Devaux and Langmuir, is an important question which, on the basis of existing data,[23] cannot be answered definitely as a general case.

Summary

1. Measurements by the drop weight method were made of the surface tension of mercury in contact with saturated vapors of organic liquids. Different values from those existing in the literature were obtained for some of the liquids, and also values were obtained for a number of liquids for which no previous values appear to have been recorded.

2. Measurements by the capillary rise method were made of the interfacial tension of water in contact with organic liquids, and of the surface tension of water saturated with organic liquids and in contact with the saturated vapor.

3. The results show that when a film is spontaneously formed on the surface of a liquid (*e. g.*, mercury or water), the surface tension of the liquid supporting the film registers at saturation vapor pressures a tension, σ_{13}, the value of which is equal to the sum given by the interfacial tension of the liquid against the liquid constituting the film, σ_{12}, plus the surface tension of the film liquid, σ_{23}, that is, $\sigma_{13} = \sigma_{12} + \sigma_{23}$ at saturation vapor pressures when the initial condition (the condition for film formation) $\sigma_1 > \sigma_{12} + \sigma_{23}$ is fulfilled. In other words, the so-called Antonoff's interfacial tension rule holds for these systems, contrary to the results of some previous investigators.

[23] For evidence of multimolecular films *cf.* Cassel [*Trans. Faraday Soc.*, **28**, 177 (1932)] and for monomolecular films *cf.* Rideal, "Introduction to Surface Chemistry," Cambridge University Press, 1930, pp. 61, 83; Adam, "Physics and Chemistry of Surfaces," Oxford University Press, 1930, p. 29.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. V. The Conductance of Some Amido Salts in Liquid Ammonia[1]

BY CHARLES A. KRAUS AND WILLIAM W. HAWES[2]

I. Introduction

This and the three succeeding papers of the present series deal with the influence of ionic constitution on the properties of electrolytic solutions. They are particularly concerned with the influence of the constitution of anions upon the dissociation of their alkali metal salts in liquid ammonia.

It is known that some electrolytes are stronger than others; for example, the dissociation constants of acids and bases in water and in other solvents extend over a wide range of values. Similarly, salts of the less electropositive metals are generally less highly dissociated in a given solvent than

[1] This and the succeeding paper of this series formed the subject matter of the Edgar F. Smith Birthday Lecture delivered by the senior author at the University of Pennsylvania, May 23, 1930.

[2] Metcalf Fellow in Chemistry.

are those of the strongly electropositive metals. Mercuric salts in water and numerous salts of heavy metals in non-aqueous solvents are not highly dissociated. The salts of the primary, secondary and tertiary amines in non-aqueous solvents are less highly dissociated than corresponding salts of the strongly electropositive quaternary ammonium ions.[3] Apparently, there is some connection between the strength of an electrolyte and the electropositiveness of its positive ion.

We have only a limited knowledge of the influence of the constitution of negative ions on the properties of solutions of their salts. This is in part due to the fact that most of these ions are weakly electronegative and their salts are, therefore, unstable in the presence of oxygen and of water. There are no common negative ions analogous to the quaternary ammonium ions, whose constitution can be varied widely and which are strongly electronegative. The only negative ions that have been studied extensively from the standpoint of constitution are the ions of the carboxylic acids. These have been studied chiefly in the form of acids rather than of salts.

We might well expect that elements other than oxygen would form negative ions analogous to the anions of the organic acids. These would not usually be stable in water, but they should be stable in solvents that do not have a high oxidizing or hydrolyzing tendency. This and succeeding papers will be concerned with anions of various elements such as nitrogen, tin, germanium, carbon, oxygen and sulfur. We shall, for the most part, deal only with univalent ions. In the case of elements of higher valence, therefore, all the valences, except one, will be satisfied by neutral atoms or groups, such as hydrogen or organic groups. The general formula of these ions is $R_{n-1}A^-$, where R is an organic group or hydrogen, and A is an atom of valence n. Anions of this type have only a low affinity for the electron and are, therefore, readily oxidized; the corresponding hydrogen derivatives are usually very weak acids and their salts are easily hydrolyzed. Salts of such anions, therefore, must be studied under rigid exclusion of oxygen and water and in solvents of low hydrolyzing power. Moreover, if a comparative study of ionic dissociation is to be made, the solvent must have a sufficiently low dielectric constant so that a measurable proportion of the electrolyte will be undissociated, that is, will be in a condition such that it takes no part in the conduction process.

