taken as the activity of hydronium ions in the inner ion layer. The latter is the case actually observed.

Acknowledgment.—The author would like to express his indebtedness and his sincere gratitude to the National Research Council for the grant of a Fellowship which made this research possible, and to Professor George Scatchard of M. I. T. for his inspiring guidance, help and encouragement during the prosecution of this problem. He would also like to express his appreciation to Professors Isadore Amdur and Walter Stockmayer of M. I. T., George Kimball of Columbia, and Samuel Glasstone of Boston College for valuable discussions.

Summary

The KGG theory, which accounts for the lack of variation of hydrogen overvoltage with *p*H by means of an "electrically saturated" layer adjacent to the electrode surface in which the concentration of hydronium ions is practically independent of *p*H, has been extended to the case where the solution contains salt as well as acid. If the metallic ions can penetrate into the "saturated" layer and contribute to its electrical charge, they displace hydronium ions from it and cause a rise, or drop, in the overvoltage depending on whether the protons discharged are postulated to come from hydronium ions or from water molecules.

The magnitude of the rise (or drop) can be calculated on the simple assumption that the two species of ions penetrate into the saturated layer with equal freedom (apart from any differences in charge). If there is a restriction to the penetration of metallic ions (*e. g.*, because of their hydration shell), the salt effect may be smaller than predicted.

The hydrogen overvoltage has been measured as a function of current density on a mercury cathode at 25° in solutions of hydrochloric acid with, and without, additions of potassium and calcium chlorides. In the pure acid, the overvoltage is almost independent of *p*H in the range 0 to 3, although the present data do indicate a slight increase in overvoltage with *p*H. With addition of potassium chloride, there is a *rise* in overvoltage of the magnitude predicted theoretically. With addition of calcium chloride, there is also a *rise* in overvoltage, at least at high current densities. At low current densities, the latter solutions show marked hysteresis and depression of the overvoltage below the pure acid values. These results are interpreted to mean that the protons discharged at a hydrogen cathode come from *hydronium ions* and not from *water molecules*. The slight variation of overvoltage with *p*H in pure acids is also consistent with this interpretation.

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[CONTRIBUTION FROM METCALF RESEARCH LABORATORY, BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XXXIX. Conductance of Several Salts in Ammonia at $-34°$ by a Precision Method[1]

BY VINCENT F. HNIZDA[2] AND CHARLES A. KRAUS

I. Introduction

The purpose of the present investigation was: first, to develop a method for measuring the conductance of solutions of salts in liquid ammonia with a precision comparable with that of solutions in water; and, second, to measure the conductance of several salts in liquid ammonia, which measurements might serve as reference standards in evaluating the precision of other methods when such were found necessary or desirable.

The chief sources of error in conductance measurements in liquid ammonia are: (1) uncertainties as to the concentration of solutions measured, particularly at low concentrations; (2) lack of control of solvent purity and uncertainty as to the correction to be applied for solvent conductance; (3) lack of proper temperature control; (4) uncertainties in resistance measurements owing to capacitance effects due to leads.

(1) **Concentration Errors.**—In all measurements hitherto carried out in liquid ammonia, the dilution method has been employed. This method consists essentially in adding a known amount of salt to a known quantity of solvent, withdrawing a known amount of solution and replacing it by a known amount of fresh solvent. This procedure is repeated until the desired low concentration has been reached.

Two methods have been employed for determining the amount of solvent: (a) The volume of the solution is measured in the conductance cell before and after each withdrawal of solution and addition of solvent. This method was employed by Franklin and Kraus[3] in their earliest measurements; a similar method was employed by Monosson and Pleskov[4] in their more recent measurements. (b) The volume of solvent introduced is measured in a special pipet external to the con-

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[1] This paper is based on a portion of a thesis presented by Vincent F. Hnizda in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of Brown University. May, 1935.

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[3] Franklin and Kraus. *Am. Chem. J.*, **43**, 277 (1900).

[4] Monosson and Pleskov, *Z. physik. Chem.*, **156A**, 176 (1933).

ductance cell; the amount of solvent withdrawn as solution and left as solution in the cell at the end of a series is absorbed in water and weighed. The latter method was employed by Kraus[5] in measuring the conductance of alkali metals in liquid ammonia and has subsequently been employed by several investigators in this Laboratory.[6] In the case of highly reactive substances which cannot be handled in air or which must be prepared in the conductance cell itself, this method seems to be the only one available.

When the volume of the solution is measured in the cell, high precision cannot be attained because the area of the exposed surface is relatively large, as much as a square centimeter or more. Another source of error in this method is due to the fact that in the withdrawal of solution, the flow of liquid is shut off at a desired point by closing a stopcock. The liquid in flowing back into the cell from the closed stopcock leaves some solution behind on the surface of the exposed tubes where the solute is deposited when the solvent evaporates. This source of error becomes particularly important if the withdrawal tube and stopcock are so arranged as to leave a pocket in the line, as in the case of the apparatus used by Monosson and Pleskov.[4] The loss of solute due to evaporation of solution in the withdrawal lines is of particular importance because it introduces a cumulative error of unknown magnitude.

In the method, such as that of Kraus,[5] in which the solvent introduced is measured by volume and that withdrawn by weight, an error, due to evaporation in the withdrawal line, is also present. But perhaps more serious is the uncertainty of the amount of ammonia remaining in the cell after withdrawal. Usually, the withdrawal is made through a fine capillary which extends from the withdrawal stopcock to a point such that a desired amount of liquid is left behind when withdrawal is completed. The stopcock is closed when the liquid in the cell reaches the bottom of the capillary and vapor, in place of liquid, begins to come over. Unless the stopcock is closed at the precise moment when all the liquid has passed through the stopcock, a certain amount of vapor comes over, thus concentrating the solution slightly. This method has the advantage that liquid which comes in contact with the stopcock is not returned to the cell.

(2) **Purity of Solvent.**—Ammonia is readily purified by evaporation from a solution of sodium or sodium amide. We have been able to obtain liquid ammonia having a specific conductance of the order of 1×10^{-11} mho. Under ordinary conditions, however, the ammonia that has been used in conductance measurements has had a conductance of the order of 1×10^{-7} mho. This corresponds to a solvent correction of the order of 3% for a solution at a concentration of 1×10^{-5} *N*. While the correction is not large, it is uncertain because the specific conductance of the ammonia actually used cannot be determined except for the first and highest concentration of a series. Previous investigators have measured the specific conductance of samples of solvent and assumed that it remained constant in the course of a series of measurements. It is to be noted that stopcock lubricants are a source of impurity; we have been unable to obtain a specific conductance below 1×10^{-8} mho with solvent that had passed through a stopcock. Possibly, modern lubricants of the silicone type would yield better results.

It may also be pointed out that ammonia evaporated from a stock cylinder usually carries impurities with it as a result of entrainment unless the vapor is passed through a very fine filter.

(3) **Temperature Control.**—Adequate temperature control is not obtained by simply surrounding the conductance cell by a bath of ammonia boiling under atmospheric pressure in a Dewar tube. Monosson and Pleskov[4] overcame this difficulty measurably by stirring the bath with a stream of air and measuring their solutions at −40°. But, even here, the temperature uncertainty was of the order of 0.1°, or more.

(4) **Lead Effects.**—Conductance cells, as ordinarily employed, have been small; leads have been rather closely spaced and they have been immersed in liquid ammonia of uncertain resistance. Such arrangement leads to no serious difficulty with solutions of higher concentration, but, with solutions of low concentration and high resistance, errors are introduced that can be eliminated only by use of a bath liquid of higher specific resistance.

