# CONDUCTANCES OF SOLUTIONS IN THE REGION

## OF MEDIUM CONCENTRATION

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by

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To My Parents

# ACKNOWLEDGMENTS

Although I cannot honestly say that I <u>wish</u> to be found in error, yet I do fervently hope that the progress of science in the hands of the many zealous cultivators will be such as, by giving us new and other developments, and laws more and more general in their applications, will make even me think that what is written and illustrated in these experimental researches, belongs to the by-gone parts of science.

Michael Faraday

# ABSTRACT

Equivalent conductances, densities, and viscosities of aqueous solutions of ammonium nitrate, silver nitrate, and lithium nitrate were determined at 25°C. and 35°C. at concentrations ranging from 0.01 molar to 1.0 molar.

Experimental equivalent conductances have been compared with those calculated by the Wishaw-Stokes and Falkenhagen-Leist equations. Suitable choice of one parameter, the distance of closest approach, permits reproduction of the experimental data with an error of less than 0.5%. A study of the deviations of calculated from experimental conductances reveals that the distance of closest approach varies appreciably with concentration and temperature.

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THEORETICAL INTRODUCTION

# THEORETICAL INTRODUCTION

This introduction will discuss briefly the equations of Debye, Hückel, and Onsager; of Wishaw and Stokes; of Falkenhagen and Leist; and show how the equation of Fuoss and Onsager may be applied to dilute solution data.

## 1. Early Quantitative Predictions

The equivalent conductance, $\Lambda$ , of a solution of an electrolyte is defined by

$$\Lambda = \frac{1000 \, L}{c} \text{ mhos,} \qquad (1)$$

where L is called the specific conductance of the solution, and c is the concentration of the electrolyte in moles per liter. L is defined by

$$L = \frac{A}{r} \text{ mho/cm.,} \qquad (2)$$

where r is the resistance of the solution measured in a cell of constant A. The specific conductance is the conductance of a one centimeter cube of solution. A is dependent on the geometry of the cell and is invariably determined by measuring the resistance of a solution of known specific conductance. $\Lambda_c$ , the limiting equivalent conductance, is a constant characteristic of the solute in a given solvent at a given temperature. It is obtained by extrapolating some theoretical or semi-theoretical conductance

function to infinite dilution.

It was observed by Kohlrausch[1] in 1916 that conductance data in extremely dilute solutions could be made to fit the equation

$$\Lambda = \Lambda_o - A\sqrt{c} \tag{3}$$

where A is an empirical constant. The extrapolation of a $\Lambda$ against $\sqrt{c}$ plot is a time-honoured method for the evaluation of $\Lambda_o$.

In 1923 Debye and Hückel[2] published a limiting law giving the activity coefficient of an electrolyte in solution as a linear function of the square root of concentration, with slope given by a group of known physical constants. A solution of an electrolyte is assumed to be completely dissociated. This is reasonable, since studies of the structure of electrolyte crystals indicate the occurrence of ordered arrangements of ions rather than molecules in the space lattice. The decrease in equivalent conductance with increase in concentration is attributed to a decrease in the velocity of the ions, a consequence of ion-ion and ion-solvent interactions, rather than to a decrease in the number of ions, as suggested earlier by Arrhenius. Each ion is treated as being surrounded by an atmosphere of ions of opposite charge. Attributing all deviations from ideality to changes in charges on the ionic atmosphere, Debye and Hückel arrived at

the equation

$$\ln \gamma = \frac{-\epsilon^2 K}{2D_o kT(1 + Ka)} , \qquad (4)$$

where

$$K^2 = \frac{\pi \epsilon^2}{125} \frac{N}{D_o kT} c , \qquad (5)$$

and "a" is the distance of closest approach between ions of opposite charge, one of the boundary conditions imposed in the derivation of equation (4). The meaning of the other symbols will be found in an appendix. $1/K$ is the distance at which the charge density of the ionic atmosphere is a maximum. In very dilute solutions $Ka \ll 1$, and

$$\ln \gamma = \frac{-\epsilon^2 K}{2D_o kT} . \qquad (6)$$

Debye and Hückel[3] then applied the ionic atmosphere model to the problem of conductance. They reasoned that the imposition of an external electric field would distort the ionic atmosphere. The central ion will move in one direction while the oppositely-charged ions of the atmosphere will be pulled in the opposite direction. This asymmetry results in a greater force behind the ion than in front of it, retarding the motion of the ion. This is known as the relaxation effect. In addition, the motion of an ion and its atmosphere will be retarded by solvent molecules obstructing its path and by ions of opposite charge. This is the electrophoretic effect.

Onsager[4] extended the treatment of Debye and Hückel
to include the effect of the Brownian motion of the ions,
and arrived at the equation

$$\Lambda = \Lambda_c - \left[ \frac{82.48}{\eta_o (D_o T)^{1/2}} + \frac{8.204 \times 10^5}{(D_o T)^{3/2}} \Lambda_c \right] \sqrt{c} \quad (7)$$

for uni-univalent electrolytes.  This is often written

$$\Lambda = \Lambda_o - (\alpha \Lambda_o + \beta) \sqrt{c} \quad (8)$$

For water at $25^o$C., $\alpha = 0.2289$, $\beta = 60.49$.

There are several difficulties inherent in the Debye-
Hückel theory and its extension by Onsager.  The most important
are:

(i) The principle of the linear superposition of fields
requires that there be a linear relationship between the
charge density around an ion and the electrical potential.
The charge density, $\rho$, is given by

$$\rho = \frac{(dn_+ - dn_-)}{dV} \epsilon,$$

where $dn_+$ is the number of positive ions in a volume $dV$
at a distance $r$ from a particular ion.  The Boltzmann dis-
tribution function predicts that $dn_+$ will be given by

$$dn_+ = n \exp\left(\frac{-\epsilon \psi}{kT}\right) dV,$$

where $n$ is the number of positive or negative ions per unit

volume, $\epsilon\psi$ is the work required to bring a unit positive
charge from infinity to a distance r from the selected ion,
and $\psi$ is the electrical potential. dn_ is defined as

$$dn_- = n \exp\left(\frac{\epsilon\psi}{kT}\right)dV \;.$$

Insertion of the last two equations into the definition of
the charge density gives

$$\rho = n\epsilon\left[\exp\left(\frac{-\epsilon\psi}{kT}\right) - \exp\left(\frac{\epsilon\psi}{kT}\right)\right].$$

If the exponentials be expanded as infinite series, and
third and higher order terms be neglected, the equation
is reduced to

$$\rho = -\frac{2n\epsilon^2\psi}{kT}\;.$$

This equation has the linear relationship between charge
density and electrical potential which the principle of
the linear superposition of fields requires. The neglect
of third and higher order terms is justifiable only when
kT, the thermal energy of the ions, is very much greater
than $\epsilon\psi$, the interionic potential energy.

(ii) The dielectric constant of the solution is taken
to be that of the solvent. This ignores the decrease of
the bulk dielectric constant with increase of concentration,
as well as the variation of the microscopic dielectric
constant with distance from an ion.

(iii) Ions are considered to be so far apart that their size is negligible with respect to the distance between them. In a 0.01 molar solution ions will be of the order of 20 $\overset{o}{A}$ apart, while the diameter of an ion is 2 - 4 $\overset{o}{A}$.

## 2. The Wishaw-Stokes Equation

The next significant advance in conductance theory did not occur until 1952 when Falkenhagen, Leist, and Kelbg[5] modified Onsager's treatment of the relaxation effect to include the effect of finite ion size. Employing a distribution function due to Eigen and Wicke[6] they arrived at the following expression for the relaxation effect in uni-univalent electrolytes

$$\frac{\Delta X}{X} = \frac{\epsilon^2}{3D_o kT} \frac{K}{Ka(1 + Ka)} \left( \exp(0.2929Ka) - 1 \right)\left( 1 - \frac{n}{N_1} \right)\left( 1 - \frac{n}{N_2} \right) \tag{9}$$

where

$$K^2 = \frac{\pi \epsilon^2 N}{125 D_o kT} c \left( 1 - \frac{n}{2N_1} - \frac{n}{2N_2} \right) \tag{10}$$

n is the number of ions of one kind per cubic centimeter of solution, and $N_1$ is the reciprocal of the volume of a cation. $N_2$ is the reciprocal of the volume of an anion. If, as is approximately correct, $N_1$ is taken as equal to $N_2$, equations (9) and (10) become

$$\frac{\Delta X}{X} = \frac{\epsilon^2}{3D_o kT} \frac{K}{a(1 + a)} \left( \exp(0.2929 a) - 1 \right)\left( 1 - \frac{n}{N_1} \right)^2 \tag{11}$$

$$K^2 = \frac{\pi \epsilon^2 N}{125 D_o kT} c \left( 1 - \frac{n}{N_1} \right) \tag{12}$$

Making the approximation $\left(1 - \dfrac{n}{N_1}\right) = 1$, Wishaw and Stokes[7]

insert the expression for the relaxation effect into their

general conductance equation

$$\Lambda = \left(\Lambda_o - \frac{10^7 \, F^2}{6\pi \eta_o N} \cdot \frac{\kappa}{(1 + \kappa a)}\right)\left(1 + \frac{\Delta X}{X}\right) \quad (13)$$

and obtain

$$\Lambda = \left(\Lambda_o - \frac{B_1 \, \kappa}{(1 + \kappa a)}\right)\left(1 - \frac{B_2 \, \kappa}{(1 + \kappa a)\kappa a} \, \frac{\exp(0.2929\kappa a) - 1}{} \right) \quad (14)$$

where

$$B_1 = \frac{10^7 \, F^2}{6\pi \eta_o N} \, ,$$

and

$$B_2 = \frac{\epsilon^2}{3D_o kT} \, .$$

Values of $B_1$ and $B_2$ are listed in an appendix.

It is useful to determine when the approximation

$\left(1 - \dfrac{n}{N_1}\right) = 1$ is justifiable. Inclusion of this term reduces

$\kappa$ by a factor $\left(1 - \dfrac{n}{N_1}\right)$ , and $\dfrac{\Delta X}{X}$ by a factor $\left(1 - \dfrac{n}{N_1}\right)^2$.

Values of these factors are compared with values of the

electrophoretic and relaxation terms in the table below.

Data are for ammonium nitrate solutions at $25^{\circ}$C., but apply

approximately to any uni-univalent electrolyte. $N_1$ is

calculated for an ionic radius of $1.5 \times 10^{-8}$ cm.

Ommision of the factor $\left(1 - \dfrac{n}{N_1}\right)^2$ would increase the

calculated equivalent conductance by 0.01% at 0.1 molar,

by 0.1% at 1 molar, and by 4% at 10 molar.

| Concentration | $\left(1 - \frac{n}{N_1}\right)$ | $\frac{B_1 \kappa}{1 + \kappa a}$ | $\left(1 - \frac{n}{N_1}\right)^2$ | $\frac{\Delta X}{X}$ |
|---|---|---|---|---|
| Moles/liter | ... | mhos | ... | ... |
| $10^{-3}$ | 1.0000 | 3 | 1.0000 | ..... |
| $10^{-2}$ | 1.0000 | 6 | 0.9998 | 0.021 |
| $10^{-1}$ | 0.9996 | 15 | 0.9984 | 0.058 |
| $10^{0}$ | 0.9959 | 30 | 0.988 | 0.13 |
| $10^{1}$ | 0.958 | 50 | 0.843 | 0.30 |

## 3. The Falkenhagen-Leist Equation

Consideration of the fact that ions, being impenetrable, must be displaced during migration led Falkenhagen[8] to evaluate the relaxation effect as

$$\Lambda_I = \frac{0.2929 \, B_2 \, \Lambda_o \, \kappa}{(1 + \kappa a)(1 + \frac{1}{2}\sqrt{2}\kappa a + \frac{1}{6}\kappa^2 a^2)} \qquad (15)$$

and the electrophoretic effect as

$$\Lambda_{II} = \frac{B_3 \, \kappa}{1 + \kappa a} , \qquad (16)$$

where $\kappa$ is defined by equation (10), but in practice equation (5) is used. The constant $B_3$ is defined by

$$B_3 = \frac{\epsilon^2 \, N}{27\pi \, \gamma_o 10^{11}}$$

Falkenhagen's general conductance equation is

$$\Lambda = \Lambda_o - \Lambda_I - \Lambda_{II} \tag{17}$$

instead of the product type proposed by Wishaw and Stokes.


## 4. The Fuoss-Onsager Equations

Fuoss[9] has recently summarized the involved theoretical treatment given earlier by Fuoss and Onsager[10] and by Fuoss.[11] The simpler case, that in which ion pair formation is negligible, will be considered first.

(i) The Conductance Equation in the Case of Negligible Association.

