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The electrochemical behavior of membranes in liquid ammonia and the analytical significance of this behavior. Part I--Glass electrode. Part II--Selectively permeable cation exchange membranes.

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THE ELECTROCHEMICAL BEHAVIOR OF MEMBRANES IN LIQUID AMMONIA AND THE ANALYTICAL SIGNIFICANCE OF THIS BEHAVIOR

Part I - Glass Electrode

Part II - Selectively Permeable Cation Exchange Membranes

by

MARTHA JANE BERGIN
(A.B., Radcliffe College, 1945; A.M. Boston University, 1950)

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Approved

by:

First Reader Arno H. A. Heyn
Assistant Professor of Chemistry

Second Reader Louis C.W. Baker
Assistant Professor of Chemistry

TO

JOHN A. AND AUGUSTA H. BERGIN

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TOPICAL OUTLINE

Part I - Glass Electrode

Part II - Selectively Permeable Cation Exchange Membranes

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PART I

THE GLASS ELECTRODE

INTRODUCTION

In 1909 Fritz Haber[19] found that a potential developed when a thin-walled glass bulb, containing an electrode and an internal solution, was immersed in a test solution which was in contact with another electrode. The potential was found to vary with the acidity of the test solution. An assembly consisting of such a thin-walled glass bulb, its internal solution, and the electrode which it contains, has since become known collectively as a "glass electrode". The Haber cell may be schematically represented as follows:

Reference Electrode	Aqueous Solutions Containing Solvated Protons	Glass Membrane	Aqueous Solution of Solvated Protons of Known Concentration	Reference Electrode

Since 1909 the phenomenon has been extensively investigated. Although many kinds of glass may be used to produce membranes which are electrochemically sensitive to their surroundings when used in such cells, only a few kinds exhibit electrochemical and physical characteristics which make them highly desirable for the determination of hydrogen ion activities. An ideal kind of glass for this purpose would be such that the potential developed would be in quantitative accord with the Nerst equation[2]:

$$E = E_0 + RT/nF \ln a_{H_1^+}/a_{H_2^+}$$

Actually no kind of glass exhibits such ideal behavior over the entire range of concentration, but a few kinds closely approach this ideal behavior over considerable ranges. The early researches demonstrated that glass electrode phenomena are highly dependent upon the nature of the surface of the glass membrane.

Dole and others(2) extended the use of the glass electrode to liquid media other than water. Such work was especially concerned with glass electrode action in organic solvents.

Part I of this dissertation reports an investigation of the possibility of extending the use of the glass electrode to liquid ammonia systems.

The starting point of this work was an attempt to discover a potential between the electrodes of the following cell:

Reference Electrode	Solution of Ammonium Salt in Liquid Ammonia	Glass Membrane	Solution of Ammonium Salt of Known Concentration in Liquid Ammonia	Reference Electrode

This cell is analogous to the Haber cell (above), since the ammonium ion in liquid ammonia corresponds to the hydronium ion in water, both representing the solvated proton in the respective media. Since the glass electrode is capable of measuring the hydronium ion activity in water, it was felt that it might be capable of measuring the ammonium ion activity in liquid ammonia.

No potential could be detected between the electrodes of the above system when it was tested under a variety of experimental conditions. A systematic elucidation of some of the possible factors involved in the failure of this system to develop a potential was then undertaken. This elucidation led directly to the developments reported in Part II of this dissertation.

THE GLASS ELECTRODE

General

The theory[2, 3, 24] which has been developed to explain the glass electrode action in water will be presented in this section. The early investigations revealed that the glass electrode was not influenced by the presence of oxidizing or reducing materials. There is no transfer of electrons at the electrode solution interface. Therefore, neither oxidation nor reduction occurs. The potential measured is dependent only on the difference of hydronium ion activity on either side of the membrane. In other words, the glass electrode serves as a junction in a concentration cell. Therefore, it can be shown that the following thermodynamic relationship holds:

$$E = E_0 + RT/nF \ln a_1/a_2 \qquad (1)$$

where a_1 and a_2 are the activities of the solvated protons on either side of the membrane.

Since one of the hydrogen ion activities is held constant, Equation (1) can be condensed to the following:

$$E = C\ (pH) \qquad (2)$$

where C is a constant and pH is defined as $-\log a_{H^+}$.

The overall EMF measured by a pH meter is the sum of all the EMF's of the system. Figure I (Appendix II) represents schematically the cell system. E_1 is the potential between the reference electrode and the internal solution. This potential will remain constant provided the temperature does not vary. E_2 is the potential between the reference electrode and the membrane and is equal to the product of the current times the resistance (IR drop). Since ionic solutions are used, their resistance will be very low. Moreover, the current through the cell is very small. Therefore, the potential (E_2) is negligible. E_3 is the potential between the glass surface and the solution. This should be constant provided the surface does not vary with time. E_4 represents the IR drop across the membrane. In early glass electrodes, this potential was large, since the resistance of ordinary glass is very high. However, when very thin bulbs of low resistance glass could be prepared[30] and the proper pH instrumentation[9, 14, 31] became available, E_4 could be made negligible. E_5 is the potential between the outer surface of the glass and the unknown solution. It is essentially a function of pH. E_6, similar to E_2, is negligible. E_7, the reference electrode potential, is constant except for minor variations caused by junction potentials.

Thus, it is apparent that, if there is no rapid temperature change, the observed EMF of the cell system is caused by E_5, which is essentially dependent on pH.

The instrument used to measure this potential is a vacuum tube electrometer calibrated in pH units (Figure II). One pH unit is equivalent to 60 millivolts at 25°C. This meter must measure voltage to an accuracy of 0.6 millivolts with an input current of roughly 10^{-12} amperes.

In 1922, W. S. Hughes[22] found that the sodium ion concentration also affected the glass electrode action. He observed that the glass surface potential is not a linear function of the logarithm of the hydrogen ion concentration beyond a pH of 10 (Figure III). This deviation is called the "sodium error". Other investigators proved that certain other monovalent ions had a similar effect when in contact with the glass electrode[21, 39]. The deviation occurred, however, only when the ion was present at a high concentration with respect to the hydrogen ion.

Later, Dole and MacInnes[28] made a systematic study to find glasses which would be pH responsive with the least alkaline error. The glass they found most satisfactory was a soda-lime silicate glass containing 21.6% Na_2O, 6.5% CaO, 71.9% SiO_2. This glass is produced commercially by the Corning Glass Company as their "015 glass". Although this glass functioned in a satisfactory manner between a pH of 1 and a pH of 9, a sodium error still occurred in the more basic region. In addition, this glass became increasingly soluble at high temperatures[18]. Later, more extensive studies resulted in the development of new types of glasses[26, 32, 33]. The pH responsive glasses have been considered to be structures consisting of a silicon-oxygen meshwork in which the alkali metal ions and other cations occupy interstitial positions within this meshwork[41]. The character and dimensions of the ions govern the fundamental exchange reactions between the glass surface and the solution. For the ideal pH-sensitive glass, both low resistivity and low sodium error are desired. It can be shown that the direct current resistance of pH sensitive glass is proportional to the ionic radii of its constituents. However, it was generally found that the use of a glass having low electrical resistance gave relatively high sodium errors. Lithium glasses, for example, were found to have the smallest sodium errors; however, they generally had a higher resistance than other glasses. On the other hand soda glasses were found to have higher sodium errors but lower resistance than other glasses. The lithium glasses[13] are in general use in the glass electrodes of today. These glasses have roughly the following composition: 28 mole % lithium oxide, 70 mole % silica content, and the remaining 2 mole % contains the oxide of an alkaline earth metal of small atomic radius.

Theory

This section will present an historical survey of the various theories which have been proposed to explain glass electrode phenomena.

Haber[19], who first investigated the phenomenon, proposed a mechanism based on phase boundary considerations. In his theory, he assumed that within the glass the hydrogen ion concentration remained constant although it varied in the solution. The results lead to the following equation:

$$E = RT/nF \ln C_{H^+} + C \quad .$$

Haber was not aware of the sodium error. Hughes[22] attempted to explain this error by assuming that the glass acted as a sodium silicate-silicic acid buffer system. He proposed further that this buffer did not become effective until a pH of 9. To substantiate this, he mentioned that the first dissociation constant for silicic acid is 1×10^{-9}. However, such a system would not allow for the variation of the alkaline error which is observed experimentally when sodium and potassium are used.

Cross and Halpern(15, 41) considered the phenomenon on the basis of equilibria existing between the glass and the solution. If an electrolyte containing alkali metal ions is added, it becomes distributed between the liquid and solid phases according to the Mass Action Law. As this electrolyte becomes more concentrated, sufficient alkali metal ion is distributed between the glass membrane and the solution to set up an additional potential, the "sodium error" potential. However, it is known that the glass electrode responds instantaneously to concentration variation. The equilibria considered by Gross and Halpern are likely to be reached more slowly.

The possibility that the glass membrane might be acting as an ion exchanger was investigated by Horowitz(21). His experimental results indicated that at high concentrations the glass electrode behaved as a sodium, potassium, or lithium electrode. The Horowitz theory was later disproved by Freundlich(12), who found that ion adsorption, as determined by the electrokinetic potential, bore no relationship to the thermodynamic potential of the glass electrode.

Another phenomenon which might serve to explain glass electrode action is the Donnan semi-permeable membrane effect. If this effect were a contributing factor, any cation should be able to diffuse through the glass and thus control the potential. To investigate the possibility of the presence of Donnan membrane action, the following cells were set up[5]:

.1N HCl	glass electrode	.1N	NaOH	(4a)
.1N HCl .1N NaCl	glass electrode	.1N	NaOH	(4b)

If the glass were acting as a semi-permeable membrane, the E.M.F. of the two cells would be different because the sodium ion would enter into the reaction. The potential of cell system 4a was 0.6098 volts while that of 4b was 0.6090 volts.

In 1931 Dole proposed his liquid junction theory[5, 36]. He assumed that the conduction through glass is electrolytic rather than electronic. Therefore, when current passes, ions move from a region of one activity to a region of another. The potential of the junction between the glass and the aqueous solution is given by the fundamental differential equation.

$$dE = -t_{H^+} RT/F \, d\ln a_{H^+} - t_{Na^+} RT/F \, d\ln a_{Na^+} \text{-----} + t_{OH^-} RT/F \, d\ln a_{OH^-} + t_{Cl^-} RT/F \, d\ln a_{Cl^-} \qquad (5)$$

If t_{H^+} approaches 1, then all the other terms would approach 0, and the equation would become that of a hydrogen electrode. The general equation cannot be integrated, however, as t is an unknown function of the concentration.

Dole then visualized the following cell system to aid in his theoretical treatment of glass electrode action.

I		Glass		II
H_2O		H^+		
H^+		Na^+		H_2O
Na				H^+
	A		B	

He also found it necessary to make the following series of assumptions, some of which seemed difficult to justify: (1) only the positive ions are important (glass electrode action has been found to be independent of the anions present), (2) the ions are mobile through the boundaries, (3) a homogeneous solvent exists throughout the system, and (4) the perfect gas laws are applicable in this case.

If the Henderson Plank equations were applied, the potential of the glass electrode was determined as follows[29]:

$$E_A = RT/F \ln \frac{u_{H^+} C^{I}_{H^+} + u_{Na^+} C^{I}_{Na^+}}{u_{H^+} C^{G}_{H^+} + u_{Na^+} C^{G}_{Na^+}}$$

$$E_B = RT/F \ln \frac{u_{H^+} C^{G}_{H^+} + u_{Na^+} C^{G}_{Na^+}}{u_{H^+} C^{II}_{H^+}} \qquad (6)$$

where u represents ionic mobility.

Adding the two potentials and substituting the activities for concentration, the following equation was obtained:

$$E_A + E_B = E_G = RT/F \ln \frac{a^{I}_{H^+} + u_{Na^+} / u_{H^+} a^{I}_{Na^+}}{a^{II}_{H^+}} \qquad (7).$$

If the glass electrode were behaving exactly like a hydrogen electrode, the potential would be:

$$E_H = RT/F \ln \frac{a^{I}_{H^+}}{a^{II}_{H^+}} \qquad (8).$$

The difference between this potential and E_G should give the glass electrode or sodium error:

$$\Delta E = E_G - E_H = RT/F \ln \frac{a^{I}_{H^+} + \frac{u_{Na^+}}{u_{H^+}} a^{I}_{Na^+}}{a^{I}_{H^+}} \qquad (9).$$

This equation for the glass electrode error predicted the following:

(1) The error would increase with diminishing hydrogen activity.

(2) The error would increase with increasing sodium activity at constant pH.

(3) The error would vary from sodium to lithium depending on mobility of the ions.

(4) If the activity of hydrogen was small enough, the error would be proportional to the logarithm of sodium ion activity and thus the glass electrode would act as a sodium electrode.

Equation 9 satisfied the experimental facts up to a pH of 12, but beyond that value it failed. Also, in order to use this equation and obtain the correct order of magnitude for the error, the mobility of the hydrogen ion had to be 10^{11} times as great as that of any other ion in the solution. Such a high value is not substantiated by other studies, e.g. transference studies at a liquid junction. The necessity of further modifications of the theory was evident.

In the interim between 1931-1934, Gurney[17] treated the problem of the plating out of alloys in a statistical manner. Dole, seeing that a similar approach might be used for the glass electrode, proposed a slightly different derivation of the equation for the error in the glass electrode[6]. In the new treatment, Dole assumed that glass was essentially a negative silicate lattice with mobile positive ions occupying equilibrium positions. These positive ions were thought to have varying energy levels following the Boltzman distribution law[7].

According to this theory, the hydrogen ion is making transitions from equilibrium positions in the water to positions of equal or lower energy on the glass surface. However, some of the hydrogen ions on the glass surface have enough energy to return into the solution. If the "d" transitions are those which the ion makes onto the glass from solution and "s" transitions are the reverse, at equilibrium the two must equal each other. If the equations for these two types of transitions are equated (i.e. equilibrium conditions), the interfacial potential is obtained.

Let $U^{og}_{H^+}$ = energy of lowest quantum level of H^+ on glass surface

$U^{os}_{H^+}$ = energy of lowest quantum level of H^+ in solution

$U^{og}_{Na^+}$ and $U^{os}_{Na^+}$ are defined in an analogous manner for sodium. All energies from U_o to U_∞ are assumed for the ions.

The number of s-situations, i.e. situations which give rise to s-transitions, per unit area of glass surface, which have energies between U and U + dU, can be expressed by:

$$1/kT \exp \frac{U^{og}_{H^+} - U}{kT} \quad dU \quad \text{(if no interfacial potential)} \qquad (10).$$

or

$$1/kT \exp \frac{U^{og}_{H^+} + \epsilon V - U}{kT} \quad dU \quad \text{(if interfacial potential)} \qquad (11).$$

The number of s-situations is dependent on the number of water molecules in the vicinity (N_W), and also on the number of desired positions occupied by sodium ions.

γ = fraction of unit surface covered by H^+ ions.

Therefore,

$$\gamma N_W/kT \exp \frac{U^{og}_{H^+} + \epsilon V - U}{kT} \quad \text{(s-situations for } H^+) \quad (12)$$

$$1 - \quad N_W/kT \exp \frac{U^{og}_{Na^+} + \epsilon V - U}{kT} \quad \text{(s-situations for } Na^+) \quad (13)$$

It is possible that the sodium and hydrogen ions cannot occupy the same positions interchangeably. Let

a = Number of lattice points per unit surface which H^+ can occupy

a γ = Fraction of total lattice points occupied by H^+

a- aγ = Total humber of lattice points not occupied by H^+.

Of these $(a-a\gamma)$ lattice points, a certain fraction, δ, can be occupied by the sodium ion.

$$\text{For } H^{+} \quad a\gamma N_W/kT \ \exp \frac{U_{H^+}^{og} + \epsilon V - U}{kT} \, dU \tag{14}$$

$$\text{For } Na^{+} \quad \delta(a-a\gamma) \ N_W/kT \ \exp \frac{U_{H^+}^{og} + \epsilon V - U}{kT} \, dU \tag{15}$$

Now the number of d transitions must be determined. These depend on the number of hydrogen ions (N_{H^+}) and sodium ions present, the number of lattice points the ions can occupy, and the energy of ions.

$$\text{d-transitions for } H^{+} \quad a \ N_{H^+}/kT \ \exp \frac{U_{H^+}^{os} - U}{kT} \, dU \tag{16}$$

$$\text{d-transitions for } Na^{+} \quad a\delta \ N_{Na^+}/kT \ \exp \frac{U_{Na^+}^{os} - U}{kT} \, dU \tag{17}$$

One more assumption had to be made before these values could be equated. A probability ratio β had to be introduced to account for the fact that some of the ions might not deposit as expected. Now equating:

$$a\gamma (N_W/kT) \ \exp \frac{U_{H^+}^{og} + \epsilon V - U}{kT} \, dU = \beta_{H^+} \ a \ (N_H/kT) \ \exp \frac{U_{Na^+}^{os} + U}{kT} \, dU \tag{18}$$

If $U_{H^+}^{os} - U_{H^+}^{og} = Q_{H^+}$; $N_{H^+}/N_W = C_{H^+}$,

the equation (18) for the proton condenses to:

$$\gamma = C_{H^+} \beta_{H^+} \ \exp \frac{Q_{H^+} - \epsilon V}{kT} \tag{19}$$

and for sodium ion:

$$1 - \gamma = C_{Na^+} \beta_{Na^+} \ \exp \frac{Q_{Na^+} - \epsilon V}{kT} \tag{20}$$

Adding equations (19) and (20):

$$C_{H^+}\beta_{H^+} \exp \frac{Q_{H^+} - \epsilon V}{kT} + C_{Na^+}\beta_{Na^+} \exp \frac{Q_{Na^+} - \epsilon V}{kT} = 1 \quad (21).$$

If no sodium is in solution, i.e. if $C_{Na^+} = 0$,

$$V_o = Q_{H^+}/\epsilon + kT/\epsilon \ \ln C_{H^+}\beta_{H^+} \quad \beta_{H^+} \approx 1 \quad (22),$$

the regular hydrogen electrode equation is obtained. The glass electrode error can then be expressed as:

$$V - V_o = \Delta E = kT/\epsilon \ \ln \frac{\beta_{Na^+}/\beta_{H^+}\, C_{Na^+} \exp \frac{Q_{Na^+} - Q_{H^+}}{kT} + C_{H^+}}{C_{H^+}} \quad (23).$$

This equation is found to fit the experimental facts quite well. Its advantages over the one obtained by the liquid junction approach are as follows:

1. No assumptions need be made concerning the mobilities of the ions.
2. It explains why negative ions have little or no effect as the silicate lattice is assumed to be negative, thus repelling anions.
3. The necessary assumption that $Q_{H^+} - Q_{Na^+}$ is greater than 15,000 cal/mole appears reasonably possible.

Since 1934, there have been no results which invalidate the statistical treatment of the glass electrode[20].

Effect of Temperature

Earlier sections indicate the importance of the resistance of glass membranes. The importance of this resistance becomes evident when it is realized that there is a point beyond which the errors inherent in the particular type of measuring equipment being used become significant. The relationship between temperature and resistance of glass electrodes can be expressed by the following equation[8, 37]:

$$\log R = A + B/T \qquad (24)$$

in which R is the observed resistance, T is the absolute temperature, and A and B are constants. The value of A is dependent upon the particular dimensions of the membrane, as well as upon the intrinsic character of the glass. Thus, the constant A is not fundamentally significant. The value B is independent on the geometry of the membrane and is related primarily to the nature of the glass.

From the above relationship, it is evident that there will be a logarithmic increase in resistance with a decrease in temperature. Because measurements in liquid ammonia are generally made below -33°C, this increase in resistance becomes significant for the research reported in this dissertation.

BEHAVIOR IN NON-AQUEOUS MEDIA

It has been found experimentally that the glass electrode does not function as a simple hydrogen electrode in solutions the pH of which is below 1. To explain this "acid error", Dole proposed a "water activity" theory in 1932[4]. This theory postulated that it was the hydronium ions, rather than free protons, which reacted at the glass surface. As the solution became more acidic, protons were not so completely solvated, and hence did not react ideally with the glass surface. During the subsequent investigations, glasses were found with no "acid error". In such cases, the proton itself must be the active agent[27].

Since the degree of solvation of the proton influences pH response in some cases, difficulty might be predicted in the use of the glass electrode in non-aqueous media where hydronium ion would not exist. However, in ethanol-water mixtures of concentrations up to 30% alcohol by volume, a linear relationship has been found between the potential and the pH[44]. Acetone-water solutions have been found to give a linear plot[38].

In many non-aqueous solutions, however, the glass electrode is found to vary in a non-linear manner with pH. However, in such cases, the potentials are generally reproducible and have been used to check changes of acid concentrations.

LIQUID AMMONIA

The study of the physical and chemical properties of solutions of electrolytes in liquid ammonia has been of considerable scientific interest[42]. Investigations in this medium have appreciably swelled the knowledge of the properties of liquid ammonia as a solvent as well as contributed to the general theory of solution chemistry.

Because liquid ammonia has an appreciably lower dielectric constant than water, i.e. 22.0 at -24°C, 760 mm. Hg and 4×10^8 cycles/sec., there is considerable strengthening of the electrostatic forces between the ions in this medium as compared with those in water. In addition liquid ammonia has a very low viscosity which generally results in an increase of the mobility of ions in the solution. This mobility could influence the glass electrode action, since this value enters into the equation derived for the glass electrode potential (see page 10).

It has been found that the affinity of the solvent molecule for the proton is exceedingly great in liquid ammonia. The effect is shown with particular clarity when it is realized that there is a difference of 17.3 calories between the heats of solution of the proton in liquid ammonia and in water. This greater affinity results in a difference between the behavior of acids in this medium and acids in water.

According to the theory of Franklin[10], in liquid ammonia the ammonium ion is an analog of the hydronium ion in water. All compounds which split off ammonium ions are considered to be acids in liquid ammonia.

This category includes ammonium salts, amides, and others. Liquid ammonia solutions of ammonium salts color acid-base indicators[1], and produce catalytic action analogous to acids in aqueous media. Similarly, some metals displace hydrogen from ammonium solutions. Franklin, Kraus[11], and Smith[40], while investigating the conductivity of amides in liquid ammonia, found that their strength paralleled that of carboxylic acids in aqueous solutions.

The mobility of the ammonium ion[16] gave further indication that the relationship between the proton and its solvating molecules in ammonia is somewhat different than that in water. The mobility of the ammonium ion is low compared to the very high mobility of the hydronium ion, in spite of the fact that the ammonia medium has very low viscosity.

Finally, liquid ammonia, being a better Bronsted base, equalizes the relative strength of various acids to a much greater extent than does water. A comparison of the dissociation constants of H_2S in water and in liquid ammonia (5.7×10^{-8} and 0.98×10^{-3} respectively) and HCN (4.7×10^{-10} and 1.9×10^{-3} respectively) indicates how great this effect is.

In summary, the proton, when solvated with liquid ammonia, becomes the ammonium ion. This solvated proton retains many of the acidic properties of the proton in water. However, because of the strong affinity of the solvating ammonia molecule for the proton, and other factors, additional properties appear which cannot be directly correlated with any of those of the hydronium ion.

PRELIMINARY EXPERIMENTAL WORK

The Cell System

The cell system chosen for investigation may be represented schematically as follows:

Lead	$Pb(NO_3)2$ 0.1 M in Liquid Ammonia	NH_4NO_3 Varying Concentrations in Liquid Ammonia	Glass Membrane Corning 015	NH_4NO_3 0.1 M in Liquid Ammonia	$Pb(NO_3)_2$ 0.1 M in Liquid Ammonia	Lead
Reference Electrode		Unknown NH_4^+ Concentration	Membrane	Known NH_4^+ Concentration	Reference Electrode	

The lead-lead nitrate electrode was used as the reference electrode[35]. The potential of a reference electrode in such a system is unimportant provided it remains constant. Although the lead-lead nitrate electrode is not useful in aqueous work since a reproducible potential cannot be obtained owing to lead hydroxide formation, this electrode is frequently used as a reference in electrochemical measurements in liquid ammonia. In many respects its significance for electrochemical measurements in liquid ammonia parallels that of the hydrogen electrode in aqueous solutions[35]. The use of this reference electrode in the above system eliminated any potential which might have occurred at the junctions between the reference electrodes and the ammonium salt solutions.

The lead electrodes were prepared by plating lead on platinum electrodes which had been cleaned in concentrated nitric acid, washed thoroughly, and ignited. The lead plating solution was made as follows: carbon dioxide was bubbled through a saturated solution of lead acetate. The precipitate (probably a basic lead carbonate) was filtered, washed with saturated carbon dioxide solution, and dried. The solution resulting from a mixture of 60 grams of the lead salt, and 40 grams of 72% perchloric acid was diluted to one liter and used as the plating bath. The lead plating was continued for 1 hour. The electrode, after being washed thoroughly with distilled water followed by acetone, was allowed to dry in a stream of dry nitrogen[35].

The ammonium nitrate used was recrystallized from methyl alcohol which had been distilled from calcium hydride. The lead nitrate was recrystallized from a slightly acidic aqueous solution and washed with alcohol. The salts were dried at 110°C. and then stored in a desiccator. Determination of the lead content of the recrystallized lead nitrate was made by the sulfate method of analysis. This indicated that the recrystallized material contained at least 99.6% lead nitrate.

EQUIPMENT

Vacuum Line

Figure VI, which shows schematically the vacuum line, is self-explanatory. The condensation vessel, which appears just before the cell proper, was used only in the early measurements. Later, sodium was placed in a stainless steel tank containing the supply of liquid ammonia. The ammonia was condensed from the tank directly into the cell. With the exception of the glass electrode unit which was made of lead glass, the line was composed of pyrex glass. The soft glass was attached to the pyrex by means of a standard taper joint - soft glass female to pyrex male. A vacuum of 2 x 10^{-6} millimeters of mercury could be obtained.

The Cell

The cell is drawn in a more detailed manner in Figure V. The preliminary design was made by Mr. Raymond Andrews and the main portion of the glass blowing was done at MacAllister Bicknell. It was made from a 71/60 standard-taper joint. The male portion of this joint was domed, and two 24/40 male joints and one 14/36 joint, were ring-sealed into the top. A side arm connected this portion of the cell to the vacuum line. The other section of the 71/60 joint was flattened to form the bottom of the cell. The 24/40 joints were used to hold the glass and lead electrodes and the 14/36 joint was used as inlet either for a thermometer or a sample addition mechanism. The outer glass electrode body was composed of lead glass except for the Corning 015 glass membrane. The volumes of the outer and inner cells were calibrated so that a known volume of ammonia could be condensed into each.

Exact amounts of various salts necessary to make up the desired concentrations were weighed and added directly to the outer and inner cells. The concentration of the solution inside the glass electrode was 0.1 M with respect to both ammonium and lead nitrate. The outer cell was maintained at 0.1 M with respect to lead nitrate and 0.001 M with respect to ammonium nitrate. Ammonia was condensed directly onto these salts from the auxiliary tank where it had been dried over metallic sodium for at least two days.

Stirring and Cooling Systems

The stirring was accomplished by magnetic means. The large Alnico horseshoe magnet (on load from Sylvania Electric Products, Inc.) had a rod, silver-soldered on the back so that it could be placed in a Cenco variable-speed stirrer. The field strength of the magnet was 4900 gausses. This field strength was necessary since the stirring bar had to be activated through the Dewar vessel which jacketed the cell.

The cell was initially cooled by an acetone-dry ice bath. Later, isopropyl alcohol was substituted for the acetone because this solvent became less cloudy at low temperatures.

Leads

Originally, the leads consisting of copper wire soldered to platinum were used. The platinum was sealed into lead glass. Platinum wire sealed into lead glass was used for the electrodes of the reference cells to insure a vacuum-tight seal. Difficulties caused by stray currents were so acute when copper wire leads were used that they were replaced by Beckman electrode cable, a coaxial cable with polyethylene insulation.

Since a temperature gradient existed along the leads, moisture from the air could condense in the tip of the lead, causing a short circuit between the shielding cable and the platinum wire. To avoid condensation of moisture on the cable, it was embedded in paraffin and silica gel was placed above the wax (Figure IV).

Results

It was necessary, as a preliminary experiment, to ascertain whether the potentials set up by the two lead electrodes were identical. Dipping the lead electrodes into the same liquid ammonia-lead nitrate solution produced zero potential.

When attempts were made to measure the potential produced by the overall cell system, the system behaved as an open circuit.

In an effort to overcome the increased resistance of the glass, membranes of various thicknesses were prepared and the cell system was tested when these were successively utilized; the cell system behaved as an open circuit at all times. The same system was used with water as the medium to check the sensitivity of the membrane. The circuit could be balanced under these conditions, proving the membranes were sensitive in this medium.

Experiments with Ammoniated Glass

To obtain normal glass electrode action, the membrane used must be solvated. In order to remove any water trapped in the interstices of the glass, the space on each side of the membrane was evacuated for a period of ten hours. Ammonia was then condensed into the outer cell only. A vacuum was maintained in the inner cell. After ten more hours, the ammonia was condensed into the inner cell also; and the membrane was allowed to remain immersed in liquid ammonia for an additional 48 hours. Even after this treatment, the circuit could not be balanced. This experiment indicated that incomplete solvation of the membrane was not the cause of lack of electrode response.

