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.
California, June, 1907.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF ADELBERT COLLEGE.]
# 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°,

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

when it was maintained by the boiling of the water.   The variations of temperature were averaged by frequent readings, it being assumed that for small intervals the curve of the vapor pressure is a straight line.

The gases used were carbon dioxide, hydrogen, and at the lowest temperatures, air.   Hydrogen was used only in one determination, namely at 100°; there was no trace of any reaction with the sulphur, and the results were the same as those obtained with carbon dioxide.   Air was used with determinations at 100° and below, but only the determinations at the lowest temperatures are included among the main results.   The others will be discussed separately.   The flow of the gas was regulated by passing it through a capillary tube of the proper proportions and by the pressure produced in the generators.   The carbon dioxide and hydrogen were prepared in the usual way and dried with sulphuric acid.   The determinations were frequently made in pairs, which fact facilitated the operations and supplied a test for the saturation of the gas, for in each pair of determinations all the conditions were the same, except the rate of passing the gas.   The amount of gas was measured by an experiment meter at the end of the system.

The saturation of the gas was established in two ways.   By one method two U-tubes, filled with sulphur, were connected in series and with all the other conditions the same as in the regular experiments, the loss of sulphur was investigated.   The results were as follows :

TABLE 1.

|  | Amount of Gas. L. | Duration of Expt. Days. | Rate of Gas. L per D. | Loss of S. 1st tube. grams. | Loss of S. 2nd tube. grams. | S. deposited at end. grams. |
|---|---|---|---|---|---|---|
| A | 103 | 7.5 | 14 | 0.0096 | 0.0001 | 0.0096 |
| B | 175 | 7.5 | 23 | 0.0165 | 0.0003 | 0.0159 |

In each case the loss of sulphur, within the limits of error of the experiment, was confined to the first tube.

Saturation was further assured by varying the rate of the flow of the gas within somewhat wide limits, when no corresponding wide limits of variation in the loss of sulphur was observed, as shown in Table 2.   The larger or smaller results shown in this table are seen to have no dependence upon the different rates of passing the gas.

TABLE 2.

| No. of Expt. | Temp. C. | Duration. Days | Am't. Gas. L. | Rate. L. per D. | Deviation of rate from mean. Per cent. | Corresponding vapor pressure. mm. | Deviation of vapor pressure from mean. Per cent. |
|---|---|---|---|---|---|---|---|
| 7 A | 100° | 9.8 | 207 | 21.1 | 4.5+ | 0.0076 | 2.0+ |
| B | 100° | 9.8 | 173 | 17.6 | 12.8— | 0.0074 | 0.6— |
| C | 100° | 12.7 | 231 | 18.2 | 9.9— | 0.0074 | 0.6— |
| D | 100° | 12.7 | 200 | 15.7 | 22.3— | 0.0075 | 0.6+ |
| E | 100° | 5.8 | 141 | 24.3 | 20.3+ | 0.0074 | 0.6— |
| F | 100° | 5.8 | 140 | 24.2 | 19.8+ | 0.0074 | 0.6— |

Mean 20.2          Mean 0.00745

The same check was applied to most of the other determinations. When this was omitted, reliance was placed on the similarity to comparable determinations when the check was applied.    Determinations 3, 4, 5. 6 and 10 were thus checked as shown in Table 3, and the differences in the results obtained, are either negligible or of such irregularity of amount and sign, that they cannot be attributed to lack of saturation.

TABLE 3.

| No. of Expt. | Temp. | Duration Days | Am't of gas L. | Rate per day L. | Deviation from mean rate. Per cent. | Corresponding vapor pressure mm. | Deviation of vapor pressure from mean. Per cent. |
|---|---|---|---|---|---|---|---|
| 3 A | 70° | 4.8 | 177 | 37 | 23 -- | 0.00045 | 5 — |
| B | 70° | 4.8 | 181 | 38 | 27 --- | 0.00050 | 6 -- |
| C | 70° | 11.8 | 183 | 15 | 50 — | 0.00047 | 1 — |
| 4 A | 80° | 5.7 | 148 | 26 | 24 — | 0.0010 | 10 — |
| B | 80° | 5.7 | 146 | 26 | 24 -- | 0.0011 | 0 |
| C | 80° | 10.9 | 115 | 11 | 48 | 0.0012 | 10 · |
| 5 A | 90° | 3.7 | 83 | 22 | 17 | 0.0039 | 4 · |
| B | 90° | 3.7 | 81 | 22 | 17 -- | 0.0050 | 4 -- |
| C | 90° | 11.9 | 140 | 12 | 34 -- | 0.0026 | 8 — |
| 6 A | 95° | 5.0 | 129 | 26 | 24 -- | 0.0044 | 3 --- |
| B | 95° | 5.0 | 108 | 22 | 4 + | 0.0041 | 4 — |
| C | 95° | 8.0 | 120 | 15 | 28 -- | 0.0043 | 1 ·· |
| 10 A | 110° | 5.0 | 72 | 14 | 15 --- | 0.0137 | 1 -- |
| B | 110° | 5.0 | 95 | 19 | 15 -- | 0.0154 | 1 --- |

