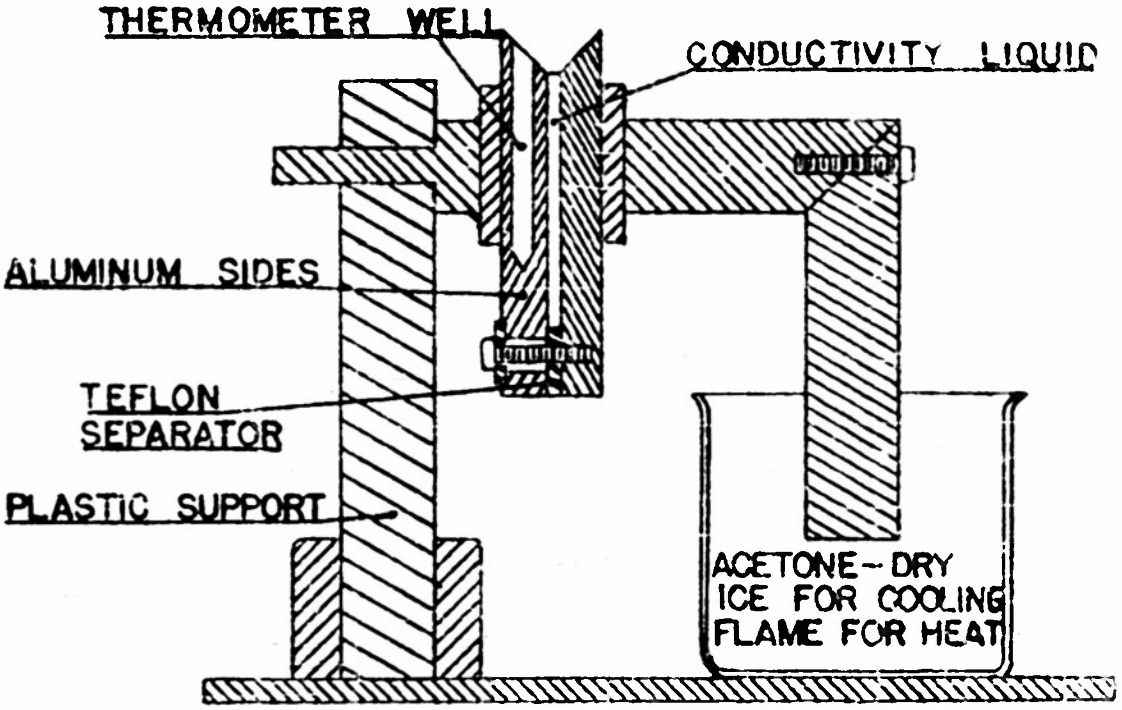
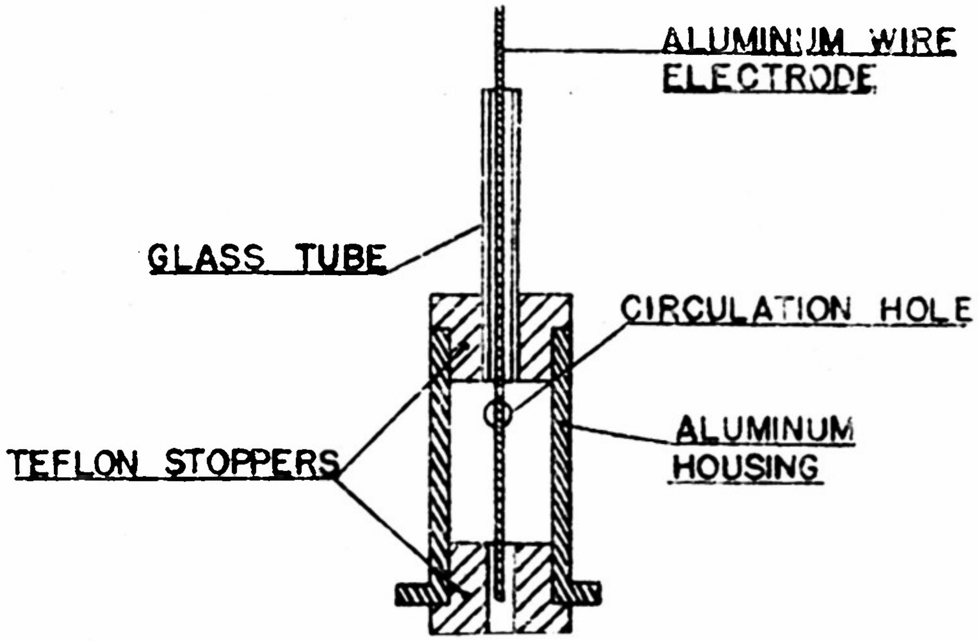


FIGURE 4-10



IMPEDANCE CELL
FIGURE 4-11



DIP CELL

FIGURE 4-12

wired across the opposing bridge arm to balance cell and stray capacity to produce a sharp null at the 1,000 cps. test frequency. The dip cell was used occasionally to measure continuous changes in resistivity.

4.1.8 Other Test Methods.

The above discussion of test methods and apparatus supplements information given in Technical Report No. 2. Other methods, relating to linearity, noise, etc. are discussed briefly in that report.

4.2 DATA SHEETS AND TABULATIONS

4.2.1 Plots of H/P, k_v, K_o and M vs. temperature.

In Figures 4-13 through 4-23 values of H/P, k_v and K_o are plotted versus temperature for several liquids and various grades of fritted glass and porous porcelain. These plots represent only a fraction of the data taken in the tests but are in more respects representative. Comparative data on a wider variety of liquids are given in Section 3.2 of Technical Report No. 2. The data presented in Figures 4-13 through 4-23 illustrate how the different electrokinetic parameters vary with temperature. Inasmuch as the quality of the porcelain test elements in the #02 and #015 grades was poor the figures for the different grades should not be compared quantitatively on the basis of pore size. The manufacturer's figures for pore size are as follows:

Grade	Pore Radius (Microns)
015	1.4
02	.85
03	.6

The manufacturer's figures for porosity are given as between 50% and 70%, but measurements on several samples of the 03 grade indicated a porosity near 30%.

4.2.2 Data on Liquid Selection

A previous investigation, conducted in connection with the fabrication of blast gages for the Naval Ordnance Laboratory, indicated acetonitrile to be superior to other common organics for use in electrokinetic transducers. A more intensive study of the problem of liquid selection has been made. This included cross tabulations based on dipole moment, viscosity, molecular weight, dielectric constant and other properties. Rejections were made in some instances on the basis of boiling point, freezing point, etc. to obtain a list of liquids to try experimentally in electrokinetic cells. A modified rule of thumb method as developed by Fairbrother (17) and including the dielectric constant was used as a basis of rejection of electrokinetically inactive liquids.

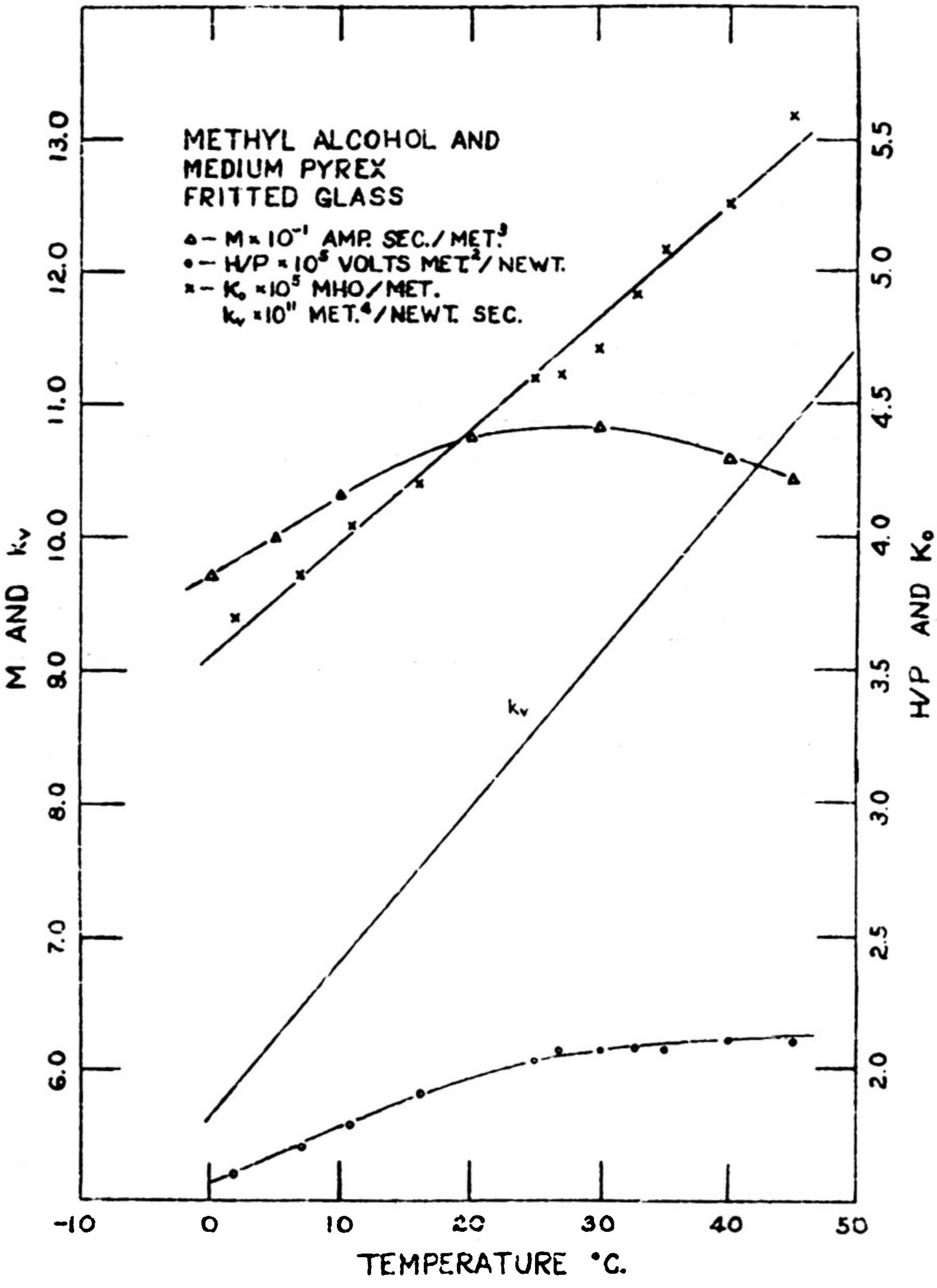

METHYL ALCOHOL AND
MEDIUM PYREX
FRITTED GLASS
△ – M × 10⁻¹ AMP. SEC./MET.³
• – H/P × 10⁸ VOLTS MET.²/NEWT.
× – K₀ × 10⁵ MHO/MET.
kᵥ × 10¹¹ MET.⁴/NEWT. SEC.
kᵥ
M AND kᵥ
H/P AND K₀
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
-10
0
10
20
30
40
50
TEMPERATURE °C.

