[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, NO. I, 30]

THE RESISTANCE-TEMPERATURE COEFFICIENT OF CONCENTRATED SOLUTIONS OF POTASSIUM IN LIQUID AMMONIA AND THE SPECIFIC CONDUCTANCE OF SOLUTIONS OF POTASSIUM IN LIQUID AMMONIA AT INTERMEDIATE CONCENTRATIONS

BY CHARLES A. KRAUS AND WALTER W. LUCASSE

RECEIVED JULY 23, 1923

In a preceding article[1] the authors have given the results of an investigation on the resistance-temperature coefficient of concentrated solutions of sodium in liquid ammonia. It appeared of interest to carry out a similar series of measurements with solutions of potassium in liquid ammonia at concentrations up to the saturation point. In the case of solutions of sodium in liquid ammonia, it was not possible to measure the temperature coefficient at lower temperatures over a considerable concentration interval, owing to the fact that this system separates into two phases with a critical point at —41.6°.[2]

The method and apparatus employed were the same as those previously employed in the case of sodium solutions. The results obtained, however, are on the whole more consistent than those obtained with sodium, partly because of the larger temperature interval which could be here employed and partly because of greater experience in the manipulation of the apparatus.

The Resistance-Temperature Coefficient of Potassium in Liquid Ammonia as a Function of Concentration.—Three independent series of measurements were carried out with solutions of potassium in liquid ammonia. Excepting the first two points in Series 1, the temperature interval employed was from the boiling point of liquid ammonia to —45°. The results are given in Table I, in which the dilution V, in liters of pure ammonia per gram-atom of potassium, is given in the first column; the upper temperature, in the second column; the lower temperature, in the third column; and, in the fourth column, the resistance-temperature coefficient:

$$\gamma = \frac{1}{R_{-33.5}}\frac{\Delta R}{\Delta t} \times 100.$$

The results are shown graphically in Fig. 1 in which the temperature coefficients are plotted as ordinates and the dilutions V, as defined above, as abscissas. The curve is similar to that obtained in the case of solutions of sodium in liquid ammonia, but is not identical with it. At the lower concentrations, the potassium solutions yielded a minimum coefficient of 1.42% as against 1.52% for sodium. At the higher

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[1] Kraus and Lucasse, THIS JOURNAL, 44, 1941 (1922).

[2] Kraus and Lucasse. *ibid.*, 44, 1949 (1922).

concentrations, the temperature coefficient in the case of potassium is markedly higher than in that of sodium. The maximum value is 4.55% per degree, whereas that of sodium is approximately 3.6%. This difference may in part be due to the fact that the temperature interval in the case of the potassium solutions is markedly greater than in that of the sodium solutions; while at the same time the temperature coefficient increases with decreasing temperature. The maximum value of the temperature coefficient occurs at a dilution of approximately 1.15 liters

TABLE I

RESISTANCE-TEMPERATURE COEFFICIENT OF POTASSIUM IN LIQUID AMMONIA

V	t_1	t_2	γ	V	t_1	t_2	γ
	Series 1				Series 2		
0.1250	−32.9	−40.0	0.0438	0.4018	−32.8	−45.0	0.806
.1297	33.1	40.1	0.0880	0.5200	32.8	45.1	1.57
.1538	33.0	45.1	0.132	0.5611	32.8	45.0	1.90
.2046	33.0	45.1	0.208	0.6501	32.8	45.0	2.80
.2831	33.0	45.0	0.388	0.7145	33.0	45.0	3.43
.3565	33.0	45.0	0.613	0.8054	33.0	45.0	4.22
.4385	33.0	45.0	1.02	0.9863	33.0	45.0	4.41
	Series 3			1.167	33.0	45.0	3.91
3.141	−33.05	−45.0	1.67	1.079	32.9	45.0	4.16
3.882	33.05	45.0	1.56	0.8933	32.9	45.0	4.50
4.508	33.05	45.0	1.47	0.9462	32.9	45.0	4.50
5.285	33.1	45.0	1.48	1.9120	33.0	45.0	4.55
6.081	33.1	45.0	1.42	1.409	33.0	45.0	3.04
5.140	33.1	45.0	1.46	1.879	33.0	45.0	2.22
4.018	33.1	45.0	1.49	2.443	33.0	45.0	1.85