II. Outline of Method

In view of these considerations, it was decided to develop a method in which concentration changes were effected by adding solute to ammonia of known specific conductance. Stopcocks were eliminated from the apparatus and temperature was controlled by means of a sensitive manostat.

The conductance cell had a capacity of about 325 cc. of liquid ammonia. Four lots of salt were sealed in four glass bulbs, the fourth bulb containing 100 mg. of salt, the third 10 to 30 mg.; the salt in both these bulbs was weighed. The salt in the second bulb was approximately one-tenth that in the third and that in the first bulb one-tenth that in the second. When the ammonia in the cell, 320 cc., had reached the proper and constant high resistance, bulb No. 1 (containing the smallest amount of salt) was crushed, the solution was mixed and its conductance measured. Then a portion of the ammonia was evaporated to concentrate the solution, the ammonia being absorbed in weighed absorption tubes containing water. The conductance of the resulting solution was measured and a portion of the solvent was again evaporated. This procedure was repeated nine or ten

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[5] Kraus, THIS JOURNAL, **43**, 749 (1921).

[6] Kraus and Hawes, *ibid.*, **55**, 2776 (1933); Kraus and Kahler, *ibid.*, **55**, 3537 (1933).

times until the solution had reached about one-fifteenth its original volume. The cell was then emptied, the ammonia was absorbed and weighed and any residual ammonia remaining in the system was determined.

The cell was then washed out, ammonia was again collected and the second lightest bulb was crushed and the conductance of the resulting solution measured. Ammonia was again evaporated and conductances were determined as in the preceding series. Thereafter, the cell was again emptied and refilled, the third bulb was crushed and a third series of measurements made. Finally, the fourth bulb was crushed and measurements carried out. Concentrations for the fourth series were computed from the weight of salt and known weights of solvent.

The dilute points of the last series (fourth) overlapped the concentrated points of the third series and, similarly, points of the third series overlapped those of the second, and so on, with the remainder of the series. An interpolation function was set up for the conductance of the fourth series and therefrom the concentration of the more concentrated points of the third series was determined. An interpolation function was then set up for the third series and the concentrations of the second series was determined therefrom. Concentrations for the first series were determined in a similar manner.

By the above described procedure, correction for solvent conductance is automatically eliminated as are also adsorption effects.

III. Experimental

A. **Purification of Solvent.**—Ammonia is best purified by evaporation from a solution of sodium or sodium amide. Unless the rate of evaporation is very slow, particles of solute are carried along in quantity sufficient to lower the specific conductance of the condensate measurably. In order to filter out particles from the vapor, it was passed through a tightly packed, silica cotton plug. The plug was surrounded with a heating coil so that volatile materials could be eliminated by pumping. The ammonia was distilled from a stock cylinder into a special supply cylinder having a capacity of several pounds and containing sodium amide. This cylinder could be refilled without detaching it from the cell system.

Ammonia vapor passing through stopcocks is contaminated and a specific conductance less than 1×10^{-8} could not be obtained with lubricants in use at the time. Accordingly, stopcocks were replaced by metal ball valves.

In preliminary experiments, a special cell with large electrodes was sealed in the ammonia line. Resistances were measured by the D. C. method of Kraus and Fuoss.[7] After thorough washing, ammonia was obtained having a specific conductance as low as 1×10^{-11}.

However, it was found very difficult to wash out the cell to a point where this low conductance could be maintained. This was due to the slow desorption of impurities from the walls of the cell and, especially from the electrodes which had to be platinized to avoid polarization effects. As much as two weeks were required to wash out the cell to a point where the specific conductance remained below 1×10^{-10} for twenty-four hours. When it came to condensing ammonia in the conductance cell, it was found impractical to work with solvent having a specific conductance below 1×10^{-9} mho. At that, it required a week, or more, to wash out the cell to a point where the conductance of the solvent remained constant at this value. The introduction of air into the system when traces of ammonia were present, contaminated the cell irretrievably. In such event, it was necessary to steam out the entire system. After such treatment, a sticking vacuum could be obtained within an hour.

To determine the nature of the impurity present in the solvent, samples of ammonia having a specific conductance of 1×10^{-7} and 2×10^{-8}, respectively, were evaporated from the cell and the conductance was measured as a function of volume. The product of specific conductance and volume was found to be constant in both instances. Evidently, the residual impurity in liquid ammonia behaves like a completely dissociated electrolyte.

It may be pointed out that, according to the method employed for determining the concentrations of the more dilute solutions, the solvent correction is automatically eliminated although, in the present investigation, the conductance of the solvent was at all times negligible, even in the most dilute solutions.

B. **Assembly.**—The conductance Cell I (capacity 350 cc.) and the general assembly are shown in Fig. 1. The cell is surrounded by a bath of ammonia contained in an unsilvered Dewar tube which is provided with a tight fitting top. The tube E connects with the manostat system. Ordinarily, a larger silvered Dewar tube is placed around the unsilvered tube to minimize evaporation due to radiation.

The cell connects with the source of ammonia (not shown) through the silica cotton plug, D, the stepseal, C,[8] and the metal to lead glass seal, B.[9]

Ammonia or solution may be withdrawn from the cell through the capillary tube, L, and the stopcock, N, into the receiver, O. The trap, M, prevents solution or solvent from running back into the cell when the stopcock is closed. This, the only stopcock in the apparatus, is used in withdrawals only.

Solvent may be condensed from the cell into the receiver, S. This may subsequently be evaporated and passed back through the capillary, L, on proper manipulation of the ball valves, R and Q, for the purpose of stirring the solution. Through proper manipulation of the ball valves, ammonia may be evaporated in the cell and absorbed in the evacuated absorption flask, Z, which is detachable at Y, so that it can be weighed. A small opening in the wall of the delivery tube of the absorption flask prevents water from sucking back when absorption is completed and serves to eliminate a stopcock.

The needle valve, V, is connected to the glass system by means of a platinum tube seal, W,[10] which will be described below. To provide mechanical strength for this seal, it is surrounded by a close fitting, strong, glass tube which is cemented to the adjoining members.

When ammonia is evaporated from the cell for absorption, vapor (from a stock cylinder, not shown) is passed through the sintered glass disc, J, in the bottom of the bath; this ammonia condenses and compensates the heat loss due to evaporation from the cell, thus maintaining the bath at approximately constant temperature. This ammonia also compensates for loss from the bath during a series of measurements so that the bath liquid does not have to be replenished. Ammonia vapor also is passed through the disc, J, during measurement in order to stir the bath for the purpose of maintaining constant thermal conditions. In order to force the ammonia to pass through the disc as vapor, it is necessary to provide the tube leading to the disc with a silvered vacuum jacket.

Stopcock T, lubricated with "Apiezon" grease, connects with the mercury vapor pump system (not shown). Stopcock X communicates with an absorption bottle; it is used to absorb discarded ammonia. U is an adjustable mercury trap and manometer.

The cell is closed at the top by means of a ground glass,

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[7] Kraus and Fuoss, This Journal, **55**, 21 (1933).

[8] Keyes and Kraus. U. S. Patent 1,014,757 (Jan. 16, 1912).

[9] Kraus, U. S. Patent 1,046,084 (Dec. 3, 1912).

[10] Kraus. U. S. Patent 1, 093,997 (Apr. 21, 1914).