The conductance of a dilute solution of a strong electrolyte is given by

$$\Lambda = \Lambda_o - Sc^{1/2} + Ec \log c + Jc . \tag{18}$$

In this equation S is defined by

$$S = \alpha \Lambda_o + \beta ,$$

where $\alpha$ and $\beta$ are Debye-Hückel-Onsager constants, defined in equation (8). E is defined through

$$0.4343 \, E = \frac{\kappa^2 a^2 b^2}{24c} - \frac{\kappa a b \beta}{16c^{1/2}} ,$$

where

$$b = \frac{\epsilon^2}{a D_o kT} .$$

"a" is, as usual, the distance of closest approach between two ions. Notice that E and S are independent of concentration

and the value of "a". J is defined by

$$J = \sigma_1 \Lambda_0 + \sigma_2 ,$$

where

$$\sigma_1 = \frac{\kappa^2 a^2 b^2}{12c} \left[ h(b) + 0.9074 + \ln \frac{\kappa a}{c^{\frac{1}{2}}} \right] ,$$

and

$$\sigma_2 = \alpha\beta + \frac{11\beta a\kappa}{12c^{\frac{1}{2}}} - \frac{\kappa ab\beta}{8c^{\frac{1}{2}}} \left( 1.0170 + \ln \frac{\kappa a}{c^{\frac{1}{2}}} \right) .$$

The function h(b) which appears in $\sigma_1$ is given by

$$h(b) = \frac{2b^2 + 2b - 1}{b^3} .$$

$\kappa$ is defined, as before, by equation (5). The functions $\sigma_1$ and $\sigma_2$ are dependent only on the choice of "a". Thus J depends only on "a" and the limiting equivalent conductance. Experience has shown that "a" and $\Lambda_0$ depend on the equation used in their evaluation. Consequently they must be determined from experimental data with the Fuoss-Onsager equation. The quantity $\Lambda'$, defined by

$$\Lambda' = \Lambda + Sc^{\frac{1}{2}} - Ec \log c , \tag{19}$$

is calculated for each conductance determination. A plot of $\Lambda'$ against concentration will have an intercept $\Lambda_0$ and slope J, from which "a" may be calculated.

(ii) The Conductance Equation in the Case of Appreciable
Association.

Two changes are made in equation (18) to accomodate
the new situation. Wherever it appears, the concentration, c,
is replaced by $c\gamma_0$, where $\gamma_0$ is the degree of dissociation
of the electrolyte in solution. The ratio of the conductance
to the limiting equivalent conductance is a satisfactory first
approximation for $\gamma_0$. An association term is introduced
to represent the effect of the ion pairs on the conductance.
The new equation is

$$\Lambda = \Lambda_0 - S(c\gamma_0)^{\frac{1}{2}} + Ec\gamma_0 \log c\gamma_0 + Jc\gamma_0 - K_a c\gamma_0 f^2 \Lambda \quad (20)$$

where f is the mean ionic activity of the electrolyte, and
$K_a$ is the association constant for ion pair formation. All
other symbols are defined as before. We are faced with
the problem of determining $\Lambda_0$, "a", and $K_a$ from experimental
data. Three new quantities are defined as shown:

$$\Lambda' = \Lambda_0 + Jc\gamma_0 - K_a c\gamma_0 f^2 \Lambda$$

$$y = \frac{\Lambda' - \Lambda_0}{c\gamma_0} = J - K_a f^2 \Lambda$$

$$x = f^2 \Lambda.$$

$\Lambda_0$ is chosen so that a plot of y against x is linear, and
$K_a$ is obtained from the slope of the plot. J is the
y-intercept of this plot. Then "a" may be calculated, since
$\Lambda_0$ is already known.

If $K_a$ be known from the extrapolation of a plot of log $K_a$ against the reciprocal of the dielectric constant, the evaluation of "a" and $\Lambda_o$ is somewhat simpler. The quantity $\Lambda_J$ is defined by

$$\Lambda_J = \Lambda_o + Jc\gamma_o .$$

A plot of $\Lambda_J$ against $c\gamma_o$ will have slope $J$ and intercept $\Lambda_o$ .

On the other hand, if "a" be known, the limiting equivalent conductance and the association constant may be calculated from a plot of $\Lambda_K$ against $c\gamma_o f^2 \Lambda$ , where

$$\Lambda_K = \Lambda_o - K_a c\gamma_o f^2 \Lambda .$$

Fuoss and Onsager[10] mention several reasons why their equation can be expected to be in error in linear and higher order terms:

(1) The change of viscosity with concentration is neglected.

(2) The change of dielectric constant is neglected.

(3) Linear superposition of fields is assumed.

(4) The volume occupied by the ions is neglected.

(5) The fact that colliding ions have finite velocity is ignored.

(6) The solvent is assumed to be continuous.

These reasons apply to the Wishaw-Stokes and Falkenhagen-Liest equations as well.

Mathematical approximations restrict the Fuoss-Onsager equation to $\kappa$ a$<$ 0.3. (For example, c $<$ 0.05 molar for "a" = 3.5 Å). In developing the theory, all the ions except the reference ion are replaced by a continuous charge distribution. The charge density in the ionic atmosphere is a maximum at $1/\kappa$ . The approach of any ion to the reference ion will have a large effect on the potential about the reference ion. It is suggested that the minimum permissible interionic distance is of the order of a few ionic diameters, and 7 x a is arbitrarily chosen. This limits the concentration to which we expect the equation to hold to 0.02 molar.

There is no doubt that some form of viscosity correction is necessary in conductance equations, particularly for concentrations above 0.1 molar. Experience has shown that the factor $\eta/\eta_o$ is probably close to the true correction. The viscosity-corrected equations are, then,

$$\Lambda \eta/\eta_o = \left(-\Lambda_o - \frac{B_1 \kappa}{1 + \kappa a}\right)\left(1 - \frac{B_2 \kappa}{(1 + \kappa a)\kappa a}\exp(0.2929\kappa a) - 1\right) \tag{21}$$

and

$$\Lambda \eta/\eta_o = \Lambda_o - \Lambda_I - \Lambda_{II} \tag{22}$$

It should be remembered that the theoretical validity of these equations is not being examined. There are good reasons for believing that none of them is applicable to

concentrations higher than 0.02 molar. The question,
"Do these equations satisfactorily reproduce experimental
data in concentrated solutions ?" is being investigated.
It is realized that the "a" values obtained in the range
0.01 molar to 0.1 molar are at best qualitative, and that
those calculated for higher concentrations can have little
physical significance.

NATURE OF THE PROBLEM

# THE NATURE OF THE PROBLEM

The applicability of the equations of Robinson and Stokes,

$$\Lambda = \left( \Lambda_c - \frac{B_1 \kappa}{1 + \kappa a} \right)\left( 1 - \frac{B_2 \kappa}{(1 + \kappa a)\kappa a} \exp(0.2929\kappa a) - 1 \right)$$

and of Falkenhagen and Leist,

$$\Lambda = \Lambda_o - \frac{B_2 \kappa}{(1 + \kappa a)(1 + \frac{1}{2}\sqrt{2}\kappa a + \frac{1}{2}\kappa^2 a^2)} - \frac{B_3 \kappa}{1 + \kappa a}$$

to salts previously studied in concentrated solutions in this laboratory has been examined in the region of moderate concentration. The effect of a simple viscosity correction on agreement between calculated and experimental equivalent conductances was investigated.

Densities, viscosities, specific conductances, and equivalent conductances were determined for solutions of ammonium nitrate, silver nitrate, and lithium nitrate at $25^{\circ}$C. and $35^{\circ}$C. at twenty concentrations between 0.01 molar and 1.0 molar.

EXPERIMENTAL PROCEDURE

# EXPERIMENTAL PROCEDURE

## 1. Purity of Materials

Ammonium nitrate, Fisher reagent grade, was recrystallized twice from conductance water, ground in an agate mortar, and stored in an oven at $100^\circ$C. until needed.

Silver nitrate from Johnson, Matthey, and Mallory, was fused carefully in a platinum dish, ground in an agate mortar, and stored in darkness over sulphuric acid.

Fisher reagent grade lithium nitrate was fused just before use, as described below.

Potassium chloride, Mallinckrodt analytical reagent, was fused in a platinum dish, ground in an agate mortar, and stored over sulphuric acid.

## 2. Preparation of the Solutions

Water obtained from a Barnstead still with a block tin condenser had a specific conductance less than $5 \times 10^{-6}$ mho/cm. at $25^\circ$C.

At least 2.5 gm. of the salt was weighed to the nearest 0.2 mg. The salt was washed into a flask, and made up to 0.5 to 2 liters with conductance water. The solution was weighed on a large balance to the nearest 10 mg. A few of the weakest solutions were prepared by weighing as little as 1.5 gm. of the salt to 0.1 mg. on a semi-micro balance.

Lithium nitrate was heated to constant weight in a platinum dish, then dissolved in water and transferred to a flask.

All weights were calibrated, and all weighings were corrected to vacuum. (Density of air: 1.16 mg./ml.). Weight concentrations are, then, known at least within 0.01%.

## 3. The Conductance Bridge

A model 200C Hewlett-Packard oscillator generated a 1000 c.p.s. alternating current for a bridge composed of a No. 1553 Leeds and Northrup shielded ratio box, a No. 4750 resistance box, and a variable capacitance. The signal from the bridge was amplified by a Heath model EA-2 12 watt amplifier, and detected with a headphone set. The standard resistances were calibrated to the nearest 0.01 ohm with a Jones Bridge. Resistances were measured to the nearest 0.005%. To avoid heating the solution in the cell, it was necessary to limit the output of the oscillator to high voltage over a brief period of time, or low voltage over a longer period. A moment's calculation will show that a resistance of 250 ohms measured at 13 volts (maximum oscillator output) may increase the temperature of the solution in the cell by 0.01°C. per second. It may be pointed out that resistances need not be calibrated with exceptional accuracy, since small errors in cell constant determinations will be compensated by similar errors in specific conductance.

## 4. The Conductance Cells

Several cells with leads and filling tubes sufficiently separated to avoid stray capacitances (the Parker effect), as recommended by Jones and Bollinger[12] were used. Cell constants determined with the solutions defined by Jones and Bradshaw[13] were constant within 0.02% throughout this investigation. The cell constants were 0.551, 3.1996, 33.701, 61.237, 101.40, and 135.11.

The variation of cell constant with temperature is given approximately by

$$\Delta A = - \beta A \Delta T$$

for a cell with large electrode separation.[14] $\beta$ is the linear coefficient of thermal expansion of glass, and A is the cell constant. In this work the cell constant change was not greater than 0.003%, and so was ignored.


## 5. The Thermostats

Two four-gallon pyrex containers were filled with oil - Marcol GX supplied by Imperial Oil Limited - and lagged with half-inch felt. Each contained two propellor-type stirrers, a mercury-toluene regulator, a 60-watt heating lamp, and a Beckmann thermometer. In addition, the $25^{\circ}$C. bath contained a copper coil for conducting cooling water at roughly constant temperature and constant rate of flow. The thermostats

maintained constant temperature within $0.002^{\circ}C$. Beckmann thermometers were calibrated periodically, with a Müller bridge, against two different platinum resistance thermometers, which ascertained the temperature within $0.005^{\circ}C$.

## 6. The Viscosity Measurements

Two viscometers of the Cannon and Fenske[15] type, having negligible drainage and kinetic energy corrections, were calibrated with water at $25^{\circ}C$. and $35^{\circ}C$. They were filled through the capillary arm to a reference mark on the capillary portion by applying suction to the opposite arm. Calibration run times were reproducible to only 0.05%, possibly because of variations in the quantity of air dissolved in the water.

## 7. The Density Determinations

Two pycnometers of 45 mls. capacity were filled and left in the thermostat for at least 30 minutes. The solution meniscus in one capillary arm was adjusted to a reference mark by withdrawing solution with filter paper through the opposite arm. The pycnometers were rinsed with acetone, dried, and left in the balance case for 1 hour before weighing. Several times during the research the instruments were calibrated with water at both temperatures. Vacuum corrections were applied to all weighings. The mean deviation of a dozen calibrations was 0.002%.

## 8. The Hydrolysis Correction

Following Campbell and Bock,[16] the equivalent conductances of ammonium nitrate solutions were corrected for hydrolysis, which occurs according to the equation

$$NH_4^+ + H_2O = NH_4OH + H^+$$
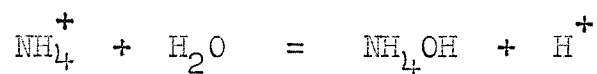
The hydrolysis constants, taken from Bates and Pinching,[17] are $K_h = 5.689 \times 10^{-10}$ at $25^\circ$C. and $K_h = 1.130 \times 10^{-9}$ at $35^\circ$C. In no case was the correction greater than 0.11 mho.

Determinations of specific conductance, density, and viscosity were done in duplicate. Measurements at $35^\circ$C. were done without refilling the instruments.

EXPERIMENTAL RESULTS

# EXPERIMENTAL RESULTS

The experimental results of this research are given in Tables I to VI. Three fundamental properties, the density, the specific conductance, and the relative viscosity are listed for each solution. In addition two derived properties, the molarity and the equivalent conductance are given. The salts described are ammonium nitrate, silver nitrate, and lithium nitrate, each at $25^{\circ}$C. and $35^{\circ}$C.

All conductances are corrected for the contribution of water. A hydrolysis correction, described on page 23, has been applied to the data on ammonium nitrate.