It was thought that if ammonium ions were made to replace protons in the glass by means of migration induced by a potential gradient, then the exchange at the surface of the membrane, necessary for glass electrode action, might occur more easily. In an attempt to cause ammonium ions to migrate into the membrane, a potential of 300 volts was applied for a period of twenty-four hours. However, this treatment proved to have no effect.

It has been found that the sodium ion in glass can be replaced partially by the ammonium ion. This method has been used in glass technology to produce high silica glass[23, 25]. Ammonium ion can be substituted for the sodium ion in a finished glass and later removed by heating or leaching. A glass poorer in alkali and richer in silica will result. A Corning 015 membrane was ammoniated in this manner. Experimentally, this was accomplished in a 50 ml. porcelain crucible containing Wood's Metal (Figure VII). Into this the glass electrode tube was placed. The tube contained a slurry of ammonium sulfate in sulfuric acid. It was necessary to choose a salt which (1) contained no cation other than the ammonium ion, (2) melted below 200°C, and (3) remained stable at this temperature. Neutral ammonium sulfate decomposes to ammonia and ammonium bisulfate at a low temperature. The bisulfate is stable up to 280°C. A mixture of this salt and sulfuric acid fit the requirements for replacement reaction. A platinum wire dipped into the slurry and a nichrome wire immersed in the Wood's metal served as contacts. After the Wood's metal had reached a temperature of 200°C, a potential of 7 1/2 volts was applied for a period of six hours. A current of between 8-10 microamperes was observed. At the end of this period, the glass tube was washed thoroughly in distilled water and acetone, dried, and sealed onto the system. Parallel runs were made on similar Corning 015 membranes in order to analyze the final composition of the ammoniated glass. The weight change which occurred when the ammonia was driven from these treated electrodes by heat, indicated that about 60% of the sodium had been replaced. A Kjeldahl analysis proved that the gas being evolved from the glass upon heating was ammonia. The use of such glasses in the liquid ammonia system proved no more successful than the use of the unammoniated Corning 015 membrane.

Discussion of Preliminary Results

From these initial experiments, it seemed apparent that there is no glass electrode action in the liquid ammonia system. Two factors had been changed as compared to normal glass electrode usage: the medium and the temperature. The experiments had been conducted at a temperature of -40°C, or 65 degrees below the usual operating temperature of the electrode.

The resistance of glass is known to increase rapidly with a decrease in temperature. Conductance through the membrane is necessary for glass electrode action. It appeared possible, therefore that the decrease in temperature had increased the resistance of the glass enough to prevent sufficient conductance for glass electrode action.

Another major factor to be considered in the failure to obtain glass electrode action was the use of liquid ammonia as a medium. It appeared possible that the ammonium ion in this medium might not, for various reasons, have sufficient energy to exchange with an ion on the surface of the glass membrane.

FURTHER EXPERIMENTAL RESULTS

Since current must flow through the membrane in order to have glass electrode action, and since an increase in applied voltage across the membrane will increase the rate of flow of this current, an increase of voltage should produce a current of measurable magnitude if the high resistance at low temperature is the limiting factor.

Equipment - The instrument used to measure the current was a Precision Multirange Test Meter (Series 856G). With this meter 0.1 microamperes can be detected. Initially, a 300 volt D.C. power supply was used for measurements but this was replaced by a 2400 volt D.C. supply. The power supply, the cell, and the ammeter were connected in series. If a pH measurement was to be attempted, the power supply was removed and a pH meter was inserted in its place.

Investigation of Corning 015 Glass

Aqueous Conditions - The first series of tests made to determine the effect of temperature on conductance through the membrane was carried out in an aqueous medium. In all other respects, the cell system used was identical to that used in liquid ammonia. Since the voltage applied was known and the resulting current was measured, the resistance of the glass could be calculated from Ohm's Law.

Numerous studies have been made of the increase of the resistance of glasses with decrease in temperature. However, it was necessary to determine whether these relationships held for a glass membrane in a cell system of the type used, i.e. one involving lead-lead nitrate reference electrodes in ammonium nitrate solutions. It was also desirable to extend the resistance measurements to a temperature well below that involved in the liquid ammonia cells.

The results obtained on application of a 300 volt potential to the cell system are presented in Table I (Appendix I). Those obtained on application of a 2400 volt potential are recorded in Table II. In the former case, the current dropped below the limit of accuracy of the meter when the temperature was decreased to approximately 7°C. Therefore, only the 2400 volt potential was used in the later measurements. The results of these measurements are plotted in Figure VIII, and it was found that all values fall on the same curve. Therefore, the resistance of the glass at a given temperature remains constant regardless of the potential applied.

<u>Liquid Ammonia Conditions</u> - In the preliminary experimental work, it had been found that 2400 volt potentials across the membranes in liquid ammonia systems produced no observable current. Careful repetition of these experiments, using the equipment described in the section immediately above, verified earlier observations. These measurements were made at -40°C. It was reasoned that if temperature alone were responsible for the lack of conduction, an increase in temperature should permit the passage of current. It was, therefore, desirable to attempt to determine how the resistance of the glass varied with temperature in liquid ammonia. The cell system was prepared as for previous measurements. However, Kronig's cement was

substituted for stopcock grease on all standard taper connecting joints in order to enable work at higher pressures. After condensing the ammonia, the cooling Dewar flask was removed, and the cell was allowed to become warmer. Constant stirring was maintained. A copper constantan thermocouple sealed into the cell permitted measurements of temperature. The results are presented in Table III. At -10°C a pH measurement was attempted; but, as in all previous attempts to obtain such measurements in liquid ammonia, the meter could not be balanced. Immediately after the last reading (-1°C) the pressure became sufficiently great to blow apart the large ground glass joint of the cell.

These data show that even at -1°C when a 2400 volt potential was applied to the cell system, the conductance of the glass membrane in liquid ammonia was less than 0.1 microampere. In the analogous aqueous system a current of 2 microamperes was observed at 6°C. The results of this experiment indicate that, although resistance might increase greatly with decreasing temperature, the temperature is not the major reason for lack of conductivity through the glass in liquid ammonia.

Alcohol-Water Condition - The final step in this series of experiments was to ascertain whether pH could be measured at as low a temperature at -33°C. It was necessary to determine experimentally whether the resistance of a glass membrane had been increased to such an extent by lowering of the temperature that a pH measurement was not possible. An alcohol-water mixture, containing 80% alcohol by volume, was chosen for these experiments. Although a linear potential response with pH change is not obtained in alcoholic solutions, a glass electrode potential can be measured and reproduced.

The alcohol-water solution in the outer cell was made .02 N with respect to hydrochloric acid and that in the inner cell was made 1.2 N with respect to the same reagent. The agar salt bridges, which served as connections between the alcohol-water solutions and calomel reference electrodes, partially crystallized at the lower temperatures; but this did not interfere with the measurements. Using such a cell arrangement, the Beckman meter could be balanced at pH = 3 when the temperature was 26°C.

Since there must be conductance through the membrane to obtain a pH measurement, the resistance of the glass membrane in the alcohol-water solution was determined at various temperatures. The results are summarized in Table IV. The resulting curve (plotted in Figure IX) is parallel to that obtained in water. The significant fact is, however, that current was observed to flow at as low a temperature as -33°C. This was not observed at a similar temperature in the liquid ammonia medium.

Investigation of Beckman General Purpose and Type "E" Glasses

The previous experiments indicated that no glass electrode action was observed in liquid ammonia using Corning 015 glass. Two Beckman glass electrode glasses were similarly tested in an effort to ascertain whether the composition of the glass might influence the results.

The Beckman General Purpose Glass has an exceptionally low electrical resistance and is used when chemical and physical strength and durability are needed. In addition, at room temperature operation, no "sodium error" correction is needed up to pH 11 when this glass is used. The second type of glass is known as Beckman Type "E". Since it is not chemically resistant to acidic solutions, this glass is employed in the pH region between 9 and 14. Beckman Amber Glass, which is especially suitable for use at elevated temperatures, was not tested because it is known to have too high a resistance below room temperature.

Liquid Ammonia Conditions

Two of the outer electrode bodies of both the General Purpose and the Type "E" glasses were obtained from Beckman Instruments, Inc. Type "E" glass was first tested. The cell was set up in the usual manner with 0.1 N lead nitrate as reference electrode solution in both cells and 0.1 N ammonium nitrate in the inner and 0.001 N ammonium nitrate in the outer cell. The system containing the glass membrane was evacuated for fifteen minutes before the ammonia was condensed. The system was allowed to stand overnight in contact with the solvent in an attempt to solvate the glass electrode. However, when the lead electrodes were inserted, the pH meter could not be balanced. A potential of 45 volts was applied across the glass but no resultant current could be measured on the ammeter. The potential was increased to 2400 volts with similarly negative results. In an effort to condition the glass further, 45 volts were applied across the electrode for a period of 24 hours. A potential of 2400 volts was then applied for four hours. During this period no flow of current could be observed. The pH meter could not be balanced at any time during this series of tests.

The All Purpose Glass was conditioned in liquid ammonia in the same manner as the Type "E". The results were identical with those described above.

Aqueous Conditions - Using a cell system with Type "E" glass as the membrane and aqueous conditions, the pH meter was balanced at 6.8 pH units. A series of measurements to check the change of resistance with temperature was started. Unfortunately, the membrane was punctured as a result of the high current which occurs with increasing temperatures. The values obtained, however, followed the pattern of the Corning 015 glass.

The temperature-resistance data of the General Purpose Glass in aqueous media are more complete and are summarized in Table V. The results are more clearly shown graphically in Figure X.

Alcohol-Water Conditions - The decrease of conductance with decreasing temperature was determined with General Purpose Glass in 80% alcohol solutions. The outer cell solution contained, 0.02 N hydrochloric acid, the inner cell 1.2 N hydrochloric acid. At 26°C the pH meter could be balanced at 7 millivolts. After the temperature had been decreased to -29°C, a value of 10 millivolts was obtained. Data are summarized in Table VI and presented graphically in Figure IX.

The current observed were noticeably higher when the General Purpose glass replaced the Corning 015 as membrane. The use of thinner membranes, as well as of glasses of lower resistance than Corning 015, account for this change. However, the shape of the curves are similar. It is significant that current flows and pH can be measured at -30°C in the aqueous-alcohol medium.

This series of experiments shows that the three types of glasses tested behave in a similar manner with respect to their change of resistance with temperature. The General Purpose glass, because of its lower resistance, permits a slightly greater current to flow at -30°C than does the Corning 015. None of these glasses show glass electrode action in liquid ammonia.

EFFECT OF SODIUM ION

If sodium ions are present in aqueous solution in a sufficiently high concentration, they will take part in the glass electrode action and cause the "sodium error". It seemed desirable to attempt to determine the effect of sodium ion on the glass in liquid ammonia. Corning 015 and also Beckman General Purpose glasses were used. The cell system was the same as that used in previous liquid ammonia work. To the outer cell enough sodium nitrate was added stepwise until a concentration of sodium ion 30 times greater than that of the ammonium ion was obtained. This ratio of sodium ions to hydronium ions in aqueous medium is more than sufficient to introduce the "sodium error". In the liquid ammonia system the pH meter could not be balanced and the application of 2400 volts produced no conduction across the membrane.

In a second experiment, sodium nitrate was substituted for ammonium nitrate (.1 M $NaNO_3$ in the inner cell and .001 M $NaNO_3$ in the outer). The glass membrane again did not respond.

The results when Beckman General Purpose Glass was used were identical.

In summary, no effect of sodium ion on glass electrode action in liquid ammonia was detected.

DISCUSSION OF RESULTS

Experiments show that there is no glass electrode action in liquid ammonia. In liquid ammonia the glass membranes do not conduct a measurable amount of current. This does not result solely from the low temperature of the system (-40°C), since raising the temperature to -1°C did not change the results, while in an alcohol-water system, pH response was observed at as low a temperature as -30°C. The plots of temperature versus resistance for aqueous and water-alochol media are similar, indicating that there had been no appreciable variation in this phenomenon as a result of a change in media.

Identical results were obtained with three different types of glass, this gave further evidence that the lack of a glass electrode action in liquid ammonia is neither the result of the low temperature, nor of the type of glass. Therefore, it is indicated that this lack of glass electrode action is ascribable to the nature of the medium.

On the whole, these results are not surprising. On solvation in liquid ammonia, the proton becomes the ammonium ion, which may be more highly solvated than that in water[32]. This ion has little tendency to dissociate into a proton and a molecule of ammonia. There has been no evidence that the ammonium ion will cause an "error" in pH measurements in water. In other words, even in aqueous media, this ion does not take part in any exchange equilibria with the sodium or hydrogen ions on the surface of the glass. Therefore, it seems improbable that the ammonium ion in liquid ammonia would have sufficient energy to react with a glass surface.

A plot of the logarithm of the resistance versus the reciprocal of the absolute temperature gives a straight line (Figures XI-XIV). This linearity is in agreement with the well-known equation representing variation of resistance with temperature, that is:

$$\log R = A + B/T$$

This relationship was found to apply down to temperatures of at least $-30^{\circ}C$.

SUGGESTED DIRECTION FOR FURTHER WORK

Since glass membranes show no electrode action in the presence of sodium as well as ammonium ions in liquid ammonia, it is likely that no ion could cause electrode action in this medium. The direction for further work, therefore, would be the substitution of a conducting exchange membrane for the glass membrane.

Recently much progress has been made in the preparation of such anion and cation exchange resin membranes. If such membranes should prove operative in the liquid ammonia medium, they would be non-specific and would indicate the total concentration of ions of the same charge.

The study of cationic exchange membranes for electrochemical measurements in liquid ammonia is presented in the second part of this dissertation.

CONCLUSION

1. It has been demonstrated that glass electrodes employing Corning 015, Beckman Type "E", or Beckman General Purpose glasses cannot be used to determine the concentration of ammonium ions in liquid ammonia.

2. It has been shown that glass electrodes employing Corning 015 or Beckman General Purpose glasses are insensitive to the concentration of sodium salts in liquid ammonia.

3. It has been established that glass electrode action does occur at temperatures as low as -35°C in water-alcohol solutions. Therefore, the increase of electrical resistance with decrease of temperature is not solely responsible for the lack of glass electrode action in liquid ammonia.

4. Temperature-resistance data has been extended to -33°C for membranes of Corning 015 and to -30°C for membranes of Beckman General Purpose glass in water-alcohol solutions. The resistance has been shown to vary with temperature in accordance with the following equation:

$$\text{Log } R = A + B/T$$

5. It has been demonstrated that imposed potentials of up to 2400 volts fail to cause membranes of the above mentioned types of glasses to pass 0.1 microampere in the temperature range -40°C to -1°C, when the membranes separate solutions of electrolytes in liquid ammonia.

APPENDIX I

TABLE I

Temperature Resistance Data
300 Volt Potential - Aqueous Conditions
Corning 015 Glass

Temperature ° Centigrade	Temperature ° Absolute	1/T	Current Microamperes	Resistance* Megohms
7	280	.00357	0.2	1500
9	282	.00355	0.2	1500
11	284	.00352	0.3	1000
14	287	.00348	0.5	600
15	288	.00345	0.6	500
18	291	.00344	0.8	376
22	295	.00339	1.1	286
26	299	.00334	2.1	150
38	311	.00322	4.2	72
45	318	.00314	8.2	37
49	322	.00311	10.0	30
52	327	.00306	13.0	22

*Resistance calculated from Ohm's Law E = IR

TABLE II

Temperature Resistance Data
2400 Volt Potential - Aqueous Conditions
Corning 015 Glass

Temperature ° Centigrade	Temperature ° Absolute	1/T	Current Microamperes	Resistance Megohms
6	279	.00358	2.0	1200
7	280	.00357	2.2	1090
8	281	.00356	2.8	860
9	282	.00355	3.0	800
14	287	.00348	4.5	533
16	289	.00346	5.2	460
20	293	.00341	8.0	300
29	302	.00331	17.0	141
31	304	.00329	21.0	114
35	308	.00325	30.0	80
41	314	.00319	49.0	49
46	319	.00316	90.0	27
50	323	.00309	105.0	22
52	325	.00307	120.0	20

*Resistance calculated from Ohm's Law E = IR

TABLE III

Temperature Resistance Data
2400 Volt Potential - Liquid Ammonia Conditions
Corning 015 Glass

Temperature ° Centigrade	Current Microamperes
-37	0.0
-20	0.0
-10*	0.0
- 4	0.0
- 1	0.0

*Unsuccessful pH measurement attempted here.

TABLE IV

Temperature Resistance Data
2400 Volt Potential - Alcohol-Water Conditions
Corning 015 Glass

Temperature ° Centigrade	Temperature ° Absolute	1/T	Current Microamperes	Resistance* Megohms
-33	240	.00416	0.1	24000
-30	243	.00412	0.1	24000
-24	249	.00402	0.1	24000
-16	257	.00389	0.2	12000
-10	263	.00380	0.5	3440
0	273	.00366	1.4	1710
9	282	.00355	2.0	1200
12	285	.00351	3.0	800
20	293	.00341	5.9	410
30	303	.00330	14.0	171
40	313	.00319	32.0	75
46	319	.00313	80.0	30

*Calculated from E = IR

TABLE V

Temperature Resistance Data
2400 Volt Potential - Aqueous Conditions
Beckman Type "E" Glass

Temperature ° Centigrade	Temperature ° Absolute	1/T	Current Microamperes	Resistance Megohms
25	398	.00336	60	40
28	301	.00332	75	32
31	304	.00329	95	24
35	Current too high - Pin hole developed			
	Beckman General Purpose Glass			
7	280	.00357	4	600
8	281	.00356	5	480
10	283	.00353	7	342
18*	291	.00344	15	160
28	301	.00332	36	67
31	304	.00329	47	51
36	309	.00323	75	32
39	312	.00321	100	24
42	315	.00317	140	17
45	318	.00314	184	13
48	321	.00312	240	10
50	323	.00309	270	9

*pH meter balanced at 6.0 pH units

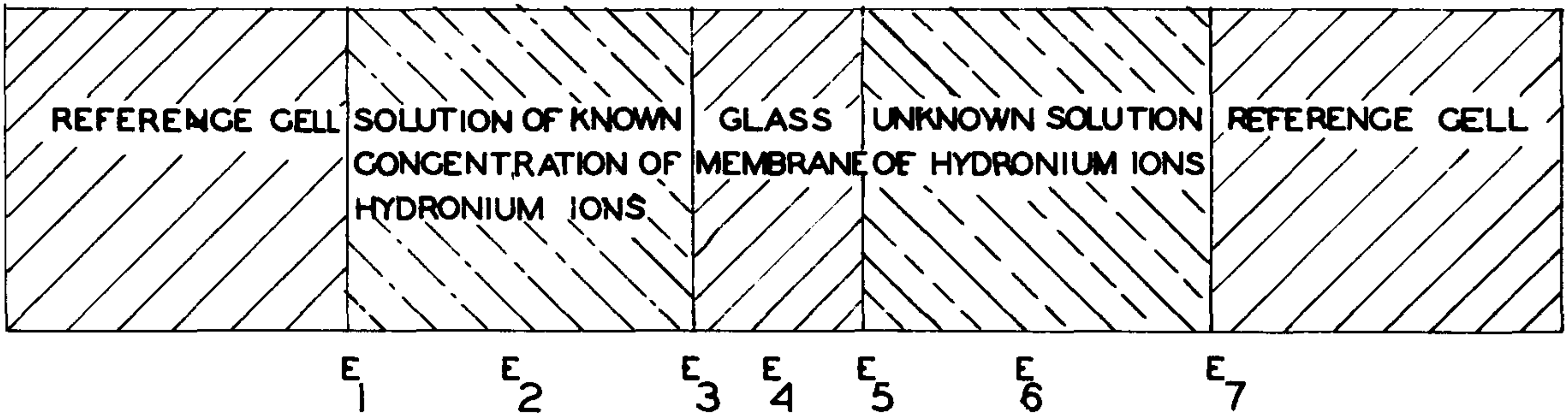
TABLE VI

Temperature Resistance Data
2400 Volt Potential - Alcohol-Water Conditions
Beckman General Purpose Glass

Temperature ° Centigrade	Temperature ° Absolute	1/T	Current Microamperes	Resistance* Megohms
-30	243	.00412	0.2	12000
-20	253	.00395	0.5	4800
-10	263	.00382	1.0	2400
0	273	.00366	2.3	1042
5	278	.00360	4.0	600
10	283	.00353	7.0	342
15	288	.00347	10.0	240
19	292	.00342	16.0	150
22	295	.00339	25.0	96
25	298	.00335	28.0	85
30	303	.00330	45.0	53
35	308	.00325	75.0	32
40	313	.00319	132.0	18
45	318	.00314	210.0	11
50	323	.00310	375.0	6