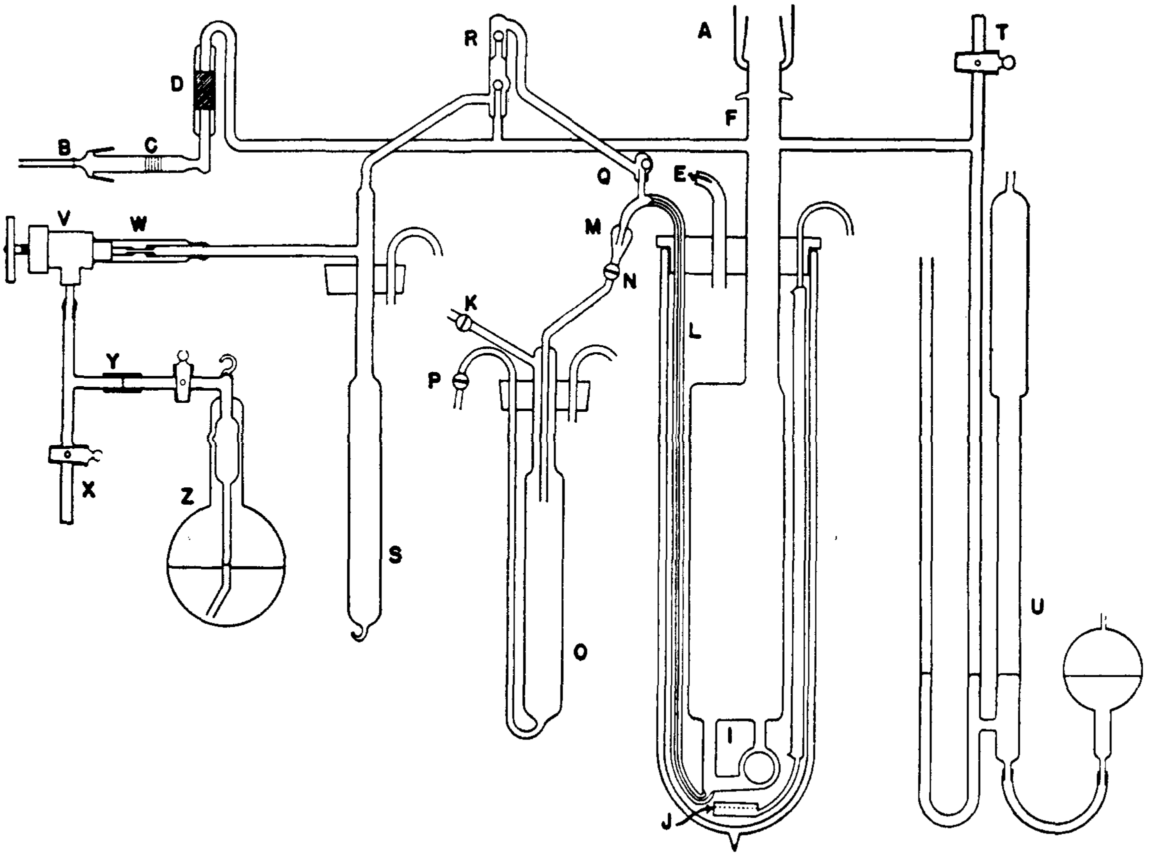

Fig. 1.—Conductance cell assembly.

mercury sealed joint, A, carrying the silver, metal bellows shown in Fig. 3.

Details of cell construction are shown in Fig. 2. The small, spherical electrode chamber, b, in which the electrodes are located, is connected to the main chamber, a, by means of the tubes i and j, g. Ammonia vapor passing up through g from l serves to stir the solution in a and circulate solution through the electrode chamber, b.

The four salt samples are contained in small, fragile bulbs, d, d, which ordinarily float on the surface of the liquid. At a proper level of liquid, the desired bulb can be floated into the fine mesh, platinum gauze basket, c, by gently rotating the bottom of the bath container. The bulb is confined in position in the basket by means of the end of the crusher rod, p, which can be manipulated by means of the flexible metal bellows to which it is clipped at U, Fig. 3. The basket is provided with a bail by means of which it can be fished out of the cell at the end of a series of measurements. It is also provided with a platinum gauze cover. The purpose of the basket is to keep chips of glass from falling into the electrode chamber after the bulb has been crushed.

After a first series of measurements, a second bulb is floated into the basket and crushed, the fragments of the earlier bulb having been left in the basket. This process is repeated until all four bulbs have been used.

The crusher rod, p, is provided with a guide, k, which keeps it properly centered. The guide is provided at a point that lies above the level of the liquid in the bath.

When ammonia is evaporated, a certain amount of solute is left on the crusher rod. A platinum iridium spring wire clip, e, is, therefore, provided which engages the crusher rod closely and a turn of which touches the interior surface of the neck of the cell. On raising the level of the ammonia in the bath to the level of the spring clip, ammonia condenses in the neck, f, and the condensate is guided onto the surface of the crusher rod by the clip. This serves to wash down any solute adhering to the surface of the crusher rod. This device is indispensable.

The bellows is provided with a support, n, n, to prevent it from collapsing when under vacuum. The support is disengaged when the crusher rod is to be manipulated. The ground joint at the bottom of the bellows was constructed of steel.

C. **Platinum Tube Seals.**—In constructing conductance cells earlier in this Laboratory, platinum tubes have been sealed through Pyrex glass according to the method of Kraus.[10] However, owing to the lack of adequate adhesion between Pyrex and platinum, the platinum tube, on continued use, draws away from the glass and the seals become leaky. Accordingly, an improved seal was developed.

It was found that "Corning No. 707" glass, a low melting glass, adheres to platinum very tenaciously. For satisfactory results it is necessary to use platinum tubing of the *highest purity;* a thickness of 0.05 mm. works very satisfactorily. The no. 707 glass cannot be sealed to Pyrex but it may be sealed in very stable fashion to "Corning No. 332" glass (Canary glass) which, in turn, is readily sealed to Pyrex. The procedure for making a seal is as follows: a rod of No. 707 glass is drawn out to about 1 mm. thickness in an air-gas flame. After degassing the platinum, a cylindrical bead of from 1 to 2 mm. thickness and 5 mm., or more, length is laid down on the tube. This is inserted into the end of the lead tube of Canary glass which should be slightly flared where the bead is inserted. The Canary glass tube is then collapsed on the 707 glass bead, being careful that the 707 glass does not run over the end of the Canary glass tube. The Canary tube may then be sealed to Pyrex. In the present instance, the entire electrode chamber was constructed of

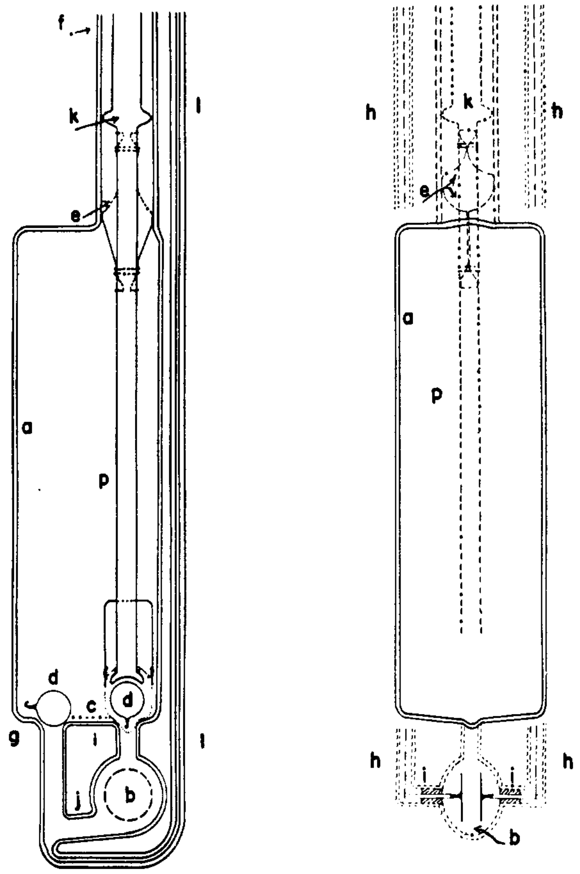

Fig. 2.—Details of cell construction.

