THE ELECTRICAL CONDUCTIVITY OF METHYLAMINE SOLUTIONS.

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Since methylamine has been shown to possess a rather wide solvent power,[1] and to give solutions which in some cases are possessed of marked electrical conductivity,[2] it has been deemed worth while to extend the work of Gibbs on the properties of methylamine, to a quantitative study of the electrical conductivities of the solutions. The plan had been formulated of making measurements on a selected list of solutions, chosen to cover the field as well as possible, but as an unfortunate result of the earthquake of last April, the investigation was brought to a sudden close just as the work of making the measurements was well under way. It has been the expectation of the authors to take up again this investigation and finish a rather extended series of observations before publishing, but as a result of the junior author's transferring his field of activities to the Philippines, it has been determined to publish the data so far obtained.

Description of the Apparatus, Method of Manipulation.—The apparatus employed was, in principle, essentially the same as that used by Franklin and Kraus,[3] in their measurements of the conductivity of liquid ammonia solutions, with such modifications as the nature of the solvent seemed to require.

A is a steel cylinder containing the stock of methylamine. C is a filter tube which is introduced into the train for the purpose of removing any solid impurities which might be carried over with the gas.[4] B is a manometer used as an aid in regulating the flow of gas. D is a receiver into which the gas is condensed and retained until the pure liquid is required in the conductivity cell. E is the conductivity cell with its connections. E^1 is the constant temperature bath of ice and water. F is a receptacle for receiving the solution after removal from the conductivity cell. Before beginning a series of measurements this tube is evacuated through the stop-cock, S^{10}, and is kept cool by a bath of liquid ammonia. After a series of measurements is finished, F is removed and sealed before the blow pipe, thus permitting the operator to recover the expensive solvent. G is a pressure regulator devised for the purpose of regulating the boiling point of the solution in the conductivity cell, E, to the temperature of the bath, E'. The tube from the stop-cock, S^7, delivers the gas through pin hole openings under the mercury column, G, which latter may be adjusted to any desired height. The methylamine which escapes from the conductivity cell by way of this pressure

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[1] Gibbs, This Journal, **28**, 1395.

[2] Gibbs, loc. cit., and Franklin and Kraus, Am. Ch. J., **24**, 90.

[3] Am. Ch. J., **23**, 277.

[4] Vide Franklin and Kraus, Am. Ch. J., **23**, 278.

regulator is condensed in the cell H, which at the end of a series of measurements is removed and sealed, thus effecting a saving of the methylamine. Liquid ammonia for condensing the methylamine in the receptacles D, F and H, is delivered from a cylinder of the commercial liquid through the tube I. Ammonia gas is carried to a carboy of water through the tube I'. Pure, dry hydrogen for stirring the solution and removing it from the conductivity cell is delivered to the apparatus under pressure at the stopcocks S^6 and S^9. It is to be noted that the methylamine after leaving the steel cylinder and the short piece of lead tubing leading from it, comes in contact only with the glass of the apparatus, the platinum electrodes of the conductivity cell, and the hydrogen used for stirring the solution, for the various glass portions of the apparatus are sealed together by means of flexible joints made by drawing the tubing to capillaries. The hydrogen which comes in contact with the solutions is produced by the electrolytic decomposition of dilute sulphuric acid in the tube, K, (Fig. 2) and is purified by passing through the three wash bottles L_1, L_2 and L_3 (containing in L_1 and L_2 an aqueous solution of potassium hydroxide and pyrogallol, and in L_3 concentrated sulphuric acid), and the three tubes, M_1, M_2 and M_3, containing respectively soda-lime, calcium chloride and phosphorus pentoxide. The hydrogen pressure is shown by the manometer N.