FIGURE 4-13

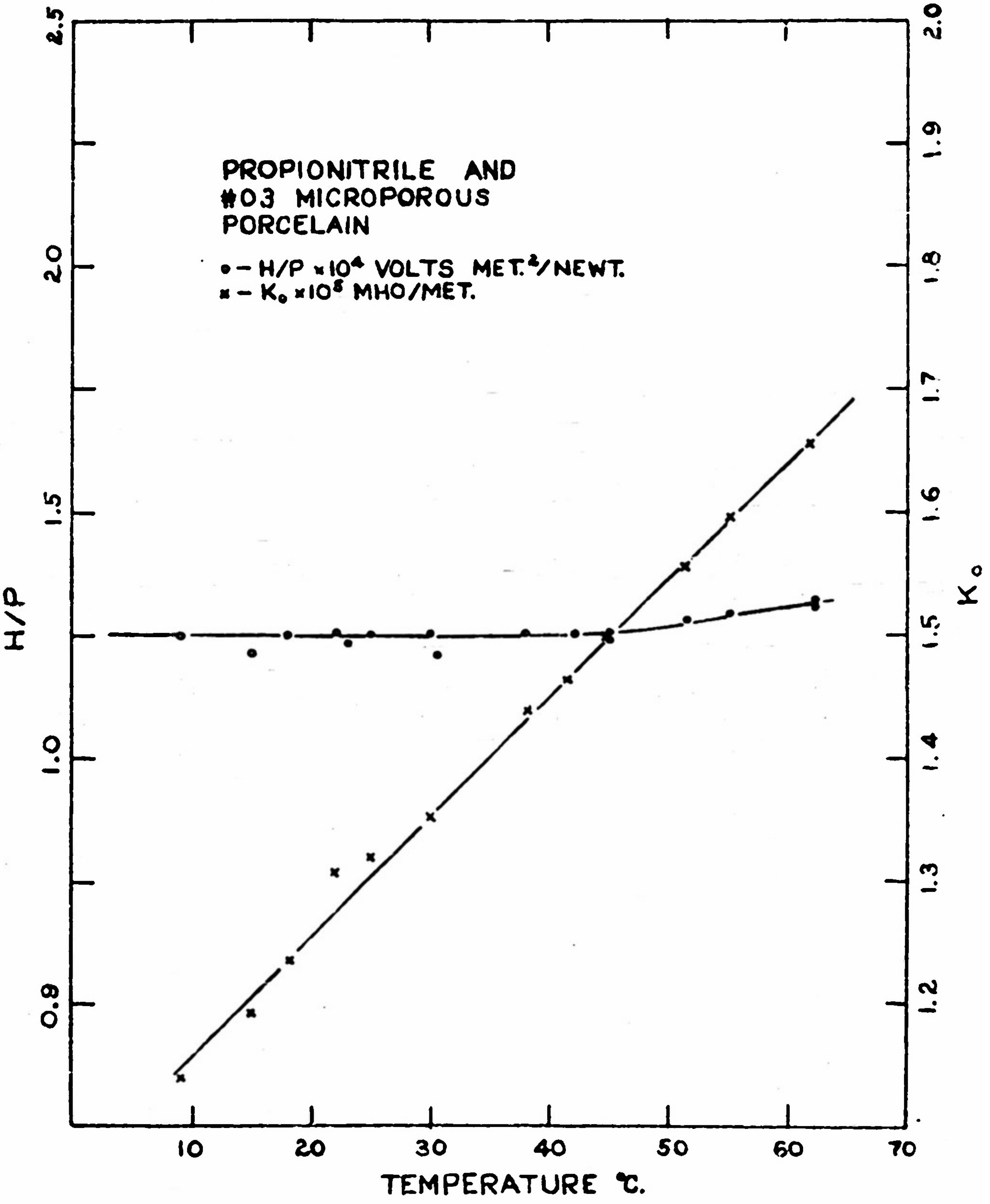
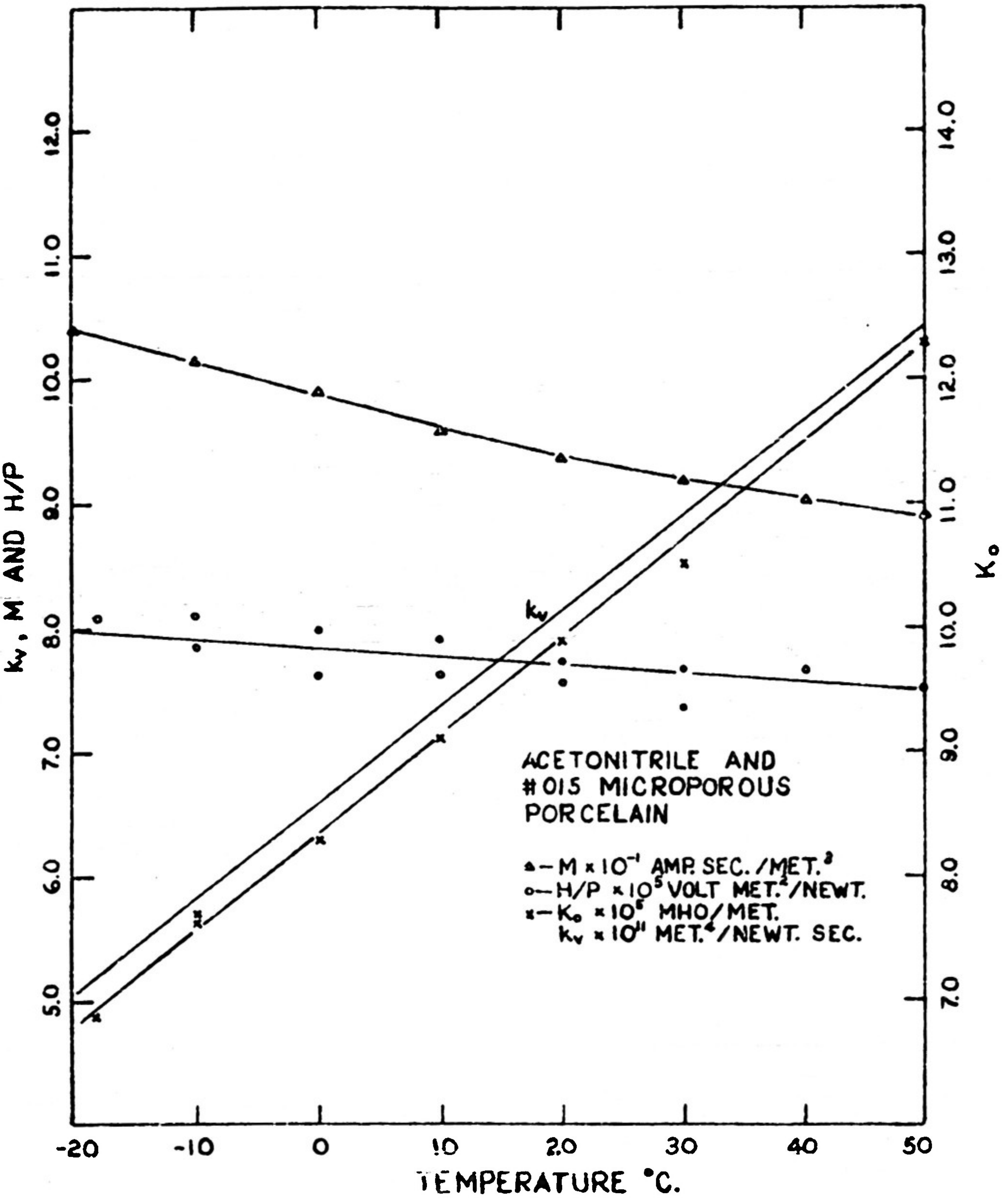

PROPIONITRILE AND #03 MICROPOROUS PORCELAIN
● – H/P × 10⁴ VOLTS MET.²/NEWT.
× – K₀ × 10⁸ MHO/MET.
H/P
K₀
2.5
2.0
1.5
1.0
0.9
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
10
20
30
40
50
60
70
TEMPERATURE °C.

FIGURE 4-14



12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
Kv, M AND H/P
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
Ko
kv
ACETONITRILE AND
#015 MICROPOROUS
PORCELAIN
▵ – M × 10⁻¹ AMP. SEC. /MET.³
○ – H/P × 10⁵ VOLT MET.²/NEWT.
× – Ko × 10⁶ MHO/MET.
kv × 10¹¹ MET.⁴/NEWT. SEC.
-20
-10
0
10
20
30
40
50
TEMPERATURE °C.

FIGURE 4-15

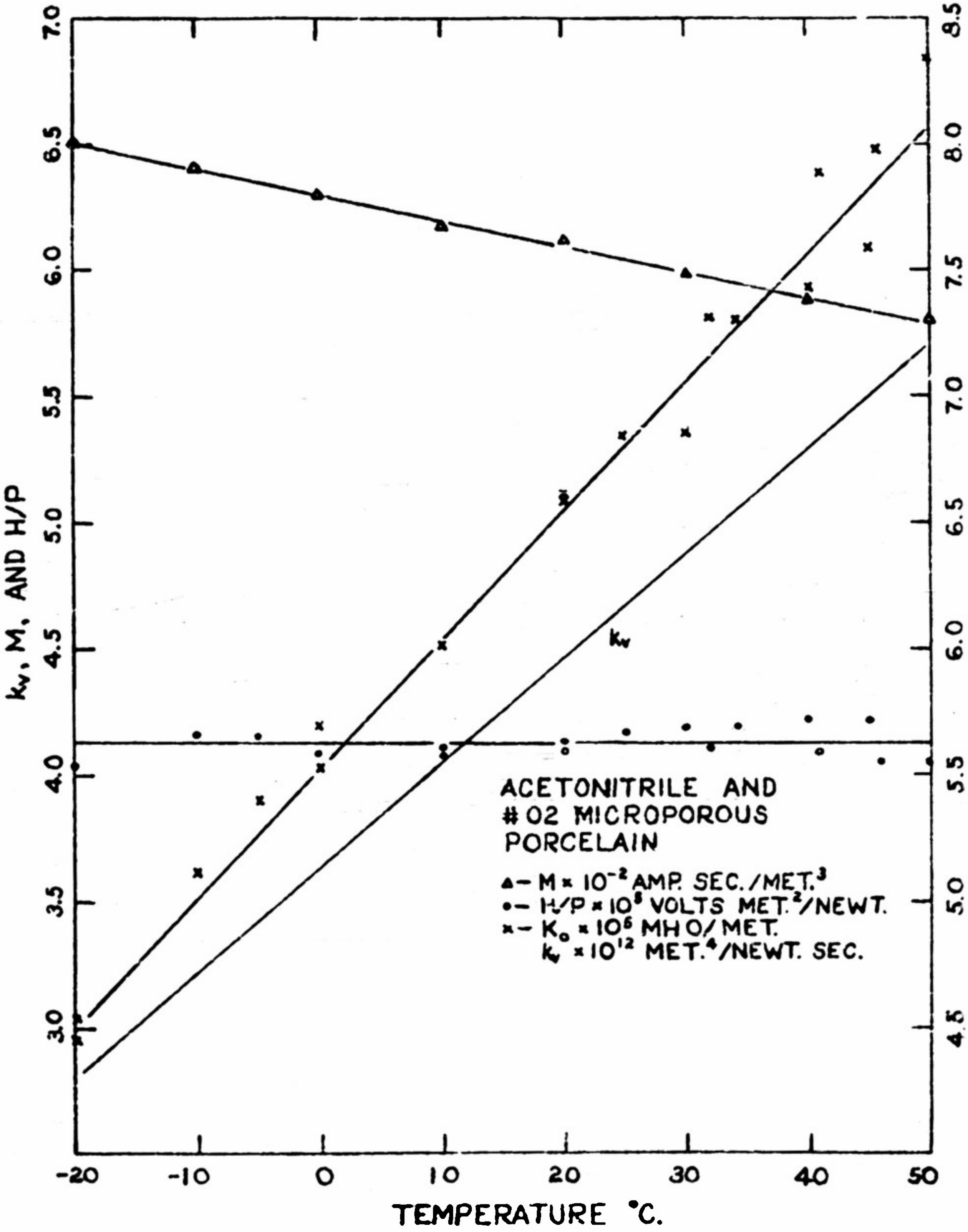

kv, M, AND H/P
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
Ko
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
kv
-20
-10
0
10
20
30
40
50
TEMPERATURE °C.
ACETONITRILE AND
#02 MICROPOROUS
PORCELAIN
▲ – M × 10⁻² AMP. SEC./MET.³
● – H/P × 10⁸ VOLTS MET.²/NEWT.
× – Ko × 10⁶ MHO/MET.
kv × 10¹² MET.⁴/NEWT. SEC.

