Summary

Measurements of the heat of adsorption of hydrogen on active and heat-treated copper catalysts have been made.

The active preparations show maxima in the curves of heat of adsorption plotted against amount adsorbed.

With partially de-activated catalysts the maximum occurs when smaller amounts of gas are adsorbed. Further de-activation eliminates such maxima.

These results are in harmony with a theory of the catalytic surface with variable elementary spaces, upon the most active of which adsorption is accompanied by an endothermic activation process.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

THE DENSITY OF SOLUTIONS OF SODIUM IN LIQUID AMMONIA

BY CHARLES A. KRAUS, E. SEATON CARNEY AND WARREN C. JOHNSON

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According to Kraus and Lucasse[1] the density of a concentrated solution of sodium or potassium in liquid ammonia is markedly lower than that of either of its components, which shows that the process of solution of these metals is accompanied by a large increase in volume. Forney[2] investigated the density of solutions of sodium in liquid ammonia at higher concentrations, using for this purpose a specially designed spring balance. This method, however, did not prove sufficiently sensitive to admit of accurate determination of the volume change. Since these solutions are very exceptional in their behavior, it was thought worth while to develop a method whereby their density could be determined with a relatively high degree of accuracy. An apparatus was therefore designed whereby the density was measured directly by means of a Westphal balance.

Apparatus and Procedure

The chief difficulty encountered in determining the density of solutions of the alkali metals in liquid ammonia is due to their extreme reactivity toward oxygen and moisture. This was overcome by maintaining an atmosphere of hydrogen over the solutions during the course of the measurements. The essential features of the apparatus are shown in outline in Fig. 1. The balance, which was equipped with suitable clamping and leveling devices, was placed in a sealed case provided with plate glass windows on opposite sides. Special riders were constructed of inverted "U" form, carrying a loop at the top. The riders were manipulated

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[1] (a) Kraus and Lucasse, THIS JOURNAL, **43**, 2538 (1921); (b) *ibid.*, **44**, 1941 (1922).

[2] Forney, *Thesis*, Clark University, 1923.

from without the case by means of a rider carrier A. A hook B was provided within the case on which the riders were placed when not in use. The beam could be fixed in position by means of the clamps CC. The balance case was connected to the density tube D by means of a short length of rubber tubing E. A special bob F was constructed of Pyrex glass and adjusted to have a volume of 5.000 cc. at —33.8°, the temperature at which the density measurements were carried out. The density of the solutions could thus be read directly in terms of the position of the riders on the beam. The beam was connected to the bob by means of a silk thread G, which passed through the rubber tube E, and which, in turn, was connected to a fine platinum wire H attached to the bob. During the weighing operations, the density tube D, as well as the balance case, was filled with pure hydrogen at a pressure slightly above that of the atmosphere. In general, a slow stream of hydrogen was maintained through the upper portion of the density tube and the case and out through the tube I, which was connected with a mercury trap, not shown in the figure. Except during the weighings, connection between the

