

941. *The Thermal Dissociation of Sodium Hydride.*

By C. C. ADDISON, R. J. PULHAM, and R. J. ROY.

Equilibrium dissociation pressures of hydrogen over sodium hydride have been determined for the temperature range 100–315°. The results support the relation $\log_{10} p_{(\text{mm})} = 11.66 - 6100/T$ and the value of $\Delta H = -13.94$ kcal./mole which apply at higher temperatures. At any given temperature, the dissociation pressures are shown to be virtually unchanged over the two-phase (sodium hydride–sodium) “plateau” region. When pure sodium hydride is heated, dissociation proceeds until the composition reaches the plateau range. At temperatures in the range 100–150°, dissociation rates corresponding to the forward reaction $\text{NaH} \longrightarrow \text{Na} + \frac{1}{2}\text{H}_2$ have been measured; they lead to values of 24.9 and 11.0 kcal./mole for the activation energies of the forward and back reactions, respectively.

PREVIOUS studies¹⁻⁷ of the dissociation of sodium hydride have employed temperatures above 280°. On thermal dissociation of the alkali metal hydrides, the metal produced may recombine with hydrogen at other parts of the apparatus unless the temperature is carefully controlled. This experimental complication has usually been overcome by enclosing the hydride in an iron or nickel ampoule, which is pervious to hydrogen but impervious to the vapour of the alkali metal. At low temperatures, pressure equilibrium is established slowly, and accurate results are therefore more difficult to obtain by this technique. In the course of a study of the hydrogen–liquid sodium system it became necessary to determine dissociation pressures at temperatures down to the melting point of sodium (97.8°). Complications resulting from the distillation of free sodium have been avoided without the use of permeable metal containers, so that the observed rates of change of hydrogen pressure represent the true behaviour of sodium hydride. Since low pressures are involved, it is necessary to prevent any surface contamination (such as a surface film of sodium hydroxide) that might arise during transfer of the hydride. A method has therefore been developed in which sodium hydride is prepared in the glass vessel to be employed for pressure measurement.

Dissociation pressures in the sodium–hydrogen system are represented by isotherms of the type shown in Fig. 1. The α region corresponds to true solutions of hydrogen in liquid sodium. Consequently, the equilibrium pressure at any given temperature increases with hydrogen concentration in solution; point A gives the solubility of hydrogen in

¹ Hautefeuille and Troost, *Ann. Chim. Phys.*, 1874, (5) **2**, 273; *Compt. rend.*, 1874, **78**, 809.

² Keyes, *J. Amer. Chem. Soc.*, 1912, **34**, 779.

³ Bardwell, *J. Amer. Chem. Soc.*, 1922, **44**, 2499.

⁴ Zhukov, *Ann. Inst. Analyt. Phys. Chim.*, 1926, **3**, 461; 1927, **3**, 600.

⁵ Herold, *Compt. rend.*, 1949, **228**, 686; *Ann. Chim. (France)*, 1951, **6**, 536.

⁶ Banus, McSharry and Sullivan, *J. Amer. Chem. Soc.*, 1955, **77**, 2007.

⁷ Sollers and Crenshaw, *J. Amer. Chem. Soc.*, 1937, **59**, 2724.

sodium, which decreases with decreasing temperature. Solubility determinations will be described in a later Paper. The pressure is constant in the plateau region β , and equilibrium is attained rapidly; the phase rule indicates the presence of two immiscible (but mutually saturated) phases consisting of sodium metal and sodium hydride. Values for these dissociation pressures in the temperature range 100–315° are reported in the present Paper.

The γ region represents a single phase consisting of the metal hydride containing "dissolved" metal. The many published studies of transition metal hydrides⁸ leave no doubt that equilibrium pressures can be obtained in this region, but all such cases appear to involve solid metals and rigid lattices. However, our results for sodium hydride, which involve temperatures at which sodium is liquid, indicate that the isotherm (Fig. 1) can only be extended beyond point B, *i.e.*, into the γ range, under particular experimental conditions. True dissociation pressures for sodium hydride are only obtained under conditions in which both forward and back reactions in the equilibrium $\text{NaH} \rightleftharpoons \text{Na} + \frac{1}{2}\text{H}_2$ can occur. The forward reaction depends only on temperature, but one of the main points that arises from the present work is that the back-reaction may or may not occur,

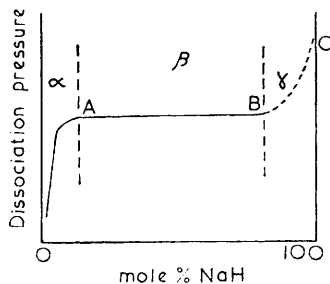


FIG. 1. The sodium-hydrogen system.

