[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY, METAL HYDRIDES INCORPORATED]

The Sodium–Sodium Hydride–Hydrogen System at 500–600°[1]

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The dissociation pressure of hydrogen in the sodium–sodium hydride–hydrogen system has been measured as a function of temperature and over-all composition of the condensed phase or phases. Measurements have been made at temperatures from 500 to 600° at pressures ranging up to 4600 cm. The results have been plotted both as pressure *versus* the over-all composition of the condensed phase or phases, and as log pressure *versus* reciprocal of absolute temperature. The latter plot consists of a series of straight lines, from the slopes of which the differential heats of dissociation were calculated. The isotherms consist of nearly horizontal lines which break away sharply at both ends of the composition axis. The non-horizontal portions of the isotherms indicate the regions of limited mutual solubility of sodium and sodium hydride in the temperature range studied.

Introduction

Previous work by Herold,[2] Keyes,[3] and others[4–7] has outlined the sodium–sodium hydride–hydrogen system to a maximum temperature of 430° with the corresponding dissociation pressure of 91 cm. Their results were in good agreement and indicated that, at constant temperature, the dissociation pressure was independent of the composition of the condensed phase. Considered from the viewpoint of the phase rule, this fact of univariance of the two-component system required that three phases be present at all times. Since gaseous hydrogen was always present, there must have been two distinct condensed phases, sodium hydride and metallic sodium, in the system over the entire range of composition. This indicated that sodium hydride and metallic sodium were insoluble in each other in all proportions at these temperatures. In general, it could be said that one need only specify the temperature of the system to define its equilibrium dissociation pressure, regardless of the relative amounts of sodium and sodium hydride present. All of the previous work with this system, which differed only in the method employed to contain the sodium hydride, could be summarized by the equation representing Herold's data

$$\log_{10} P_{\text{mm.}} = -6100/T + 11.66$$

In extending the available data on this system to higher temperatures, it was expected that the univariant character of the system would continue. It was found, however, in preliminary experiments in this Laboratory between 500 and 600° that the results obtained could be explained only by a limited mutual solubility of sodium and sodium hydride, which solubility increased with temperature. Experimental techniques were, therefore, modified to permit study of a composition-dependent system with excellent results.

Experimental

The experimental techniques employed for this high-pressure study of the sodium–sodium hydride–hydrogen system have been used previously in this Laboratory[8,9] for both high- and low-pressure studies of hydrides. Essentially, two techniques have been used. The equilibrium temperature–pressure curve for sodium hydride has been determined by the method previously employed for titanium and uranium hydrides,[8,9] where the hydride is heated under a pressure of hydrogen. The sample is heated slowly, and the pressure developed is plotted as a function of temperature. Initially, a linear thermal-expansion curve is obtained, and, as the temperature increases further, dissociation occurs and the pressure increases over that obtained by extrapolation of the linear expansion curve. The intersection of the linear expansion curve and the dissociation–pressure curve can be determined by graphical methods and represents a point on the dissociation–pressure curve for 100% sodium hydride. Typical dissociation curves are shown in Fig. 1.

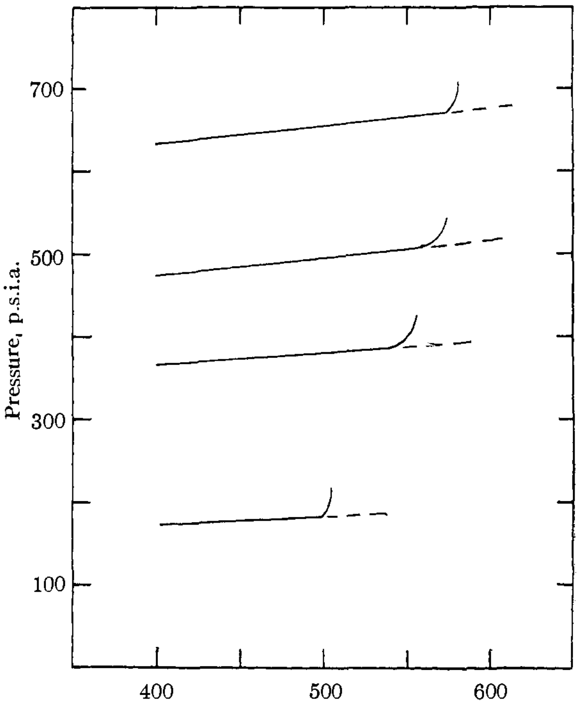

Fig. 1.—Typical thermal dissociation curves.