## TABLE I

### DATA FOR AMMONIUM NITRATE SOLUTIONS AT 25.00°C.

| Concentration (mole/liter) | Density (gm/ml) | Specific Conductance (mho/cm x $10^6$) | Equivalent Conductance (mhos) | Relative Viscosity |
|---|---|---|---|---|
| 0.009893 | 0.99740 | 1350.9 | 136.47 | 0.999 |
| 0.020033 | 0.99776 | 2671.8 | 133.32 | 0.998 |
| 0.029175 | 0.99801 | 3830.7 | 131.26 | 0.998 |
| 0.039970 | 0.99839 | 5170.5 | 129.33 | 0.997 |
| 0.047956 | 0.99866 | 6146.3 | 128.13 | 0.996 |
| 0.050005 | 0.99872 | 6395.0 | 127.86 | 0.998 |
| 0.059997 | 0.99901 | 7601.0 | 126.66 | 0.996 |
| 0.070046 | 0.99938 | 8792.6 | 125.50 | 0.997 |
| 0.079920 | 0.99967 | 9955.0 | 124.54 | 0.996 |
| 0.089968 | 1.00003 | 11130.3 | 123.70 | 0.996 |
| 0.10001 | 1.00036 | 12285.5 | 122.83 | 0.995 |
| 0.15363 | 1.00208 | 18344 | 119.39 | 0.993 |
| 0.20090 | 1.00360 | 23529 | 117.10 | 0.990 |
| 0.30230 | 1.00684 | 34302 | 113.46 | 0.986 |
| 0.39993 | 1.00990 | 44327 | 110.83 | 0.982 |
| 0.49647 | 1.01296 | 53993 | 108.74 | 0.977 |
| 0.59710 | 1.01613 | 63832 | 106.90 | 0.975 |
| 0.69976 | 1.01937 | 73640 | 105.23 | 0.973 |
| 0.79943 | 1.02246 | 82966 | 103.77 | 0.968 |
| 0.90237 | 1.02566 | 92510 | 102.51 | 0.967 |
| 0.99976 | 1.02868 | 101306 | 101.32 | 0.963 |

## TABLE II

### DATA FOR AMMONIUM NITRATE SOLUTIONS AT 35.00°C.

| Concentration (mole/liter) | Density (gm/ml) | Specific Conductance (mho/cm x 10$^6$) | Equivalent Conductance (mhos) | Relative Viscosity |
|---|---|---|---|---|
| 0.009864 | 0.99439 | 1616.0 | 163.73 | 0.999 |
| 0.019972 | 0.99472 | 3192.9 | 159.78 | 0.999 |
| 0.029087 | 0.99498 | 4577.8 | 157.31 | 0.999 |
| 0.039851 | 0.99540 | 6177.1 | 154.94 | 0.998 |
| 0.047808 | 0.99559 | 7341.2 | 153.49 | 0.997 |
| 0.049851 | 0.99566 | 7637.5 | 153.14 | 0.998 |
| 0.059813 | 0.99594 | 9073.9 | 151.65 | 0.998 |
| 0.069828 | 0.99628 | 10495.5 | 150.28 | 0.998 |
| 0.079673 | 0.99658 | 11880.9 | 149.08 | 0.997 |
| 0.089684 | 0.99687 | 13280.7 | 148.04 | 0.997 |
| 0.099691 | 0.99720 | 14661.3 | 147.03 | 0.998 |
| 0.15315 | 0.99894 | 21863 | 142.73 | 0.996 |
| 0.20026 | 1.00041 | 28020 | 139.89 | 0.995 |
| 0.30130 | 1.00353 | 40792 | 135.37 | 0.992 |
| 0.39859 | 1.00650 | 52637 | 132.04 | 0.992 |
| 0.49478 | 1.00951 | 64031 | 129.40 | 0.988 |
| 0.59498 | 1.01251 | 75588 | 127.03 | 0.987 |
| 0.69727 | 1.01575 | 87124 | 124.94 | 0.987 |
| 0.79655 | 1.01877 | 98031 | 123.06 | 0.984 |
| 0.89905 | 1.02189 | 109146 | 121.39 | 0.984 |
| 0.99578 | 1.02458 | 119441 | 119.94 | 0.982 |

## TABLE III

### DATA FOR SILVER NITRATE SOLUTIONS AT $25.00^\circ$C.

| Concentration (mole/liter) | Density (gm/ml) | Specific Conductance $(10^6 \times (mhos)/cm)$ | Equivalent Conductance (mhos) | Relative Viscosity |
|---|---|---|---|---|
| 0.010156 | 0.99842 | 1267.0 | 124.75 | 1.001 |
| 0.019394 | 0.99981 | 2354.2 | 121.39 | 1.003 |
| 0.029459 | 1.00125 | 3503.3 | 118.92 | 1.004 |
| 0.039998 | 1.00278 | 4675.2 | 116.89 | 1.004 |
| 0.049659 | 1.00411 | 5720.5 | 115.20 | 1.003 |
| 0.058313 | 1.00530 | 6643.7 | 113.93 | 1.003 |
| 0.068343 | 1.00675 | 7691.4 | 112.54 | 1.004 |
| 0.080014 | 1.00842 | 8895.5 | 111.18 | 1.005 |
| 0.089961 | 1.00978 | 9902.2 | 110.07 | 1.005 |
| 0.10063 | 1.01127 | 10968.2 | 109.00 | 1.005 |
| 0.14915 | 1.01809 | 15655 | 104.96 | 1.008 |
| 0.19797 | 1.02494 | 20148 | 101.77 | 1.011 |
| 0.29997 | 1.03920 | 28982 | 96.62 | 1.016 |
| 0.39976 | 1.05316 | 37051 | 92.68 | 1.022 |
| 0.55271 | 1.07455 | 48674 | 88.06 | 1.027 |
| 0.59523 | 1.08033 | 51646 | 86.77 | 1.030 |
| 0.69928 | 1.09476 | 58860 | 84.17 | 1.038 |
| 0.79154 | 1.10758 | 64962 | 82.07 | 1.046 |
| 0.89509 | 1.12196 | 71594 | 79.99 | 1.053 |
| 1.00088 | 1.13649 | 77977 | 77.91 | 1.062 |

## TABLE IV

### DATA FOR SILVER NITRATE SOLUTIONS AT 35.00°C.

| Concentration (mole/liter) | Density (gm/ml) | Specific Conductance (mho/cm x $10^6$) | Equivalent Conductance (mhos) | Relative Viscosity |
|---|---|---|---|---|
| 0.010127 | 0.99549 | 1519.5 | 150.04 | 1.002 |
| 0.019335 | 0.99678 | 2824.9 | 146.10 | 1.003 |
| 0.029369 | 0.99820 | 4199.9 | 143.00 | 1.004 |
| 0.039873 | 0.99966 | 5604.3 | 140.55 | 1.004 |
| 0.049507 | 1.00104 | 6854.4 | 138.45 | 1.005 |
| 0.058136 | 1.00224 | 7958.2 | 136.89 | 1.005 |
| 0.068130 | 1.00362 | 9212.8 | 135.22 | 1.007 |
| 0.079763 | 1.00526 | 10652.4 | 133.55 | 1.007 |
| 0.089681 | 1.00663 | 11858 | 132.23 | 1.008 |
| 0.10032 | 1.00811 | 13143 | 131.01 | 1.008 |
| 0.14867 | 1.01485 | 18738 | 126.04 | 1.011 |
| 0.19734 | 1.02167 | 24108 | 122.16 | 1.016 |
| 0.29899 | 1.03580 | 34657 | 115.91 | 1.022 |
| 0.39842 | 1.04961 | 44288 | 111.16 | 1.029 |
| 0.55080 | 1.07082 | 58120 | 105.52 | 1.037 |
| 0.59314 | 1.07654 | 61665 | 103.96 | 1.038 |
| 0.69679 | 1.09087 | 70246 | 100.81 | 1.050 |
| 0.78873 | 1.10364 | 77488 | 98.24 | 1.058 |
| 0.89180 | 1.11783 | 85278 | 95.63 | 1.066 |
| 0.99713 | 1.13225 | 92985 | 93.25 | 1.076 |

## TABLE V

### DATA FOR LITHIUM NITRATE SOLUTIONS AT 25.00°C.

| Concentration (mole/liter) | Density (gm/ml) | Specific Conductance (mho/cm x 10$^6$) | Equivalent Conductance (mhos) | Relative Viscosity |
|---|---|---|---|---|
| 0.010572 | 0.99751 | 1083.0 | 102.44 | 1.000 |
| 0.021061 | 0.99793 | 2105.4 | 99.97 | 0.999 |
| 0.029775 | 0.99830 | 2920.0 | 98.07 | 1.004 |
| 0.038848 | 0.99866 | 3770.3 | 97.05 | 1.005 |
| 0.050821 | 0.99897 | 4861.3 | 95.66 | - |
| 0.059158 | 0.99949 | 5604.1 | 94.73 | 1.007 |
| 0.069872 | 0.99991 | 6533.8 | 93.51 | 1.009 |
| 0.076234 | 1.00010 | 7095.4 | 93.07 | 1.008 |
| 0.091701 | 1.00079 | 8448.0 | 92.13 | 1.011 |
| 0.10111 | 1.00112 | 9247.6 | 91.46 | 1.011 |
| 0.14980 | 1.00332 | 13290 | 88.72 | 1.017 |
| 0.19937 | 1.00506 | 17267 | 86.61 | 1.022 |
| 0.29918 | 1.00902 | 24887 | 83.19 | 1.043 |
| 0.39900 | 1.01293 | 32130 | 80.53 | 1.042 |
| 0.45941 | 1.01532 | 36341 | 79.10 | 1.050 |
| 0.58142 | 1.02009 | 44546 | 76.62 | 1.060 |
| 0.71135 | 1.02509 | 52771 | 74.18 | 1.075 |
| 0.81640 | 1.02930 | 59193 | 72.51 | 1.087 |
| 0.91191 | 1.03301 | 64745 | 71.00 | 1.098 |
| 1.00464 | 1.03667 | 69959 | 69.64 | 1.114 |

(30)

## TABLE VI

### DATA FOR LITHIUM NITRATE SOLUTIONS AT 35.00°C.

| Concentration (mole/liter) | Density (gm/ml) | Specific Conductance (mho/cm x 10$^6$) | Equivalent Conductance (mhos) | Relative Viscosity |
|---|---|---|---|---|
| 0.010540 | 0.99446 | 1306.2 | 123.93 | 1.000 |
| 0.020996 | 0.99485 | 2534.9 | 120.73 | 1.002 |
| 0.029683 | 0.99523 | 3525.9 | 118.79 | 1.003 |
| 0.038729 | 0.99559 | 4540.1 | 117.23 | 1.006 |
| 0.050664 | 0.99589 | 5848.5 | 115.44 | - |
| 0.058975 | 0.99640 | 6745.2 | 114.37 | 1.008 |
| 0.069654 | 0.99679 | 7861.2 | 112.86 | 1.010 |
| 0.075999 | 0.99700 | 8531.6 | 112.26 | 1.008 |
| 0.091418 | 0.99770 | 10157.2 | 111.11 | 1.012 |
| 0.10079 | 0.99798 | 11114.3 | 110.27 | 1.014 |
| 0.14929 | 0.99997 | 15960 | 106.91 | 1.020 |
| 0.19874 | 1.00186 | 20724 | 104.28 | 1.024 |
| 0.29821 | 1.00576 | 29822 | 100.00 | 1.044 |
| 0.39769 | 1.00960 | 38460 | 96.71 | 1.045 |
| 0.45787 | 1.01192 | 43479 | 94.96 | 1.055 |
| 0.57945 | 1.01662 | 53234 | 91.87 | 1.066 |
| 0.70889 | 1.02154 | 62894 | 88.86 | 1.081 |
| 0.81351 | 1.02566 | 70605 | 86.79 | 1.094 |
| 0.90862 | 1.02929 | 77198 | 84.96 | 1.106 |
| 1.0010 | 1.03287 | 83338 | 83.26 | 1.117 |

DISCUSSION OF THE RESULTS

# DISCUSSION OF THE RESULTS

## 1. Estimation of the Possible Error

Allowing for the same error in density determinations as in calibration, the mean deviation of the densities from their true values should be 0.004%. Data for ammonium nitrate solutions for the equations (obtained by least mean square calculations)

$$d^{25} = 0.997091 + 0.0040552 \ P$$

and

$$d^{35} = 0.994077 + 0.0039351 \ P,$$

with a mean deviation of 0.002% at 25°C. and 0.0035% at 35°C. P is the weight percent of ammonium nitrate in the solution. Deviations are random, indicating that the introduction of a term in $P^2$ is not necessary. The densities for P = 0 agree with those of water within 0.0018%. As pointed out earlier, weight percent concentrations are known to at least 0.01%. The molar concentration is then known to at least 0.015%.

The accuracy of the specific conductance determinations depends on the cell constants, which are known to 0.02%, and the resistances, known to 0.01%.

Equivalent conductances may then be expected to be within 0.05% of their true values, making some allowance for the possibility that several errors may operate in the same direction.

(33)

## 2. Comparison with Previous Work

The least mean square equation for the densities of ammonium nitrate solutions at $25^\circ$C. is

$$d^{25} = 0.99710 + 0.032364\ c - 0.00079\ c^2 ,$$

within 0.002% for $0 < c < 1$ mole per liter. Gucker[18] gives the equation

$$d^{25} = 0.997077 + 0.032628\ c - 0.000963\ c^{3/2}$$
$$- 0.0000473\ c^2 .$$

For $0 < c < 1$ these equations do not differ by more than 0.002% in $d^{25}$. The differences in the $35^\circ$C. data for ammonium nitrate solutions from the data of Campbell and Bock[16] and Campbell, Gray, and Kartzmark[19] are no greater than 0.01%, except in the case of Bock's 0.023 molar solution, which differs by 0.03%, and Gray's 1 molar solution, which differs by 0.14%.

