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Conductance Studies of Concentrated Solutions of Sodium Hydroxide and Potassium Hydroxide Electrolytes

Andrew Ling-Wei Woo

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CONDUCTANCE STUDIES OF CONCENTRATED SOLUTIONS
OF SODIUM HYDROXIDE AND POTASSIUM
HYDROXIDE ELECTROLYTES

BY

ANDREW LING-WEI WOO

A thesis submitted
in partial fulfillment of the requirements for the
degree Master of Science, Major in
Chemistry, South Dakota State
University

1968

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CONDUCTANCE STUDIES OF CONCENTRATED SOLUTIONS
OF SODIUM HYDROXIDE AND POTASSIUM
HYDROXIDE ELECTROLYTES

This thesis is approved as a creditable and independent investigation by a candidate for the degree, Master of Science, and is acceptable as meeting the thesis requirements for this degree, but without implying that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Thesis Adviser

Date

Head, Chemistry Department

Date

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ALW

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INTRODUCTION

Most of the basic assumptions for the theory of conductance were originated by Onsager. Debye and Falkenhagen extended the Onsager theory in their studies with the use of alternating current methods. To this day, theories of conductance in electrolytic solutions are founded principally upon developments of these early basic ideas. However, the theoretical treatment in the case of concentrated solutions is still inadequate. This is due to the circumstance that the general molecular theory of irreversible processes is still in a developmental stage. In addition, the electrolytic solution comprises a complex system whose exact treatment encounters formidable mathematical difficulties. It has been possible, with the aid of a few general assumptions and the introduction of the concept of ionic diameter, to extend the range of validity of the limiting laws for the dilute solutions by a considerable margin. But for the highly concentrated electrolytic solutions, the uncertainty as to the best approach in the explanation of the experimental results still exists. The object of this research is to investigate the conductances of the concentrated solutions of sodium hydroxide, potassium hydroxide, and their mixtures in order to help understand the nature of these electrolytic solutions. Furthermore, the conductance data obtained should have immediate applicability in the technology of alkaline electrolyte systems.

A literature survey reveals that only a relatively small amount of work on concentrated electrolytic solutions has been done. Campbell and co-workers (1-10) have studied the concentrated aqueous solutions of sulfuric acid, silver nitrate, lithium nitrate, ammonium nitrate and mixtures in two of the three salts: lithium nitrate, ammonium nitrate and silver nitrate at various temperatures. Haase and collaborators (19-23) have investigated the concentrated aqueous solutions of nitric acid, perchloric acid, lithium perchlorate, hydrochloric acid, hydrobromic acid, hydroiodic acid, and sulfuric acid in a temperature range of minus twenty to sixty degrees centigrade. Klochko and Godneva (31) have studied concentrated solutions of sodium hydroxide, potassium hydroxide and their one-to-one mixture in a temperature range of twenty-five to two hundred degrees centigrade. They have found that with sodium hydroxide and potassium hydroxide, just like the other electrolytes, when a plot of conductivity, K , versus concentration is made, a concave downward curve with a maximum at five to seven normal is obtained. When plotted as equivalent conductivity, Λ , versus concentration, a concave upward curve with no minimum is usually obtained. At moderate concentrations and in a temperature range of eighteen to one hundred degrees centigrade Gantman and co-workers (16) have found that the relation between temperature and conductance is almost linear. Robinson, Wishaw and Stokes (36, 40) have attempted

to explain these results by constructing the conductance, Λ , as the sum of the partial conductances Λ_I (relaxation effect) and Λ_{II} (electrophoretic effect) in the following manner:

$$\Lambda = \frac{\eta_{(0)}}{\eta_{(c)}} (\Lambda^\circ - \Lambda_I) \left(1 - \frac{\Lambda_{II}}{\Lambda^\circ}\right) \doteq \frac{\eta_{(0)}}{\eta_{(c)}} (\Lambda^\circ - \Lambda_I - \Lambda_{II})$$

A viscosity correction factor has also been applied. This semi-empirical statement was tested by Campbell and co-workers (1, 2, 6, 8, 10). While the calculated results show good agreement with experimental values up to quite high concentrations in the case of lithium nitrate, they were less accurate for potassium chloride solutions.

In this study, the aqueous solutions of sodium hydroxide, potassium hydroxide, and their mixtures with a concentration range of approximately 2.5 to 12 normal at temperatures of 25⁰, 35⁰, 45⁰, 55⁰ and 65⁰C are carefully investigated. The results of these strongly basic concentrated solutions are found to be similar to the concentrated solutions of salts and acids. A pronounced maximum at around five to seven normal is also found on the conductivity curve and the equivalent conductivity curve shows that equivalent conductivity varies with concentration in a typical manner. The relationship between conductivity and temperature is found not to be simply linear for higher concentrations. Some quite obvious deviations from the mixture addition rule are also observed. These not well-understood phenomena undoubtedly lead to some interesting but controversial discussions and conclusions. The

Robinson and Stokes equation is tested with the results of this research. Good agreement is found when the viscosity correction factor is applied, but it requires an unusually large value for the distance of closest approach of the ions. Some other equations have also been tested. The results indicate that it should be possible to correctly explain the conductance of concentrated solutions by the proper acknowledgement of the interionic interaction effects rather than resorting to the use of ion pair formation for all types of electrolytes.

HISTORICAL

Basic Concepts

Metallic conductors are known to obey Ohm's law,

$$I = \frac{E}{R}$$

where I is the current (amperes), E is the electromotive force (volts) and the proportionality constant R is called the resistance (ohms). The resistance depends on the dimensions of the conductor:

$$R = \frac{\rho l}{A}$$

here l is the length and A the cross-sectional area of the conductor.

The specific resistance, ρ , is called the resistivity. The reciprocal of the resistance is called the conductance (ohm^{-1}) and the reciprocal of the resistivity, the specific conductance or conductivity, κ ($\text{cm}^{-1}\text{ohm}^{-1}$).

The earliest studies of the conductance of solutions were made with rather large direct currents. The resulting electrochemical action was so great that erratic results were obtained, and it appeared that Ohm's law was not obeyed; that is, the conductivity seemed to depend on the voltage. The result was largely due to polarization at the electrodes of the conductivity cell; that is, a departure from equilibrium conditions in the surrounding electrolyte.

These difficulties were overcome by the use of an alternating current bridge such as that shown in Figure 1. With frequencies in the audio range (1000-4000 cycles per second), the direction of the current changes so rapidly that polarization effects are essentially eliminated. One difficulty with the alternating current bridge is that the cell acts as a capacitance in parallel with a resistance, so that even when the resistance arms are balanced there is a residual unbalance. This effect can be partially overcome by inserting a variable capacitance in the other arm of the bridge, but for the very precise work further refinements are necessary (38).

A typical conductivity cell (25, 26, 27, 28, 29, 30, 35) is also shown in Figure 1. Instead of measuring the dimensions of the electrodes of the cell, one usually calibrates the cell before use with a solution of known conductivity. Calibration of the conductivity cell will be discussed in detail in the Experimental section.

The literature survey (4, 20, 39, 40) reveals that the conductance measurements of concentrated electrolytic solutions are essentially the same as those of dilute solutions.

Kohlrausch defined a function called the equivalent conductivity,

$$\Lambda = \frac{1000 K}{C} = \frac{K}{C^*} \quad (1)$$

The concentration C^* has the units of equivalents per cubic centimeter, and C has the units of equivalents per liter. The

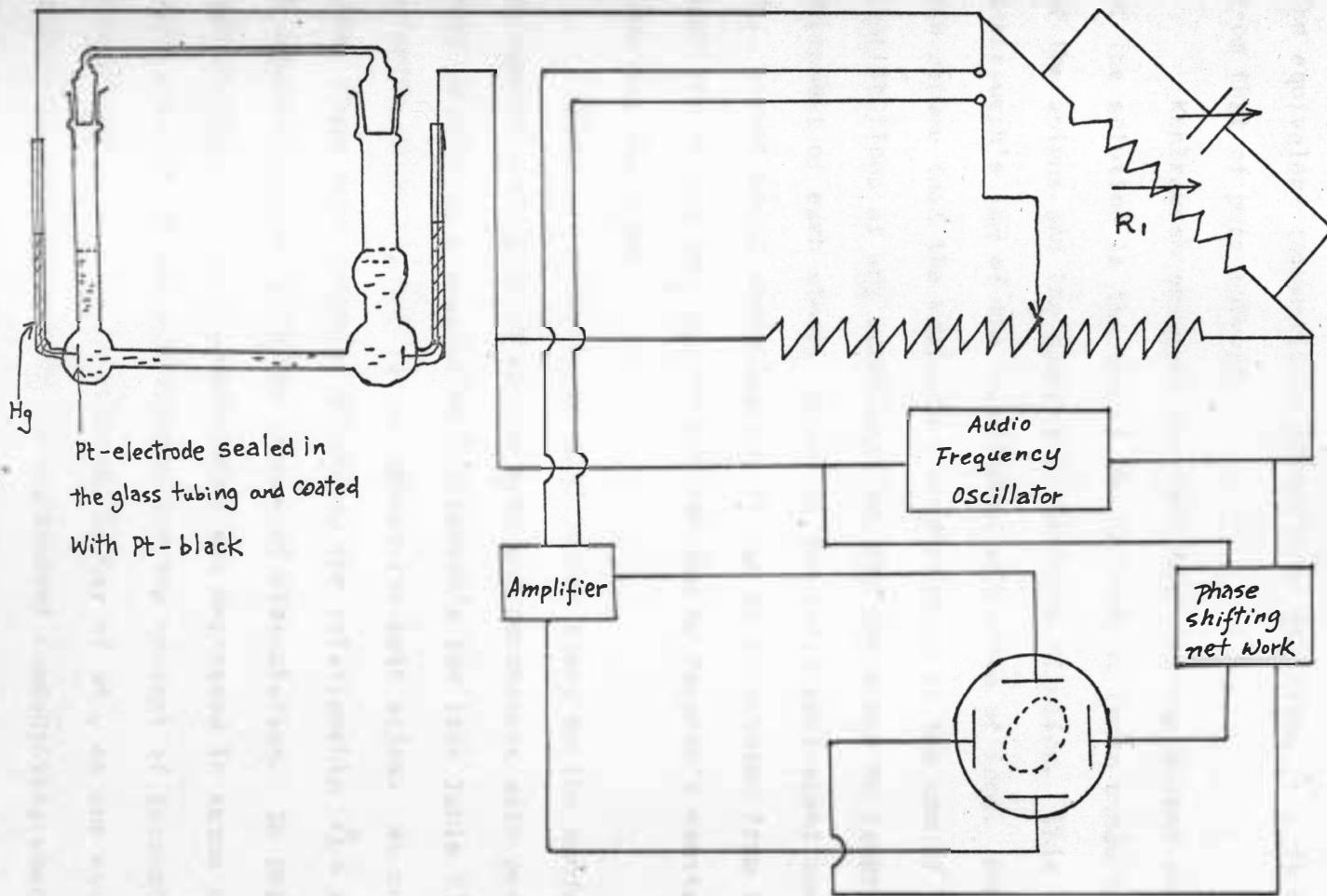


Figure 1. A-C Wheatstone bridge for measurement of conductance of electrolytic solutions (12, 34).

equivalent conductivity is almost, but not quite, independent of concentration. It does approach a limiting value upon dilution. The equivalent conductivity at infinite dilution, Λ° , is different from that of pure solvent.

Kohlrausch observed the fact that the equivalent conductivity of the solution is the sum of the equivalent ionic conductivities of the anions and the cations at infinite dilution. This is Kohlrausch's law of the independent migration of ions. One also can assume that the equivalent conductivity is the sum of ionic contributions at any concentration, but these are no longer independent of each other. Although the ionic equivalent conductivity, λ_i , is not known individually, it can be calculated from the mobility of the ion, u_i , by multiplying by Faraday's constant, F ; that is, $\lambda_i = Fu_i$.

Haase and co-workers' (20) recent study on the conductance of aqueous solutions of nitric acid and perchloric acid provides a good example of illustrating Kohlrausch's law (see Table 1). At infinite dilution, the law is upheld for both acids. At concentrations other than infinite dilution, the relationship $\Lambda = \alpha(\lambda_+ + \lambda_-)$ is applied, where α is the degree of dissociation. In this application the ionic conductances are expressed in terms of the concentration of the electrolyte and the concept of incomplete dissociation has been introduced, by way of α , as one way of explaining the decrease in the equivalent conductivity when the concentration increases.

Table 1. Equivalent Conductivities of HNO_3 and HClO_4 at 25°C ; α is the degree of dissociation (20).

System	c moles/liter	α	Δ $\text{cm}^2/\text{equiv}\cdot\text{ohm}$	$\lambda_+ + \lambda_-$ $\text{cm}^2/\text{equiv}\cdot\text{ohm}$
HNO_3	0	1.000	421.3	421.3
	1	0.985	328.6	333.6
	5	0.829	170.5	205.7
	10	0.520	73.81	141.9
HClO_4	0	1.000	417.2	417.2
	1	0.984	330.7	336.1
	5	0.902	152.5	169.1

Debye-Hückel Theory of Dilute Electrolytic Solutions.

The strong electrolytes are assumed to dissociate completely into their ions in dilute solutions. The observed deviations from ideal behavior are then ascribed to electrical interactions between the ions. For an ion in the solution, the opposite charged particles are more likely to be found in the immediate neighborhood. On the average, a given ion will be surrounded by a spherically symmetrical distribution of oppositely charged ions. This ionic atmosphere is formed by the compromise between the electrostatic interactions tending to produce ordered configurations and the thermal kinetic collisions tending to destroy them.

To obtain theoretically the equilibrium properties of solutions, it is necessary to calculate the extra free energy arising from these electrostatic interactions. The extra electric free energy is simply related to the ionic activity coefficient, since both are a measure of the deviation from ideality.

By applying Boltzmann's distribution theorem, the charge density for the atmosphere of ions, σ , can be calculated:

$$\sigma = - \frac{e^2 U}{kT} \sum_i N_i z_i^2 \quad (2)$$

where U is the potential energy, e is the unit electric charge, k is Boltzmann's constant, T is the absolute temperature, N_i is the average number of ions of kind i in unit volume in the solution, and z_i is number of charges on the ion.