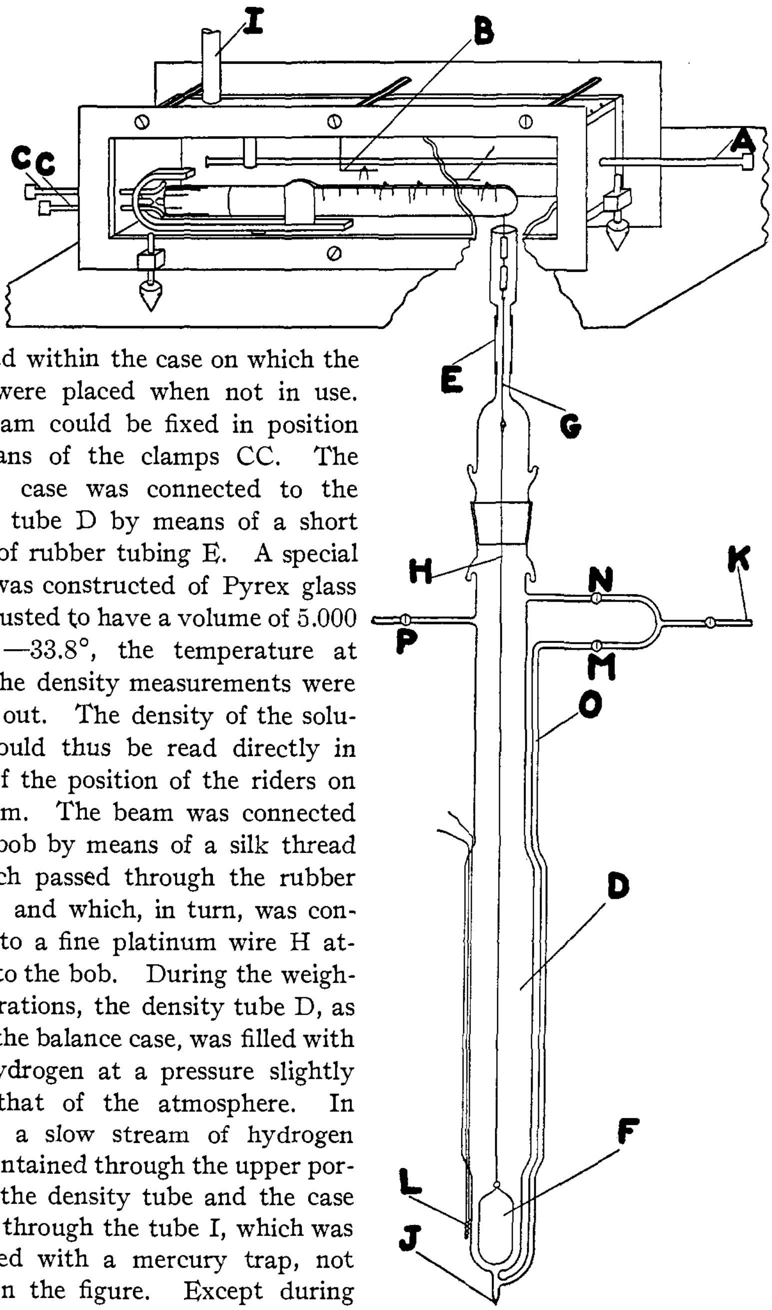

Fig. 1.

balance case and the density tube was shut off by compressing the rubber tube E with a small screw clamp.

Sodium was introduced into the bottom of the density tube through a fine capillary by the method of Kraus and Lucasse,[1] the tube being sealed off at J on completion of this operation. The tube K was connected with a source of pure ammonia, a high-vacuum pump, a source of pure hydrogen and a Toepler pump. The procedure used in introducing liquid ammonia into the tube D was similar to that described by Kraus and Lucasse.[1] The volume of the solvent was measured, prior to introduction, by means of pipet cells having a volume of from 2 to 10 cc. and graduated in 0.01 cc.

In making a series of density determinations, the following procedure was employed. After introducing the sodium, the density tube was thoroughly evacuated. It was then surrounded by a bath of ammonia (in a Dewar tube) boiling freely under the pressure of the atmosphere. An electric current was passed through the small nichrome wire coil L for the purpose of maintaining constant ebullition. Liquid ammonia, whose volume had been measured in the pipet cells, was then condensed in the tube D, the ammonia vapor passing through the tubes K and O and the stopcock M. The solution was thus stirred by the vapor passing through it. The stopcock P connected the density tube with the external atmosphere through a mercury trap and wash bottle in which any ammonia carried over was absorbed and later determined by titration. After condensing the ammonia in the density tube, a stream of hydrogen was passed through the stopcock M and tube O for the purpose of stirring the solution until equilibrium was established. Any ammonia carried over with the escaping hydrogen was absorbed in the wash bottle already mentioned and later determined by titration. The screw clamp attached to E was then removed, the balance beam was set free and the density read by means of the Westphal balance. The clamp was then replaced and the hydrogen present in the density tube, together with a small quantity of ammonia which varied with the concentration of the solution, was removed by means of a Toepler pump. The ammonia carried over in this process was absorbed in water and determined by titration. The stopcock N was used for the purpose of equalizing the pressure between the density tube and the auxiliary tube O.

After having removed the hydrogen from the density tube, another measured quantity of ammonia was introduced and the density determined as before. The procedure, as above described, was repeated until the limit of capacity of the density tube was reached.

The ammonia present in the tube was then evaporated and the last trace removed by means of a high-vacuum pump. The tube J was broken off near the tip and the sodium dissolved in a mixture of 50% of absolute alcohol and ether. When the metal was completely dissolved, the solution was allowed to run into a large platinum dish and sulfuric acid was added until it was neutral or slightly acid. The solvent was then evaporated, an excess of acid was added and the sodium finally determined as sodium sulfate.

