the temperature coefficient increases markedly with increasing temperature.

We wish to acknowledge our indebtedness to the Warren Fund of the American Academy of Arts and Sciences for a grant which made the present investigation possible.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, I, 13]

THE COMPOSITION OF THE LIQUID PHASES IN A MONOVARIANT SYSTEM, LIQUID-LIQUID-VAPOR, FOR MIXTURES OF SODIUM AND AMMONIA

BY CHARLES A. KRAUS AND WALTER W. LUCASSE

Introduction

It has been shown that at low temperatures concentrated solutions of sodium in liquid ammonia separate into two liquid phases which have an upper critical end-point in the neighborhood of —45°.[1] Ruff and Zedner[2] have determined the composition of the liquid phases in equilibrium with each other and the vapor, by determining the temperature at which the 2-phase equilibrium disappeared. According to their determinations, the critical end-point lies in the neighborhood of —45° and at a composition of approximately 2 atom per cent. of sodium. This value for the composition of the critical phase is not in accord with the vapor-pressure curves of Kraus[3] which, at higher temperatures, exhibit an inflection point at approximately 3.5 atom per cent. of sodium. It would appear, therefore, that the determinations of Ruff and Zedner are subject to considerable error.

In the course of the determination of the resistance-temperature coefficients of concentrated solutions of sodium in liquid ammonia, it was found that, when the temperature reached that of the 3-phase equilibrium, the electrical resistance, as measured in the spiral, underwent an abrupt change as the second liquid phase appeared. Preliminary measurements indicated that this break came sharply at a definite temperature. It seemed, therefore, that this method might be applicable in studying the composition of the two liquid phases.

Procedure

The measurements were carried out with the apparatus already described in an earlier article,[4] with special provision for placing the liquid under a

[1] Kraus, THIS JOURNAL, **29,** 1556 (1907).

[2] Ruff and Zedner, *Ber.,* **41,** 1948 (1908).

[3] Kraus, THIS JOURNAL, *30,* 1197 (1908).

[4] Kraus and Lucasse, *ibid.,* **43,** 2529 (1921).

pressure of hydrogen as previously described.[5]   The method consisted in cooling the bath slowly by boiling the ammonia under reduced pressure, the temperature and the resistance of the solution in the spiral being read in the meantime.   When a discontinuous change appeared in the resistance change, the temperature at which this break occurred was noted.   The temperature of the bath was then raised several degrees above that at which the break occurred, the solution was mixed, and the capillary again filled, after which the procedure was repeated, the temperature, however, being varied more slowly.   In this manner the temperature at which the resistance change occurs was checked.   The second readings were looked upon as being more precise than the first, in view of the slower rate of cooling.

In general, check determinations of the temperature at which the separation into two phases occurred were found to agree within a few tenths of a degree.   Only in a few instances, in the immediate neighborhood of the critical point, were larger divergences found, and in these cases close checks were obtained on carrying the measurements out more carefully. In a few instances, also, at low concentrations of sodium, where the temperature at which separation occurs is low and where the fraction of the second phase separated is small, the point was at times overrun without observing a sharp break in the resistance of the thread in the capillary tube.   On repeating the measurements, however, it was found possible to extend the measurements to —60° on both branches of the curve.

The concentration of the solution in the capillary was obtained from the specific resistance at the boiling point of liquid ammonia, the resistance-concentration curve having previously been determined by the writers.[4]
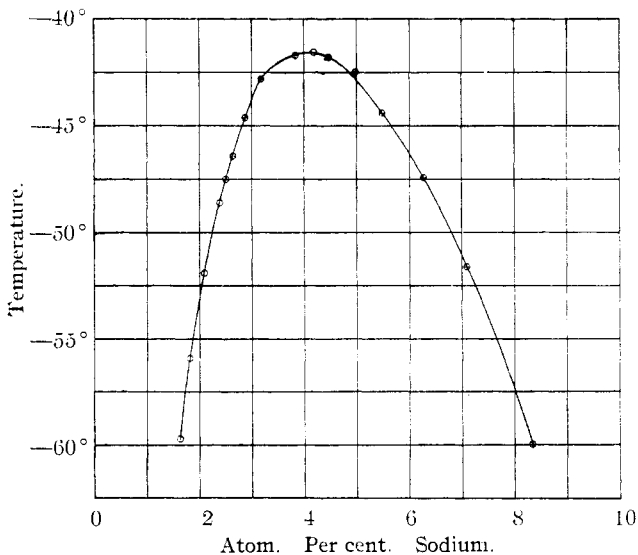
Experimental Results

In the following table are given values of the temperature and of the concentration of the predominating liquid phase for various compositions. In the third column, V is the volume of pure ammonia, density 0.674, in which one gram atom of sodium is dissolved.

The results are shown graphically in the accompanying figure, where the points represented by combined crosses and circles were obtained in a first series of determinations and the circles in a second.   It will be observed that the two series of determinations are in excellent agreement.   Furthermore, it will be seen that the points throughout lie upon a smooth curve, indicating that the method employed for determining the appearance of the second liquid phase is an extremely delicate one.