By substituting this expression into Poisson's equation,

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dU}{dr} \right) = - \frac{4\pi\sigma}{D} \quad (3)$$

where r is the distance from the central ion, and D is the dielectric constant of the solvent, one obtains the Poisson-Boltzmann equation

$$\frac{d}{dr} \left(r^2 \frac{dU}{dr} \right) = b^2 r^2 U \quad (4)$$

where

$$b^2 = \frac{4\pi e^2}{DkT} \sum_i N_i z_i^2 \quad (4a)$$

When dilute solutions are considered, and when the ionic strength is introduced, b can be expressed as

$$b = \left(\frac{8\pi N^2 e^2 d_0}{1000 DRT} \right)^{\frac{1}{2}} I^{\frac{1}{2}} = BI^{\frac{1}{2}} \quad (5)$$

where N is Avogadro's number, d_0 is the density of the solvent, I is the ionic strength (defined as $I = \frac{1}{2} \sum_i m_i z_i^2$, and m_i is the ion concentration in molality). The quantity $1/b$ has the dimension of a length, and is called the Debye length. It is the approximate measure of the thickness of the ionic atmosphere and is the distance to which the electrostatic field of an ion extends with any appreciable strength. For a very dilute solution the Poisson-Boltzmann equation gives

$$U = \frac{ze}{Dr} \exp(-br) \quad (6)$$

Since b is a function of concentration, the expansion of the exponential gives

$$U = \frac{ze}{Dr} \exp(-br) \approx \frac{ze}{Dr}(1-br) \quad (7)$$

Here it is evident that the first term ze/Dr is simply the potential at a distance r due to an ion of charge ze in a medium of dielectric constant D . The term zeb/D is then the potential due to the other ions, or those forming the ionic atmosphere of the given ion. It is this extra potential that is related to the extra free energy of the ionic solution.

Utilizing the relationship, μ_i (electric) = $kT \ln \gamma_i$, where $\mu_i = -bz^2e^2/2D$ is the extra electric free energy per ion and γ_i is the activity coefficient of the ion, one gets

$$\ln \gamma_i = - \frac{z^2e^2b}{2DkT} \quad (8)$$

Since the individual ion activity coefficient can not be measured, the mean activity coefficient is calculated as

$$\ln \gamma_{\pm} = - |z_+z_-| \cdot \left(\frac{e^2b}{2DkT} \right) \quad (9)$$

When the expression for b and the value of the universal constants are introduced, the result is

$$\log \gamma_{\pm} = - 1.825 \times 10^6 |z_+z_-| \left(\frac{I_d}{D^3T^3} \right)^{\frac{1}{2}} \quad (10)$$

or,

$$\log \gamma_{\pm} = - A |z_+ z_-| I^{\frac{1}{2}} \quad (10a)$$

This is the Debye-Hückel limiting law for the activity coefficient.

For water at 25°C, $D = 78.54$, and $d_o = 0.997$, so the equation

becomes

$$\log \gamma_{\pm} = - 0.509 |z_+ z_-| I^{\frac{1}{2}} \quad (11)$$

In the derivation of the limiting law it was consistently assumed that the analysis applied only to dilute solutions. It is not to be expected therefore that the equation should hold for concentrated solutions, nor does it. As solutions become more and more dilute, however, the equation should represent the experimental data more and more closely. This expectation has been fulfilled by numerous measurements, so that the Debye-Hückel theory for very dilute solutions may be considered to be well substantiated.

Onsager's Theory of Conductance.

Based on Debye-Hückel's interionic attraction theory, Onsager derived an equation for electrolytic conductance. This Debye-Hückel-Onsager theory is only valid for very dilute solutions (17).

Under the influence of an electric field, an ion moves through a solution not in a straight line, but in a series of zigzag steps similar to those of Brownian motion. The persistent effect of the potential difference ensures an average drift of the ion in the field direction. Opposing the electric force on the ion is first of all the frictional drag of the solvent, $f_i v_i$. Here f_i is the coefficient of frictional resistance of the solvent opposing the motion of the ion of the i th kind, and v_i is the velocity of the ion when it is moving through a solution steadily.

In addition to this viscous effect, two additional important effects must be considered even in the dilute solutions.

1. Asymmetric effect.

An ion in any static position is surrounded by an ionic atmosphere of oppositely charged ions. If the ion jumps to a new position, it will tend to drag with it this opposite charged aura. The ionic atmosphere, however, has a certain inertia and cannot instantaneously readjust itself to the new position of its central ion. Thus, around a moving ion there is a net accumulation of

opposite charge which is no longer symmetrically distributed and thus exerts an electrostatic drag, decreasing the ionic velocity in the field direction. Onsager derived the equation of this relaxation force,

$$\text{relaxation force} = \frac{e^3 z_i b}{6DkT} wX \quad (12)$$

where X is the applied potential, and w is defined by

$$w = z_+ z_- \frac{2q}{1 + \frac{1}{q}}$$

and,

$$q = \frac{z_+ z_-}{z_+ + z_-} \frac{\lambda_+ + \lambda_-}{z_+ \lambda_- + z_- \lambda_+}$$

$q = \frac{1}{2}$ for symmetrical electrolytes.

2. Electrophoretic effect.

The ions comprising the atmosphere around a given central ion are themselves moving, on the average in the opposite direction, under the influence of the applied field. If they are solvated, they tend to carry along with them their associated solvent molecules, so that there is a net flow of solvent in a direction opposite to the motion of any given central ion, which is thus forced to "swim upstream" against the current. The expression for this electrophoretic force on an ion of the i th kind is

$$\text{Electrophoretic force} = \frac{ez_i b}{6\pi\eta} f_i X \quad (13)$$

where η is the viscosity of the medium.

By equating the forces acting on the ion of the i th kind, when it is moving through a solution with a steady velocity v_i , the driving force due to the applied electrical field is $ez_i X$. This is opposed by the frictional force of the solvent, $f_i v_i$, together with the relaxation and electrophoretic forces; hence

$$ez_i X = f_i v_i + \frac{ez_i b}{6\pi\eta} f_i X + \frac{e^3 z_i b}{6DkT} w X \quad (14)$$

On dividing through by $f_i X$ and rearranging, this becomes

$$\frac{v_i}{X} = \frac{ez_i}{f_i} - \frac{ez_i b}{6\pi\eta} - \frac{e^3 z_i b}{6DkT} \frac{w}{f_i} \quad (15)$$

By definition, ionic mobility is the velocity of the ion per unit field strength; that is, $u_i = v_i/X$. If the field strength, or potential, is taken as 1 volt per centimeter; that is, X is 1/300 in electrostatic units, then

$$u_i = \frac{ez_i}{300f_i} - \frac{eb}{300} \left(\frac{z_i}{6\pi\eta} + \frac{e^2 z_i}{6DkT} \frac{w}{f_i} \right) \quad (16)$$

At infinite dilution, indicated by the superscript zero, this equation becomes

$$u_i^0 = \frac{ez_i}{300f_i} \quad (17)$$

and since $Fu_i^0 = \lambda_i^0$, it follows that

$$\frac{ez_i}{300f_i} = \frac{\lambda_i^0}{F} \quad (18)$$

Since $u_i = \lambda_i/F$, this substitution in equation 16 gives

$$\frac{\lambda_i}{F} = \frac{\lambda_i^0}{F} - \frac{eb}{300} \left(\frac{z_i}{6\pi\eta} + \frac{e}{6DkT} \frac{ez_i}{f_i} w \right) \quad (19)$$

Introducing the expression for b given by equation 5 and utilizing the standard values of e , k , and N , yields

$$\lambda_i = \lambda_i^0 - \left[\frac{29.15z_i}{(DT)^{\frac{1}{2}}\eta} + \frac{9.90 \times 10^5}{(DT)^{\frac{3}{2}}} \lambda_i^0 w \right] \sqrt{C_+z_+^2 + C_-z_-^2} \quad (20)$$

The quantities C_+ and C_- represent the concentrations of the ions in moles per liter. These may be replaced by the corresponding concentration C in equivalents per liter of the electrolyte, since $C = C_+z_+$. The equivalent conductivity of an electrolyte is equal to the sum of the ionic equivalent conductivities of the constituent ions, so that

$$\Lambda = \Lambda^0 - \left[\frac{29.15(z_+ + z_-)}{(DT)^{\frac{1}{2}}\eta} + \frac{9.90 \times 10^5 w \Lambda^0}{(DT)^{\frac{3}{2}}} \right] \sqrt{C(z_+ + z_-)} \quad (21)$$

In the simple case of a uni-univalent electrolyte, $z_+ = z_- = 1$, and w is $2\sqrt{2}$, so equation 21 reduces to

$$\Lambda = \Lambda^0 - (A + B \Lambda^0) \sqrt{C} \quad (22)$$

where A and B are constants dependent only on the nature of the solvent and the temperature, and are given by

$$A = \frac{82.4}{(DT)^{\frac{1}{2}} \eta} \quad (22a)$$

$$B = \frac{82.0 \times 10^5}{(DT)^{\frac{3}{2}}}$$

Equations 20, 21 and 22 represent the well known Onsager equation. These relationships, based on the assumption that dissociation of the electrolyte is complete, attempt to account for the falling off of the equivalent conductivity at appreciable concentrations in terms of a decrease in ionic velocity resulting from interionic forces. The decrease of conductance due to these forces is represented by the quantities in the square brackets. The first term gives the effect due to the electrophoretic force, and the second term represents the influence of the relaxation, or asymmetric force.

Modification of the Onsager Equation.

Three distinct methods have been used for extending the range of Onsager's equation to somewhat higher concentrations. The first applies mainly to electrolytes for which the conductance falls below the predicted "limiting law" values in dilute solutions, and interprets this "conductance deficiency" in terms of finite ionization constants. The second assumes complete dissociation and attempts to account for all departures from the limiting equation by more elaborate theoretical approximations or inclusion of the "mean distance of closest approach" in the physical picture. The third method is the purely empirical addition of terms in higher powers of concentration than the one-half power.

Shedlovsky (37) rearranged the limiting equation to obtain an empirical equation

$$\Lambda' = \frac{\Lambda + A\sqrt{C}}{1 - B\sqrt{C}} = \Lambda^{\circ} + DC \quad (23)$$

or,

$$\Lambda = \Lambda^{\circ} - \mathcal{J}(\Lambda) C^{\frac{1}{2}} + DC - DBC^{\frac{3}{2}} \quad (24)$$

The conductance of strong 1-1 electrolytes can usually be expressed by this equation up to 0.1 normal within experimental error.

Fuoss and Onsager (18) estimated the effect of the mathematical simplifications involved in the derivation of Onsager's limiting equation. The deviation of Λ from linearity with concentration is represented by addition of two terms. Thus

$$\Lambda = \Lambda^{\circ} - \mathcal{J}(\Lambda) \sqrt{C} + AC \log C + BC \quad (25)$$

As originally proposed, this expression was semi-empirical in that the numerical values of the constants A and B had not yet been completely evaluated from theoretical consideration.

In 1957, Fuoss and Onsager (14) derived an improved conductance equation for symmetrical valence type electrolytes. The relaxation field for dissociated electrolytes was obtained as a function of concentration by solving the Onsager-Fuoss equation of continuity, subjected to boundary conditions for charged spheres rather than considering the ions as point charges. The retention of higher order terms in the previous expression of the electrophoretic effect provided a conductance equation which has the limiting form

$$\Lambda = \Lambda^{\circ} - (A \Lambda^{\circ} + B)C^{\frac{1}{2}} + D \ln C + (J_1 C - J_2 C^{\frac{3}{2}})(1 - \alpha C^{\frac{1}{2}}) \quad (26)$$

in which the constants J_1 and J_2 are explicit functions of the ion size, Λ° and properties of the solvent. The dielectric constant, D , is independent of ion size. Up to concentrations of the order of a hundredth normal, the equation reduces to

$$\Lambda = \Lambda^{\circ} - (A \Lambda^{\circ} + B)C^{\frac{1}{2}} + CD(ba) \quad (27)$$

By using the potential of the total directed force on charged spheres moving in a continuum under an external field and correcting for electrophoresis, Fuoss, Onsager and Skinner (15) derived another modified conductance equation for the symmetrical electrolytes,

$$\Lambda = \Lambda^{\circ} - \mathcal{S} C^{\frac{1}{2}} + E' \ln(6E_1' C) + LC - A_c f^2 \quad (28)$$

This equation reproduces conductance data for 1-1 electrolytes in solvents of high dielectric constant. This result confirms

Other Conductance Equations.

Among the numerous empirical equations which have been suggested for extrapolation of conductivity data for strong electrolytes, the square root law of Kohlrausch

$$\Lambda = \Lambda^{\circ} - A \sqrt{C} \quad (29)$$

has been rendered the most noteworthy service in aqueous solutions, and is formally in agreement with the interionic attraction theory. Because of the success of this equation at extreme dilutions, most of the interpolation equations proposed for use at higher concentrations reduces to the above equation at low concentrations. The simplest of these is the relation

$$\Lambda = \Lambda^{\circ} - A \sqrt{C} + BC \quad (30)$$

Walden proposed the equation

$$\Lambda = \frac{\Lambda^{\circ}}{1 + B \sqrt{C}} \quad (31)$$

which is considerably less accurate than equation 30 but covers the same range up to 0.01 molar. Lattey (18) combined features of both these equations by writing

$$\Lambda = \Lambda^{\circ} - \frac{A \sqrt{C}}{1 + B \sqrt{C}} \quad (32)$$

This expression is fairly successful at concentrations below 0.1 N. By addition of a linear term in concentration, Jones and Dole (18) showed that the relation

$$\Lambda = \Lambda^{\circ} - \frac{A\sqrt{C}}{1 + B\sqrt{C}} + DC \quad (33)$$

will describe their data for barium chloride up to 2 N with a very small experimental error. The results for potassium bromide (28) can be expressed with equal success at 0° and 25°C.

Kuzenetsov, Antipina and Buryankovskaya (32) reported their investigations of conductivity of saturated aqueous sodium chloride solutions containing up to 4.08 N of sodium hydroxide at 75° and 95°C in 1959. Plots of conductivity, \mathcal{K} , versus sodium hydroxide concentration were functions expressed by

$$\mathcal{K} = A + BC - KC^2 + LC^3 \quad (34)$$

where C is the concentration of sodium hydroxide in moles per liter at 20° and the values of the constants A, B, K and L at 75° and 95°C were given.

A modified Onsager equation derived by Robinson and Stokes (36) and Wishaw and Stokes (40) in 1953 is found to be very interesting. Combining Falkenhagen's (13) derivation of the relaxation effect with the conventional expression of electrophoretic effect, the equation of conductance for uni-univalent electrolytes takes the form

$$\Lambda = \Lambda^{\circ} - \left(\frac{82.5}{\eta(DT)^{\frac{1}{2}}} \frac{C^{\frac{1}{2}}}{1 + b_0} \right) \left(1 + \frac{\Delta X}{X} \right) \quad (35)$$

where b is defined by equation 4a and a^0 is the closest approach of the ions expressed in Angstroms. The relaxation term for the 1-1 electrolytes is

$$\frac{\Delta X}{X} = - \frac{e^2}{3DkT} \frac{0.2929 b}{1 + ba^0} \quad (35a)$$

which differs from Onsager's limiting formula, equation 12, by the factor $1/(1 + ba^0)$. By substituting $\Delta X/X$ into equation 35, one obtains

$$\Lambda = \Lambda^0 - \frac{(B_1 \Lambda^0 + B_2) C^{\frac{1}{2}}}{1 + Ba^0 C^{\frac{1}{2}}} \quad (36)$$

where $B_1 = 8.20 \times 10^5 / (DT)^{\frac{3}{2}}$

$$B_2 = 82.5 / [\eta (DT)^{\frac{1}{2}}]$$

$$B = 50.29 / (DT)^{\frac{1}{2}} \quad (36a)$$

It is interesting to note the similarity of the equations 24, 27, 30 and 34, as they are all in power series form and reduce to equation 29 in the limiting case. However, most of these equations fail to accurately describe the conductance of highly concentrated solutions. But equation 36, with the proper correction of viscosity, gives good agreement with experimental results in the case of lithium chlorate (10) up to 6 normal.