In order to determine the volume change accompanying the formation of the saturated sodium solution from its components, it was necessary to make a precise determination of the concentration of this solution. This was done by the method of Kraus and Johnson,[3] a detailed description of which need not be repeated here. It consists essentially

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[3] Kraus and Johnson, This Journal, **47**, 725 (1925).

in measuring the equilibrium pressure for a series of mixtures of sodium and ammonia of known composition. So long as sodium is present in excess, the pressure remains fixed, but as soon as the amount of ammonia is in excess of that necessary for complete solution of the sodium, a rapid rise in pressure occurs. By graphical means the point corresponding to the saturated solution can be evaluated with considerable precision. The pressure measurements were extended to fairly dilute solutions in order to obtain the data necessary for correcting the concentrations, in the density determinations, for ammonia present in the vapor phase.

Results

The density values as obtained are presented in Table I, in which the weight of ammonia in the solution is given in the first column, the number of moles of ammonia per atom of sodium in the second column, the density of the solution in the third column and the volume change per atom of sodium, ΔV, in the last column. The volume change is calculated by means of the equation

$$\Delta V = \frac{N \times 17.032 + 22.997}{D_s} - \left(\frac{N \times 17.032}{D_{NH_3}} + \frac{22.997}{D_{Na}}\right)$$

where N is the number of moles of ammonia per atom of sodium, D_s is the density of sodium at the temperature of the solution and D_{NH_3} is the density of pure ammonia at the same temperature. The reduced barometric reading during the experiment was 742.25 mm. of mercury, which corresponds to a temperature of —33.8° for the boiling point of liquid ammonia.[4] The density of pure ammonia at this temperature is 0.6824[5] and that of sodium 0.9805. The latter value was obtained by

TABLE I

DENSITY OF SOLUTIONS OF SODIUM IN LIQUID AMMONIA AT DIFFERENT CONCENTRATIONS

t = —33.8°. Sodium sulfate = 6.9190 g. ≏ 2.2402 g. of sodium

NH_3, g.	NH_3/Na	Density	V
7.562	5.48	0.5782	40.96
11.160	6.731	.5888	42.26
14.700	8.867	.6044	43.15
18.278	11.025	.6163	43.37
21.713	13.097	.6251	43.29
25.271	15.243	.6322	43.13
28.857	17.406	.6376	43.13
32.544	19.630	.6423	42.93
36.054	21.747	.6462	42.54
39.901	24.072	.6494	42.48
45.200	27.263	.6535	41.82
54.061	32.608	.6582	41.40

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[4] Cragoe, Meyers and Taylor, Bureau of Standards, *Scientific Papers*, No. 369, p. 33, **1920**.

[5] Cragoe and Harper, *ibid.*, No. 420, p. 313, 1921.

interpolating data due to Dewar at 17 and —182.6°,[6] and combining this with a value determined by Richards and Brink[7] at 20°.

TABLE II

VAPOR PRESSURE OF SOLUTIONS OF SODIUM IN LIQUID AMMONIA AT DIFFERENT CONCENTRATIONS AT —33°

Series 1

Conc. NH_3/Na	4.824	5.424	5.566	5.711	5.774	5.869
Press., mm.	405.0	398.0	421.0	445.0	461.0	469.0
Conc. NH_3/Na	5.932	6.051	6.146	6.295	6.700	7.243
Press., mm.	483.5	493.0	516.0	533.5	577.5	623.6
Conc. NH_3/Na	7.812	8.383	8.934	9.521	10.745	13.561
Press., mm.	656.5	686.5	707.5	732.2	745.5	769.0

Series 2

Conc. NH_3/Na	2.839	3.995	4.532	5.097	5.461	5.602
Press., mm.	397.0	397.0	401.0	403.0	403.0	431.5
Conc. NH_3/Na	6.008	6.469	6.910	7.314	7.922	8.367
Press., mm.	486.0	544.5	592.5	625.0	661.5	681.5

In Table II are given the values of the equilibrium pressures as measured for solutions of sodium in liquid ammonia at various concentrations, including saturated solutions.