Canary glass. Canary glass is not available at this time but Corning "H-R green sealing glass No. 3321" is equally satisfactory. The above described seals are very stable and withstand temperature changes to liquid air temperatures.

D. Manostat.—At the boiling point of liquid ammonia, the vapor pressure change per degree is approximately 38 mm. Satisfactory temperature control may, therefore, be had by equipping the bath with an effective manostat. Such a device is illustrated in Fig. 4. The manostat connects with the bath through E (Fig. 1) and the stopcock B and the tube T (Fig. 4). The control device consists of a column of mercury, L, evacuated at the top through stopcock N, and connecting with a large bulb, H, which is connected with the interior of the bath through stopcock B. The tungsten contacts, G, Q, are connected with a vacuum tube relay system F[11] which operates the control valve E by means of a solenoid. The manostat is connected to an aspirator pump through D. A carboy, C, of five gallon capacity is connected with the system to serve as ballast and thus prevent sudden pressure changes.

Ammonia from the bath, through E (Fig. 1), passes to the pump by this route. In order to control the suction on the bath, an adjustable air inlet valve, K, is provided. This valve and the bypass, M, are so adjusted that the temperature of the bath rises slowly when the control valve, E, is closed and falls slowly when open. This requires a pressure difference of about 2 cm. as registered on the manometer, J. At X, the manometer tube is provided with a ball check valve to prevent mercury from being drawn into the system on sudden change of pressure; the ball floats on the mercury.

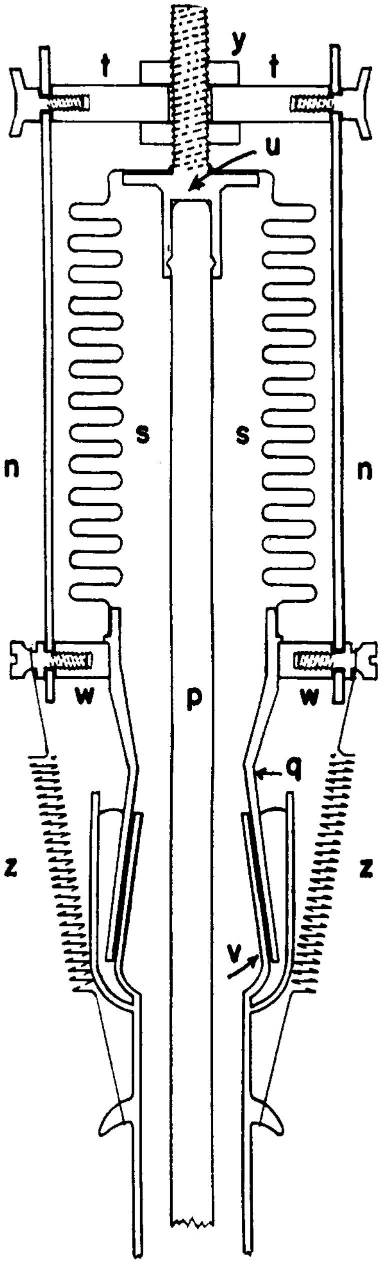

Fig. 3.—Details of metal bellows.

The manostat operates as follows: as the bath warms up and the pressure increases, the mercury makes contact with the contact point, G, closing the circuit through the relay, F, and opening the control valve, E. As the pressure then falls, contact is broken and the control valve closes, allowing the bath to warm up again. It is to be noted that the bath is not boiling freely under the pressure indicated by the manometer, L; a rapid stream of ammonia vapor is being passed through the bath in the form of very fine bubbles that originate in the bottom of the bath at the surface of the fritted glass filter, J, Fig. 1. This stream of vapor stirs the bath and maintains equilibrium in it. The adjustment of the bypass, M, and the air inlet valve, K, depends on the rate of flow of ammonia vapor through the bath.

With proper adjustment of the manostat, the pressure change on the oil manometer, I, which registers the pres-

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[11] We are indebted to Dr. W. W. Hawes for the design and construction of the relay systems.

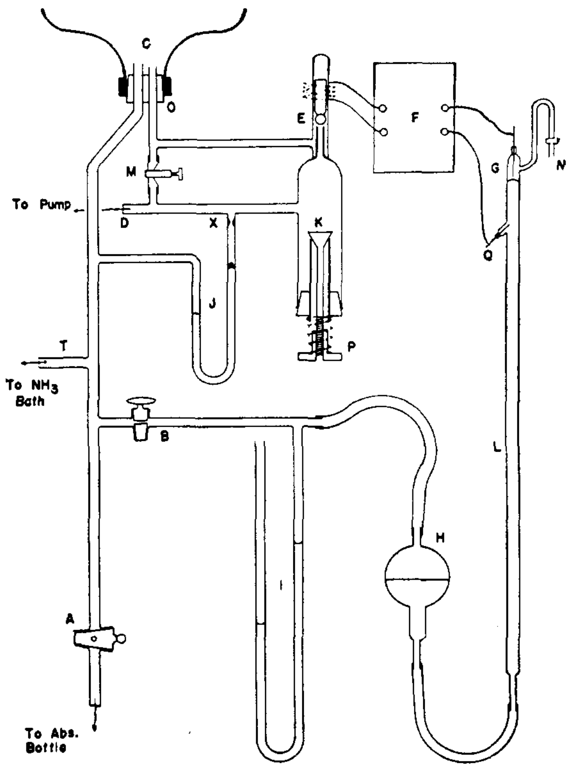

Fig. 4.—Details of manostat connections.

sure difference between the bath and the atmosphere, does not exceed 2 mm. Since the pressure change of liquid ammonia at −34° is 38 mm. per degree, the bath temperature is controlled to better than 0.01°. The vapor pressure of ammonia is a sensitive thermometric agent; the temperature of the solution in the cell may at all times be deduced from its vapor pressure. The vapor pressure of ammonia at −34° is 735.4 mm. and the manostat is so adjusted that the manometer (not shown) which is connected with the cell system registers this pressure. The temperature is readily changed by adjusting the height of the column in L.

E. Miscellaneous

1. Computation of Concentration.—The total ammonia in the system during a series of measurements is absorbed in water and weighed, with the exception of 70 mg., which remains in the system when the last lot is absorbed down to a pressure of from 8 to 10 cm. To compute the concentration, the following data are required: (1) the amount of ammonia in the system at any pressure with the bath at −34°, the external atmosphere at 23° (room temp.) and the bath filled to the normal operating level; (2) the volume of ammonia adhering to the spring clip, e (Fig. 2), and to the interior walls of the cell for any desired level of liquid in the cell; and (3) the amount of ammonia present as vapor with the solution at −34° and the room temperature at 23°.

