

of accuracy of the observations and calculations the entire effect of the hydrogen-ion concentration on the osmotic pressure of the casein chloride solution is covered by the correction required and that there is little if anything left for the dispersion hypothesis to explain.

6. This is in harmony with the conclusion previously reached by the writer that the influence of electrolytes on the osmotic pressure of protein solutions is entirely or almost entirely the consequence of the difference in the concentration of crystalloidal ions inside the protein solutions and the outside aqueous solutions at equilibrium, this difference being caused by the establishment of a membrane equilibrium.

The writer is indebted to the editorial board for some valuable suggestions which have been incorporated in the text.

NEW YORK, N. Y.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, I, 12]

## THE RESISTANCE-TEMPERATURE COEFFICIENT OF CONCENTRATED SOLUTIONS OF SODIUM IN LIQUID AMMONIA

BY CHARLES A. KRAUS AND WALTER W. LUCASSE

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### Introduction

In a previous article, the writers<sup>1</sup> have shown that the order of magnitude of the electrical conductance of concentrated solutions of sodium and potassium in liquid ammonia approaches that of typical metallic substances. For example, the specific conductance of a saturated solution of sodium in liquid ammonia has a value of 5047.0, which is about one-half that of mercury at ordinary temperatures. The atomic conductance of these solutions, however, is much higher than that of many metallic elements. Thus, the atomic conductance of sodium<sup>2</sup> in liquid ammonia is  $1.1 \times 10^6$ ,

<sup>1</sup> Kraus and Lucasse, *THIS JOURNAL*, **43**, 2529 (1921).

<sup>2</sup> This value of the atomic conductance is based upon the value 0.54 for the density of a saturated solution of sodium in liquid ammonia, which was determined approximately. The great increase in volume accompanying the formation of this saturated solution, which amounts to 53 cc. per atom of sodium, or an increase of 33%, strikingly illustrates the enormous change which the physical properties of these solutions undergo with respect to those of the constituent substances. It is interesting to note that the volume of solutions of sodium and potassium of the same atomic composition is practically identical. Thus the volume of a saturated solution of sodium containing one atom of metal ( $V=0.1353$ ) is 211.5 cc., assuming the density given above. The volume of a solution containing one atom of potassium ( $V=0.1295$ ) is 211.4 cc., assuming as density the value 0.632 (Ref. 1). The difference in the density of sodium and potassium solutions of a given composition is, therefore, due to the difference in the weight of the metallic atoms. This serves to illustrate the striking similarity in the physical properties of solutions of different metals in ammonia.

which is about  $\frac{1}{5}$  that of metallic sodium and  $\frac{2}{3}$  that of metallic lithium. The atomic conductance is of the order of magnitude of that of osmium and tin and is greater than that of a large number of typical metallic elements.

It may be expected that the resistance-temperature coefficient of these solutions will vary as a function of the concentration, and that at high concentrations the temperature coefficient will approach that of typical metallic substances. Kraus<sup>3</sup> has shown that the temperature coefficient of dilute solutions of sodium in liquid ammonia is positive and that in the neighborhood of the boiling point of liquid ammonia it has a value of approximately 2.25% per degree in terms of the resistance at the boiling point. It appeared worth while, therefore, to examine the temperature coefficient of these solutions at higher concentrations.

### Apparatus and Procedure

The apparatus employed in determining the temperature coefficients was the same as that already described by the authors in their previous paper.<sup>1</sup> A few modifications of the auxiliary apparatus were, however, introduced. One of the difficulties met with in the preceding investigation was due to the breaking of the thread of liquid in the resistance capillary, due to the formation of small bubbles of vapor. This effect was greatly accentuated when the temperature of the surrounding bath was lowered. In order to overcome this, the solution was placed under an excess pressure of pure hydrogen. This hydrogen was derived from a tank of electrolytic hydrogen by diffusion through a palladium tube. The palladium tube was fused into a lead glass tube which in turn was sealed into a quartz tube by means of de Khotinsky cement. The glass tube into which the palladium tube was sealed was, in turn, connected with the conductance apparatus. The diffusion chamber was introduced into an electric tube furnace by means of which the temperature could be maintained at any desired point. Hydrogen was passed through the quartz tube around the exterior surface of the palladium under an excess pressure of about 30 cm. of mercury. The hydrogen diffusing through the palladium was allowed to accumulate in a reservoir over mercury, the pressure thereon being adjusted by means of a second reservoir of mercury connected with it and open to the atmosphere. The diffusion of hydrogen takes place very rapidly at red heat and yields a very pure product. The apparatus proved very convenient in manipulation and obviated entirely the difficulties previously experienced due to the breaking of the conducting thread in the capillary.

