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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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

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[12] Unpublished observations made in this Laboratory.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).

within rather narrow limits are suited for use with a cell having that particular resistance capacity.

The latter show that the value of the cell constant depends upon the resistance of the solution by means of which it is determined, and should be known for all resistances within the range of the measurements for which the cell is to be used.

The use by the writer[4] of a conductivity cell containing three electrodes provided a striking corroboration of the above conclusions, probably on account of the design of the cell and the method of making the measurements. The electrodes consisted of three co-axial cylinders open at the ends, two of which were concentric and close together, and the third, at some distance from the others, presented its edge to the edges of the others.

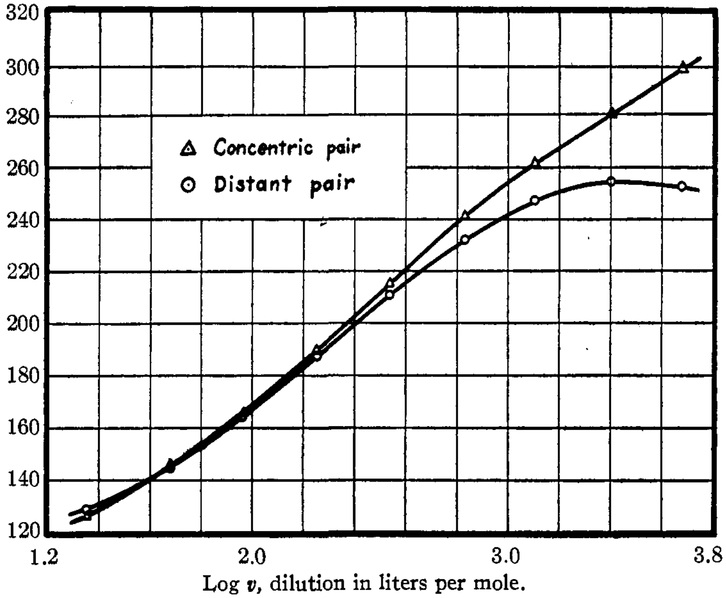

Fig. 1.—Conductivity curves of NH_4NO_3 in liquid NH_3, resulting from measurements of resistances of two cells formed by three electrodes in the same solution.

The measurements were made by diluting a measured volume of a solution of known concentration and resistance with successive measured portions of pure solvent, calculating the new concentration, and measuring the new resistance after each dilution.

Fig. 1 shows the ordinary conductivity curves of ammonium nitrate in liquid ammonia solution. The values of Λ for one of the curves were calculated from the measured resistances of the cell formed by the con-

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[4] See preceding paper.

centric pair of electrodes, and the values for the other curve, from the distant pair of electrodes, using the corresponding cell constants, determined as described in the preceding paper.

It is evident that as the resistance changes there is a change not only in the cell constants, but also in the ratio which they bear to one another, and that the values of Λ determined from the two cells are concordant only in that region of concentration and resistance in which the 0.02 M and 0.01 M potassium chloride solutions used to determine the cell constants also fall.

The intersection of the two curves (Fig. 1) occurs at a concentration near 0.02 M, and the resistances of the concentric and distant cells at the near-by plotted points were 17.73 ohms, and 3574 ohms, respectively.

The resistances of the same cells containing aqueous potassium chloride are set forth in Table I.

TABLE I

THE RESISTANCES AND RESISTANCE RATIOS OF THE CELLS CONTAINING THE AQUEOUS POTASSIUM CHLORIDE SOLUTIONS WITH WHICH THE CELL CONSTANTS WERE DETERMINED

KCl	Concentric cell		Distant cell	
aq.	R(ohms)	$R_{0.01\,M}/R_{0.02\,M}$	R(ohms)	$R_{0.01\,M}/R_{0.02\,M}$
0.01 M	43.80		8860	
		2.033		2.033
0.02 M	21.55		4357	

It is seen that the ratio of the resistances of these two solutions is the same for both cells. Thus the criterion of reliability imposed by Taylor and Acree[5] is complied with by these cells, notwithstanding their demonstrated unreliability, when used with solutions the resistances of which vary greatly from those of the potassium chloride solutions referred to in Table I.

In Fig. 2, values of the ratio of the resistance measured by means of the distant pair of electrodes to that measured by means of the concentric pair, are plotted against values of the logarithm of the resistance of the distant pair. The data were obtained from solutions of ammonium nitrate, and ammonium chloride, in liquid ammonia, and of potassium chloride in water.

It is evident that the resistance measured between the distant pair of electrodes increases more and more rapidly than that measured between the concentric pair, until the limiting resistance of the former is reached.

It had previously been found that when the walls of the cell vessel were wet with either water or ammonia, the order of magnitude of the resistance measured between either pair of electrodes never exceeded 10^6 ohms. Consequently, on diluting a solution, as the resistance meas-

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[5] Taylor and Acree, THIS JOURNAL, **38**, 2409 (1916).

ured between the distant pair of electrodes reaches this maximum value, any further dilution causes a sharp decrease in the ratio of the resistances of the two cells. This condition is evidenced in Fig. 2 by the break at *m*.