The rates (liters per day) in other determinations were :

Expt. 1, 50°, rate = 46 ; Expt. 2, 55°, rate = 35 ; Expt. 9, 105°, rate = 13 ; Expt. 11, 120°, rate = 11.

It is certain from the following considerations that the volatilized sulphur was completely redeposited in the exit tube.

1. The temperature of the warmest portion of this tube was 40°, and of the colder portion 30°. The vapor pressure corresponding to this temperature is 0.00001 mm. involving a maximum loss of 0.03 milligram for each determination.

2. The layer of sulphur was deposited within narrow limits, with no sign of it in the more distant portions of the tube.   When a bend in the tube was kept in ice-water during the entire progress of one determination, there was noticed a just discernible breath of sulphur, far too small in amount to affect the results.

The determinations of the vapor pressure are shown in Table 4.

More attention was paid to the vapor pressure at 100° than to that at any other temperature.  This was determined for prismatic sulphur by four determinations with carbon dioxide, and two determinations with hydrogen.  The prismatic condition was assured by crystallizing the sulphur as above indicated, and introducing it into the chamber heated to 100° within 30 minutes from the time of its cooling.  The six determi-

## TABLE 4.

| No of Expt. | Gas used | Temp. | | Volume of gas at meter. | Temp. at meter. | Amount of Sulphur volatilized. grams. | Calculated vapor-pressure. mm. | Temp. in round nos. | Vapor-pressure corresponding. mm. | Mean. mm. | Vapor-pressure calculated from formula. mm. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Air | 48.6 | | 199.53 | 18.0 | 0.00021 | 0.00007 | 50° | 0.00008 | | 0.00008 |
| 2 | Air | 56.1 | | 266.02 | 17.2 | 0.00055 | 0.00015 | 55° | 0.00013 | | 0.00012 |
| 3 | $CO_2$ | 68.8 | | 183.06 | 19.0 | 0.00110 | 0.00043 | 70° | 0.00047 | | 0.00049 |
| 4 | $CO_2$ | 81.1 | | 114.57 | 15.5 | 0.00216 | 0.0013 | 80° | 0.0012 | | 0.0012 |
| 5 | $CO_2$ | 91.0 | | 139.73 | 14.8 | 0.0058 | 0.0029 | 90° | 0.0026 | | 0.0030 |
| 6 | $CO_2$ | 94.9 | | 119.52 | 15.0 | 0.0072 | 0.0042 | 95° | 0.0043 | | 0.0047 |
| 7 A | $CO_2$ | 99.7 | Prismatic Sulphur | 207.10 | 23.4 | 0.0212 | 0.0074 | 100° | 0.0076 | | |
| B | $CO_2$ | 99.7 | | 172.61 | 22.8 | 0.0173 | 0.0072 | 100° | 0.0074 | | |
| C | $CO_2$ | 99.6 | | 230.86 | 22.7 | 0.0231 | 0.0072 | 100° | 0.0074 | | |
| D | $CO_2$ | 99.6 | | 199.74 | 22.1 | 0.0203 | 0.0073 | 100° | 0.0075 | 0.00745 | 0.00745 |
| E | H | 99.8 | | 140.90 | 23.3 | 0.0142 | 0.0072 | 100° | 0.0074 | | |
| F | H | 99.8 | | 140.20 | 22.5 | 0.0142 | 0.0072 | 100° | 0.0074 | | |
| A | $CO_2$ | 99.7 | Rhombic Sulphur | 242.88 | 23.0 | 0.0235 | 0.0069 | 100° | 0.0071 | 0.0072 | |
| B | $CO_2$ | 99.7 | | 173.05 | 22.3 | 0.0171 | 0.0071 | 100° | 0.0073 | | |
| 9 | $CO_2$ | 104.4 | | 73.76 | 21.3 | 0.0103 | 0.0100 | 105° | 0.0104 | | 0.107 |
| 10 A | $CO_2$ | 109.8 | | 71.83 | 21.4 | 0.0136 | 0.0135 | 110° | 0.0137 | 0.0136 | 1.0154 |
| B | $CO_2$ | 109.8 | | 95.05 | 20.8 | 0.0176 | 0.0132 | 110° | 0.0134 | | |
| 11 | $CO_2$ | 120.5 | | 55.64 | 21.3 | 0.0233 | 0.0351 | 120° | 0.0339 | | 0.0320 |