*Calculated from E = IR

APPENDIX II



E_1 = CONSTANT

E_2 = 0

E_3 = CONSTANT

E_4 = 0 OR AT LEAST CONSTANT

E_5 = VARIABLE ESSENTIALLY WITH PH

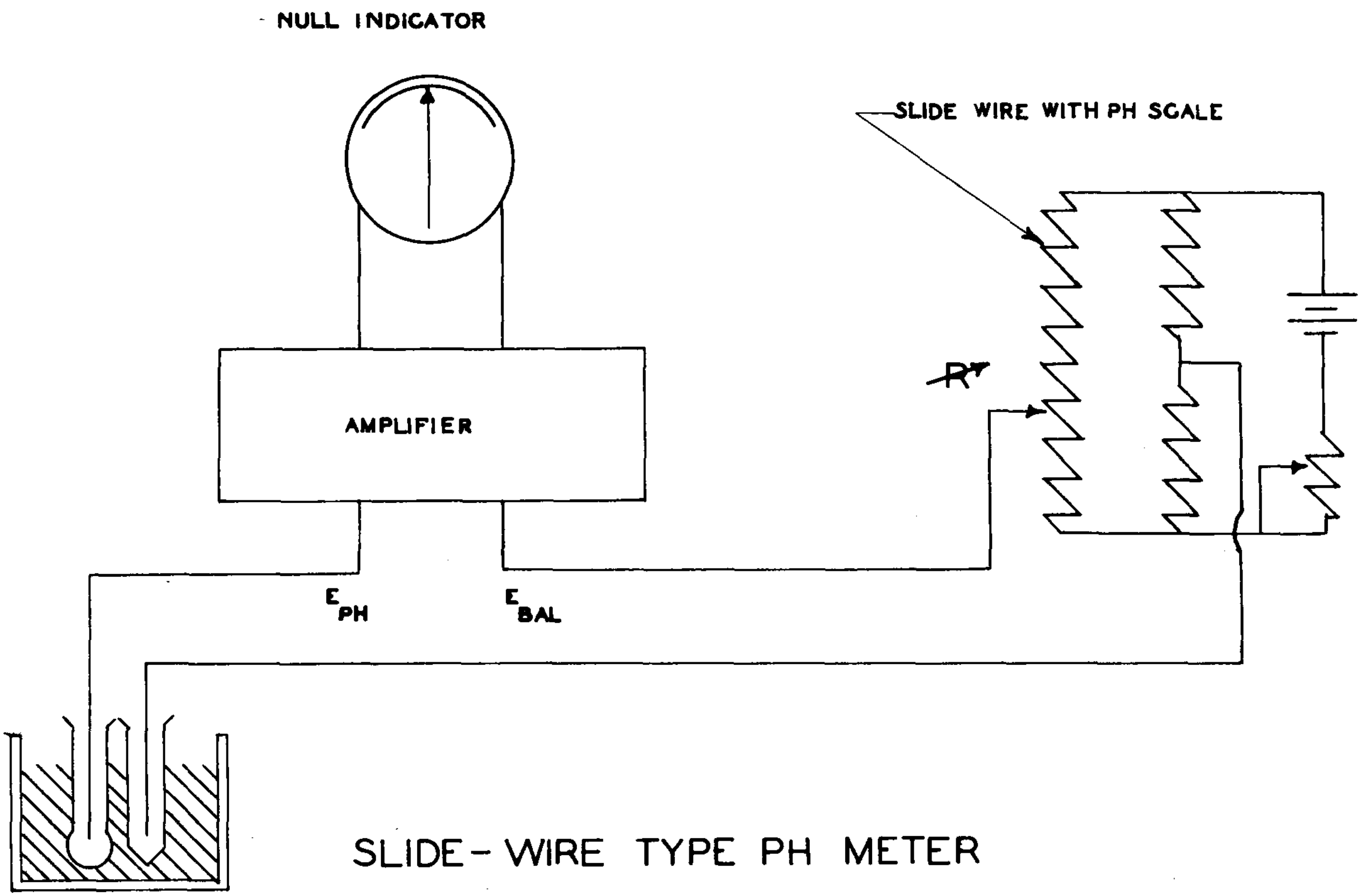
E_6 = 0

E_7 = CONSTANT

$$\Delta EMF = \Delta E = C \cdot \Delta PH$$

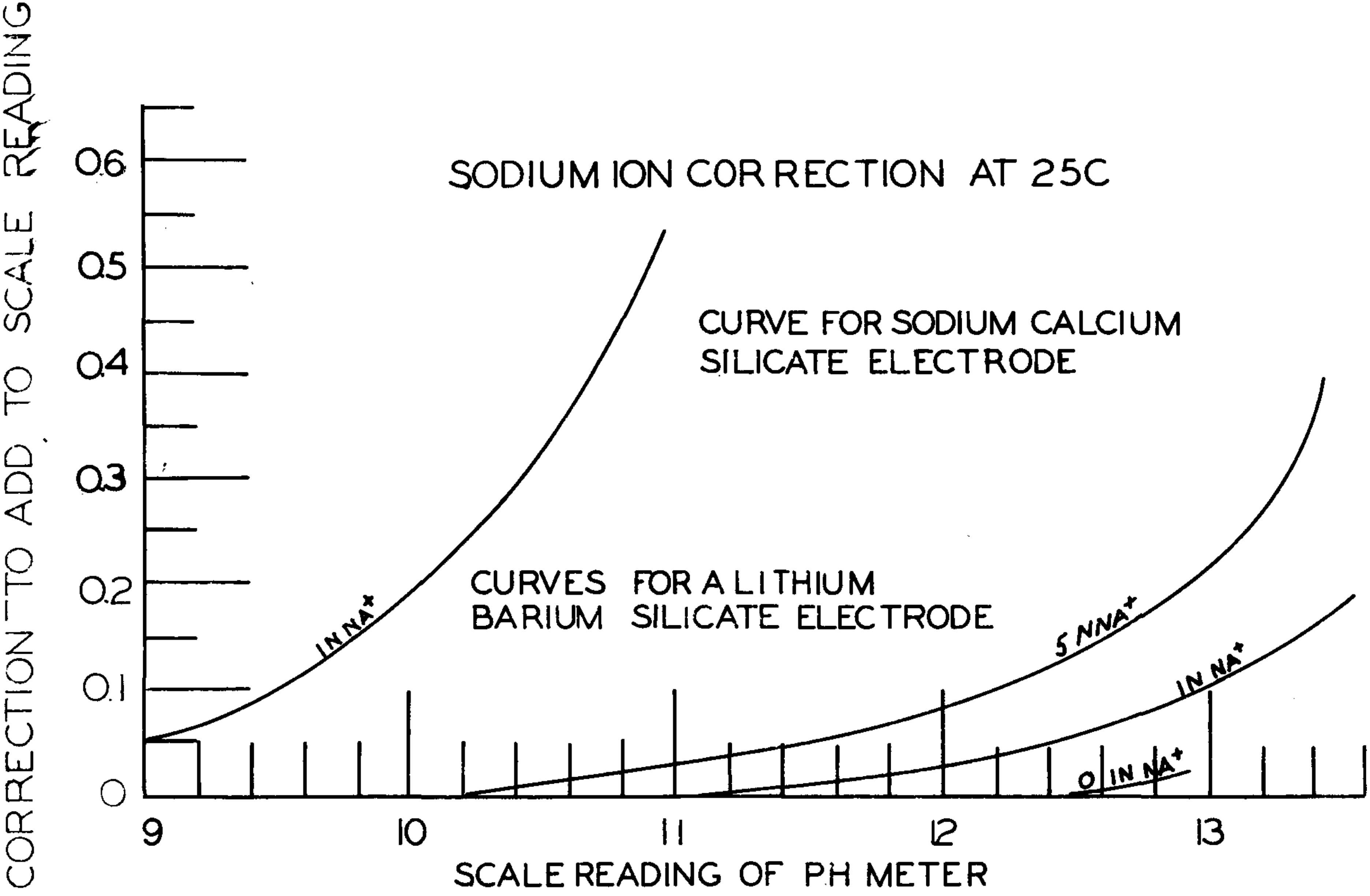
POTENTIALS INVOLVED IN PH MEASUREMENT

FIGURE I



SLIDE - WIRE TYPE PH METER

FIGURE II

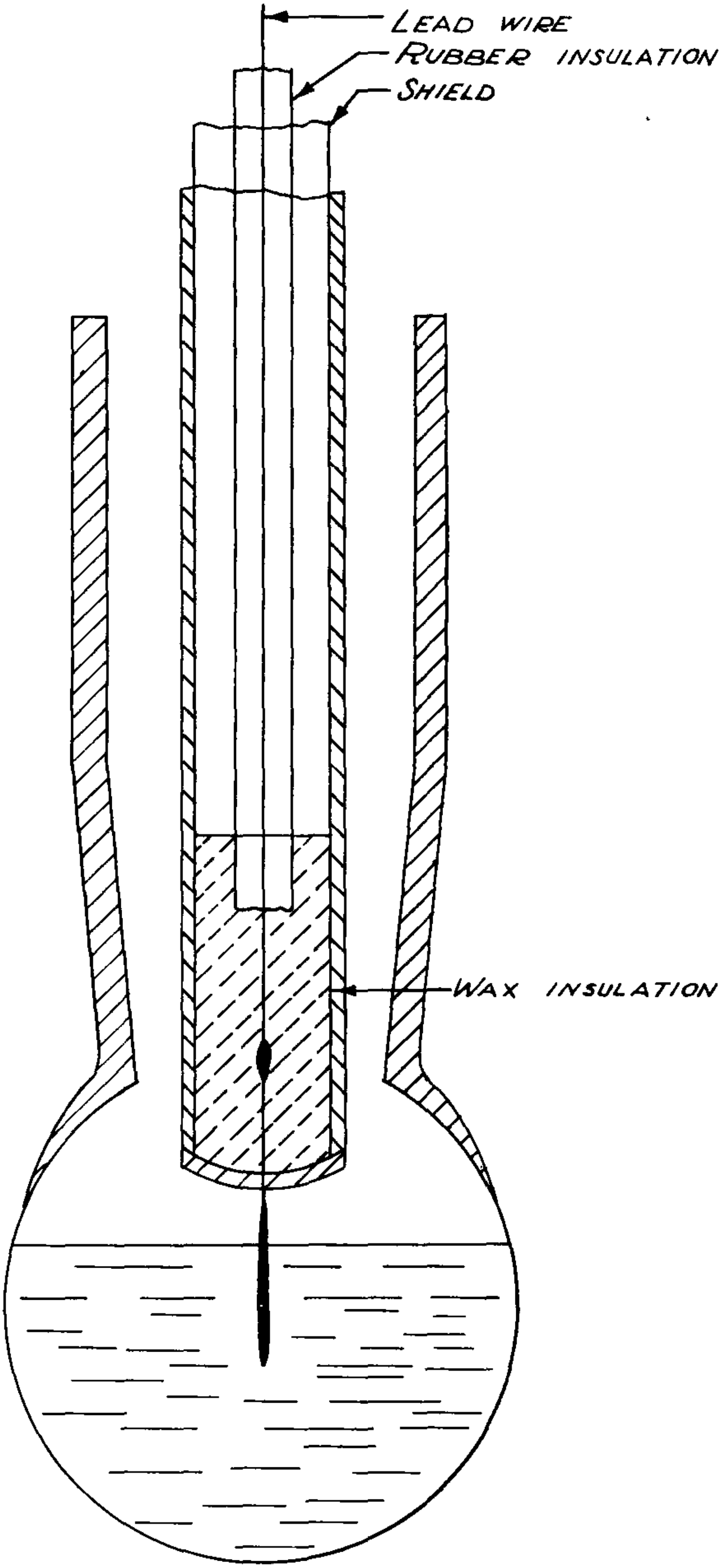


SODIUM ION ERRORS

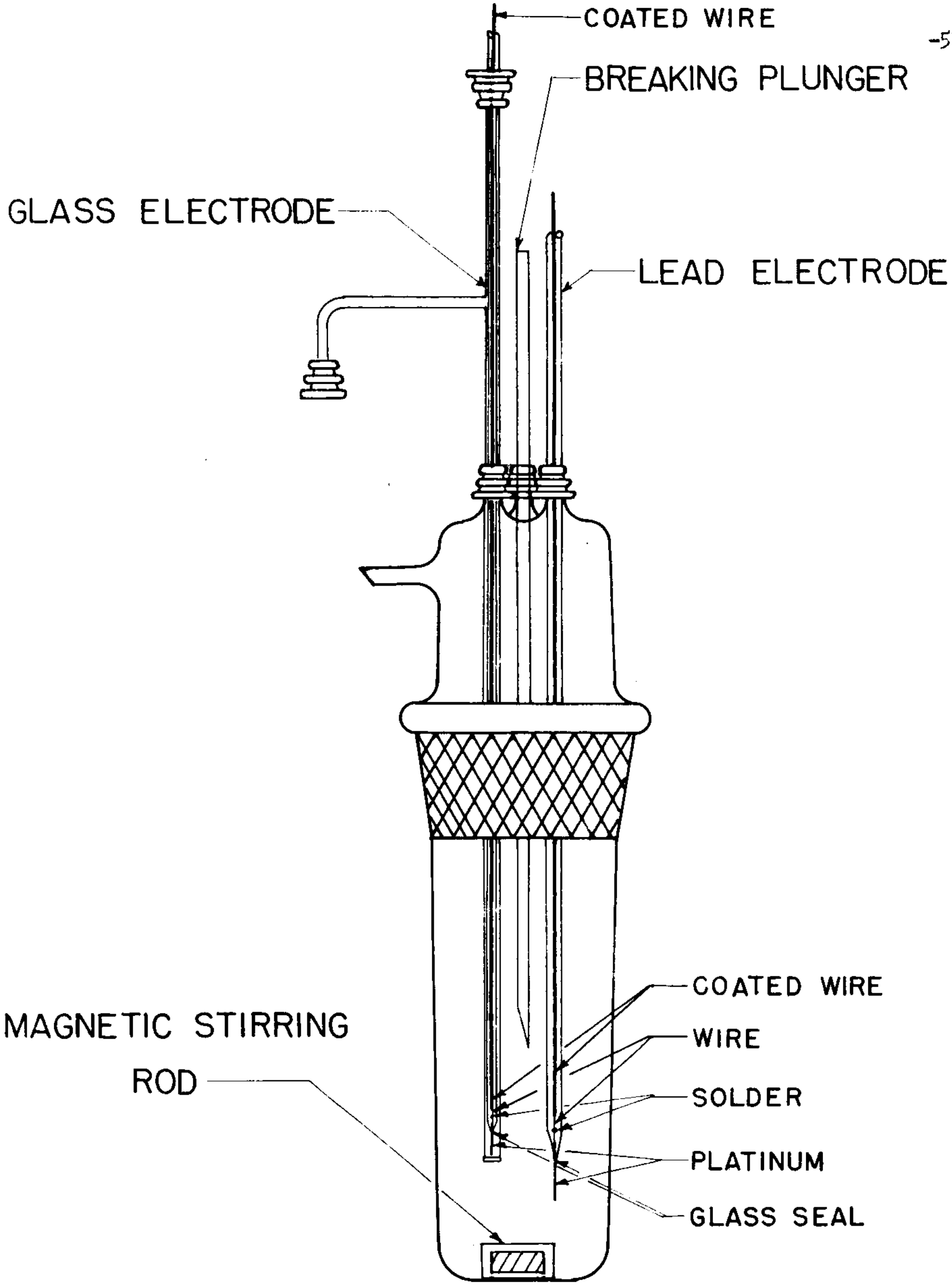
FIGURE III

Beckman Instruments

FIGURE IV



GLASS ELECTRODE



REACTION CELL

FIGURE V

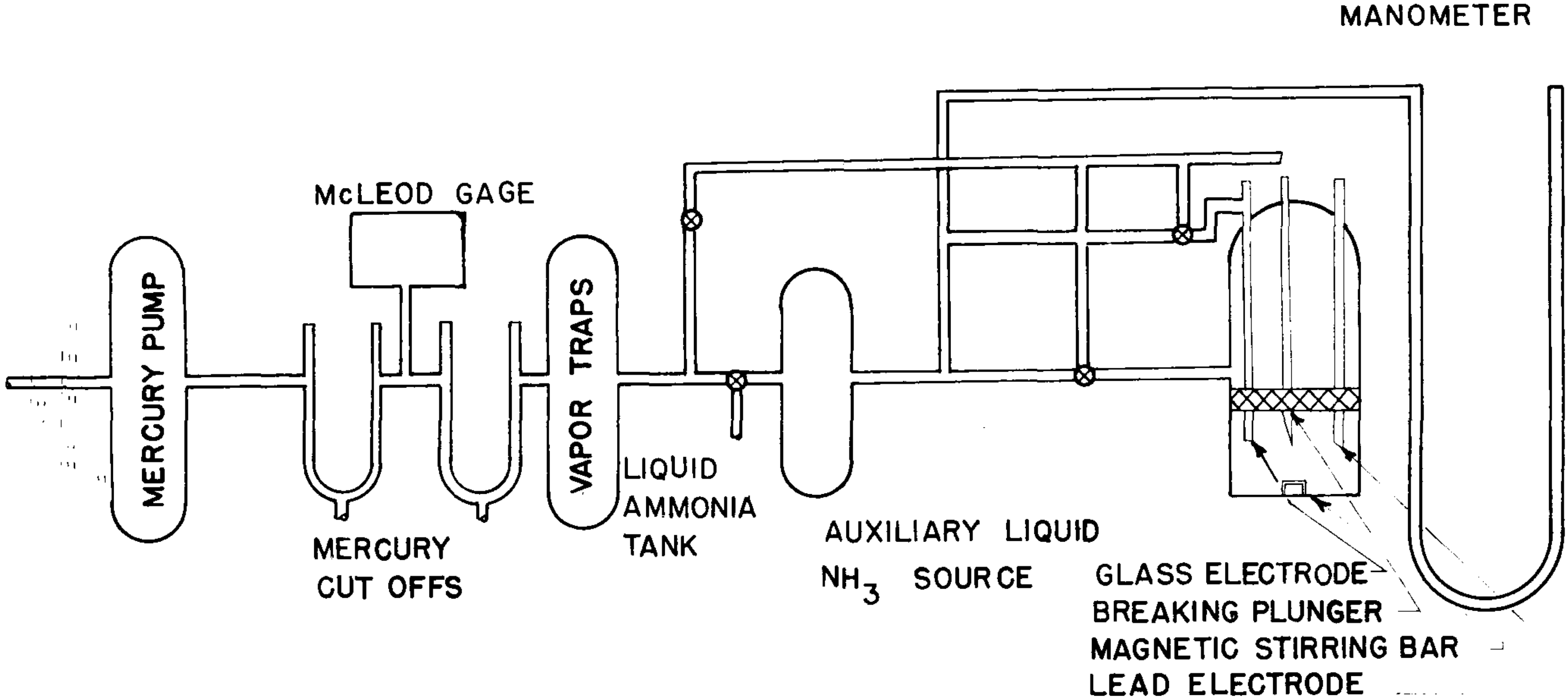
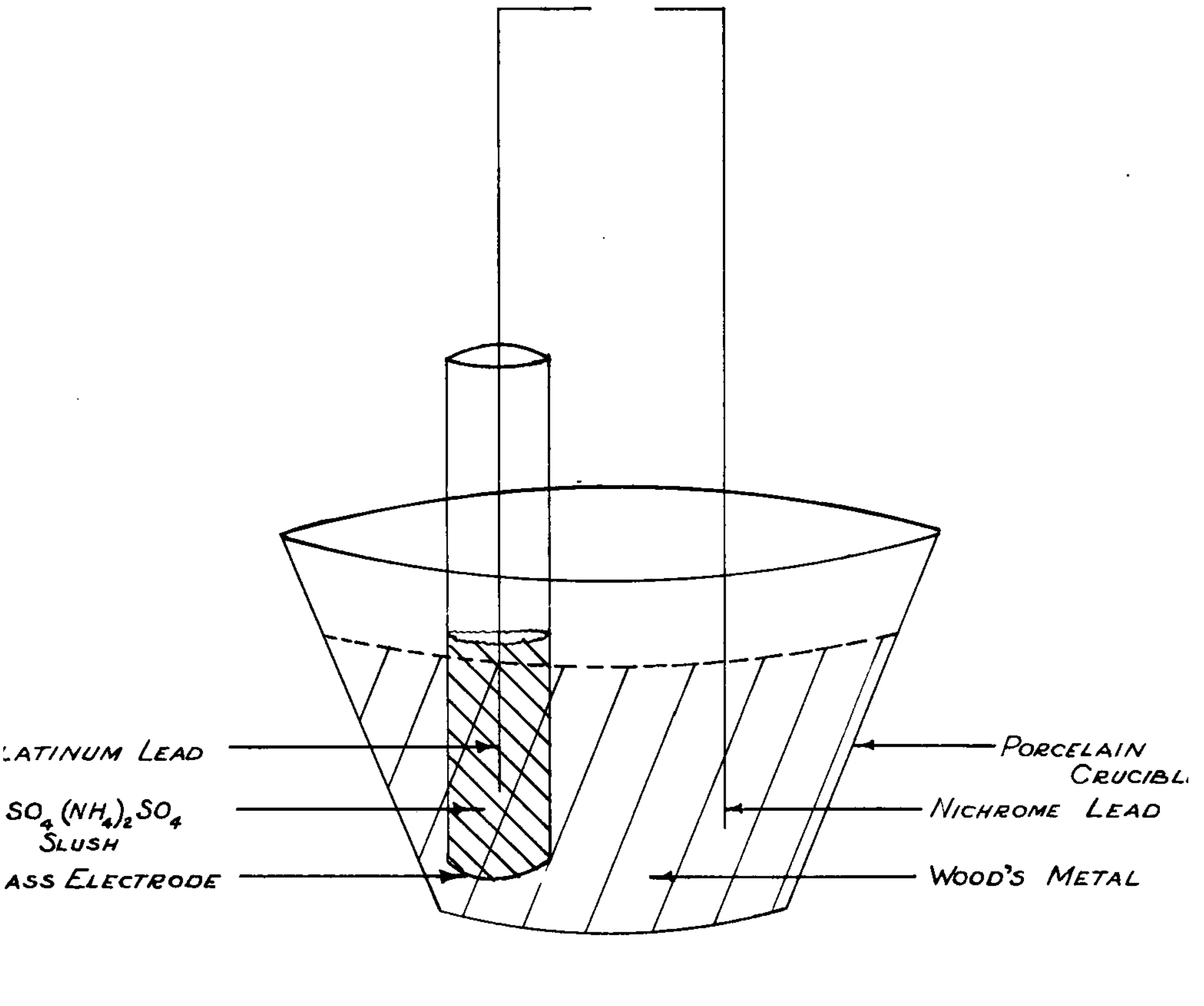

MANOMETER
McLEOD GAGE
MERCURY PUMP
VAPOR TRAPS
LIQUID
AMMONIA
TANK
MERCURY
CUT OFFS
AUXILIARY LIQUID
NH3 SOURCE
GLASS ELECTRODE
BREAKING PLUNGER
MAGNETIC STIRRING BAR
LEAD ELECTRODE

FIGURE VI

FIGURE VII



SYSTEM FOR AMMONIATING GLASS

FIGURE VIII

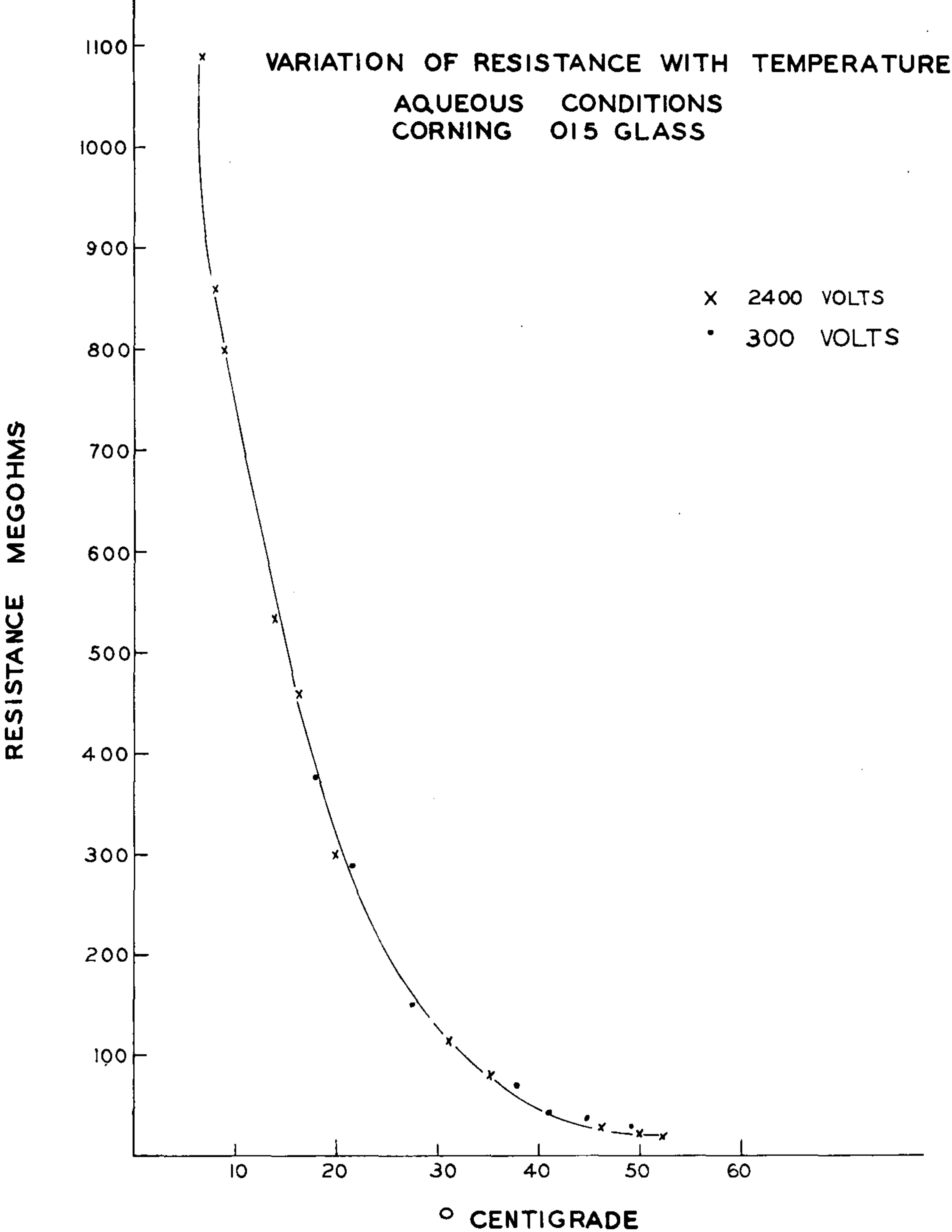

VARIATION OF RESISTANCE WITH TEMPERATURE
AQUEOUS CONDITIONS
CORNING 015 GLASS
X 2400 VOLTS
• 300 VOLTS
RESISTANCE MEGOHMS
1100
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
° CENTIGRADE

FIGURE IX

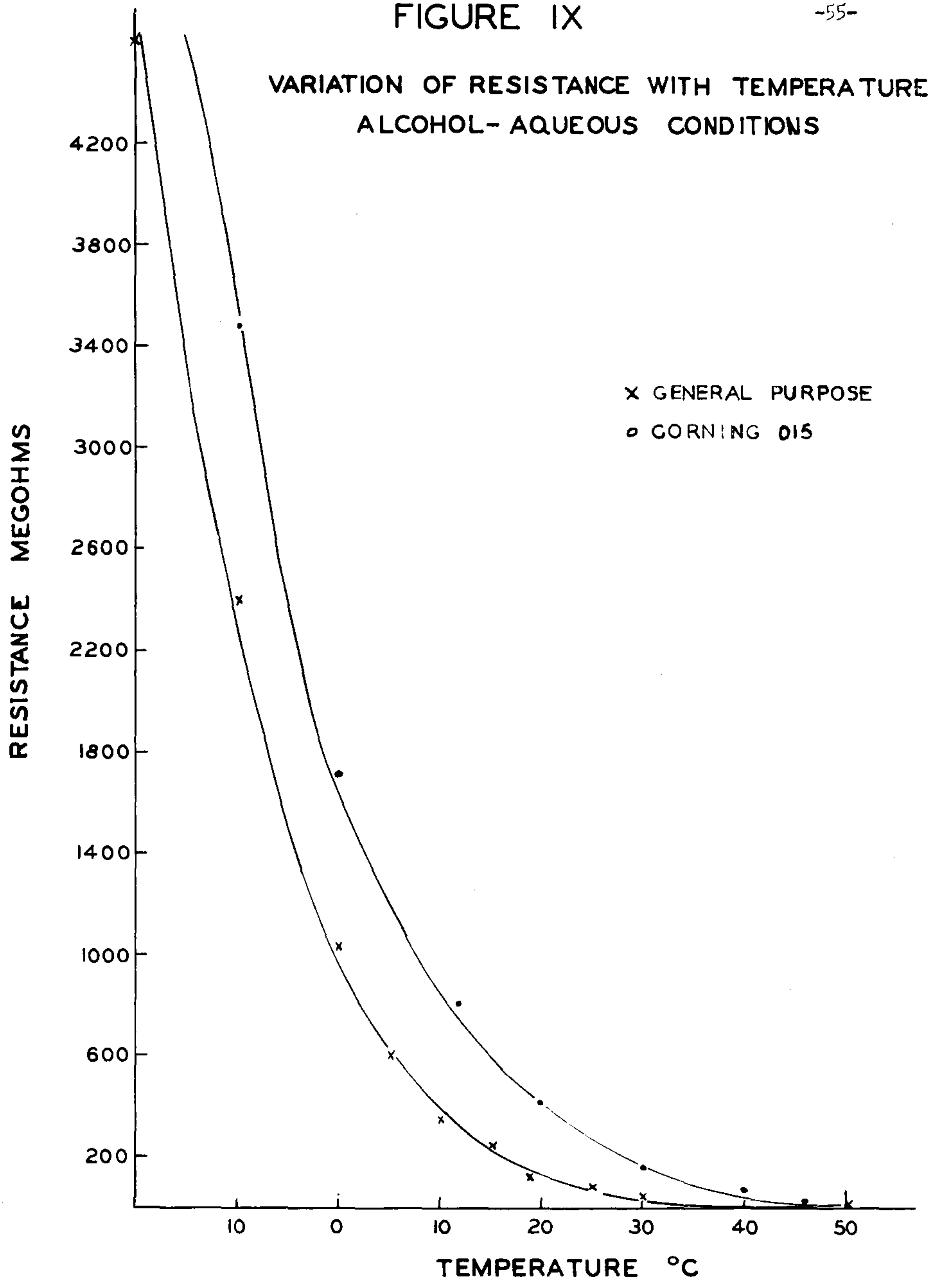

VARIATION OF RESISTANCE WITH TEMPERATURE
ALCOHOL-AQUEOUS CONDITIONS
X GENERAL PURPOSE
o CORNING 015
RESISTANCE MEGOHMS
4200
3800
3400
3000
2600
2200
1800
1400
1000
600
200
10
0
10
20
30
40
50
TEMPERATURE °C

FIGURE X

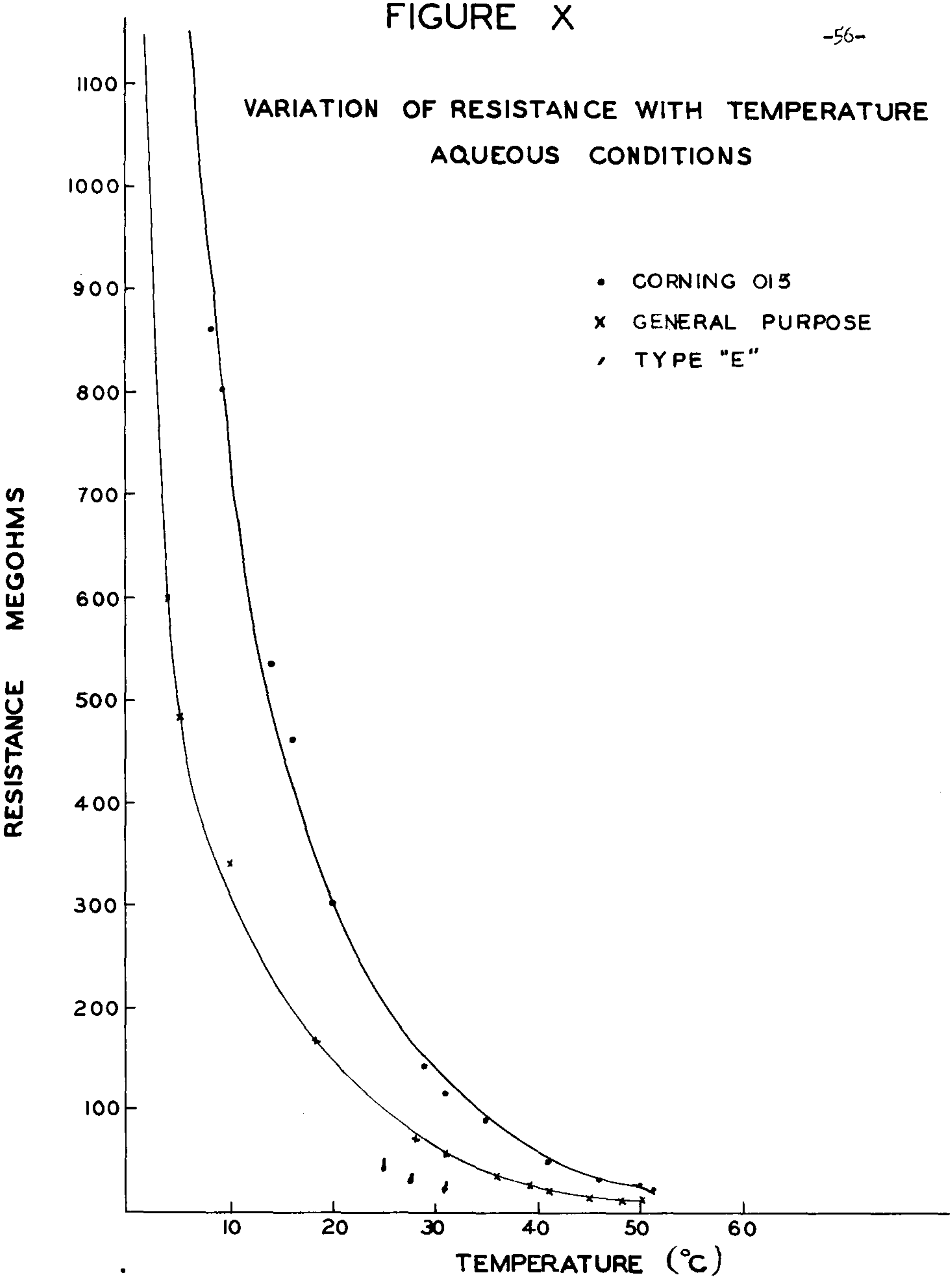

VARIATION OF RESISTANCE WITH TEMPERATURE
AQUEOUS CONDITIONS
• CORNING 015
x GENERAL PURPOSE
/ TYPE "E"
RESISTANCE MEGOHMS
1100
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
TEMPERATURE (°C)