[5] Kraus and Lucasse, THIS JOURNAL, **44**, 1942 (1922).

TABLE I

COMPOSITION OF PREDOMINATING LIQUID PHASE AT DIFFERENT TEMPERATURES

No.	Specific Cond. at −33.5°	V	Mol % Na	t
		Run No. 1		
2	647.73	0.3304	7.09	−51.6
3	126.99	0.5408	4.46	−41.8
4	199.11	0.4819	4.97	−42.5
5	284.23	0.4355	5.47	−44.4
6	444.15	0.3776	6.27	−47.4
7	1007.2	0.2773	8.34	−60.0
8	60.885	0.6339	3.83	−41.7
9	19.693	0.7691	3.18	−42.8
10	9.379	0.8551	2.87	−44.6
11	5.625	0.9290	2.64	−46.4
		Run No. 2		
1	94.050	0.5794	4.18	−41.5
2	3.9707	0.9840	2.50	−47.5
4	3.0860	1.035	2.38	−48.6
5	1.7714	1.183	2.09	−51.9
6	1.0852	1.371	1.81	−55.9
7	0.8139	1.531	1.62	−59.7

The Composition of the Liquid Phases at Different Temperatures.

Discussion

The reliability of the method is demonstrated by the concordance of the results obtained and the reproducibility of the experiments. *A priori*, it would hardly be expected that the method would lead to results so readily reproducible. However, it should be borne in mind that the

conductance of these solutions is greatly affected by even a very minute change in concentration. A comparatively slight separation into 2 phases, therefore, might be expected to lead to a marked change in the resistance. Judging by the reproducibility of the results, the system has little tendency to pass into the metastable regions. The second phase appears to separate immediately when the composition along the solubility curve is reached.

The curve obtained differs considerably from that determined by Ruff and Zedner. The temperature at the critical point is several degrees higher, being —41.6°, and the composition of the more dilute phase lies at markedly higher concentrations. The critical composition is found to lie at approximately 95.85 mol per cent. of ammonia. This composition is much higher in sodium than is indicated by the results of Ruff and Zedner, but is in good agreement with the vapor-pressure curves of Kraus.

Perhaps the most interesting feature of the system lies in the low concentration of sodium at which the critical phase makes its appearance. In ordinary systems the critical phase often has a composition in the neighborhood of 50 molar per cent. of the constituents, and it is only seldom that the critical phase contains less than 15% of one of the constituents. The composition of the critical phase in the present case corresponds to a concentration of approximately 1.7 N.[6] That a critical phase should appear at so low a concentration of one constituent illustrates in a striking manner the unusual character of this system.

This system is also interesting from another point of view. From available data it may be inferred that with a single pair of constituents it is possible to obtain two monovariant systems in which we have present equilibria of the type liquid–liquid–vapor.[7] For compositions rich in ammonia, the equilibrium is that studied in the present investigation. At temperatures above the melting point of sodium, however, it appears probable that it will be found possible to obtain another series of equilibria between the vapor phase and 2 liquid phases, in which one of the liquid phases consists practically of pure sodium with a small amount of ammonia dissolved and the other of a concentrated solution of sodium

⁶ The concentration is expressed in terms of the volume of pure ammonia. See above.

⁷ The solubility of sodium in liquid ammonia has been measured by Ruff and Zedner from approximately —115° to +20°, the solubility decreasing as the temperature rises over this interval from 16.5 to 14.0 atom per cent. of sodium. If ammonia and liquid sodium were completely miscible, then the solubility curve for sodium would ultimately have to meet the sodium axis at the melting point under the pressure of the system in question. In view of the fact that the solubility curve shows a distinct inclination toward the ammonia axis from —115° to +20°, it is improbable that, through the remaining interval of 80°, the curve will change its course sufficiently to meet the sodium axis at the melting point. If such were the case, very large thermal effects would necessarily have to appear in this region.

in liquid ammonia.   Unfortunately, because of the reaction which occurs between sodium and ammonia at higher temperatures, which results in the formation of sodium amide and hydrogen, it will probably not be possible to realize the second series of equilibria over a considerable temperature range.   It is very likely, however, that the equilibria might be realized at temperatures only slightly above the melting point of sodium.   Whether or not the liquid phases in this second series of equilibria would likewise have a critical end-point cannot be stated, but it is not improbable that such would be the case.   It is known, for example, that ammonia is appreciably soluble in liquid alloys of sodium and potassium at ordinary temperatures.[8]   If such a point exists it is doubtless quite unrealizable.

Summary

1.   The concentrations of the liquid phases which appear at low temperatures in the more concentrated solutions of sodium in liquid ammonia have been studied.

2.   It has been found that this system has an upper critical end-point at a temperature of $-41.6°$ and a composition of 4.15 atom per cent. of sodium.

3.   The compositions were determined by the discontinuous change in the conductance of the mixture which occurs when the system separates into 2 phases.

4.   The phase relations in the system, sodium-ammonia, are briefly discussed.

WORCESTER, MASSACHUSETTS

[8] Kraus, THIS JOURNAL, **43**, 756 (1921).