The temperature of the ammonia bath was determined by means of a

<sup>3</sup> Kraus, *THIS JOURNAL*, **43**, 758 (1921).

pentane thermometer. At the upper temperature, the normal boiling point of liquid ammonia itself served as a fixed point, while the lower temperatures were obtained by boiling the ammonia under reduced pressure. The rate of boiling of the ammonia in the bath was adjusted by means of a pinchcock on the rubber tube connecting the bath with the pump. It was possible to regulate temperatures to  $0.1^\circ$  by this means. At higher and lower concentrations the temperature measurements were extended to  $-60^\circ$ , but in the neighborhood of a concentration of 4 atom per cent. of ammonia the mixture exhibits an upper critical end-point at a temperature near  $-42^\circ$ . In this region, therefore, it was not possible to study the temperature coefficient over an interval greater than  $7.5^\circ$ . In most instances, the results were checked by bringing the temperature of the bath back to the normal boiling point of liquid ammonia and re-determining the resistance.

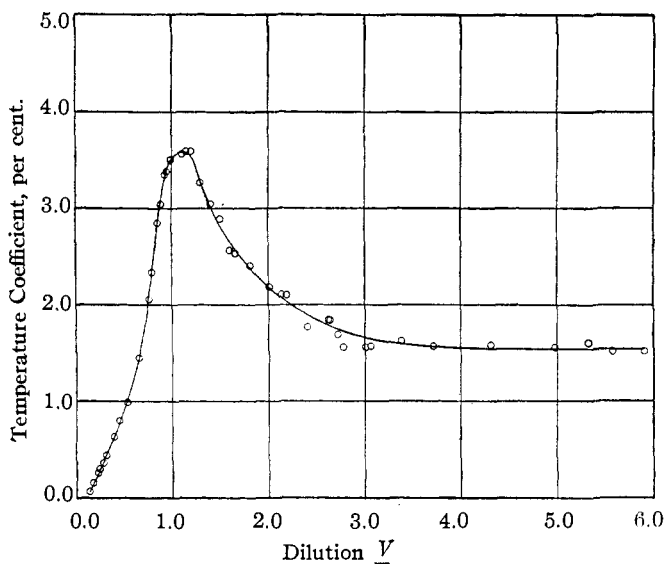
In order to reduce the time necessary to bring the bath back to the boiling point of liquid ammonia, a coil of Nichrome wire, suspended on a glass framework, was introduced near the bottom of the bath. With a current of 2 or 3 amperes, the temperature of the bath could be raised from  $-60^\circ$  to the boiling point of ammonia in a comparatively short time.

The concentrations at which the temperature coefficients were measured were determined from the conductance curves of the writers' earlier measurements. This method proved to be a very convenient one and saved a great deal of time.

The resistance was measured by means of a telephone and drum-wound bridge. At high concentrations, the resistance change was small while the minimum was less sharp than at lower concentrations. In these regions the chief source of error was due to the bridge setting. At lower concentrations, the chief source of error was due to the difficulties of temperature control and to the smallness of the temperature interval. It is believed that the errors affecting the coefficients under favorable conditions do not exceed 5%. In the most dilute solutions measured, the resistance reached a value of about 300,000 ohms. In these regions a Vreeland oscillator was employed as a source of e.m.f., and capacity and inductance effects were balanced out.

In other respects the procedure did not differ materially from that employed in the conductance measurements. In most instances, several independent observations were carried out at a given concentration. These appear averaged in the table.

The temperature coefficients, as a function of concentration, for an interval of approximately  $7.5^\circ$  below the boiling point, are shown graphically in the accompanying figure. The dilutions in liters of pure ammonia per gram atom of sodium are plotted as abscissas and the temperature coefficients as ordinates.



Figure, showing the Temperature Coefficient of Sodium in Ammonia as a Function of Concentration.

### Experimental Results

The results obtained are given in the following tables.

