

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

The Dissociation Pressures of Sodium Deuteride and Sodium Hydride

BY EDITH FORD SOLLERS¹ AND J. L. CRENSHAW

In a previous paper² the authors have presented data on the dissociation pressures of potassium deuteride and potassium hydride. This paper contains the results of a similar study of sodium deuteride and sodium hydride. The discussion of the problem and the bibliography may be found in the earlier paper.

Experimental Part

The experimental procedure was exactly the same as that followed in the study of the potassium salts² with three exceptions. Dry sodium (Merck) was used. Treatment with dioxane to remove oil was, therefore, unnecessary. Freshly cut sodium was placed in a glass boat. The glass boat was placed in the reaction tube and the tube was sealed off. From this point the procedure was the same as in the case of the potassium salts.

The second change in procedure was the lining of the reaction tube with special glass resistant to sodium vapor.³

The third change was in the construction of the reaction tube. The thermocouple entry tube was omitted as it could not be easily coated with sodium-resisting glass. The jacketed thermocouple was placed in the nitrate-bath as near the reaction chamber as possible. This made no appreciable change in the temperature readings since the temperature was constant to 0.1° except within less than an inch (2.5 cm.) from the surface and sides of the bath.

Experimental Difficulties

The difficulties encountered with potassium deuteride and hydride were still present. Distillation of the metal up the capillary tube was much less, as would be expected from the lower vapor pressures of sodium. Sodium, however, reacted with the glass to a greater extent, as Keyes⁴ has noted. The reaction may not be the same as that observed by Keyes since the pressures obtained after the sodium had been in contact with the glass for some time at high temperatures were lower than the equilibrium pressures, whereas Keyes' were higher. In fact, at temperatures above 360° with the deuteride and above 380° with the hydride, a slow but continuous decrease in pressure occurred at constant temperature. This fall in pressure was noticed at somewhat lower temperatures when sodium-resisting glass was not used. The difference between our results and those of Keyes may be due to the difference in the composition of the glass used. In the work on potassium² we attributed this fall in pressure at high temperatures to the distillation of potassium into the cooler parts of the system and its subse-

quent conversion into hydride. Since the fall in pressure was even more noticeable in the case of sodium when ordinary Pyrex glass was used, some other explanation is necessary since, at the temperatures of the experiments, the vapor pressure of sodium is much less than that of potassium. It seems probable that the fall in pressure may be due to the production of a small amount of metallic calcium as a result of the reaction of sodium (or potassium) with the glass. This calcium would combine with hydrogen (or deuterium) to form calcium hydride (or deuteride) whose dissociation pressure would be very low at the temperatures used.⁵

Experimental Results

Measurements were made on sodium hydride from 310 to 380° and on sodium deuteride from 270 to 360°. The reaction of sodium with the glass made measurements at higher temperatures impossible. The fact that it was possible to make sodium hydride measurements up to 380°, whereas the deuteride measurements could not be made past 360°, may be an indication that sodium deuteride reaches equilibrium more slowly than sodium hydride. Reaction of sodium with the glass is probably occurring at 360° when sodium hydride is in the tube, but the glass reaction is so much slower than the dissociation that the error in the measurements below 380° is undetectable.

Nine determinations were made on three different preparations of sodium hydride. The results are in very good agreement with those of Keyes.⁴ The twenty-three determinations on six different deuteride preparations are recorded in Table I.

TABLE I
OBSERVED DISSOCIATION PRESSURES OF SODIUM
DEUTERIDE

°C.	Pressure, mm.	°C.	Pressure, mm.	°C.	Pressure mm.
271.2	2.8	319.5	37.0	352.3	137.1
272.7	3.3	321.5	39.1	354.3	144.7
298.0	12.2	323.1	40.7	354.6	140.8
301.3	14.8	324.0	42.9	354.9	146.8
312.8	26.1	329.3	57.6	355.7	155.8
314.1	27.6	334.1	67.4	355.9	155.4
316.0	28.9	334.1	67.8	356.7	157.3
317.7	29.2	349.0	124.3		

The experimental data on sodium deuteride and sodium hydride are plotted in Fig. 1. In

(1) Alice Freeman Palmer Fellow of Wellesley College.

(2) Edith Ford Sollers and J. L. Crenshaw, *THIS JOURNAL*, **59**, 2015 (1937).

(3) The authors wish to thank Professor Frederick G. Keyes of the Massachusetts Institute of Technology, who very kindly supplied this glass and gave many valuable suggestions for using it.

(4) Keyes, *THIS JOURNAL*, **34**, 779 (1912).

(5) Remy-Genneté, *Ann. chim.*, **19**, 263 (1933).