With the temperature of the bath at −34°, room temperature at 23° and the bath at normal level, the ammonia in the system was determined as a function of pressure by absorbing the ammonia and weighing. By a short extrapolation, the total ammonia in the system at saturation pressure, 735.4 mm., was found to be 544 mg. The amount of liquid held on the spring clip was determined by lowering the level of the bath so that the liquid evaporated off the clip and condensed in the solution; from the conductance change of the solution in the cell, the amount of ammonia condensed was computed. The ammonia held by the spring clip amounted to 36 mg. The ammonia held on the walls as a function of level was determined in the same way; the total ammonia held by clip and walls when 20 cc. of ammonia was present in the cell amounted to 75 mg., or 110 cu.mm. The density of saturated ammonia vapor at −34°[12] is 0.863 mg. per cc.,[8] yielding a vapor correction of 1.266 mg. per gram of liquid.

In computing the concentration of the last and most concentrated solution of a series, the weight of ammonia left in the system at end of absorption, at a pressure of 8 to 10 cm. and an additional 5 mg. for the ammonia trapped in the tube between the needle valve V (Fig. 1) and the stopcock of the absorption flask, Z, totalling about 70 mg., are added to the weight of ammonia absorbed in the flask; this is the total amount of ammonia present in the system as liquid and vapor when the conductance of the solution was measured. From the total weight of ammonia is subtracted 544 mg. (the weight of ammonia in the system when filled with saturated vapor) less the weight of a volume of ammonia vapor equal to the volume of solution. If the volume of the final solution was 20 cc., for example, the vapor correction would amount to 17.3 mg. which, subtracted from 544, leaves 526.7 mg., the weight of ammonia present in the system as vapor. Subtracting this from the total weight of solvent, yields the total weight of liquid in the system. From this must further be subtracted the liquid held on the walls and clip amounting to from 40 to 75 mg., depending on the volume of solution. Assuming the density of the solution to be the same as that of pure ammonia, the volume of solution containing a known weight of salt is obtained. The volume of the next more dilute solution is simply determined by adding, to the weight of the preceding solution, the weight of solvent absorbed in going to the final solution, increased by the weight of a volume of vapor equal to that of the liquid absorbed and correcting this by adding the weight of ammonia held on the walls over the area that corresponds to the volume of the ammonia absorbed. In this manner, the concentration of all solutions of a series of measurements may be calculated. It may be pointed out that the corrections discussed above are of the utmost importance if precision is to be achieved; for the most concentrated solutions, having a volume of 20 cc. and a weight of approximately 14 g., the total correction amounts to as much as 3%; precise corrections are, therefore, necessary. How-

(12) Cragoe, McKelvy and O'Conner, Scientific Papers, Bureau of Standards, No. 467 (1923).

ever, the importance of these corrections diminishes rapidly as the concentration of the solution in a given series decreases.

2. **Electrical Measurements.**—Solvent resistances were measured by the d. c. method of Kraus and Fuoss.[7] While this method does not yield precision, values are not greatly in error; the specific conductance of the solvents was negligible in comparison with that of the most dilute solutions measured.

The resistance of solutions was measured by means of a Jones bridge, a variable frequency, audio-range oscillator and an amplifier. Additional resistances were available up to several hundred thousand ohms. The leads to the bridge were shielded by one inch brass tubes in which a heavy copper conductor was held in position by Bakelite spacers. The lead resistance to the cell was measured, and corrections were made when necessary.

Since the electrodes could be platinized only lightly because of adsorption effects that rendered it difficult to wash all electrolytes out of the cell in starting a series of measurements, polarization effects appeared, particularly with the more concentrated solutions. Settings were made at a series of frequencies from 600 to 4000 cycles and the results extrapolated to infinite frequency. It is believed that no considerable error was introduced in this way.

The leads of the conductance cell necessarily pass up through a considerable depth of liquid ammonia in the bath. This introduces lead effects that cannot well be eliminated readily. The effect may be reduced by using a bath liquid of lower specific conductance. This was shown by immersing the cell in alcohol and by increasing the conductance of the alcohol by addition of electrolyte. If the ammonia of the bath were purified, it would probably be possible to carry out measurements to well below 1×10^{-5} *N*. A solution of sodium bromide showed deviation of 0.5% at 3×10^{-6} *N*. With potassium chloride and iodide the deviations were below 0.1% at 0.7×10^{-5} *N*.

3. **Calibration of Cell.**—A primary cell was calibrated with a demal solution of potassium chloride. Three independent measurements were made; the constant was based on specific conductance values of Jones and Bradshaw.[12a] The constant was found to be 21.656 with a mean deviation of 0.025%. A comparison cell was constructed and compared with the primary cell; the mean of three measurements yielded a constant of 0.36743 with a deviation of 0.025%. Finally, the cell to be used was checked against the comparison cell at three different resistances with an extreme range of 1:20. This yielded 0.6580 for the cell constant with a mean deviation of 0.03%. Measurements were carried out in an oil-bath at 25 ± 0.002° and temperature was checked against a platinum resistance thermometer.

4. **Salts** of highest purity were recrystallized, potassium iodide from specially purified alcohol. They were kept in a vacuum desiccator over phosphorus pentoxide.

The salts were weighed in sealed, fragile, Pyrex glass bulbs. They were four in number, the weight in consecutive bulbs being in the approximate ratio of 1:10, excepting the fourth and heaviest which always contained very nearly 100 mg. The salts were introduced into the bulbs through a platinum tube funnel; they were then attached to the pump system and evacuated to a sticking vacuum while heated in a bath at 250°. They were then sealed off and weighed against an evacuated counterpoise. The volume of the bulbs was determined by weighing in air and in water. A hook was attached to the seal of the bulb to facilitate introduction into the cell. The next heaviest bulb, containing from 10 to 30 mg., was also weighed to serve as a check to the heaviest one.

5. **Temperature Coefficients.**—At times, when the temperature of the cell differed slightly from −34°, it was found more convenient to apply a correction to the observed resistance rather than to readjust the manostat. Accordingly, the temperature coefficient was determined for sodium bromide at a series of concentrations. The pressure was lowered from 30 to 40 mm. which corresponds to a temperature interval of approximately 1°. The results are given in Table I for different bridge resistances and approximate concentrations. Corrections were applied on the basis of bridge resistance since the concentrations of the solutions were not known when readings were made.

TABLE I

TEMPERATURE COEFFICIENTS FOR SODIUM BROMIDE SOLUTIONS AT −34° (CELL CONSTANT, 0.6580)

Resistance $\times 10^{-2}$	760	300	80	25	10	2.4
$C \times 10^5$ (approx.)	2.9	8.7	30	100	300	1900
%/mm. $\times 10^2$	2.95	2.90	2.55	2.65	2.45	2.22
%/deg.	1.12	1.10	1.08	1.00	0.93	0.84

In making temperature corrections for salts other than sodium bromide, the same coefficient was used as for this salt. Since the corrections never exceeded 0.05%, this could not introduce a significant error. These data could also be used in reducing conductance data at the boiling point to the present temperature of −34°.

6. **Constants.**—Following are values of constants that have been employed throughout this paper: density of liquid ammonia at −34°, 0.6826[13]; density of saturated ammonia vapor at −34°, 0.863 mg./cc.[12]; pressure of saturated ammonia vapor at −34°, 735.4 mm.[14]; temperature coefficient of vapor pressure at −34°, 37.15 mm./deg.[14]; dielectric constant at −34° 22[15]; viscosity at −34°, 2.558×10^{-3}.

(12a) Jones and Bradshaw, THIS JOURNAL, **55**, 1780 (1933).

(13) Cragoe and Harper, Scientific Papers, Bureau of Standards, No. 420 (1921).

(14) Cragoe, Magee and Taylor, Scientific Papers, Bureau of Standards, No. 369 (1920).