The lower composition values were obtained from desorption isotherms, a method which has been used for study of the calcium–hydrogen system at low pressures,[10] as well as in the study of titanium–hydrogen and uranium-hydro-

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 125th Meeting of the American Chemical Society, Kansas City, Missouri, March 1954.

[2] A. Herold, *Compt. rend.*, **228**, 686 (1949).

[3] F. G. Keyes, THIS JOURNAL, **34**, 779 (1912).

[4] P. Hautefeuille and L. Troost, *Compt. rend.*, **78**, 809 (1874).

[5] I. I. Zhukov, *Ann. inst. anal. phys. chim.*, **3**, 461 (1926).

[6] I. I. Zhukov, *ibid.*, **3**, 600 (1927).

[7] D. C. Bardwell, THIS JOURNAL, **44**, 2499 (1922).

[8] J. J. McSharry, R. W. Bragdon and T. R. P. Gibb, Jr., *ibid.*, **73**, 1751 (1951).

[9] J. J. McSharry, T. R. P. Gibb, Jr., and H. W. Kruschwitz, Jr., *ibid.*, **74**, 6203 (1952).

[10] W. C. Johnson, *et al.*, *ibid.*, **61**, 318 (1930).

gen systems[8,11] and is adaptable to high-pressure work. The measurement of absorption curves to check desorption data was prevented by the formation of a hydrogen-impervious layer of sodium hydride on the surface of the sodium.

The main difficulties encountered in the dissociation study of the sodium–hydrogen system are the effects of corrosion, distillation of the sodium metal from the low-composition hydride, and the loss of hydrogen because of diffusion. An apparatus to overcome these difficulties was realized by the use of a double-wall system, with an outer container constructed of 316 stainless steel to hold 1,000 p.s.i. gas pressure at 1000° and a smaller sealed liner constructed from Armco iron[10,12] to contain the alkali hydride within the steel container.

Hydrogen diffusion from the system through the stainless steel pressure container was almost negligible at 500° but increased markedly near 600°. To combat the effect of diffusion loss at 600°, the alternative of using a single sample to determine only a few points on the isotherm curve before replacement was used, rather than fabricating an extremely heavy-walled container and using this single sample over the entire composition range. For the measurement of points at the low-composition end of the 600° isotherm, the composition was lowered to the desired region at 500° by repeated removal of measured amounts of hydrogen before heating to 600°.

The Armco liners successfully overcame the corrosion and distillation difficulties encountered in this system. These liners resisted corrosion by sodium hydride and sodium metal in the presence of hydrogen and served as selective membranes which allowed only hydrogen to diffuse readily, while retaining sodium liquid and vapor. These sealed liners served satisfactorily at 550° and above, but, at the lower temperatures, the diffusion of hydrogen proved to be extremely slow as equilibrium was approached. This characteristic of the Armco iron liners was overcome by using a controlled gas leak in the liners. During the hydrogen-removal procedure, known quantities of gas were removed at a very slow rate to prevent loss of material, which might be caused by high-velocity gas flow from the container.

The Armco iron liners were loaded through their stems with sodium hydride in the inert atmosphere of the dry-box. They were then fitted with rubber tube connections, which were pinched off before their removal from the dry-box and arranged on a hydrogen-vacuum line source. The liners were then carefully evacuated, refilled with hydrogen, the stems pinched tight by means of a die and press constructed for this operation, and sealed by welding. The sodium hydride-filled Armco liners were placed within the steel pressure containers, which were closed by welding the top end to the previously fabricated body. The stem leading from the shell was fitted with an adapter containing a needle valve, and the container was connected with a high-pressure capillary line leading to the gage system.

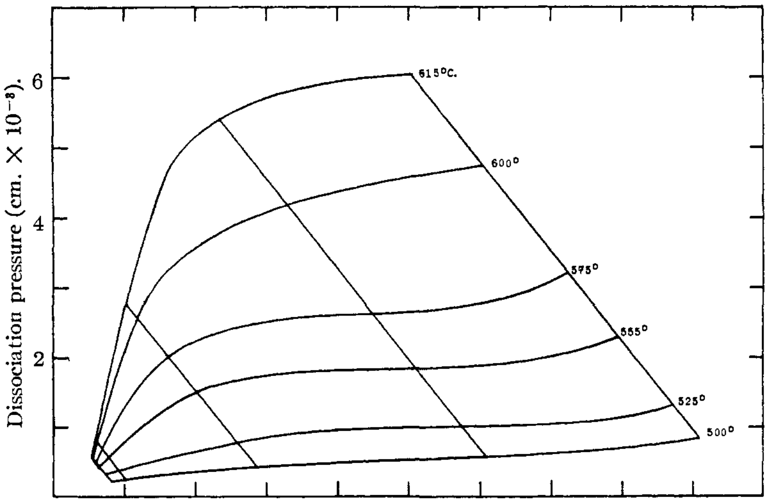

Fig. 2.—Isotherms derived from early data.