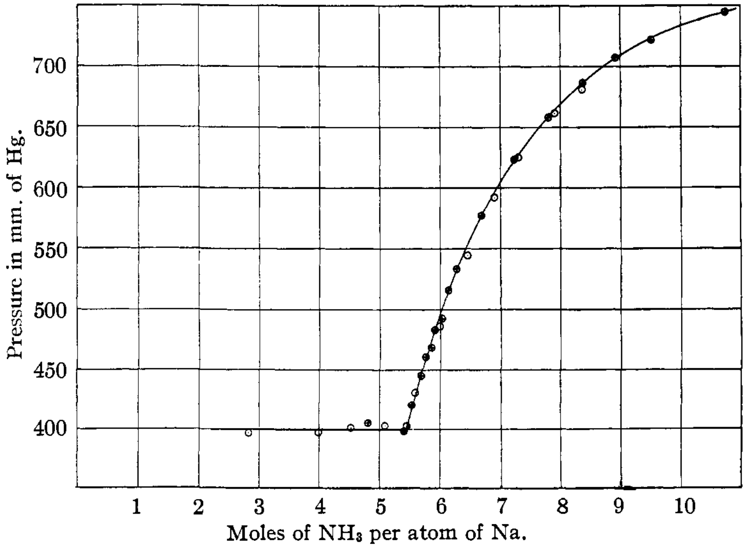

Fig. 2.

These results presented in Table II are shown graphically in Fig. 2, where pressures are plotted as ordinates against moles of ammonia per

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[6] Dewar, *Chem. News*, **85**, 277 (1902).

[7] Richards and Brink, THIS JOURNAL, **29**, 117 (1907).

atom of sodium as abscissas. Points of Series 1 are represented by combined crosses and circles and of Series 2 by crosses.

From the plot the composition of the saturated solution of sodium in liquid ammonia was found to be 5.48 moles of ammonia per atom of sodium.

Discussion

The density of solutions of sodium in liquid ammonia is shown as a function of the concentration in Fig. 3, in which densities are plotted as ordinates. In Curve 2, the number of moles of ammonia per atom of sodium are plotted as abscissas, while in Curve 1 the number of atoms of sodium per mole of ammonia are correspondingly plotted. In Fig. 4 values of ΔV are plotted as a function of the concentration expressed in moles of ammonia per atom of sodium.

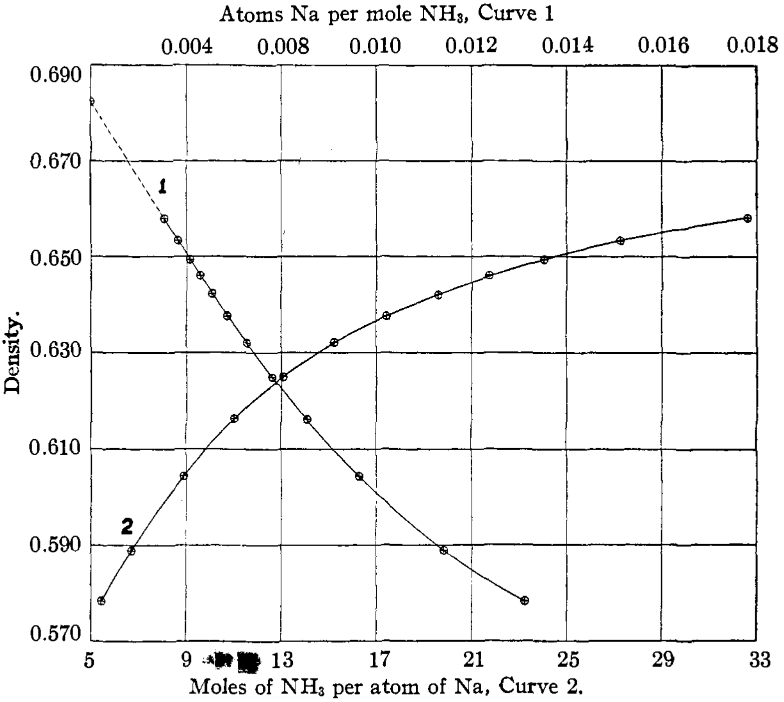

Fig. 3.

The relative values of the density are consistent with one another within less than two units in the fourth place. This is well illustrated by the ΔV curve (Fig. 4), which is quite sensitive to errors in the density values. The maximum deviation of the values of ΔV, as determined, from those of the smooth curve, as drawn, lies well within an error limit of two units in the fourth place in the value of the density.