Concentration Dependence and Temperature Dependence of Conductance.

Campbell and collaborators (1-10) have studied the conductance of concentrated solutions of silver nitrate, ammonium nitrate, lithium nitrate, lithium chlorate, and the mixtures of two of the three salts, silver nitrate, ammonium nitrate and lithium nitrate at various temperatures. The molten salts of silver nitrate and ammonium nitrate were also investigated. When the conductivity was plotted against concentration at various temperatures, all the curves obtained were similar in character; they all exhibit a pronounced maximum at a concentration around five to seven normal. When plotted as equivalent conductivity versus concentration, a concave upward curve with no minimum was obtained. And, when plotted as equivalent conductivity versus $\log C$ an almost straight line was usually found. It was also found that when plotted as equivalent conductivity versus temperature at constant concentration an apparent straight line was usually obtained.

Haase and co-workers (19, 21, 22, 23) have measured the conductances of concentrated aqueous solutions of nitric acid (from minus twenty to fifty degrees centigrade), perchloric acid, and lithium perchlorate (from zero to sixty degrees centigrade), and hydrochloric acid, hydrobromic acid and hydroiodic acid (from minus twenty to fifty degrees centigrade), and sulfuric acid (from ten to fifty degrees centigrade). The tabulated results and graphs showed that the relationships among conductivity, equivalent

conductivity, concentration and temperature of these acids were essentially the same as those of the uni-univalent salt solutions.

Manvelyan and co-workers (33) have reported the results of their study on the conductance of concentrated solutions of sodium and potassium hydroxides, their mixtures, and their carbonates at twenty-five degrees centigrade. The conductivity curves for sodium hydroxide and potassium hydroxide passed through a sharp maximum at 4.5 and 6 normal, respectively.

In 1959, Klochko and Godneva (31) investigated the conductances of the concentrated aqueous solutions of sodium hydroxide, potassium hydroxide and their one-to-one mixture in a temperature range of twenty-five to two hundred degrees centigrade. The characteristic conductivity curves for sodium hydroxide and potassium hydroxide were found to be similar to those of the acids and salts. The conductivity of the one-to-one mixture fell in between the values of sodium hydroxide and potassium hydroxide.

Gantman and co-workers (16) have found that at moderate concentrations and in a temperature range of eighteen to one hundred degrees centigrade the relationship between temperature and conductance is linear.

EXPERIMENTAL

Description of the Equipment.

The equipment used is shown in Figure 2. The conductivity bridge (model RC 16B2, Industrial Instruments Inc.) was connected with a variable capacitor (model EUW-29, Heath) in order to get a sharp balance on the conductivity cell. The water bath could be regulated to get a constant temperature in a range from 15° to 95°C within an error of $\pm 0.05^\circ$.

A pyrex tubing (11 mm in outer diameter, 42 cm in length) bent into a U-shape was used as a conductivity cell. The platinum wire was sealed into one end of the pyrex glass tubing (7 mm in outer diameter, 15 cm in length) to construct the electrode. Mercury was used for the connection of the platinum and copper lead wire. A special rubber stopper was fixed on the electrode so that the electrode would be located at the same position for each measurement.

The electrodes were plated with a platinum black coating. Platinization of the electrodes was found to be necessary, because it was almost impossible to get a sharp balance on the conductivity bridge when measuring the resistance of the concentrated solutions with the unplatinized electrodes.

Potassium chloride, used for calibration of the cell, was recrystallized twice in distilled water, and dried in the oven (110°C) overnight. In order to double check the results, two potassium chloride solutions (24) of different concentrations were made.

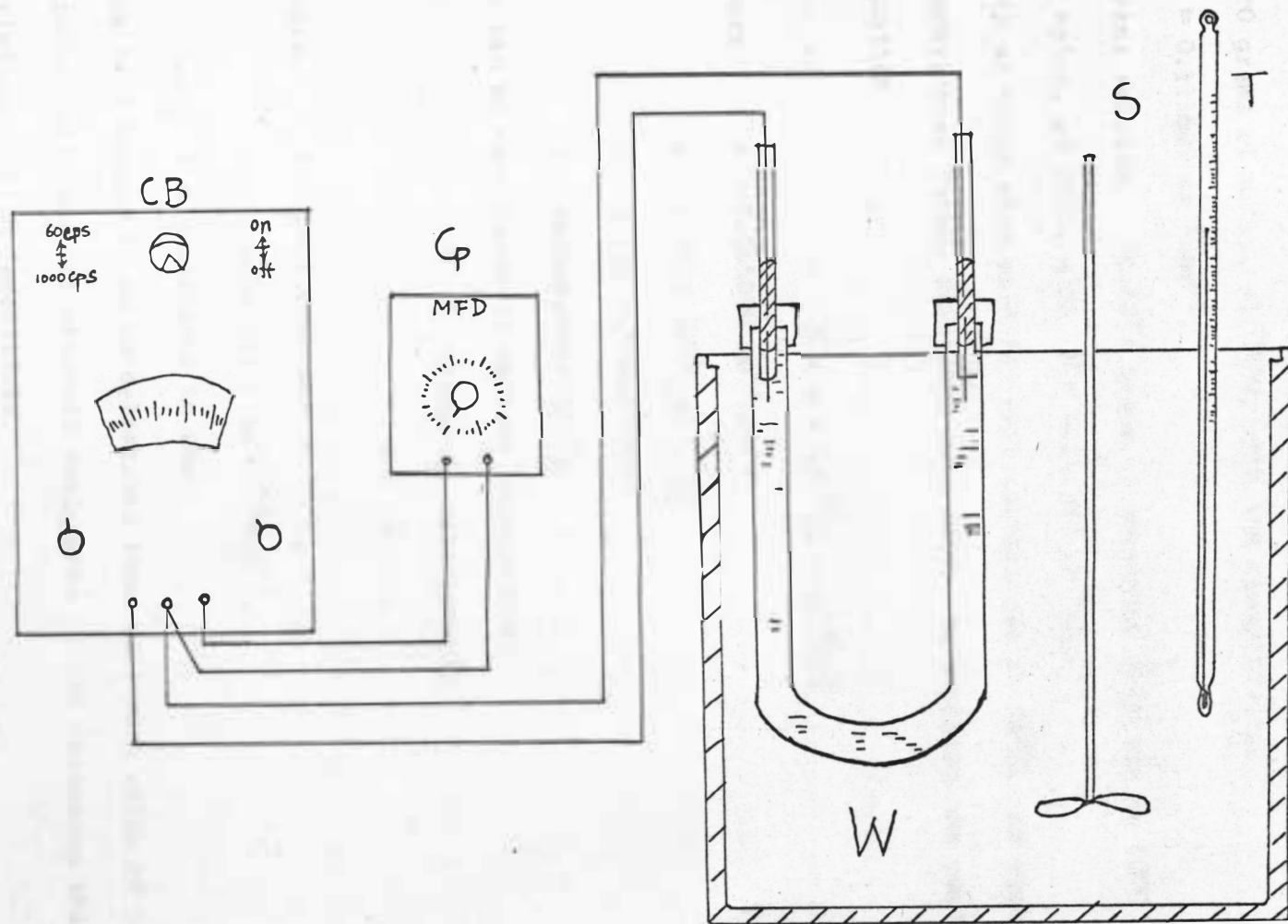


Figure 2. The apparatus used for conductivity measurements.

Kohlrausch solution: 76.9153 grams of potassium chloride in 1000 grams of water, at 25°C, with the conductivity,
 $\kappa = 0.111687 \text{ cm}^{-1}\text{ohm}^{-1}$.

Parker solution: 76.6276 grams of potassium chloride in 1000 grams of water, at 25°C, with $\kappa = 0.111322 \text{ cm}^{-1}\text{ohm}^{-1}$.

Both of these were used for cell calibration at 25°C. At higher temperatures Parker solutions were used. By applying the empirical equation

$$\kappa = A + 10^{-3}BT + 10^{-6}CT^2$$

where $A = 0.065098 \text{ cm}^{-1}\text{ohm}^{-1}$

$B = 1.7319 \text{ cm}^{-1}\text{ohm}^{-1}/^{\circ}\text{C}$

$C = 4.681 \text{ cm}^{-1}\text{ohm}^{-1}/^{\circ}\text{C}^2$

$T = \text{temperature in } ^{\circ}\text{C}$

κ can be calculated at various temperatures.

From the relationship

$$k = \kappa \cdot R$$

where $k = \text{cell constant in cm}^{-1}$,

$\kappa = \text{conductivity in cm}^{-1}\text{ohm}^{-1}$,

and, $R = \text{resistance in ohm}$,

the cell constant can be calculated from the known value of the conductivity and the measured resistance of the potassium chloride solution at each temperature.

Preparation of the Solutions.

The water used was purified by double distillation. A small quantity of potassium permanganate was added to the water before distillation. The purified water was then kept in a pyrex bottle fitted with an ascarite trap and stoppered air-tight to prevent absorption of carbon dioxide from the air.

A 12.04 N sodium hydroxide solution and a 11.86 N potassium hydroxide solution were made by dissolving solid sodium hydroxide (98.4% pure) and potassium hydroxide (85.0% pure) directly into water without further purification, then analyzed by titration with standardized hydrochloric acid (2.000 N). The solutions were kept in the pyrex bottles with ascarite traps, and stoppered air-tight to keep out carbon dioxide.

The mixtures, in various ratios, were made by mixing appropriate amounts of the concentrated sodium hydroxide and potassium hydroxide solutions. For example, a mixture of a ratio of 1.015 : 1 was made from 20.00 ml of 12.04 N sodium hydroxide and 20.00 ml of 11.86 N potassium hydroxide. The total volume of the mixture was adjusted with water to 40.00 ml. The concentration of sodium hydroxide in the mixture was $(20.00/40.00) \times 12.04 \text{ N} = 6.020 \text{ N}$ and that of potassium hydroxide was $(20.00/40.00) \times 11.86 \text{ N} = 5.930 \text{ N}$. So the ratio of sodium hydroxide to potassium hydroxide was $6.020 : 5.930 = 1.015 : 1$. The ratios of all the other mixtures were calculated in the same way.

Measurements and Data.

For each series (aqueous sodium hydroxide, potassium hydroxide or each of the mixtures in different NaOH:KOH ratios), ten measurements were made at different concentrations of hydroxide ions. For example, the 12.04 sodium hydroxide solution was measured and found to have a resistance of 260 ohms. Then 25.00 ml of the 12.04 N sodium hydroxide was diluted to 30.00 ml. The C_{OH^-} was $(25.00/30.00) \times 12.04 \text{ N} = 10.03 \text{ N}$ and the resistance of the solution of first dilution was 213 ohms. Again, 25.00 ml of 10.03 N solution was diluted to 30.00 ml and C_{OH^-} changed to $(25.00/30.00) \times 10.03 \text{ N} = 8.360 \text{ N}$. Nine solutions of more dilute concentrations were made and the resistances were measured in the usual manner.

All three cells used had cell constants around 56 cm^{-1} . The cell constant was checked carefully before and after the measuring of each of the series. All the measurements were made with the conventional alternating current bridge circuit at a frequency of 1000 cps. The resistance of the solution was read directly from the dial of the conductivity bridge. With the known cell constant, the conductivity can be calculated by applying the relationship, $k = \mathcal{K} \cdot R$, or $\mathcal{K} = k/R$. Applying equation 1, the equivalent conductivity can be calculated. The results are tabulated in Tables 2 through 6.

Table 2. Conductances of Aqueous Solutions of Sodium Hydroxide and Potassium Hydroxide Electrolytes at 25°C.

Ratio NaOH:KOH	C_{OH^-} equiv/l	K $cm^{-1}ohm^{-1}$	Δ $cm^2/equiv \cdot ohm$	Ratio NaOH:KOH	C_{OH^-} equiv/l	K $cm^{-1}ohm^{-1}$	Δ $cm^2/equiv \cdot ohm$
1:0	12.04	0.2168	18.01	1.015:1	4.802	0.5005	104.2
	10.03	0.2646	26.38		4.002	0.4839	120.9
	8.358	0.3166	37.87		3.335	0.4539	136.1
	6.965	0.3636	52.17		2.779	0.4153	149.4
	5.804	0.3969	68.31		2.316	0.3754	162.1
	4.837	0.4114	85.00	0.3384:1	11.91	0.3924	32.86
	4.031	0.4055	100.4		9.920	0.4736	47.74
	3.359	0.3887	115.7		8.267	0.5292	64.01
	2.799	0.3660	130.7		6.889	0.5580	81.00
2.030:1	2.332	0.3296	141.5	5.741	0.5693	99.16	
	11.98	0.2819	23.53	4.784	0.5472	114.3	
	9.983	0.3436	34.42	3.987	0.5170	129.7	
	8.319	0.3997	48.05	3.323	0.4776	143.7	
	6.933	0.4403	63.51	2.769	0.4352	157.1	
	5.777	0.4620	79.97	2.307	0.3887	168.5	
	4.815	0.4658	96.74	0:1	11.86	0.4658	39.28
	4.012	0.4473	111.5		9.883	0.5525	55.90
	3.343	0.4237	126.7		8.236	0.6028	73.19
	2.786	0.3914	140.5		6.863	0.6297	91.75
2.322	0.3567	153.6	5.719		0.6227	108.9	
1.015:1	11.95	0.3290	27.53	4.766	0.6060	127.2	
	9.958	0.3984	40.01	3.972	0.5680	143.0	
	8.298	0.4504	54.28	3.310	0.5285	159.7	
	6.915	0.4910	70.27	2.758	0.4725	171.3	
	5.763	0.5092	88.36	2.299	0.4156	180.8	

Table 3. Conductances of Aqueous Solutions of Sodium Hydroxide and Potassium Hydroxide Electrolytes at 35°C.