In the present investigation, we have employed ammonia as solvent. Salts of weakly negative ions are usually readily soluble in ammonia and without ammonolysis. The dissociation of salts in ammonia varies over a very wide range, depending upon the constitution of their constituent ions. No electrolyte thus far studied has been found to be completely dissociated in liquid ammonia.

(3) Walden, *Z. physik. Chem.*, **162**, 1 (1932).

In the present paper we recount the results of a study of the conductance of electrolytes in which nitrogen is the central element of the negative ion. The simplest negative ion of this type is the amide ion, NH_2^-, the conductance of whose sodium and potassium salts has been measured by Franklin[4] and by Franklin and Kraus.[5] One or both of the hydrogen atoms of the amide ion may be replaced by phenyl groups, yielding the ions $C_6H_5NH^-$ and $(C_6H_5)_2N^-$. Finally, we have taken advantage of the remarkable property of triphenylboron to combine with the amide ion to form the stable complex ion $(C_6H_5)_3B{\cdot}NH_2^-$. This ion is in many respects similar to the ammonium ion; the charge is probably not localized on any one atom or valence of the complex ion, but the group as a whole has an excess negative charge of unity. All the above ions are weakly negative and, with the exception of the ammidotriphenylboron ion, are very readily oxidized. By analogy with positive ions, it might be expected that the salts of such weakly negative ions would prove to be weak electrolytes. This, however, is not the case. Certain of these salts are much stronger than those which we ordinarily term typical electrolytes. The affinity of a negative ion for its electron has little or nothing to do with the dissociation of its salts in solution. The tendency of a given salt to dissociate is primarily determined by the size of its ions or, in other terms, by the energy necessary to separate an ion-pair. Our present results tend to confirm the view of Fuoss and Kraus[6] that the dissociation process for a given solvent medium is controlled by Coulomb forces and that the larger the ions, and therefore, the lower the energy of dissociation, the greater the degree of dissociation of the electrolyte under otherwise comparable conditions.

II. Apparatus and Materials

The general procedure in measuring the conductance of the solutions was similar to that used earlier by Kraus[7] in measuring the conductance of solutions of the alkali metals. Known volumes of liquid ammonia were distilled into the conductivity cell, containing a known original weight of salt, and approximately known volumes of solution were withdrawn before each dilution, the exact volumes being determined from the weight of ammonia withdrawn after absorption in water. Since all the salts measured are extremely sensitive to moisture and oxygen, they necessarily had to be prepared in the conductivity cell itself. The preparation consisted in treating a known weight of the alkali metal amide with an equivalent amount of the amine in liquid ammonia. The reaction is $MNH_2 + R_2NH = MNR_2 + NH_3$. Since the amides cannot be manipulated in air, they were prepared in the conductivity cell by the interaction of a

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(4) Franklin, *Z physik. Chem.*, **69**, 290 (1909).

(5) Franklin and Kraus, *Am. Chem. J.*, **23**, 292 (1900).

(6) Fuoss and Kraus, THIS JOURNAL, **55**, 1019 (1933).

(7) Kraus, *ibid.*, **43**, 749 (1921).

known weight of metal with the solvent, a bit of oxidized iron wire serving as catalyst.[8]

In the case of diphenylamine and triphenylboron ammine, which could be handled in air, the materials were made up into pellets and added as needed. Aniline was sealed in a fragile glass bulb and introduced into the conductivity cell at the beginning of an experiment. The aniline bulb was broken after preparation of the alkali metal amide.