Calculated vapor pressure for 20° = 0.000005 ; for 30° = 0.000013 ; for 40° = 0.00003 ; for 60° = 0.00020.

nations agreed fairly closely, ranging from 2 per cent. above to 0.6 per cent. below the mean.

Under experiment 8 are given the results for rhombic sulphur. These determinations were made with crystals like those used in the above experiment, converted into the rhombic form by standing for days. The results may, however, be taken only as qualitative, since the point in time was not determined when the temperature of 100° was influential in reproducing the prismatic form.

The values for the vapor pressure for the temperatures above, 100°, are probably not so accurate as for this temperature, inasmuch as the apparatus was not so well suited for the purpose. The bath surrounding the warm chamber consisted of a calcium chloride solution. At 120° the sulphur was placed in a tube about 30 cm. long and inclined at a small angle, so that the gas passed in slow bubbles through the liquid sulphur.

When the values of the logarithms for the vapor pressure at and below 100° are plotted, they lie near a straight line whose prolongation, however, does not include the higher values. From this a general expression may be obtained for the vapor pressure of sulphur :

$$p = a\, b^t$$

For temperatures from 50° to 100°, log. $a = 7.9225$, log. $b = 0.0395$, $t =$ temperature centigrade. For temperatures somewhat above 100°, log. $a = \overline{3}.8725$, log. $b = 0.0316$, $t =$ temperature centigrade — 100. The values for the vapor pressures thus calculated are given in the last column of Table 4.

It seemed desirable to try another gas besides carbon dioxide and hydrogen. Dry air was used in a series of determinations at 100° and below. It was evident from preliminary trials that the sulphur was oxidized only slightly, if at all, and this was confirmed by the results shown in Table 5. These determinations were a repetition of those of Table 4, except that air was used instead of carbon dioxide.

TABLE 5.

| No. of Expt. | Corrected temp. | Amount of sulphur deposited in exit tube for 100 L gas. g. for CO₂ | for air. | Corresponding vapor pressure. for CO₂. | for air. | Amount of sulphur oxidized (as determined by amount of SO₂). |
|---|---|---|---|---|---|---|
| 3 | 70° | 0.00057 | 0.00057 | 0.00047 | 0.00047 | very slight |
| 4 | 80° | 0.0014 | 0.0012 | 0.0012 | 0.0011 | very slight |
| 5 | 90° | 0.0030 | 0.0034 | 0.0026 | 0.0030 | |
| 6 | 95° | 0.0048 | 0.0048 | 0.0043 | 0.0043 | very slight |
| 7 | 100° | 0.0083 | 0.0078 | 0.0075 | 0.0071 | 0.00033 g. |

The results show that at 100°, the oxidizing action of dry air upon sulphur in this form is very slight, yet it is enough to vitiate the results. (The odor noticeable when sulphur is heated to this temperature is that of the volatilized sulphur, not of sulphur dioxide.) At temperatures below 100°, the loss cannot be determined, the results being apparently independent of this condition. This was confirmed by submitting sulphur in the same form to the action of dry oxygen at these temperatures

and determining the sulphur dioxide formed. Only at 100° could an appreciable amount be observed, namely, that corresponding to an oxidation of 0.0001 g. sulphur per day of contact.

During the progress of some experiments recently performed in this laboratory, it was found desirable to know the possible loss of sulphur when water holding it in suspension was evaporated. This suggested a method for determining the vapor pressure of sulphur at 100°. Accordingly, water with sulphur in suspension was boiled, and the steam passed over a column of sulphur in the form of shot. The column was 50 cm. long, 1.5 cm. in diameter, and contained about 100 g. of sulphur. This sulphur column was surrounded by a jacket through which steam was passed to maintain the sulphur at the proper temperature. The steam which had passed over the sulphur column was condensed, and the sulphur contained in the distillate determined. It was weighed as barium sulphate after oxidation with hydrogen peroxide in alkaline solution.