FIGURE XI

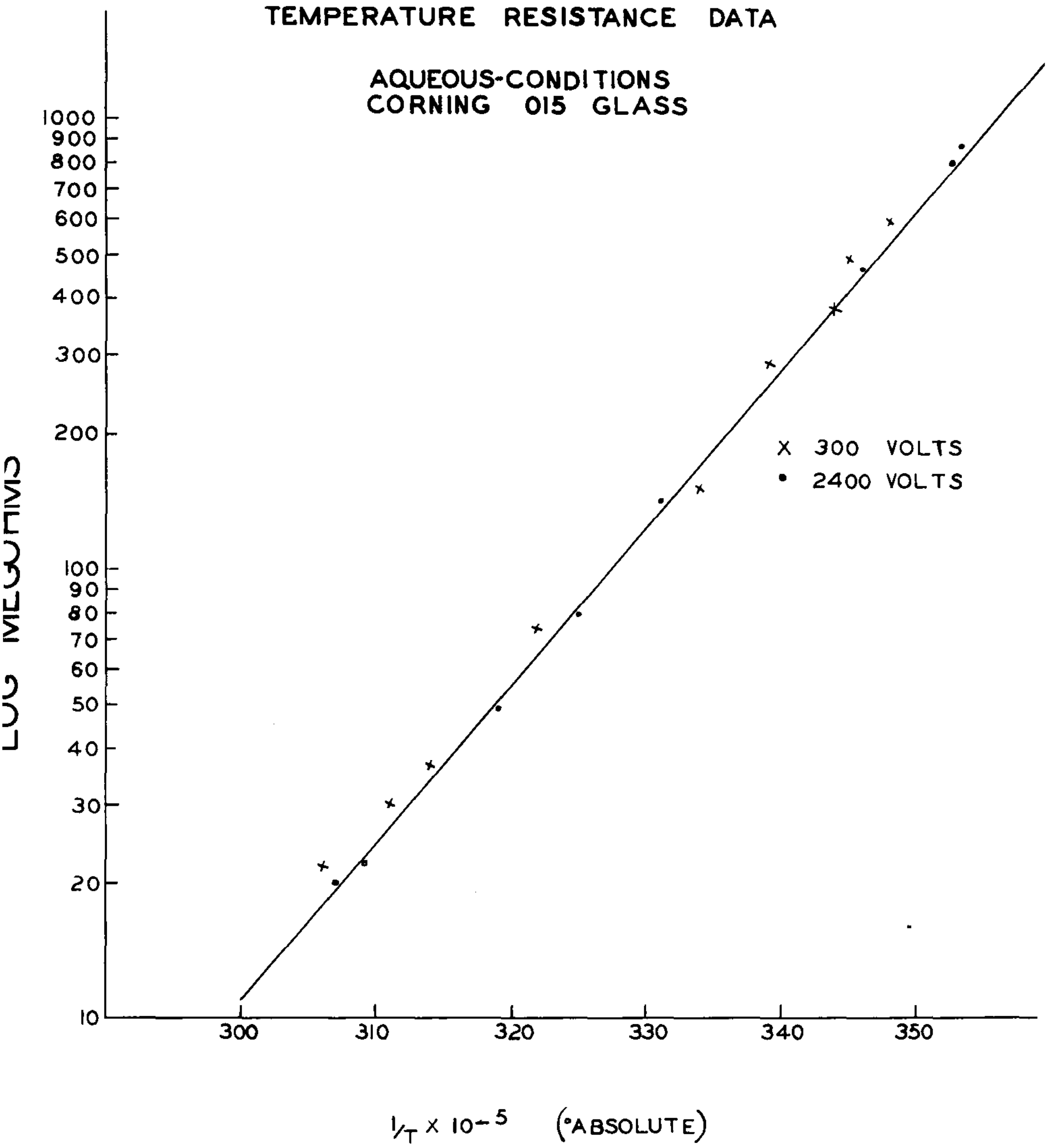
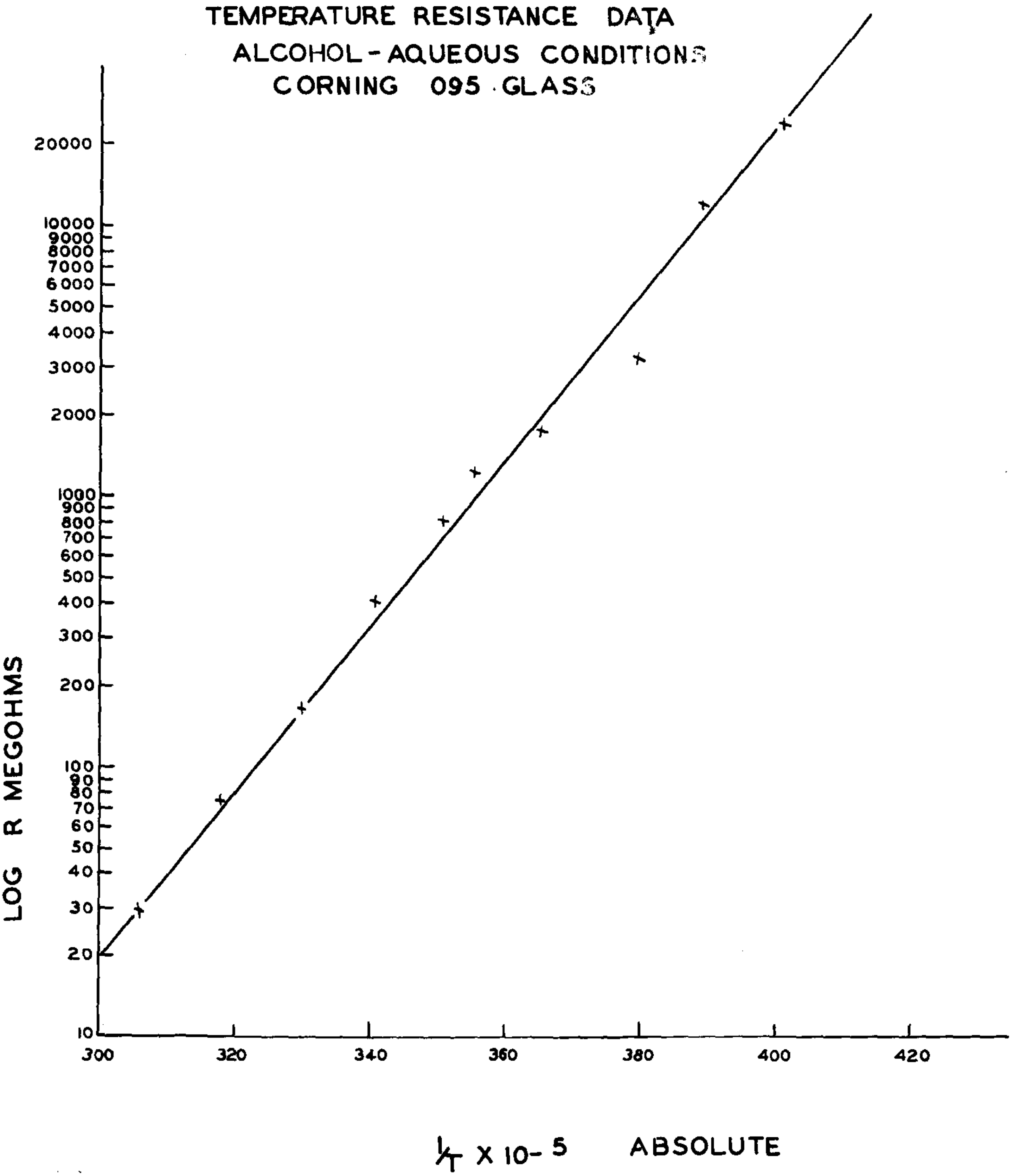

TEMPERATURE RESISTANCE DATA
AQUEOUS-CONDITIONS
CORNING 015 GLASS
LOG MEGOHMS
1000
900
800
700
600
500
400
300
200
100
90
80
70
60
50
40
30
20
10
X 300 VOLTS
• 2400 VOLTS
300
310
320
330
340
350
1/T × 10-5 (°ABSOLUTE)

FIGURE XII


TEMPERATURE RESISTANCE DATA
ALCOHOL-AQUEOUS CONDITIONS
CORNING 095 GLASS
LOG R MEGOHMS
20000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
900
800
700
600
500
400
300
200
100
90
80
70
60
50
40
30
20
10
300
320
340
360
380
400
420
1/T X 10-5 ABSOLUTE

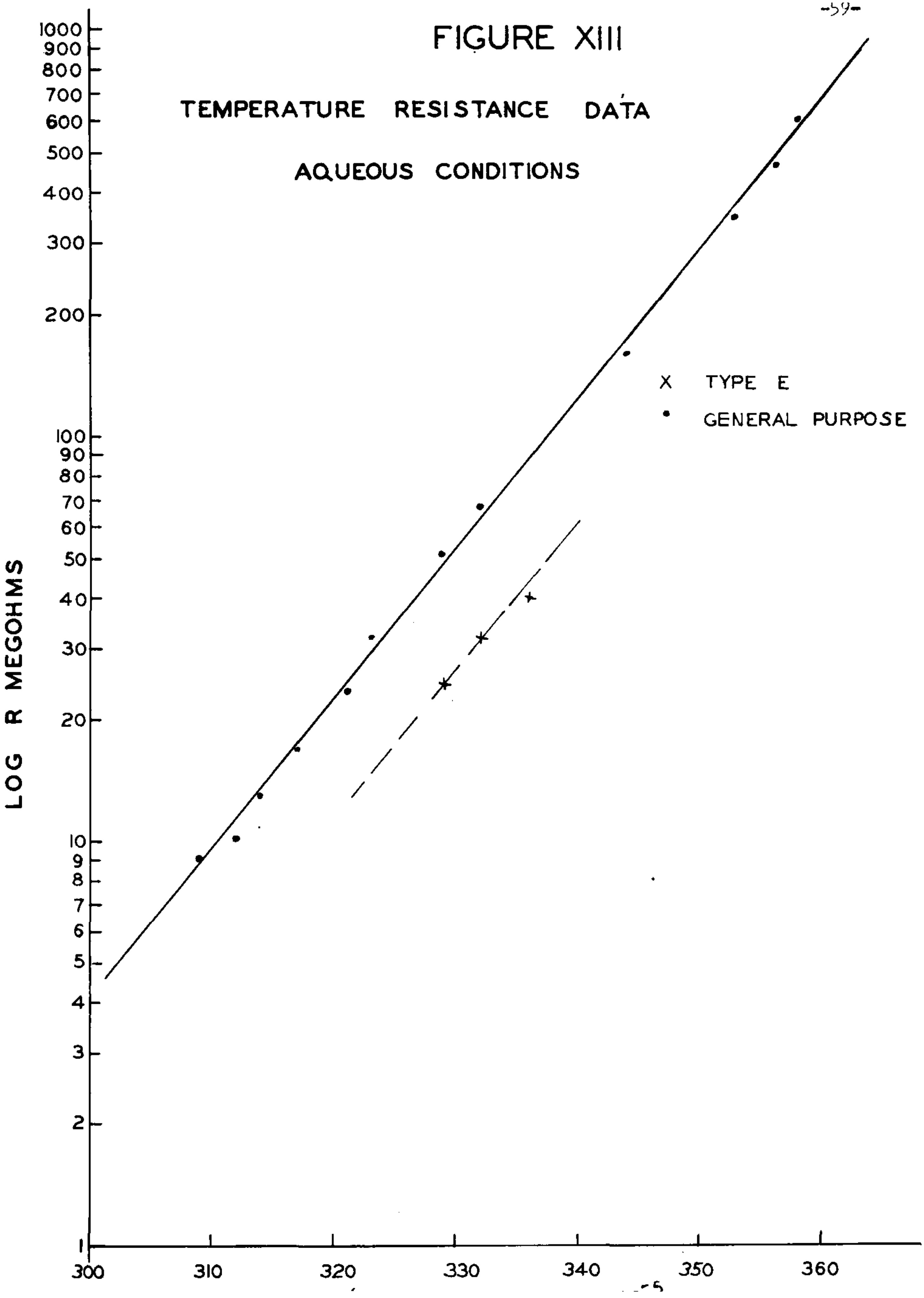
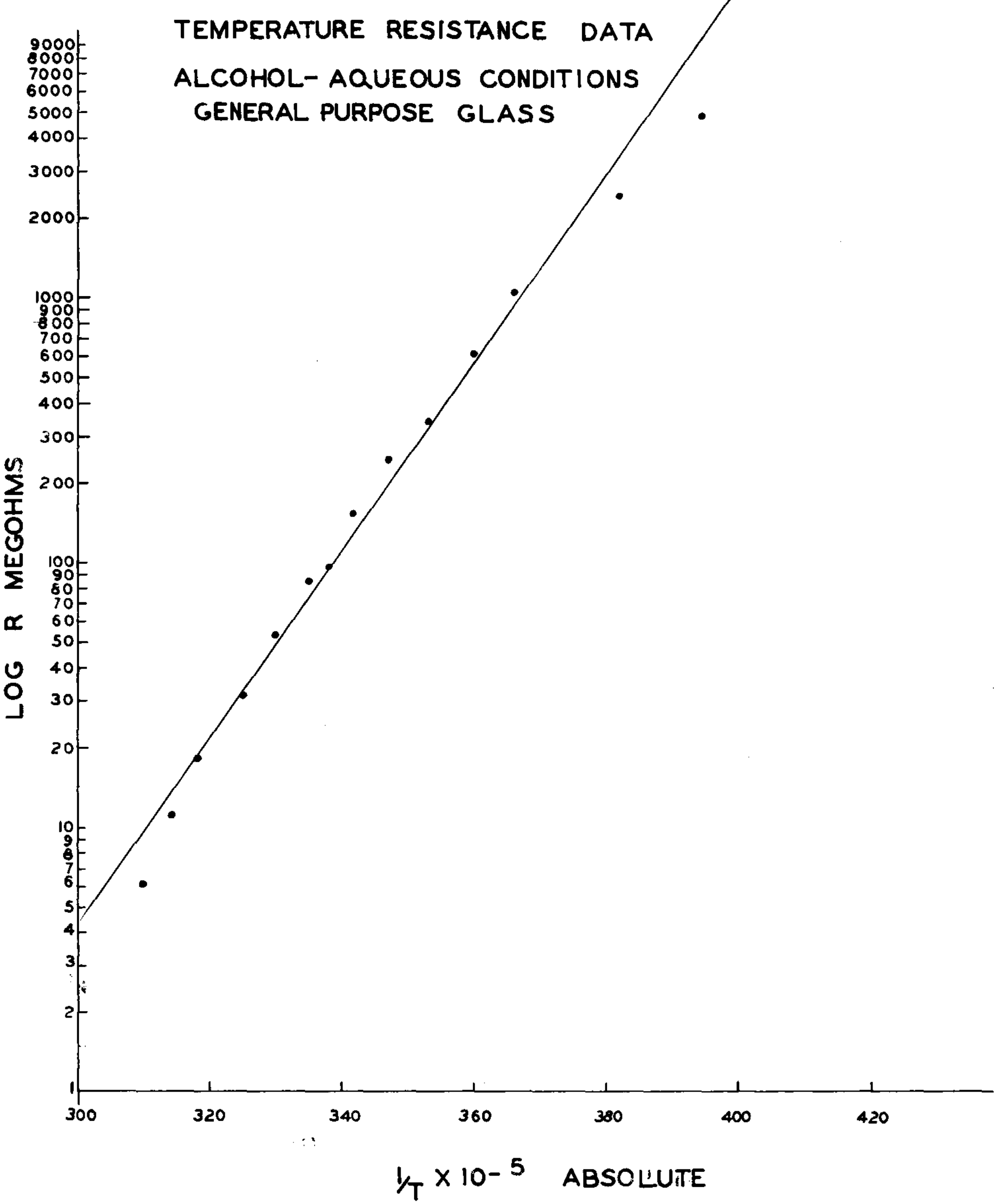


FIGURE XIII
TEMPERATURE RESISTANCE DATA
AQUEOUS CONDITIONS
X TYPE E
• GENERAL PURPOSE
LOG R MEGOHMS
1000
900
800
700
600
500
400
300
200
100
90
80
70
60
50
40
30
20
10
9
8
7
6
5
4
3
2
1
300
310
320
330
340
350
360

FIGURE XIV


TEMPERATURE RESISTANCE DATA
ALCOHOL- AQUEOUS CONDITIONS
GENERAL PURPOSE GLASS
LOG R MEGOHMS
9000
8000
7000
6000
5000
4000
3000
2000
1000
900
800
700
600
500
400
300
200
100
90
80
70
60
50
40
30
20
10
9
8
7
6
5
4
3
2
1
300
320
340
360
380
400
420
1/T X 10- 5 ABSOLUTE

BIBLIOGRAPHY

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PART II

SELECTIVELY PERMEABLE CATION EXCHANGE MEMBRANES

INTRODUCTION

In Part I of this dissertation, it was demonstrated that the glass electrode is not sensitive to changes of ammonium ion concentration in liquid ammonia. It may be considered that in aqueous media the response of the glass electrode to a change in hydrogen ion concentration results from a change in the dynamic equilibrium which exists between the hydrogen ions in solution and those on the surface of the glass. Therefore, the glass which separates the reference electrode solution from a test solution may be considered to behave as a membrane made of ion exchange material. In contrast to the glass membrane, the ion exchange membranes have a high conductivity in electrolytic solutions at -50°C as well as at 25°C[2, 18]; and it was reasonable to expect that they would conduct electricity in liquid ammonia. For these reasons, the study of cells with an ion exchange membrane in place of the glass membrane was undertaken. In this part of the dissertation, the successful use of an ion exchange membrane in place of the glass membrane is reported.

In aqueous media, membranes made of ion exchange resins have been used to determine activity coefficients and to study membrane equilibria[11, 5, 7]. The research reported in this dissertation demonstrates that ion exchange membranes can be used in liquid ammonia in cells analogous to those used for the glass electrode. Measurements made with such cells enable the calculation of many cationic or anionic concentrations (rather than specifically hydrogen ion concentrations, which alone are calculable when the glass electrode is used), and ratios of activity coefficients may be calculated for certain of the salts in the test solutions.

In the first section, the mechanics of the ion exchange membrane and the findings of previous workers will be discussed. The second section includes a description of the cell system used in the research reported herein and a derivation of necessary equations. This is followed by the experimental section which demonstrates that in the dilute region the logarithm of the cationic concentration is a linear function of the cell potential. Finally, the relationship between the cell potential and the cationic concentration is used to calculate ratios of activity coefficients which are compared with those found previously by other workers[15].

This work represents the first reported study of the use of ion exchange membranes in liquid ammonia systems.

JUNCTION POTENTIALS PRODUCED BY SELECTIVELY PERMEABLE ION EXCHANGE MEMBRANES

The electrochemical properties and uses of ion exchange membranes are dependent upon the fact that they create a rather special type of junction between two solutions. It will be helpful in the development of an understanding of the nature of the ion exchange membrane junctions to review very briefly two familiar types of junctions; the metallic junction which is specifically reversible to one of the ions in solution and the non-specific liquid junction. It will be shown that the membrane junction is similar in certain respects to the liquid junction and in other respects to the metallic junction. A simplified schematic representation of the membrane's mode of action will be utilized to make clear the relationship of the membrane junction to the other two types of junctions. This will be followed by a brief discussion of factors controlling the use of ion exchange membranes as electrochemical junctions.

Liquid Junction - When two solutions containing different concentrations of the same electrolyte are in contact, a potential will generally exist at the junction[5].

Reference Electrode	$Ag^{+}NO_3^{-}$ a_1	Liquid Junction	$Ag^{+}NO_3^{-}$ a_2	Reference Electrode
		E_1		

In the cell system shown above, the more concentrated solution will tend to diffuse into the more dilute one. The rate of migration of each ion is dependent upon its mobility and concentration. Differences in speeds of migration of various ions cause a potential which, for the case of constant mobility of ions in the junction region, may be expressed by the well known equation[3, 18]:

$$E_1 = (2t_+^+ - 1)\ RT/F \ln a_1/a_2$$

or (1)

$$E_1 = \frac{t_+ - t_-}{t_+ + t_-}\ RT/F \ln a_1/a_2$$

in which $t_+ + t_- = 1$.

Obviously, E is a function of the transference numbers of anions and cations (t_+ and t_-). Frequently these transference numbers have a value of approximately 0.5, and the resultant liquid junction potential is extremely small if it exists at all. If the migration of the nitrate ion in the cell illustrated could be completely restrained ($t_- = 0$ and $t_+ = 1$), the potential would be caused by the diffusion tendency of the silver ion and equation (1) would then become:

$$E = RT/F \ln a_1/a_2 \qquad (2).$$

There are two types of junctions in which this restriction of nitrate ion migration may be attained, namely a metallic junction and an ion exchange membrane junction.

Metallic Junction - A familiar cell system in which two solutions are separated by a metallic junction which is specifically reversible to one of the ions in solution is shown below:

Reference Electrode	$Ag^{+}NO_3^{-}$ a_1	Silver	$Ag^{+}NO_3$ a_2	Reference Electrode

E_2

Any current passing through the junction of this cell must be carried by the silver ion; thus t_{Ag^+} and $t_{NO_3^-}$ are equal to unity and zero respectively. The junction potential in this system, which is expressed by equation (2), represents the maximum value which can be obtained for such a junction potential involving two solutions of silver nitrate.

Ion Exchange Membrane Junction - The use of the metallic junction to restrict the migration of the negative ions limits the study of concentration cells to salts of metals which form satisfactory metallic junctions. For example, the activities of salts of the alkali metals in water cannot be studied by using a cell with metallic junctions because these metals would not form suitable junctions with aqueous solutions. A more general method for eliminating the migration of negative ions may be found in the use of ion exchange membranes as junctions. Membranes made of ion exchange material act as ion sieves. An ideal membrane made of a cation exchange material would allow only cations to pass through. This simulates a metallic junction, but it can be used for salts of any metal.

Consider the cell system represented by:

Reference Electrode	$Ag^{+}NO_3^{-}$ a_1	Ion Exchange Membrane	$Ag^{+}NO_3^{-}$ a_2	Reference Electrode.

E_L

A cation-exchanger forms the junction between the two solutions. The ideally selective cation exchange membrane is one for which $t_+ = 1$ and $t_- = 0$. Equation (1) is valid for any junction and here reduces to the equation found for the metallic junction (equation (2)).

Sollner[18] has demonstrated experimentally that an ideally selective membrane may be achieved in practice. He studied the behavior of a number of electrolytes at various concentrations in a cell system such as that described above. By keeping the ratio of the concentrations of the solutions in the cells constant at 2:1 he minimizes the effect of changes of activity coefficients with increasing concentration. The following table compares the junction potentials calculated according to equation (2) with the values found experimentally.

Concentration of Electrolyte C_2/C_1 (equivalents/liter)	Electrolyte	$E_{Calc.}$ mv	$E_{Expt.}$ mv
.002/.001	KCl	17.5	17.5
.004/.002	KCl	17.3	17.3
.04/.02	KCl	16.6	16.6
.002/.001	K_2SO_4	17.4	17.4
.02/.01	K_2SO_4	16.7	16.7
.002/.001	HCl	17.4	17.4

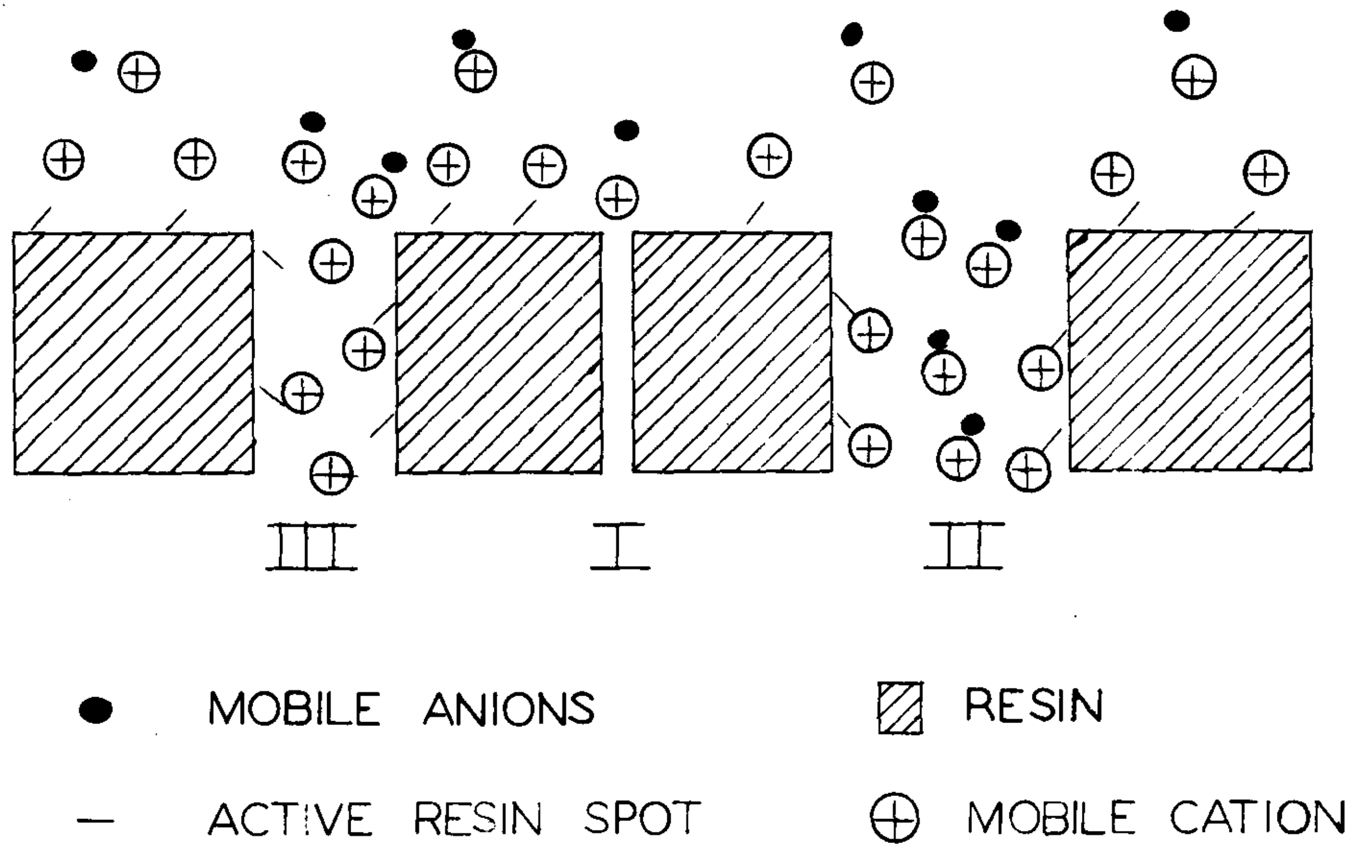
A new tool in electrochemistry was established by this experimental verification of the fact that under certain conditions cation exchange membranes are permeable only to cations. The type of information that this method yields is obvious from equation (2). Activities and activity coefficients for a solution of a single electrolyte can be determined easily and rapidly. Similarly, changes in concentrations can be determined. The applications of the membranes in the study of electrolytic solutions are not restricted to aqueous media; but, as shown in this research, may be applied to liquid ammonia solutions.

Discussion of Membrane

The membrane consists of a three dimensional meshwork of cross-linked chains of an organic polymer. A simplified diagram of the membrane is shown in Figure I[7].

Either actively or potentially charged functional groups are located on the chains. Examples of such groups are SO_3^- and COO^- in the case of cation exchange resins and RNH_3^+ and R_4N^+ for the anion exchangers. To maintain electrical neutrality a mobile ion of opposite charge must be associated with each charged spot on the membrane lattice. If this membrane is placed in a salt solution, these mobile ions can be exchanged or replaced by ions of a like charge from the solution. If a membrane has an ideal physical structure, only ions of the same sign as the mobile ion in the membrane will diffuse through, for example, only positive ions may be transported through cation exchanging resins.

The function of the membrane is comparable to that of an ionic sieve or screen[13, 14, 20]. The mechanics of this screening effect and the factors contributing to it can be shown graphically by means of the following diagram:



Three situations can occur in a membrane which has a variable pore size. Condition I results if the ion in solution is too large to pass into the pore. This pore would not make any contribution to any electrochemical action and may, therefore, be disregarded. The opposite extreme of condition I would arise when the pore is of such a size that no screening effect exists (II). Such pores exist very infrequently in the membrane but are mentioned to make the discussion completely general. Finally, the ideal pore size is that which is large enough to allow the cations of the solution to flow through, but small enough that the anions are repelled (III). The anions are repelled by the negatively charged groups existing throughout the membrane. Electrical neutrality within the membrane is maintained between the mobile cations and negative functional groups. The concentration of the functional groups and mobile cations within the membrane is very great (often five to seven molar), compared to the concentration of anions in the solution outside the membrane. In order for an anion to enter such a pore in the membrane, it would not only have to overcome the repulsion of the negative lattice, but also move from a region of lower salt concentration to one of much higher within the membrane. Therefore, the cations alone carry the current through this pore; the transference number of the positive ion (t_+) would be 1. The potential existing across the membrane at pore II would be equal to that calculated by equation (1), whereas that at pore III could be obtained by use of equation (2). The desirable membrane should have pores of the type III.

Controlling Conditions for Ideal Ionic Selectivity

As previously discussed, the pore size of the membrane controls to a large extent the ionic selectivity. By careful regulation of experimental conditions during the preparation of the membrane, the pore size can be controlled to such an extent that the resulting transference number (t_+) approaches, and in most cases equals unity for moderately dilute solutions. This ionic selectivity may be referred to as "Permselectivity".

As a corollary to the pore size of the membranes, the size of the ionic species in the solution also governs the permselectivity. A membrane which is to be used with large ions can maintain a high ionic selectivity with a relatively greater distribution of pore size. Indeed, a membrane may exhibit a positive transference number of unity in the presence of a cation of one size and a positive transference number less than unity in the presence of a cation of different size[18]. This, however, does not present an insurmountable problem in the use of membranes prepared from ion exchange materials, if proper caution is observed in selecting membranes suitable to the solutions under study.

It has been found experimentally that the transference number (t_+) deviates from unity in more concentrated solutions (Figure II)[7]. As the salt solution in contact with the membrane becomes more concentrated, the probability of diffusion of anions into the membrane increases (t_+ decreases). Data bearing on this point are summarized in the following table[18].

Concentration of Electrolyte KCl	Positive Transference Number
.002/.001	1.000
.04/.02	1.000
.1/.05	.994
.2/.1	.971
.4/.2	.935

In conclusion, it is evident that in aqueous solutions, the membrane will serve as a valuable tool in electrochemical studies. Its uses as a reversible non-specific electrode are potentially manyfold.

SELECTIVELY PERMEABLE ION EXCHANGE MEMBRANES AS A TOOL IN THE CHEMISTRY OF LIQUID AMMONIA

The work to be presented concerns the extension of the use of ion exchange membranes to liquid ammonia and, incidentally, to alcohol. The type of information which can be obtained in these media is identical with that which was obtained in aqueous solutions, i.e. the interrelationship of activity coefficients, cationic concentrations, and transference numbers[18].