With this preliminary survey of the apparatus, it will be easy to follow the details of a series of measurements. Operations are begun by drawing liquid ammonia into the Dewar tubes, D, F and H. The valve of A is then opened and methylamine is distilled into the receptacle D, whence it is run through the stop-cock, S^1, into the conductivity cell E, and thence, for the purpose of washing the cell and the connecting tubes,— a portion through the tube, E^3, and the stopcocks, S^3, S^5, S^8, and S^{10}; the remainder through the tube, E, and the stopcocks, S^7, S^5, S^8 and S^{111}, —to the cell, F. Fresh solvent is then run into the conductivity cell in sufficient quantity to cover well the bottom of the cell, after which a weighed quantity of the solute, contained in the platinum spoon, E^9, is introduced through the tubulure, E^{10}. Any particles of the solute remaining attached to the spoon or to to the sides of the tube, E^6, are then washed into the cell by drawing additional methylamine from the receiver, D. The introduction of solvent is continued until the glass pointer, E^1 is just submerged. The solution is then stirred by means of a stream of hydrogen through the stopcocks, S^9, S^5, S^7, and the capillary tube, E, until the solution is homogeneous and the surface of the solution is adjusted accurately on the pointer. The passage of hydrogen through the solution and thence by way of the stopcock, S^6 to the receiver, H, carries methylamine vapor with it, thus enabling the operator to bring about the desired adjustment to the pointer. Since the capil-

lary tubes, E and E³, have an appreciable volume, the adjustment of the surface of the solution to the pointer must take place with the stopcocks, S⁵ and S⁷, set to give gaseous connection between these and the neck of the cell at E. The level of the solution within the capillaries will then come into equilibrium with that of the contents of the cell. Corrections for difference in capillarity between methylamine and water, which latter was used in calibrating the cell, have not been made. The resistance of the solution between the electrodes, E, is then measured by the familiar method of Kohlrausch, connection with the exterior being made through the tubes, E², filled with mercury. An aliquot part of the solution is then removed by turning hydrogen under pressure on to the surface of the solution through S⁶, after setting the stopcocks S⁵, S⁸, S⁹ and S¹⁰, to deliver into the cell, F and allowing the solution to flow out until the tip of the "J" tube, E³, is just uncovered. Fresh solvent is then introduced, and the operations described above are repeated until the desired dilution is reached.

The Solvent.—The methylamine used in this investigation was a part of a kilogram obtained from Kahlbaum.[1] It was purified by distillation after long contact with metallic sodium to remove any water and ammonia, which might have been present. No tests were made to prove the purity of the solvent, although its essential purity is to be assumed from the observed constancy of its boiling point[2] and the high specific conductivity of the purified liquid. Methylamine of a specific conductivity, $\kappa = 0.7 \times 10^{-6}$ to 1.2×10^{-6}, was easily obtained in the cell of the conductivity apparatus. No attempt has been made to determine the conductivity of the purest methylamine.

Constants and Units.—The units of Kohlrausch have been used.[3] The resistance capacity of the cell at 20.3° was found by means of a fiftieth normal solution of potassium chloride[3] to be 0.1886 Kohlrausch units.

The volumes of the conductivity cell, determined by weighing at 16°, the amount of water required to fill the cell to the respective glass pointers, are for the points E³ and E⁴, 3.92 cc. and 7.83 cc. respectively.

Numerical Results.—In the following tables are given the results of measurements on the five substances studied. The dilutions are expressed in liters per gram molecule, and are denoted by $\varphi/1000$. The molecular conductivities are denoted by the symbol Λ.

TABLE 1.—*Potassium Iodide.*

$\phi/1000$	Λ	$\phi/1000$	Λ
21.8	12.2	174.	17.9
43.5	12.2	348.	23.4
87.0	14.0		

[2] Cf. Gibbs, This Journal, 27, 859.
[3] Kohlrausch and Holborn: Leitfähigkeit der Elektrolyte, p. 77.

TABLE 2.—*Potassium Iodide.*

13.5	13.1	428.	24.4
27.0	12.4	856.	32.7
53.9	12.6	1710.	44.2
107.5	14.4	3420.	64.5
214.5	18.4		

TABLE 3.—*Acetamide.*

12.1	0.031	11.8	0.030
5.9	0.028		

TABLE 4.—*Benzenesulphonamide.*

29.6	0.56	59.1	0.74

TABLE 5.—*Metanitrobenzenesulphonamide.*

16.8	5.64	33.5	5.40

TABLE 6.—*Metanitrobenzenesulphonamide.*

13.4	5.15	106.6	6.88
26.7	4.81	213.0	8.73
53.4	5.40	425.5	15.5

TABLE 7.—*Silver Nitrate.*

0.66	25.9	10.5	22.1
1.32	35.3	21.1	19.6
2.68	30.8	42.1	19.4
5.28	26.4		

TABLE 8.—*Silver Nitrate.*

0.61	27.0	38.8	17.8
1.22	33.3	77.5	22.2
2.44	31.5	154.8	26.2
4.87	26.9	309.0	33.3
9.72	22.8	618.0	44.8
19.4	20.4		