Apparatus.—Some of the equipment and techniques employed in this work have been described in a previous paper from this Laboratory.[8] The arrangement of equipment is shown in Fig. 1 of reference 8, with the sole exception that the pressure vessel was submerged in a molten lead-bath to give better temperature control in the present study. The outer containers were of 316 stainless steel, 1.75 inches i.d., 2 inches o.d., and 3 inches long. The end plates were $^1/_2$-inch thick. An 18-inch stem of $^3/_8$-inch o.d., $^1/_4$ inch i.d. stainless steel tubing was welded in a hole at one end and soldered to a brass adapter containing in series a needle valve and a $^1/_8$-inch brass fitting. The Armco iron liners were 1.5 inches i.d, $1^9/_{16}$ inches o.d., and $1^7/_8$ inches long with a 2-inch length of $^1/_4$ inch tubing welded to a hole in one end. The liners were pretreated at 1000° by alternate 30-minute periods of hydrogen atmosphere and vacuum for 4 hours to reduce any oxides present. The pressure gages were Brown Instrument Company 0- to 1000-p.s.i. recording gages which were calibrated to ±1% by a standard dead-weight gage.

Materials.—The sodium hydride was obtained from the Chemical Hydrides Production Department of Metal Hydrides Incorporated and sieved, the +60 mesh portion being discarded. The −60 mesh material analyzed between 99.4 and 99.8% sodium hydride by hydrogen evolution. This underwent further hydriding under high hydrogen pressure *in situ* and averaged 99.8% from absorption measurements. Typical carbon analyses were less than 0.1%.

Spectrographic analysis showed that other metal impurities were present in the following amounts

Ca	~0.1%	Fe	<0.05%
Li	<0.0005	Mg	<0.001
K	<0.01	C	<0.1

Tank hydrogen with a 99.9% analysis was purified by passage over lump zirconium at 500° to remove oxygen, nitrogen, moisture and carbonaceous impurities before use in this study.

Results and Discussion

As was mentioned in the introduction, the results of early experiments at 500–600° in this Laboratory did not agree with those of previous workers at lower temperatures and could be explained only on the basis of a limited mutual solubility of the components of the system. The results of these experiments were recalculated as isotherms, corrections being made for the changes in composition due to dissociation. The derived isotherms are plotted in Fig. 2. The diagonal straight lines in Fig. 2 indicate the temperature–pressure data from which the isotherms were derived.

The experimental isotherm data, obtained under conditions where extreme variations of pressure were observed with temperature and composition changes, demonstrate that the dissociation pressures of the sodium–hydrogen system are dependent on composition. The results obtained are conveniently summarized in Figs. 3 and 4. Figure 3 is a plot of isotherms that were obtained from actual experimental measurement. These show increasingly large plateaus that approach the horizontal with diminishing temperature and indicate the presence of two con-

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(11) T. R. P. Gibb, Jr., and H. W. Kruschwitz, Jr., This Journal, **72**, 5365 (1950).

(12) Remy-Gennetè, *Ann. chim.*, [10] **19**, 263 (1933).

densed phases. In the high sodium hydride composition region, the dissociation pressure rises with increasing composition. In the low sodium hydride composition end, the dissociation pressure falls off with decreasing composition. It is apparent that, as the temperature range of the previous work is approached, the two-phase horizontal portion will extend over nearly the entire range of composition. Figure 4 shows the data expressed by means of isocomposition curves, where the common logarithm of the pressure is plotted *versus* the reciprocal of the absolute temperature. These curves offer a method, by use of the Clausius–Clapeyron equation, of thermodynamically evaluating the system in its various phase regions. These plots are mathematically expressed by the equation

$$(\log_{10}P_{\text{cm.}} = -a/T + b)$$

where temperature is expressed in degrees absolute, and a and b are derived constants given in Table I for compositions from 10 to 100% sodium hydride. The 30 to 80% composition range has been expressed by one curve on this isocomposition plot because of the extremely small variance of the curves in this range.