FIGURE 4-16

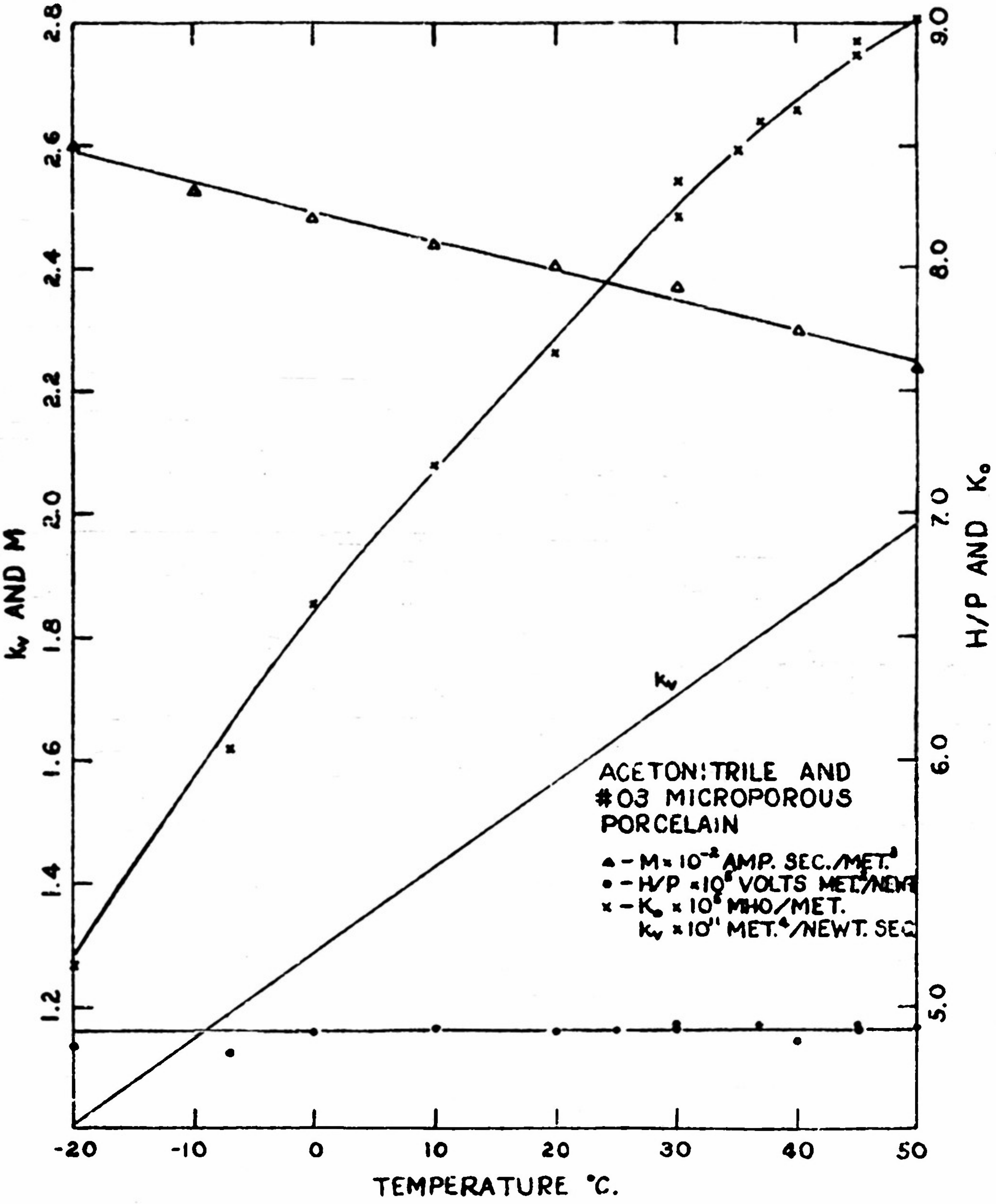

2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
k_v AND M
9.0
8.0
7.0
6.0
5.0
H/P AND K_o
-20
-10
0
10
20
30
40
50
TEMPERATURE °C.
k_v
ACETONITRILE AND
#03 MICROPOROUS
PORCELAIN
▲ - M × 10^{-2} AMP. SEC./MET.^{3}
● - H/P × 10^{6} VOLTS MET.^{2}/NEW
× - K_o × 10^{6} MHO/MET.
k_v × 10^{11} MET.^{4}/NEWT. SEC

FIGURE 4-17

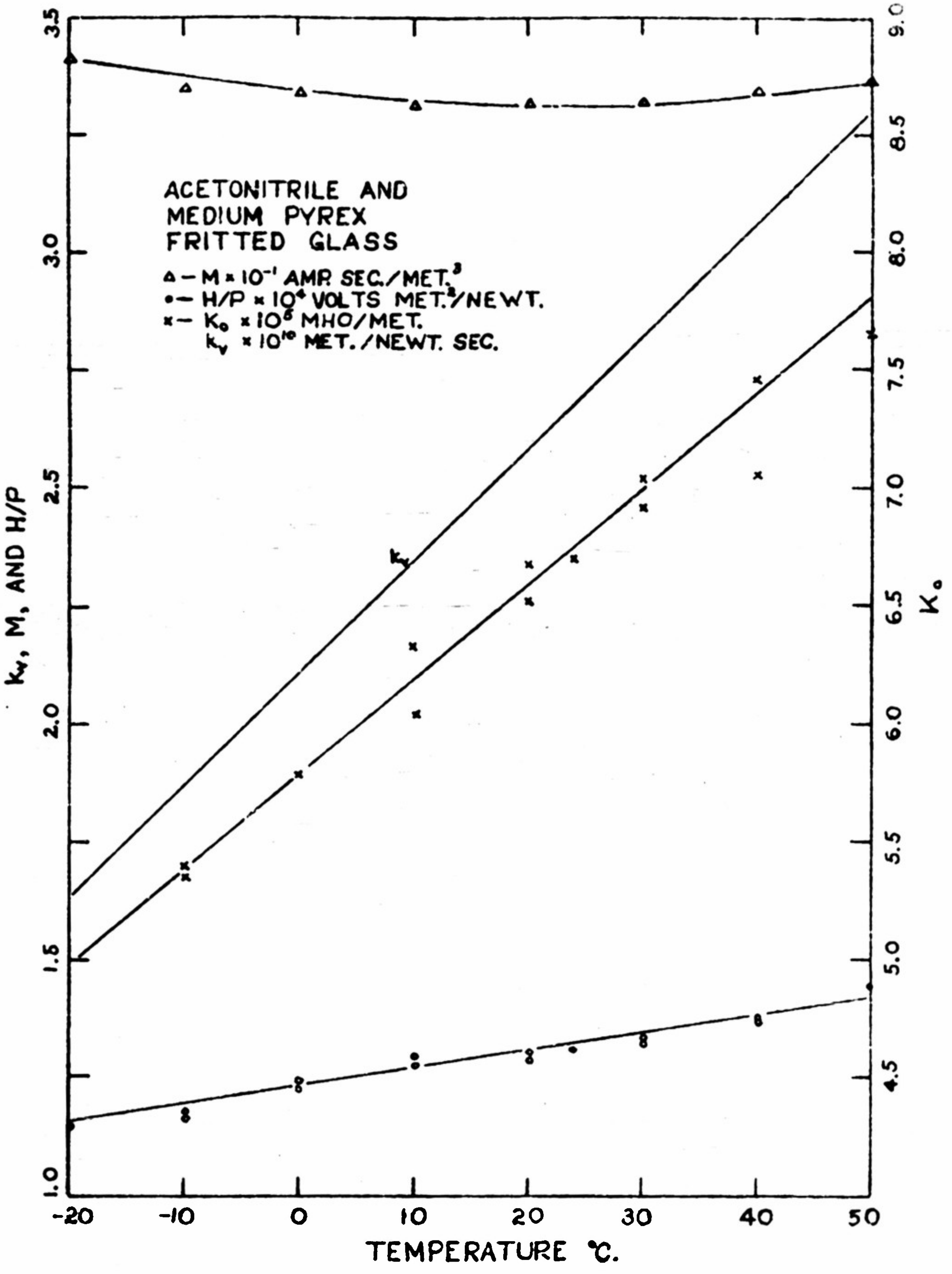

ACETONITRILE AND
MEDIUM PYREX
FRITTED GLASS
△ – M × 10⁻¹ AMP. SEC./MET.³
● – H/P × 10⁴ VOLTS MET.³/NEWT.
× – K₀ × 10⁶ MHO/MET.
k_v × 10¹⁰ MET./NEWT. SEC.
k_v
k_v, M, AND H/P
1.0
1.5
2.0
2.5
3.0
3.5
K₀
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
-20
-10
0
10
20
30
40
50
TEMPERATURE °C.

FIGURE 4-18

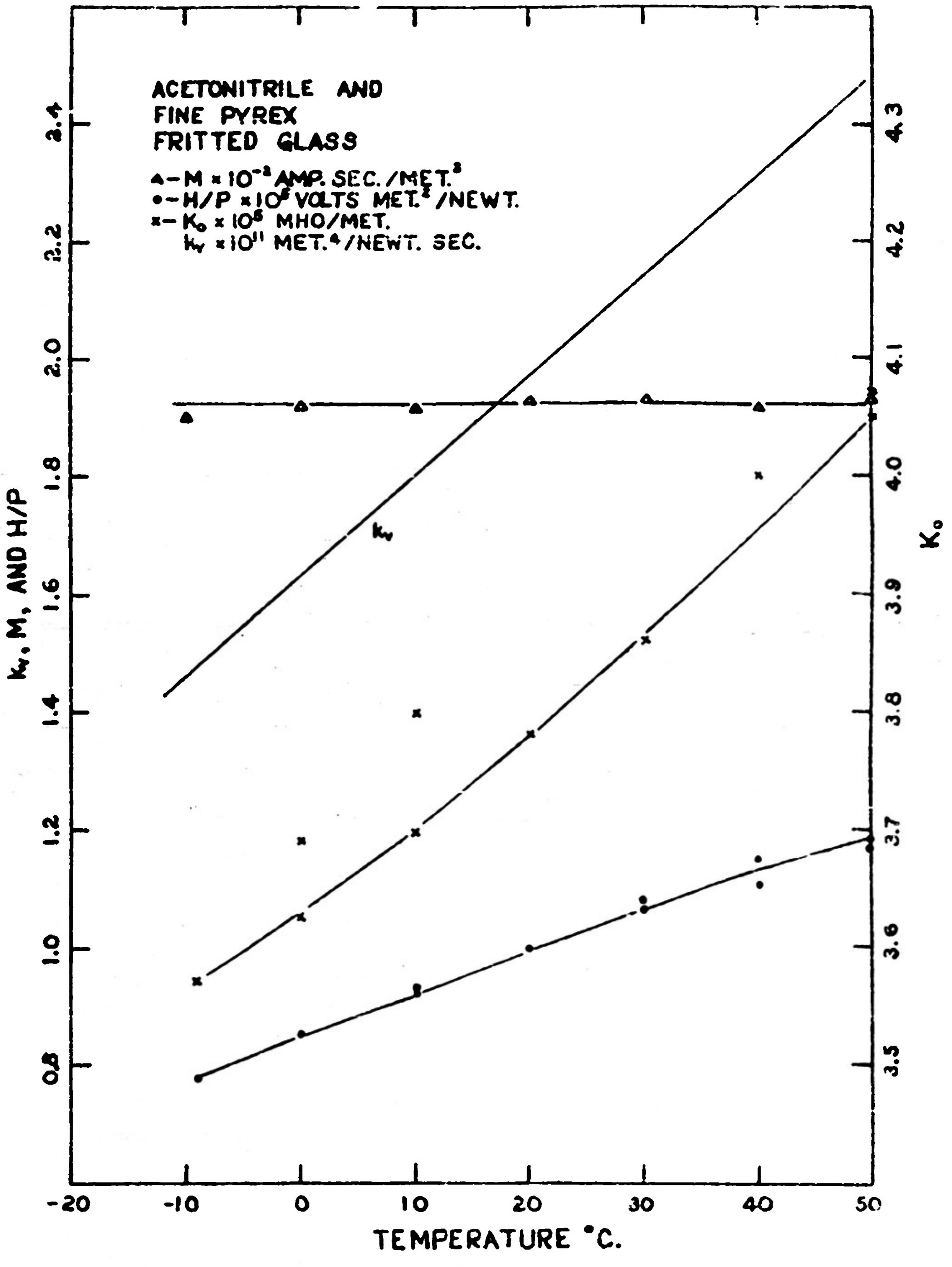

ACETONITRILE AND
FINE PYREX
FRITTED GLASS
▲–M × 10⁻² AMP. SEC./MET.²
●–H/P × 10⁵ VOLTS MET.²/NEWT.
×– K₀ × 10⁶ MHO/MET.
kᵥ × 10¹¹ MET.⁴/NEWT. SEC.
kᵥ
kᵥ, M, AND H/P
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
K₀
3.5
3.6
3.7
3.8
3.9
4.0
4.1
4.2
4.3
-20
-10
0
10
20
30
40
50
TEMPERATURE °C.