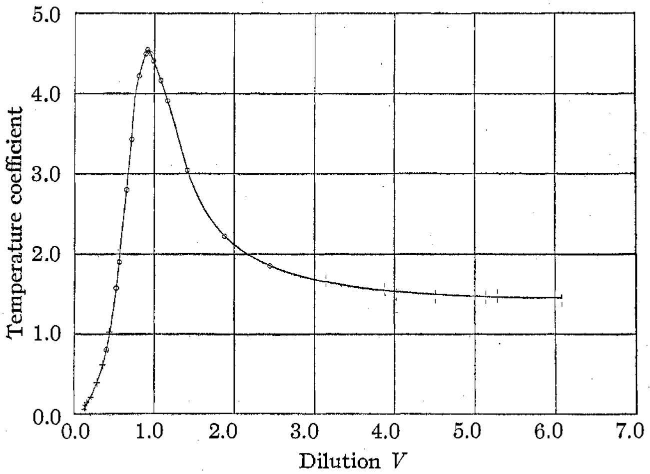

Fig. 1.—Variation of temperature coefficient of solutions of potassium in liquid ammonia as a function of concentration

in the case of sodium, while in that of potassium solutions it lies at a dilution of 0.91 liters.

Beyond the maximum, the temperature coefficient falls off very rapidly to a value of 0.0438% per degree for the saturated solution, which does not differ greatly from the corresponding coefficient of a solution of sodium. In the case of potassium, as in that of sodium, the coefficient would have a negative value if the concentration of the metal were slightly higher.

The Resistance-Temperature Coefficient as a Function of Temperature.—The resistance-temperature coefficient of solutions of potassium in liquid ammonia was measured at a series of temperatures down to approximately —70° for concentrations up to approximately normal. The results are given in Table II, in which the point in the series is given in the first column, the dilution V in the second column, the limits of the temperature intervals in the third and fourth columns, and the value of the coefficient γ in the last column.

TABLE II

RESISTANCE-TEMPERATURE COEFFICIENTS OF POTASSIUM SOLUTIONS IN LIQUID AMMONIA FOR DIFFERENT TEMPERATURE INTERVALS

Point No.	V	t_1	t_2	γ
1	0.1250	-32.9	-40.0	0.0438
		40.0	50.0	0.0918
		50.0	60.0	0.119
		60.0	67.0	0.122
2	0.1303	33.1	25.5	0.0537
	0.1297	33.1	40.1	0.0880
		40.1	50.1	0.103
		50.1	60.1	0.119
		60.1	67.5	0.155
12	0.9099	33.0	40.0	4.35
		40.0	50.0	5.30
		50.0	60.0	6.73
		60.0	70.2	7.29
	0.9120	33.0	45.0	4.55

The results here obtained are again similar to those obtained in the case of solutions of sodium. With decreasing temperature, the value of the coefficient increases. This is particularly marked at the higher concentrations, where the temperature coefficient increases approximately three times in passing from the interval of —32.9° to —40° to that of —60° to —67°. Very remarkable is the value which the coefficient assumes for the interval —60° to —70°, at a concentration in the neighborhood of the maximum, which amounts here to 7.29%.

Up to the present time it is not possible to indicate the factors to which the variation of the temperature coefficient may be due. It is a fact, however, that, at higher concentrations, the density of solutions of the alkali metals in liquid ammonia undergoes a phenomenally large change, the density increasing with decreasing concentration.[3]

The Specific Conductance of Solutions of Potassium in Liquid Ammonia at its Boiling Point at Intermediate Concentrations.—In an earlier paper[4] the authors have given data on the specific conductance of solutions of potassium in liquid ammonia by direct comparison with mercury at dilutions as high as $V = 0.7229$. Since that time a further series of measurements has been made carrying the dilution to $V = 1.597$. The results are given in Table III, in which the dilution, as defined above, appears in the first row, and the specific conductance l in reciprocal ohms, in the second.