Ideally, the following cell system would be preferred:

Solid Reference Electrode	Ammonium Nitrate c_1 Liquid Ammonia	Membrane	Ammonium Nitrate c_2 Liquid Ammonia	Solid Reference Electrode

The expression for the potential of the total system would be:

$$E = (2t_+ - 1)\, RT/F \ln \frac{(\gamma'_{\pm})(c_2)}{(\gamma_{\pm})(c_1)} + C \qquad (4)$$

where $\gamma_{\pm}$ is the mean activity coefficient of ammonium nitrate in liquid ammonia and t_+ is the positive transference number across the membrane. The transference number of the membrane can be determined by the method of Sollner[19], and then one can proceed directly to determine the activity coefficients or to measure ammonium ion concentrations.

Experimentally, this cell system was found impractical. The solid electrodes were not used and a metal-metallic ion electrode, i.e., lead-lead ion or silver-silver ion, served as reference. Although the initial experiments were made with cells in an all ammonia system, such cells were abandoned because the membranes could not withstand the vacuum technique used for the handling of liquid ammonia. Accordingly, a system was designed in which the membrane was not endangered by evacuation. It is schematically represented by:

Silver	Silver Nitrate .001 M	Ammonium Nitrate Varying Concentrations	Membrane	Ammonium Nitrate .001 M	Silver Nitrate .001 M	Silver
	Liquid Ammonia			Alcohol		

This arrangement introduced an unusual combination of features which requires a more complete theoretical treatment. These features are: (a) the use of mixed media for which there does not appear to be a precedent, and (b) the use of mixed electrolytes.

Two sets of experiments were used to determine the applicability of a cell system involving two separate solvents. First, the constancy of the potential of a cell system, which was identical to the one diagramed above except that a liquid junction replaced the membrane, was investigated. Second, in order to test the action of the membrane itself when used in different media, a water-water, then alcohol-water, and finally an alcohol-ammonia system were studied. The data demonstrated that the migration of the anion was, indeed, restricted in a reproducible manner regardless of the medium used.

The use of reference electrodes which were dependent on the concentration of a cation in solution makes the theoretical interpretation of the potentials produced by the system more complicated from a mathematical point of view[10]. Nevertheless, clear interpretation of the factors contributing to the potential of the cell system is possible.

The change in potential upon addition of NH_4NO_3 to one side of the cell system can be represented by an equation analogous to equation (3):

$$E = (2t_+ - 1)\ RT/F \ln \frac{(\gamma_\pm)_B\ (C_B)}{(\gamma_\pm)_A\ (C_A)} \quad . \qquad (4)$$

This equation, the derivation for which is given in the next section, can be used to evaluate the ratio of activity coefficients of the ammonium salt at various concentrations, once the transference number of the membrane is known.

THE JUNCTION POTENTIAL PRODUCED ACROSS A MEMBRANE WHICH SEPARATES DIFFERENT SOLVENTS CONTAINING MIXED ELECTROLYTES

Electrochemical Considerations

The cell design described in the preceding section introduces new factors with regard to the membrane potential. Since the chemical potential of a substance does not depend directly on the nature of the solvent, the fundamental electrochemical equations which are known to be valid for aqueous media, can be applied to any solvent. Therefore, a general equation for the potential of the cell system may be derived.

For the cell:

Silver Metal	Ag^+ (.001 M)	NH_4^+		Membrane	NH_4^+(.001 M)	Ag^+(.001 M)	Silver Metal
	NO_3^-(.001 M)	NO_3^-			NO_3^-(.001 M)	NO_3^-(.001 M)	
	Liquid Ammonia I				Alcohol II		
E_1				E_2			E_3 .

The electrode potential E_1 may be expressed by:

$$E_1 = RT/F \ln (a_{AgNO_3})_I$$

where a_{AgNO_3} is the mean activity of silver nitrate in liquid ammonia.

In an analogous manner, E_3 may be represented by:

$$E_3 = - RT/F \ln (a_{AgNO_3})_{II}$$

where $(a_{AgNO_3})_{II}$ is the mean activity of silver nitrate in alcohol.

The potential at the membrane (E_2) depends on the activity of two cations, Ag^+ and NH_4^+. The Henderson-Plank[6, 12] equation, which has been used successfully in the calculations of liquid junction potentials for mixed electrolytes, may be applied to the above system. The derivation of this equation utilizes the concept that the junction consists of a continuous series of solutions produced by the mixing of the two solutions. This condition may be considered to be satisfied in the case of the membrane junction. The general form of the equation is:

$$E_L = RT/F \frac{\sum_n \left(u_i^{II}/z_i\right)a_i^{II} - \left(u_i^{I}/z_i\right)a_i^{I}}{\sum_n \left(u_i^{II}\, a_i^{II} - u_i^{I}\, a_i^{I}\right)} \quad \ln \frac{a_i^{I}\, u_i^{I}}{a_i^{II}\quad u_i^{II}} \qquad (5)$$

where u_i represents the mobility and z_i the charge of the ith ion. $\sum_n$ indicates a summation over all the ions, and the superscripts I and II distinguish between the ions in the solutions on either side of the junction.

For the membrane junction in a cell in which all of the ions are univalent, this equation reduces to:

$$E_L = RT/F \frac{(U_I - V_I) - (U_{II} - V_{II})}{(U_I + V_I) - (U_{II} + V_{II})} \;\ln\; \frac{(U_I + V_I)}{(U_{II} + V_{II})} \qquad (6)$$

where U, the total contribution of positive ions to the transport of current, and V, the total contribution of negative ions, may be more specifically defined as:

$$U_I = a^{+I}_{Ag^+} \; u^{+I}_{Ag^+} + a^{+I}_{NH_4^+} \; u^{+I}_{NH_4^+}$$

$$V_I = a^{-I}_{NO_3^-} \; u^{-I}_{NO_3^-}$$

$$U_{II} = a^{+II}_{Ag^+} \; u^{+II}_{Ag^+} + a^{+II}_{NH_4^+} \; u^{+II}_{NH_4^+}$$

$$V_{II} = a^{-II}_{NO_3^-} \; u^{-II}_{NO_3^-} \quad .$$

The ionic mobilities, u_+ and u_-, and the ionic activities, a_+ and a_- , for the mixture of electrolytes ($AgNO_3$ and NH_4NO_3) must be known in order to use equation (6) in calculating junction potentials. No such data are available for liquid ammonia or ethyl alcohol media, or for electrolytes within the exchange resin. Since the concentrations of the solutions in which the measurements were made were sufficiently low, properties which have been found to hold in dilute solutions of uni-univalent salts in many media may be used in the simplification of equation (6).

Assuming that the mobility of an ion is dependent only on the concentration of that ion and not on the ionic strength of the solution (Kohlrausch principle[4]), the mobility of the silver ion is independent of the concentration of other electrolytes. The same is true for other ions. Also, it is assumed that in dilute solution, the mobility of a specific ion does not change significantly with concentration.

Differences in mobilities may be expected between the various ionic species. However, the data below show that the mobilities of Ag^+

and NH_4^+ in liquid ammonia and in ethyl alcohol are very nearly equal. The ratio of equivalent conductances of NH_4NO_3 and $AgNO_3$ in liquid ammonia (-33.5°C) in the concentration range of 0.001 M to 0.004 M is between 1.01 and 1.04[8]. In ethyl alcohol the ratio of ionic conductances of NH_4^+ to Ag^+ at infinite dilution is 1.11[10], and the ratio of equivalent conductances of NH_4NO_3 and $AgNO_3$ at 0.005 M is 1.05[9]. Although the absolute mobilities in the membrane phase are unknown, it is to be expected that the relation between mobilities of ions found in a conventional solution will also hold true in the membrane.

Therefore, under the assumptions of independent ionic mobilities, of constant ionic mobilities over the concentration range investigated, and of a ratio of Ag^+ mobility to NH_4^+ mobility equal to 0.95 (NH_4/Ag^+ = 1.05) equation (6) becomes:

$$E_L = \frac{RT}{F} \frac{\left[u^o_{NH_4^+}\left(.95\, a^{+I}_{Ag^+} + a^{+I}_{NH_4^+}\right) - u^o_{NO_3^-} a^{-I}_{NH_4^+}\right] - \left[u^o_{NH_4^+}\left(.95\, a^{+II}_{Ag^+} + a^{+II}_{NH_4^+}\right) - u^o_{NO_3^-} a^{-II}_{NO_3^-}\right]}{\left[u^o_{NH_4^+}\left(.95\, a^{+I}_{Ag^+} + a^{+I}_{NH_4^+}\right) + u^o_{NO_3^-} a^{-I}_{NH_4^+}\right] - \left[u^o_{NH_4^+}\left(.95\, a^{+II}_{Ag^+} + a^{+II}_{NH_4^+}\right) + u^o_{NO_3^-} a^{-II}_{NO_3^-}\right]}$$

$$\ln \left[\frac{u^o_{NH_4^+}\left(.95\, a^{+I}_{Ag^+} + a^{+I}_{NH_4^+}\right) + u^o_{NO_3^-} a^{-I}_{NO_3^-}}{u^o_{NH_4^+}\left(.95\, a^{+II}_{Ag^+} + a^{+II}_{NH_4^+}\right) + u^o_{NO_3^-} a^{-II}_{NO_3^-}}\right] \qquad (7)$$

where u^{o}'s are the ionic mobilities of the indicated ions throughout the whole transition region.

The 0.95 coefficient of the activity of the silver ion in the above equation is of importance only when the concentrations of silver ions and of ammonium ions are nearly equal. For the case in which NH_4^+ concentration is several times as great as that of Ag^+, 1.00 may be used in place of 0.95 for the coefficient without changing the results significantly.

This simplification still leaves equation (7) unusable in the absence of some information about ionic activities. It has been found in water (and in other media) that activity coefficients of uni-univalent salts in dilute solutions are very nearly equal to each other(11); and the same may be expected to be true in liquid ammonia. It has been found to be true in alcohol solution(11). This assumption may only be well justified for liquid ammonia solutions which are very dilute. However, because the concentration of ammonium nitrate far exceeded that of silver nitrate at all times, except when very dilute solutions were used, the assumption was only of significance when the conditions existed for which it was most valid. If the same solvent were used on each side of the membrane, the effect of any inequality in the activity coefficients of the two salts would be minimized because the ratio of such activity coefficients would be nearly the same for each solution. Although different media were used on each side of the membrane, any difference between the ratio of activity coefficients of the univalent salts in one medium and the corresponding ratio in other medium cancel out because only differences in cell potentials (corresponding to different concentrations of ammonium nitrate in liquid ammonia) were utilized. Equation (7) may be further simplified to:

$$E_L = \frac{u_+ - u_-}{u_+ + u_-} \ln \frac{\gamma'^{I}_{\pm} (C_{AgNO_3} + C_{NH_4NO_3})^{I}}{\gamma'^{II}_{\pm} (C_{AgNO_3} + C_{NH_4NO_3})^{II}} \quad (8).$$

Since the transference number, t_+, of the positive ion is $u_+/u_+ + u_-$ and the transference number, t_-, of the negative ion is $u_-/u_+ + u_-$, equation (8) may be rewritten as:

$$E_L = (2t_+ - 1)\ RT/F \ln \frac{\gamma'^{I}_{\pm} (C_{AgNO_3} + C_{NH_4NO_3})^{I}}{\gamma'^{II}_{\pm} (C_{AgNO_3} + C_{NH_4NO_3})^{II}} \quad (9).$$

The total potential of the cell is equal to the sum of all potentials present.

$$E_{total} = E_1 + E_2 + E_3 \quad \text{where } E_2 = E_L$$

$$E_{total} = RT/F \ln \frac{(a_{AgNO_3})^{I}}{(a_{AgNO_3})^{II}} - (2t_+ - 1)\ RT/F \ln \frac{\gamma'^{I}_{\pm} (C_{AgNO_3} + C_{NH_4NO_3})^{I}}{\gamma'^{II}_{\pm} (C_{AgNO_3} + C_{NH_4NO_3})^{II}}$$

(10).

or

$$E_{total} = RT/F \ln \frac{(a_{AgNO_3})^{I}}{(a_{AgNO_3})^{II}} - (2t_+ - 1) \ln \gamma_{\pm}^{II} (C_{AgNO_3} + C_{NH_4NO_3})^{II}$$

$$+ (2t_+ - 1) RT/F \ln \gamma_{\pm}^{I} (C_{AgNO_3} + C_{NH_4NO_3})^{I} \qquad (11).$$

II - Alcoholic I - Liquid Ammonia

Since the ammonium nitrate concentration is varied in the liquid ammonia half of the cell, the ionic strength of the solution will vary, thereby affecting the activity of the silver nitrate $(a_{AgNO_3})^{I}$ in that solution. However, a calculation of this change over the concentration range investigated (.002 M - .016 M), using activity coefficients obtained from a modified Debye-Huckel[15] equation, indicates that the potential change over the entire range would not be greater than 4 millivolts. This change is within the experimental error. Therefore, the first two terms of equation (11) are constant, within experimental error, because all of the other terms they contain are held invariant.

The equation for the potential of the cell may then be expressed by:

$$E_{total} = (2t_+ - 1) RT/F \ln \gamma_{\pm}^{I} (C_{AgNO_3} + C_{NH_4NO_3})^{I} + C \qquad (12).$$

Thus, the change of potential which occurs as the concentration of NH_4NO_3 in the liquid ammonia is increased from A to B may be expressed by:

$$E_B - E_A = \Delta E = (2t_+ - 1)\ RT/F\ \ln \frac{\gamma_\pm (C_{AgNO_3} + C_{NH_4NO_3})_B}{\gamma_\pm (C_{AgNO_3} + C_{NH_4NO_3})_A} \qquad (13).$$

This equation is then a general representation for the potential change accompanying a change of electrolyte activity. It predicts that a plot of the logarithm of the cationic concentration versus the potential will result in a straight line since it was found that, in the dilute region under discussion, activity coefficients change linearly with concentration. The slope of the straight line should be dependent upon both $(2t_+ - 1)\ RT/F$ and the activity coefficient ratios.

Calculation of Activity Coefficient Ratio and Transference Numbers

If the proper numerical values are substituted into equation (13), the following relationship is obtained:

$$E = (2t_+ - 1)\ (.039) \quad \log \frac{(\gamma_\pm)_B}{(\gamma_\pm)_A} + \log C_B/C_A \qquad (14).$$

at $-50^\circ C$.

where C_B and C_A represent cationic concentrations and $\gamma_\pm$ is the mean activity coefficient of ammonium nitrate. The solutions to which the calculations have been applied had a molar ratio of ammonium nitrate to silver nitrate of at least 5:1. In this concentration region, the errors introduced by previous assumptions become negligible.

Both the transference number (t_+) and ratio of activity coefficients cannot be determined by the same series of experiments. However, if either is known, the other may be determined.

Transference Numbers - In aqueous media, the activity coefficients for ammonium nitrate have been accurately determined; and their values may be substituted into the equation. In this manner the positive transference number may be evaluated, and the degree of ionic selectivity of the membrane thus determined.

In an analogous manner, the transference number of the membrane in liquid ammonia was determined, using the mean activity coefficients for ammonium nitrate which have been calculated by Debye-Huckel type of treatment. These calculated activity coefficients are practically identical, in this range of concentrations, with those experimentally determined by these workers.

Activity Coefficient Ratios

It was found experimentally that the change of the positive transference number in going from an all water system to a liquid ammonia-alcohol system is not appreciable. The transference number can, therefore, be determined (as indicated above) in the all water system and this value can be used in the calculation of the activity coefficient ratios in liquid ammonia.

Both methods have been applied to the data obtained with very close agreement between the results.

EXPERIMENTAL

THE CELL

Cell A - Cell A, used for a portion of the experimental work described in this section, was the cell used for the work reported in Part I of this dissertation. The soft glass sections, which were necessary in the glass electrode investigations, were replaced by pyrex glass.

Cell B - Cell B was made from a 500 ml round-bottomed flask which had four necks, three of which carried 24/40 standard tapered ground glass joints and one of which carried a 14/36 ground glass joint. (See Figure IV.) One of the 24/40 joints was fitted with a "Y" ground glass adapter. A thermometer was inserted through one of the arms of the "Y" adapter. The other arm was attached to a "cold finger" type of condenser which in turn was connected to a vacuum line. The central 24/40 neck contained the ion exchange membrane. The remaining large neck accommodated the sample addition unit. The fourth joint contained the reference electrode for the outer half-cell.

The body of the round-bottomed flask was used as a container for the silver-silver nitrate reference electrode and the liquid ammonia solutions. The ammonia was condensed into a separate, calibrated flask which was attached to the vacuum line just before the cell. (See Figure V.) The two were separated by stopcocks so that they could be operated independently.

The remaining portions of the cell will be discussed in the following sequence: reference electrodes; the membrane unit which contains the membrane junction, the alcoholic solution of ammonium nitrate, and the inner silver-silver ion reference electrode; and the sample addition unit. Finally, a separate treatment of the liquid junction unit will be presented.

Reference Electrodes

Most of the measurements were made using a silver-silver ion reference electrode in the outer cell and either a silver-silver ion electrode or a silver-silver chloride electrode for reference in the inner cell. The outer silver electrode was made by sealing, by means of sealing wax, a piece of metallic silver (connected to a lead wire) into a glass tube. A platinum wire plated with silver was used as the metal in the inner electrode.

The silver-silver chloride electrode was prepared in the following manner[1]. The plating solution was prepared by adding silver nitrate to a filtered 20% potassium cyanide solution until a permanent white precipitate just appeared. The resulting solution was filtered and used for plating. With platinum as anode, the plating was continued for three hours. The plated electrode was rinsed thoroughly with distilled water and finally allowed to stand in distilled water overnight. The silver electrode was then used as anode for the electrolysis of 0.1 M hydrochloric acid at a current density of 2 milliamperes per square centimeter for two hours. The resulting silver-silver chloride electrode was used after being rinsed in distilled water. This electrode, after being placed in the alcoholic internal half-cell solution, did not change its potential during the period when the experiments were made.

For the measurements made in the all-ammonia system, lead-lead nitrate electrodes were used. Since lead nitrate is insoluble in alcohol and since the presence of divalent cations would complicate the theoretical interpretation of the results, the lead-lead nitrate electrodes were replaced by silver-silver nitrate electrodes for the experiments where alcoholic solutions were employed.

The Membrane Unit

The membranes used in this work were prepared at the laboratories of Ionics, Inc. in Cambridge, Massachusetts. The ion exchange material was formed directly on fritted glass discs of medium porosity. The fritted discs had previously been sealed into 10 mm glass tubing. By forming the ion exchange membrane directly in the pores of the glass, the mechanical strength of the resulting membrane was greatly increased.

The membranes were received in contact with dilute sulfuric acid solution, and the resin was in its acid form The water had to be removed from the membranes before they could be used. If this were not done, the membranes were unservicable for the following reasons:

(1) as the membrane was cooled for use in liquid ammonia, the water would freeze and expand, thereby destroying the membrane, and (2) even if the membrane were not mechanically injured in the cooling process, the membrane would be in solid solution condition which would not be desirable. Replacement of water with alcohol eliminated these difficulties. The membrane was bathed in 100 ml of 10% alcohol solution for two hours, then in 20% alcohol solution for two hours, and so on, until finally the membrane was stored in absolute alcohol. In spite of these precautions, only one-fourth of the membranes prepared did not develop leaks.

The tube containing the membrane was sealed onto a 24/40 ground glass joint. The alcoholic reference solution (.001 M with respect to both silver nitrate and ammonium nitrate) was added, and the inner reference electrode was inserted. These components comprised the membrane unit. The unit was stored in a large test tube with the outside surface of the membrane dipping into alcohol. The test tube and membrane unit were cooled to $-50^{o}C$ before the membrane was inserted into the liquid ammonia.

Sample Addition Unit

A simple and direct method of increasing the concentration of solutions in the closed system, by the addition of known amounts of non-volatile solutes, was developed. The customary procedures of breaking bulbs which contain the samples[16] or of titrating a measured amount of concentrated solution into the system from a thermostated buret[21], require complex equipment, the operation of which is both time-consuming and unreliable. The equipment required for the simple method described below may be easily constructed from items which are generally available. This method of addition has been found to be as accurate as previous procedures and may be adapted for use over a wide range of sample sizes.

The method consists of the lowering of a series of boats, containing weighed amounts of the desired non-volatile solute, one by one into a well-stirred solution. A schematic diagram of the apparatus is shown in Figure III.

The apparatus used consisted of a small pyrex glass chamber which had two standard-taper joints at right angles to each other. The size of the joints could be varied to fit the needs of the equipment. A glass tube was attached to a standard taper plug (of larger diameter than the tube) in such a way that the glass tube projected into the chamber when the plug was in place. The end of the glass tube was fashioned into a bobbin-like shape, with two glass ridges 1/4 inch apart and with a small hole between the ridges. Pyrex glass fiber thread was knotted at one end and threaded through the hole. The knot served to hold one end of the fiber securely. Rotation of the plug served to wind or unwind the thread.

Boats were constructed from glass tubing of the appropriate size (in this case 8 mm. tubing). They were loosely joined together by platinum wire, so that all might stand upright while being filled. One-half to three-quarters of an inch of wire was allowed between each boat. Samples were weighed and transferred quantitatively to the desired boat. A pyrex glass weight was attached to the lowest boat to overcome the initial bouyancy effect.

Before the chamber was attached by means of an intermediate chamber (see Figure IV) to the proper ground glass joint at the top of the reaction cell, the glass fiber thread was unwound until the series of boats might be attached to it. By rewinding the fiber thread, the samples were then raised into the intermediate chamber, where they were stored until needed.

The samples were kept sufficiently high in the system so that solvent did not condense on them. The boats were lowered one by one into the solution. The time required for complete solution depended upon the solubility of the salt and the degree of stirring.

The Liquid Junction Unit

The unit used is illustrated in Figure VI. A 24/36 ground glass joint was ground down further with emery cloth so that a liquid-tight fit could no longer be obtained(5). A very slow leak was observed, and there was a thin layer of liquid from the inner cell between the two parts of the joint. The male portion of the joint was sealed onto the 24/40 interjoint in the same manner as the membrane had been. The other portion of the joint was filled with the reference solution and attached. The two portions were held together by means of glass fiber which was wound about the "ears". This unit was stored until used in a large test tube containing the alcoholic solution.

When the unit was to be used, the storage test tube and its contents were cooled in acetone-dry ice to $-50^{\circ}C$. The unit was then quickly removed, and the alcoholic solution was wiped off. The unit was immediately inserted into the central 24/40 joint in the cell. Liquid ammonia had previously been condensed into the cell. This procedure was used because the vacuum necessary to condense the ammonia was sufficiently great to draw the solution from the inner cell into the outer one. By creating a slight pressure of ammonia in the system during the interchanging of the 24/40 plug and the liquid junction unit, no moisture from the atmosphere could condense in the cell system.

GENERAL PROCEDURE

To obtain a series of measurements, the following general procedure was used. The desired amount of silver nitrate was weighed into the outer cell (the final concentration being .001 M), and a magnetic stirring bar was added. The outer reference electrode, the sample adding unit with the samples in the boats, and the Y tube containing the low temperature thermometer were inserted into the cell. A 24/40 plug replaced the membrane unit in the middle joint at this time. The cell was then evacuated. (See Figure II, Part I.) The calibrated flask was cooled to $-50^{\circ}C$ by means of isopropyl alcohol and dry ice in a Dewar flask, and 330 ml of ammonia were condensed into the flask. Then the cell was cooled, and the 330 ml of ammonia were recondensed into the main cell. When all the ammonia had been condensed, the pressure in the system was allowed to increase to slightly above one atmosphere. At this point, the membrane unit, which had been pre-cooled in alcohol to $-50^{\circ}C$, was inserted; and the whole system was recooled to $-50^{\circ}C$. The potentiometer (Beckman Model G pH meter) was connected in series with the cell. Equilibrium was shown by a constant potential which was generally established within several minutes. Since this constant potential, once obtained, was found in the early experiments to remain unchanged for periods ranging from an half hour to twelve hours, the criterion for a recordable value of the potential was taken to be constancy of voltage for a period of ten minutes.

EXPERIMENTAL RESULTS

Experiment I - Determination of Membrane Junction Potential in an All-Aqueous System

The potential for the following cell system was determined as a function of the ammonium ion concentration.

Silver	Silver Nitrate 10^{-3} M	Ammonium Nitrate, Varying Concentrations	Membrane	Ammonium Nitrate 10^{-3} M	Silver Nitrate 10^{-3} M	Silver
	WATER			WATER		

The potentials observed at 24°C over a concentration range from .002 M to .036 M with respect to ammonium nitrate are presented in Table VII. These values were reproduced within ± 1 millivolt in two additional runs using duplicate membranes. The plot of potential versus the logarithm of the cationic concentration is linear (Figure XII).

In order to decrease the importance of the contribution of the silver ion to the potential, the silver nitrate concentration was decreased to 10^{-4} M. With such reference cells a comparable linear plot was obtained (Table VII, Figure XIII). The values of the potentials in Table VII are the average of five runs using duplicate membranes. The maximum variation of any value from the average is ± 1 millivolt. The potentials obtained upon the addition of the ammonium salt were steady and reproducible. When the silver nitrate concentration was decreased to 10^{-5} in both reference cells, a constant potential could not be obtained.

Experiment II - Determination of Membrane Junction Potentials in a Cell System with One Half-Cell Aqueous and the Other Half-Cell Alcoholic

This system may be represented schematically as follows:

Silver	Silver Nitrate 10^{-4} M	Variable NH_4NO_3 Concentrations	Membrane	Ammonium Nitrate 0.001 M	Silver Nitrate 10^{-4} M	Silver
	WATER			ALCOHOL		

Again the concentration range was varied from .002 M to .036 M with respect to ammonium nitrate and the resultant potentials are recorded in Table VIII. The temperature was at 24°C. Four runs checked within the experimental error of the method (± 1 millivolt).

A plot of potential vs. cationic concentration (Figure XII) again yields a straight line; however, at higher concentrations the slope changes in this case.

Experiment III - Determination of Membrane Junction Potentials with Alcohol in Both Half-Cells

The following cell was used in this series of experiments:

Silver	Silver Nitrate 10^{-4} M	Varying NH_4NO_3 Concentrations	Membrane	Ammonium Nitrate 10^{-2} M	Silver Nitrate 10^{-4} M	Silver
	ALCOHOL			ALCOHOL		

This system is the same as those used in Experiments I and II, except for the use of an all-alcohol system in place of an all-aqueous or alcohol-aqueous system. The temperature was again maintained at 24°C. Initially, it was difficult to obtain a constant potential; however, when the cell was allowed to equilibriate for a period of two hours, the system became stabilized; and steady potentials were observed for the subsequent solutions. The results representing an average of three series of measurements using two membranes are tabulated in Table VIII and plotted in Figure XII.

Thus, a plot is obtained which is linear at the lower concentrations but shows a change of slope at the higher concentrations.

Experiment IV - Determination of Membrane Junction Potentials in a Cell System with Liquid Ammonia in One Half-Cell and Alcohol in the Other (Concentration Range .001 M to .012 M)

The cell system used for the major portion of the experiments may be designated schematically as follows:

Silver Metal	Silver Nitrate .001 M	Varying NH_4NO_3 Concentrations	Membrane	Ammonium Nitrate .001 M	Silver Nitrate .001 M	Silver
	LIQUID AMMONIA			ALCOHOL		

Using this cell, the concentration range of .001 M to .012 M with respect to ammonium nitrate was investigated thoroughly at a temperature of -50°C. Seven different membranes were used during fifteen series of measurements. The results obtained in this range could be reproduced within ± 1 millivolt, not only for all consecutive series of measurements using the same membrane, but also for all series of measurements using different membranes. Figure IX is a plot of the average values of all potentials obtained versus the logarithm of the cationic concentration.

The specific values obtained in duplicate series of measurements using Membrane II are recorded in Table IV and are plotted as the upper line in Figure X. The variation of results is well within the experimental error of the meter used for the measurements.

Membrane I, however, behaved in a manner slightly different from that of the other membranes. This variation is apparent in a comparison of the values recorded in Tables III and IV and the plots of these data (Figure X). However, this was the only membrane which gave results at variance with those obtained when the other seven membranes (mentioned above) were used.

Using Membrane III an additional series of measurements was made using ammonium chloride as the ammonium salt in the test solution. The results obtained were identical with those obtained using ammonium nitrate with the same or other membranes.

Experiment V - Determination of Membrane Junction Potential in Cell System with Liquid Ammonia in One Half-Cell and Alcohol in the Other (Concentration Range .012 M to .036 M)

The cell system used in the previous experiment was used in this experiment. Typical results obtained for solutions of concentrations above .015 M are presented in Table V. A plot of the measured potentials versus the logarithm of the cationic concentration indicates that the points deviate from a straight line (Figure XI). Moreover, the results in this more concentrated region were less reproducible than those obtained in Experiment IV. The deviations were greater than those to be expected to arise from the functioning of the pH meter. The deviations were frequently as great as 4 millivolts.

The points in Figure XI represent averages derived from the results of twelve series of experiments in which a total of five membranes were used. Six of these series extended over the entire range of concentrations represented, while the other six extended only over the range .003 M to .012 M.