Equivalent conductances for ammonium nitrate solutions at $35^\circ$C. were compared with the results of Campbell and Bock[16] by means of a plot of the difference between experimental conductance and that calculated from the Fuoss-Onsager equation, against concentration. In the range checked, 0.01 molar to 0.07 molar, the present results are consistently 0.08 mho, or 0.05% higher than those of Campbell and Bock. This is not unusual, however, when one remembers that a difference of 0.10% would still be within the experimental error. The fact

that one set of results differs consistently from the other may be attributed to a calibration difference, such as might occur in a cell constant determination.

Conductances in the range 0.01 molar to 0.1 molar were fitted to the Shedlovsky extrapolation function[20],

$$\Lambda = \Lambda_c - \frac{(\alpha \Lambda_c + \beta)\sqrt{c}}{1 - \alpha\sqrt{c}} + Ac$$

where $\alpha = 0.2289$ and $\beta = 60.32$ at $25^\circ$C. and $\alpha = 0.2334$ and $\beta = 75.09$ at $35^\circ$C. The values of $\Lambda_c$ obtained are shown below:

$$\Lambda_c$$

|  |  | Shedlovsky | Literature | Reference |
|---|---|---|---|---|
| Ammonium nitrate | 25°C. | 145.0 | 145.01 | 21 |
|  | 35°C. | 174.2 | 174.21 | 16 |
| Silver nitrate | 25°C. | 133.2 | 133.36 | 21 |
|  | 35°C. | 161.0 | 161.53 | 22 |
| Lithium nitrate | 25°C. | 110.5 | 110.14 | 21 |
|  | 35°C. | 133.7 | 133.48 | 21 |

In view of the relatively high concentrations to which the extrapolation function was applied, and in view of the effect of association of most nitrates on conductance, agreement may be considered as good.

The viscosity results agree with those of Campbell, Gray, and Kartzmark[19] and of Campbell, Debus, and Kartzmark[23] within 0.2%.

## 3. Self-consistency of Equivalent Conductances

Plots of the $\overset{o}{a}$ values necessary for agreement of experimental conductances with those calculated by one of the conductance equations against a convenient function of concentration are a rigid test of the self-consistency of experimental data. Figure 1 shows such a plot for ammonium nitrate solutions at $25^{o}$C., using the Falkenhagen-Leist equation. That none of the points deviates from the average line by more than the experimental error, shown in Figure 2, is evidence that the conductances are self-consistent within 0.05%.

## 4. Description of the Calculations with the Experimental Results

The Falkenhagen-Leist and Robinson-Stokes equations contain but one parameter, $\overset{o}{a}$, the distance of closest approach between ions. This parameter is chosen to give good agreement between experimental and calculated equivalent conductances in dilute solutions. The calculations in this work force $\overset{o}{a}$ to absorb all imperfections of the conductance equations.

The data from which the figures were drawn appear in an appendix. In the figures, the size of the circles is not indicative of the experimental error.

## (i) Ammonium Nitrate and the Falkenhagen-Leist Equation

Figure 1 shows how $\overset{o}{a}$, calculated by the Falkenhagen-Leist equation (17), varies with concentration. The effect of the

viscosity correction, equation (22), is also shown. Above
1 molar the data of Campbell and Kartzmark[24] were used.
Note that:

(a) The $\overset{o}{a}$ values from the viscosity-corrected equation
show greater scatter than those from equation (17).
This is due to the relatively large uncertainty in the
viscosity determinations, 0.2%.

(b) The $\overset{o}{a}$ values from the viscosity-corrected equation
generally lie below those from equation (17). The fact
that ammonium nitrate solutions below about 4 molar
at $25^{o}$C. have viscosities smaller than that of water
explains this.

(c) One would expect $\overset{o}{a}$ values calculated from equations
(17) and (22) to be closer the more dilute the solution.
It will be evident from the discussion below that an accuracy
of 0.005% or better in the viscosity determinations would
be necessary to show that two $\overset{o}{a}$ values do not differ by
more than 0.2 $\overset{o}{A}$ at 0.01 molar.

(d) $\overset{o}{a}$ determinations in dilute solutions show greater
scatter than in concentrated solutions. The reason lies
in the nature of the Falkenhagen-Leist equation. $\overset{o}{a}$ is
used only in the linear and quadratic divisors, $(1 + \kappa a)$
and $(1 + \frac{1}{2}\sqrt{2}\kappa a + \frac{1}{2}\kappa^2 a^2)$, both of which approach unity
with increasing dilution. Consequently the more dilute
the solution, the greater the uncertainty in the
determination of $\overset{o}{a}$ from the conductance.

FIGURE 1
å(F-L) vs. log c
$NH_4NO_3$ at 25°C.

log concentration

Falkenhagen - Leist  å (Å)
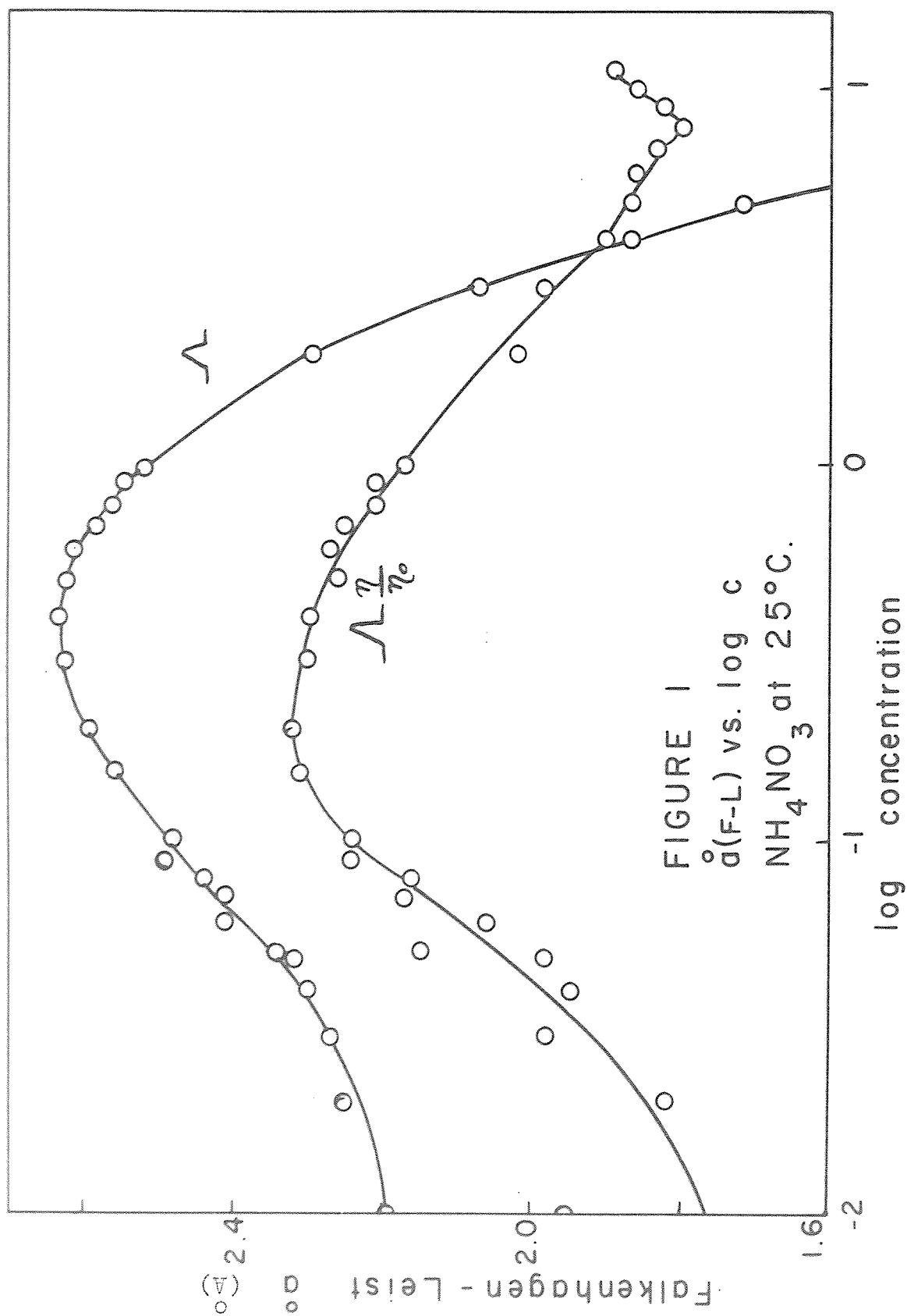
Figure 2 shows how the uncertainty, $\Delta \overset{\circ}{a}$, in the determination of $\overset{\circ}{a}$ varies with concentration. There is no significant difference between plots at $25^{\circ}$ C. and $35^{\circ}$ C. The information given is for ammonium nitrate solutions but also applies, within 20%, to solutions of the two other salts. Points were obtained by calculating the effect of a 0.05% change in conductance on the value of $\overset{\circ}{a}$, at constant concentration. Figure 2 is useful for estimating the accuracy of $\overset{\circ}{a}$ values. For example, if conductance data accurate to 0.01% are available for 0.01 molar solutions, $\overset{\circ}{a}$ may be calculated to the nearest 0.04 $\overset{\circ}{A}$, within 2% of most $\overset{\circ}{a}$ values, and no better. For 0.001 molar solutions $\overset{\circ}{a}$ may be calculated with a possible error of 0.4 $\overset{\circ}{A}$, which is about 25% of an $\overset{\circ}{a}$ value. Data for solutions weaker than 0.001 molar will not contribute to the determination of $\overset{\circ}{a}$. It should be remembered that the bulk of conductance data does not meet this criterion of low experimental error.

By applying Figure 2 to Figure 1, it may be seen that the change in $\overset{\circ}{a}$ for a 0.05% change in conductance is 0.20 $\overset{\circ}{A}$ at 0.01 molar, 0.026 $\overset{\circ}{A}$ at 0.1 molar, and 0.005 $\overset{\circ}{A}$ at 1 molar. If $\overset{\circ}{a}$ were constant the experimentally determined $\overset{\circ}{a}$ values would lie within a funnel-shaped area opening wider and wider in the direction of lower concentration. Since this is not the case, we may expect the Falkenhagen-Leist equation to show appreciable deviations from the experimental results.

FIGURE 2

$\Delta \mathring{d}$ at constant concentration

for $\Delta \Lambda = 0.05\%$ of $\Lambda$,

vs. log c, $NH_4 NO_3$

(1) Falkenhagen - Leist

(2) Robinson - Stokes

(3) Fuoss - Onsager

log concentration

$\Delta \mathring{d}$
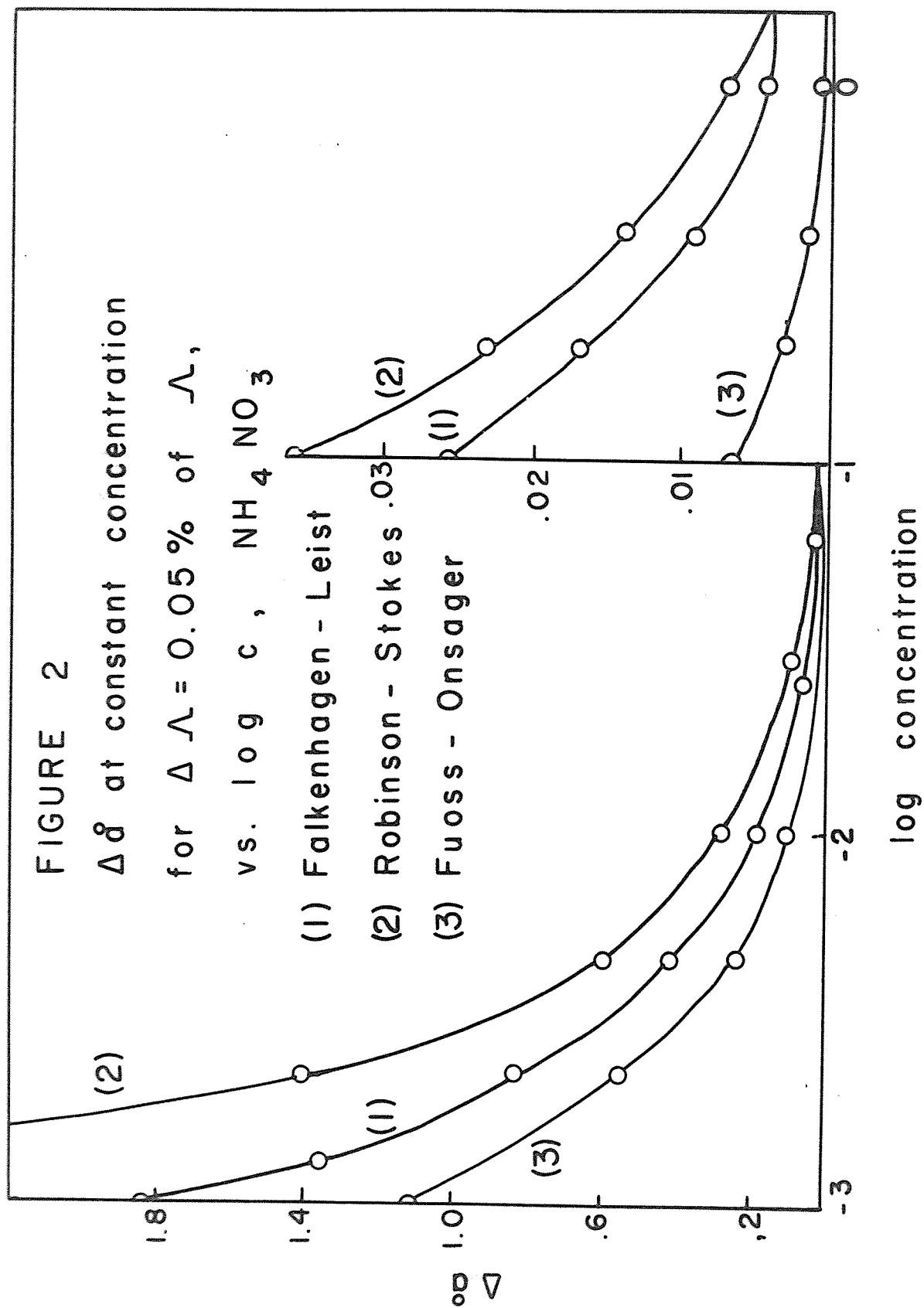
The temperature dependence of $\overset{\circ}{a}$ is examined in Figure 3. Because of the magnitude of the uncertainty in the determination of $\overset{\circ}{a}$, it is not possible to state indisputably whether or not $\overset{\circ}{a}$ varies with temperature for solutions less than 0.1 molar. The fact that $\overset{\circ}{a}$ values at $35^{\circ}$C. are consistently higher than those at $25^{\circ}$C. does, however, suggest that $\overset{\circ}{a}$ varies with temperature. Above 0.1 molar there is no doubt that two different $\overset{\circ}{a}$ values will be necessary to reproduce the experimental results.