Ratio NaOH:KOH	C_{OH^-} equiv/l	κ $cm^{-1}ohm^{-1}$	Δ $cm^2/equiv \cdot ohm$	Ratio NaOH:KOH	C_{OH^-} equiv/l	κ $cm^{-1}ohm^{-1}$	Δ $cm^2/equiv \cdot ohm$
1:0	12.04	0.3050	25.33	1.015:1	4.802	0.6164	128.4
	10.03	0.3592	35.80		4.002	0.5775	144.3
	8.358	0.4243	50.77		3.335	0.5422	162.6
	6.965	0.4800	68.92		2.779	0.4962	178.6
	5.804	0.5025	86.58		2.316	0.4354	188.0
	4.837	0.5070	104.8	0.3384:1	11.91	0.5137	43.13
	4.031	0.4921	122.1		9.920	0.5975	60.23
	3.359	0.4722	140.6		8.267	0.6579	79.58
	2.799	0.4403	146.8		6.889	0.6971	101.2
	2.332	0.4038	161.5		5.741	0.6889	120.0
2.030:1	11.98	0.4011	33.48	4.784	0.6640	138.8	
	9.983	0.4684	46.92	3.987	0.6294	157.9	
	8.319	0.5275	63.41	3.323	0.5798	174.5	
	6.933	0.5577	80.44	2.769	0.5228	188.8	
	5.777	0.5798	100.2	2.307	0.4685	203.1	
	4.815	0.5741	119.2	0:1	11.86	0.6006	50.64
	4.012	0.5524	137.7		9.883	0.6930	70.12
	3.343	0.5182	155.0		8.236	0.7459	90.57
	2.786	0.4761	170.9		6.863	0.7705	112.3
	2.322	0.4274	184.1		5.719	0.7654	133.8
1.015:1	11.95	0.4436	37.12	4.719	0.7274	152.6	
	9.958	0.5182	50.02	3.972	0.6809	171.4	
	8.298	0.5768	69.52	3.310	0.6196	187.2	
	6.915	0.6164	89.14	2.758	0.5550	201.2	
	5.763	0.6296	109.2	2.298	0.4962	215.9	

Table 4. Conductances of Aqueous Solutions of Sodium Hydroxide and Potassium Hydroxide Electrolytes at 45°C.

Ratio NaOH:KOH	C_{OH^-} equiv/l	K $cm^{-1}ohm^{-1}$	Δ $cm^2/equiv \cdot ohm$	Ratio NaOH:KOH	C_{OH^-} equiv/l	K $cm^{-1}ohm^{-1}$	Δ $cm^2/equiv \cdot ohm$	
1:0	12.04	0.4279	35.54	1.015:1	4.802	0.7167	149.2	
	10.03	0.4992	49.77		4.002	0.6676	166.8	
	8.358	0.5537	66.25		3.335	0.6281	188.3	
	6.965	0.5918	84.97		2.779	0.5744	206.7	
	5.804	0.6085	104.2		2.316	0.5146	222.2	
	4.837	0.6085	125.9					
	4.031	0.5930	147.1		0.3384:1	11.91	0.6638	55.73
	3.359	0.5562	165.6			9.920	0.7329	73.88
	2.799	0.5124	170.8			8.267	0.7946	96.12
	2.332	0.4581	183.2			6.889	0.8227	119.4
2.030:1	11.98	0.5262	43.92		5.741	0.8113	141.3	
	9.983	0.5960	59.70		4.784	0.7788	162.8	
	8.319	0.6526	78.45		3.987	0.7301	183.1	
	6.933	0.6872	99.09		3.323	0.6575	197.9	
	5.777	0.6954	120.4		2.769	0.5942	214.6	
	4.815	0.6725	139.6		2.307	0.5359	232.3	
	4.012	0.6415	159.9	0:1	11.86	0.7422	62.58	
	3.343	0.6085	182.0		9.883	0.8403	85.02	
	2.786	0.5563	199.7		8.236	0.8985	109.1	
	2.322	0.5035	216.8		6.863	0.9054	131.9	
1.015:1	11.95	0.5727	47.92		5.719	0.8808	154.0	
	9.958	0.6490	65.17		4.766	0.8425	176.8	
	8.298	0.6995	84.30		3.972	0.7840	197.4	
	6.915	0.7301	105.6		3.310	0.7080	213.9	
	5.763	0.7394	128.3		2.758	0.6419	232.7	
					2.298	0.5671	246.8	

Table 5. Conductances of Aqueous Solutions of Sodium Hydroxide and Potassium Hydroxide Electrolytes at 55°C.

Ratio NaOH:KOH	C_{OH^-} equiv/l	K $cm^{-1}ohm^{-1}$	Λ $cm^2/equiv \cdot ohm$	Ratio NaOH:KOH	C_{OH^-} equiv/l	K $cm^{-1}ohm^{-1}$	Λ $cm^2/equiv \cdot ohm$
1:0	12.04	0.5788	48.07	1.015:1	4.802	0.8466	176.3
	10.03	0.6373	63.54		4.002	0.7878	196.8
	8.358	0.6960	83.27		3.335	0.7272	218.0
	6.965	0.7205	103.4		2.779	0.6596	237.4
	5.804	0.7366	126.9		2.316	0.5848	252.5
	4.837	0.7366	152.3	0.3384:1	11.91	0.7989	76.08
	4.031	0.7002	173.7		9.920	0.9003	90.76
	3.359	0.6520	194.1		8.267	0.9565	116.1
	2.799	0.5971	213.3		6.889	0.9746	142.0
	2.332	0.5507	236.2		5.741	0.9565	167.2
2.030:1	11.98	0.6697	55.90	4.784	0.9046	189.8	
	9.983	0.7386	74.01	3.987	0.8403	211.6	
	8.319	0.7989	96.03	3.323	0.7717	233.1	
	6.933	0.8268	119.3	2.769	0.6960	252.4	
	5.777	0.8305	143.8	2.307	0.6163	268.2	
	4.815	0.7953	164.8	0:1	11.86	0.8686	73.24
	4.012	0.7563	183.1		9.883	1.0021	101.4
	3.343	0.6825	204.2		8.236	1.0602	128.7
	-	-	-		6.863	1.0602	154.5
	-	-	-		5.719	1.0093	176.5
1.015:1	11.95	0.7366	61.64	4.766	0.9533	200.0	
	9.958	0.8046	80.80	3.972	0.8794	221.4	
	8.298	0.8660	104.4	3.310	0.8046	243.1	
	6.915	0.8794	127.2	2.758	0.7180	260.3	
	5.763	0.8794	152.6	2.298	0.6338	275.8	

Table 6. Conductances of Aqueous Solutions of Sodium Hydroxide and Potassium Hydroxide Electrolytes at 65°C.

Ratio NaOH:KOH	C_{OH^-} equiv/l	K $cm^{-1}ohm^{-1}$	Λ $cm^2/equiv \cdot ohm$	Ratio NaOH:KOH	C_{OH^-} equiv/l	K $cm^{-1}ohm^{-1}$	Λ $cm^2/equiv \cdot ohm$	
1:0	12.04	0.7298	60.62	1.015:1	4.802	0.9690	201.8	
	10.03	0.8008	79.84		4.002	0.9080	226.9	
	8.358	0.8541	102.2		3.335	0.8356	250.6	
	6.965	0.8736	125.4		2.779	0.7488	269.4	
	5.804	0.8736	150.5		2.316	0.6552	282.9	
	4.837	0.8605	177.9		0.3384:1	11.91	0.9856	82.75
	4.031	0.8178	202.9			9.920	1.0736	108.2
	3.358	0.7537	224.4			8.267	1.1158	134.1
	2.799	0.6888	239.0			6.889	1.1305	164.1
	2.332	0.6233	267.3			5.741	1.0928	190.4
2.030:1	11.98	0.7952	66.38	4.784		1.0483	219.1	
	9.983	0.9195	92.11	3.987	0.9609	241.0		
	8.319	0.9690	116.5	3.323	0.8736	262.9		
	6.933	0.9770	140.9	2.769	0.7791	281.4		
	5.777	0.9740	168.6	2.307	0.6704	290.6		
	4.814	0.9375	194.7	0:1	11.86	1.0677	90.02	
	4.012	0.8802	219.4		9.883	1.1695	118.3	
	3.343	0.8120	242.9		8.236	1.2138	147.4	
	2.786	0.7373	264.6		6.863	1.2138	176.9	
	2.322	0.6627	285.4		5.719	1.1766	205.7	
1.015:1	11.95	0.9009	75.39		4.766	1.1088	232.6	
	9.958	0.9772	98.11	3.953	1.0115	255.9		
	8.298	1.0204	123.0	3.313	0.9152	276.2		
	6.915	1.0277	148.6	2.761	0.8120	294.1		
	5.763	1.0115	175.5	2.301	0.7207	313.2		

DISCUSSION AND CONCLUSION

Concentration Dependence of Conductance.

When plotted as equivalent conductivity versus concentration, a concave upward curve with no minimum was obtained for sodium hydroxide and potassium hydroxide electrolytes in the temperature range from 25° to 65°C. When the results of this research at 25° were compared with those of Darken and Meier (11), very good agreement was found (see Figure 3). The results of Manvelyan and his co-workers (33) were also checked and were found to be slightly lower.

As shown in Figures 4, 5, 6, 7 and 8, the conductivity curves of sodium hydroxide and potassium hydroxide electrolytes are essentially the same in character as those of the acids and salts previously discussed. For sodium hydroxide, the concave downward curves have a maximum around 5 N. For potassium hydroxide the maxima are around 7 N. The conductivity curves become concave upward at high concentrations. The points of inflection of the sodium hydroxide curves are around 9 N, while those of potassium hydroxide are at higher concentrations. The existence of maxima in the conductivity curves is of interest, since it means that for concentrations beyond that of the maximum, solutions containing more electrolyte have a lower conductance than the solutions containing less electrolyte. Thus, either the total number of ions is decreasing, or their mobility or both. The concentration corresponding to the maximum doesn't shift noticeably with temperature. If it is assumed that

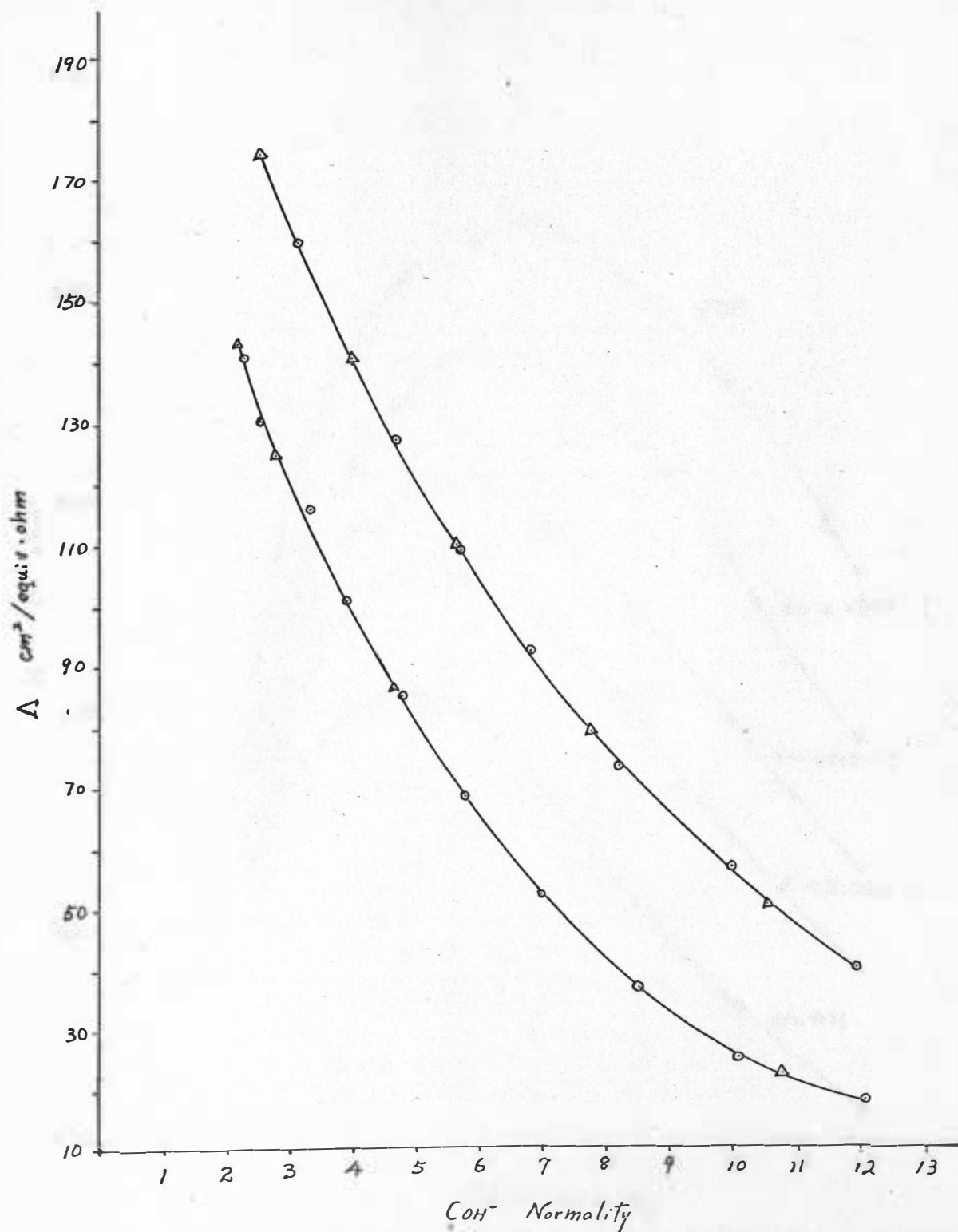


Figure 3. Equivalent conductivities of aqueous NaOH and KOH at 25°C.
 • this research, Δ Darken and Meier (11).