TABLE 9.—*Silver Nitrate.*[1]

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0.244	8.14	0.868	30.4
0.362	17.2	1.28	31.4
0.581	26.4		

Graphical Representation of the Results.—In the accompanying plate are plotted the results obtained for silver nitrate, potassium iodide and metanitrobenzenesulphonamide in methylamine together with a curve representing the behavior of silver nitrate in amylamine.[2] The molecular conductivities are plotted as ordinates, the logarithms of the dilutions as abscissas. The logarithms of the dilutions rather than the dilutions themselves, or even the cube roots of the dilutions, are used for the reason that this method gives a better distribution of points in the more concentrated solutions.

[1] This set of measurements was made with a cell of the following constants: Volume to point 1, 2.98 cc.; point 2, 4.43 cc.; point 3, 7.11 cc.; point 4, 10.63 cc.; point 5, 15.66 cc. The cell constant was, 0.1905.

[2] Kahlenberg and Ruhoff, J. Phys. Chem., 7, 254.

PLATE I.
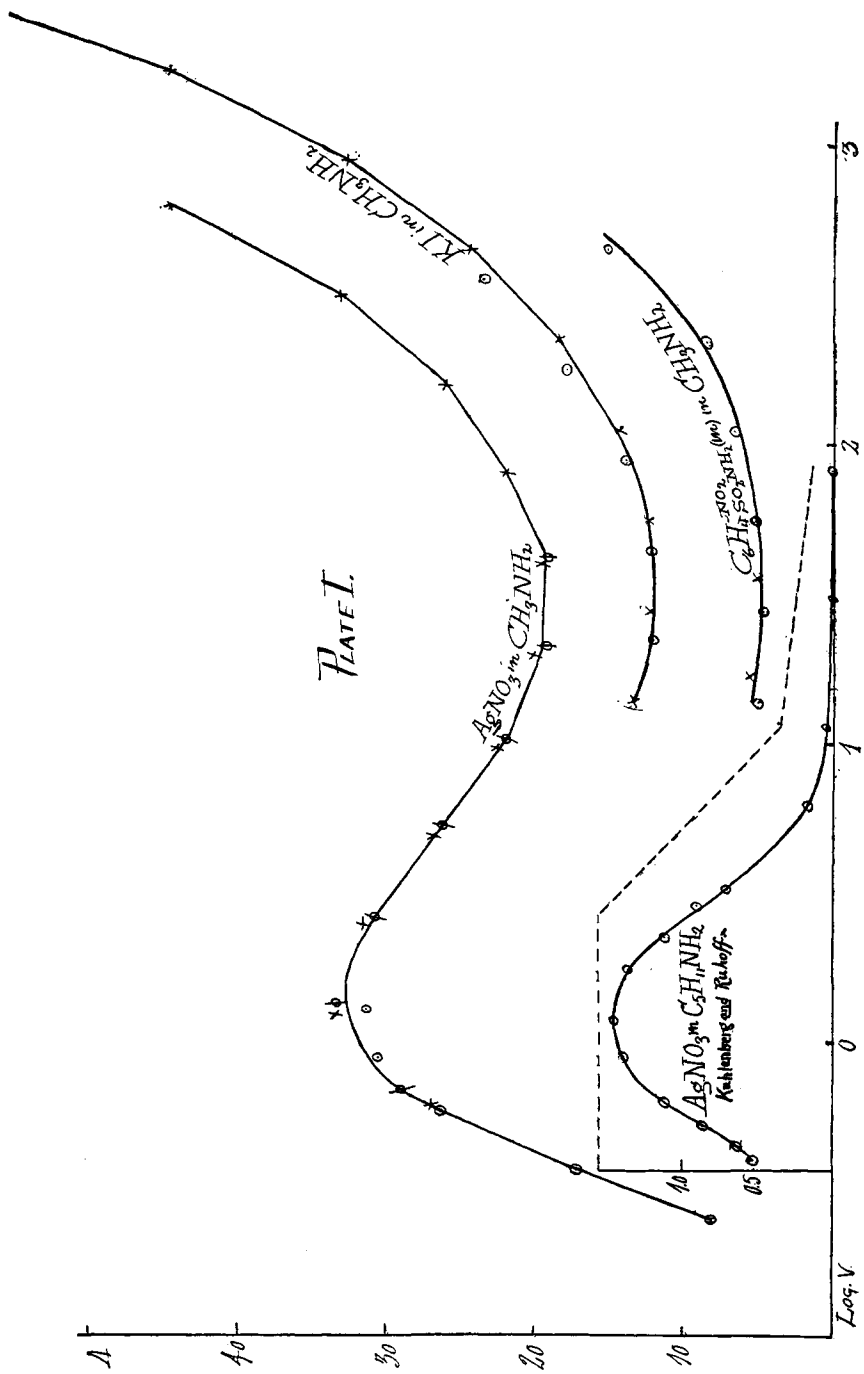
Discussion of Results.—It has been noted that certain non-aqueous solutions not infrequently exhibit the phenomenon of diminishing molecular conductivity with increasing dilution.[1] In other cases[2] the molecular conductivity falls to a minimum, after which with further dilution it rises continuously. Lewis[3] has found that the molecular conductivity of potassium iodide in liquid iodine at first increases with the dilution to be followed by a striking fall. A similar behavior of silver nitrate in amylamine has been observed by Kahlenberg and Ruhoff[4].