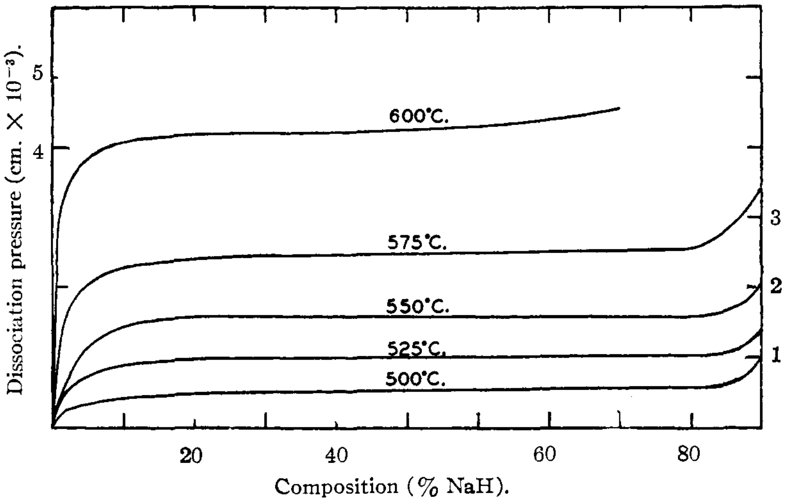

Fig. 3.—Experimental isotherms.

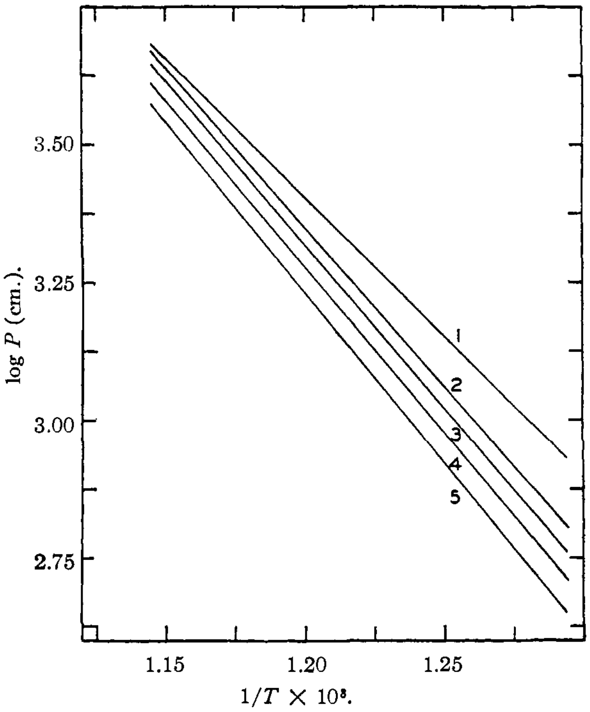

Fig. 4.—Isocomposition curves: 1, 100% NaH; 2, 90% NaH; 3, 80–30% NaH; 4, 20% NaH; 5, 10% NaH.

TABLE I

EMPIRICAL CONSTANTS FOR THE INTEGRATED CLAUSIUS–CLAPEYRON EQUATION FOR NaH

$(\log_{10}P_{\text{cm.}} = -a/T + b)$

NaH, %	a	b
100	5070	9.49
90	5806	10.32
80–30	5958	10.47
20	6058	10.55
10	6222	10.70

When the equation

$$\log P_{\text{cm.}} = -6100/T + 10.66$$

as reported by Herold[2] for the sodium–hydrogen system over the range 250–415° for all compositions, is extrapolated on the isocomposition plot, it lies between the 80 and 90% isocomposition curves.

An important consideration in any hydride dissociation pressure study, which appears to have been overlooked by many of the earlier workers, has been the need of the highest purity hydride and hydrogen atmospheres. These factors are important not only because of the effect impurities have on dissociation data, as has been shown by experimental work in this Laboratory and by others,[13] but also because they influence the rate of attainment of equilibrium. It is also important for the calculation of equilibrium compositions that the volumes of the dissociation system be exactly known in order that the weight of hydrogen in the condensed phases may be calculated within close limits.