(15) Goodwin and Thompson, *Z. Elektrochem.*, **6**, 338 (1900).

The value of the viscosity is based on Elsey's[16] value of 2.543×10^{-3} at the boiling point of ammonia. We have corrected for a temperature 0.35° below the boiling point assuming a temperature coefficient of 1%/deg.

All experimental values in this paper have been adjusted to $-34 \pm 0.01°$.

IV. Experimental Results

The results of all measurements, without exception, are given in Table II, A, B, C and D, for sodium bromide, potassium chloride, potassium iodide and potassium bromide, respectively. The specific conductance of the solvent for the most dilute series is given at the head of the table in each case. In Table II, A, B and C, are given the concentration of the solution, C, in moles per liter of solution (first column), the equivalent conductance, Λ, of the solute (column 2) and the percentage deviation of the experimental values from the Fuoss linear plots (last column). In Table II, D, for potassium bromide, there are also given computed values for the degree of dissociation, γ, of the electrolyte (column 3) and its activity coefficient, f (column 4). In the tables, an additional space separates the four series for a given salt.

TABLE II

CONDUCTANCE OF SALTS IN LIQUID AMMONIA AT −34°

$C \times 10^5$	Λ	% Deviation	$C \times 10^5$	Λ	% Deviation
$\kappa = 1.6 \times 10^{-9}$ mho: A.			Sodium Bromide (Fig. 5)		
0.28127	313.74	−0.47	29.429	277.79	0.00
.36355	313.65	− .55	36.965	272.49	+ .01
.51705	313.11	− .57	47.573	266.12	+ .04
.84957	311.78	− .44	63.081	258.26	.00
1.74972	309.31	− .38	96.306	245.42	− .29
2.90940	306.56	− .22	134.186	234.25	− .40
4.72057	303.35	− .17	209.983	218.60	−1.00
2.6652	307.10	−0.24	320.701	202.98	−1.73
3.3646	305.67	− .21	437.977	190.77	−1.60
4.2566	304.08	− .15	303.61	205.08	−1.70
5.7931	301.56	− .09	389.43	195.68	−2.43
8.7060	297.22	.00	537.29	184.27	−2.60
12.5503	292.80	− .01	875.27	166.89	....
19.0083	286.39	.00	1872.95	143.97	....
31.3199	276.38	.00			
44.133	268.16	.00			
$\kappa = 1.1 \times 10^{-9}$ mho: B.			Potassium Chloride (Fig. 5)		
0.86842	343.14	−0.43	82.200	228.26	+0.05
1.16897	340.74	− .20	104.204	216.62	+ .18
1.58970	338.61	− .19	137.596	202.81	+ .40
2.47067	334.27	− .01	209.907	182.23	+ .75
3.9574	328.27	.00	311.937	163.74	+1.40
5.7655	322.00	.00	453.25	147.42	+2.43
9.3195	311.77	+ .02	702.29	130.21	+3.60
12.9191	302.52	+ .24	973.98	118.45	+5.20
7.5576	316.48	+0.06	438.80	148.68	+2.30
9.1474	312.22	+ .02	575.58	138.15	+2.75
12.0303	305.08	.00	809.56	125.20	+3.40
15.6187	297.48	.00	1307.13	109.21	+11.2
24.021	282.42	.00	1651.3[a]	102.86	....
33.413	268.63	+ .10			
50.785	250.93	.00			
80.515	229.28	− .01			
107.713	215.18	.00			
$\kappa = 2.5 \times 10^{-9}$ mho: C.			Potassium Iodide (Fig. 6)		
0.66289	341.51	−0.08	52.669	297.29	−0.17
.84547	340.86	− .07	69.907	289.50	− .20
1.16552	340.08	− .07	101.469	278.97	− .45
1.84918	338.25	.00	151.505	265.87	−1.18
3.02938	336.05	.00	247.023	248.88	−2.30
4.53294	333.84	−0.04	399.610	232.05	−4.08
6.48507	330.91	+ .01	534.114	221.62	−5.35
8.88137	328.13	− .01	188.13	258.32	−1.50
5.1127	332.79	.00	249.30	248.60	−2.35
6.4647	330.94	+0.01	335.63	237.81	−3.35
8.3253	328.64	.00	509.47	222.96	−5.20
11.2706	325.44	.00	837.02	205.81	....
16.7546	320.04	+0.04	1581.58	186.04	....
28.457	311.04	.00			
38.507	304.84	−0.09			
52.809	297.20	− .17			
72.382	288.87	− .40			

$C \times 10^4$	Sp. cond. $\kappa \times 10^5$	Λ	γ	f	% Deviation
$\kappa = 3.0 \times 10^{-9}$ mho: D.		Potassium Bromide (Fig. 6)			
0.74448	0.25506	342.61	0.9988	0.9714	−0.01
.97846	.33416	341.51	.9969	.9673	+ .02
1.33340	.45392	340.42	.9954	.9620	− .01
2.17036	.73361	338.01	.9918	.9518	.00
3.57948	1.19724	334.47	.9857	.9387	.00
5.07066	1.71127	330.95	.9793	.9270	.00
7.52495	2.45650	326.45	.9707	.9130	.00
10.4255	3.35252	321.59	.9610	.8989	.00
7.1395	2.3359	327.19	.9721	.9151	.00
9.1680	2.9677	323.70	.9654	.9046	.00
11.8787	3.7932	319.33	.9564	.8921	.00
16.2678	5.0991	313.45	.9445	.8763	−0.09
24.267	7.3770	303.99	.9243	.8525	− .16
36.054	10.5574	292.82	.8999	.8254	− .20
54.668	15.2683	279.29	.8701	.7927	− .30
76.349	20.4018	267.22	.8433	.7631	− .55
108.641	27.5176	253.29	.8123	.7286	− .80
76.234	20.376	267.29	.8435	.7632	−0.55
98.644	25.365	257.14	.8208	.7384	− .61
121.323	30.167	248.66	.8018	.7173	− .87
185.581	42.811	230.68	.7619	.6698	−1.25
295.98	62.289	210.46	.7185	.6118	−1.70
463.53	88.869	191.72	.6817	.5494	−2.48
673.55	119.015	176.70	.6558	.4925	−2.55
1035.713	166.485	160.75	....	....	....
295.83	62.265	210.47	.7186	.6118	−1.70
391.13	77.803	198.91	.6956	.5737	−1.87
536.80	99.667	185.67	.6708	.5275	−2.00
787.95	134.335	170.49	.6465	.4674	−2.40
1532.63	223.579	145.87	....	....	....

[a] This solution was saturated and its concentration was determined from its specific conductance.

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(16) Elsey, THIS JOURNAL, **42**, 2459 (1920).