Fig. 2, $\log_{10} p$ is plotted against $1/T$, and within experimental error straight lines are obtained. The heavy lines in both plots are the graphs of the following equations which were obtained by the method of least squares.

$$\text{For sodium deuteride: } \log_{10} p = \frac{-6915.00}{T} + 13.1994$$

$$\text{For sodium hydride: } \log_{10} p = \frac{-6318.41}{T} + 11.9250$$

$$\text{Keyes gives for sodium hydride: } \log_{10} p = \frac{-5700}{T} + 2.5 \log_{10} T + 3.956^6$$

These equations give for the heats of formation, which are assumed constant throughout the temperature range used, 15,800 calories for sodium deuteride, 14,440 calories for sodium hydride. For the hydride, Keyes gives 14,740 calories at 350°.

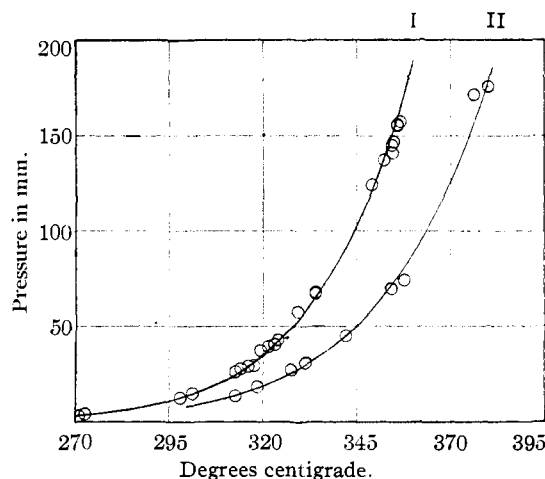


Fig. 1.—I, NaD; II, NaH.

As may be seen from the plots, the experimental error is rather large. The probable errors of the least squares equations are: for sodium hydride 0.030, for sodium deuteride 0.017, in $\log_{10} p$. These values correspond to probable errors of something over 7% in the calculated pressures of the hydride and somewhat less than 4% in those of the deuteride. The heat of formation of sodium deuteride appears to

(6) The best line drawn through the points for the deuteride plotted in Fig. 2 would have a slight curvature and a least square solution in which a term in $\log T$ is included gives the equation

$$\log_{10} p = (-13,114.7/T) - 24.1516 \log_{10} T + 90.6392$$

Since the heat capacity of the dissociation products is almost certainly greater than that of the deuteride, the heat of formation should increase with rising temperature and hence the logarithmic term in the above equation should be positive. The curvature shown by the data for the deuteride in Fig. 2 is therefore in the wrong direction and is due to experimental error. For this reason, we have drawn the best possible straight line through the points and have assumed that, within the experimental error, the heat of the reaction is constant in the temperature range investigated.

be slightly larger than that of the hydride. The dissociation pressure of sodium deuteride is about twice as great as that of sodium hydride in the range studied.

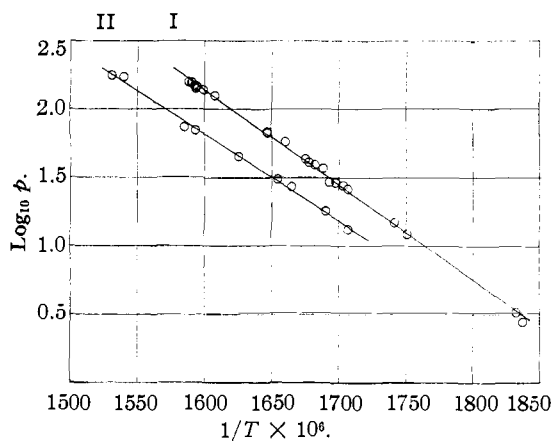


Fig. 2.—I, NaD; II, NaH.

Table II contains the dissociation pressures of sodium deuteride and sodium hydride as calculated for round temperatures from the above equations. Keyes' calculated values for sodium hydride are included for comparison. The agreement between the sodium hydride pressures calculated from Keyes' equation and from the authors' is excellent.

TABLE II

°C.	CALCULATED DISSOCIATION PRESSURES OF SODIUM DEUTERIDE AND SODIUM HYDRIDE		
	Pressure NaD calcd., mm.	Pressure NaH calcd., mm.	Pressure NaH calcd., mm. (Keyes)
270	2.9
280	5.0
290	8.3	...	5.2
300	13.6	...	8.0
310	21.9	12.3	12.4
320	34.7	18.7	18.8
330	54.2	28.1	28.3
340	83.2	41.6	42.0
350	126.3	60.9	61.6
360	189.3	88.1	90.7
370	...	125.9	127.9
380	...	178.0	181.4

Summary

1. The dissociation pressures of sodium hydride have been measured from 310 to 380°. They are in very good agreement with those of Keyes.
2. The dissociation pressures of sodium deuteride have been measured from 270 to 360°. In this range, the dissociation pressures of sodium

deuteride are approximately twice as great as those of sodium hydride.