The Falkenhagen-Leist equation reproduces the data for ammonium nitrate solutions remarkably well up to 1 molar, in spite of the inconstancy of $\overset{\circ}{a}$ required for a perfect fit. Figure 4 is a plot of the difference between observed and experimental conductances for two arbitrary values of $\overset{\circ}{a}$, 2.560 $\overset{\circ}{A}$ and 2.625 $\overset{\circ}{A}$. Experimental data are reproduced within 0.4 mho up to 1 molar for $\overset{\circ}{a}$ = 2.560 $\overset{\circ}{A}$, but the deviations are systematic and greater than the experimental error. Most disturbing is the failure of the equation to reproduce dilute solution ( < 0.1 molar) data with a physically reasonable $\overset{\circ}{a}$ value. For agreement within 0.1 mho, an $\overset{\circ}{a}$ of about 2.3 $\overset{\circ}{A}$ would be necessary, but the sum of the crystallographic radii of ammonium and nitrate ions is only about 3.5 $\overset{\circ}{A}$.

The effect of replacing the original Debye-Hückel definition of $K$, equation (5), by that of Falkenhagen, Leist, and Kelbg, equation (10), is also illustrated in Figure 4. Below 0.1 molar the effect on the calculated conductance is negligible, but at 1 molar the calculated conductance is increased by 0.2 mho by the use of $K$ from equation (10).

FIGURE 3

å(F-L) vs. log c

$NH_4NO_3$, 25°C. and 35°C.

K, Equation (10)

K, Equation (5)

å = 2.560 Å

FIGURE 4

$\Lambda$(exp.) $- \Lambda$(F-L)

vs. log c

$NH_4NO_3$, 25°C.

å = 2.625 Å

log concentration

Falkenhagen - Leist Deviations
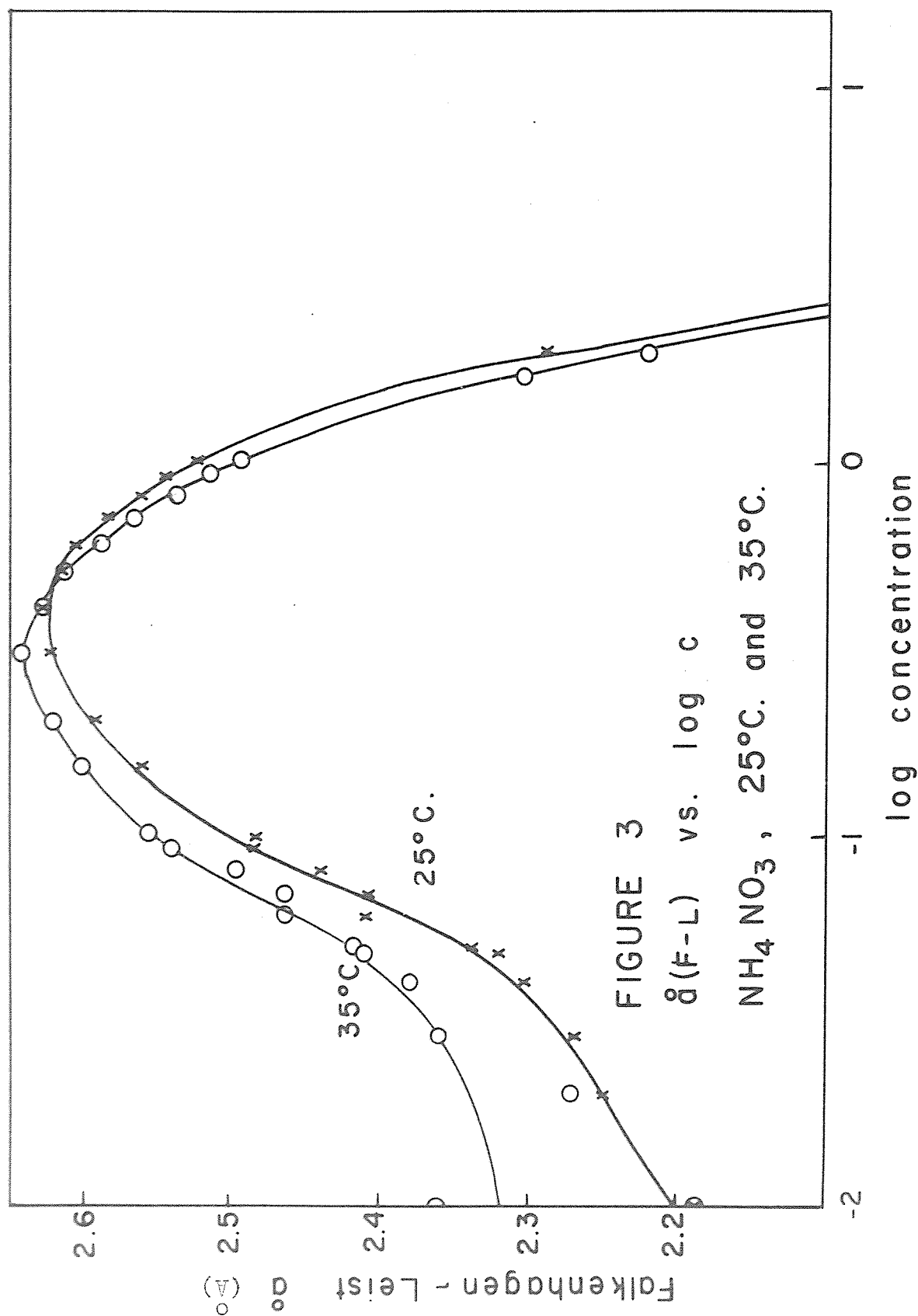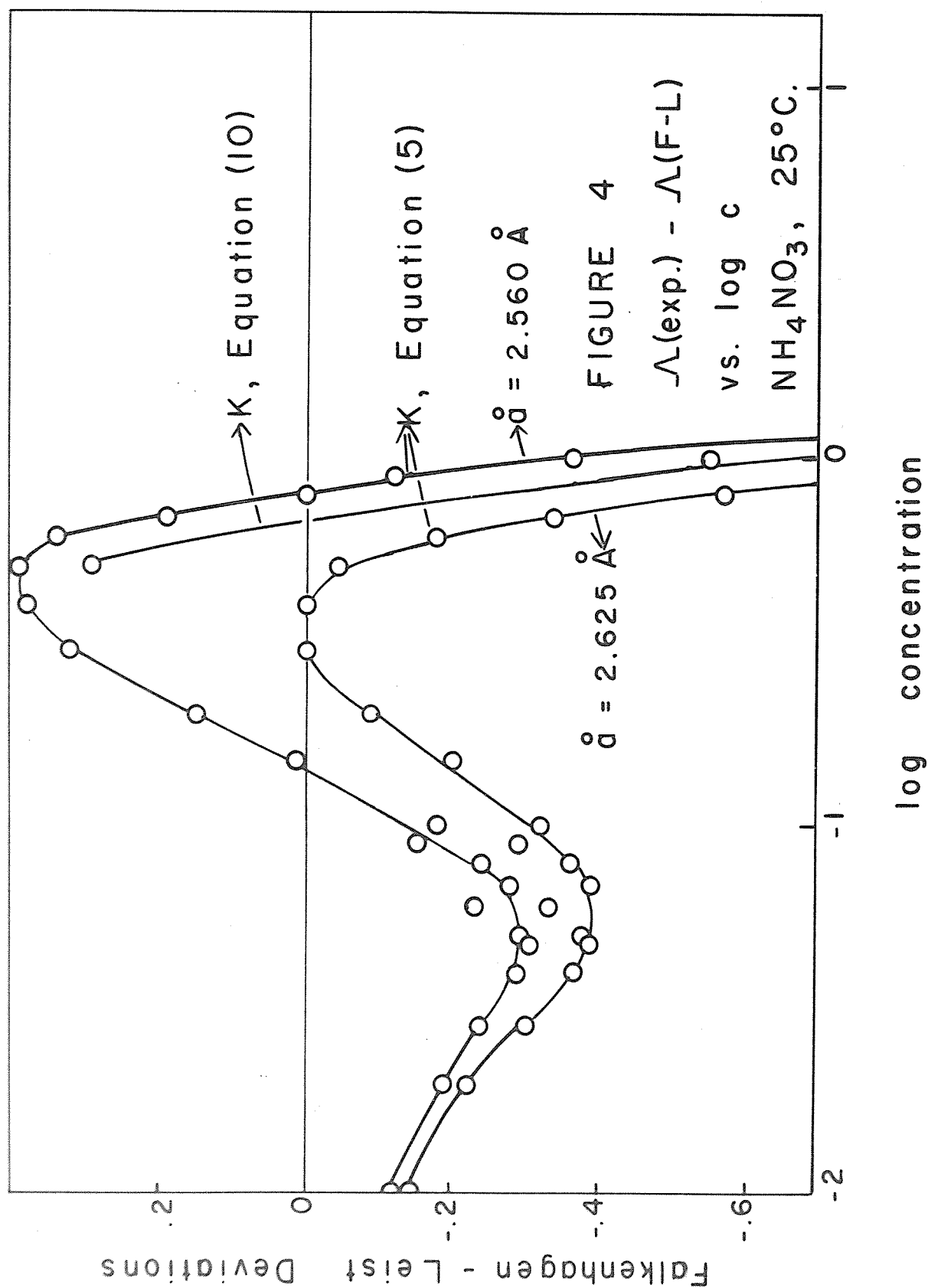
(ii) Ammonium Nitrate and the Robinson-Stokes Equation

The variation of the Robinson-Stokes $\overset{o}{a}$ with concentration,
and the effect on $\overset{o}{a}$ of a first power viscosity correction
are illustrated in Figure 5.  Equations (14) and (21) were
used in the calculations.  Three observations made earlier
in connection with the Falkenhagen-Leist equation (page 37)
may be applied to this plot.  $\overset{o}{a}$ values calculated with the
viscosity-corrected equation show greater scatter than those
with equation (14).  The $\overset{o}{a}$ values calculated by equations
(14) and (21) do not become identical with increasing dilution.
The viscosity-corrected $\overset{o}{a}$ values lie below those from equation (14).
Examination of Figure 2 will show that the uncertainty in $\overset{o}{a}$
for data accurate to 0.05% is 0.3 $\overset{o}{A}$ at 0.01 molar, 0.035 $\overset{o}{A}$
at 0.1 molar, and 0.008 $\overset{o}{A}$ at 1 molar.  The uncertainty in
a Robinson-Stokes $\overset{o}{a}$ is about 50% higher than that in a
Falkenhagen-Leist $\overset{o}{a}$.

For equation (14), $\overset{o}{a}$ increases up to 0.6 molar, has the
constant value 3.37 $\overset{o}{A}$ up to 1 molar, then decreases rapidly.
$\overset{o}{a}$ values from equation (21) reach a maximum at 2.82 $\overset{o}{A}$ (0.7 molar)
and a minimum at 2.53 $\overset{o}{A}$ (5 molar).  A comparison of Figures
1 and 5 shows that Robinson-Stokes $\overset{o}{a}$ values are higher, and
consequently more plausible physically, than Falkenhagen-
Leist $\overset{o}{a}$ values.

Experimental conductances and those calculated with the
Robinson-Stokes equation corrected for viscosity ($\overset{o}{a}$ = 2.75 $\overset{o}{A}$)

FIGURE 5
$\overset{\circ}{a}(R-S)$ vs. log c
$NH_4NO_3$ at 25°C.