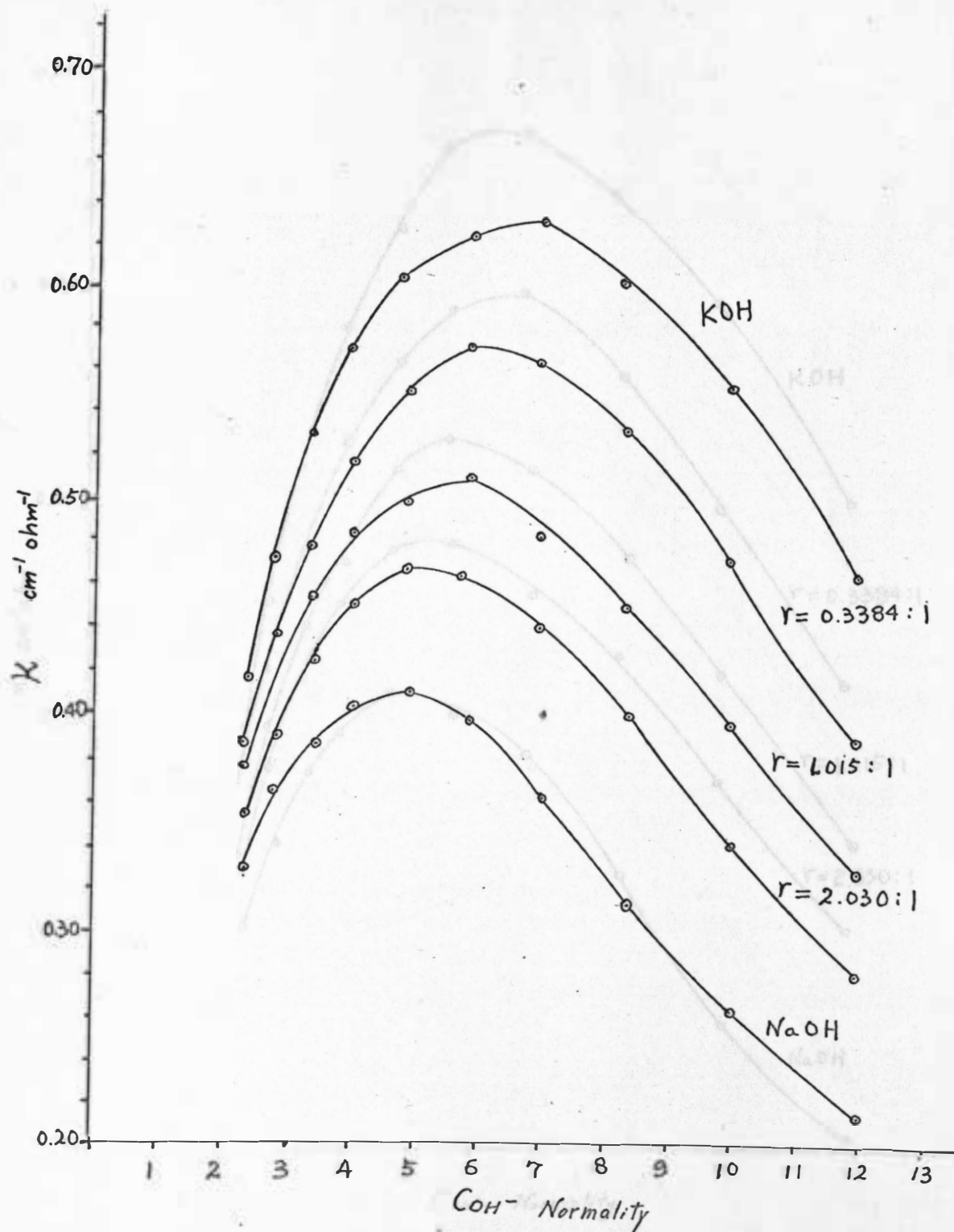


Figure 4. Relation of concentration and conductivity of aqueous NaOH and KOH electrolytes at 25°C. r is the ratio of NaOH to KOH for the mixtures.

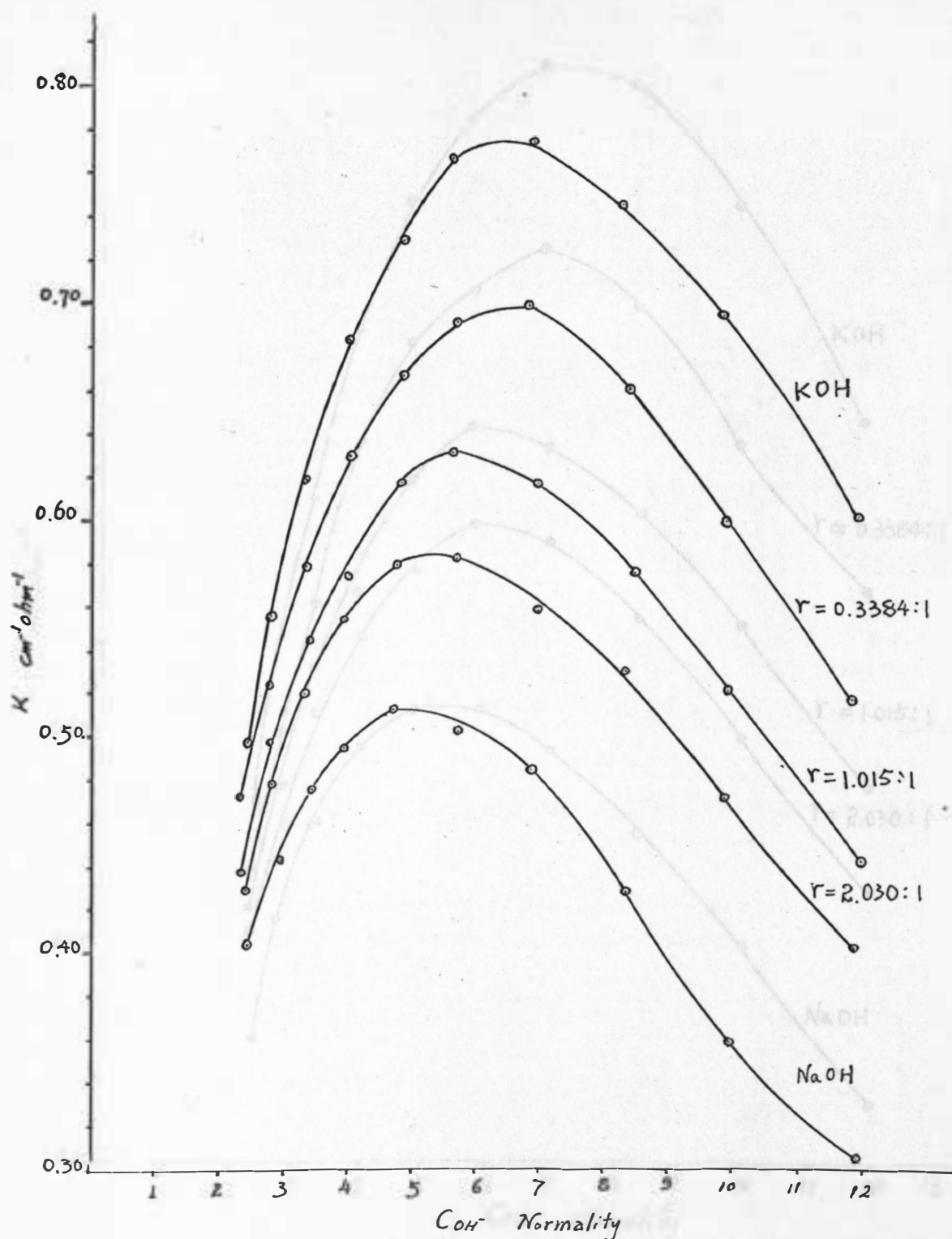


Figure 5. Relation of concentration and conductivity of aqueous NaOH and KOH electrolytes at 35°C.

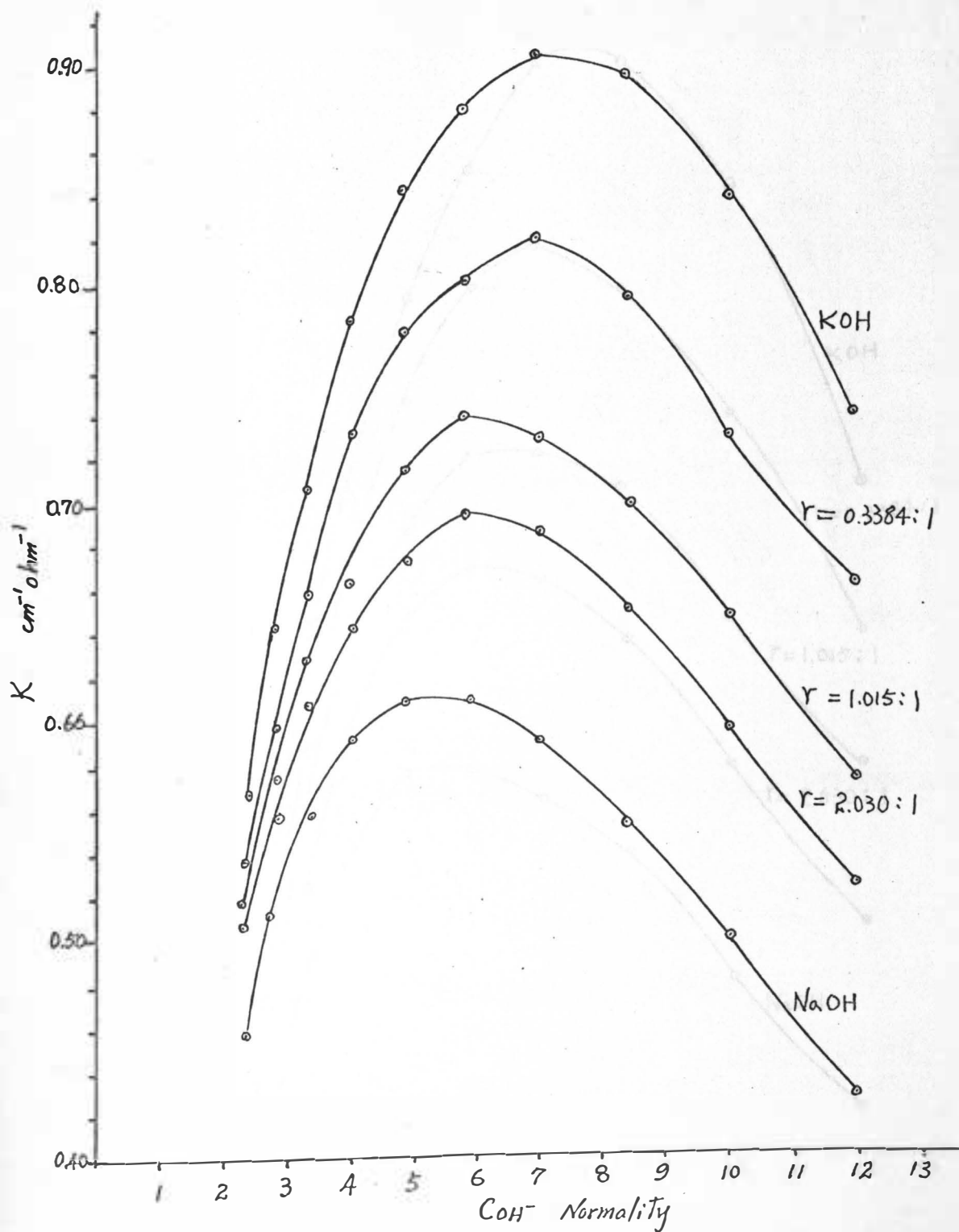


Figure 6. Relation of concentration and conductivity of aqueous NaOH and KOH electrolytes at 45°C .

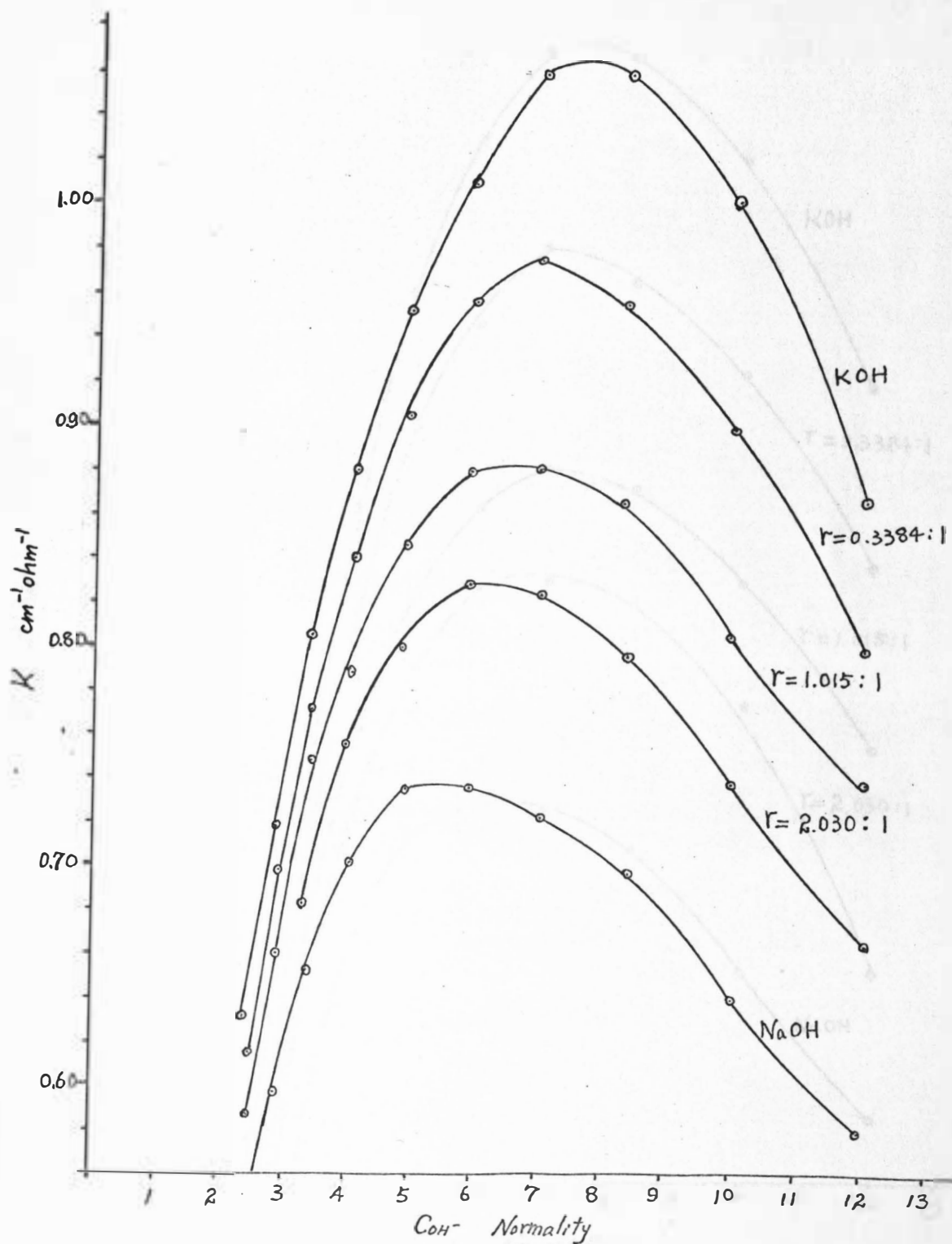


Figure 7. Relation of concentration and conductivity of aqueous NaOH and KOH electrolytes at 55°C.

