contains two $R_2CuCl_4.2H_2O$. The space-group symmetry is probably D_{4h}^{14} with 2Cu at (a), 4 alkali at (d), 4Cl at (f), 4Cl at (g) and $4H_2O$ at (e). The compounds seem to have "double salt" characteristics.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

THE CONDUCTIVITY OF ACIDS AND SALTS IN LIQUID AMMONIA[1]

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In the course of the development of the system of compounds derived from liquid ammonia as a solvent, by Franklin[2] and his associates, it was desired to know the extent to which certain acids and salts would ionize when dissolved in liquid ammonia. This information was designed to indicate whether or not metallic salts of acids derived from the ammonia system, when dissolved in liquid ammonia, would ionize to a greater extent than their respective acids. This conspicuous property of salts of aquo-acids in water solution would thus serve to test the validity of the classification of the former as true salts.

Also it was hoped that such information would be a useful addition to existing knowledge of the properties of substances dissolved in liquid ammonia.

Some of the data obtained by Franklin[3] and by Franklin and Kraus[4] are made use of for purposes of comparison.

Treatment and Expression of Results

The following notation has been used to express the designated quantities: R, measured resistance; C, cell constant; v, dilution, in liters per mole; Λ, molecular conductivity; Λ_∞, the value approached by Λ as the dilution increases; K, the ionization or equilibrium constant.

The conductivity curves of the substances measured, with some of the curves of Franklin and of Franklin and Kraus, have been plotted together in Fig. 1 for comparison.

The graphical methods of Kraus and Bray[5] have been used, where applicable, to evaluate Λ_∞ and K, and these values are given in Tables I and II.

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[1] From a thesis presented to the Department of Chemistry and the Committee on Graduate Study of Stanford University in 1925 in partial fulfilment of the requirements for the degree of Doctor of Philosophy. The work herein described was done under the direction of Dr. E. C. Franklin.

[2] Franklin, "Liquid Ammonia as a Solvent," A. C. S. Monograph in preparation.

[3] Franklin, *Z. physik. Chem.*, **69**, 270 (1909).

[4] (a) Franklin and Kraus, *Am. Chem. Jour.*, **23**, 277 (1900); (b) THIS JOURNAL, **27**, 191 (1905).

[5] Kraus and Bray, THIS JOURNAL, **35**, 1315 (1913).

Experimental

The measurements were made at —33.5°, using cells described by Elsey,[6] and technique which differs only in certain details from that described by him, or by Franklin and Kraus.[4a]

The cell constants were redetermined, using 0.02 *M* potassium chloride at 20 and at 0°, and 0.01 *M* potassium chloride at 18°, prepared by the method of Kraus and Parker,[7] and using the values for the specific conductivity given by Kohlrausch and Holborn,[8] and by Kraus and Parker, respectively.

The resistance measurements were made by comparison with a standard 1–100,000 ohm box of Curtis coils, by means of a Kohlrausch drum slide wire, both made by Leeds and Northrup, and used by Elsey.

The alternating current was obtained from a micro-hummer giving a sine wave current with a frequency of 1000.

The telephone current was amplified by means of a device described by Hall and Adams.[9]

The entire apparatus was shielded with grounded metal. The wires leading from the cell vessel were No. 18 double cotton covered copper, enclosed in separate grounded lead tubes. These wires under operating conditions had a resistance of 0.16 ohm, which was deducted from all resistance measurements.

Satisfactorily sharp minima were obtained by the use of capacity in parallel with the resistance box.

For reasons set forth in the following paper, the resistance measurements herein described were made by means of the concentric pair of electrodes only.

A measured volume of a solution of determined concentration and resistance was diluted with successive measured portions of pure solvent, distilled from the reservoir and condensed directly in the conductivity cell. The new concentration was calculated, and the new resistance measured, after each dilution.

All results have been corrected by subtracting the specific conductivity of the solvent, as obtained before and after each series of measurements, from that of the solution.

The specific conductivity of the solvent was usually from 0.1 to 0.2 $\times 10^{-6}$ mhos.

Preparation of Materials

The substances used in making these measurements have been obtained from several sources. Two were Kahlbaum preparations, ten were

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[6] Elsey, This Journal, **42**, 2454 (1920).

[7] Kraus and Parker, This Journal, **44**, 2422 (1922).

[8] Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," B. G. Teubner, Leipzig, 1916.

[9] Hall and Adams, This Journal, **41**, 1515 (1919).

prepared or purified by the writer, and ten were prepared and purified by other workers, notably W. L. Burdick, J. S. Blair and F. W. Bergstrom, to whom thanks are due. In cases of uncertainty the purity has been verified by analysis and, with the exception of dicyanodiamide and melamine, the purity of all are within the limits of the experimental error of the measurements.

Results

The molecular conductivity at log v = 3.0 of seven acids and their respective alkali-metal salts is shown in Table I.