FIGURE 6

$(\Lambda \frac{\eta}{\eta_o}) - (\Lambda \frac{\eta}{\eta_o})(R-S)$  vs.  log c

$NH_4NO_3$ at 25°C.

$\overset{o}{a} = 2.75 \text{ Å}$

log concentration

Robinson - Stokes Deviations
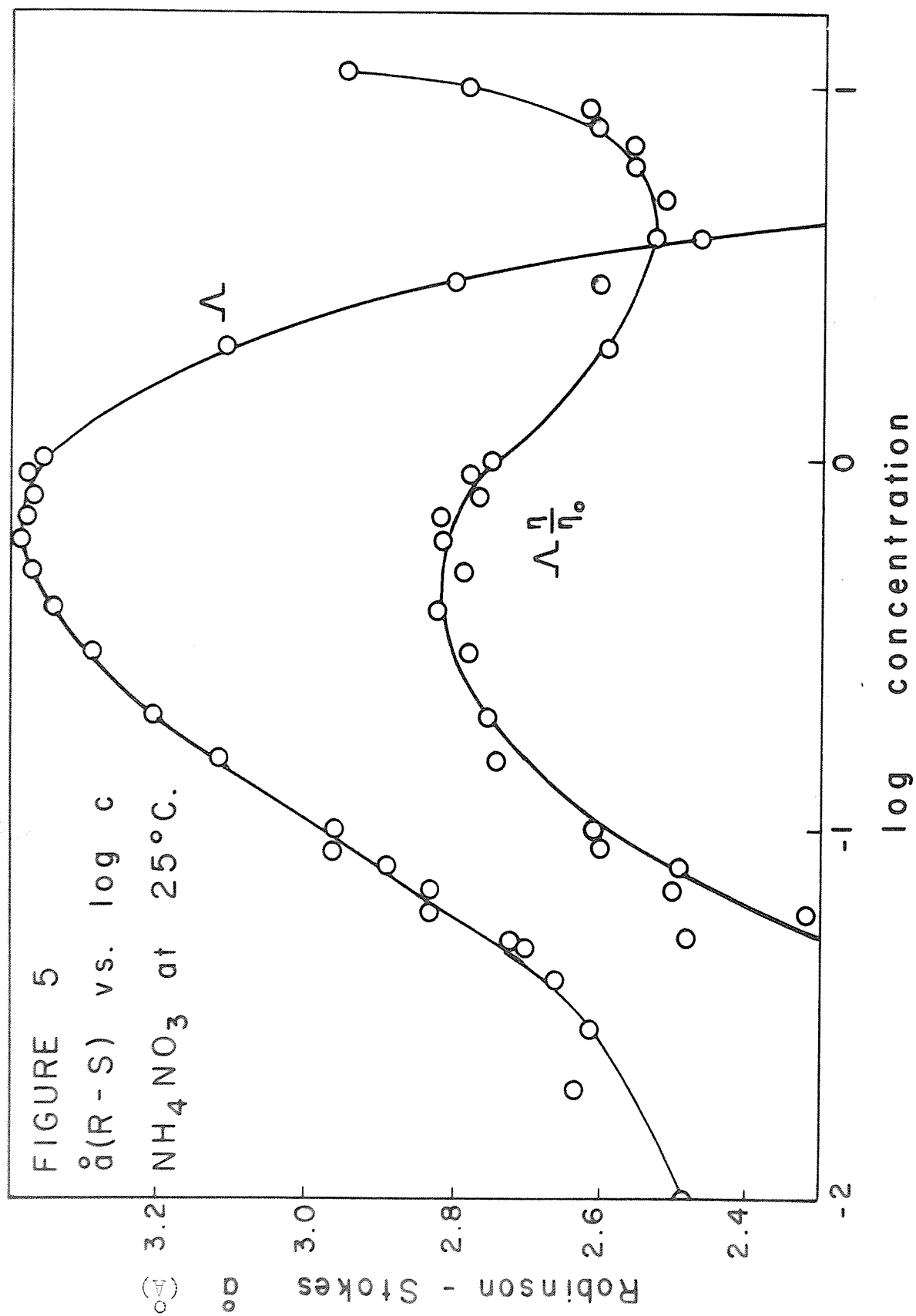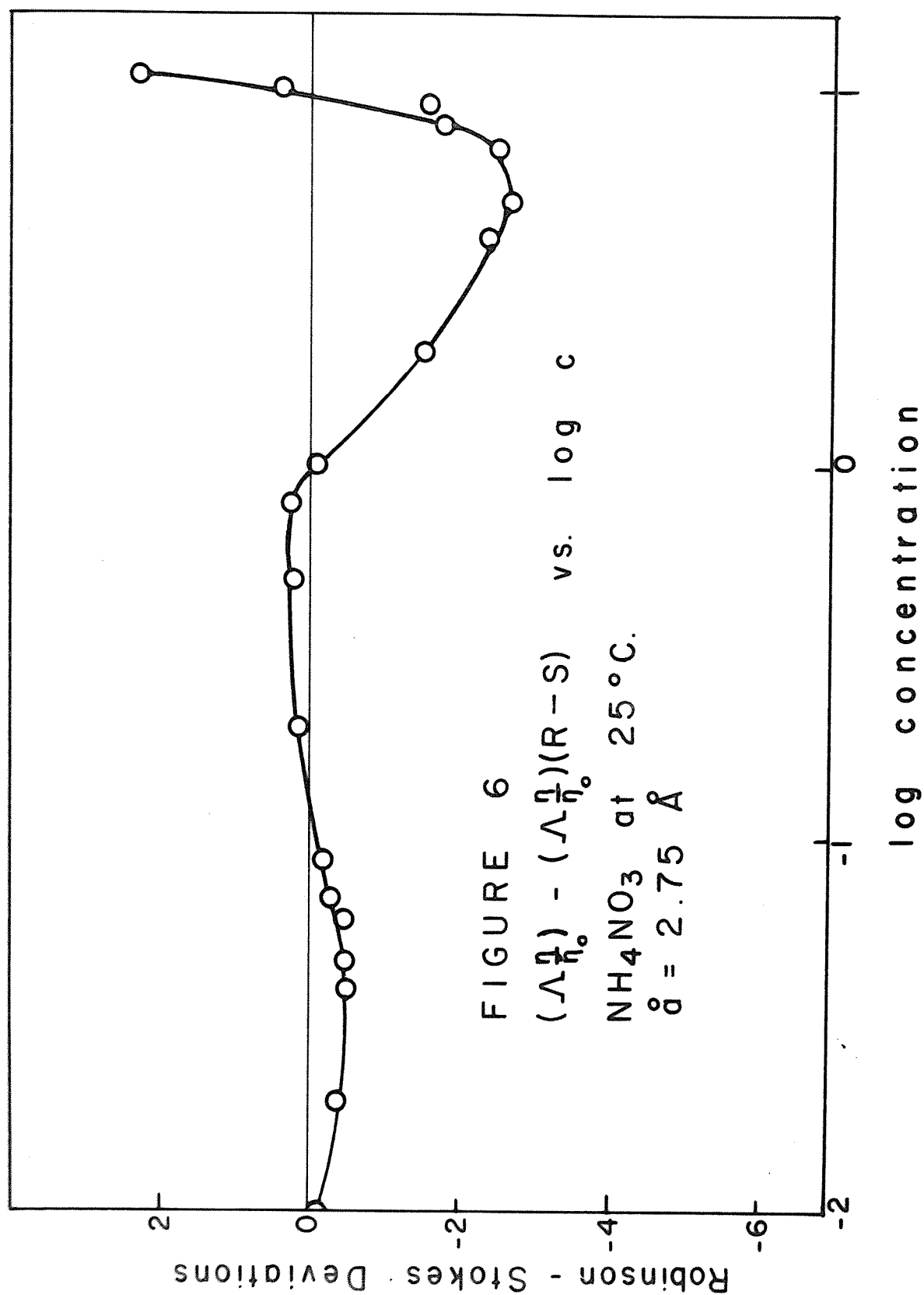
are compared in Figure 6. Up to 1 molar, agreement is within
0.5 mho. Equation (14), with $\overset{o}{a}$ = 3.37 $\overset{o}{A}$ (not illustrated),
reproduces the data equally well below 1 molar.


(iii) Ammonium Nitrate and the Fuoss-Onsager Equation

An attempt was made to fit the 35$^o$C. data of Campbell
and Bock[16] and some of the present data to the Fuoss-Onsager
equation, (18). The procedure, which neglects ion association,
is described on page 11. A plot of the quantity $\Lambda'$ against
concentration is linear below 0.003 molar, with intercept
$\Lambda_o$ = 174.18 $\pm$ 0.08 mhos and slope J = 350. This corresponds
to $\overset{o}{a}$ = 4.6 $\overset{o}{A}$. Data in the range 0.003 molar to 0.04 molar
also lie on a straight line but the intercept is 174.5 mhos
and the slope 180, corresponding to $\overset{o}{a}$ = 2.2 $\overset{o}{A}$. The failure
of this treatment no doubt lies in the fact that ammonium and
nitrate ions form ion pairs; consequently the simpler Fuoss-
Onsager equation is not applicable.


(iv) Silver Nitrate and the Falkenhagen-Leist Equation

The Falkenhagen-Leist $\overset{o}{a}$ is plotted against log concentration
in Figure 7. As with ammonium nitrate, results from the
viscosity-corrected equation show considerable scatter because
of the uncertainty in viscosity determination, and dilute
solution $\overset{o}{a}$ values are less certain than calculations in
concentrated solutions. A recent review by Stern and Amis[25]

FIGURE 7

å(F-L) vs. log c

AgNO₃ at 25° C.
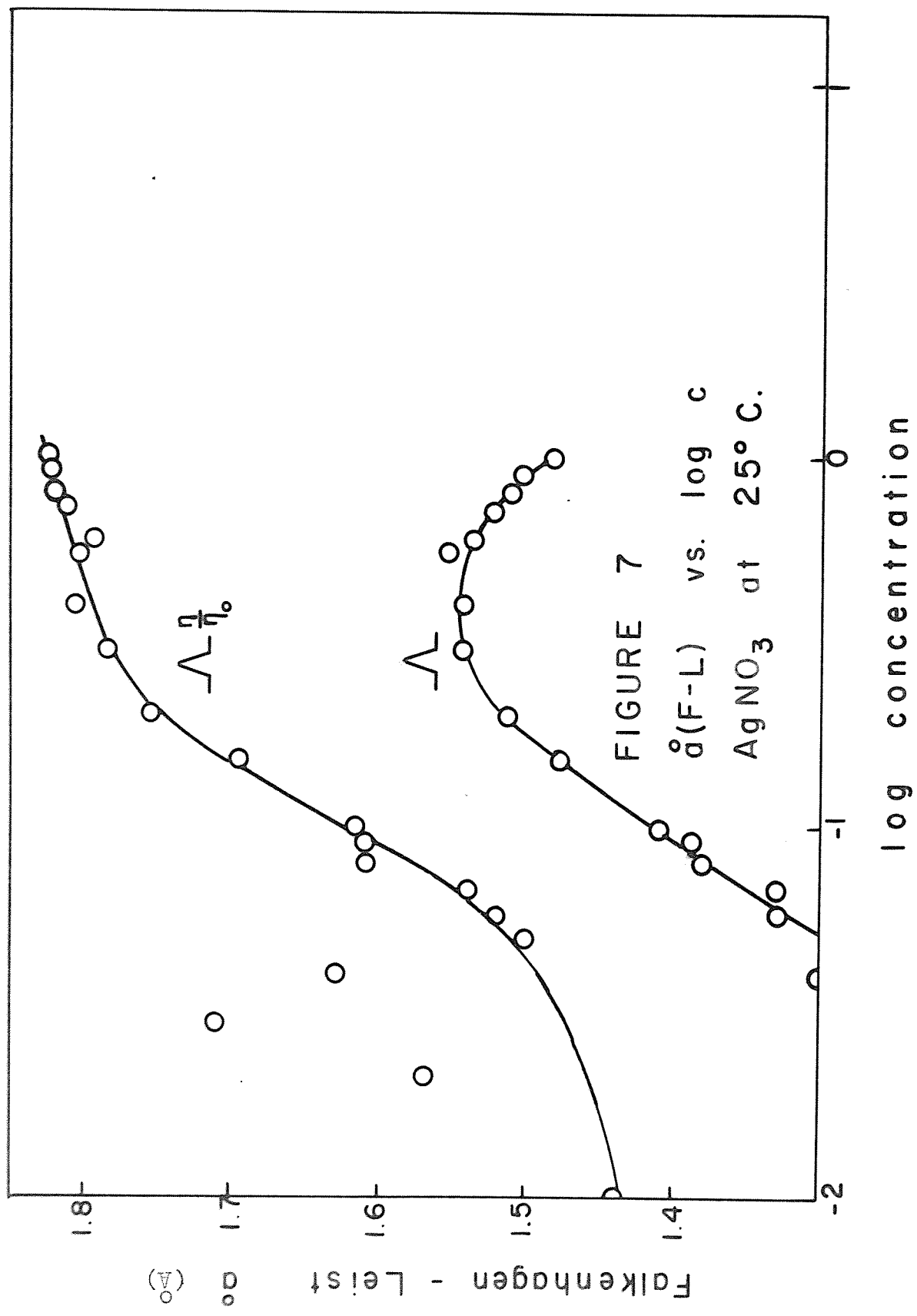
gives the following radii, determined from ionic constituent mobilities: $Ag^+ = 1.13 \overset{o}{A}$, $NO_3^- = 2.25 \overset{o}{A}$. The sum of the ionic radii obtained in these calculations is always less than $1.9 \overset{o}{A}$, no doubt because ion association has been ignored.