FIGURE 4-19

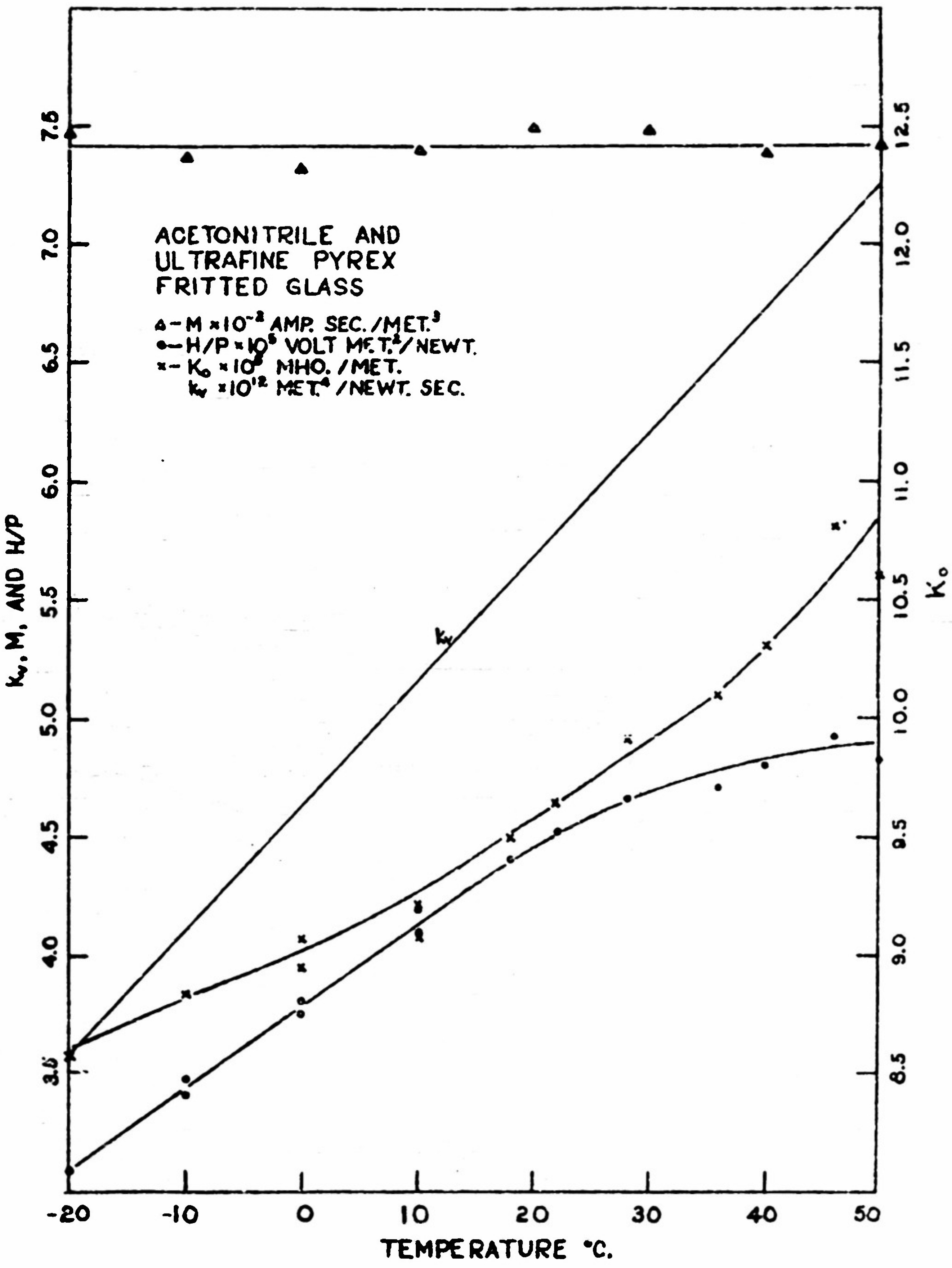

ACETONITRILE AND
ULTRAFINE PYREX
FRITTED GLASS
▲ – M × 10⁻² AMP. SEC./MET.³
● – H/P × 10⁵ VOLT MET.²/NEWT.
× – K₀ × 10³ MHO./MET.
kᵥ × 10¹² MET.⁴/NEWT. SEC.
kᵥ
kᵥ, M, AND H/P
K₀
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
-20
-10
0
10
20
30
40
50
TEMPERATURE °C.

FIGURE 4-20

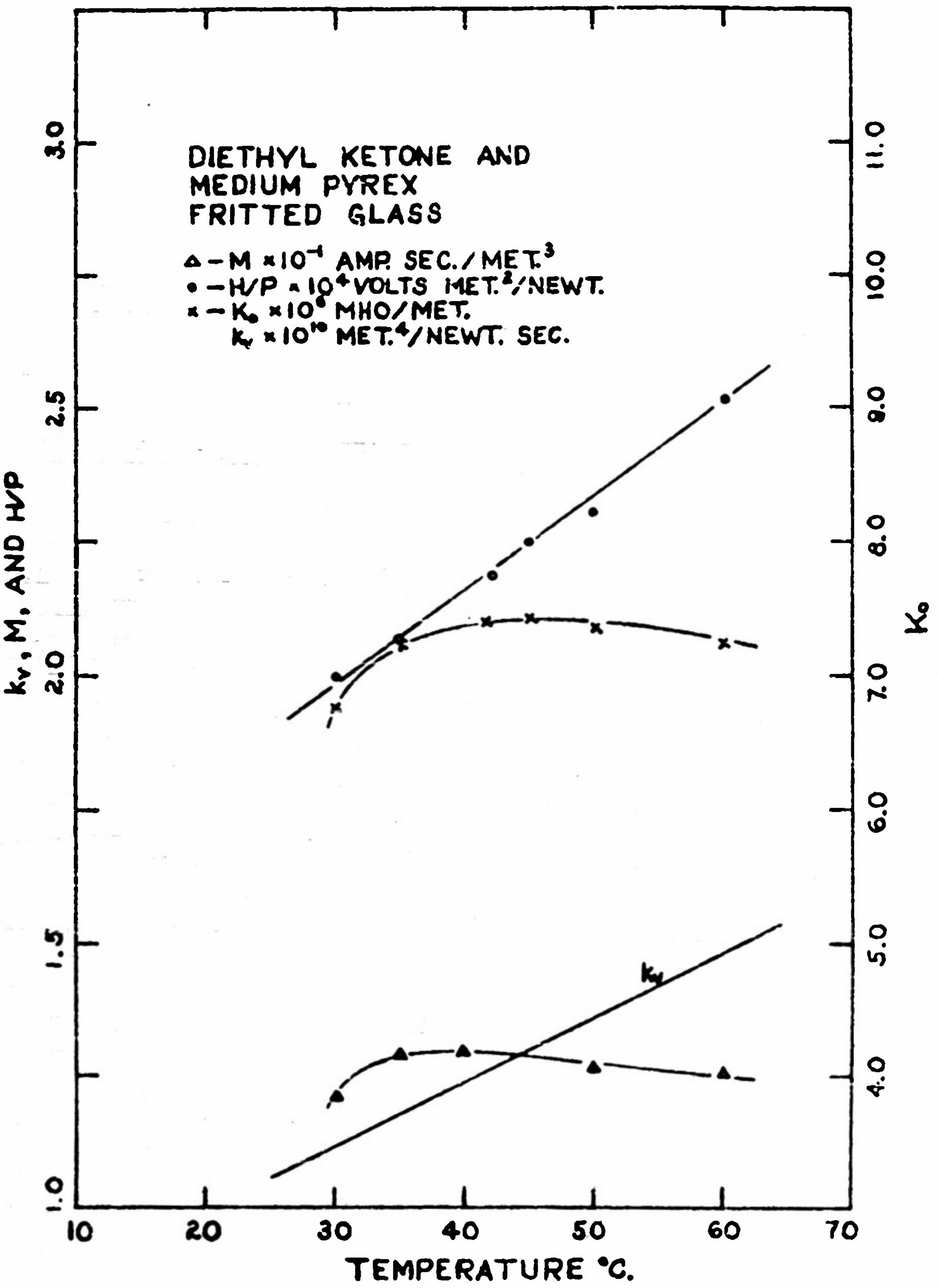

DIETHYL KETONE AND
MEDIUM PYREX
FRITTED GLASS
▲ – M × 10^-4 AMP. SEC./MET.^3
● – H/P × 10^4 VOLTS MET.^2/NEWT.
× – K_o × 10^6 MHO/MET.
k_v × 10^10 MET.^4/NEWT. SEC.
k_v
k_v, M, AND H/P
1.0
1.5
2.0
2.5
3.0
K_o
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
10
20
30
40
50
60
70
TEMPERATURE °C.

FIGURE 4-21

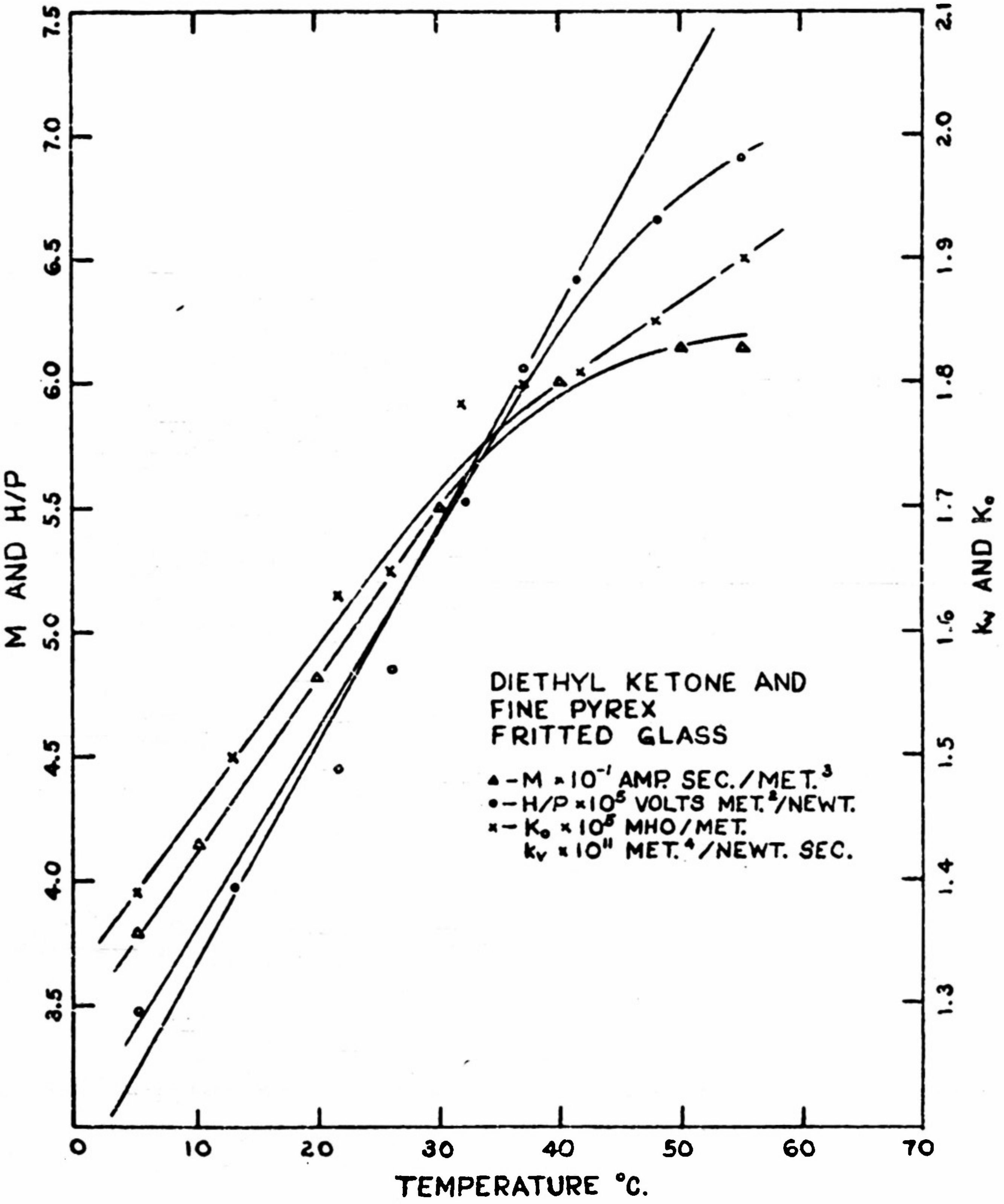

M AND H/P
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
k_v AND K_o
0
10
20
30
40
50
60
70
TEMPERATURE °C.
DIETHYL KETONE AND
FINE PYREX
FRITTED GLASS
▲ – M × 10^{-1} AMP. SEC./MET.^{3}
● – H/P × 10^5 VOLTS MET.^{2}/NEWT.
× – K_o × 10^5 MHO/MET.
k_v × 10^{11} MET.^{4}/NEWT. SEC.