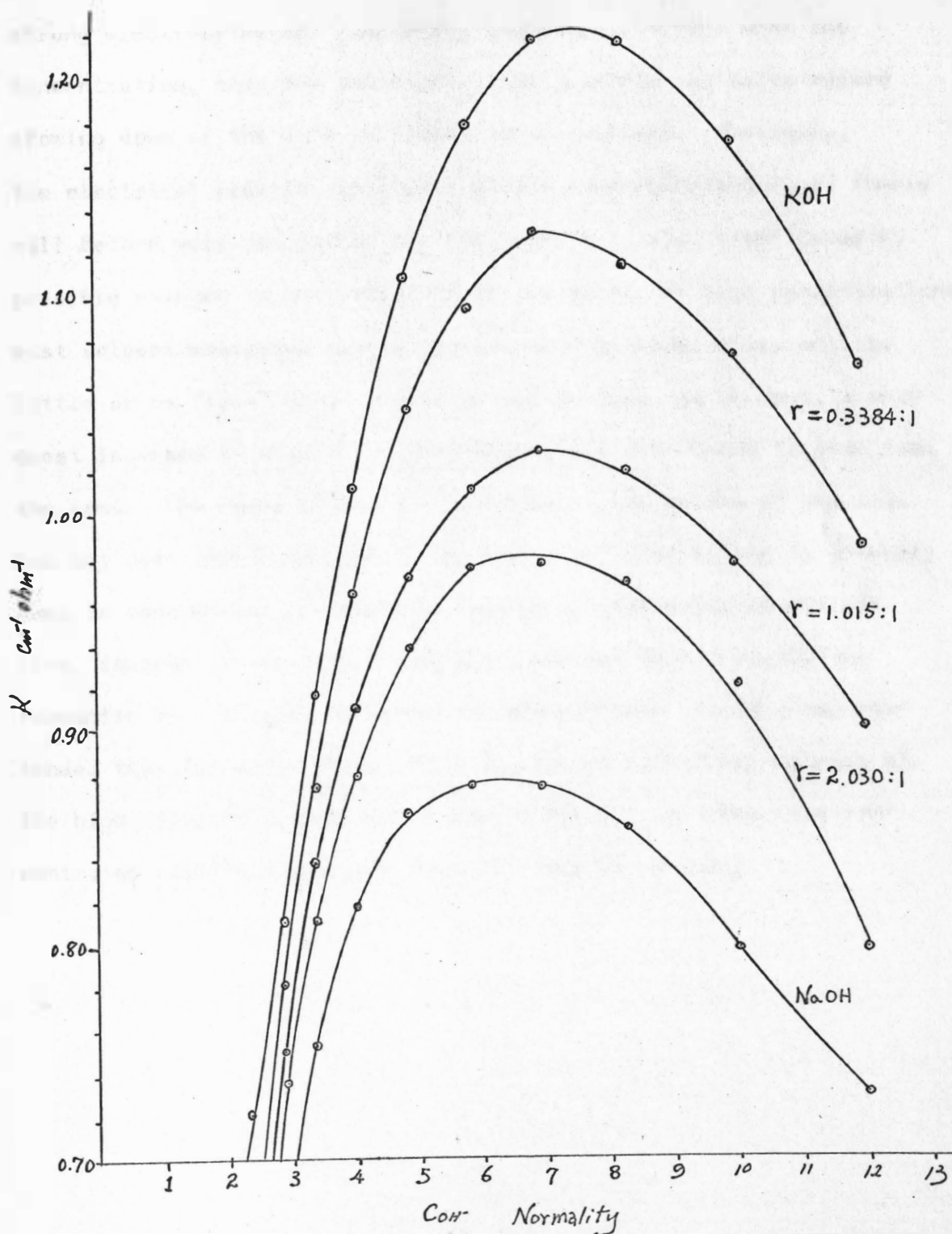


Figure 8. Relation of concentration and conductivity of aqueous NaOH and KOH electrolytes at 65°C.

strong electrolytes are completely ionized, no matter what the concentration, then the existence of the maximum indicates marked slowing down of the ions at higher concentrations. Obviously, the electrical effects considered by the Debye-Hückel-Onsager theory will become very pronounced but the picture is also complicated by possible changes in the hydration of the ions. At high concentrations most solvent molecules may be tightly held by ions; there will be little or no "free" water. This should produce, as it does, a very great increase in viscosity, and this factor also tends to slow down the ions. The exact effect of viscosity on the motion of the ions has not been formulated but it must be considerable, and is probably due, in concentrated solutions, largely to electrostatic effects. Also, instead of complete ionization, another factor may be the formation of ion pairs at higher concentrations. It is often contended that ion pairs cannot form in aqueous solutions, because of the high dielectric constant of the medium but in these very concentrated solutions ion pair formation may be possible.

Temperature Dependence of Conductance.

When plotted as conductivity versus temperature, an apparent straight line is obtained for sodium hydroxide and potassium hydroxide electrolytes at moderate concentrations. At high concentrations ($C_{OH^-} > 7 N$) a concave upward curve is obtained. Figures 9, 10, 11, 12, and 13 illustrate the relationship of conductivity and temperature at various concentrations. It is found that the conclusion made by Gantman and co-workers (16) that "there is a linear dependence of the electrical conductance of sodium hydroxide solutions on temperature in the range from 18° to 100°C" is somewhat inaccurate. When the graphs of the relation of conductivity and temperature are examined very carefully, it is found that even at the hydroxide ion concentration as low as 3 N some slight curvature can still be found. From the relationship $\lambda_i = Fu_i$, equivalent conductivity of the ion is directly proportional to the ionic mobility, but temperature is not the only factor which governs the ionic mobility, whose temperature dependence is quite complicated as one would suspect. Therefore, it is wrong to say that the relationship between conductance and temperature is simply linear as was earlier supposed.

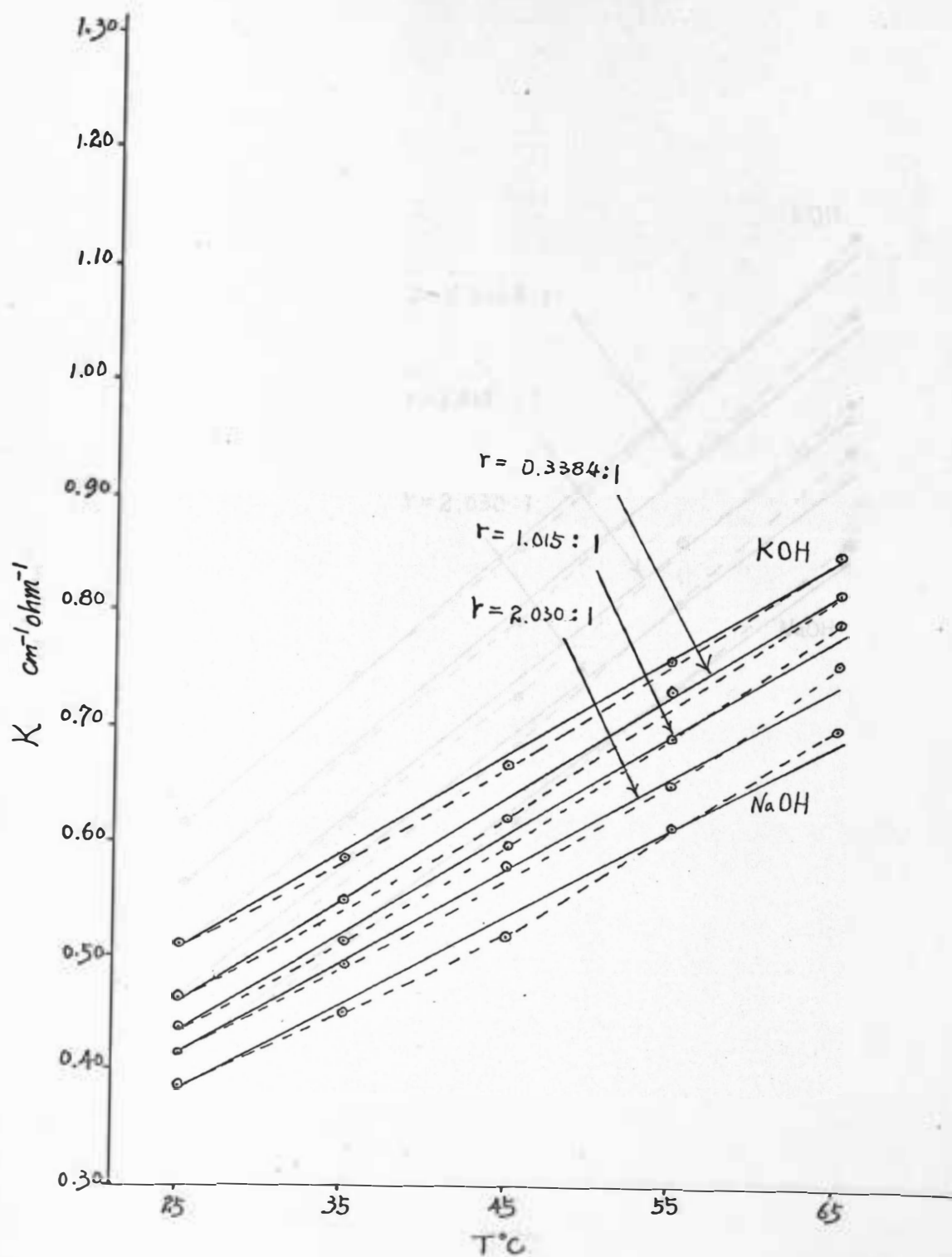


Figure 9. Relation of conductivity and temperature of aqueous NaOH and KOH electrolytes at hydroxide ion concentration of 3 N.

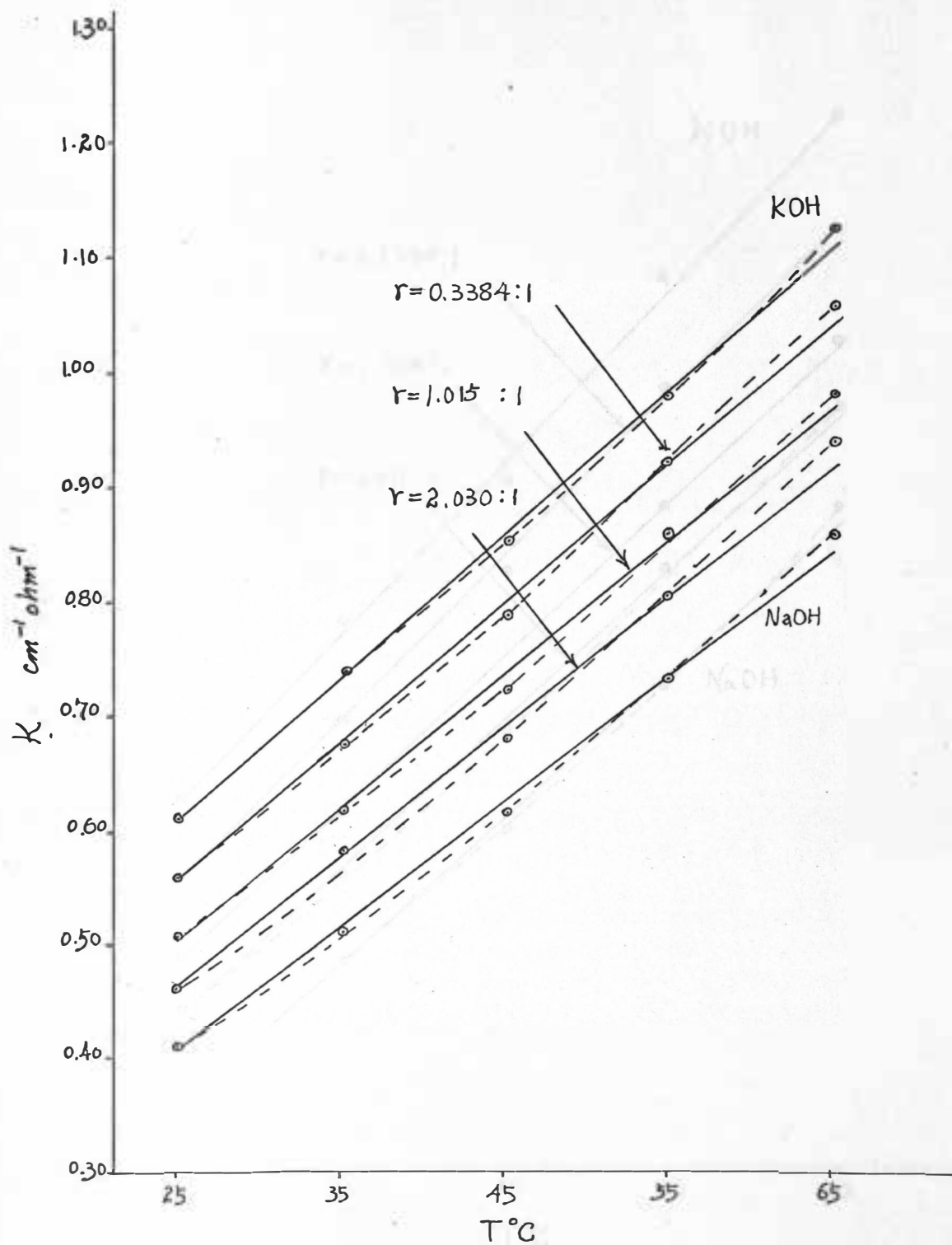


Figure 10. Relation of conductivity and temperature of aqueous NaOH and KOH electrolytes at hydroxide ion concentration of 5 N.