As the curve for silver nitrate in methylamine in the above plate shows, the authors have now found that a methylamine solution of silver nitrate combines the earlier observed effects with those described by Lewis. The behavior of Lewis' solution is represented by the first portions of our curve, that of the solutions studied by Kablukoff, Euler, and MacIntosh and Archibald, by the middle portions, while the latter portions coincide in their graph with the more dilute solutions of the cyanides in liquid ammonia as observed by Franklin and Kraus.

What, in the light of the theory of electrolytic dissociation, the explanation for the unique behavior of our methylamine solutions may be, it is difficult to say. Steele, McIntosh and Archibald[5] explain the behavior of solutions in the liquefied halogen acids by assuming the formation of polymeric forms of the solute, or by the union of more than one molecule of the solute with more or less of the solvent to form aggregates which are in equilibrium on the one hand with their original constituents and on the other with the products of their electrolytic dissociation. They show that by this hypothesis they may explain the observed falling molecular conductivity with increasing dilution. It is not obvious, however, how this conception may be extended to account for the maximum and minimum of our curve, or to follow the curve to concentrations above and below these points.

According to Walden[6] the normal conductivity curve is shown by solutions which are essentially physical mixtures, while the abnormal curves are the result of chemical changes either in the solvent alone or between the solvent and solute. He accordingly explains the increase of conductivity of certain relatively concentrated solutions in acetaldehyde on the assumption that under these conditions, the normal dissociation obscures

[1] Kablukoff : Z. physik. Chem., 4, 429; Euler, Ibid., 28, 623; Kahlenberg and Ruhoff, J. phys. Chem., 7, 254; Platinkoff, Z. physik. Chem., 48, 220; Sakur, Ber., 35, 1242; Walden, Z. physik. Chem., 43, 385, and 54, 141; McIntosh and Archibald, Phil. Trans. A., 205, 120.

[2] Walden, loc. cit. Franklin and Kraus, This Journal, 27, 215.

[3] Proc. Acad. Arts and Sci., 41, 419.

[4] Loc. cit.

[5] Loc. cit., p. 148.

[6] Z. physik. Chem., 54, 145.

the chemical effects. The molecular conductivity therefore increases with the dilution and reaches a maximum. On further dilution, "aldo-lytic" decomposition, giving rise to poorer electrolytes, becomes conspic-uous with the result that continued dilution brings with it a depression of the molecular conductivity to a minimum beyond which the normal dissociation of the products of aldolysis gives a conductivity curve rising with further increase of the dilution, in the familiar manner, to a maxi-mum. While such an hypothesis may account for the observed behavior of aldehyde solutions, it is not clear how a similar explanation may be applied to solutions of silver nitrate in methylamine. In any event, in view of the behavior of silver nitrate in ammonia solutions,[1] it seems impossible to assume "aminolytic decomposition" in these methylamine solution.