FIGURE 4-22

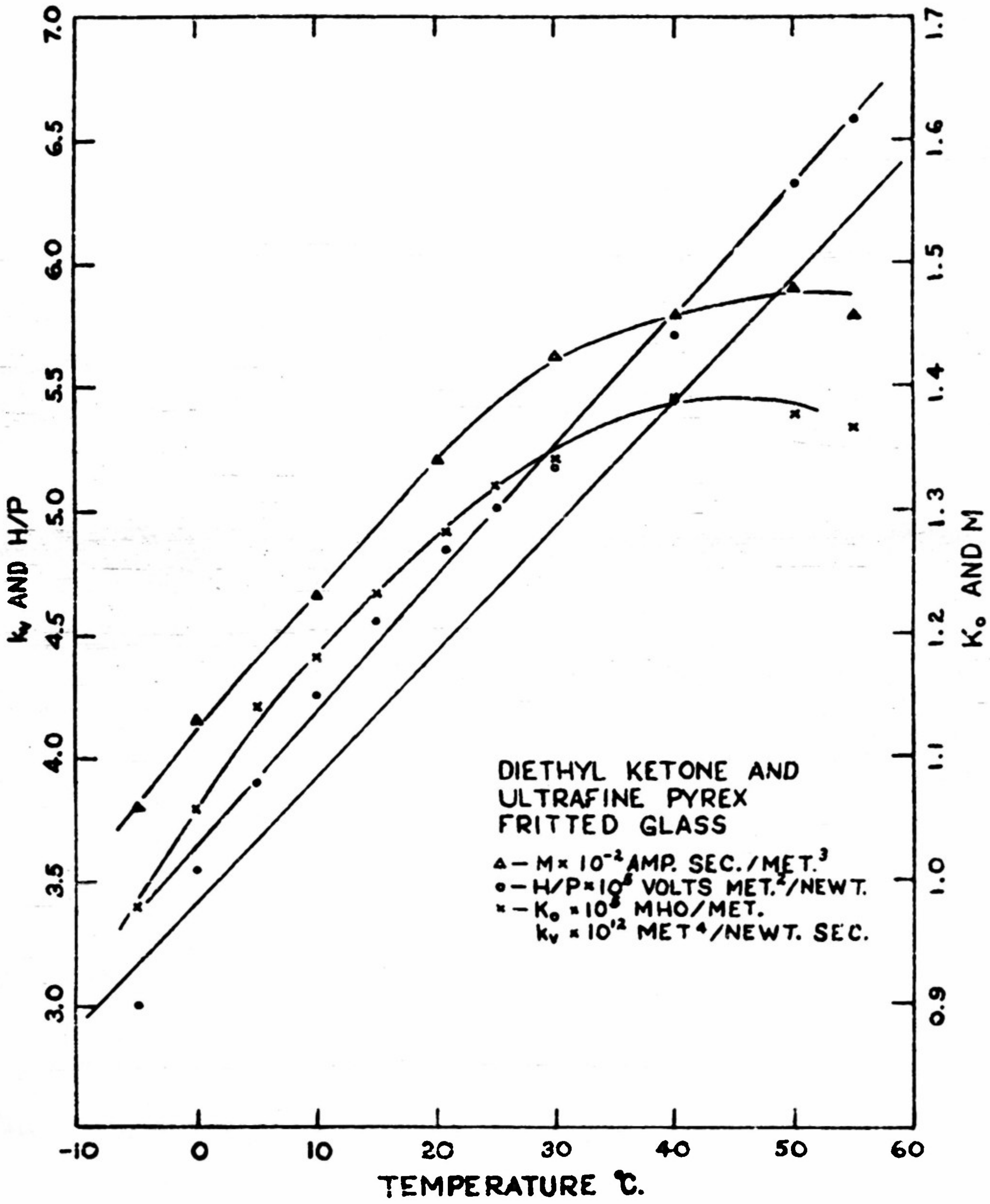

7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
k_v AND H/P
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
K_o AND M
-10
0
10
20
30
40
50
60
TEMPERATURE °C.
DIETHYL KETONE AND
ULTRAFINE PYREX
FRITTED GLASS
△ – M × 10^{-2} AMP. SEC./MET.^{3}
○ – H/P × 10^5 VOLTS MET.^{2}/NEWT.
× – K_o × 10^8 MHO/MET.
k_v × 10^{12} MET^4/NEWT. SEC.

FIGURE 4-23

The degree of validity of this method of selection is illustrated in Figures 4-24 and 4-25 for different solid materials. In general it shows that, (with the exception of acetone), any liquid which has a poor "figure of merit" is likely to be inefficient in a transducer. A very large number and variety of compounds were considered. The relatively simple, low molecular weight compounds are in general superior. Acetonitrile has more advantageous properties than any tested. These are tabulated in Appendix B.

4.2.3 Comparison of Porous Solids.

The number of very pure and inert porous solid materials which may be procured in a microporous state with a high ratio of porosity to permeability is very limited. Although limited experiments were conducted on other solids such as sulfur, alundum, and powdered resins, most data were obtained using fritted glass or porous porcelain. For the two types of solids, it is interesting to compare the changes of relative cell conductivity and relative liquid viscosity with temperature. Ideally if ion mobility were to vary inversely with viscosity one would expect the relative inverse conductivity curves in Figure 26 to coincide with the relative viscosity curve. It may be noted that for the medium grade Pyrex material with the largest pore size, the ideal relation holds more closely. All substantial departures are believed due to surface conductance effects in the pores. A similar set of curves for the porcelains in Fig. 4-27 shows the effects of surface conductance to be far less pronounced. This difference lacks a simple theoretical explanation but accounts for the superiority of porcelain to glass with respect to the effect of temperature on sensitivity.

4.2.4 Liquid Mixtures.

Several tests were conducted on mixtures of different liquids to determine the effects of mixing pure compounds on electrokinetic properties. In each instance the electric moments were of the same sign, i.e. the inner layer being positively charged. As was expected the current-pressure sensitivity of the mixtures varied linearly with the percentage of each liquid. This is illustrated in Fig. 4-28. The numerical sensitivity values are only significant in a relative sense.

4.2.5 Addition Agents and Cleaning Methods.

It would be expected that certain addition agents added to the liquid might strongly affect phenomena occuring at the liquid-solid interface. They might also affect the conductivity, the temperature co-efficient and the rate at which stability is approached. In some instances variations in performance between cells, some being improvements, could only be accounted for in terms of unknown contaminants. Different addition agents were, therefore, added with the general results noted in the following table.

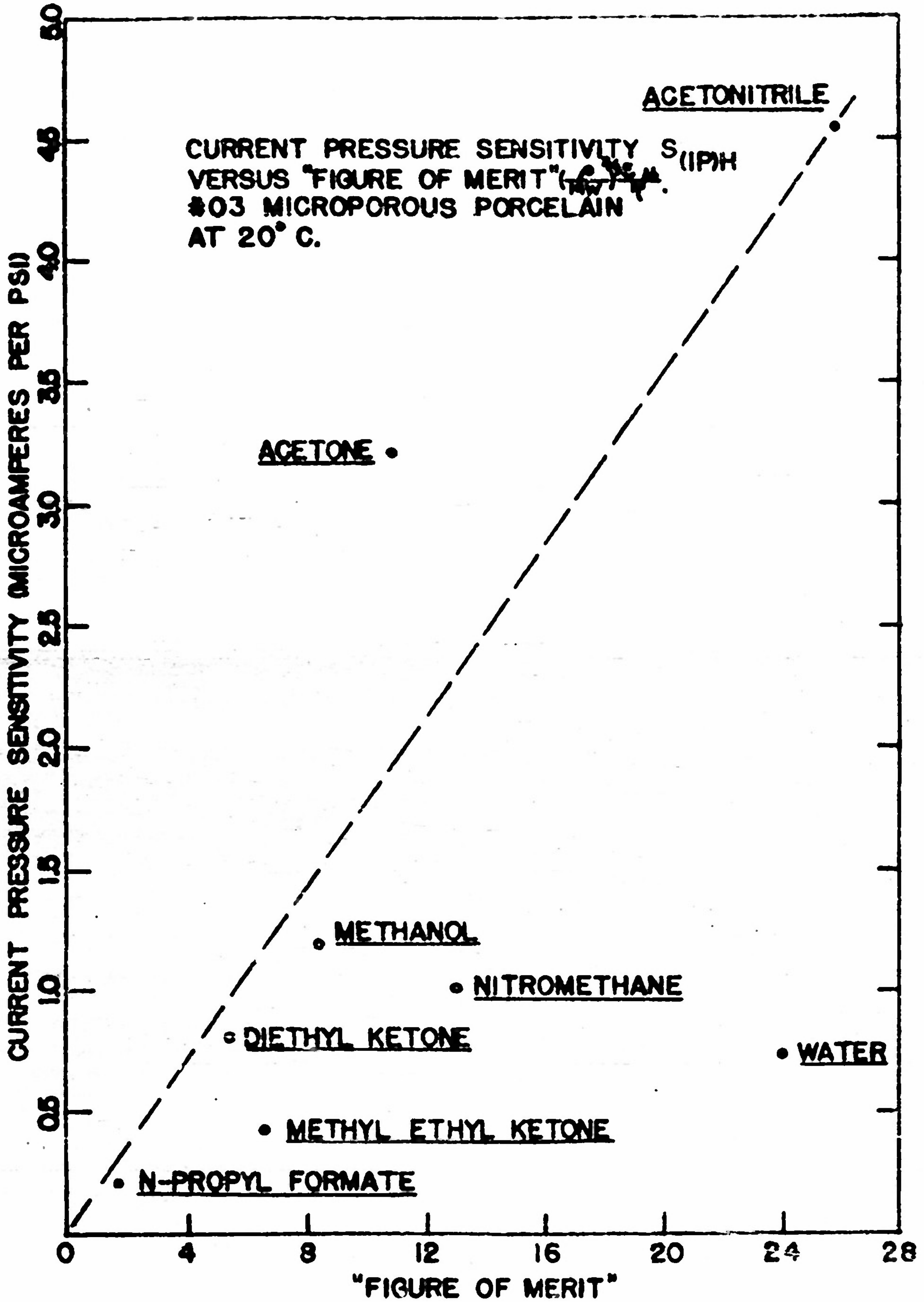

CURRENT PRESSURE SENSITIVITY S(IP)H
VERSUS "FIGURE OF MERIT" [illegible].
#03 MICROPOROUS PORCELAIN
AT 20° C.
ACETONITRILE
ACETONE
METHANOL
NITROMETHANE
DIETHYL KETONE
WATER
METHYL ETHYL KETONE
N-PROPYL FORMATE
CURRENT PRESSURE SENSITIVITY (MICROAMPERES PER PSI)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
4
8
12
16
20
24
28
"FIGURE OF MERIT"