Apparatus.—The conductance was measured in a cell A (Fig. 1), which was provided with a pair of electrodes at B and a single electrode at C. Electrical connection was made by means of wires and a few drops of mercury in the lead tubes DD. The pair of electrodes, of about 0.5 sq. cm. area and 1 mm. distance, was used to measure the more dilute solutions. The electrode C, of 0.2 sq. cm. area, was used in conjunction with the pair to measure the more concentrated solutions. As indicated in Fig. 1, the electrodes B were located in a small chamber underneath the main body of the cell and this chamber was connected with the larger chamber above by a tube of about 6 mm. diameter and was also connected with the same chamber from below by a small tube which connected at the bottom with a larger tube of about 10 mm. diameter, which was coaxial with the neck E of the cell. This construction was adopted in order that the solution might be prepared in the cell by crushing the bulb F, attached to the end of the crushing rod G, which passed through the neck of the cell and was attached to the ground-glass cap at the top by means of a rubber slip-joint H. The capillary tube I, extending to the bottom of the cell, served the purpose of emptying the cell through the stopcock J. It likewise served in stirring the contents of the cell by means of a stream of ammonia vapor. A second capillary K, which did not reach to the bottom of the cell, was used to draw off solution in the process of dilution, a volume of about 13.8 cc. of solution being left behind.

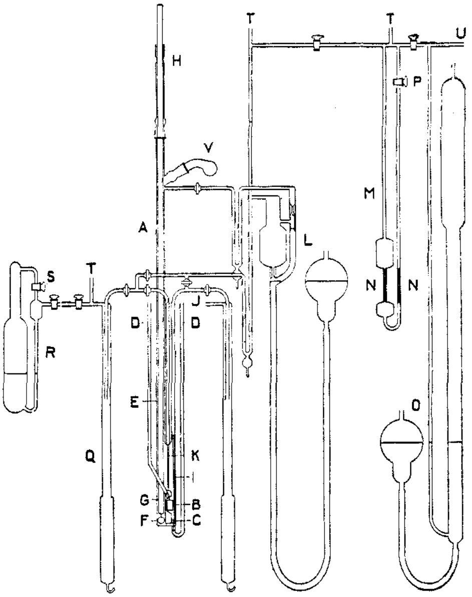

Fig. 1.

Stirring was accomplished by withdrawing vapor from the cell above the solution by means of a modified Toepler pump L and returning it to the cell through the two capillaries I and K as described. The ammonia introduced into the cell was measured in the pipet M, the two tubes NN being graduated to 0.01 cc. and volumes being estimated to 0.001 cc. The ammonia, dried with sodium in the stock cylinder, was condensed in the pipet under a pressure of about 15 cm. of mercury, the pressure being regulated by the height of mercury in the trap O.

The pipet was cooled by a bath of boiling ammonia. Before reading the pipet, the level of the liquid in the bath was adjusted to be the same as that of the liquid in the

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[8] Franklin, THIS JOURNAL, **27**, 831 (1905).

capillaries NN. On removing the bath and closing stopcock P, the ammonia boiled in the pipet and was condensed in the conductivity cell. Solution was withdrawn from the cell through the capillary K into the receiver Q, which was cooled by a bath of ammonia boiling under reduced pressure. The pressure of vapor in the cell served to force the solution into the receiver, from which the solvent was evaporated and absorbed in water in a special absorption tube R, cooled in ice water. The stopcock S served to control the flow of vapor into the absorption tube. The apparatus is connected with a vacuum pump and suitable manometer at T and with a source of ammonia at U.

Before preparing the salt, the cell was washed with pure solvent until its conductance reached a desired low value. The weighed bulb F, containing the metal, was crushed under ammonia and converted to amide. The hydrogen generated in this process was removed, usually along with the entire quantity of solvent. The crusher rod, along with the cap to which it was attached, was in most cases removed and the cell was closed by a second cap. Substances that could be formed into pellets in air were introduced as needed from the addition tube V, which was attached to the neck of the cell near the top by means of a ground joint. Aniline was sealed in a weighed bulb which was broken after preparation of the sodium amide.