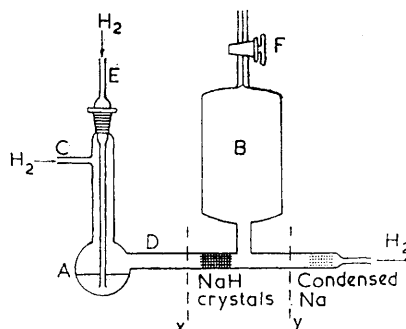


FIG. 2. Preparation of sodium hydride *in situ*.

depending on experimental conditions. Thus, in the presence of an excess of liquid sodium the back-reaction always occurs, so that the dissociation pressure is rapidly established for all compositions in the β (plateau) region. When such mixtures are heated *in vacuo*, the hydrogen pressure rises rapidly to the true dissociation pressure, and not beyond this. In the γ region, however, sodium metal is dispersed in the sodium hydride lattice, and whether or not this sodium is accessible for the back-reaction appears to depend (*inter alia*) on the hydrogen pressure. Thus Banus, McSharry, and Sullivan⁶ present a series of continuous isotherms for the range 500–600°, which include the region BC (Fig. 1) and extend to the 100% NaH axis. The axis points (corresponding to point C, Fig. 1) were obtained by heating the hydride under an imposed high pressure of hydrogen until an increase in pressure beyond that due to expansion was detected, and the imposed hydrogen pressure was then regarded as the dissociation pressure at that temperature. In contrast, all our experiments involve heating sodium hydride in an initial vacuum; low pressures (less than 1 mm.) are involved, and the only hydrogen present in the system is that produced by thermal decomposition of the hydride. Under these conditions, the hydrogen pressure continues to increase to values that may exceed fifty times the true dissociation pressure (as indicated by the plateau region), and it is clear that the back-reaction is not occurring at these low hydrogen pressures. The hydrogen pressure continues to increase until sufficient decomposition has occurred to give rise to a separate sodium phase (*i.e.*, composition B). The pressure reached under these conditions has no significance, being merely a function of the quantity of hydride present and the volume of

⁸ Gibb, "Progress in Inorganic Chemistry," Interscience Publishers, New York, Vol. 3, p. 315.

the vessel. When this hydrogen is removed from the system, true dissociation pressures are subsequently obtained. It follows, therefore, that in the temperature range 100—300°, where low pressures of hydrogen are involved, the isotherm cannot be extended into the γ region of Fig. 1. These experimental conditions have been specifically chosen, however, since they are the conditions under which the forward reaction alone can be studied.

In the temperature range 100—150°, dissociation rates are small but constant; they give a direct measure of the rate of the dissociation process $\text{NaH} \longrightarrow \text{Na} + \frac{1}{2}\text{H}_2$, and thus the activation energies for dissociation and formation. From the variation with temperature of the parabolic rate-constant for the uptake of hydrogen by sodium, Longton⁹ deduced a value for the activation energy. However, this process involves penetration through surface films, and the results are not directly comparable.

EXPERIMENTAL

Argon was purified as already described,¹⁰ and hydrogen (British Oxygen Co. Ltd., 99.9%) was treated similarly. The sodium used contained 8 p.p.m. of oxygen, and the calcium content was reduced to 0.01 wt. % by passage through glass sinter plates.

Preparation of Sodium Hydride.—Liquid sodium was run into the glass bulb A (2 cm. diam.) under an argon atmosphere (Fig. 2). The temperature of the bulb was then maintained within the range 375—400°. By the use of appropriate electrical windings, a temperature gradient was set up along tube D so that the temperature in D was about 320° where vessel B was joined to D, and about 300° at the hydrogen exit. The argon supply was then stopped; hydrogen was passed into the apparatus through C (1 l./min.) and was also bubbled through the liquid sodium *via* tube E. This disturbed the sodium surface, and prevented the formation of a cohesive film of sodium hydride, which would otherwise have prevented further reaction. Below 300°, the rate of hydride formation was very slow indeed, and above 400° there was pronounced attack of bulb A by the liquid sodium. Under the conditions described above, hydrogen reacted with sodium vapour; the hydride collected at the position shown in Fig. 2, whereas unchanged sodium vapour condensed at a separate position at the cooler end of the tube. The hydride was obtained as a matt of needles, which were quite colourless and thus free from excess of sodium. Tube D was sealed off at positions X and Y; by this means the pure hydride was enclosed in the vessel B, which was then used for the study of the thermal decomposition.

The quantities of sodium hydride used were determined both from the total quantity of hydrogen produced on decomposition, and by analysis of the remaining sodium.

Measurement of Dissociation Pressures.—Vessel B (Fig. 2) of about 0.5 to 1 l. capacity was attached through tap F to a vacuum line, which incorporated two McLeod gauges covering the pressure ranges 10^{-6} — 10^{-2} and 10^{-3} —2 mm. A bath of silicone oil controlled to $\pm 1^\circ$ was counter-balanced in such a way that it could be raised rapidly to immerse B up to the level of tap F. Vessel B was first evacuated at room temperature and tap F closed; the oil bath was brought to the required temperature, then raised to surround B. The hydride was allowed to decompose for a measured time; the oil bath was then rapidly removed, and the cooling of B was assisted by a stream of cold air. This had the effect of "freezing" the equilibrium $\text{NaH} \rightleftharpoons \text{Na} + \frac{1}{2}\text{H}_2$, since the rate of the back-reaction to reform the hydride is negligible at the lower temperatures. The hydrogen in B was then expanded into the calibrated vacuum frame; the pressure was measured on the appropriate McLeod gauge, and from this the original pressure of hydrogen in B at room temperature was determined. This was corrected for temperature and bulb expansion to give the dissociation pressure of hydrogen at the temperature of the experiment. Vessel B was again evacuated, and the procedure for pressure measurement was repeated allowing different time intervals for dissociation. By this means it was possible to determine rates of dissociation, and to recognise equilibrium pressures.