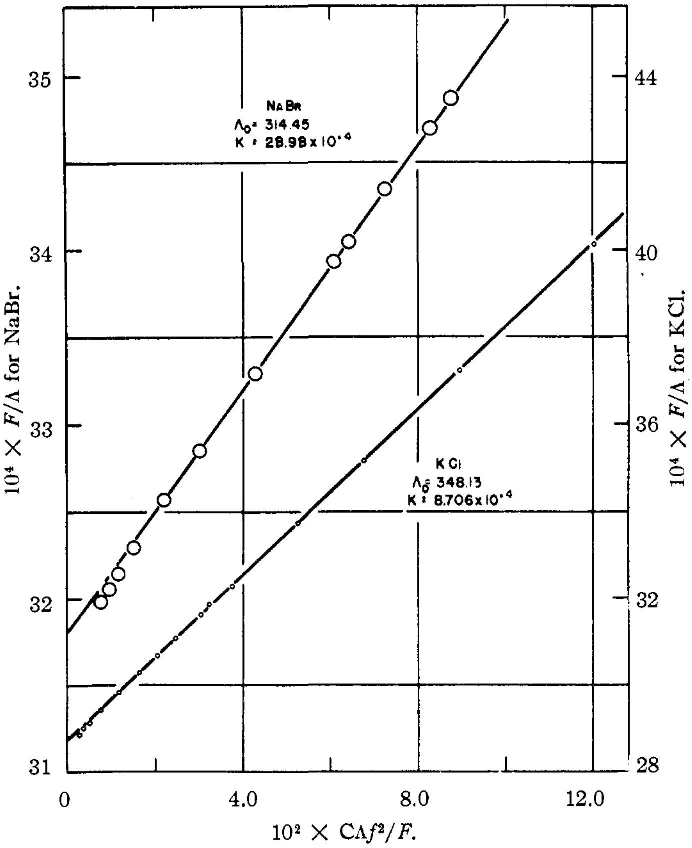

Fig. 5.—Fuoss plots for sodium bromide and potassium chloride in ammonia at −34°.

Fuoss plots (in the dilute region) for sodium bromide and potassium chloride are shown in Fig. 5 and for potassium bromide and potassium iodide in Fig. 6. The radii of the circles in these figures have been drawn to correspond to an error of 0.1% in the value of Λ. Deviations that correspond to Λ values greater than those called for by the Fuoss relation are accounted positive, and in the reverse, negative.

V. Discussion

1. Consistency of Results.—Since there are no data available that might be used as a basis for reference, the adequacy of the method and the precision of the results of the present investigation can only be inferred from the internal consistency of the results obtained. We have a rough, although not a precision, check on the reproducibility of the measured values in that the contents of the third, as well as of the fourth bulbs were weighed directly. However, the weights of salts in the third bulb varied between 10 and 30 mg. and were intended to give only a rough check on the concentration, based on the weights of salts in the fourth bulb (100 mg.). In Table III, are compared concentration ratios in the overlapping regions for the four salts, based on the weights of salts in bulbs 3 and 4, respectively.

It will be noted that the greatest deviation is 0.7% in the case of sodium bromide, in which case, only 10 mg. was weighed out in bulb 3. For the other salts, the discrepancy amounts to 0.1, 0.23, and 0.02%. These variations are within the limit of error of weighing in the case of the third bulb. In any case, it seems clear that the results, based on bulb 4, are not grossly in error.

In solvents of high dielectric constant, such as water, some knowledge of the internal consistency of experimental values may be obtained by their conformance to the requirements of Onsager's theory. In the present instance, with a solvent of dielectric constant 22, this *cannot be done.* However, we can compare the experimental values with the requirements of the Bjerrum–Fuoss theory of short range ion interaction.

TABLE III

COMPARISON OF CONCENTRATION RATIOS BASED ON SALT WEIGHTS IN BULBS 3 AND 4

Salt	No. 3, bulb, mg.	No. 4 bulb, mg.	Concn. ratio
NaBr	9.80	100.13	0.9938
KCl	20.43	101.03	0.9990
KBr	29.67	100.01	1.0023
KI	29.24	99.73	1.0002

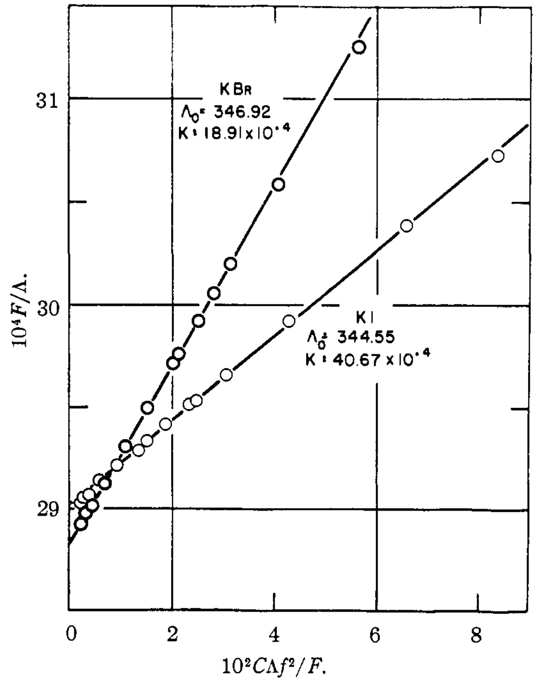

Fig. 6.—Fuoss plots for potassium bromide and potassium iodide in ammonia at −34°.

In the last column of Table II are given the deviations of the individual experimental values from the linear relation of the Fuoss plots. In dilute solutions of concentrations from 9.7×10^{-5} to 6.6×10^{-6}, depending on the series, deviations appear, always in the same direction, which (for sodium bromide) increase from 0.1 to 0.47% at the lowest concentration (2.8×10^{-6}). These deviations, which are always negative, are clearly due to lead effects (Sec. III,E,2). The fact that these effects appeared at lower concentration in the later series was probably due to the higher purity of the ammonia in the thermostat bath in the later series.

At higher concentrations, above 1×10^{-4} *N*, deviations occur due to the inadequacy of the theory. These deviations may be either positive or negative, depending on the nature of the salt, and the magnitude of the deviation likewise depends on the salt. Thus, for sodium bromide, potassium chloride, potassium bromide and potassium iodide at a concentration of approximately 5×10^{-3} *N*, the deviations are, respectively, -2.6, $+2.7$, -2.0 and -5.2%; at 13×10^{-3} *N*, the deviation for potassium chloride is $+11.2$%.

Since deviations occur at low concentrations, on the one hand, and high concentrations, on the other, we can best gain an idea of the consistency of the experimental values by averaging the deviations for all points, beginning with the first point at which the deviation is 0.1%, or less, at low concentration, and continuing to where it becomes 0.1%, or more, at high concentration. For potassium iodide and potassium bromide, the deviabelow 0.1% at the lowest concentration measured, *ca.* 7×10^{-6} *N*.

The results of such a study of the data are summarized in Table IV; the formula of the salt is given in the first column, the range of concentrations in the second column, the number of experimental points (all points in the given concentration range) in the third column and the average percentage deviation in the last column.

TABLE IV

AVERAGE DEVIATION OF INDIVIDUAL CONDUCTANCE VALUES FROM FUOSS LINEAR RELATION OF SALTS IN NH_3 AT $-34°$

Salt	Concn. range	Pts.	Av. dev. %
NaBr	$5.7 \times 10^{-5} - 6.3 \times 10^{-4}$	10	0.016
KCl	$2.4 \times 10^{-5} - 8.2 \times 10^{-4}$	15	.034
KBr	$7.4 \times 10^{-6} - 1.6 \times 10^{-4}$	12	.011
KI	$6.6 \times 10^{-6} - 3.8 \times 10^{-4}$	15	.028

These deviations, ranging from 0.011% for potassium bromide to 0.034% for potassium chloride, indicate a high degree of consistency for the experimental values. *Per contra,* they lend a large measure of support for the validity of the Bjerrum–Fuoss theory of short-range ion interaction.

The fact that, at higher concentrations, weaker salts show positive deviation while stronger salts show negative deviations (see Table II), is significant. Similar observations have been made in the case of solutions in pyridine[17] and nitrobenzene.[18]

2. Constants.—From the Fuoss plots may be determined the limiting conductance, Λ_0, and the dissocation constant, *K*. These constants are collected in Table V; the formula of the salt is given in the first column, the value of Λ_0 in the second column and the dissociation constant, *K*, in the last column.