After making up the solution with a known quantity of ammonia, its conductivity was measured. The solution was then stirred and its conductance again measured, and this process was repeated until a constant value was obtained. A second pipet full of ammonia was then condensed in the cell and the conductance of the solution measured as before. Solution was then withdrawn from the cell as described above and the conductance of the residual solution was again measured. The solution was now diluted by ammonia from the pipet. Approximately, the volume of the pipet was 9.8 cc., and the volume remaining in the cell was 13.8 cc., so that the dilution ratio was 1.41. The ammonia entering the cell was measured by volume in the pipet and that withdrawn was determined by weight in the absorption tubes. The two were found to check well within 0.1%. A correction was made for ammonia in the vapor phase. To determine this correction, known quantities of ammonia were introduced into the cell at pressures below one atmosphere, the cell being surrounded by a bath of boiling ammonia. The temperature of the solution was determined from its vapor pressure. Bureau of Standards data[9] were employed for vapor pressures and for the density of liquid ammonia.

The conductance was measured by means of a Kohlrausch bridge with Curtis wound coils up to 100,000 ohms. A Vreeland oscillator served as source of current, a telephone as indicating instrument, and induction and capacity effects were balanced out by means of suitable condensers. The cell constant of the high resistance electrodes was determined by intercomparison with a second cell which was standardized at 0° by means of 0.1 N potassium chloride solution, using values of Parker and Parker[10] for the specific conductance. The constant of the low resistance electrodes was determined during each experiment by comparison with the high resistance combination. The constant of the high resistance electrodes was 3.986 and that of the low resistance pair in the neighborhood of 0.22.

Materials.—Metallic sodium and potassium were used without further purification. They were melted *in vacuo* and run through fine capillaries into weighed, fragile bulbs. Between one and two m. atoms of metal were used in a preparation. Diphenylamine was recrystallized from ether by addition of benzene, m. p. 54°. Aniline was twice distilled over barium oxide at low pressure, the middle fraction only being retained in each case. It was introduced into a weighed, fragile bulb. Triphenylboron amides were prepared by the direct action of sodium or potassium amide or triphenylboron ammine.

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[9] Cragoe, Meyers and Taylor, Scientific Papers of Bur. of Standards, No. 369, April 10, 1920; Cragoe and Harper, *ibid.*, No. 420, October 15, 1921.

[10] Parker and Parker, THIS JOURNAL, **46**, 312 (1924).

The latter compound was purified by repeated recrystallization from benzene, and finally from ether, m. p. 250°. Sodium and potassium triphenylboron ammides are readily soluble in liquid ammonia and yield colorless solutions. The sodium salt crystallizes with three molecules of ammonia and the potassium salt with one. Corrections were applied for solvent retained by these salts in computing the concentrations. Sodium and potassium diphenyl amide yield yellow solutions. Sodium monophenyl amide also yields a yellow solution. Attempts to prepare this salt by the action of sodium on aniline or hydrazobenzene, according to the method of White[11] and White and Knight,[12] proved unsuccessful. A reddish colored solution resulted, indicating side reactions.

The ammonia used was a synthetic product which was treated with metallic sodium in the supply cylinder. It was not found practicable to reduce the specific conductance of the ammonia in the cell below 4×10^{-7}. Conductance values have been corrected for this value. That the correction is not greatly in error is indicated by the fact that the Λ–log V curves show no sudden change of direction down to fairly low concentrations.