Experiment VI - The Determination of Liquid Junction Potentials Occurring in Cell Systems Studied

The liquid junction potentials were measured by the same general method used for the membrane measurements. The liquid junction unit, (described on page 91), replaced the membrane unit in the cell. It was found that electrical effects caused by slight stray magnetic fields were important when this unit was used. As a result, before a measurement could be made, all electrical appliances had to be turned off. Stirring had to be stopped. Under such conditions, results were obtained for the liquid ammonia-alcohol cell system. Two of the four tests made are included in Table VI. Results of all tests were identical and were reproducible within $\pm$ 1 millivolt.

Further work proved, however, that the junction potential did not remain constant for more than fifteen minutes, after which time an increase in potential occurred. Variation of the potential with time may be attributed to the slow diffusion of the alcohol into the liquid ammonia. An example of this effect is shown by that fact upon the addition, all at one time, of sufficient ammonium nitrate to produce a .018 M concentration, a change of junction potential of 8 millivolts was observed; whereas, in Table VI, a value of 15 millivolts is reported for the case when the stepwise method of addition was used to arrive at the same concentration.

However, irrespective of the method used, the change in liquid junction potential upon addition of ammonium nitrate does not become significant until at least .012 M. Therefore, below this concentration, any changes of potential which were observed when a membrane was used, were not caused by variation in liquid junction potential.

Experiment VII - Determination of Membrane Junction Potential in All Liquid Ammonia System (With Notes on Preliminary Work)

The first experimental work was performed in an all ammonia system using lead-lead nitrate reference electrodes.

Lead	Lead Nitrate .03 M	Varying NH_4NO_3 Concentrations	Membrane	Ammonium Nitrate .001 M	Lead Nitrate .03 M	Lead
	LIQUID AMMONIA			LIQUID AMMONIA		

The data obtained are presented in Table I. A plot of the logarithm of the cationic concentration (including the lead ion concentration) versus the resulting potential is linear (Figure VII). Comparison of the results of measurements made with each of two membranes show that in both cases the response was linear. However, the slopes of the plots are different. This change in slope may be interpreted as the result of a different degree of ionic perselectivity of one membrane as compared to the other (t_+ across the membrane may not have been identical in both cases).

To obtain these data, the membrane was first treated with alcohol and then the main portion of alcohol was removed from the membrane by evacuating the cell system for about 30 minutes before the ammonia was allowed to condense into the cell. This evacuation caused the membrane to dry and pull away from the glass disc. In most cases, the swelling of the membrane upon solvation of the membrane by liquid ammonia was not sufficient to prevent leakage, and these measurements had to be abandoned.

The large number of experimental failures during the period of these experiments indicated that the mechanical strength of the membranes, as prepared, was not sufficient to withstand the experimental procedures necessary for all-liquid ammonia measurements. Furthermore, some of the measurements of the values of the potential were extremely erratic. This occurred because the changing liquid ammonia level in the inner cell caused a variation in the concentration of the reference solution. At this point in the research, the alcohol inner reference solution was introduced. (See Experimental Section.) A more stable, less volatile, constant reference cell was obtained in this manner. In addition, the lead-lead nitrate reference electrodes were replaced by silver-silver nitrate electrodes.

Experiment VIII - The Determination of the Effect of Temperature on the Membrane Junction Potential

In order to determine the effect of temperature changes on the measured potential, the following cell system was set up:

Silver	Silver Nitrate .001 M	Ammonium Nitrate .002 M	Membrane	Ammonium Nitrate .001 M	Silver Nitrate .001 M	Silver
	LIQUID AMMONIA			ALCOHOL		

The potential of the system was measured at various temperatures. The temperature was controlled by adding appropriate quantities of dry ice to the isopropyl alcohol in the Dewar vessel. The potentials observed at various temperatures are listed in Table II. These data were plotted (Figure VIII). The variation of the potential with temperature is linear. These data indicate that control of the temperature in the cell system to within ± 1°C is sufficient for the experimental accuracy required.

Experiment IX - Determination of the Effect of Barium Nitrate on Membrane Junction Potential

In order to determine the behavior of divalent ions toward the membrane, the following cell system was investigated:

Silver	Silver Nitrate .001 M	Varying $Ba(NO_3)_2$ Concentrations	Membrane	Ammonium Nitrate .001 M	Silver Nitrate .001 M	Silver
	LIQUID AMMONIA -50°C			ALCOHOL		

The resulting potentials are presented in Table IX and plotted in Figure XIII and XIV. A duplicate set of measurements gave identical results. To compare the results, so obtained, with data collected previously, the same membrane was checked using changing ammonium nitrate concentrations in the outer solution. The results obtained are plotted in Figure XIII and are identical with those described previously (Experiment IV) for such systems.

It will be noted that a linear plot is obtained with barium ion concentrations between .002 M and .008 M. A comparison of the resultant slopes of ammonium and barium ion data indicates that the effect of the two ions are not identical. This to be expected, since some of the assumptions involved in the derivation of Equation (13) only apply to uni-univalent salts.

CALCULATIONS

Transference Numbers

It has been shown in an earlier section that either transference numbers or activity coefficient data can be obtained from the experimental results. The equation developed on page 84,

$$E = (2t_+ - 1)\ RT/F\ \left(\ln \frac{(\gamma_\pm)_B}{(\gamma_\pm)_A} + \ln \frac{C_B}{C_A}\right),$$

will give a value for t_+ upon insertion of the values for (1) the ratios of cationic concentrations and of activity coefficients and (2) the change in potential expressed in volts. In the aqueous cell system, for the concentration range studied (.002 - .030 M), $(\gamma'_\pm)_B/(\gamma'_\pm)_A$ is unity: therefore the log $(\gamma'_\pm)_B/(\gamma'_\pm)_A$ is equal to zero. The above equation then reduces to:

$$E = (2t_+ - 1)\ RT/F\ (\ln C_B/C_A).$$

Taking the values for E and C_B/C_A from Figure XVI, the following numerical calculation was made:

$$E = .042 = (2t_+ - 1)\ \frac{(297)\ (8.314)\ (2.303)}{96500}\ \log .03/.004$$

$$t_+ = .94$$

The constancy of the slope shows that the value of the transference number remains constant over this range of concentrations. The value of .94 indicates that 94% of the current across the membrane was carried by the positive ions and that in aqueous media the membrane is very nearly ideal in its selectivity.

In an analogous manner the positive transference number of the membrane when it is in the liquid ammonia-alcohol system may be determined. The values used were obtained from Figure IX over a cationic concentration range of .005 M to .013 M. The ratio of activity coefficients was obtained from a plot of those calculated by Pleskov and Monoszon[15], who used a modified Debye-Huckel equation (Figure XV).

$$E = .0125 = (2t_+ - 1)\ (.039)\ \log\left(\frac{0.013}{0.005} + \frac{.475}{.580}\right)$$

$$t_+ = .98\ .$$

This shows that there was a very slight difference between the proportion of current carried across the membrane by the positive ions in aqueous media and that so carried in the ammonia-alcohol system. The ionic selectivity of the membrane apparently does not change appreciably in going from one system to the other.

Activity Coefficient Ratios

Using the transference number obtained in aqueous media, the activity coefficient ratios of ammonium nitrate in liquid ammonia may be determined. The cationic concentration of .005 M was chosen as a reference point. Since the ratio of concentration of ammonium ions to that of silver ions at this point is 5/1, any contribution by the silver ion was minimized. An example of the method of calculation is shown below for the change in concentration from .005 - .007 M (see Figure IX):

$$E = .004 = (.94)\ (.039)\ \log\left(\frac{C_{.007}}{C_{.005}} + \frac{(\gamma'_{\pm})_{.007}}{(\gamma'_{\pm})_{.005}}\right)$$

$$(\gamma'_{\pm})_{.005}/(\gamma_{\pm})_{.007} = 1.09$$

The ratios calculated over the entire concentration range are presented in Table X.

Pleskov and Monoszon(15) experimentally determined the mean activity coefficients of ammonium nitrate in liquid ammonia by measurement of the electromotive force of a concentration cell of the type:

$$\mathrm{Pt}\left|\begin{array}{cc} H_2 & NH_4NO_3 \\ & c, \end{array}\right|\begin{array}{c} KNO_3 \\ \mathrm{Sat.} \end{array}\left|\begin{array}{cc} NH_4NO_3 & H_2 \\ .1N & \end{array}\right|\mathrm{Pt} \quad .$$

The values obtained in this manner are plotted against the logarithm of the concentration (Figure XV). From this graph, ratios of activity coefficients were obtained and are listed in Table X.

It is of considerable interest to compare the results with those calculated theoretically from the Debye-Huckel equation. Because, in the concentration range investigated, ammonium salts are not completely dissociated in liquid ammonia, both the degree of dissociation and the dissociation constant were introduced into the calculation of the activity coefficients by the Debye-Huckel treatment(15).

In this manner activity coefficients were calculated by Pleskov and Monoszon which agreed fairly closely with those experimentally determined. These values are plotted in Figure XV and ratios of these resulting activity coefficients are also recorded in Table X.

DISCUSSION OF RESULTS

The experiments presented in this study were devised so as to simulate the glass electrode cell system; i.e., to have a constant reference cell and vary the external solution. The method used offers a convenient means of determining not only hydrogen ion activity but any cationic activity. Such a use of ion exchange membranes has not been reported even in aqueous systems. Therefore, before any application was made to liquid ammonia solutions, aqueous systems were studied to determine the validity of reproducible variation of membrane potentials with changes in concentration. The experimental necessity of introducing alcohol as a medium in one half of the cell system made it desirable to study systems which had different media on either side of the membrane.

Equation (14), page 84 is:

$$E = (2t_+ - 1)\ (.039)\ \log\ (\gamma_\pm)_B/(\gamma_\pm)_A + \log C_B/C_A\ .$$

This equation is applicable only when uni-univalent salts are present in the system. Before this equation can be used simply to interrelate the potential measured and the cationic concentration in the test solution, values for the other two terms (transference number, t_+, and ratio of activity coefficients, $((\gamma'_\pm)_B/(\gamma'_\pm)_A)$ must be established.

Aqueous System

In this system all terms in the above equation, except the positive transference number, are known either by experiment or from the literature. It was found that the slope of the plot prescribed by the equation, i.e., the logarithm of the cationic concentration versus the potential, revealed $t_{NH_4^+} = 0.94$. This is in excellent agreement with values obtained by others (Figure II) by an entirely different method which was developed by Sollner[19]. Sollner's method involved a concentration cell in which the concentrations on both sides of the membrane were varied in such a manner that they always remained in the absolute ratio of 2:1. Such control kept the activity coefficient ratio close to 1, thus facilitating the determination of the transference numbers. The technique used for the present investigation did not incorporate this simplification. However, this limitation is not serious since at concentrations at which ratios of activity coefficients begin to vary appreciably, the membrane itself also begins to deviate from ideality. Therefore, as a consequence of this work, a new method for the determination of the transference numbers across a membrane has been developed.

Water-Alcohol System

Over a limited concentration range, the plots of the results for the alcohol-water system and the all-water system have slopes which are essentially the same (Figure XII). Therefore, a change in the medium did not change the transference number of the membrane. These data establish that, over a definite concentration range, a cell containing two media may be used successfully. Therefore, the membrane can be used as an electrochemical tool in non-aqueous media.

Liquid Ammonia-Alcohol System

The experimental data discussed above have established that ion exchange membranes can be used if two media are present in the cell system and that the transference number across the membrane may be determined.

With the liquid ammonia-alcohol system, the permselective membranes may be used to determine ratios of activity coefficients at a temperature as low as -50°C. In this system, the value of the transference number was found to remain constant over a concentration range which was somewhat smaller than the range over which the transference number remained constant in the cell water system. This range was .002 - .017 M for liquid ammonia-alcohol system and .003 - .03 M for the water system. The values of t_+ agree closely for the two systems. The ratios of activity coefficients were calculated over the concentration region investigated. Two sets of activity coefficient ratios for ammonium nitrate in liquid ammonia are available in the literature for comparison. One set was calculated by means of a modified form of the Debye-Huckel equation. The other was obtained by Pleskov and Monoszon[15] from a series of measurements of a concentration cell wherein hydrogen electrodes were used as the specific electrodes. The experimental data presented in this study strongly support their experimental values.

The permselective membranes present a general method for determining activity coefficients and other properties in non-aqueous media. The membrane is not specific but can be used with any cation. Its successful use with ammonium ion in liquid ammonia, alcohol, and water promises wide application with other salts and media.

One of the limitations of the experimental method described results from the use of silver-silver ion reference electrodes. There are relatively few solid electrodes which have been developed for use in liquid ammonia. However, the use of such solid electrodes would be desirable for future work on the electrochemical behavior of ion exchange membranes in liquid ammonia, and would greatly simplify the experimental techniques and augment the value and scope of the data obtainable. The experiments involving the divalent barium ion gave reproducible results, which, though they illustrate that the present method can have analytical application for polyvalent ions, are not susceptible to theoretical interpretation. If solid electrodes were available, the results obtained with their use would be susceptible to a straightforward theoretical interpretation when divalent ions are present. This is not possible when silver-silver nitrate electrodes are used because the presence of the silver ion in solution complicates the solution.

Analytical Applications

It is of analytical interest that a plot of the logarithm of the cationic concentration versus the membrane junction potential is a straight line. It is at once apparent that this technique may be used to determine absolute values of, or monitor changes in, the cationic concentration in aqueous and non-aqueous media. The kinetics of numerous reactions may, therefore, be determined in various media by proper utilization of cell systems such as those herein reported.

Another potential analytical application is the determination of end-points of various electrometric titrations, for example those involving neutralization, precipitation, or complex forming reactions.

CONCLUSION

1. The reproducible operation, in water, alcohol, and liquid ammonia systems, of selectively permeable ion exchange membrane electrodes has been demonstrated.

2. A new method has been established for the determination of cationic concentrations in these media.

3. These electrodes have been applied in the determination of transference numbers across such membranes in these media.

4. It has been demonstrated that selectively permeable ion exchange membrane electrodes are useful electrochemical and analytical tools whether the solvents on either side of the membrane are the same or not.

5. A new method for the determination of the ratios of activity coefficients of a salt at various concentrations has been presented. This method is applicable to solutions in numerous media, including liquid ammonia.

6. Ratios of activity coefficients of ammonium nitrate at various concentrations in liquid ammonia have been determined.

7. Methods have been indicated, applicable to reactions in various media, for monitoring of cationic concentration changes during studies of kinetics, and for the determination of end-points of electrometric titrations.

APPENDIX III

TABLE I

Variation of Membrane Potential with Concentration
(All Ammonia System)

Concentration of Ammonium Nitrate (Molarity)	Cationic Concentration	Potential (Millivolts) Membrane I	Membrane II A	Membrane II B
.001	.031	(-2)	-20	-26
.005	.035	-18	-10	-20
.01	.040	+1	-4	-10
.015	.045	+22	+10	-1
.020	.050	+31	+20	+10

TABLE II

Variation of Membrane Potential with Temperature

Temperature (° Centigrade)	Potential (Millivolts)
-68.9	238
-59.5	242
-56.7	244
-51.1	248
-46.7	250

TABLE III

Variation of Membrane Potential with Ammonium Nitrate

Membrane I

Concentration of Ammonium Nitrate (Molarity)	Membrane Potential (Millivolts)	Change in Potential (Millivolts)
--	250	
.001	253	3
.002	258	8
.003	263	13
.004	265	15
.005	268	18
.006	270	20

TABLE IV

Variation of Membrane Potential with Ammonium Ion Concentration

Membrane II

Concentration of Ammonium Ion (Molarity)	Membrane Potential (Millivolts)	Change in Potential (Millivolts)
--	258	
.002	265	7
.004	268	10
.006	273	15
.008	275	17
.010	277	19
.012	282	22
--	260	--
.002	268	8
.004	271	11
.006	276	16
.008	278	18
.010	280	20
.012	282	22

TABLE V

Variation of Membrane Potential with High Ammonium Ion Concentrations

Membrane II

Concentration of Ammonium Ion (Molarity)	Potential (Millivolts)	Change in Potential (Millivolts)
	274	
.006	290	16
.012	300	26
.014	303	29
.016	306	32
.018	309	35
.020	306	32

Membrane VI

Concentration of Ammonium Ion (Molarity)	Potential (Millivolts)	Change in Potential (Millivolts)
	310	
.006	327	17
.012	337	27
.018	343	33
.024	353	43
.030	370	60
.036	383	73

TABLE VI

Liquid Junction Potential Variation with Concentration

Concentration of Ammonium Ion (Molarity)	Potential (Millivolts)	Change in Potential (Millivolts)
	538	
.002	538	
.004	539	1
.006	542	4
.008	544	6
	Second Test	
	525	
.006	528	3
.012	532	7
.018	540	15
.024	550	25
.030	554	29
.036	560	35

TABLE VII

Variation of Membrane Potential with Ammonium Nitrate Concentration
Aqueous Conditions
Reference Cell Solution - 10^{-3} M Silver Nitrate - Temp. 24°C.

Ammonium Nitrate Concentration Moles	Potential (Millivolts) 1	2
.002	-45	
.004	-33	
.006	-22	-28
.008	-21	
.010	-18	
.012		-12
.014	-10	
.018	-5	-3
.022	0	
.024		2
.026	3	
.030	6	5
.034	10	
.036		11

TABLE VIII

Variation of Membrane Potential with Ammonium Nitrate Concentration
Reference Cell Solution - 10^{-4} Silver Nitrate - Temp. 24°C.

Ammonium Nitrate Concentration (Moles)	Aqueous	Potential (Millivolts) Alcoholic	Alcohol-Water
.004	-22	+10	-53
.008	-8	+30	-38
.012	+2	+45	-28
.016	+8	+50	-19
.020	+12	+55	-12
.024	+15	+62	-8
.028	+19	+70	0
.032	+22	+80	+3

TABLE IX

Variation of Membrane Potential with Barium Ion Concentration

Barium Ion Concentration Moles	Change in Potential Millivolts	
	Run 1	Run 2
.0020		8
.0025	12	
.004	18	16
.006	22	20
.008	28	
.010	36	38
.012		43
.014		48
.016		50

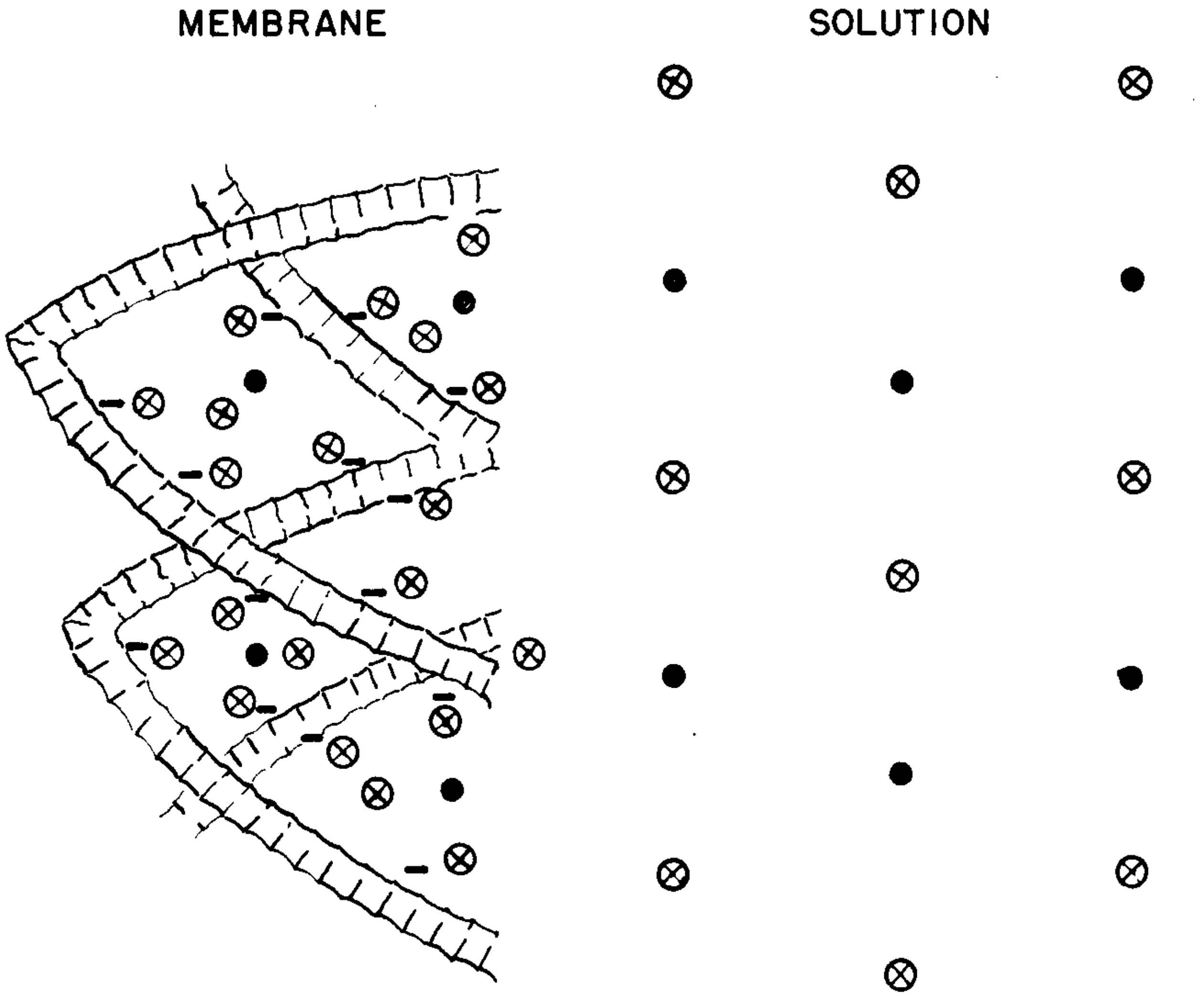
TABLE X

Activity Coefficient Ratios

Concentration Ratio (Molarity)	As Determined By Membrane Junction	As Determined By Pleskov & Monoszon	Calculated Debye Huckel
.005/.007	1.09	1.08	1.08
.005/.009	1.16	1.17	1.13
.005/.011	1.26	1.25	1.19
.005/.013	1.35	1.32	1.23
.005/.015	1.39	1.38	1.27

APPENDIX IV

FIGURE I
SIMPLIFIED MOLECULAR MODEL OF A PERMIONIC CATION MEMBRANE IN SOLUTION



LEGEND

– ACTIVE (NEGATIVE) RESIN SPOT

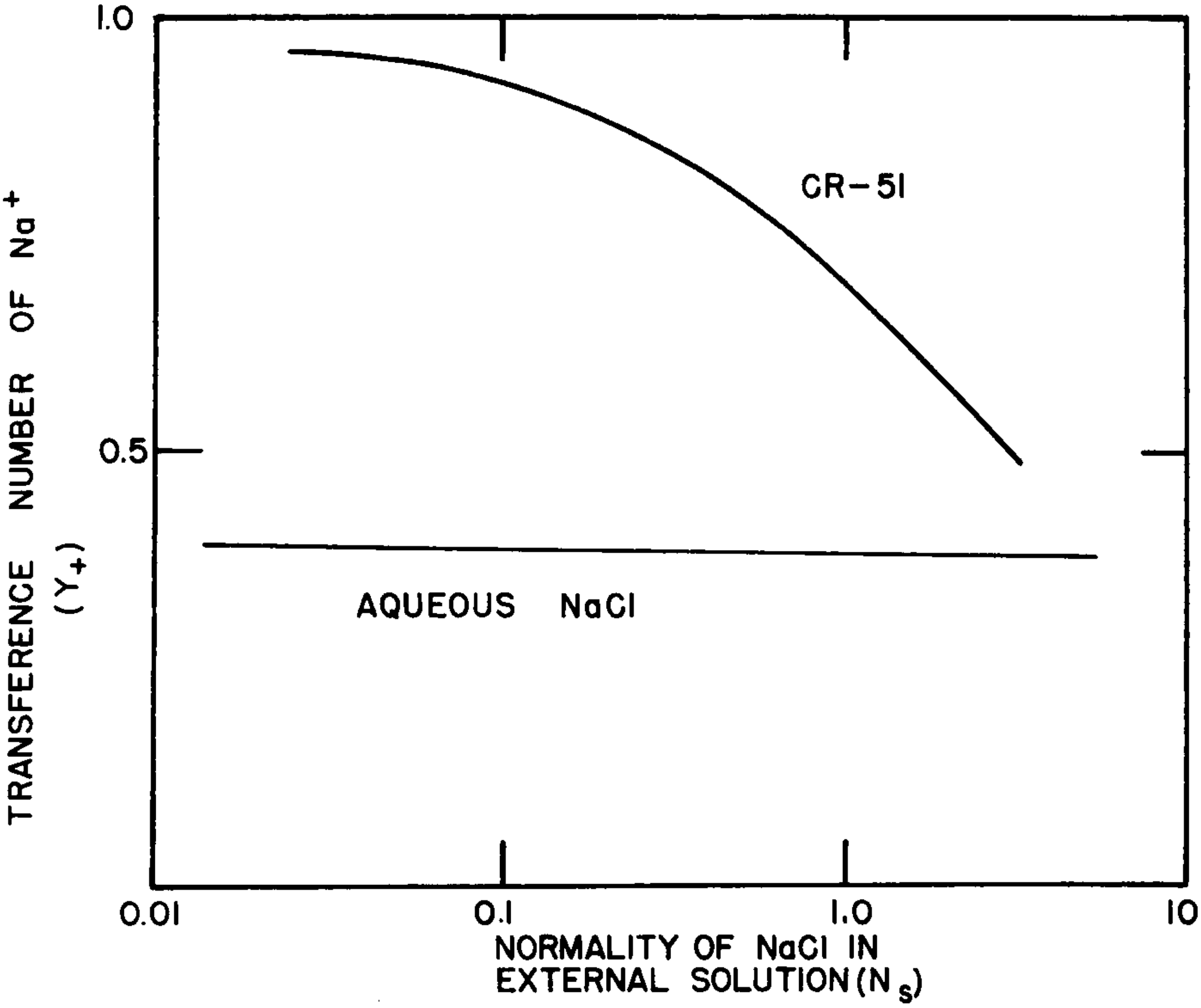
⊗ MOBILE POSITIVE ION

● MOBILE NEGATIVE ION

RESIN MATRIX

FIGURE II

PERMSELECTIVITY
OF PERMIONIC CR-51 IN NaCl SOLUTIONS
(MEASURED AS TRANSFERENCE NUMBER
OF THE SODIUM ION)