TABLE I

THE CONDUCTIVITY OF ACID AND SALT COMPARED

	Electrolyte	Formula	$\Lambda_{\log v = 3.0}$	Λ_{∞}	$10^4 K$
1.	Potassium *m*-nitrobenzenesulfonamide	$NO_2.C_6H_4.SO_2NHK$	201	275	15.0
II.	*m*-Nitrobenzenesulfonamide	$NO_2.C_6H_4.SO_2NH_2$	162	231	12.5
4.	Potassium succinimide	$\begin{matrix}CH_2.CO\\CH_2.CO\end{matrix}:NK$	135	298	3.03
3.	Succinimide	$\begin{matrix}CH_2.CO\\CH_2.CO\end{matrix}:NH$	138	286	2.45
7.	Monosodium cyanamide	$NC.NHNa$	205	...	...
III. 5.	Cyanamide	$NC.NH_2$	35	...	...
16.	Dipotassium α-triphenylguanidine	$C_6H_5N:C(KNC_6H_5)_2$	154	...	...
6.	α-Triphenylguanidine	$C_6H_5N:C(HNC_6H_5)_2$	0.75	...	...
14.	Potassium *iso*butyramide	$(CH_3)_2CH.CONHK$	126	290	2±0.2
10.	*Iso*butyramide	$(CH_3)_2CH.CONH_2$	0.025	...	...
15.	Potassium valeramide	$C_4H_9.CONHK$	123	287	1.8
11.	Valeramide	$C_4H_9.CONH_2$	0.5	...	...
22.	Potassium acetamide	CH_3CONHK	155	328	1.8
V.	Acetamide	CH_3CONH_2	0.9	...	...

TABLE II

THE CONDUCTIVITY OF OTHER ACIDS AND SALTS

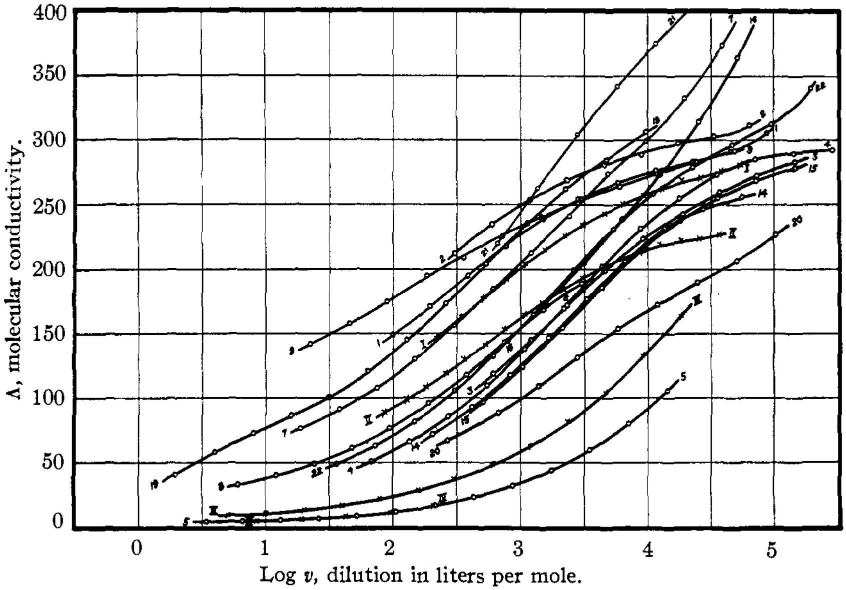
	Electrolyte	Formula	$\Lambda_{\log v = 3.0}$	Λ_{∞}	$10^4 K$
1.	Ammonium azide	NH_4N_3	227	291.5	15.0
2.	Sodium dicyanimide	$NaN(CN)_2$	249	305±3	17±3
8.	Monosodium ammono-aluminate	$NaAl(NH_2)_4$	155	227	14.0
9.	Sulfur nitride	S_4N_4	233	298	0.8
19.	Sodium cyanide	$NaCN$	230	349±2	0.88
12.	*o*-Nitrobenzamide	$NO_2.C_6H_4.CO.NH_2$	2	...	...
13.	*p*-Nitrobenzamide	$NO_2.C_6H_4.CO.NH_2$	0.5	...	...
17.	Dicyanodiamide	$(NC.NH_2)_2$	0.7	...	...
18.	Melamine	$(NC.NH_2)_3$	0.8	...	...
20.	Trisodium tricyanomelamine	$[NaN(CN)_2]_3$	100	...	...
21.	Tripotassium hydromelonate	$K_3C_9N_{13}$	244	...	...

Values of Λ at this same dilution for other acids and salts are given in Table II.

The dilution $\log v = 3.0$ was chosen because the values of Λ are perhaps better distributed in this region than in any other which includes as many curves.

Values of Λ_∞ and K could not be determined by the graphical method of Kraus and Bray with substances not binary electrolytes; and the use of this method with binary electrolytes of very low conductivity leads to unreasonably low values for Λ_∞, with correspondingly high values for the degree of dissociation and for K. Therefore, no attempt has been made to assign values to those substances.

The number assigned to a substance in the tables is the same as that which designates the curve for that substance in Fig. 1. The Roman numerals refer to substances measured by Franklin and Kraus.