TABLE I  
RESISTANCE-TEMPERATURE COEFFICIENTS OF SOLUTIONS OF SODIUM IN LIQUID AMMONIA

| No.   | $V$    | $^{\circ}\text{C. negative upper } t$ | $^{\circ}\text{C. negative lower } t$ | $\frac{1}{R_{-33.5}} \frac{\Delta R}{\Delta t} \times 100$ |
|-------|--------|---------------------------------------|---------------------------------------|--|
| Run 1 |        |                                       |                                       |  |
| 1     | 0.1766 | 32.3                                  | 50.1                                  | 0.158  |
| Run 4 |        |                                       |                                       |  |
| 1     | 0.1409 | 32.2                                  | 50.0                                  | 0.0656   |
| Run 5 |        |                                       |                                       |  |
| 1     | 0.2317 | 32.2                                  | 40.0                                  | 0.262  |
| 2     | 0.3184 | 32.2                                  | 42.5                                  | 0.447  |
| Run 6 |        |                                       |                                       |  |
| 1     | 0.2838 | 32.2                                  | 46.1                                  | 0.369  |
| 2     | 0.3908 | 32.2                                  | 45.4                                  | 0.633  |
| 3     | 0.4539 | 32.2                                  | 42.0                                  | 0.807  |
| 4     | 0.5321 | 32.2                                  | 40.0                                  | 1.000  |
| 5     | 0.6561 | 32.2                                  | 40.0                                  | 1.45   |
| Run 8 |        |                                       |                                       |  |
| 1     | 0.2466 | 32.2                                  | 40.1                                  | 0.290  |
| 9     | 0.7691 | 32.2                                  | 40.0                                  | 2.06   |
| 10    | 0.8551 | 32.2                                  | 40.0                                  | 2.84   |
| 11    | 0.9290 | 32.2                                  | 41.0                                  | 3.35   |

| Run 11 |       |      |      |      |
|--------|-------|------|------|------|
| 1      | 0.984 | 32.6 | 40.0 | 3.50 |
| 2      | 0.889 | 32.6 | 40.0 | 3.04 |
| 3      | 0.793 | 32.6 | 40.0 | 2.34 |
| 4      | 0.942 | 32.6 | 40.0 | 3.38 |
| 5      | 1.102 | 32.6 | 40.0 | 2.57 |
| 6      | 1.197 | 32.6 | 40.0 | 3.60 |
| 7      | 1.406 | 32.4 | 40.0 | 3.05 |
| Run 12 |       |      |      |      |
| 1      | 1.143 | 32.3 | 40.0 | 3.60 |
| 2      | 1.291 | 32.3 | 40.0 | 3.27 |
| 3      | 1.507 | 32.3 | 40.0 | 2.89 |
| 4      | 1.600 | 32.3 | 40.0 | 2.57 |
| 5      | 1.660 | 32.3 | 40.0 | 2.54 |
| 6      | 1.811 | 32.3 | 40.0 | 2.41 |
| 7      | 2.014 | 32.3 | 40.0 | 2.19 |
| 8      | 2.138 | 32.3 | 40.0 | 2.11 |
| Run 13 |       |      |      |      |
| 1      | 2.193 | 32.7 | 40.0 | 2.10 |
| 2      | 2.624 | 32.7 | 40.0 | 1.85 |
| 3      | 2.404 | 32.7 | 40.0 | 1.77 |
| 4      | 2.636 | 32.7 | 40.0 | 1.84 |
| 5      | 3.069 | 32.7 | 40.0 | 1.57 |
| 6      | 2.780 | 32.5 | 40.0 | 1.57 |
| 7      | 3.381 | 32.5 | 40.0 | 1.63 |
| 8      | 3.724 | 32.5 | 40.0 | 1.57 |
| 9      | 4.315 | 32.5 | 40.0 | 1.59 |
| 10     | 4.977 | 32.5 | 40.0 | 1.56 |
| 11     | 5.572 | 32.5 | 40.0 | 1.52 |
| 12     | 5.902 | 32.5 | 40.0 | 1.52 |
| 13     | 5.321 | 32.4 | 40.0 | 1.61 |
| 14     | 3.013 | 32.4 | 40.0 | 1.57 |
| 15     | 2.723 | 32.4 | 40.0 | 1.70 |