III. Experimental Results

Below are tabulated the conductance values, at various dilutions, for the following salts: sodium monophenyl amide, $NaNHC_6H_5$, sodium diphenyl amide, $NaN(C_6H_5)_2$, sodium triphenylboron ammide, $NaNH_2{\cdot}B(C_6H_5)_3$,

TABLE I

CONDUCTANCE VALUES OF SALTS IN AMMONIA

V	Λ	V	Λ	V	Λ
Sodium Monophenyl Amide (−33.1°)					
12.40	59.5	93.28	101.7	795.9	186.0
18.69	65.2	159.2	119.3	1362	209.1
31.98	74.9	271.9	139.6	...	...
54.62	86.9	466.7	162.7	...	...
Sodium Diphenyl Amide (−33.0°)					
15.97	95.3	157.6	143.7	2243	206.9
24.04	103.0	268.3	157.7	3823	215.2
32.09	108.4	456.6	172.4	6515	222.0
54.56	119.1	776.9	186.4	11100	228.8
92.45	130.8	1321	197.4	...	...
Sodium Triphenylboron Ammide (−32.9°)					
12.28	92.3	270.1	156.3	6503	202.2
18.55	100.7	460.1	167.9	11030	205.2
31.74	111.4	784.5	177.4	18910	207.1
54.65	121.3	1333	185.4	32100	209.3
93.11	133.4	2261	192.5	...	...
159.1	145.3	3821	198.0	...	...
Potassium Diphenyl Amide (−33.1°)					
9.48	104.3	119.2	159.5	1718	227.9
14.31	111.8	204.1	174.2	2927	237.4
24.50	121.7	349.7	187.6	4957	245.0
40.94	132.7	593.4	203.3	8396	250.8
69.38	145.1	1007	216.4	14300	256.3

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[11] White, THIS JOURNAL, **45**, 779 (1923).

[12] White and Knight, *ibid.*, **45**, 1780 (1923).

TABLE I (*Concluded*)

Potassium Triphenylboron Ammide (−33.2°)

V	Λ	V	Λ	V	Λ
17.41	130.5	373.3	197.8	7521	243.5
26.20	140.2	632.8	208.3	12820	246.8
44.74	149.5	895.5	214.7	21880	249.8
76.21	160.6	1525	225.2	37260	251.5
129.9	172.3	2603	233.1	...	...
219.9	186.4	4429	239.2	...	...

potassium diphenyl amide, $KN(C_6H_5)_2$, and potassium triphenylboron ammide, $KNH_2 \cdot B(C_6H_5)_3$. At the head of each table is given the temperature at which the measurements were carried out.

IV. Discussion

The results for sodium and potassium salts are shown graphically in Figs. 2 and 3, respectively. Values for sodium amide and potassium amide, due to Franklin and Kraus[5] and Franklin,[4] are shown for comparison. It is evident that the substitution of a hydrogen atom of the amide ion by a phenyl group results in a greatly increased conductance of the electrolyte at higher concentrations. Combining the amide ion with the large triphenylboron molecule increases the conductance still more. In the more dilute solutions, where all the salts are highly ionized, the salts with smaller ions exhibit a higher conductance, owing to their greater mobility. In all cases, the curves of salts with larger ions are less steep than those of salts with smaller ions. Dissociation, therefore, is primarily determined by the size of the ions and, to some extent, by their configuration; the

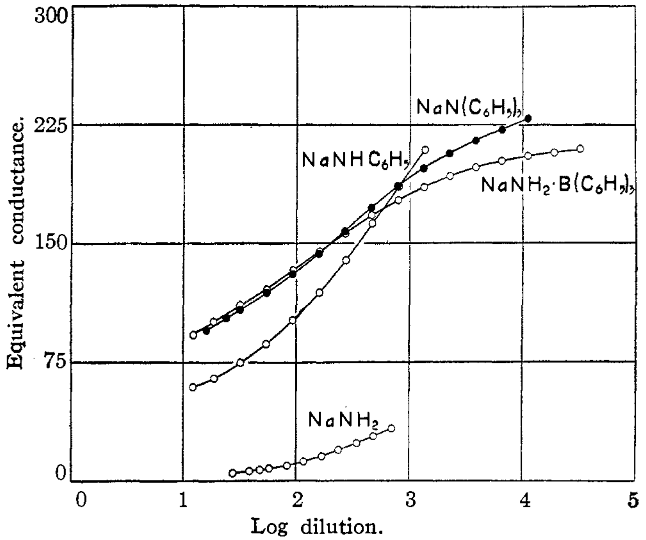

Fig. 2.

electron affinity of the negative ions bears no relation to the phenomenon of ionic dissociation.