It might be expected that the ratio of the resistances of the two cells would be constant, if the various factors such as effective electrode area and effective distance between electrodes remain constant. Evidently this is not the case.

The conditions assumed by Washburn[2] as a basis for the design of conductivity cells are, among others, plane parallel electrodes having a relatively large surface area, and separated by a relatively small distance. These conditions obviously are not fulfilled in the case of the cell formed by the distant pair of electrodes arranged edge to edge.

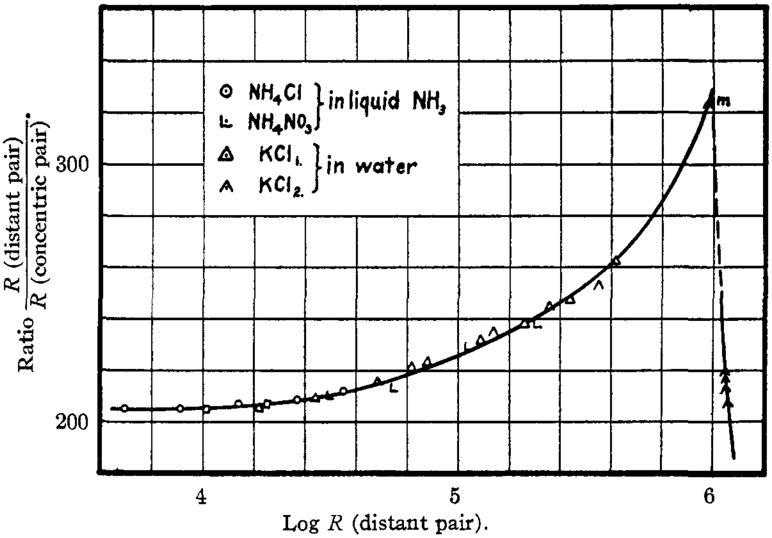

Fig. 2.—The effect of dilution on the ratio of the resistances of two cells formed by three electrodes in the same solution.

Obviously, unless the cell constant has been evaluated by means of suitably prepared solutions of known specific conductivity, which have resistances up to the highest value to be measured with the cell, all measurements made over a considerable range of resistances with a single cell are in error because the cell constant changes with resistance.

Especially liable to such error are such measurements as have been made by Franklin and Kraus,[6] and by Franklin,[7] Elsey,[8] the writer[4] and others, over a wide range of resistances by the process of dilution.

In this type of work it was the usual procedure to change from the

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[6] Franklin and Kraus, *Am. Chem. J.*, **23**, 277 (1900).

[7] Franklin, *Z. physik. Chem.*, **69**, 272 (1909).

[8] Elsey, THIS JOURNAL, **42**, 2454 (1920).

distant pair to the concentric pair of electrodes as soon as the resistance measured between the latter exceeded 100 ohms, in order to minimize the heating effect of the current at low resistances. So long as this procedure was followed, no discrepancy became apparent, since the change was made in the region in which the corresponding values of Λ were concordant.

Elsey[8] states that in case the change was made to the concentric pair of electrodes when their resistance was below 100 ohms, the heating effect of the current was noticeable, and that below 75 ohms there was a marked discrepancy between the corresponding values of Λ obtained from the two pairs of electrodes.

This discrepancy is indicated in Fig. 1 by the divergence of the curves for ammonium nitrate below their point of intersection, and is bound up with a shift in the bridge setting due to polarization, treated by Washburn,[9] rather than with the heating effect of the current, or a changing cell constant. A rising temperature would produce a change in the direction opposite to that of the error indicated. The effect of a changing cell constant in this region is undoubtedly negligibly small. The shift in the bridge setting resulting when capacity is used to sharpen the telephone minimum which had been rendered indeterminate by polarization in a concentrated solution, most marked in "set-up B,"[10] was in the direction of increasing resistance or decreasing values of Λ, and is probably the source of the discrepancy noted by Elsey.

Summary

The writer offers data in support of conclusions of Washburn and of Schlesinger and Read, showing that the use of a conductivity cell should be restricted to solutions having resistances of the same order of magnitude as those of the solutions used to determine the cell constant, on account of the fact that the cell constant changes with the resistance of the solution measured.

The effect of doubling the resistance of the solution between the concentric pair of electrodes of a three electrode cell was to slightly more than double the resistance of the solution between one of the concentric pair and the distant electrode. This effect amounted to about 5% at a dilution of one thousand liters per mole, and increased with dilution up to the highest resistance that could be measured between the distant pair of electrodes.

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[9] Ref. 2, p. 2458.

[10] (a) Ref. 3. (b) The usual bridge set-up with the alternating current connected to the ends of the slide wire.