×—Franklin and Kraus: I, Potassium *m*-nitrobenzenesulfonamide; II, *m*-Nitrobenzenesulfonamide; III, Mercury succinimide; IV, Cyanamide. ○—Smith: 1, Ammonium azide; 2, Sodium dicyanimide; 3, Succinimide; 4, Potassium succinimide; 5, Cyanamide; 7, Monosodium cyanamide; 8, Monosodium ammono-aluminate; 9, Sulfur nitride; 14, Potassium *iso*butyramide; 15, Potassium valeramide; 16, Dipotassium α-triphenylguanidine; 19, Sodium cyanide; 20, Trisodium tricyanomelamine; 21, Tripotassium hydromelonate; 22, Potassium acetamide.

Fig. 1.—The conductivity of acids and salts in liquid ammonia.

Discussion

On account of several considerations treated in the following paper, and because with many of the substances it is difficult to attain and maintain any considerable degree of purity, no great accuracy can be claimed for the results presented above. However, the least accurate of them is probably not in error by more than 5%.

It is immediately evident from Fig. 1 that only a few of the curves correspond more than approximately to the dilution law of Kraus and Bray.[5] Obviously many of the substances do not behave as simple binary electrolytes.

A point of inflection at about log $v = 4.5$ seems to be common to most of the curves in Fig. 1, at which point the slope again increases.

The curves as a group approach a value just under 300 for Λ_∞. The fact that in certain cases curves of nearly ideal form were obtained, serves as a check upon the manipulation as well as upon the accuracy with which the dilutions could be made.

The curves of the acid amides, the polymers of cyanamide and α-triphenylguanidine have not been plotted in Fig. 1 because of the extremely small values of Λ involved.

One might expect the acid amides to be poor conductors, since they are analogs of the weak carboxylic acids. Although they are formally dibasic acids, only one hydrogen atom can be replaced by potassium in liquid ammonia solution, and it is probable that the ionization of the second is immeasurably small. This is in harmony with the fact that their salts behave essentially as binary electrolytes.

As may be seen from Table I, the salt is in every case but one a better conductor than the corresponding acid. The difference, however, is small in case the acid is one of the so-called "strong" acids. Possibly since the "strong" acid is capable of forming a stable ammonium salt, it does so, and the conductivity measured is that of the ammonium salt. Succinimide, for example, is stable and has weak acid properties in water solution.

The mercury salt of succinimide (Fig. 1) runs true to the form of mercury salts in general, exhibiting a very low conductivity, as compared with most salts, in liquid ammonia, as in water.

In considering the ammono-carbonic acids,[10] it is interesting to note that the conductivity of both acids and salts, in so far as it has been measured, increases with de-ammonation of the acids, and decreases with polymerization. The most completely ammonated acid, and the more polymerized acids, are very poor conductors, while the monomolecular de-ammonation product, $HN(CN)_2$, is a strong acid even in water solution. This is in harmony with results reported by Madelung and Kern,[11] who show that dicyanimide, $HN(CN)_2$, is a strong acid in water solution, and that the triamer, tricyanomelamine, is a somewhat weaker

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[10] Franklin, This Journal, **44**, 486 (1922).

[11] Madelung and Kern, *Ann.*, **427**, 1 (1922).

one in practically the same ratio that has been found by the writer for the conductivity of their respective salts in liquid ammonia solution.

Sulfur nitride is noteworthy for the reason that it is a good conductor, and that the form of the curve is that of a binary electrolyte. Sulfur nitride has been shown[12] to be a mixed anammonide of ammono-sulfurous, and ammono-thiosulfuric acids. The possibility of ammonation, with the resulting formation of the above acids, is precluded by the small slope of the curve, and the absence of insoluble material. It is suggested that the substance dissociates into the two anammonous radicals which on ammonation would give the respective acids.

In conclusion, the writer wishes to express the most sincere thanks to Dr. E. C. Franklin for assistance, suggestions and advice which always have been readily available.

Summary

Conductivity measurements have been made in liquid ammonia solution at —33.5° on twenty-two substances.

In every case but one, the alkali metal salt of an acid proved to be a much better conductor than the acid itself.

The acid amides are very poor conductors, while their alkali metal salts are good conductors and behave as binary electrolytes.

The conductivity of the ammono-carbonic acids, and their alkali metal salts, increases with de-ammonation of the acid, and decreases with polymerization.

The graphical method of Kraus and Bray has been used to evaluate Λ_∞ and K, for twelve substances.

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A SOURCE OF ERROR IN CONDUCTIVITY MEASUREMENTS[1]

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In studying the literature on the measurement of electrolytic conductivity, one meets with statements of conclusions such as those of Washburn,[2] and of Schlesinger and Read.[3]

The former states, in substance, that a cell should be designed, in resistance capacity, for the particular solution the resistance of which is to be measured in it; and that only solutions having resistances varying

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[12] Unpublished observations made in this Laboratory.

[1] See preceding paper. Since this paper was first prepared, a paper by Randall and Scott, THIS JOURNAL, **49**, 636 (1927), has appeared which presents similar results.

[2] Washburn, THIS JOURNAL, **38**, 2431 (1916).

[3] Schlesinger and Read, *ibid.*, **41**, 1727 (1919).