We have computed the values of the limiting conductance Λ_0 and the dissociation constant K according to the method of Fuoss and Kraus.[13] We have also calculated the parameter a,[14] which may be pictured as the distance between ions in the ion pairs. In calculating Λ_0 and K, we have depended largely on the conductance values between 0.001 and 0.0001 N.

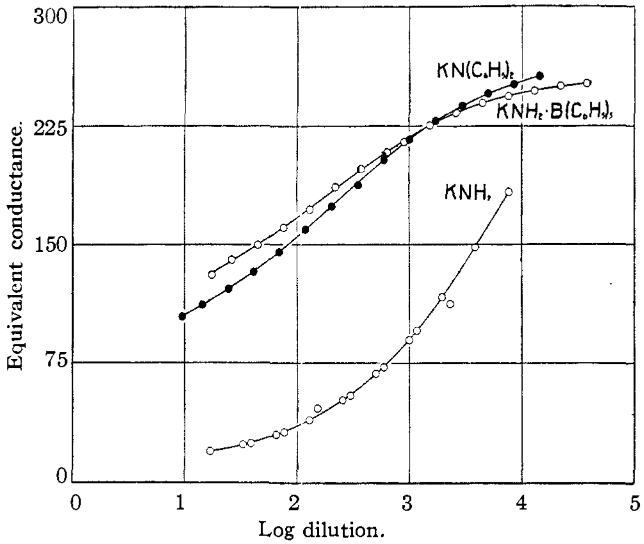

Fig. 3.

All the salts measured are highly sensitive to oxygen and other impurities, and conductance values below $10^{-4}N$ become increasingly uncertain as the concentration diminishes. The conductance values for sodium phenyl amide seem to be somewhat high, but it is believed that the value of K is not greatly in error. Since the dissociation of the salts of triphenylboron ammide is about 96% at $10^{-3}N$, the precision of the measurements is not sufficiently high to make an accurate determination of K possible. The values given in the table are substantially correct and serve for purposes of comparison.

As may be seen from the table, the dissociation constants are consistently higher for salts having larger negative ions; correspondingly, salts of lower Λ_0 values have higher K values. Sodium monophenyl amide has about the same dissociation constant as cesium nitrate (9.66×10^{-4}). The K values of most inorganic salts lie between 10×10^{-4} and 35×10^{-4}. Therefore, the two diphenyl amides are distinctly better electrolytes than ordinary salts, and the two triphenylboron ammides are much better electrolytes.

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(13) Fuoss and Kraus, THIS JOURNAL, **55**, 476 (1933).

(14) Fuoss and Kraus, *ibid.*, **55**, 1019 (1933).

TABLE II

CONSTANTS OF ELECTROLYTES IN AMMONIA

Salt	Λ_0	$K \times 10^4$	$a \times 10^8$
$NaNH \cdot C_6H_5$	316	8.2	3.1
$NaN(C_6H_5)_2$	235	58	6.7
$NaNH_2 \cdot B(C_6H_5)_3$	215	150	10.9
$KN(C_6H_5)_2$	266	50.5	6.0
$KNH_2 \cdot B(C_6H_5)_3$	257	130	10.4
KNH_2 (Franklin)	351	0.70	2.2

Adding triphenylboron to the amide ion raises the dissociation constant of the potassium salt from 0.7×10^{-4} to 130×10^{-4}. There is much evidence in the literature indicating that the relation between dissociation and ion size found in ammonia holds quite generally for all solvents. It is unnecessary to give a detailed review of the literature here, but those who are familiar with the subject will recall, for example, that the quaternary ammonium salts generally exhibit a higher relative conductance than do corresponding alkali metal salts at the same concentrations.[15]