3. The following heats of formation per mole

have been calculated: for sodium hydride, 14,440 calories; for sodium deuteride, 15,800 calories.

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A Semi-micro Calorimeter for Measuring Heat Capacities at Low Temperatures¹

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In view of the trend toward micro and semi-micro apparatus it seemed to be of interest to construct a calorimeter for small amounts of organic liquids which would enable measurements of specific heats and heats of transition to be made in the range 100 to 320°K. The calibrated heat conductivity calorimeter developed by Andrews,² Haworth,³ and Smith,⁴ was selected as the basis for the experiments.

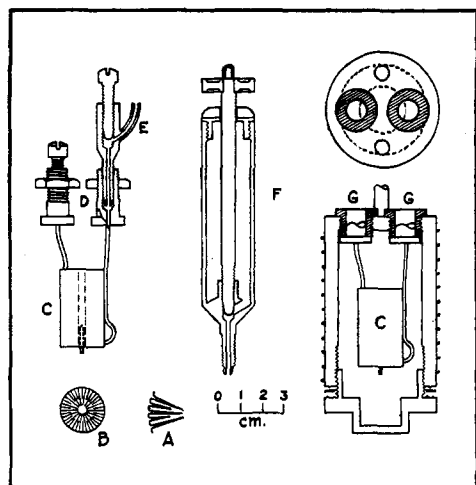


Fig. 1.

Calorimeter Construction

A pilot calorimeter was first built which was used to try out several ideas of design and construction.⁵ With the experience obtained on this calorimeter as a guide, the apparatus was constructed in its final form as follows: a can with vanes inside was formed by bending a strip of gold 0.05 mm. thick, 3.5 cm. wide and nearly a meter long as shown in the end view at A and B of Fig. 1. To add strength the outside was plated with copper, and the ends were closed by plated copper, thus producing a

container possessing no joints or fissures. In this way the vanes were an integral part of the can.

Entrance and exit tubes of 1-mm. German silver tubing were soldered in place (shown at C) and also a thermocouple well reaching up 1 cm. from the bottom of the can. In order to simulate "black body" conditions better the can was plated finally with a fine grained spongy layer of copper, washed and dried, and placed in a 110° oven for three hours, thereby converting the surface to a velvet black copper oxide.

After the plating was completed, the entrance and exit tubes were soldered to brass bushings D threaded in the manner shown. The screws had spherical ends which made gas and liquid tight valves when in contact with the conical seats of the bushings. The brass fitting E was designed to permit control of the gas and liquids which were passed through the can for cleaning purposes.

At F is shown the brass container in which the liquids under investigation were weighed. It was threaded to fit the bushing D and contained a sphere-cone valve in the bottom. After the sample had been weighed in this container, it was inserted into the bushing D and the valve opened to permit the sample to drain by gravity into the can. The opposite bushing valve which had been serving as a vent and the valve in the weighing container were then closed and, after withdrawal from the bushing, the former was reweighed. The amount clinging to the tip was found to be negligible. Independent preliminary transfers showed that the difference between the weight lost by the weighing container and that gained by the receiver averaged less than 0.1% on a 5-g. sample of benzene. The total volume of the can was about 6 ml. although the samples taken in most of the work were about 3 to 3.5 ml.

The shield was of copper 5.2 cm. in diameter, 7.5 cm. long with a wall thickness of 6.5 mm. (see Fig. 1). The bottom was closed by a threaded copper plug and made gas tight with a lead gasket. In addition the joint was finally sealed with low melting solder. The inside of the shield was given a velvet black surface similar to that of the can. The top of the can was pierced by four holes. Into the two smaller were soldered 6.5-mm. German silver tubes, one carrying the thermocouple wires and the other providing gas connection with the outside. The can was suspended in the shield by the bushings D (Fig. 1) which were secured in the hard rubber plugs G and bakelited in position. This was necessary for electrical insulation. Twenty ohms of no. 30 constantan wire was bakelited on the outside of the shield as a heater.

(1) Part of a dissertation presented to the Faculty of Philosophy of The Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) D. H. Andrews, *THIS JOURNAL*, **48**, 1287 (1926).

(3) E. Haworth and D. H. Andrews, *ibid.*, **50**, 2998 (1928).

(4) R. H. Smith and D. H. Andrews, *ibid.*, **53**, 3644 (1931).

(5) It was with this apparatus that the data cited by R. C. Lord, Jr., and E. R. Blanchard, *J. Chem. Phys.*, **4**, 707 (1936), were obtained.