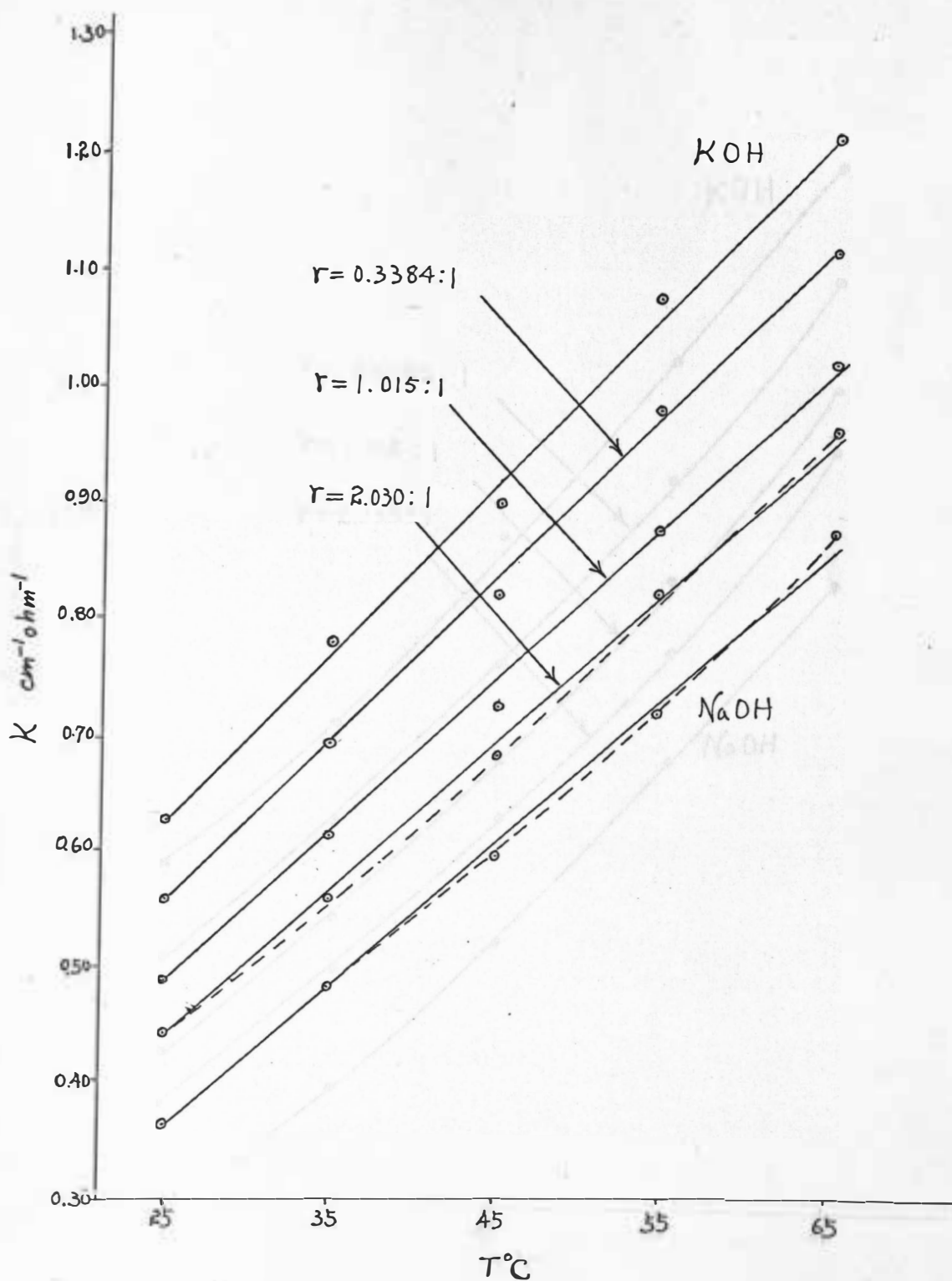


Figure 11. Relation of conductivity and temperature of aqueous NaOH and KOH electrolytes at hydroxide ion concentration of 7 N.

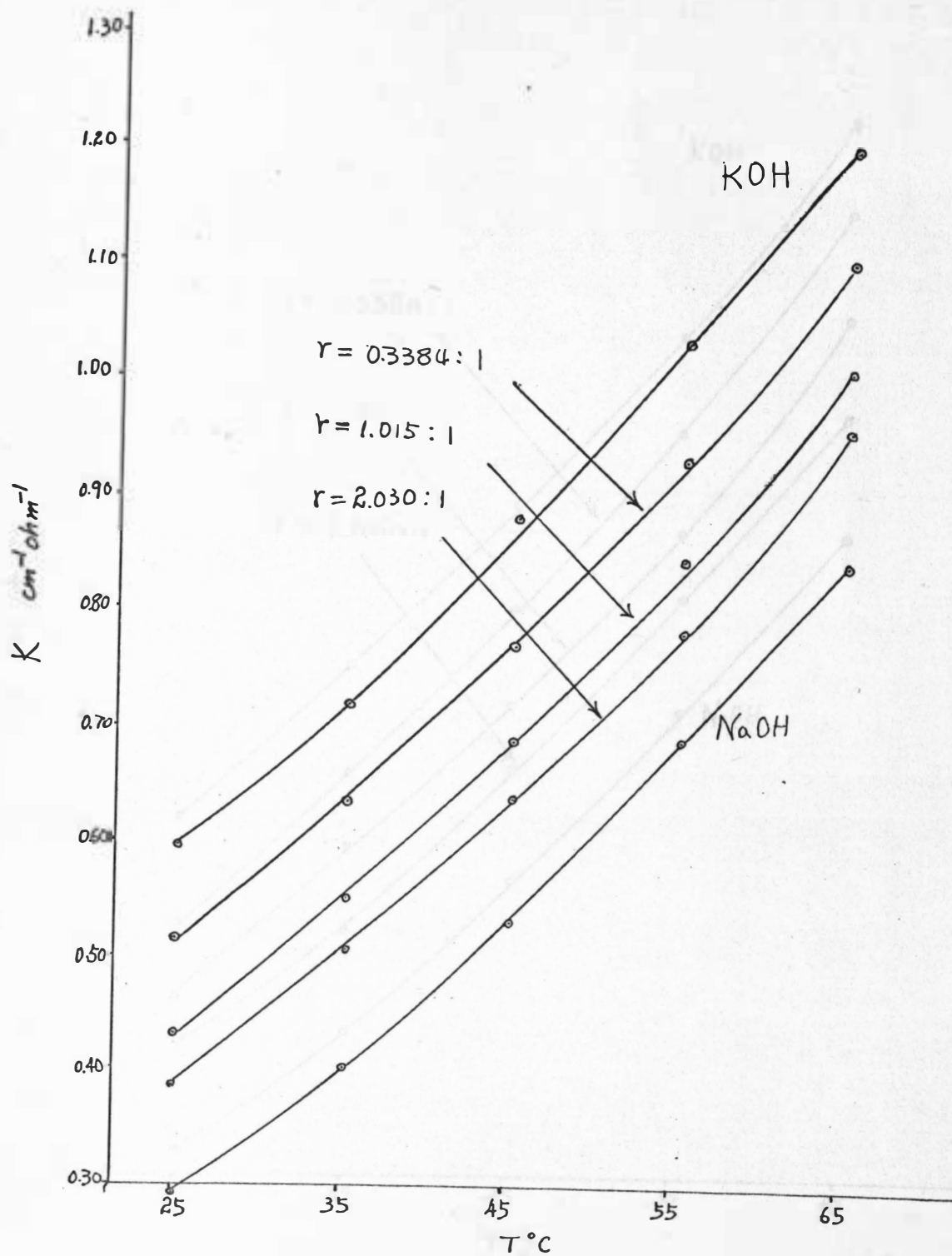


Figure 12. Relation of conductivity and temperature of aqueous NaOH and KOH electrolytes at hydroxide ion concentration of 9 N.

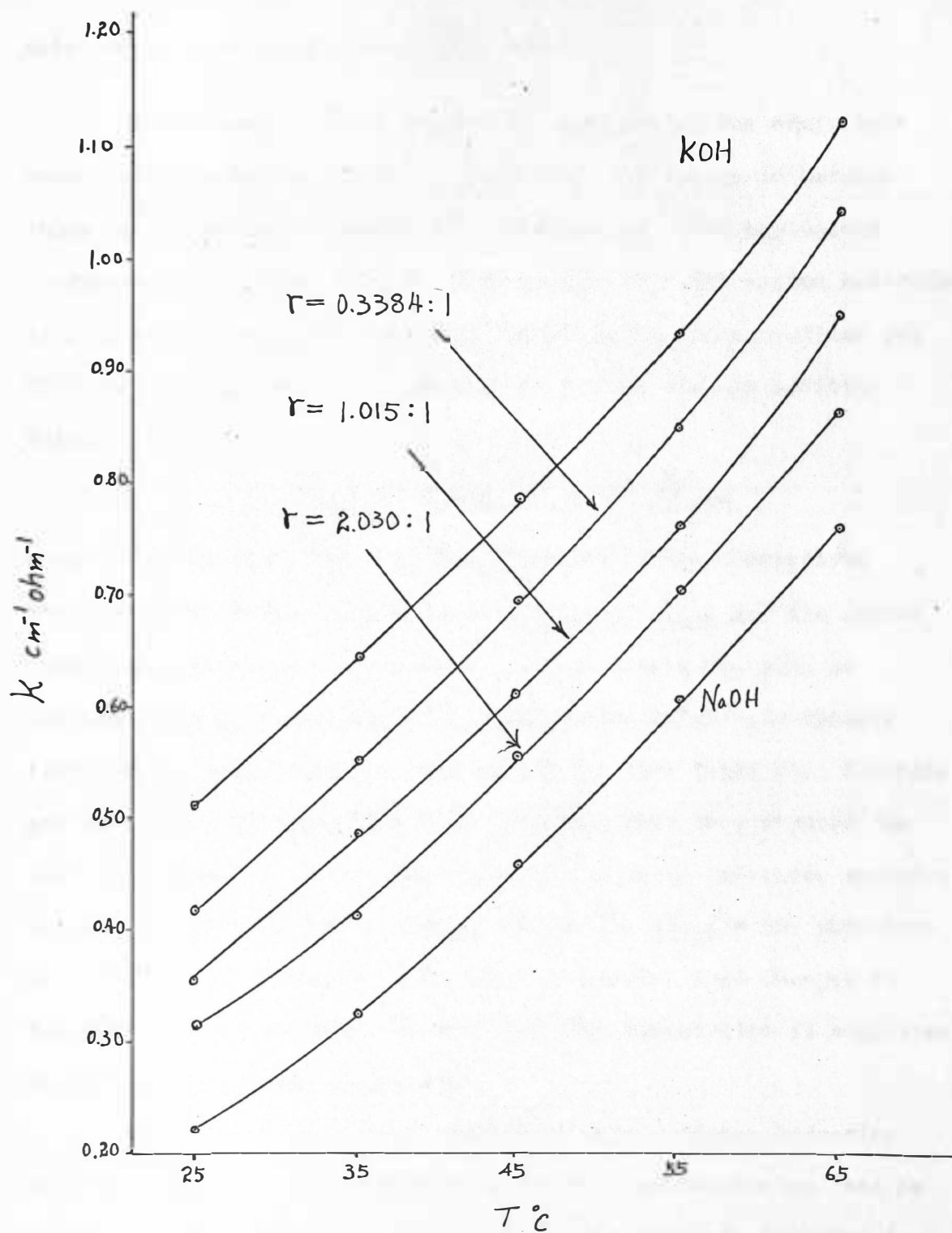


Figure 13. Relation of conductivity and temperature of aqueous NaOH and KOH electrolytes at hydroxide ion concentration of 11 N.

Relation of Composition and Conductance.

As observed from the results of this study, the equivalent conductivities of the mixtures always have the values in between those of the two pure constituent electrolytes. The equivalent conductivities of the mixtures with a ratio of 1.015 sodium hydroxide to 1 potassium hydroxide at various electrolyte concentrations and different temperatures are calculated from the mixture addition rule:

$$\Lambda_{\text{cal.}} = x \Lambda_{\text{NaOH}} + (1-x) \Lambda_{\text{KOH}}$$

where x is the fraction of sodium hydroxide in the electrolyte mixture, $1.015/2.015 = 0.504$, and, Λ_{NaOH} and Λ_{KOH} are the equivalent conductivities for the pure constituent electrolytes at corresponding concentrations. The calculated values are usually found to be larger than the observed values (see Table 7). Campbell and co-workers (9) found the same situation when they studied the various mixtures of two of the three salts, silver nitrate, ammonium nitrate and lithium nitrate, and attempted to explain the phenomena by hydration and change of dielectric constant. That changes in the hydration of the ions may be a possible explanation is suggested by the following type of argument.

Sodium ions are always assumed to have a higher hydration ability. Suppose, in the solution, one half of the sodium ions be replaced by potassium ions. Since potassium ions are hydrated to a smaller extent than are sodium ions, the remaining sodium ions have

Table 7. Equivalent Conductivities ($\text{cm}^2/\text{equiv}\cdot\text{ohm}$) of the Mixtures with the NaOH KOH Ratio of 1.015 : 1 at (a) 25°C and (b) 65°C.

(a)

C_{OH^-}	Λ_{KOH}	Λ_{NaOH}	$\Lambda_{\text{mix(expl)}}$	$\Lambda_{\text{mix(calc)}}$	$\Delta\Lambda$
3N	162.3	123.6	143.5	142.8	-0.7
4	142.2	100.2	120.9	121.0	+0.1
5	122.3	81.3	100.9	101.6	+0.7
6	104.6	65.1	84.0	84.7	+0.7
7	89.4	52.0	69.4	70.5	+1.1
8	76.0	41.0	58.3	58.4	+0.1
9	64.4	32.5	47.7	48.3	+0.6
10	54.3	26.4	39.9	40.2	+0.3
11	45.5	21.7	33.0	33.5	+0.5

(b)

C_{OH^-}	Λ_{KOH}	Λ_{NaOH}	$\Lambda_{\text{mix(expl)}}$	$\Lambda_{\text{mix(calc)}}$	$\Delta\Lambda$
3N	274.5	236.4	255.8	255.3	-0.5
4	252.9	202.1	226.1	227.3	+1.2
5	225.0	172.2	194.4	198.4	+4.0
6	197.2	146.3	167.0	171.6	+4.6
7	172.5	124.4	145.8	148.3	+2.5
8	151.8	107.3	128.3	129.4	+1.1
9	132.8	92.0	111.8	112.2	+0.4
10	116.1	80.0	97.6	97.9	+0.3
11	101.6	71.4	85.3	86.4	+1.1

more water available for hydration and would therefore behave as if they were in more dilute solution. In general then, the more highly hydrated ions will be in effect in a more dilute solution. An increase in solvation and hence of the effective radius of the ion would, in the sense of Stokes' law, cause a decrease in mobility of the ion. The increase in equivalent conductivity observed on dilution of an electrolytic solution (despite a possible increase in hydration) is due to a decrease in the interionic forces. When hydrated ions are replaced by less hydrated ions of the same charge, the interionic forces are only slightly altered. Hence, in the case considered, the remaining sodium ions being more highly hydrated, their mobility will decrease. The contribution of the potassium ions to the conductance of the mixture will be effected less, since they are less hydrated. Hence it appears that the hydration effect would operate in the direction of lowering the conductance of the mixture below the value calculated by the mixture rule.

A consideration of the dielectric constant of the mixed solution leads to the same conclusion. No measurements of dielectric constant in the mixed solutions were made in this study but certain theoretical deductions are possible. The equation for the dielectric constant

$$D = D_0 + 2 \delta C^{\frac{1}{2}}$$

where δ is a characteristic coefficient of the electrolyte and can be either positive or negative, suggests that D is linear in $C^{\frac{1}{2}}$. Strict obedience of this equation is usually observed only up to a

concentration of about two molar. This is due to the inclusion of all the water molecules in the fields of the ions; the highest possible orientation of water molecules has been attained and further addition of ions can have little effect. In replacing sodium ions by potassium ions, which are less highly hydrated, more water molecules are made available to the strong fields of the remaining sodium ions and their power of depressing the dielectric constant of the mixed solution will be larger than that calculated from the mixture rule. The lower dielectric constant will increase the interionic forces resulting in a lower conductance than the calculated value.

Some Conclusions about Conductance Equations.