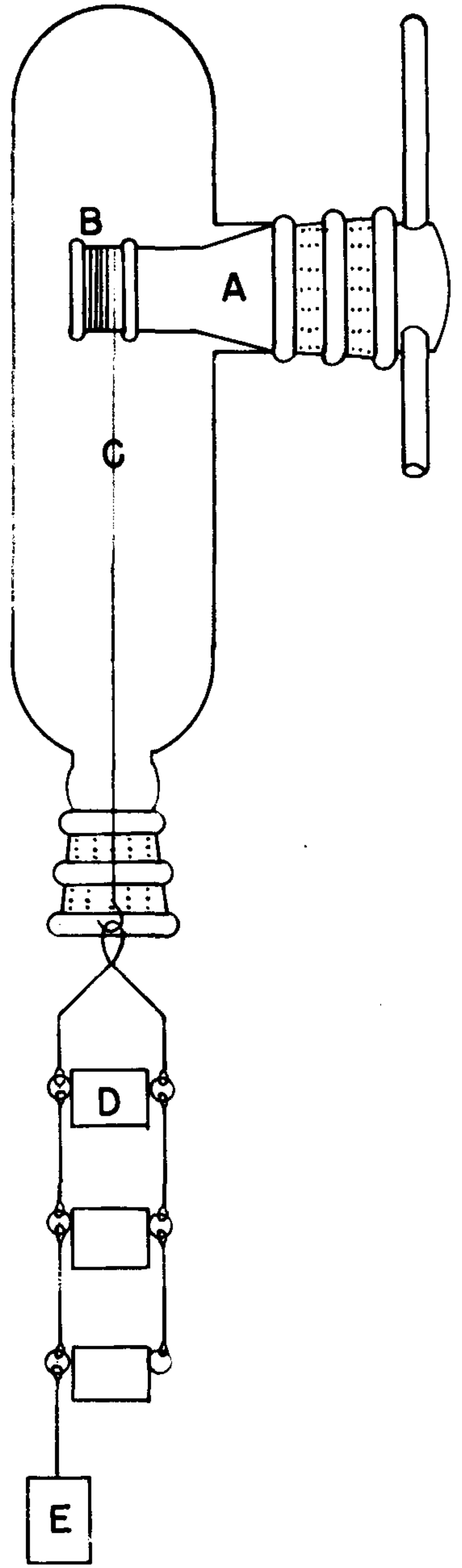
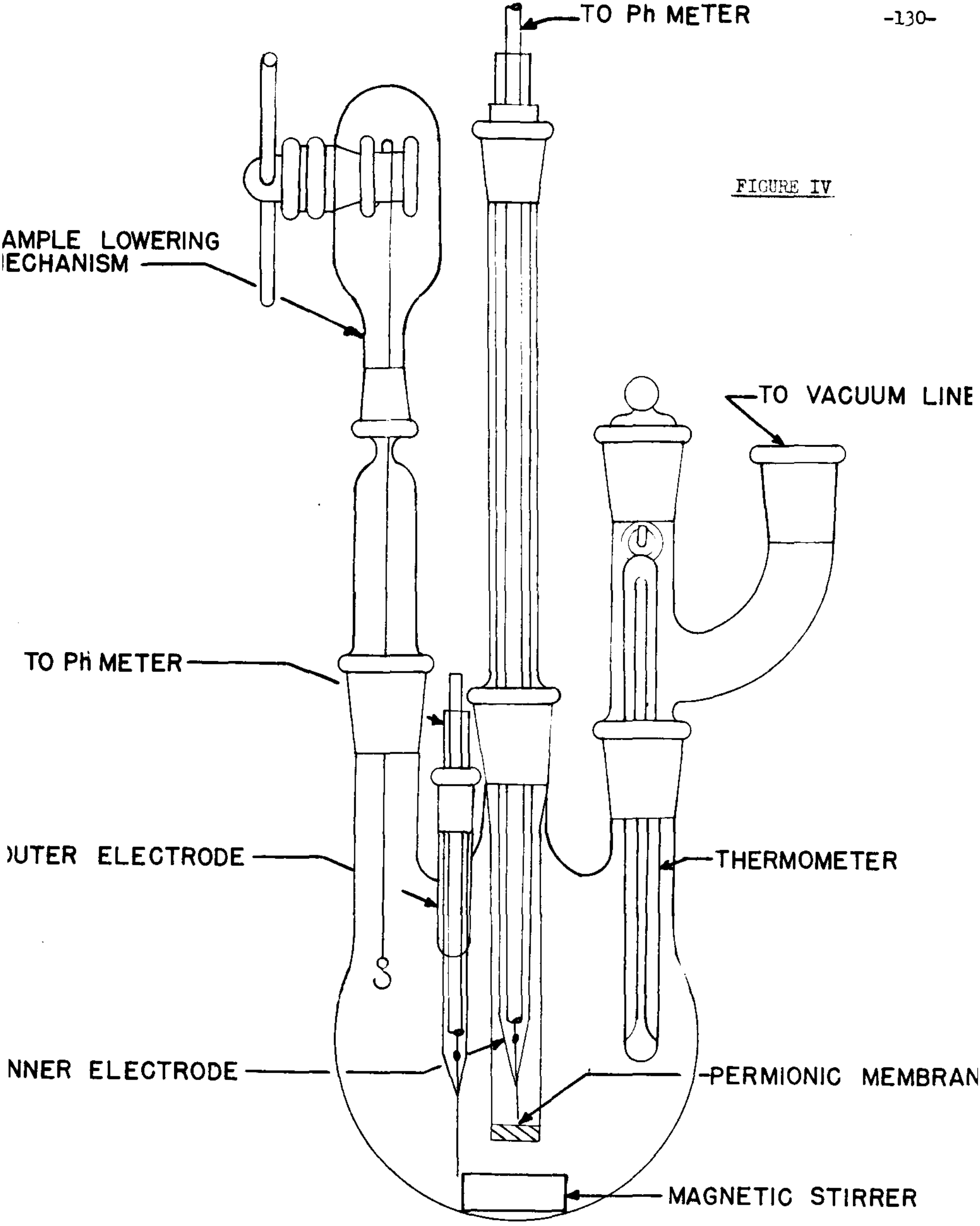


FIGURE III

FIGURE IV



CELL ASSEMBLY FOR MEASUREMENTS

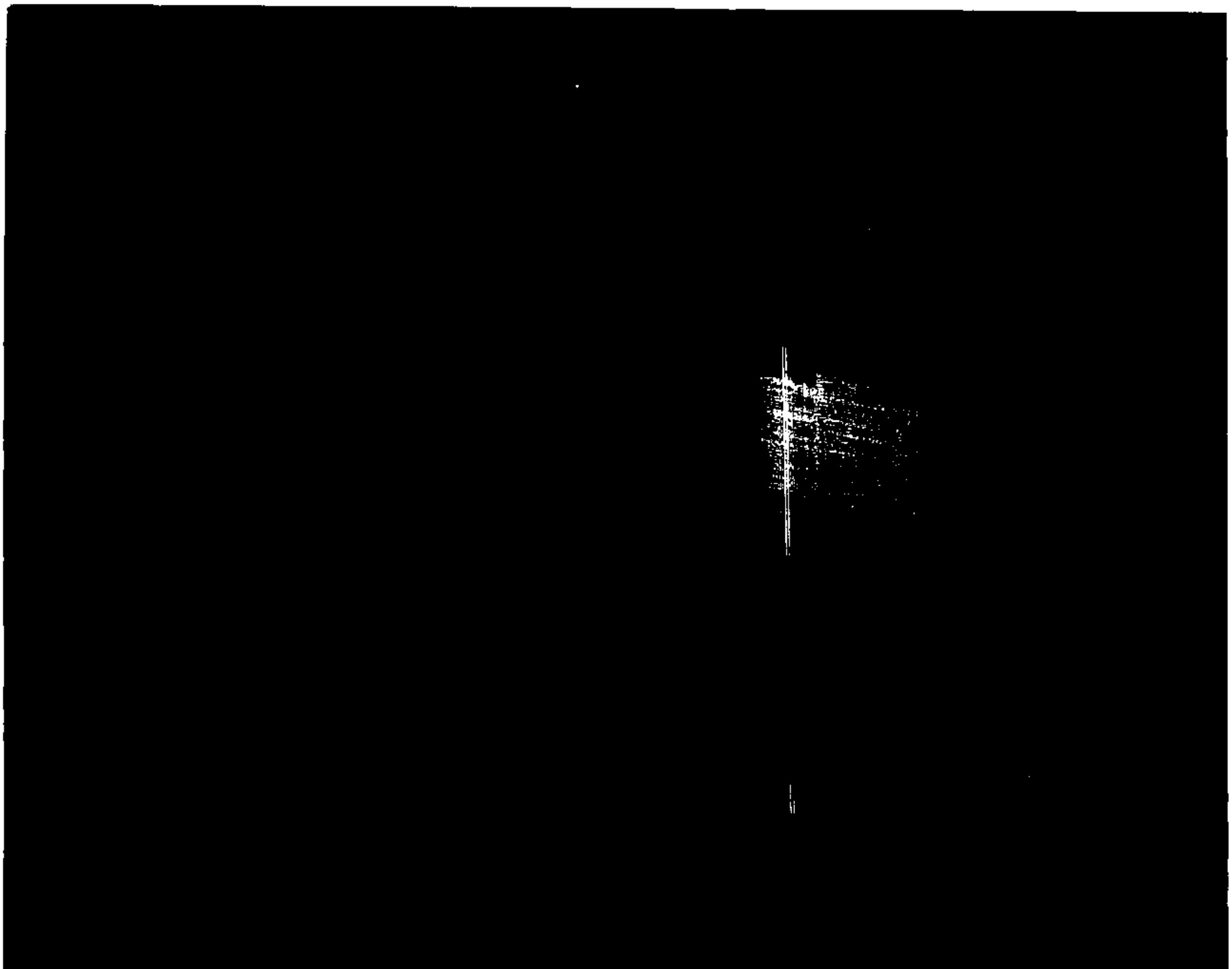


FIGURE V

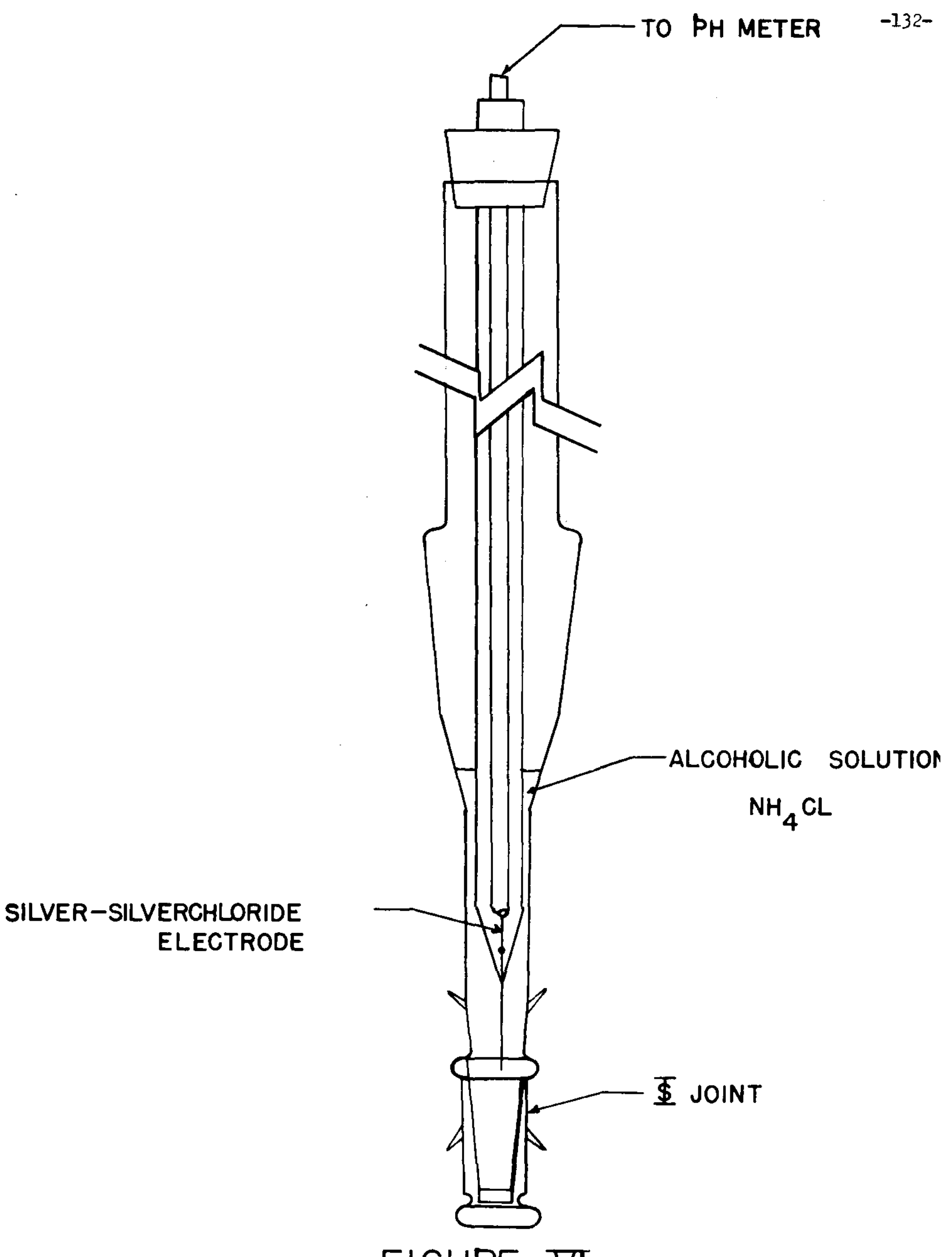

TO PH METER
ALCOHOLIC SOLUTION
NH4CL
SILVER–SILVERCHLORIDE ELECTRODE
$ JOINT

FIGURE VI

FIGURE VII

VARIATION OF MEMBRANE POTENTIAL WITH CATIONIC CONCENTRATIO
(ALL AMMONIA SYSTEM)

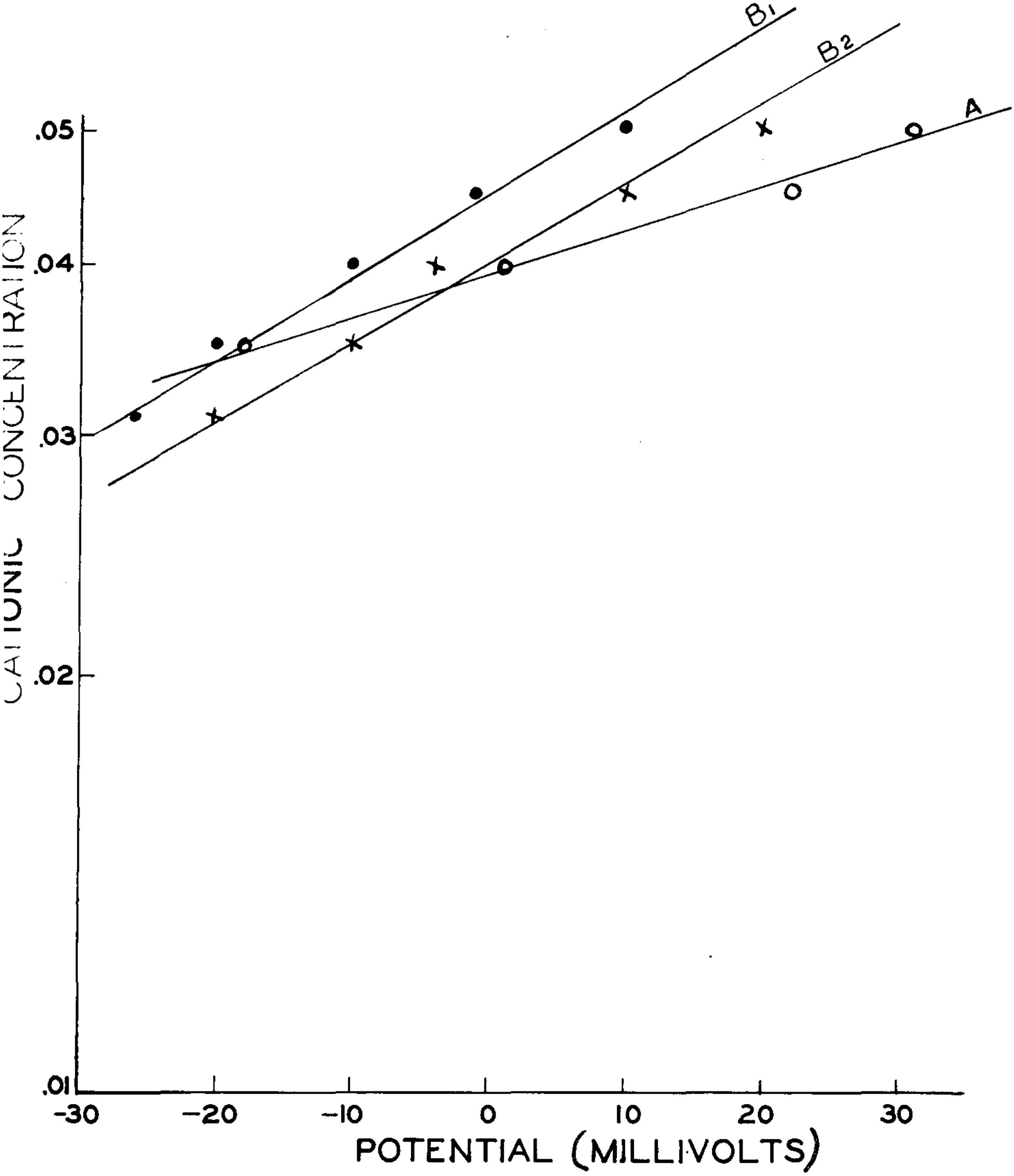


FIGURE VIII

VARIATION OF MEMBRANE POTENTIAL WITH TEMPERATURE

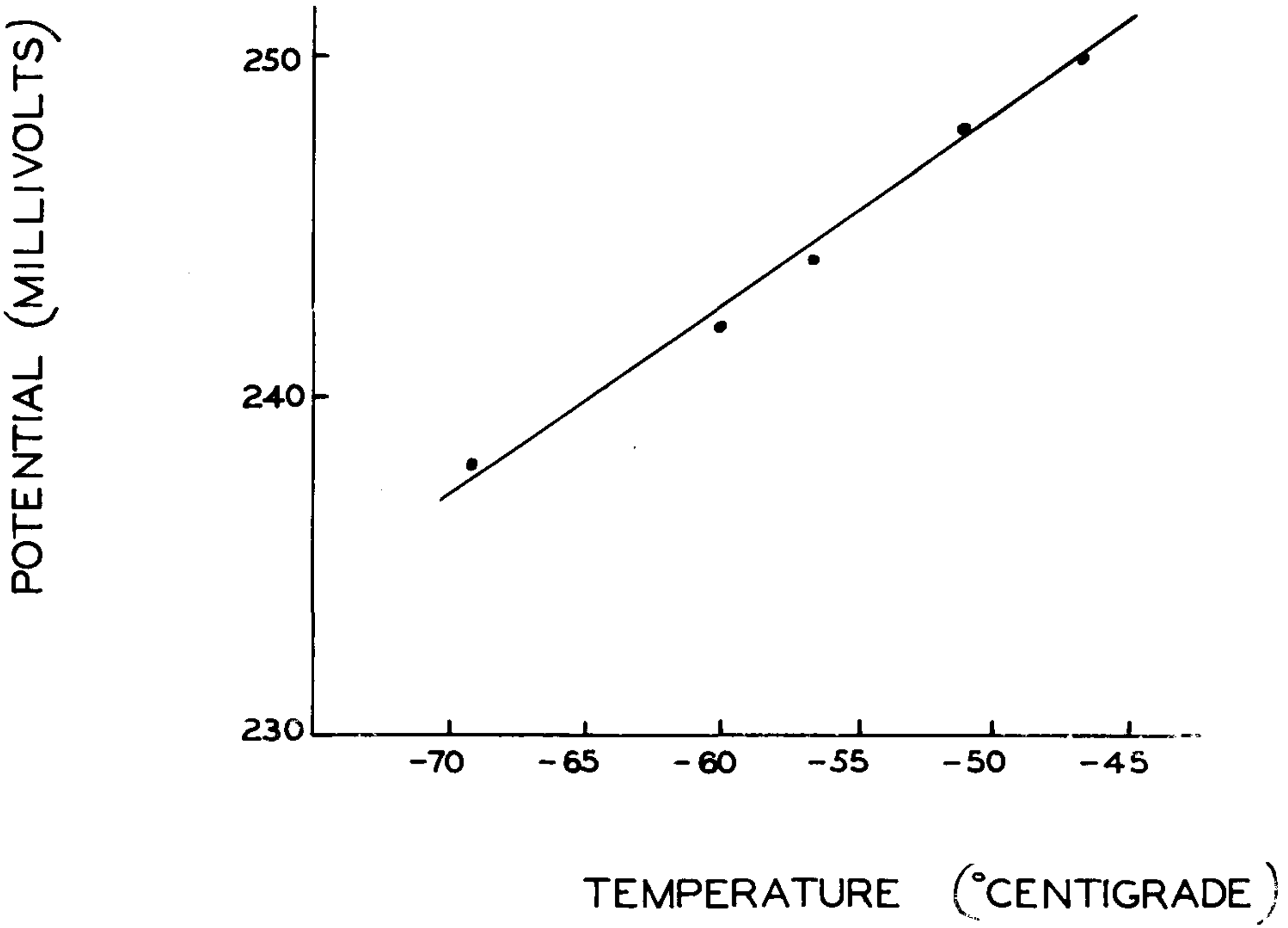


FIGURE IX

VARIATION OF MEMBRANE POTENTIAL WITH CATIONIC CONCENTRATION

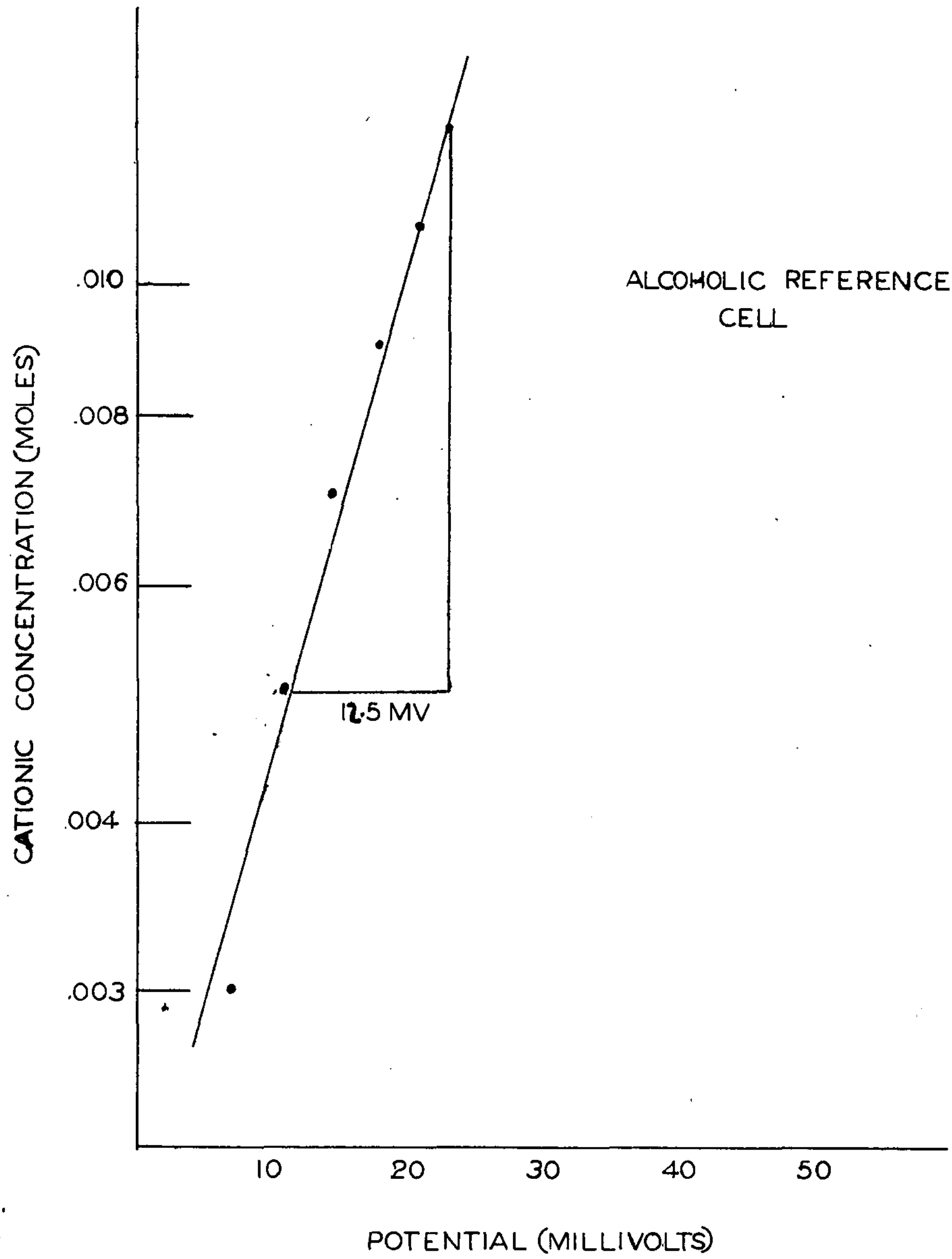


FIGURE X

VARIATION OF MEMBRANE POTENTIAL WITH CATIONIC CONCENTRATI

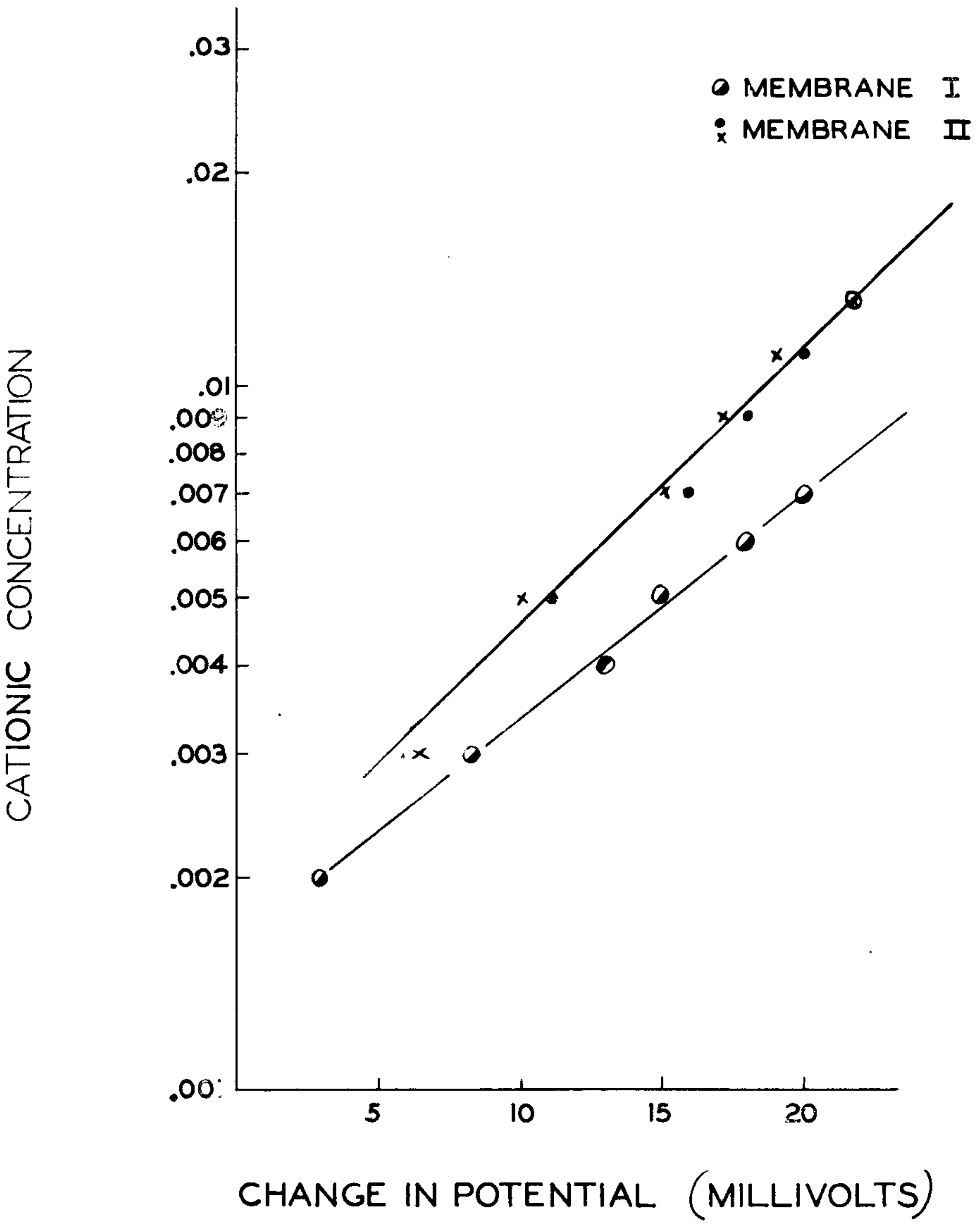


FIGURE XI

VARIATION OF MEMBRANE POTENTIAL

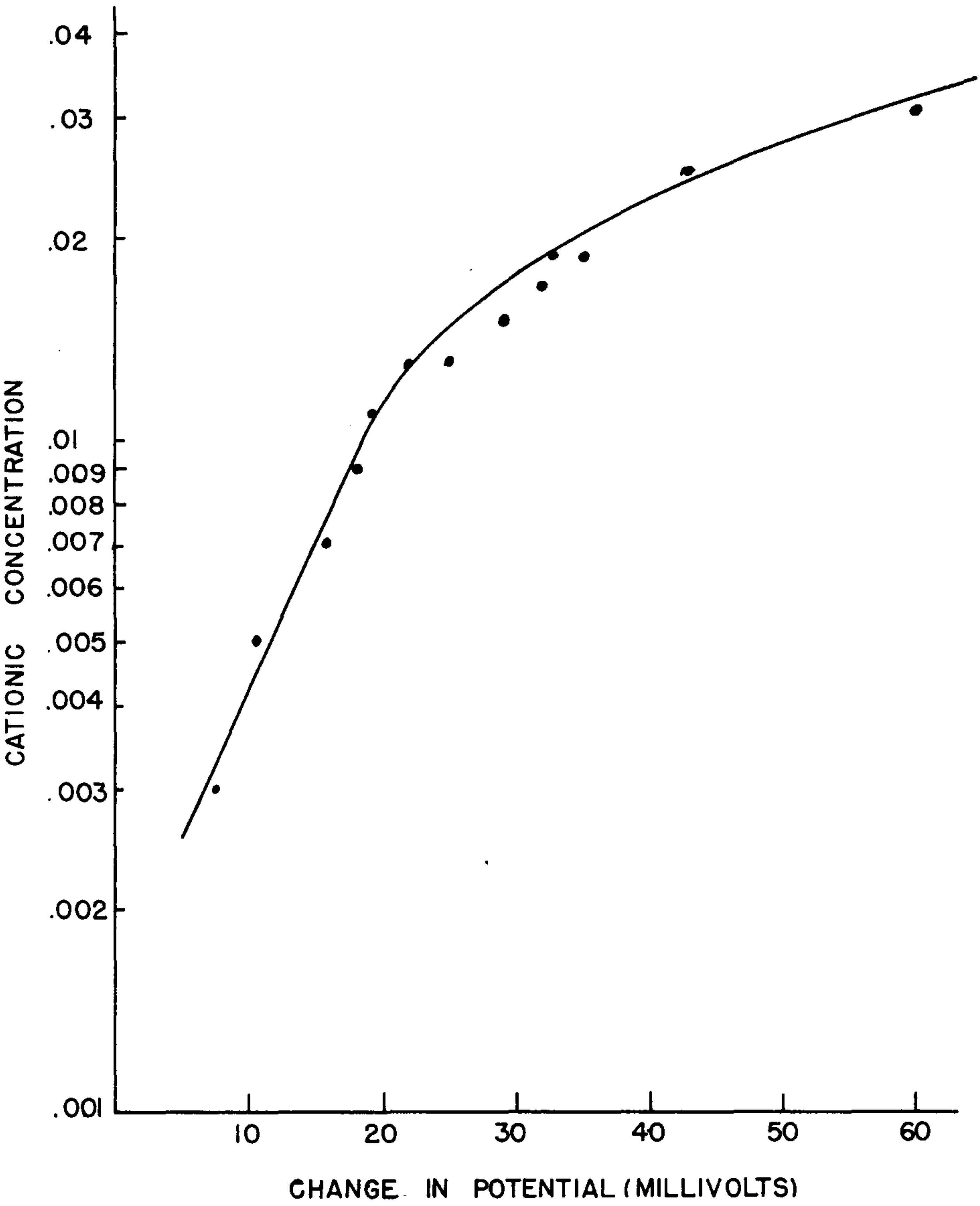


FIGURE XII

VARIATION OF MEMBRANE POTENTIAL WITH CATIONIC CONCENTRATIC

(VARIOUS MEDIA)