The only guaranty of the saturation of the steam was the uniformity òf results obtained, although the rate of passing the steam over the sulphur was varied. The steam escaping from the flask in which the water was boiled with sulphur was evidently not saturated, but when it was passed in addition over this column of sulphur, the results became reasonably uniform. The rate varied in eleven determinations from 4.4 g to 0.6 g. water distilled per minute. If these be roughly divided into those whose rate is greater than 2 g. per minute and those whose rate is less than 2 g. per minute, it developes that the more rapid average 2.3 per cent. above the mean, while the slower average 1.6 per cent. below. There were values, however, in both cases, with the opposite sign. One result, number 9, differed so much from the others that it is not included in the first summary, although no reason is apparent for this discrepancy unless it be that the rate of distillation was slower than that of the other experiments. The results are shown in Table 6.

TABLE 6.

| No. of Expt. | Am't water distilled. Grams. | Am't S found. Grams. | Am't S per 100 g. water. Grams. | Deviation from mean. Per cent. |
|---|---|---|---|---|
| 1 | 127.41 | 0.0184 | 0.0145 | 7.9+ |
| 2 | 132.30 | 0.0185 | 0.0140 | 4.2+ |
| 3 | 122.64 | 0.0159 | 0.0130 | 3.3— |
| 4 | 141.86 | 0.0198 | 0.0139 | 3.4+ |
| 5 | 54.52 | 0.0076 | 0.0139 | 3.4+ |
| 6 | 116.12 | 0.0151 | 0.0130 | 3.3— |
| 7 | 83.50 | 0.0113 | 0.0135 | 0.5+ |
| 8 | 30.39 | 0.0039 | 0.0130 | 3.3— |
| 10 | 40.42 | 0.0051 | 0.0126 | 6.3— |
| 11 | 94.52 | 0.0124 | 0.0131 | 2.5— |
| 12 | 65.62 | 0.0087 | 0.0133 | 1.0— |
| | | Mean | 0.01344 | |
| 9 | 48.83 | 0.0053 | 0.0108 | 18.0— |
| | | Mean | 0.01322 | |

The temperature was taken as that of the boiling point of water, 99.3° at the mean barometric pressure, 740.7 m.m., for the days during which the experiment was performed. Number 9 is omitted from the calculations. Using the mean of the other eleven determinations for the calculation, the vapor pressure for this temperature was found to be 0.0070 mm. The vapor pressure calculated from the results of the other method for this temperature is 0.0070 mm., which agrees with this result. If determination 9 be included the vapor pressure calculated is 0.0069, a result not materially different from the other.

Cleveland, Ohio.

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# IONIZATION OF WATER AT 0°, 18° AND 25° DERIVED FROM CONDUCTIVITY MEASUREMENTS OF THE HYDROLYSIS OF THE AMMONIUM SALT OF DIKETO-TETRAHYDROTHIAZOLE.

By C. W. Kanolt.

## 1.  Plan of the Investigation.

The degree of ionization of water at ordinary temperatures has been determined by a number of different methods—namely (1) from the hydrolysis of sodium acetate[1] as derived from the rate at which it saponifies an ester,[2] and from that of aniline acetate[3] as derived from conductivity measurements[4]; (2) from the rate of saponification of methyl acetate by water itself;[5] (3) from the electromotive force of the alkali-acid hydrogen cell;[6] and (4) from the conductivity of the purest water thus far obtained.[7] Although these entirely independent measurements have all given for the ionization of water values of the same order of magnitude and have thereby furnished one of the most striking evidences of the ionic theory, yet for none of the values so obtained can any considerable percentage accuracy be claimed. It has therefore seemed advisable to make a special study of this constant at ordinary temperatures by the same method that has been employed at higher temperatures by Noyes and Kato and by Sosman,[8] that is, by measuring the increase

[1] Arrhenius, Z. physik Chem., 11, 822 (1893).

[2] Shields, Ibid., 12, 184 (1893).

[3] Arrhenius, Ibid., 5, 19 (1890); Bredig, Ibid., 11, 829 (1893).

[4] Walker, Ibid., 4, 334 (1889).

[5] Wijs, Ibid., 11, 492 (1893).

[6] Ostwald, Ibid., 11, 521 (1893); Nernst, Ibid., 14, 155 (1894); Löwenherz, Ibid., 20, 293 (1896).

[7] Kohlrausch and Heydweiller, Ibid., 14, 330 (1894).

[8] These articles together with the present one are being published by the Carnegie Institution of Washington.