FIGURE 4-24

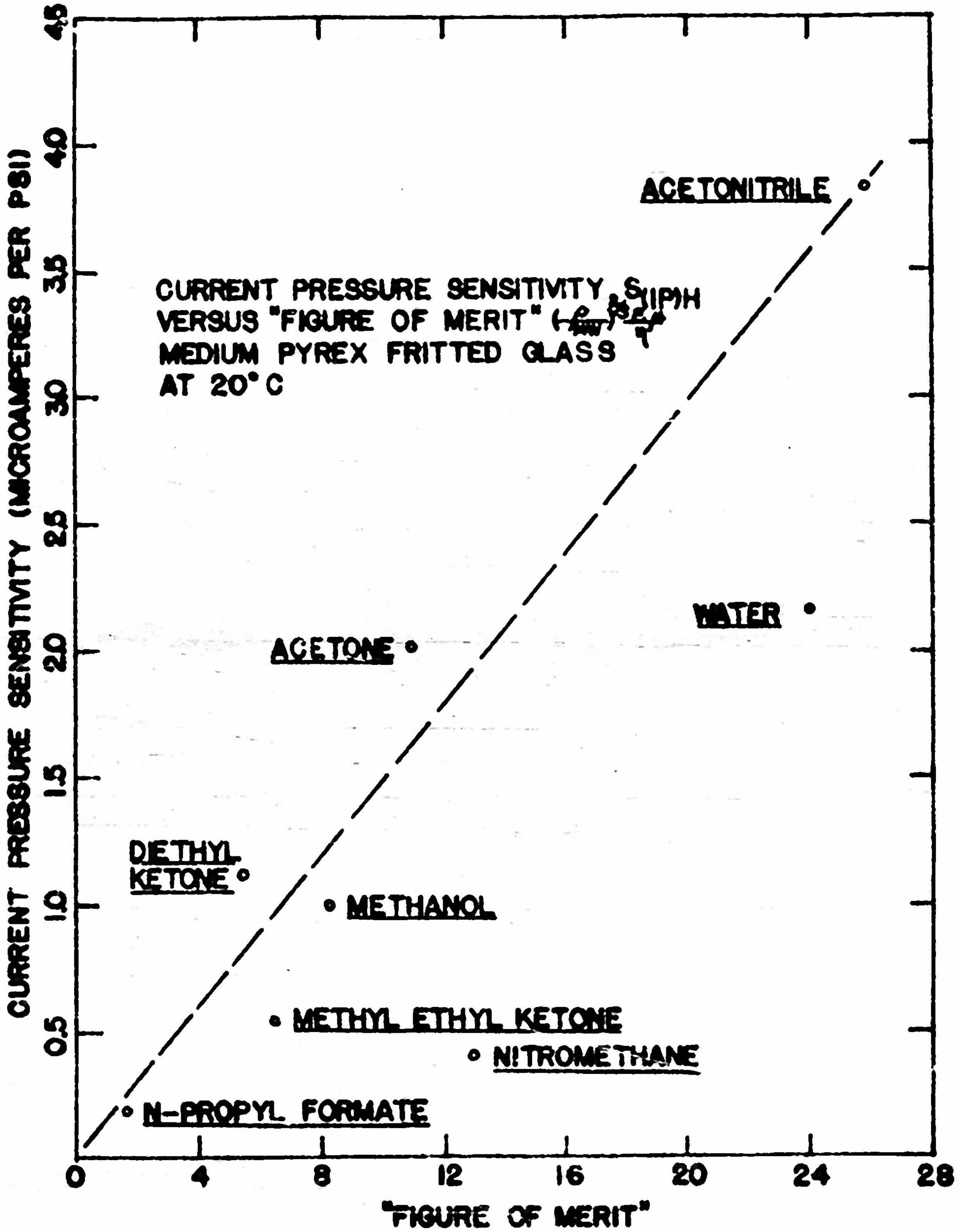

CURRENT PRESSURE SENSITIVITY, $S_{(IP)H}$
VERSUS "FIGURE OF MERIT" $(\frac{\rho}{MW})^{.3}\frac{\epsilon^{4}}{\eta}$
MEDIUM PYREX FRITTED GLASS
AT 20° C
ACETONITRILE
WATER
ACETONE
DIETHYL KETONE
METHANOL
METHYL ETHYL KETONE
NITROMETHANE
N-PROPYL FORMATE
CURRENT PRESSURE SENSITIVITY (MICROAMPERES PER PSI)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
0
4
8
12
16
20
24
28
"FIGURE OF MERIT"

FIGURE 4-25

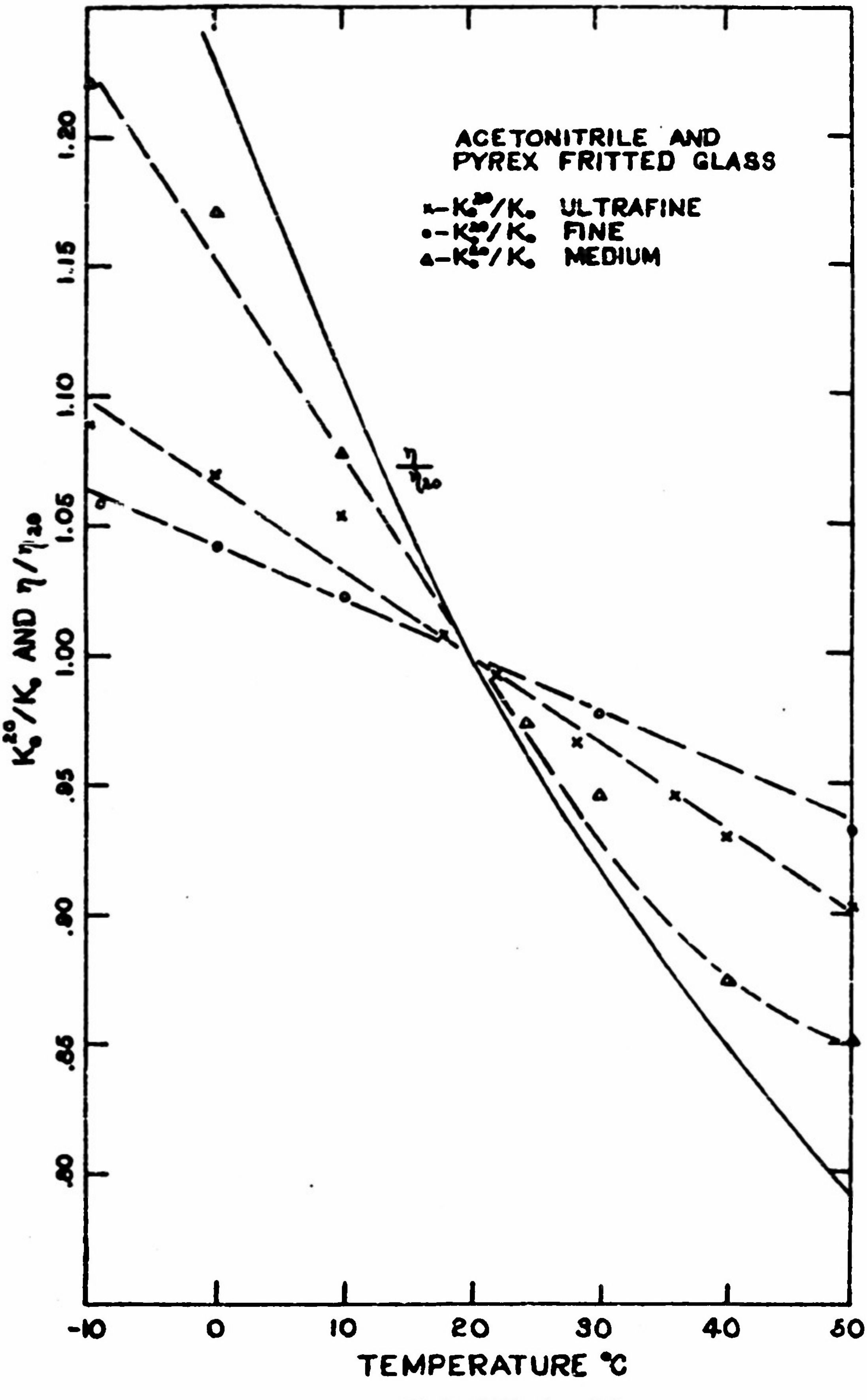

ACETONITRILE AND
PYREX FRITTED GLASS
×–K_o^{20}/K_o ULTRAFINE
•–K_o^{20}/K_o FINE
△–K_o^{20}/K_o MEDIUM
η/η_{20}
K_o^{20}/K_o AND η/η_{20}
1.20
1.15
1.10
1.05
1.00
.95
.90
.85
.80
-10
0
10
20
30
40
50
TEMPERATURE °C