Lewis[2] has proposed an hypothesis, one also touched upon by Frank-lin and Kraus,[3] which, as it seems to the authors, may account for the observed behavior of our solutions. The hypothesis, modified to include the present case, may be outlined as follows : Salts dissolved in a weak ionizing solvent may be expected to give solutions in which the self-ionization of the salt shows itself conspicuously.[4] Methylamine, such a solvent, dissolves silver nitrate abundantly, forming solutions, which, when very concentrated, are possessed of a high degree of viscosity. The conductivity of the most concentrated solutions, in that they ap-proach the condition of the melted salt, is therefore, for the most part, due to the autoionization of the salt. As the solution is diluted its viscosity diminishes rapidly with the result that the increasing speed of the ions, which has been shown by Walden[5] to accompany diminishing viscosity, more than counteracts the effect of diminishing self-ionization which may be assumed to accompany the dilution, and which of itself would cause a diminution of the conductivity. The observed conduc-tivity therefore increases. The viscosity, however, falls off at a rapidly diminishing rate as the dilution increases, so that after a time the oppos-ing effects of viscosity and self-ionization balance each other, when a maximum of molecular conductivity is reached. From this point on, for a time, increasing dilution is most conspicuous in its effects on the auto-ionization of the salt. The rate at which the autoionization diminishes becomes smaller as the dilution continues to increase with the result that, beyond a certain point, the dissociating action of the solvent be-comes conspicuous as the curve passes through the minimum and then ascends after the familiar manner of salts in aqueous solution.

[1] Cf. Franklin, This Journal, **27**, 833.

[2] Proc. Am. Acad. Arts and Sci., **41**, 427.

[3] This Journal, **27**, 216.

[4] Obviously, this cannot be true in all cases. Cf., for example, Kahlenberg's solutions of copper oleate in benzene (J. phys. Chem., **6**, 1).

[5] Z. physik. Chem., **55**, 207.

This seems to give a fairly satisfactory qualitative explanation of the conductivity relations of silver nitrate in methylamine solution. It will be noticed that potassium iodide and metanitrobenzenesulphonamide in methylamine, and the cyanides of the heavy metals in liquid ammonia,[1] give very similar curves, excepting that they have not yet been continued into the more concentrated solutions.

Summary.

It is shown that methylamine, a liquid of rather wide solvent power, is also a good electrolytic solvent.

The electrical conductivity of a short series of substances in methylamine have been measured.

Silver nitrate in solution in methylamine has been found to give a unique conductivity curve for which a tentative explanation is offered.

STANFORD UNIVERSITY.
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THE VAPOR PRESSURE OF SULPHUR AT LOW TEMPERATURES.
BY HIPPOLYTE GRUENER.

Matthies[2] has recently determined the vapor pressure of sulphur at temperatures between 200° and 400°. The vapor pressure at lower temperatures, varying from 50° to 120°, was determined by the writer by passing known amounts of a dry inert gas over sulphur heated to the desired temperature. The sulphur volatilized was collected on the walls of a cold tube and from its weight the pressure was calculated. Independently a series of determinations was undertaken at the boiling point of water. The vapor pressure in these determinations was calculated from the amount of sulphur volatilized with known amounts of water. Although the agreement among the individual determinations of this second method was not very close, the mean result was the same as that obtained by the first method.

For the first method sulphur was enclosed in a U-tube with ground connections. This enabled the exit tube, on the cold walls of which the sulphur was deposited, to be removed and weighed. The loss of weight upon heating the tube in a current of air gave the weight of the sulphur. The sulphur was used in the form of small crystals, obtained by stirring melted sulphur as it solidified, and this form was well adapted to the purpose. The total length of the column was 20 to 25 cm., its diameter 1.5 cm., and its weight about 25 g. The U tube was placed in a copper box surrounded by water or a solution of calcium chloride. The temperature was maintained constant by a gas regulator, except at 100°,

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[1] This Journal, **27**, 215.
[2] Phys. Z., **7**, 395.