It may be pointed out that, while the equilibrium between neutral molecules (ion pairs) and ions is subject to the law of mass action after the manner of the classical theory, the mechanism of the dissociation process as here postulated has no counterpart in the classical theory. The combination of oppositely charged ions to form ion pairs is due to Coulomb forces and dissociation occurs only when the energy necessary to separate a pair of ions is supplied in the form of collision energy.[14,16] The dissociation energy is measured by the value of $-RT \log_e K$. For the electrolytes in Table II, the energy varies from 1950 calories, for sodium triphenylboron ammide, to 4600 calories for potassium amide. If we had salts with still larger ions, we should expect correspondingly larger ionization constants, *i. e.*, smaller dissociation energies. It is quite possible that electrolytes may be found which will prove to be completely ionized in liquid ammonia.

Assuming spherical ions with uniform charge distribution, the a-values of Table II may be considered as distances between the centers of ionic charges in the ion pairs. As may be seen from the table, the values vary from 2.2×10^{-8}, for potassium amide, to 10.9×10^{-8}, for sodium triphenylboron ammide. The a-values as calculated are in reasonably good agreement with distances as they might be inferred from atomic dimensions and structure. For an a-value of approximately 16, the electrolyte would be completely ionized in liquid ammonia.

For a K-value of 1×10^{-6}, the a-value for liquid ammonia is 1.57×10^{-8}. The simple model of spherical ions under the action of Coulomb

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(15) Walden and Centnerszwer, *Z. physik. Chem.*, **39**, 513 (1902); Dutoit and Gyr, *J. chim. phys.*, **7**, 189 (1909).

(16) Bjerrum, *Kgl. Danske Vidensk. Selskab.*, **7**, No. 9 (1926); Falkenhagen, "Elektrolyte," Hirzel, Leipzig, 1932, p. 257 ff.

forces may well prove inadequate for extremely small ions. Unfortunately, such salts are not usually soluble, particularly in solvents of lower dielectric constant. The fact remains that in liquid ammonia, at any rate, a dissociation constant of approximately 10×10^{-4} is about the lower limit of this constant for ordinary electrolytes, which corresponds to an a-value of about 3×10^{-8}. It is only the acids and bases that exhibit extremely low K-values, and it may well be that quantum mechanical forces are here involved.

V. Summary

The electrical conductance of the following electrolytes has been measured in liquid ammonia: sodium phenyl amide, sodium diphenyl amide, sodium triphenylboron ammide, potassium diphenyl amide, and potassium triphenylboron ammide.

The dissociation constants have been evaluated. They range from 8.2×10^{-4} for sodium phenyl amide to 150×10^{-4} for sodium triphenylboron ammide. The dissociation constant increases with increasing size of the negative ion. The results are in agreement with the theory developed by Bjerrum and by Fuoss and Kraus, which attributes the process of ion association to Coulomb forces.

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[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Atomic Weight of Lead from Katanga Pitchblende

BY GREGORY P. BAXTER AND CHESTER M. ALTER

The atomic weights of several samples of lead from uranium ores occurring in East Africa have already been determined. Hönigschmid and St. Horowitz[1] obtained their material from selected crystals of uraninite from Morogoro. Hönigschmid and Birckenbach[2] used material which had been extracted from the yellow and green secondary minerals associated with Katanga pitchblende. Richards and Putzeys[3] started with metal extracted from a mixture of primary and secondary minerals from Katanga. Perette[4] determined the densities of common lead and a specimen extracted from Katanga pitchblende.[3]

		Atomic weight
Hönigschmid and St. Horowitz	Morogoro	206.046
Hönigschmid and Birckenbach	Katanga	206.048
Richards and Putzeys	Katanga	206.20
Perette	Katanga	206.14

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(1) Hönigschmid and St. Horowitz, *Sitzber. Kais. Akad. Wiss. Wien.*, **123**, 19 (1914).

(2) Hönigschmid and Birckenbach, *Ber.*, **56**, 1837 (1923).

(3) Richards and Putzeys, THIS JOURNAL, **45**, 2954 (1923).

(4) Perette, *Compt. rend.*, **180**, 1589 (1925).