The usefulness of equations (17) and (22) for reproducing experimental data is examined in Figure 8. Either equation will give, at concentrations below 1 molar, a conductance within 0.5 mho of the experimental value if $\overset{o}{a}$ is chosen properly.

(v) Silver Nitrate and the Robinson-Stokes Equation

Figure 9 shows the variation of the Robinson-Stokes $\overset{o}{a}$ for silver nitrate solutions at $25^oC$. with concentration. The curves are of the same shape as those for the Falkenhagen-Leist equation, but Robinson-Stokes $\overset{o}{a}$ values are higher. Figure 10, a comparison of calculated and experimental conductances, shows that the Robinson-Stokes equation is as satisfactory as the Falkenhagen-Leist equation.

(v) Lithium Nitrate and the Falkenhagen-Leist Equation

The $25^oC$. data are summarized in Figure 11. Stern and Amis[25] give $3.40 \overset{o}{A}$ as the radius of the lithium ion. We expect, therefore, that $\overset{o}{a}$ will be about $5.7 \overset{o}{A}$. All $\overset{o}{a}$ values calculated here are less than $4.2 \overset{o}{A}$. Once more, the discrepancy may be attributed to ion association. Figure 12 presents the deviation of calculated from experimental conductances. The equation fails rather badly above 0.5 molar.

FIGURE 8

F-L Deviations

vs. log c

$AgNO_3$ at 25°C.

$\Lambda \frac{\eta}{\eta_o} - \Lambda \frac{\eta}{\eta_o} (R-S)$

$\overset{\circ}{a} = 1.80 \text{ Å}$

$\Lambda - \Lambda (F-L)$

$\overset{\circ}{a} = 1.51 \text{ Å}$

log concentration

Falkenhagen - Leist Deviations

FIGURE 9

$\overset{\circ}{a}$(R-S) vs. log c

$AgNO_3$ at 25°C.

FIGURE 10

R - S Deviations

vs. log c

$AgNO_3$ at 25°C.

$\Lambda \frac{\eta}{\eta_o} - \Lambda \frac{\eta}{\eta_o}(R-S)$

$a = 2.00$ Å

$\Lambda - \Lambda (R-S)$

$a = 1.54$ Å

log concentration

Robinson - Stokes Deviations

FIGURE II
$\mathring{a}$(F-L) vs. log c
$LiNO_3$ at 25° C.

FIGURE 12

F-L Deviations

vs. log c

$LiNO_3$ at 25°C.

$\Lambda - \Lambda (F-L)$
$\overset{\circ}{a} = 3.00 \overset{\circ}{A}$

$\Lambda - \Lambda \frac{\eta}{\eta_o} (F-L)$
$\overset{\circ}{a} = 4.00 \overset{\circ}{A}$

Falkenhagen - Leist Deviations

SUMMARY AND CONCLUSIONS

## SUMMARY AND CONCLUSIONS

Equivalent conductances, densities, and viscosities of aqueous solutions of ammonium nitrate, silver nitrate, and lithium nitrate have been determined at $25^{O}$C. and $35^{O}$C. at concentrations in the range 0.01 molar to 1.0 molar.

Conductance data for solutions weaker than 0.005 molar are of little value for determining the distance of closest approach for an electrolyte in solution.

Ammonium nitrate data up to 1 molar may be reproduced within 0.4 mho by the Falkenhagen-Leist equation if $\overset{O}{a}$ is taken as 2.56 $\overset{O}{A}$, or within 0.5 mho by the Robinson-Stokes equation with viscosity correction, using $\overset{O}{a}$ = 2.75 $\overset{O}{A}$. Silver nitrate data up to 1 molar may be reproduced within 0.4 mho by the Falkenhagen-Leist equation using $\overset{O}{a}$ = 1.51 $\overset{O}{A}$. The same accuracy is obtainable with the Robinson-Stokes equation and $\overset{O}{a}$ = 1.54 $\overset{O}{A}$. Lithium nitrate data up to 0.5 molar may be reproduced within 0.3 mho by the Falkenhagen-Leist equation with viscosity correction using $\overset{O}{a}$ = 4.00 $\overset{O}{A}$.

These distances of closest approach are smaller than we expect, but they increase in the same order as the sizes of the cations: $Ag^{+} > NH_{4}^{+} > Li^{+}$.

APPENDICES

# TABLE OF SYMBOLS

| | |
|---|---|
| $a$, $\overset{\circ}{a}$ | Distance of closest approach between ions in solution, in cm. and $\overset{\circ}{A}$, respectively |
| $A$ | Empirical constant |
| $b$ | Fuoss-Onsager constant, page 10 |
| $B_1$, $B_2$, $B_3$, | Theoretical constants, pages 8 and 9 |
| $c$ | Concentration in moles per liter |
| $D_o$ | Dielectric constant of a pure solvent |
| $E$ | Fuoss-Onsager constant, page 10 |
| $f$ | Mean ionic activity coefficient of an electrolyte; see Fuoss-Onsager equation, page 12 |
| $F$ | Value of the Faraday, coulombs |
| $J$ | Fuoss-Onsager constant, page 10 |
| $k$ | Boltzmann's constant in ergs per degree |
| $K_a$ | Association constant for ion pair formation |
| $L$ | Specific conductance in mhos per cm. |
| $n$ | Concentration in ions per unit volume |
| $N$ | Avogadro's number in molecules per gram mole |
| $N_1$, $N_2$ | Reciprocal of the volume of ions 1 and 2 |
| $S$ | Fuoss-Onsager constant, page 10 |
| $T$ | Temperature in degrees absolute |
| $V$ | Volume in ml. |

$\alpha, \beta$      Debye-Hückel constants, page 5

$\gamma$      Activity coefficient of an electrolyte in solution, Debye-Hückel equation, page 4

$\gamma_o$      Degree of dissociation of an electrolyte in solution, Fuoss-Onsager equation, page 12

$\epsilon$      Charge on the electron, e.s.u.

$\kappa$      Reciprocal of the "radius" of the ionic atmosphere

$\Lambda, \Lambda_o$      Equivalent conductance and limiting equivalent conductance in mhos

$\eta, \eta_o$      Viscosity of solution and pure solvent, poises

$\psi$      Electrical potential around an ion

$\rho$      Charge density around an ion

$\sigma_1, \sigma_2$      Fuoss-Onsager constants, page 11

## VALUES OF PHYSICAL CONSTANTS

| | |
|---|---|
| Faraday, coulombs/equivalent | $9.6493 \times 10^3$ |
| Charge on the proton, e.s.u. | $4.8022 \times 10^{-10}$ |
| Boltzmann constant, erg/degree | $1.3803 \times 10^{-16}$ |
| Avogadro's number | $6.0238 \times 10^{23}$ |
| pi, $\pi$ | 3.14159 |
| Base of natural logarithms | 2.71828 |
| $Log_e 10$ | 2.30259 |
| Molecular weight, $NH_4NO_3$ | 80.048 |
| $AgNO_3$ | 169.888 |
| $LiNO_3$ | 68.948 |
| $KCl$ | 74.557 |

Constants relevant to water at absolute temperature, degrees,

| | | 298.16 | 308.16 |
|---|---|---|---|
| Density, g/ml. | | 0.997074 | 0.994059 |
| Dielectric constant | | 78.54 | 75.03 |
| Viscosity, poises | | $8.910 \times 10^{-3}$ | $7.203 \times 10^{-3}$ |
| $\Lambda_o$, mhos, | $NH_4NO_3$ | 145.01 | 174.21 |
| | $AgNO_3$ | 133.36 | 161.53 |
| | $LiNO_3$ | 110.14 | 133.48 |
| $\left(\dfrac{\pi \epsilon^2 N}{125 D_o kT}\right)^{\frac{1}{2}}$ | (page 4) | $3.2866 \times 10^7$ | $3.3076 \times 10^7$ |
| $B_1$ | (page 8) | $1.8407 \times 10^{-8}$ | $2.2768 \times 10^{-8}$ |
| $B_2$ | (page 8) | $2.3783 \times 10^{-8}$ | $2.4087 \times 10^{-8}$ |
| $B_3$ | (page 9) | $1.8381 \times 10^{-6}$ | $2.2737 \times 10^{-6}$ |

# DATA PERTINENT TO THE FIGURES

## 1. <u>Falkenhagen-Leist å values, $NH_4NO_3$, $25^{\circ}C$. and $35^{\circ}C$.,</u>

### <u>Figures 1 and 3.</u>

(c is in moles per liter, $\kappa$ in $cm.^{-1}$, $\overset{o}{a}$ in cm.)

| c | $\kappa_{25} \times 10^{-6}$ | $\overset{o}{a}_{25}$ | $\Lambda_{25}$ | $\overset{o}{a}_{\gamma 25}$ | $\kappa_{35} \times 10^{-6}$ | $\overset{o}{a}_{35}$ |
|------|---------|-------|-------|------|---------|-------|
| 0.01 | 3.2691 | 2.19 | 136.4 | 1.95 | 3.2849 | 2.36 |
| 0.02 | 4.6519 | 2.25 | 133.0 | 1.82 | 4.6743 | 2.27 |
| 0.03 | 5.6135 | 2.27 | 131.0 | 1.98 | 5.6411 | 2.36 |
| 0.04 | 6.5706 | 2.30 | 128.9 | 1.95 | 6.6030 | 2.38 |
| 0.048 | 7.1973 | 2.32 | 127.7 | 1.98 | 7.2321 | 2.41 |
| 0.05 | 7.3495 | 2.34 | 127.6 | 2.15 | 7.3849 | 2.42 |
| 0.06 | 8.0502 | 2.41 | 126.1 | 2.06 | 8.0894 | 2.47 |
| 0.07 | 8.6983 | 2.41 | 125.1 | 2.17 | 8.7403 | 2.47 |
| 0.08 | 9.2912 | 2.440 | 124.0 | 2.16 | 9.3360 | 2.500 |
| 0.09 | 9.8582 | 2.485 | 123.2 | 2.24 | 9.9053 | 2.542 |
| 0.10 | 10.396 | 2.482 | 122.3 | 2.24 | 10.443 | 2.557 |
| 0.15 | 12.882 | 2.562 | 118.6 | 2.31 | 12.944 | 2.602 |
| 0.2 | 14.731 | 2.594 | 116.0 | 2.32 | 14.802 | 2.623 |
| 0.3 | 18.070 | 2.624 | 111.8 | 2.30 | 18.156 | 2.642 |
| 0.4 | 20.785 | 2.625 | 108.9 | 2.30 | 20.882 | 2.629 |
| 0.5 | 23.158 | 2.618 | 106.2 | 2.26 | 23.269 | 2.615 |
| 0.6 | 25.396 | 2.605 | 104.3 | 2.27 | 2.5513 | 2.591 |
| 0.7 | 27.493 | 2.584 | 102.4 | 2.25 | 27.620 | 2.568 |

1. (continued)

| c | $K_{25}{}^{\times}10^{-6}$ | $\overset{\circ}{a}_{25}$ | $-\Delta\%_{25}$ | $a_{\gamma 25}$ | $K_{35}{}^{\times}10^{-6}$ | $\overset{\circ}{a}_{35}$ |
|---|---|---|---|---|---|---|
| 0.8 | 29.386 | 2.561 | 100.5 | 2.21 | 29.520 | 2.538 |
| 0.9 | 31.220 | 2.547 | 99.1 | 2.21 | 31.362 | 2.516 |
| 1.0 | 32.862 | 2.523 | 97.6 | 2.17 | 33.006 | 2.495 |
| (The following were calculated from data in references 19 and 24.) | | | | | | |
| 1.0 | 32.932 | 2.527 | 97.3 | 2.15 | 33.248 | 2.47 |
| 1.7 | - | - | - | - | 42.776 | 2.305 |
| 1.9 | - | - | - | - | 45.427 | 2.22 |
| 2.0 | 46.400 | 2.290 | 87.54 | 2.016 | - | - |
| 3.0 | 56.756 | 2.072 | 82.34 | 1.976 | - | - |
| 4.0 | 65.897 | 1.873 | 77.47 | 1.900 | - | - |
| 5.0 | 73.594 | 1.716 | 74.27 | 1.865 | - | - |
| 6.0 | 80.745 | 1.575 | 72.21 | 1.856 | - | - |
| 7.0 | 87.049 | - | 70.00 | 1.830 | - | - |
| 8.0 | 93.024 | - | 68.79 | 1.799 | - | - |
| 9.0 | 98.835 | - | 67.26 | 1.816 | - | - |
| 10.0 | 103.952 | - | 67.83 | 1.858 | - | - |
| 11.3 | 110.394 | - | 67.9 | 1.888 | - | - |

2. <u>Falkenhagen-Leist Deviations, $NH_4NO_3$, $25°C$., $\overset{\circ}{a} = 2.625$ Å</u>