TABLE II  
THE RESISTANCE-TEMPERATURE COEFFICIENT AS A FUNCTION OF THE TEMPERATURE INTERVAL

| Run | Point No. | $V$    | $^{\circ}\text{C. negative}$<br>upper $t$ | $^{\circ}\text{C. negative}$<br>lower $t$ | $\frac{1}{R_{-33.5}} \frac{\Delta R}{\Delta t} \times 100$ |
|-----|-----------|--------|---|---|--|
| 4   | 1         | 0.1409 | 32.2                                      | 50.0                                      | 0.0656   |
|     |           |        | 50.0                                      | 60.0                                      | 0.0930   |
| 1   | 1         | 0.1766 | 32.3                                      | 50.1                                      | 0.158  |
|     |           |        | 50.1                                      | 61.0                                      | 0.183  |
|     |           |        | 61.0                                      | 68.0                                      | 0.201  |
| 5   | 1         | 0.2317 | 32.2                                      | 40.0                                      | 0.262  |
|     |           |        | 40.0                                      | 51.0                                      | 0.318  |
| (7) | 8         | 1.702  | 32.5                                      | 40.0                                      | 2.48   |
|     |           |        | 40.0                                      | 50.0                                      | 2.80   |
|     |           |        | 50.0                                      | 60.0                                      | 3.44   |
| 12  | 8         | 2.138  | 32.3                                      | 40.0                                      | 2.11   |
|     |           |        | 40.0                                      | 50.0                                      | 2.24   |

TABLE II (Continued)

| Run | Point No. | $V$   | $^{\circ}\text{C. negative upper } t$ | $^{\circ}\text{C. negative lower } t$ | $\frac{1}{R-33.5} \frac{\Delta R}{\Delta t} + 100$ |
|-----|-----------|-------|---------------------------------------|---------------------------------------|--|
|     |           |       | 50.0                                  | 59.0                                  | 2.64   |
|     |           |       | 59.0                                  | 68.0                                  | 3.08   |
| 13  | 13        | 5.321 | 32.4                                  | 40.0                                  | 1.61   |
|     |           |       | 40.0                                  | 50.0                                  | 1.56   |

### Discussion of Results

An inspection of the figure shows that the temperature coefficient varies as a function of the concentration in an extremely complex manner. For a nearly saturated solution of sodium in liquid ammonia at a dilution  $V = 0.14$ , the coefficient has a value of 0.066%. With decreasing concentration the temperature coefficient increases markedly. In the neighborhood of  $V = 0.6$ , the temperature coefficient increases very greatly with the concentration, passing through a rather abrupt maximum at a dilution of approximately  $V = 1$ , after which the coefficient decreases more slowly as the concentration decreases. Above a dilution of  $V = 2.0$ , the temperature coefficient approaches a value of approximately 1.55%. Evidently, this represents a minimum value, since the coefficient determined by Kraus at much lower concentrations has a value of 2.25%. It is evident, therefore, that the temperature coefficient passes through a minimum value at concentrations somewhere below  $V = 2.0$ .

The course of the curve as the saturated solution is approached is of great interest. On reference to the figure, it will be seen that the temperature coefficient is not approaching a value of zero at higher concentrations, but that the curve, extended, intersects the axis of concentrations at a concentration a little above that of the saturation point; and that the temperature coefficient of the solutions would be negative beyond this point. While it is obviously impossible to carry out measurements on these solutions which lie in the metastable region, it may clearly be inferred that the temperature coefficients are undergoing a change which would ultimately lead to negative values. In other words, at high concentrations the temperature coefficients of these solutions approach those of metallic substances both in sign and in magnitude. There can be little question but that the concentrated solutions of sodium in liquid ammonia are, in fact, true metallic substances.

The manner in which the temperature coefficient varies as a function of the temperature is likewise very interesting. In the most dilute solution, at a concentration  $V = 5.32$ , the coefficient for the temperature interval from  $-32.4^{\circ}$  to  $-40^{\circ}$  is 1.61%, while from  $-40^{\circ}$  to  $-50^{\circ}$  it is 1.56%. Evidently, in this region, the temperature coefficient varies only very little, if at all, with the temperature. In the more concentrated solutions, however, the temperature coefficient increases markedly as the temperature decreases. Thus, from  $-32.3^{\circ}$  to  $-50.1^{\circ}$  the temperature

coefficient at  $V = 0.177$  is  $0.158\%$ , while from  $-61^\circ$  to  $-68^\circ$  it is  $0.201\%$ . As the concentration decreases, the influence of temperature upon the temperature coefficient likewise decreases. Thus, at a concentration  $V = 1.70$ , the temperature coefficient from  $-32.5^\circ$  to  $-40.0^\circ$  is  $2.48\%$ , while from  $-50^\circ$  to  $-60^\circ$  it is  $3.44\%$ . It is evident from the earlier work of Kraus,<sup>3</sup> that at very low concentrations the temperature coefficient increases markedly with rising temperature.