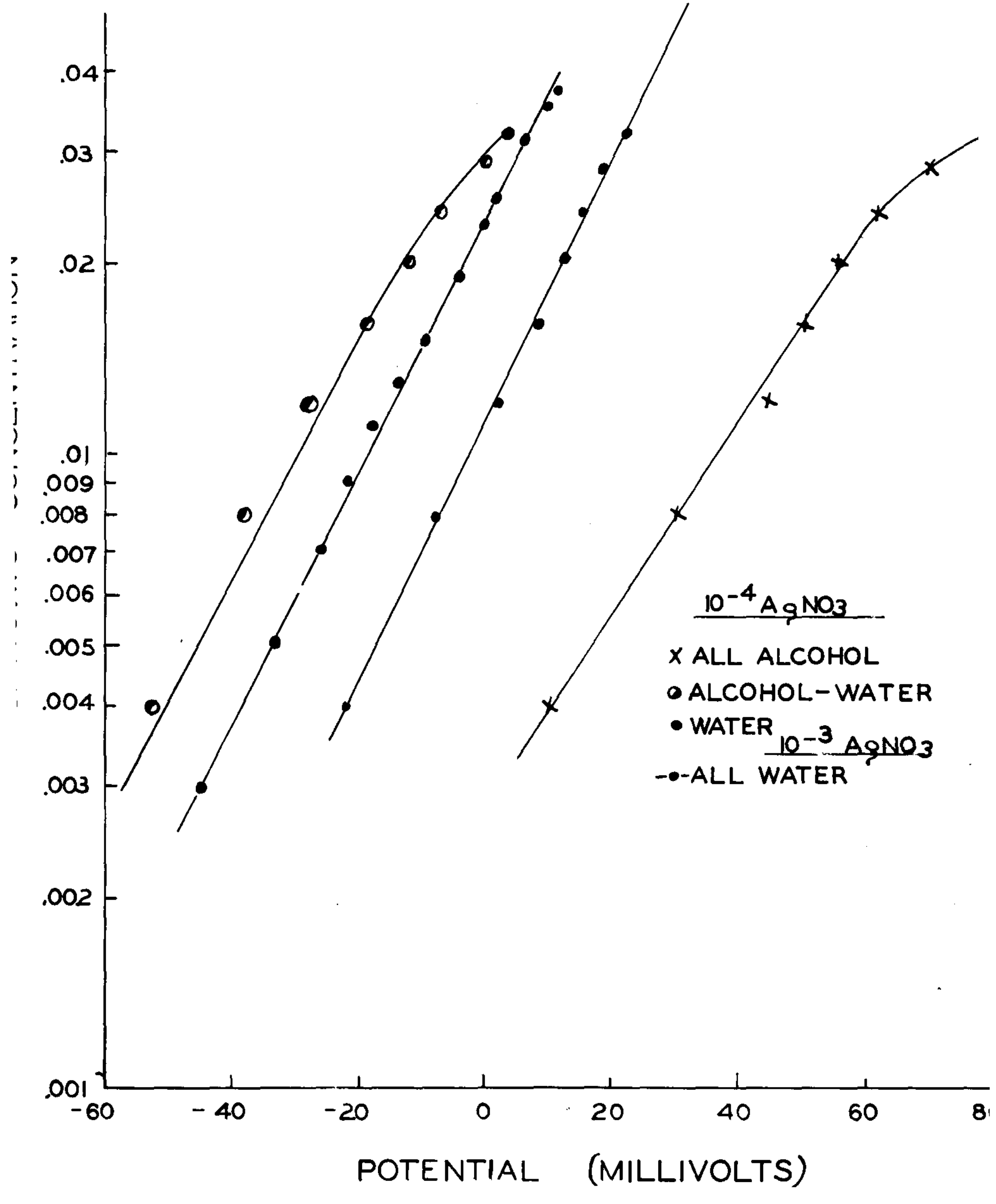


FIGURE XIII

VARIATION OF MEMBRANE POTENTIAL WITH CATIONIC CONCENTRATION

(BARIUM AND AMMONIUM IONS)

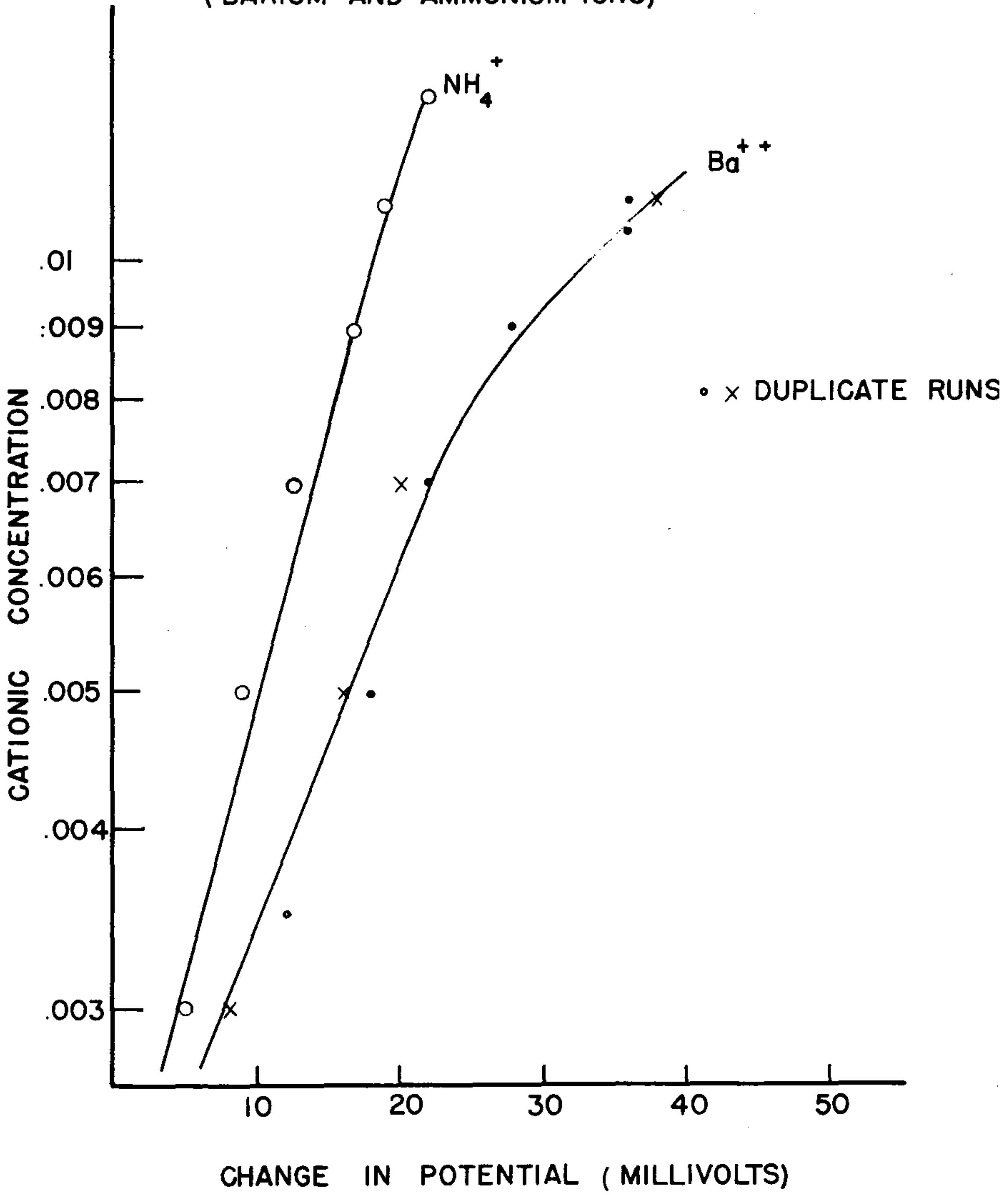


FIGURE XIV

VARIATION OF MEMBRANE POTENTIAL WITH CATIONIC CONCENTRATION

(BARIUM IONS)

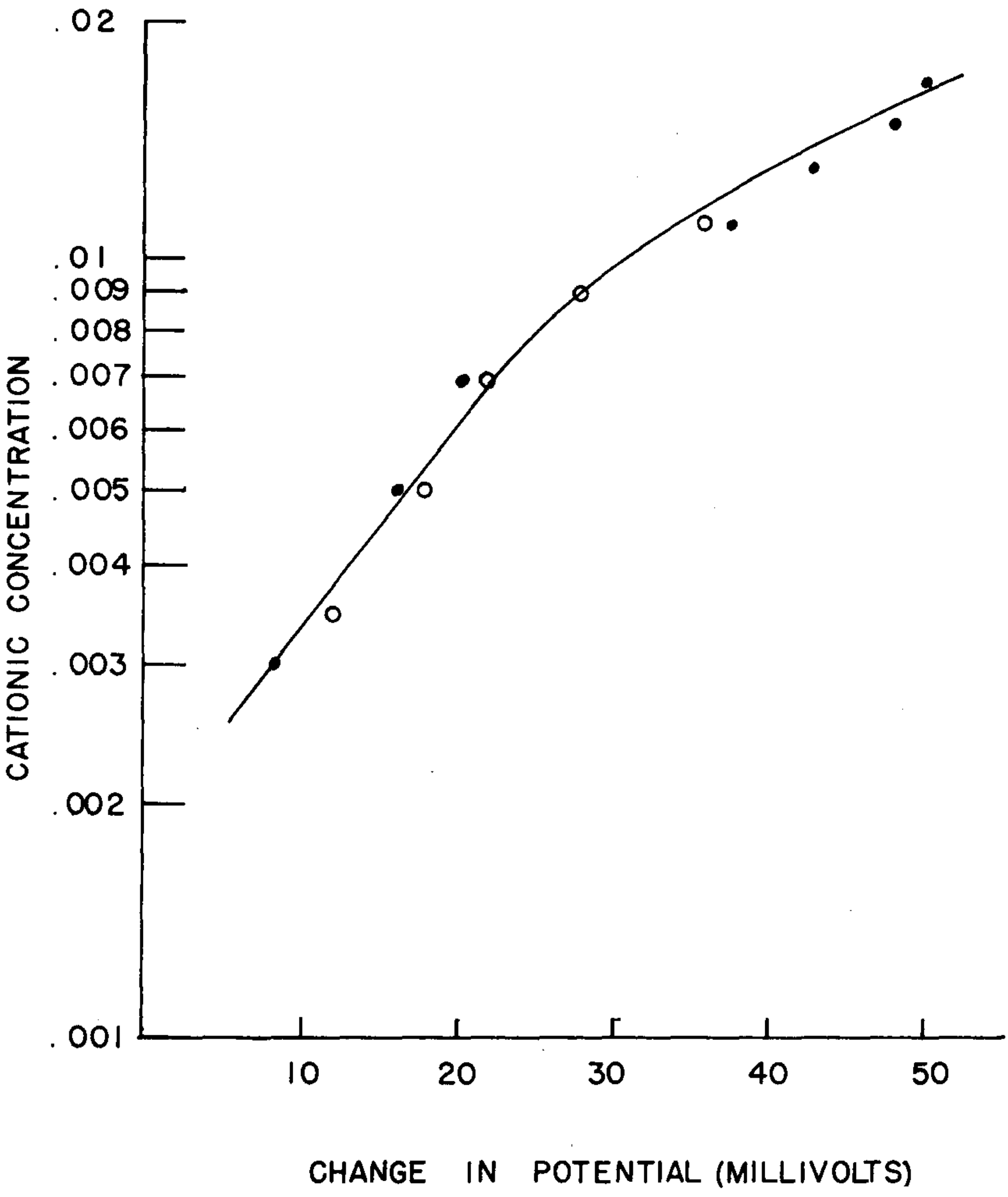


FIGURE XV

VARIATION OF ACTIVITY COEFFICIENT WITH CONCENTRATION

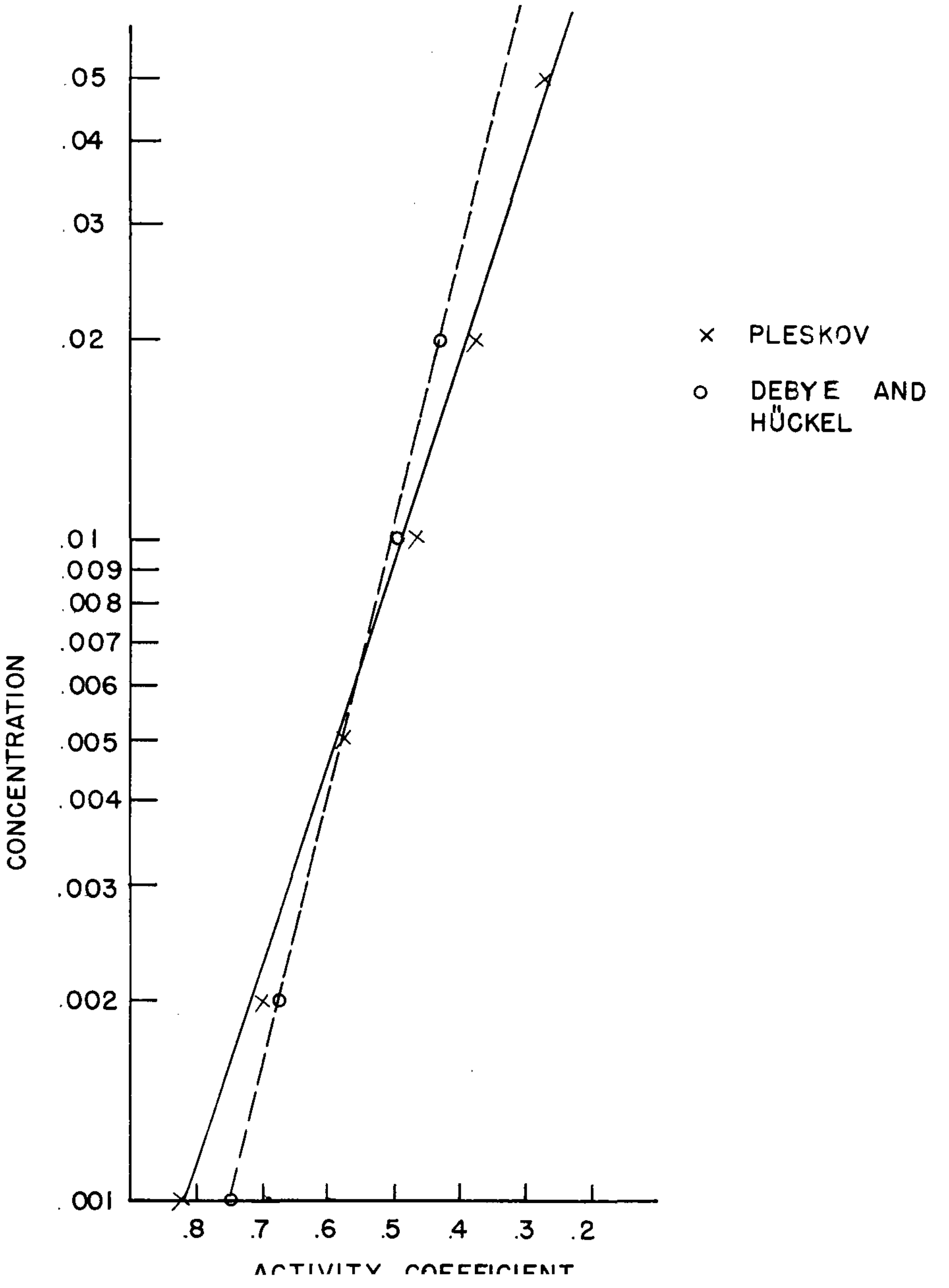
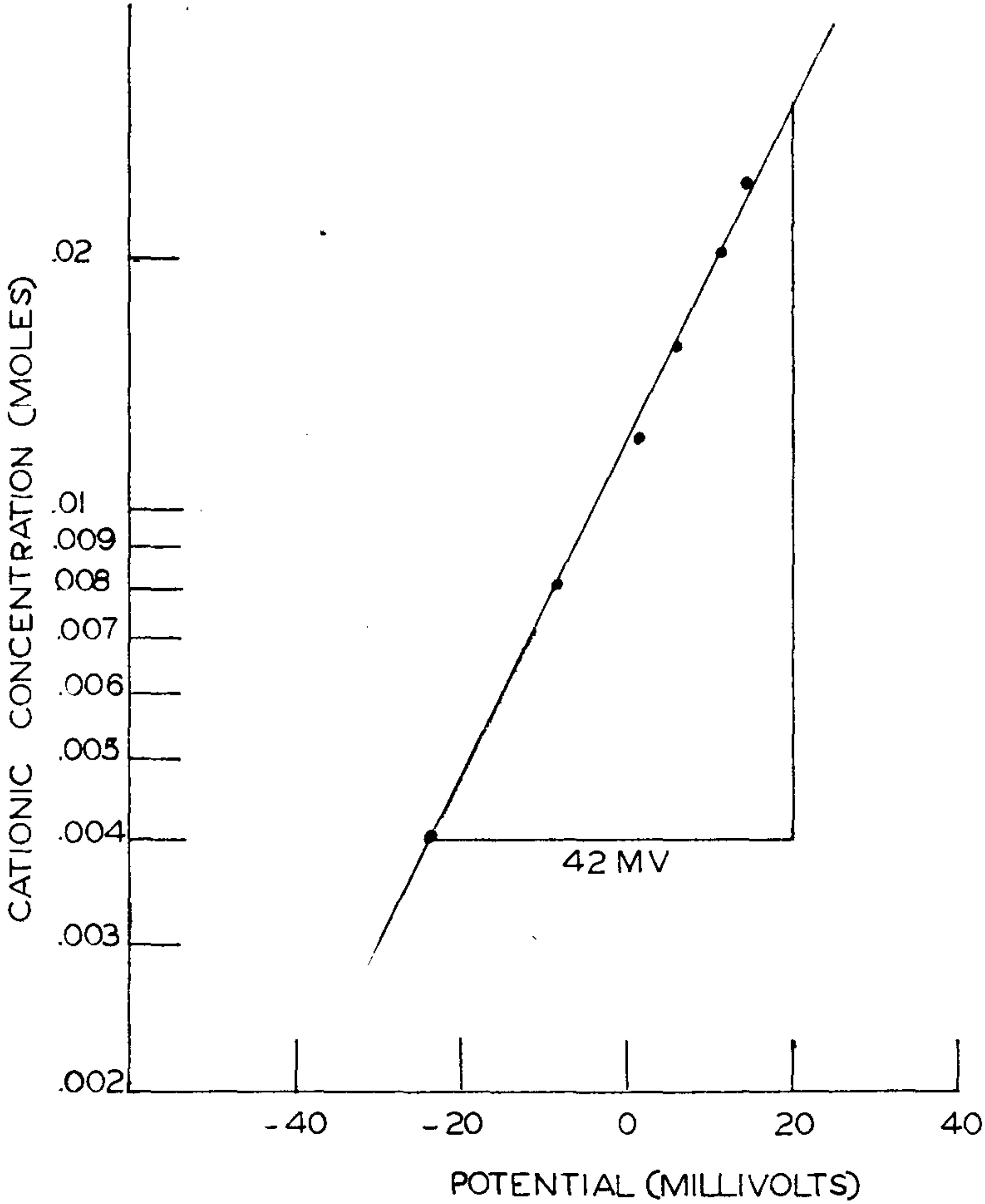


FIGURE XVI
VARIATION OF MEMBRANE POTENTIAL WITH CATIC
CONCENTRATION
(ALL AQUEOUS MEDIUM)



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THE AUTHOR

Name: Martha Jane Bergin

Home Address: 55 Fenwood Road
Boston, Massachusetts

Date of Birth: March 13, 1926

Parents: John A. and
Augusta (Harris) Bergin

Education:

High School: Girls' Latin School

College: Radcliffe College
A.B. (with Honors) 1945

Boston University
A.M., 1950

Teaching and Research Experience

Teaching Fellows during academic years of 1949-50 and 1950-51 in the undergraduate analytical chemistry and the graduate semi-micro organic analysis course.

Fellowship from Research Corporation, inter session and summer session 1951.

Professional Experience

Analytical chemist in General Engineering Laboratories of Sylvania Electric Products, Inc., Salem, Massachusetts from 1945 up to the present time. Leave-of-absence granted from September 1949 to September 1951.

ABSTRACT

Part I - The Glass Electrode

The glass electrode is a convenient instrument for the determination of the activity of the solvated proton ($H\ (H_2O)_x^+$) in water. This investigation was undertaken to determine whether the glass electrode could similarly be used for the determination of the activity of the solvated proton ($H\ (NH_3)_x^+$) in liquid ammonia.

The cell system generally used to measure the activity of the hydronium ion is represented by:

Reference Electrode	Test Solution Containing Hydronium ion	Glass Membrane	Reference Solution Containing Hydronium ion	Reference Electrode.
	a_1		a_o	

In this system, the relationship between the measured potential and the hydronium ion activity is:

$$E = RT/F \ln a_1/a_o + C.$$

The theoretical derivation of this equation is predicated on two ideas: (1) that protons are transported by the membrane, and (2) that a rapidly established exchange equilibrium exists between the protons in the glass and the hydronium ions in solution.

A similar cell system was used to investigate the possibility of glass electrode action in liquid ammonia:

Lead	Lead Nitrate	Ammonium Nitrate	Glass Membrane	Reference Solution Ammonium Nitrate	Lead Nitrate	Lead
	LIQUID AMMONIA			LIQUID AMMONIA		

The lead-lead nitrate electrodes serve as reference electrodes in the liquid ammonia system. Glass membranes were used which were made of three different kinds of glass: Corning 015, Beckman General Purpose, and Beckman Type "E".

The glass electrode action of each glass membrane was first established in water by the measurement of the resultant potential. However, when liquid ammonia was used as the solvent, the cell behaved as an open circuit; and, therefore, no potential could be measured. To encourage the necessary exchange reaction, the glass membrane was modified by replacing a portion of the sodium ions in the silicate lattice by ammonium ions. The "ammoniated" glass membrane also failed to produce any electrode response.

The electrical resistance of glass is an inverse function of the temperature. In order to ascertain whether the lack of glass electrode action in liquid ammonia solutions was a result of the high resistance of the glass membranes at the temperature ($-35^{\circ}C$) of the measurements, the relationship between the resistance of the membrane and the temperature was determined experimentally. The resistance of the membrane was studied over the temperature range $7^{\circ}C$ to $50^{\circ}C$ in an aqueous system, and over the temperature range $-35^{\circ}C$ to $45^{\circ}C$ in a water-alcohol system. In both cases, the resistances were found to follow the relationship:

$$\text{Log } R = A + B/T$$

where R is the observed resistance, T is the absolute temperature, and A and B are constants.

In liquid ammonia, over a temperature range of $-40^{\circ}C$ to $0^{\circ}C$, no passage of current through the membrane was detected when external potentials of up to 2400 volts were applied to the system. Since easily measurable conduction through a glass membrane can be obtained in the water-alcohol medium at $-35^{\circ}C$, the temperature alone is not responsible for the extremely high resistance of the membrane in liquid ammonia. Since conductance through the membrane is required for glass electrode action, it is evident that such action will not occur in liquid ammonia.

In summary, this part of the investigation has demonstrated experimentally that the glass electrode cannot be used to determine the concentration of ammonium ion in liquid ammonia. An exchange action between the protons in the glass and the solvated protons in the solution is necessary for glass electrode action in water. It must be concluded, therefore, that an analogous exchange involving the ammonium ion in liquid ammonia and the proton on the glass surface, does not occur.

Part II - Selectively Permeable Cation Exchange Membranes

In Part I of this investigation it was demonstrated that the glass electrode does not respond to a change of ammonium ion concentration in liquid ammonia. In aqueous media, the response of the glass electrode to a change in hydrogen ion activity may result from a change in the dynamic exchange equilibrium which exists between the hydrogen ions in solution and those on the surface of the glass. Therefore, the glass which separates the reference solution from the test solution may be considered to behave as a membrane made of ion exchange material. Part II of this investigation reports the successful use of a membrane made of a synthetic cation exchange resin in place of the glass membrane.

In aqueous media, membranes made of ion exchange resins have been used to determine activity coefficients and to study membrane equilibria. The research reported herein demonstrated that ion exchange membranes can also be used in liquid ammonia in cell systems analogous to those used for the glass electrode.

Two cell systems were studied. The first may be represented schematically as follows:

Silver	Silver Nitrate	Ammonium Nitrate (Varying Concentrations)	Membrane	Ammonium Nitrate (Reference)	Silver Nitrate	Silver
	WATER			WATER		

This cell system was used to establish that the cation exchange membrane behaved as an electrode which was reversible to cations in solution. The potential of the cell varied in a linear manner with the logarithm of the cationic concentration over the concentration range 0.004M to 0.04M with respect to ammonium nitrate.

During the study of the action of the membranes in liquid ammonia, some initial experiments were performed in all liquid ammonia cell systems. The use of such cells had to be abandoned because most of the membranes could not withstand the vacuum technique necessary for the use of liquid ammonia.

The cell system which was used for the major portion of the investigation may be represented schematically as follows:

Silver	Silver Nitrate	Ammonium Nitrate (Varying Concentrations)	Membrane	Ammonium Nitrate (Reference)	Silver Nitrate	Silver
	LIQUID AMMONIA			ALCOHOL		

It was found experimentally that the presence of two media in the system did not alter the fundamental nature of the membrane's electrode action.

The use of this cell system necessitated the derivation of an equation for the junction potential produced across the membrane. Since the chemical potential of a substance does not depend directly on the nature of the solvent, fundamental equations found valid in aqueous media can be applied to any solvent. Utilizing the Henderson-Plank equation for liquid junction potentials, the following relationship between the change of membrane potential resulting from a change in cationic concentration was obtained:

$$\Delta E = (2t_+ - 1)\ RT/F\ \ln\frac{(\gamma_\pm C)_B}{(\gamma_\pm C)_A}$$

where ΔE is the change in potential, t_+ represents the fraction of current carried across the membrane by the positive ions, C_A and C_B represent cationic concentrations, and $\gamma_\pm$ signifies the mean activity coefficients of the salts.

The equation predicts that, at constant temperature, a plot of the potential versus the logarithm of the cationic concentration should be linear; and the slope of such a line should be dependent on the transference number of the cation across the membrane. The ratio of activity coefficients can be obtained from this relationship.

Within the concentration range 0.002M to 0.016M with respect to ammonium nitrate, a straight line plot was obtained in accordance with the above predictions. A value for the transference number (t_+) of 0.98 was calculated from the experimental data obtained. Moreover, ratios of activity coefficients of ammonium nitrate in liquid ammonia were calculated within this concentration range. These values agreed closely with those obtained by earlier investigators who used a different electrochemical method.

In summary, in Part II of this dissertation it is demonstrated that if a membrane, made of a cation exchange resin, be substituted for the glass membrane, and if certain other experimentally necessitated modifications of the internal solvent are made, potentials are produced, the variation of which is in quantitative agreement with theoretical equations deduced. That is, this dissertation reports an electrode which may be used in liquid ammonia, and other media, to determine cationic activities in a manner analogous to the use of the glass electrodes in determining hydronium ion activities in aqueous media. A major difference between the reported electrode and the glass electrode lies in the fact that the former is sensitive to changes in the activity of any cation, while the latter is generally sensitive only to changes in hydronium ion.

In addition to enabling easy measurement of cationic activities, the experimental results have been used to calculate ratios of activity coefficients in liquid ammonia; and a method is clearly indicated for use of the new electrode for determination of the activity coefficients themselves in liquid ammonia.