<u>and $\overset{\circ}{a} = 2.560$ Å, Figure 4.</u>

2. (continued)

| c | $a = 2.625$ Å | | $a = 2.560$ Å | |
| | Calc. Cond. | Deviation | Calc. Cond. | Deviation |
|---|---|---|---|---|
| 0.01 | 136.61 | − 0.14 | 136.59 | − 0.12 |
| 0.02 | 133.54 | − 0.22 | 133.51 | − 0.19 |
| 0.03 | 131.56 | − 0.30 | 131.50 | − 0.24 |
| 0.04 | 129.69 | − 0.36 | 129.62 | − 0.29 |
| 0.048 | 128.52 | − 0.39 | 128.44 | − 0.31 |
| 0.05 | 128.24 | − 0.38 | 128.15 | − 0.29 |
| 0.06 | 126.99 | − 0.33 | 126.89 | − 0.23 |
| 0.07 | 125.89 | − 0.39 | 125.78 | − 0.28 |
| 0.08 | 124.90 | − 0.36 | 124.78 | − 0.24 |
| 0.09 | 123.99 | − 0.29 | 123.85 | − 0.15 |
| 0.10 | 123.15 | − 0.32 | 123.01 | − 0.18 |
| 0.15 | 119.59 | − 0.20 | 119.38 | + 0.01 |
| 0.2 | 117.19 | − 0.09 | 116.95 | + 0.15 |
| 0.3 | 113.46 | 0.00 | 113.14 | + 0.32 |
| 0.4 | 110.83 | 0.00 | 110.45 | + 0.38 |
| 0.5 | 108.78 | − 0.04 | 108.35 | + 0.39 |
| 0.6 | 107.08 | − 0.18 | 106.56 | + 0.34 |
| 0.7 | 105.56 | − 0.33 | 105.04 | + 0.19 |
| 0.8 | 104.34 | − 0.57 | 103.77 | 0.00 |
| 0.9 | 103.23 | − 0.72 | 102.63 | − 0.12 |
| 1.0 | 102.30 | − 0.98 | 101.68 | − 0.36 |

3. Robinson-Stokes $\overset{o}{a}$ values, $NH_4NO_3$, $25^\circ C$., Figure 5; Robinson-Stokes Deviations for $\overset{o}{a} = 2.75$ Å (with viscosity correction), Figure 6.

| c | $\overset{o}{a}$ | $\overset{o}{a}_\chi$ | $\overset{o}{a} = 2.75$ Å | |
|---|---|---|---|---|
| | | | Calc. Cond. | Deviation |
| 0.01 | 2.48 | 2.16 | 136.5 | − 0.1 |
| 0.02 | 2.63 | 2.07 | 133.4 | − 0.4 |
| 0.03 | 2.61 | 2.21 | − | − |
| 0.04 | 2.66 | 2.18 | 129.4 | − 0.5 |
| 0.048 | 2.70 | 2.19 | 128.2 | − 0.5 |
| 0.05 | 2.72 | 2.48 | − | − |
| 0.06 | 2.83 | 2.32 | 126.6 | − 0.5 |
| 0.07 | 2.83 | 2.50 | 125.4 | − 0.3 |
| 0.08 | 2.89 | 2.49 | − | − |
| 0.09 | 2.96 | 2.60 | 123.4 | − 0.2 |
| 0.10 | 2.96 | 2.61 | − | − |
| 0.15 | 3.114 | 2.74 | − | − |
| 0.2 | 3.205 | 2.76 | 115.9 | + 0.1 |
| 0.3 | 3.293 | 2.79 | − | − |
| 0.4 | 3.340 | 2.82 | − | − |
| 0.5 | 3.368 | 2.78 | 106.1 | + 0.1 |
| 0.6 | 3.384 | 2.82 | − | − |
| 0.7 | 3.379 | 2.82 | − | − |
| 0.8 | 3.366 | 2.76 | 100.4 | + 0.1 |
| 0.9 | 3.375 | 2.78 | − | − |
| 1.0 | 3.357 | 2.75 | 97.7 | − 0.1 |

3. (continued)

| c | $\overset{o}{a}$ | $\overset{o}{a}_\eta$ | $\overset{o}{a} = 2.75 \overset{o}{A}$ | | |
|---|---|---|---|---|---|
| | | | Calc. Cond. | Deviation | |

(The following were calculated from data in reference 24).

| c | $\overset{o}{a}$ | $\overset{o}{a}_\eta$ | Calc. Cond. | Deviation |
|---|---|---|---|---|
| 1.0 | 3.366 | 2.70 | 89.0 | - 1.5 |
| 2.0 | 3.107 | 2.591 | 89.0 | - 1.5 |
| 3.0 | 2.798 | 2.606 | 83.8 | - 1.5 |
| 4.0 | 2.474 | 2.532 | 79.9 | - 2.4 |
| 5.0 | 2.205 | 2.518 | 77.0 | - 2.7 |
| 6.0 | 1.953 | 2.559 | 73.5 | - 1.3 |
| 7.0 | - | 2.555 | 72.5 | - 2.5 |
| 8.0 | - | 2.607 | 70.6 | - 1.8 |
| 9.0 | - | 2.620 | 68.9 | - 1.6 |
| 10.0 | - | 2.785 | 67.4 | + 0.4 |
| 11.3 | - | 2.95 | 65.6 | + 2.3 |

4. <u>Falkenhagen-Leist $\overset{o}{a}$ values, $AgNO_3$, $25^{o}C$., Figure 7;</u>

<u>Falkenhagen-Leist Deviations for $\overset{o}{a} = 1.51 \overset{o}{A}$ (no correction)</u>

<u>and $\overset{o}{a} = 1.80 \overset{o}{A}$ (with viscosity correction), Figure 8.</u>

| c | $K \times 10^{-6}$ | $\overset{o}{a}$ | $\Lambda \mathcal{Y}_{\eta_o}$ | $\overset{o}{a}_\eta$ | Deviations $\overset{o}{a} = 1.51, 1.80$ | |
|---|---|---|---|---|---|---|
| 0.01 | 3.3122 | 1.7 | 124.7 | 1.44 | + 0.65 | - 0.1 |
| 0.02 | 4.5769 | 1.1 | 121.7 | 1.57 | - 0.26 | - 0.2 |
| 0.03 | 5.6411 | 1.19 | 119.4 | 1.71 | - 0.30 | - 0.3 |
| 0.04 | 6.5729 | 1.30 | 117.3 | 1.63 | - 0.25 | - 0.3 |

4. (continued)

| $c$ | $K \times 10^{-6}$ | $\overset{\circ}{a}$ | $-\Delta\gamma/\gamma_0$ | $\overset{\circ}{a}_x$ | Deviations $\overset{\circ}{a} = 1.51,$ | 1.80 |
|------|---------|-------|-------|-------|--------|-------|
| 0.05 | 7.3239  | 1.29  | 115.5 | 1.50  | - 0.33 | - 0.5 |
| 0.06 | 7.9365  | 1.33  | 114.3 | 1.52  | - 0.30 | - 0.5 |
| 0.07 | 8.5919  | 1.33  | 113.0 | 1.54  | - 0.36 | - 0.5 |
| 0.08 | 9.2968  | 1.38  | 111.7 | 1.61  | - 0.31 | - 0.5 |
| 0.09 | 9.8575  | 1.39  | 110.6 | 1.61  | - 0.30 | - 0.5 |
| 0.10 | 10.4258 | 1.41  | 109.6 | 1.63  | - 0.26 | - 0.5 |
| 0.15 | 12.693  | 1.478 | 105.8 | 1.70  | - 0.12 | - 0.4 |
| 0.2  | 14.623  | 1.514 | 102.9 | 1.76  | + 0.02 | - 0.1 |
| 0.3  | 18.001  | 1.545 | 98.11 | 1.79  | + 0.23 | - 0.1 |
| 0.4  | 20.780  | 1.546 | 94.68 | 1.81  | + 0.28 | + 0.1 |
| 0.55 | 24.434  | 1.555 | 90.42 | 1.803 | + 0.48 | 0.0   |
| 0.6  | 25.357  | 1.538 | 89.36 | 1.795 | + 0.30 | - 0.1 |
| 0.7  | 27.484  | 1.526 | 87.36 | 1.811 | + 0.18 | + 0.1 |
| 0.8  | 29.241  | 1.514 | 85.82 | 1.823 | + 0.05 | + 0.3 |
| 0.9  | 31.094  | 1.504 | 84.20 | 1.825 | - 0.08 | + 0.3 |
| 1.0  | 32.881  | 1.486 | 82.71 | 1.826 | - 0.36 | + 0.3 |

5. <u>Robinson-Stokes $\overset{\circ}{a}$ values, AgNO$_3$, 25°C., Figure 9;</u>
   <u>Robinson-Stokes Deviations for $\overset{\circ}{a}$ = 1.54 Å (no correction)</u>
   <u>and $\overset{\circ}{a}$ = 2.00 Å (with viscosity correction), Figure 10.</u>

5. (continued)

| c | $\overset{o}{a}$ | $\overset{o}{a}_{\varkappa}$ | Deviations $\overset{o}{a} = 1.54,$ | 2.00 |
|---|---|---|---|---|
| 0.01 | 1.8 | 1.5 | + 0.07 | - 0.1 |
| 0.02 | - | 1.62 | - | - 0.2 |
| 0.03 | 1.03 | 1.71 | - 0.36 | - 0.2 |
| 0.04 | 1.18 | 1.62 | - 0.31 | - 0.3 |
| 0.05 | 1.18 | 1.47 | - 0.40 | - 0.6 |
| 0.06 | 1.28 | 1.50 | - 0.39 | - 0.8 |
| 0.07 | 1.24 | 1.53 | - 0.43 | - 0.6 |
| 0.08 | 1.32 | 1.63 | - 0.36 | - 0.6 |
| 0.09 | 1.33 | 1.63 | - 0.35 | - 0.7 |
| 0.10 | 1.37 | 1.66 | - 0.33 | - 0.7 |
| 0.15 | 1.466 | 1.77 | - 0.21 | - 0.6 |
| 0.2 | 1.524 | 1.87 | - 0.05 | - 0.4 |
| 0.3 | 1.582 | 1.93 | + 0.19 | - 0.3 |
| 0.4 | 1.595 | 1.98 | + 0.31 | - 0.2 |
| 0.55 | 1.619 | 1.99 | + 0.53 | - 0.1 |
| 0.6 | 1.597 | 1.99 | + 0.40 | - 0.2 |
| 0.7 | 1.586 | 2.02 | + 0.36 | + 0.2 |
| 0.8 | 1.571 | 2.049 | + 0.26 | ± 0.4 |
| 0.9 | 1.563 | 2.063 | + 0.20 | + 0.5 |
| 1.0 | 1.540 | 2.075 | 0.00 | + 0.7 |

6. <u>Falkenhagen-Leist å values, $LiNO_3$, 25°C., Figure 11;</u>

<u>Falkenhagen-Leist Deviations for å = 3.00 Å (no correction)</u>

<u>and å = 4.00 Å (with viscosity correction), Figure 12.</u>

| c | $K \times 10^{-6}$ | å | $\Lambda \eta/\eta_0$ | $å_\eta$ | Deviations å = 3.00, 4.00 | |
|------|--------|-------|--------|------|--------|--------|
| 0.01 | 3.3793 | 3.47 | 102.4 | 3.44 | + 0.13 | − 0.2 |
| 0.02 | 4.7696 | 3.77 | 99.90 | 3.64 | + 0.40 | − 0.2 |
| 0.03 | 5.6711 | 3.19 | 98.51 | 3.85 | + 0.13 | − 0.1 |
| 0.04 | 6.4778 | 3.60 | 97.53 | 4.19 | + 0.48 | + 0.2 |
| 0.05 | 7.4092 | 3.61 | 96.20 | 4.15 | + 0.61 | + 0.1 |
| 0.06 | 7.9938 | 3.53 | 95.37 | 4.10 | + 0.62 | + 0.1 |
| 0.07 | 8.6876 | 3.33 | 94.36 | 3.98 | + 0.44 | 0.0 |
| 0.08 | 9.0745 | 3.39 | 93.86 | 3.96 | + 0.56 | − 0.1 |
| 0.09 | 9.9525 | 3.52 | 93.09 | 4.15 | + 0.83 | + 0.2 |
| 0.10 | 10.4508 | 3.48 | 92.49 | 4.10 | + 0.89 | + 0.2 |
| 0.15 | 12.7203 | 3.40 | 90.25 | 4.10 | + 0.92 | + 0.2 |
| 0.2 | 14.675 | 3.348 | 88.47 | 4.06 | + 0.85 | + 0.2 |
| 0.3 | 17.977 | 3.203 | 86.68 | 4.27 | + 0.76 | + 0.8 |
| 0.4 | 20.760 | 3.091 | 83.90 | 3.90 | + 0.42 | − 0.3 |
| 0.5 | 22.277 | 3.023 | 83.07 | 3.94 | + 0.12 | − 0.3 |
| 0.6 | 25.061 | 2.918 | 81.22 | 3.82 | − 0.49 | − 0.8 |
| 0.7 | 27.720 | 2.799 | 79.71 | 3.71 | − 1.30 | − 1.5 |
| 0.8 | 29.696 | 2.728 | 78.78 | 3.73 | − 2.66 | − |
| 0.9 | 31.385 | 2.665 | 77.96 | 3.69 | − | − |
| 1.0 | 32.942 | 2.600 | 77.59 | 3.73 | − | − |

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