With the experimental material on hand it is difficult to interpret the complex manner in which the temperature coefficient varies with the temperature and with the concentration. That the temperature coefficient should depend upon these variables in a somewhat complex manner is not unexpected, for in these solutions a greater number of factors are involved than in the case of ordinary electrolytic solutions. In the first place, the ionization of the electrolyte, in this case the metal, may be an important factor. In the case of ordinary electrolytic solutions in solvents of relatively low dielectric constant, the temperature coefficient at very low and very high concentrations is usually positive, while for intermediate concentration the temperature coefficient often has a relatively low or even a negative value. At very low concentrations the temperature coefficient of normal electrolytes lies in the neighborhood of  $2\%$  per degree, corresponding approximately with the temperature coefficient of the fluidity of the pure solvent. At very high concentrations, however, the temperature coefficient for normal electrolytes often has values reaching 4 or  $5\%$  or even greater. It is not unlikely that these same factors influence the temperature coefficient of solutions of the metals in liquid ammonia. The phenomenon here, however, is complicated, owing to the fact that in addition to the ionization of the electrolyte we have to take into account the influence of temperature upon the solvation of the negative electron. Kraus has shown that in dilute solutions in liquid ammonia the negative electron, to which the greater portion of the conductance of these solutions is due, is in all likelihood ammoniated, but that at high concentrations a portion of the current is carried by negative electrons which are not associated with ammonia molecules. Thus, the maximum possible mean ammoniation of the negative electrons at a concentration in the neighborhood of normal is  $0.67$  mols per equivalent, which indicates that at least one third of the charge in these solutions is carried by carriers not associated with ammonia. From the manner in which the electromotive force of concentration cells varies as a function of the concentration at higher concentrations, it is clear that the mean ammoniation of the electrons at the higher concentrations must fall off to extremely low values. This, moreover, is in agreement with the high value obtained for the conductance of these solutions.

In considering the influence of temperature upon the temperature

coefficient, therefore, the change in the relative ammoniation of the negative electrons must be taken into account. At the present time there are no data available making it possible to determine in what manner the ammoniation varies as a function of the temperature.

At very high concentrations, the temperature coefficient may be expected to decrease with increasing concentration, in view of the fact that these solutions are approaching the metals in their properties. The influence of temperature on the coefficient cannot here well be predicted, for even in the case of pure metallic substances the nature of the mechanism involved in the conduction process is uncertain. Throughout, it should be borne in mind that the physical properties of these solutions undergo a tremendous change at higher concentrations. This is indicated not alone by the enormous density change which these solutions undergo, but likewise by the fact that, in the neighborhood of four mol per cent. of ammonia, the solutions separate into two liquid phases at lower temperatures.

### Summary

1. The resistance-temperature coefficients of concentrated solutions of sodium in liquid ammonia have been measured from the saturation point up to  $V = 5.02$  and at temperatures from the boiling point of liquid ammonia down to  $-60^\circ$ .

2. Near the saturation point the temperature coefficient of sodium in liquid ammonia has a value of approximately 0.066 per cent. With decreasing concentration, the temperature coefficient increases markedly, passing through a maximum value of approximately 3.6% at  $V = 1.1$  and thereafter decreasing to a value of approximately 1.55 at dilutions above 4.0 liters per atom. Taking into account the earlier work on the temperature coefficient of more dilute solutions, it is evident that the temperature coefficient passes through a minimum value.

3. From the form of the curve at high concentrations, it is evident that the temperature coefficient is approaching a negative value at high concentrations, although this value is not actually realizable since the saturation point of the solution is reached. At the highest concentrations the solutions of the metals in liquid ammonia closely resemble metallic alloys.

4. At lower temperatures, the temperature coefficient increases markedly at higher concentrations. As the concentration decreases, the influence of temperature on the coefficient decreases, and at a dilution  $V = 5.3$  the coefficient is relatively independent of temperature. From previous work on the influence of temperature on the temperature coefficient of more dilute solutions, it is clear that the influence of temperature on the temperature coefficient changes sign, since at low concentrations



the temperature coefficient increases markedly with increasing temperature.

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WORCESTER, MASSACHUSETTS

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[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

Received June 20, 1922

### 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  $-45^{\circ}$ .<sup>1</sup> Ruff and Zedner<sup>2</sup> 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  $-45^{\circ}$  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<sup>3</sup> 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,<sup>4</sup> with special provision for placing the liquid under a

<sup>1</sup> Kraus, *THIS JOURNAL*, **29**, 1556 (1907).

<sup>2</sup> Ruff and Zedner, *Ber.*, **41**, 1948 (1908).

<sup>3</sup> Kraus, *THIS JOURNAL*, **30**, 1197 (1908).

<sup>4</sup> Kraus and Lucasse, *ibid.*, **43**, 2529 (1921).