TABLE III

SPECIFIC CONDUCTANCES OF SOLUTIONS OF POTASSIUM IN LIQUID AMMONIA AT —33.5°

V....	0.3205	0.4031	0.4881	0.5782	0.7310	0.8893	1.240	1.597
l.....	692.8	359.2	174.4	78.65	19.95	6.279	1.415	0.7470

The results of this series of experiments are in accord with those previously recorded and require no further comment. Attention should be called to a typographical error in an earlier paper,[5] where the value of the equivalent conductance as given under Observation No. 1, in Table III, at dilution $V = 0.4229$ should read "125,600.0." Calculating the value of the specific conductance of a lithium solution from this value, it is found to correspond very closely with the value for solutions of sodium and potassium at the same concentration.

Summary

The resistance-temperature coefficient of concentrated solutions of potassium in liquid ammonia has been measured from a dilution of 6 liters to the saturation point. The change of the temperature coefficient as a function of the concentration parallels that previously observed in the case of solutions of sodium. At higher concentrations, the temperature coefficient is somewhat greater for solutions of potassium than for sodium and the maximum temperature coefficient is found at a somewhat higher concentration.

The temperature coefficient has been measured as a function of the temperature at a number of concentrations. The temperature coefficient increases as the temperature decreases and the percentage change of the coefficient is greater at higher concentrations.

Some additional values are given for the specific conductance of potassium solutions in liquid ammonia at certain intermediate concentrations. These agree with previous observations.

[3] Unpublished observations in this Laboratory.

[4] Kraus and Lucasse, THIS JOURNAL, 43, 2529 (1921).

[5] Kraus, *ibid.*, 43, 756 (1921).

This investigation has received support from the Warren Fund of the American Academy of Arts and Sciences, of which aid we wish to express our grateful acknowledgment.

WORCESTER, MASSACHUSETTS

[CONTRIBUTION FROM THE LABORATORIES OF GENERAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

A STUDY OF THE TERNARY SYSTEM, TOLUENE-ACETONE-WATER

BY JAMES H. WALTON AND JOHN D. JENKINS

RECEIVED JULY 23, 1923

Toluene and acetone are miscible in all proportions, as are also acetone and water. Water and toluene, however, are practically insoluble in each other. This investigation was undertaken for the purpose of determining the solubility curve for these three compounds.

Reagents.—Acetone was dried over calcium chloride and fractionated, the fraction distilling between 56.05° and 56.16° at 760 mm. being used.

The toluene was dried over sodium, distilled and fractionated. The fraction boiling between 110.65° and 110.75° at 760 mm. was collected.

The water used was a high grade of conductivity water.

Apparatus and Method.—The pipets, burets and flasks were carefully calibrated with air-free water and the pipet also with toluene.

The apparatus in which the determinations were made is shown in Fig. 1. A is a 20 × 2.5cm. test-tube in which the liquids were mixed; P and P′ are two capillary delivery tubes, leading from the burets B and B′ containing the acetone and one of the other liquids. The method of making a determination was as follows. A definite amount, usually 10 cc., of either water or toluene was pipetted into the test-tube, which was then immediately stoppered, placed in the thermostat and allowed to stand for 15 minutes to come to the temperature of the bath. A small amount of the immiscible liquid, 0.2 to 0.5 cc., was then slowly added, the mixture vigorously stirred by means of the motor stirrer and acetone run in slowly, until the solution just cleared. The volumes of the liquids were then read and the temperatures of the burets noted. A new portion of the immiscible liquid was then added, and the process repeated. This was continued until the test-tube was about $^2/_3$ full, when another run was made in exactly the same manner, starting with the other immiscible liquid in the test-tube. This was found necessary because of the small solubility of one liquid in the other in the presence of a small percentage of acetone.

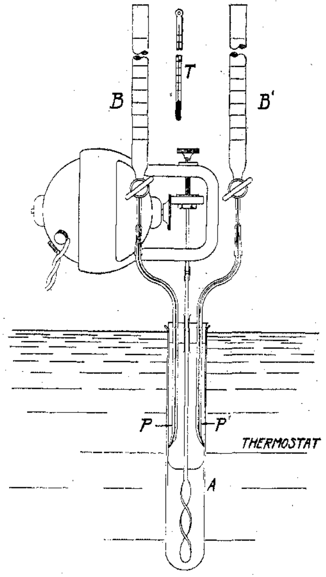

Fig. 1.—Apparatus used for solubility determinations

In order to obtain satisfactory determinations of the parts of the curves where there is only a small percentage of one component in the other