TABLE V

CONSTANTS FOR SALTS IN LIQUID AMMONIA AT $-34°$

Salt	Λ_0	$K \times 10^4$
NaBr	314.45	28.98
KCl	348.13	8.706
KBr	346.92	18.91
KI	344.55	40.67

The conductances of the three halide ions in ammonia, as in water, differ but little. In ammonia, however, the chloride has the highest conductance and the iodide the lowest. In ammonia, as in water, the sodium ion has a lower conductance than the potassium ion, but, percentage-wise, the difference is smaller in ammonia than in water.

The dissociation constant of sodium bromide is approximately 50% greater than that of potassium bromide, indicating strong interaction of the sodium ion with ammonia in the ion-pairs. The dissociation constant of potassium bromide is approximately twice that of the chloride and that of the iodide twice that of the bromide. This indicates a much lower degree of interaction of the halide ions with the solvent molecule than is the case with the sodium and potassium ions.

The only transference data that we have for electrolytes in ammonia are those of Franklin and Cady.[19] From their data, Kraus and Bray[20] have derived the value 130 as the most probable value for the conductance of the sodium ion at the boiling point of liquid ammonia. Using this value for the conductance of the sodium ion, we have 162.5 for the conductance of the potassium ion and 185.7 for the chloride ion. It seems not unlikely that the value of 130 for the sodium ion is too low.

Columns 4 and 5 of Table II, D for potassium bromide, illustrate well the importance of measurements at low concentration in the case of solvents of low dielectric constant. At a concentration of 0.74×10^{-5} *N*, the value of γ is 0.9982 and that of f, 0.9714; at $C = 1 \times 10^{-4}$, the values are 0.9810 and 0.8989, respectively. Thus, there is already marked association of ions to ion pairs at these low concentrations. The activity coefficient decreases rapidly as concentration increases and differs markedly from unity even at 10^{-5} *N*.

3. Comparison with Earlier Work.—The earliest measurements of Franklin and Kraus,[3]

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[17] Luder and Kraus, THIS JOURNAL, **69**, 2481 (1947).

[18] C. R. Witschonke, Thesis, Brown University, May, 1941, p. 32.

[19] Franklin and Cady, THIS JOURNAL, **26**, 499 (1904).

[20] Kraus and Bray, *ibid.*, **35**, 1315 (1913).

which are more consistent than later ones by the same authors, show deviations from ours on $\Lambda-\sqrt{C}$ plots of 2.1% for potassium bromide, 3.2% for potassium iodide and 0.1% for sodium bromide. Values of K, as computed by Kraus and Bray,[20] do not deviate so greatly; this is probably due to compensation of errors arising from a faulty theoretical basis for the computation of K by errors in Λ_0.

More recently, Monosson and Pleskov[4] measured the conductance of the series of alkali metal nitrates at −40°. While a direct comparison cannot be made with the present work, the difference between the conductance of the sodium and potassium ions may be compared. On the basis of Monosson and Pleskov's measurements and values of Λ_0 for potassium nitrate and sodium nitrate, as derived by extrapolation of $\Lambda-\sqrt{C}$ plots, the difference in the conductance of the two ions is 38. From our values for the limiting conductance of potassium bromide and sodium bromide, the difference is 32.47. If Monosson and Pleskov's values were corrected approximately 6% to a 6° higher temperature, their difference would be 40.

We have analyzed the data of Monosson and Pleskov by the method of Fuoss and, while the data are not sufficiently consistent for accurate evaluations of Λ_0, we have obtained the approximate values 331.1 and 296.7 for potassium nitrate and sodium nitrate, respectively. This yields 34.4 for the difference in the conductance of the potassium and sodium ions at −40° and 36.4 at −34°. At −34°, Monosson and Pleskov's value thus differs from ours by approximately 3.9 Λ-units.

VI. Summary

1. Apparatus and techniques have been developed which permit of measuring the conductance of salts in liquid ammonia solution with a high degree of precision.

2. The conductance of sodium bromide and of potassium chloride, bromide and iodide have been measured to low concentrations at −34°.

3. The experimental values have been analyzed by the method of Fuoss and values of the limiting conductance and the dissociation constant have been derived.

4. In the dilute region over a considerable range of concentration, the values conform to the Fuoss relation with mean deviation varying between 0.011 and 0.034%.

5. An improved seal is described by means of which platinum electrodes may be introduced into apparatus constructed of Pyrex glass.

6. An effective manostat is described for controlling the temperature of a liquid ammonia bath.

7. The solubility of potassium chloride in liquid ammonia at −34° was determined to be 0.01651 as determined by the specific conductance of its solution.

PROVIDENCE, R. I. RECEIVED NOVEMBER 15, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE JOHNS HOPKINS UNIVERSITY]

Ionization of Organic Esters in Sulfuric Acid. II. Alkyl Oxygen Fission[1,2]

BY LESTER P. KUHN[3]

Previous workers have shown that organic acids and esters of the formula RCOOR′, where R is a substituted or unsubstituted alkyl or aryl group and R′ is H or a substituted or unsubstituted alkyl group, may ionize in concentrated sulfuric acid either according to equation I[4] or equation II[5,6]

$$\text{RCOOR}' + \text{H}_2\text{SO}_4 = \text{RCOOR}'\text{H}^+ + \text{HSO}_4 \qquad \text{I}$$

$$\text{RCOOR}' + 3\text{H}_2\text{SO}_4 = \text{RCO}^+ + \text{H}_3\text{O}^+ + \text{R}'\text{OSO}_3\text{H} + 2\text{HSO}_4^- \qquad \text{II}$$

The former has been called normal and the latter complex ionization, or acylization. Evidence has been presented[7] which indicates that the acyl cation formed in II may combine with a bisulfate anion to yield an acyl sulfate, in which case II is replaced by equation III.

$$\text{RCOOR}' + 3\text{H}_2\text{SO}_4 = \text{RCOOSO}_3\text{H} + \text{H}_3\text{O}^+ + \text{R}'\text{SO}_3\text{H} + \text{HSO}_4^- \qquad \text{III}$$

In the present work we have studied the ionization of esters of isopropyl and *t*-butyl alcohol and we are led to the conclusion that these esters do not ionize according to either of these equations but in a manner which has hitherto not been observed in concentrated sulfuric acid.

Two methods were used to measure the extent of the ionization. The first was the determination of the van't Hoff "*i*" factor from freezing point depression measurements which tells the number of molecules and ions formed from each molecule of solute. Thus the "*i*" factors for equations I, II, and III when R′ is not H, are 2, 5 and 4, respec-

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(1) From the doctoral dissertation of Lester P. Kuhn, The Johns Hopkins University.

(2) Presented at the New York Meeting of the American Chemical Society, September, 1947.

(3) Present address: Ballistic Research Laboratories, Aberdeen Proving Ground, Maryland.

(4) Hantzsch, *Z. physik. Chem.*, **61**, 257 (1908); **65**, 4 (1909).

(5) (a) Hammett and Deyrup, THIS JOURNAL, **55**, 1900 (1933); (b) Treffers and Hammett, *ibid.*, **59**, 1708 (1937); (c) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 45–48, 54–56, 277–285.

(6) (a) Newman, THIS JOURNAL, **63**, 2431 (1941); (b) Newman, Kuivila and Garrett, *ibid.*, **67**, 1704 (1945).

(7) Kuhn and Corwin *ibid.*, **70**, 3370 (1948).