FIGURE 4-26

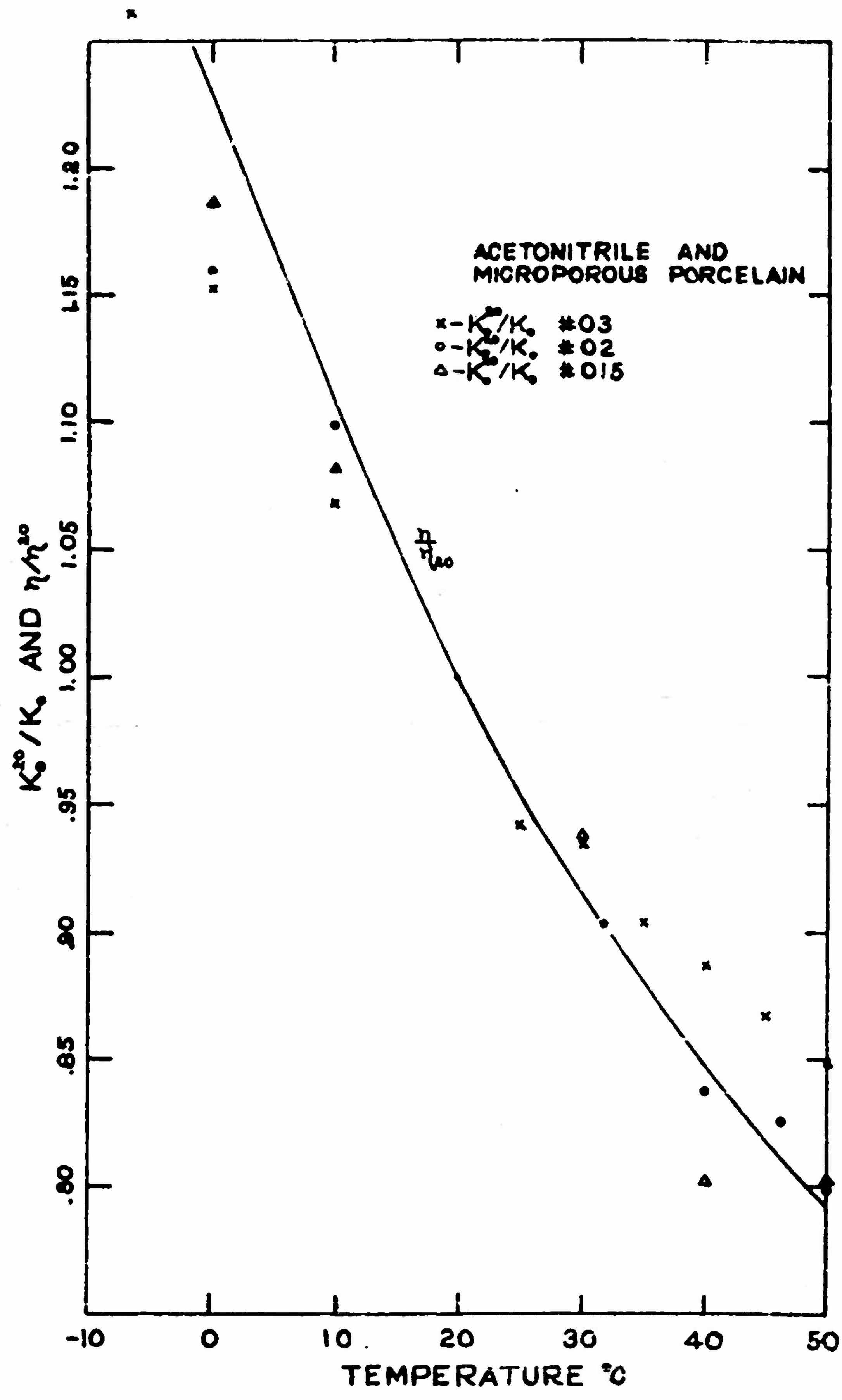
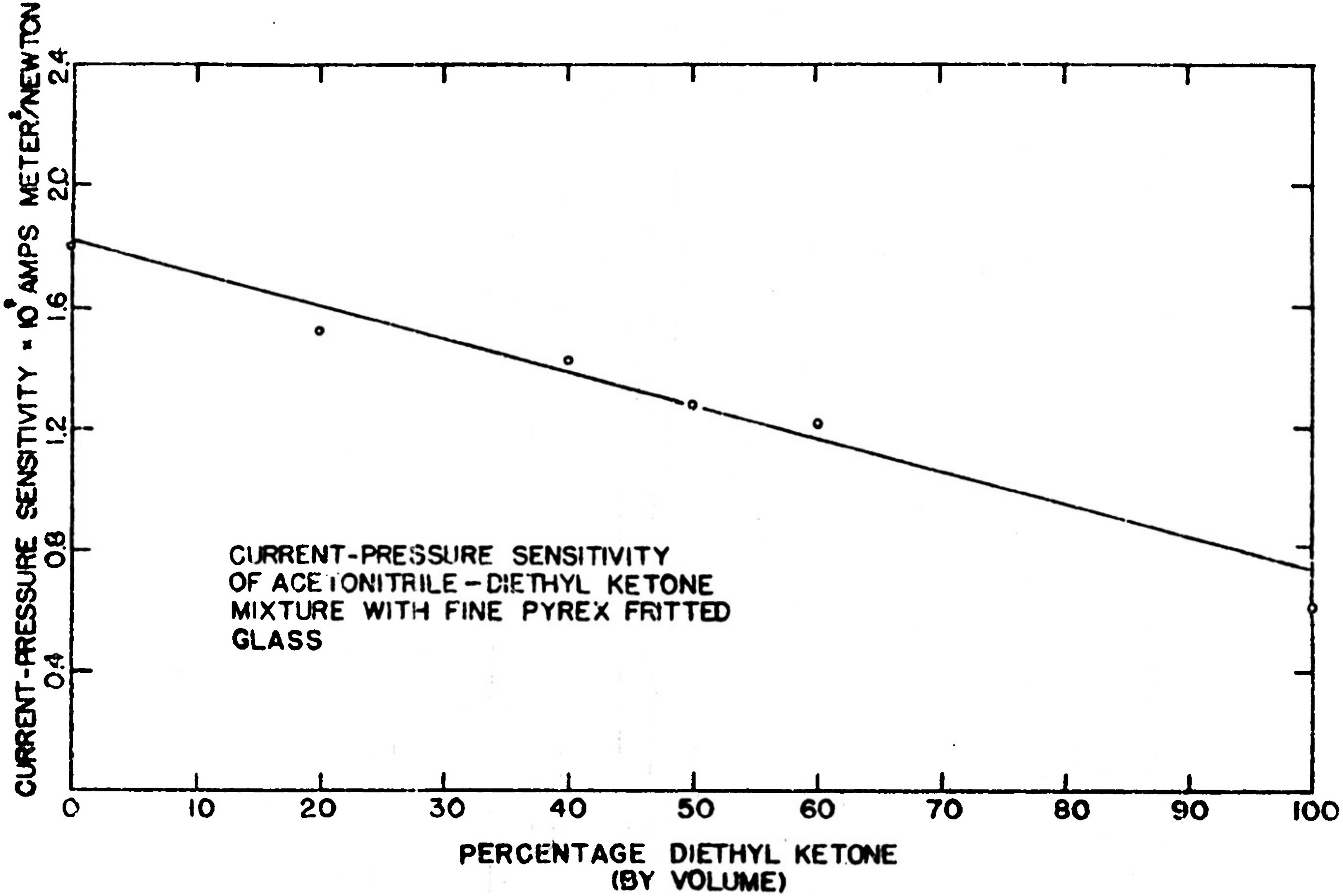
ACETONITRILE AND MICROPOROUS PORCELAIN
×-K₀²⁰/K₀ #03
○-K₀²⁰/K₀ #02
△-K₀²⁰/K₀ #015
η/η₂₀
K₀²⁰/K₀ AND η/η²⁰
1.20
1.15
1.10
1.05
1.00
.95
.90
.85
.80
-10
0
10
20
30
40
50
TEMPERATURE °C

FIGURE 4-27



CURRENT-PRESSURE SENSITIVITY OF ACETONITRILE-DIETHYL KETONE MIXTURE WITH FINE PYREX FRITTED GLASS

FIGURE 4-28

Tetraethyl ammonium bromide was tried in various concentrations in highly polished acetonitrile with the conductivity ranging as high as 5×10^{-6} mhos/cm. It was chosen as a compound with large molecular dimensions least likely to have its ions affected by solvation and likely to produce a small temperature coefficient. The results were initially good, but with a large positive coefficient developing after several days, possibly because of a chemical reaction with the aluminum electrodes. The results were inconclusive.

Other addition agents were tried for various reasons including glycine, di-sodium versenate, di-n-butylamine, sodium benzene sulfonate, sodium sulfanilate, thio-urea, and various detergents with no outstanding effects noted.

Various cleaning methods for the porous discs were employed which included strong bases, strong acids with oxidizing agents, firing to burn out organic traces, etc. The past surface history of the porous plug has a pronounced effect on what may be expected of it once it is sealed in a cell. A method of permanent "activation" found very succesful was to stream a 2% solution of hydrofluoric acid through the plug followed by a flushing with water and a volatile solvent such as acetonitrile or acetone. The plug may then be thoroughly dried by firing or heating to 300° to 400°F.

4.2.6 Coating Agents:

Various materials, some selected for their dielectric properties, were deposited in the pores of porcelain plugs to attempt to increase the electric moment to a value greater than that for porcelain. These included dyes, shellacs, polystyrene, sulfur, and various exchange resins. No significant results were obtained in the short time alloted to such experimentation. It was noted, however, that anion resin coatings reversed the sign of the electric moment and streaming potential.

4.3 Discussion of Results:

In all of the curves included in Figures 4-13 through 4-21 it may be noted that the variations of the sensitivity and coupling constant M are small in comparison with K_e and k_v as functions of temperature. In all figures pertaining to acetonitrile the variation of M is either quite small or is negative. Recalling that:

$$M = \frac{\beta F}{B}$$

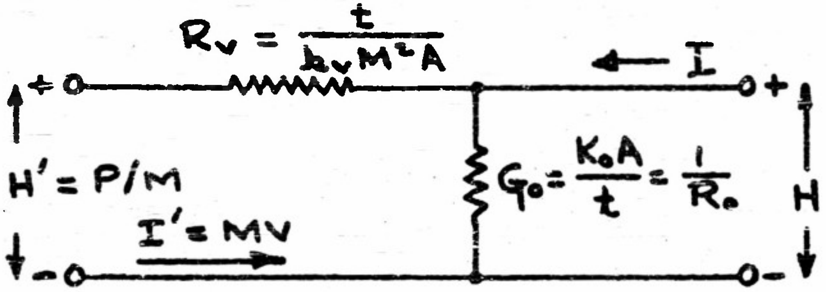
where F and B are temperature independent constants of the solid, it is evident that "μ", the electric moment, has a relatively small coefficient, substantially smaller than "ζ" or "ε", the zeta potential and dielectric constant of the classical theory. Since the value of the zeta potential may only be inferred by arbitrarily assuming the value of the dielectric constant in the polarized double layer to be the same as that in the bulk of the liquid, it is suggested that the zeta potential concept commonly appearing in the literature is an artificial concept and should be abandoned. (The porosity factor "F" is subject to measurement by filling a plug with a liquid of a low conductivity and measuring its resistance.) The suggestion that the zeta potential concept be abandoned has been made several times and for the same reasons but it continues to appear. By using the experimentally determined values for B, F, M, K_0, K_L, theory and experimental results may be readily correlated. M was used rather than μ and F in the work on this project as little control could be exercised over the properties of the porous materials tested. The other approach would only be worthwhile when accurately graded elements were available.

5. EQUIVALENT CIRCUITS

Equivalent circuits were discussed and derived in Sections 2.4 and 3.5 of Technical Report No. 2. Because of the variety of mechanical, acoustic and electrical sources and leads possible no attempt will be made here to derive a variety of equivalent circuits. Impedances may be transferred and voltages, pressures, etc. converted to equivalents by the use of the lectromechanical coupling constant "   ".

An example of how the data given in the MKS system of units may be applied to the electrokinetic element, omitting the frequency dependent parameters is given below.

For steady flow the equivalent circuit of a porous plug element is as shown:



In the above circuit M is the electromechanical coupling constant, H' is the voltage equivalent of pressure, and I' is the current equivalent of volume velocity. The above circuit is applicable to the conversion of energy in either direction. In its application, however, the following factors must be kept in mind:

1. Electrode polarization potentials for steady flow or at low frequencies when I is appreciable.

2. Changes in liquid conductivity due to electrolytic polishing for steady values of H.

3. Changes in viscosity and conductivity due to heating for large values of I.

None of the above factors is important when the transducer is used open circuit as a receiver, and polarization effects are only important at low frequencies when the load is comparable to R_o.

The equations describing the above network are:

$$I = I' + K_o \frac{A}{t} H$$

$$H' = -H + \frac{t}{k_v M^2 A} I'$$

If I' is replaced by MV and the second equation is multiplied by M, with MH' being replaced by P, it will be seen that the relations are identical with those developed in section 3.

As an illustrative example from data in Figure 4-19 at 20°C:

$H/P = 4.9 \times 10^{-5}$ volts/newton/meter^2

$k_v = 1.56 \times 10^{-11}$ meters^4/newton second

$K_o = 7.7 \times 10^{-5}$ mhos/meter

$M = 240$ Amp. Sec./meter^2

Assume now a porous disc 2" O.D. x 1/8":

$t = .00318$ meters
$A = .002$ meters

Then:

$$R_o = 1/Go = \frac{t}{K_o A} = 20{,}600 \text{ ohms}$$

$$R_v = \frac{t}{k_v M^2 A} = 1.76 \text{ meghohms}$$

For an applied pressure P = MH' the voltage H is therefore:

$$H = H' \frac{20{,}600}{20{,}600 + 1{,}760{,}000}$$

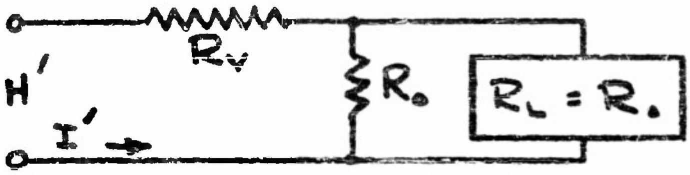
$$H = -\frac{P}{M}(.0115)$$

$$\frac{H}{P} = -\frac{.015}{240} = -4.83 \times 10^{-5} \text{ volts/Nets./Met.}^2$$

$$\frac{H}{P} = -332 \text{ mv/psi}$$

A departure of about 1.5% from the value of H/P taken from the plot is a result of the approximations in smoothing the curves between the plotted points. If the plotted points are used the values should check closely since the values for M were derived from H/P, K_o, and k_v.