The density of the saturated solution has a value of 0.5782 as against 0.6824 for pure ammonia and 0.9805 for sodium. From the determined concentration of the saturated solution, the volume change accompanying the formation of this solution from its components is found to be 40.96 cc. per atom of sodium. With decreasing concentration, the value of ΔV increases, reaching a maximum of 43.37 cc. per atom of sodium at a concentration of 11.25 moles of ammonia per atom of sodium. Beyond this concentration, the value of ΔV diminishes slowly. Judging by the form of Curve 2 (Fig. 3), as well as by that of the ΔV curve (Fig. 4), it is probable that, with decreasing concentrations, the value of ΔV approaches a constant value somewhat less than 40 cc. per atom of sodium. The most dilute solution measured contained 32.6 moles of ammonia per atom of sodium with a density of 0.6582, which corresponds to a volume concentration of 1.138 N. At this concentration the solutions are rapidly approaching a constant condition as regards the state of the dissolved substance.

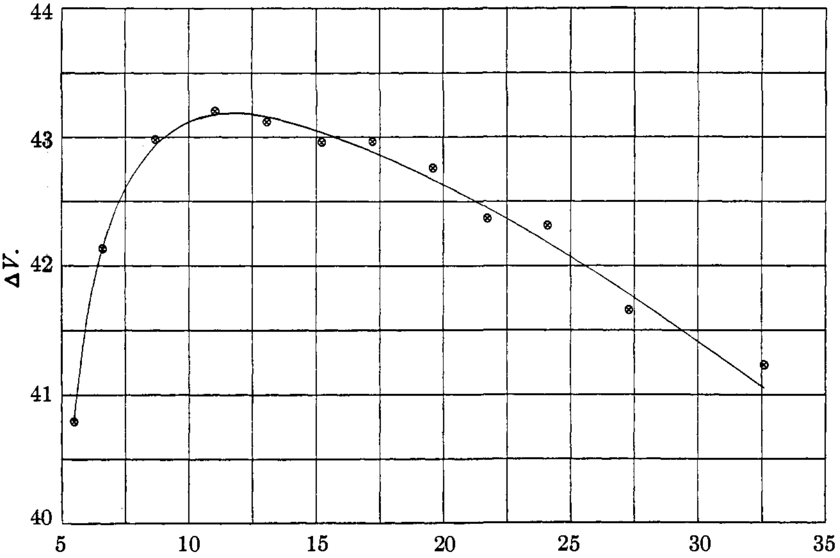

Fig. 4.

The volume change accompanying the formation of these solutions is a striking fact. It amounts to almost twice the original volume of the sodium. The heat effect accompanying the solution of sodium in liquid ammonia is inconsiderable. About 1500 calories are absorbed per atom of sodium and the value diminishes with increasing concentration.[8] If we bear in mind the fact that, in these solutions, sodium is present as a

[8] This value is based on measurements carried out by Mr. J. A. Ridderhof in this Laboratory. The detailed results will be published later.

normal sodium ion, we must ascribe the volume change chiefly to the electron which, freed from the constraints under which it exists in the solid metal, occupies a relatively large volume in the solution. In no other case heretofore investigated, either in processes of solution or of compound formation, has a volume change of this magnitude been observed. It is known that the electron in liquid ammonia solution at higher concentrations is free to move as it is in metals. Since we have no adequate conception of the state of the electron in metals, we are unable to draw any definite conclusions regarding its state in liquid ammonia. However, it may be safely concluded that the electron is not combined with the sodium ion and that at low concentrations, at any rate, the electron is associated with ammonia molecules.

The peculiar form of the ΔV curve at higher concentrations cannot be accounted for at this time. It is known that in concentrated solutions of the alkali metals in liquid ammonia, many properties exhibit singularities. The electrical conductance, for example, undergoes a tremendous increase in value with concentration as was shown by Kraus and Lucasse, while the temperature coefficient of the conductance exhibits a sharp maximum in the neighborhood of normal concentration.[1] The concentrations at which these singularities occur differ in the case of different properties.

Summary

The density of solutions of sodium in liquid ammonia has been determined at —33.8° at concentrations ranging from 32.6 moles per atom of sodium up to the saturation point.

The density of these solutions is lower than that of either constituent.

From the density values the increase in volume accompanying the solution of sodium in liquid ammonia has been calculated. The volume increase amounts to 40.96 cc. for a saturated solution and increases with increasing dilution to a maximum of 43.14 cc. for a solution containing 11.2 moles of ammonia per atom of sodium. On further dilution the value gradually diminishes and apparently approaches a limiting value in the neighborhood of 40 cc. At —33.8° the saturated solution of sodium in ammonia contains 5.48 moles of ammonia per atom of sodium.

PROVIDENCE, RHODE ISLAND