Examination of the curves in Figs. 3 and 4 shows that the dissociation pressure of sodium hydride is essentially independent of composition over the 25 to 90% composition range. The equilibrium pressures of both richer and poorer sodium–hydrogen composition phases are, however, dependent on composition, as shown by the curves. The significance of the isotherm plots, based on the phase-rule interpretation, has been covered adequately by Johnson, *et al.*,[10] in their paper on the calcium hydride system. Their explanation of the calcium–hydrogen system is analogous to the present study of the sodium–hydrogen system, the only variation being in the temperature and pressure ranges studied.

Probable Error of Measurements.—There were three major sources of error in these experiments.

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(13) M. N. A. Hall, S. L. H. Martin and A. L. G. Rees, *Trans. Faraday Soc.*, **41**, 306 (1945).

The first of these was encountered in measuring the volume of the high-pressure stainless steel container and the copper tubing leading to the recording pressure gage. This type of measurement has been checked and found to be good to within 3 cc. in approximately 100 cc. (~3%). The second source of error lay in the recording pressure gage itself. Pressures read directly from the gage were in general good to about 3 p.s.i. Percentage-wise they were difficult to evaluate, since the individual pressure reading may have been anywhere from a few p.s.i. to 900 p.s.i., giving a percentage of error of from 100 to 0.3%. For purposes of this evaluation, however, the error in these readings was taken as being less than 3%, since the majority of these readings were in excess of 100 p.s.i. The third source of error resulted from reading the closed-end manometer after removal of an increment of gas from the closed system. The mercury level in each arm of the manometer could be read accurately only to ±0.5 mm., giving an error of ±1 mm. in the pressure, which is the difference between the two levels. As was the case with the pressure-gage readings, the pressures themselves varied considerably but in general were about 30 cm. (0.3%). Other factors such as the temperature of the system and the weights of the hydride samples were known much more accurately, and errors in their determination were comparatively insignificant. From considerations of the above type, the over-all probable error in the experiments is known to be less than 5% and approximately 3%.

Thermodynamic Properties.—The values of ΔH listed in Table II are for the equilibria represented below, depending on the over-all composition of the system.

Over-all compn.	Equilibrium
100% NaH	$NaH(s) \rightleftarrows Na$(s, infinitely dilute soln. in NaH) + $^1/_2H_2$
98% NaH (sodium hydride-rich phase region)	NaH(s, containing 2% dissolved Na) $\rightleftarrows$ Na(s, 2% soln. in NaH) + $^1/_2H_2$
50% NaH (two-phase region)	NaH(s, saturated with Na) $\rightleftarrows$ Na(l, saturated with NaH) + $^1/_2H_2$
10% NaH (sodium rich phase region	NaH(l, 10% soln. in Na) $\rightleftarrows$ Na(l, containing 10% NaH) + $^1/_2H_2$

Since the compositions from 30 to 80% sodium hydride are clearly in the two-phase region, the dissociation pressures and ΔH values are constant and characteristic of the composition of the two individual saturated phases, rather than the overall composition.

Table II

Heat of Formation of NaH

Over-all compn. (% NaH)	$\Delta H^0_{500-600°}$ (cal./mole NaH)
100	11,610
90	13,300
80–30	13,590
20	13,860
10	14,250

The equilibrium constant for the dissociation may be expressed by the equation

$$K_a = \frac{a_{Na}(a_{H_2})^{1/2}}{a_{NaH}}$$

As a first approximation, the activities of sodium and sodium hydride are taken as unity and the activity of hydrogen as being equal to the pressure. With these assumptions

$$K_p = P_{H_2}{}^{1/2}$$

is established. It should be pointed out, since this study has shown sodium and sodium hydride exhibit mutual solubilities at the temperature range under consideration, the assumption of unit activities is somewhat in error. Using the value of K_p as obtained above, the ΔH values listed in Table II, and a ΔC_p value of 1.1 obtained from Kopp's rule,[14] the thermodynamic values tabulated in Table III have been calculated.

Table III

Standard Thermodynamic Properties of NaH

	100% NaH	30–80% NaH
$\Delta H^0{}_{550}$, cal./mole NaH	11,610	13,590
ΔF^0_T	11,610–17.41T	13,590–19.62T
$\Delta F^0_T = 0$	393°	419°
$\Delta F_{25°}$, cal./mole NaH	+6,410	7,730
$\Delta S^0_{25°}$, e.u.	15.5	17.7

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Beverly, Massachusetts

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(14) G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 472.