It is possible in the above example to approximate the efficiency of transferring energy into a matched load:



The input energy is approximately given by:

$$I'H' \cong I'^2 R_v$$

And the portion of energy delivered to the load is:

$$\frac{1}{2} I'^2 \left(\frac{1}{2} R_o\right)$$

Therefore, the efficiency is:

$$E_{ff.} \cong \frac{1}{4} \frac{R_o}{R_v} = 0.3\%$$

6. CONCLUSIONS AND SUGGESTIONS FOR FUTURE INVESTIGATIONS

The results obtained thus far indicate that acetonitrile with microporous porcelain (with pore radii of about 0.6 microns), forms a very satisfactory transducing combination with voltage sensitivities up to 500 mv/psi or -103 DB. Higher sensitivities may be achieved at a sacrifice of greater resistance and a greater temperature coefficient by the addition of traces of certain non-ionic detergents.

The electric moment with many combinations undergoes only small changes with temperature. It is a fundamental electrokinetic parameter unique to a given liquid solid combination and should be used rather than the zeta potential in describing the characteristics of the double-layer. Relations expressing the relation of the electric moment, the porosity, and the permeability to the electromechanical coupling constant have been derived and suggest future studies of the origin of electrokinetic phenomena.

A discussion of applications was given in Technical Report No. 2. The outlined suggestions which follow relate to possible basic investigations suggested by the work done in the past on this project.

(1.) A study of the effects of porosity and permeability and their ratio (using carefully graded materials) on the electrokinetic parameters, M, $\sqrt{\bar{S}}$, and $\bar{K}_e$.

(2.) A study of the electric moments of selected liquids with a variety of solid materials under carefully controlled conditions to identify the properties of the solids most important in affecting the magnitude of the electric moment.

(3.) A study of the action of detergents on the double-layer. (Such a study should not only throw light on the origin of the phenomena but also on the action of detergents.)

(4.) A detailed study of the nature of polarization of aluminum or tin electrodes in acetonitrile and methods of reducing polarization by the use of addition agents, coatings or methods of increasing the effective area.

(5.) A study of electrokinetic activity at high temperatures and hydrostatic pressures, well beyond the sea level boiling range.

7. REFERENCES

1. Abramson, H. A., "Electrokinetic Phenomena", ACS Monograph Series No. 66, The Chemical Catalog Publishing Co., Inc., New York 1934.

2. Reuss, F. F., "memoirs de la Societe Imperiale des Naturalistes de Moskou", 2,327 (1809).

3. Quincke, G., "Pogg. Ann.", 107, 1 (1859).

4. Helmholtz, H., "Wied. Ann.", 7,337 (1879).

5. Smoluchowski, M., "Krak. Anz.", 1903, p. 182.

6. Gouy, G., "J. Phys.", 9,457 (1910).

7. Briggs, D. R., "J. Physical Chem.", 32,641 (1928).

8. Schlumberger, C., U.S.Patent No. 1,913,293, (1932).

9. Doll, Henri-Georges, U.S.Patent No. 2,433,746, (1947).

10. Williams, M., "Review of Scientific Instruments", Vol. 19, No. 10, 640-646, October 1948.

11. Williams, M., U.S.Patent 2,615,940, (1952).

12. Ueda, S., Watanabe, A., and Tsuji, F., "Memoirs of College of Agriculture", Kyoto Univ. No. 57, July 1950.

13. White, H. L., Urban, F., and Atta, E. A., "J. Phys. Chem." 36,3152 (1932).

14. Komagata, S.; "Researches Electrotech. Lab.", Tokyo (1934).

15. Bull, H. B. and Moyer, L. S. - "J. Physical Chem", 40, 9 (1936).

16. Bikerman, J. J., "Z. Physik, Chem." A, 163, 378 (1933).

17. Fairbrother and Balkin, "J. Chem. Society", 1931 p. 389.

18. Hardway, E. V., U. S. Patents 2,644,900 - 2,644,902, and others pending.

Appendix A

SYMBOLS, UNITS, AND CONVERSION FACTORS

A-1 Symbols Used in the Report

A = Face area of porous plug perpendicular to direction of flow.

B = Permeability characteristic of porous plug material.

C = Electrical capacity.

d = Thickness of Helmholtz double layer.

e = Charge per unit area of double layer.

E = Potential gradient.

F = Porosity characteristic of porous plug material.

g_v = Flow conductance of porous plug

G_o = Electrical conductance of porous plug.

H = Potential difference.

H' = Potential equivalent of pressure difference.

i = Current density (average) in porous plug material.

I = Current flowing through cell from an external circuit.

I' = Current equivalent of bulk velocity.

k_v = Flow conductivity of liquid in porous solid.

K_o = Overall conductivity of liquid filled porous solid.

L = Inductance.

M = Electromechanical coupling constant of liquid filled porous solid material.

m = Mass.

N = Average number of pores per unit area.

p = Pressure gradient.

P = Pressure difference across plug.

Q = Volumetric quantity of liquid.

r = Radius of pore or capillary.

r_v = Flow resistance of plug.

R_o = Resistance of liquid filled porous plug, or cell, i.e. $1/G_o$

R_v = Electrical equivalent of flow resistance of plug.

s(ip)h = Unit current density-pressure gradient sensitivity with no potential gradient.

S(IP)H = Current-pressure sensitivity of plug with H zero.

t = Thickness of porous plug.

T = Time

v_d = Velocity of inner layer.

v = Velocity (effective) of liquid in plug.

V = Volume velocity of liquid.

Z = Impedance

β = Electric moment of double-layer at liquid solid interface.

ε = Dielectric constant of liquid.

ζ = Zeta potential across double-layer.

η = Viscosity.

π = 3.14159

A-2 Conversions from ESU to MKS units:

Quantity	ESU	Multiply by to Obtain	MKS
A	Cm.^{2}	10^{-4}	Met.^{2}
B	Cm.^{2}	10^{-4}	Met.^{2}
C	Statfarads	$\frac{1}{9 \times 10^{[illegible]}}$	Farads
d	Cm.	10^{-2}	Met.
e	Statcoulombs/Cm.^{2}	3.33×10^{-6}	Coul./Met.^{2}
E	Statvolts/Cm.	3×10^4	Volts/Met.
F(Force)	Dynes	10^{-5}	Newtons
F(Porosity)	- - - -	- - - -	- - - -
g_v	Cm.^{5}/Dyne Sec.	10^{-5}	Met.^{5}/New
G_o	Statmhos	$\frac{1}{9 \times 10^{[illegible]}}$	Mhos
H	Statvolts	300	Volts
i	Statamperes/Cm.^{2}	$\frac{1}{3 \times 10^5}$	Amps./Met.^{2}
I	Statamperes	$\frac{1}{3 \times 10^9}$	Amperes.
k_v	Cm.^{4}/Dyne Sec.	10^{-3}	Met.^{4}/New
K_o	Statmhos/Cm.	$\frac{1}{9 \times 10^9}$	Mhos/Met.
L	Stathenries	$9 \times 10^{[illegible]}$	Henries
m	Grams	10^{-3}	Kilograms
N	Cm.^{2}	10^4	Met.$^{-2}$
p	Dynes/Cm.^{3}	10	Newtons/Met
P	Dynes/Cm.^{2}	10^{-1}	Newtons/Met
Q	Cm.^{3}	10^{-6}	Met.^{3}
r	Cm.	10^{-2}	Met.
r_v	Dyne Sec./Cm.^{5}	10^5	Newt. Sec./M

Quantity	BSU	Multiply by to Obtain	MKS
R	Statohms	9×10^{11}	Ohms.
s(ip)h	Statamp.Cm./Dyne	$\frac{1}{3 \times 10^{6}}$	Amp.Met./New
S(ip)H	Statamp.Cm.^{2}/Dyne	$\frac{1}{3 \times 10^{8}}$	Amp.Met.^{2}/New
t	Cm.	10^{-2}	Meters
T	Sec.	- - - -	Sec.
v_d	Cm./Sec.	10^{-2}	Met./Sec.
v	Cm./Sec.	10^{-2}	Met./Sec.
V	Cm.^{3}/Sec.	10^{-6}	Met.^{3}/Sec.
Z	Statohms	9×10^{11}	Ohms.
β	Statcoulombs/Cm.	3.33×10^{-8}	Coul./Met.
ε	e.s.u.	$\frac{1}{9 \times 10^{9}}$	m.k.s.u.
ξ	Statvolts	300	Volts
η	Dyne Sec./Cm.^{2}	10^{-1}	Newt.Sec./Met.
ρc *	Dyne Sec./Cm.^{3}	10	Newt.Sec./Met

A-3 Other Convenient Conversions

1" Hg. = 3.38×10^4 Dynes/Cm.^{2}

Hg. = 13.5951 Gm./Cm.^{3} @ 0°C

1 psi = 6.8947×10^4 Dynes/Cm.^{2}

1 psi = 6.8947 x 103 Newtons/Met.^{2}

(water 25°C) = .00896 poise

(acetonitrile 20°C) = .00358 poise

1 Cm. Hg. = .19337 psi = .44604 Ft.(H_2O)

= 1.333×10^4 Dynes/Cm.^{2}

1 mv/psi = -157 DB re 1 Volt/Dyne/Cm^2

* Characteristic acoustic impedance of a media.

A-3 (Continued)

1 Volt/Newt./Met.^{2} = -20DB re 1 volt/Dyne/Cm.^{2}

1 Newton Meter = 1 Watt Second = Ergs x 10^{-7}

Appendix B

PROPERTIES OF ACETONITRILE
(Methyl Cyanide)

Acetonitrile has been found to be the most efficient elecktrokinetic liquid of all those tested to date. Its ratio of electric moment (with glass and porcelain) to viscosity is greater than for any other known liquid. Fortunately its mechanical, thermodynamic, chemical, and physiological properties all make it convenient to use in laboratory tests or for the construction of transducers. In view of the above and since much of the data in Section 4 relates to acetonitrile, a number of its important properties are given below.

B-1 Conductivity: A principle supplier lists the conductivity of his acetonitrile as 7×10^{-6} mhos/Cm. at 20°C. It has, however, been purchased on many occasions in a commercial grade with the conductivity ranging from 1.6×10^{-6} mhos/Cm. The material may be electrolytically polished using aluminum electrodes in from 10 to 30 minutes at 100 volts/inch to a conductivity as low as 0.24×10^{-6}. It will, however, return on standing to a range from 1 to 2×10^{-6}. Contact with the noble metals and with copper, zinc, and a number of others will cause a marked increase in conductivity. It is, however, complete inert to glass, high grade porcelains, aluminum, magnesium, antimony, tin and certain other metals. It is mutually insoluble with microcrystalline hydrocarbon waxes which may be used as sealing compounds.

B-2 Molecular Weight: 41.05

B-3 Density (15/4°C): 0.78746

B-4 Freezing Point: -44.9°C

B-5 Boiling Point: 81.6°C

B-6 Vapor Pressure: (20°C): 50.2 mm Hg

B-7 Flash Point: 68°F

B-8 Specific Heat (g.cal/g.mol.): 0.541

B-9 Heat of Fusion (Cal./g.mole): 2130

B-10 Heat of Vaporization (g.cal/g. 80.5°C): 173.6

B-11 Surface Tension (dyne/cm.air 20°C): 29.3

B-12 Adiabatic Compressibility (26°C): 52.2×10^{6}

B-13 Dipole Moment: 3.94×10^{18} esu

B-14 Velocity of Sound: 1303 m/Sec.

B-15 Characteristic Acoustic Impedance: 1.025×10^{-5} g/Cm.^{2}Sec.

B-16 Odor: Mild Ethereal

B-17 Dielectric Constant:

0°C	42
20°	38.8
81.6	26.2

B-18 Viscosity:

Temp. °C	Viscosity (cp)
-10	0.493
0	0.440
10	0.394
20	0.358
30	0.328
40	0.304
50	0.283
60	0.264

B-19 Toxicity: Close to that of acetic acid, Not irritating to or readily absorbed by the skin. It is reported that in the animal body the compound hydrolyzes to form acetic acid and does not liberate hydrocyanic acid. Prolonged breathing of the vapors should be avoided.

B-20 Chemical Formula: $CH_3 - C \equiv N$

Many of the above figures are quoted from the Carbide and Carbon Chemicals Company "Niacet Bulletin No. 30".