It is ensured, from the previous discussions, that there are several important factors which affect the conductance of the concentrated electrolytic solutions. In the derivation of Onsager's equation for the dilute solutions the electrostatic effects between the ions are carefully considered. The attempts to account for the departures of the conductance of concentrated solutions from the limiting equation by theoretical and empirical arguments of electrostatic effects has been discussed in the Historical section. The assumptions made in the derivation of Onsager's equation for the very dilute solutions that the dielectric constant and viscosity are those of the pure solvent are inaccurate. Actually, they both change with concentration. The changes of the dielectric constant have been discussed in the preceding section. It is found that viscosity does increase to an appreciable extent with increasing concentration. For example, for sodium hydroxide at 25°C, $\eta = 1.75$ at 3 N, and $\eta = 8.32$ at 10 N (31). The correction of viscosity, when used by Campbell and Paterson (10), brought significant changes to their results and led to a good fit with the Robinson and Stokes equation. An illustration of the use of hydration concepts has also been given in the previous discussion. Presumably, most ions are hydrated to some degree and this must have an influence on their mobilities but unfortunately the degree of hydration and its influence are not easily ascertained. The possibility of ion pair formation, equivalent to the concept of incomplete dissociation,

should not be completely eliminated. Although this theory is very popular at present, the description of concentrated electrolytic solutions can definitely be made without using the ion pair formation assumption. The presence of ions, the charged particles, in the solution causes changes in the structural arrangement of the solvent. This factor causes some chemists to suggest that the approach to the theory of concentrated solutions should start by an adequate theory of molten salts, which should then be followed by a theoretical treatment of the effects on the radial distribution function of adding uncharged (solvent) molecules. The factors discussed above are all closely interrelated. It is impossible and also unrealistic to consider any one of them separately as the complete explanation of the conductance behavior.

In the hope of throwing more light on the subject, the data of this study for aqueous sodium hydroxide at 25°C have been correlated with several different equations. A plot of equivalent conductivity versus $\log C_{\text{OH}^-}$, as first suggested by Campbell (7, 8) is made, an apparent straight line is obtained over a considerable range of concentration. In the same graph, the plot for potassium hydroxide is also made (Figure 14). For these same electrolytes at 65°C, plots of similar character are obtained (Figure 15). The fit of a straight line is quite amazing but it is obviously not completely adequate for all concentration.

Another equation which shows considerable promise, in the sense that it apparently can be applied at higher concentrations, is the Robinson and Stokes (36) equation

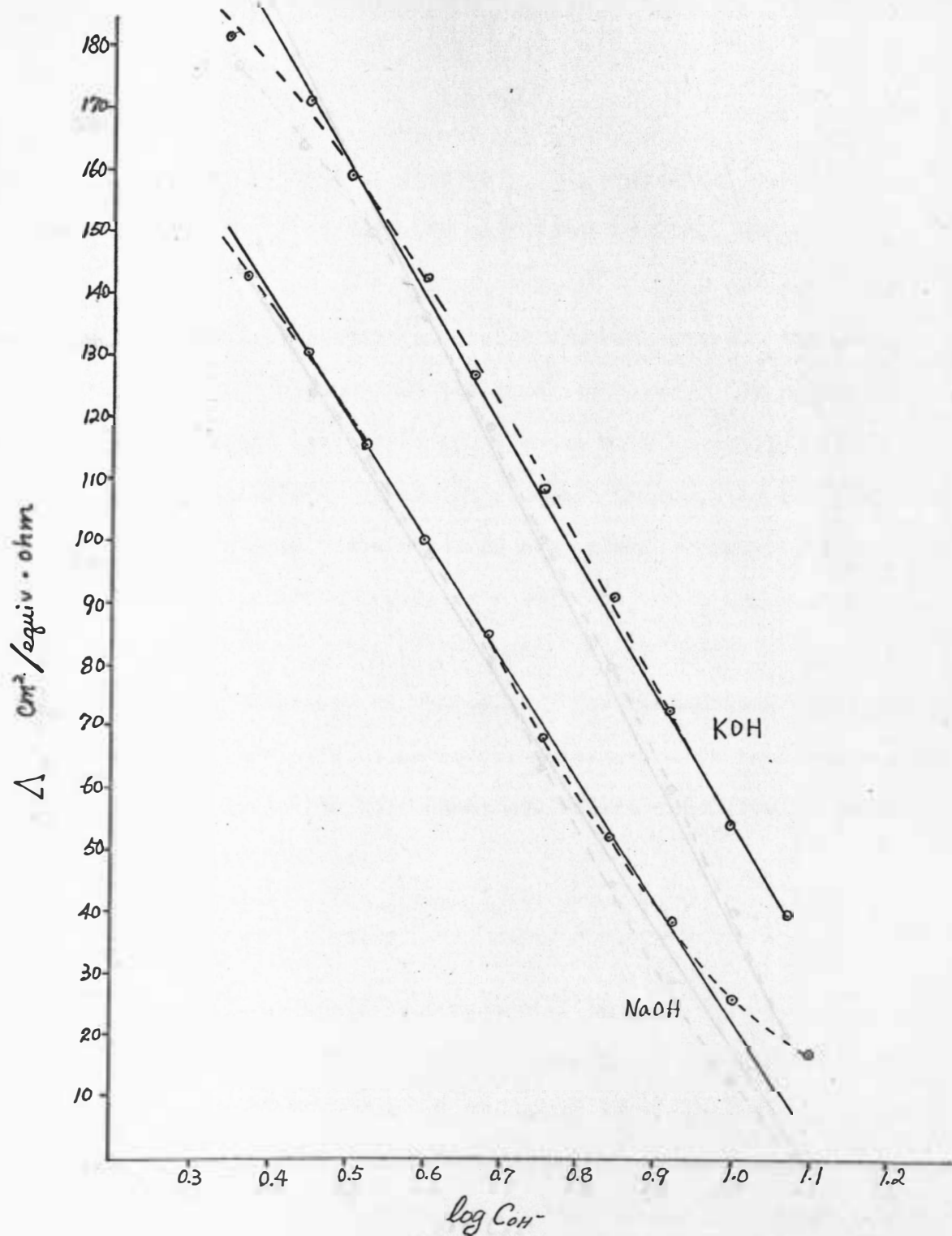


Figure 14. Relation of equivalent conductivity to the logarithm of the hydroxide ion concentration at 25°C.

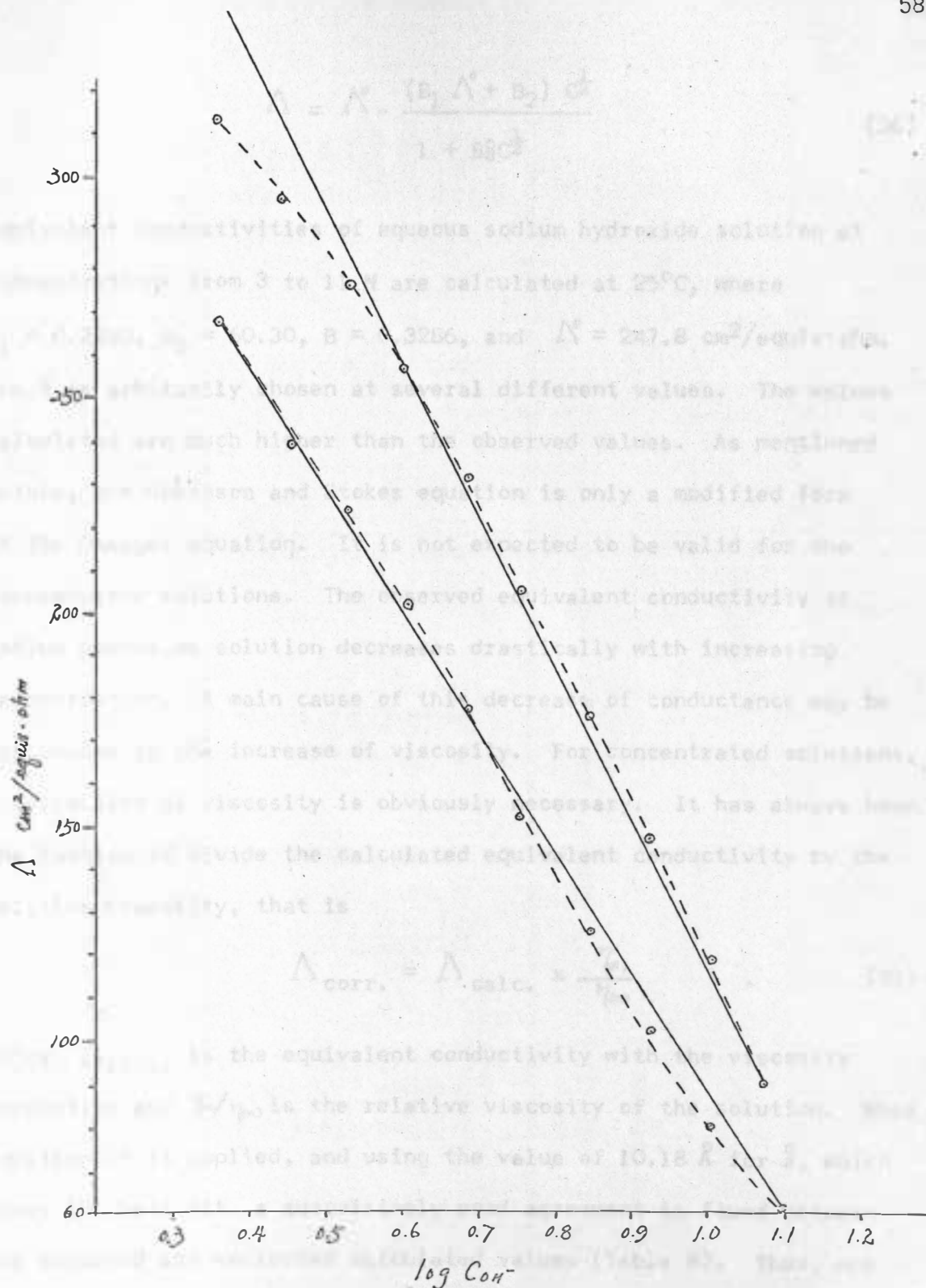


Figure 15. Relation of equivalent conductivity to the logarithm of the hydroxide ion concentration at 65°C.

$$\Lambda = \Lambda^{\circ} - \frac{(B_1 \Lambda^{\circ} + B_2) C^{\frac{1}{2}}}{1 + B_3 C^{\frac{1}{2}}} \quad (36)$$

Equivalent conductivities of aqueous sodium hydroxide solution at concentrations from 3 to 11 N are calculated at 25°C, where $B_1 = 0.2289$, $B_2 = 60.30$, $B_3 = 0.3286$, and $\Lambda^{\circ} = 247.8 \text{ cm}^2/\text{equiv}\cdot\text{ohm}$, and a is arbitrarily chosen at several different values. The values calculated are much higher than the observed values. As mentioned before, the Robinson and Stokes equation is only a modified form of the Onsager equation. It is not expected to be valid for the concentrated solutions. The observed equivalent conductivity of sodium hydroxide solution decreases drastically with increasing concentration. A main cause of this decrease of conductance may be attributed to the increase of viscosity. For concentrated solutions, a correction of viscosity is obviously necessary. It has always been the fashion to divide the calculated equivalent conductivity by the relative viscosity, that is

$$\Lambda_{\text{corr.}} = \Lambda_{\text{calc.}} \times \frac{\eta_{(0)}}{\eta_{(m)}} \quad (37)$$

where $\Lambda_{\text{corr.}}$ is the equivalent conductivity with the viscosity correction and $\eta_{(0)}/\eta_{(m)}$ is the relative viscosity of the solution. When equation 37 is applied, and using the value of 10.18 Å for a , which gives the best fit, a surprisingly good agreement is found between the observed and corrected calculated values (Table 8). Thus, one gets the conclusion that with the proper choice of a value and

Table 8. The Comparison of the Observed and Calculated Equivalent Conductivity of Concentrated Aqueous Sodium Hydroxide Solutions at 25°C.

C_{NaOH} equiv/l	obsv. cm ² /equiv·ohm	Λ^a calc. cm ² /equiv·ohm	η^b	corr. cm ² /equiv·ohm	$\Delta\Delta$	error%
3	123.8	218.0	1.75	124.6	+0.8	0.65%
4	100.2	217.4	2.16	100.6	+0.4	0.04%
5	81.2	216.8	2.66	81.5	+0.3	0.37%
6	65.5	216.6	3.32	65.2	-0.3	0.46%
7	51.4	216.4	4.23	51.2	-0.2	0.39%
8	40.8	216.2	5.33	40.6	-0.2	0.49%
9	32.3	216.0	6.69	32.3	0.0	0.00%
10	26.2	215.8	8.32	25.9	-0.3	1.14%
11	21.6	215.7	9.95	21.7	+0.1	0.46%

a. Λ calc. is calculated from the Robinson and Stokes equation.

b. Klochke and Godneva (31).

correction of viscosity, the Robinson and Stokes equation can be used to calculate the equivalent conductivity of concentrated aqueous sodium hydroxide solutions. As stated, by Campbell and Paterson (10), the choice of a value is quite arbitrary. For example, Falkenhagen and Leist (13) use a value of 4.8 \AA ; the calculation of Wishaw and Stokes (40) are based on $\bar{a} = 5.2 \text{ \AA}$; and Fuoss and Onsager use 4.31 \AA in their calculations for the dilute region. The closest approach of the ions in the solution, \bar{a} , for highly hydrated ions, like sodium and hydroxide, would be expected to be larger than those of less hydrated ions, but the value obtained here is unrealistically large to be just an ionic dimension. Although the arbitrary choice of an \bar{a} value and the viscosity correction give a very good fit with the results of this research, they do not necessarily and can not sufficiently explain the real structure of the concentrated solutions of aqueous sodium hydroxide. The combination of the Robinson and Stokes equation and equation 37 should be considered only a semi-empirical equation.

Another semi-empirical equation of the form

$$\Lambda = \Lambda^{\circ} - kC^{\frac{1}{2}}e^{-dC}$$

where k and d are constants determined by a least-squares calculation, was also tested. With $k = 77.728$ and $d = 0.010$, the calculated values are found to be in fairly good agreement with the observed values except at very high and very low concentrations. No viscosity

corrections were made. Modifications of this equation were also tried but no definite conclusions have yet been reached as to their usefulness and generality.

It is found from the above discussions that more data on viscosity and dielectric constants of the concentrated electrolytic solutions at various temperatures are needed to really devise and test the more accurate equations. With the limited information, up to the present, one still can get the following conclusions:

1. From the success of the Robinson and Stokes equation with the viscosity correction, it is definitely indicated that proper treatment of electrostatic effects with the allowance for the changes in solvent properties can explain conductance without needing to consider ion pair formation.

2. The effect that all electrolytes (acids, bases and salts) show similar behavior with maximum conductivity around 5 to 7 normal would imply that the solvent characteristics are of fundamental importance and implies the decreasing importance of specific ionic effects such as hydration, etc., except that they are probably the cause of the minor variations in conductance behavior.

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