RESULTS AND DISCUSSION

The Plateau Region.—In this region, the dissociation pressure (Table 1) is independent of time of heating.

Our values, for the temperature range 100—250°, are compared in Fig. 3 with values

⁹ Longton, U.K.A.E.A. Report, IGR-TN/C. 435, 1957.

¹⁰ Addison, Iberson, and Raynor, *Chem. and Ind.*, 1958, 96.

obtained by Banus *et al.*⁶ at 500—600° and by Herold⁵ at 280—415°. The line in Fig. 3 corresponds to the equation

$$\log_{10} p = 11.66 - 6100/T \quad (1)$$

proposed by Herold,⁵ and it is clear that this equation represents the pressure-temperature relationship satisfactorily over the full temperature range. The scatter of results increases somewhat at very low pressures, and the slight departure from the line at temperatures near the melting point of sodium, may not be a real effect. These results therefore support Herold's value of 13.94 kcal./mole for the heat of formation of sodium hydride, rather than

TABLE I.

Equilibrium dissociation pressures (p) of sodium hydride.

Temp.	p (mm.)	Temp.	p (mm.)
100°	2.69×10^{-4}	185°	1.26×10^{-2}
120	1.16×10^{-3}	200	5.65×10^{-2}
135	1.25×10^{-3}	220	0.153
151	1.21×10^{-3}	225	0.341
165	6.65×10^{-3}	250	1.193

the value 14.4 kcal./mole obtained by Sollers and Crenshaw⁷ from results within the narrow temperature range 310—380°. A value of $\Delta H_{298} = -13.6 \pm 0.27$ kcal./mole has also been determined from heats of reaction of sodium hydride with water.¹¹

All the dissociation pressures discussed above relate to the hydride-rich end of the plateau, and Banus *et al.*⁶ have deduced that Herold's results⁵ were also obtained on sodium

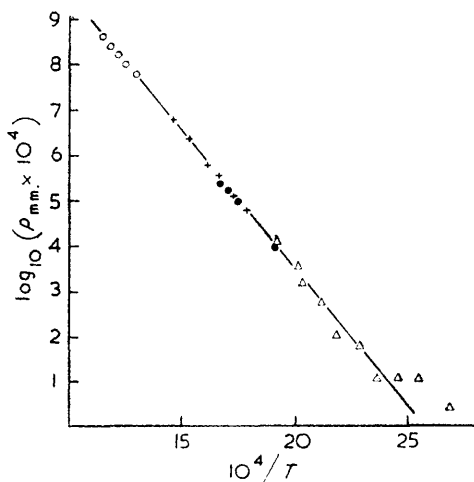


FIG. 3. Equilibrium dissociation pressures of sodium hydride.

○ ○ Banus *et al.*⁶. × × Herold.⁵
 ● ● Present work; large excess of sodium.
 △ △ Present work; partially dissociated sodium hydride.

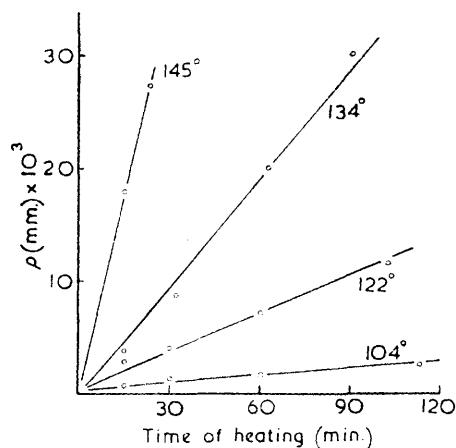


FIG. 4. Linear variation of dissociation pressure with time at low temperatures. (0.103 g. of fresh sodium hydride, vessel volume 922 ml.)

hydride that was 10—20% decomposed. The extent to which the dissociation pressure varies throughout the plateau region at different temperatures is of particular interest. Extrapolation of the solubility values of Williams, Grand and Miller¹² indicates that the solubility of sodium hydride in liquid sodium at 500° is about 10—15 mole %. Banus *et al.*⁶ have observed that at 500—600° the variations in pressure over the composition

¹¹ Messer, Fasolino, and Thalmayer, *J. Amer. Chem. Soc.*, 1955, **77**, 4524.

¹² Williams, Grand, and Miller, *J. Phys. Chem.*, 1957, **61**, 379.

range of the plateau are extremely small. In a study of the solubility of hydrogen in sodium at lower temperatures, we have obtained equilibrium dissociation pressures for two-phase sodium hydride/sodium systems containing over 99.7 mole % of liquid sodium. These values are superimposed in Fig. 3, and are compared with values for hydride-rich systems in Table 2.

TABLE 2.

Variation in equilibrium dissociation pressure (p) in the plateau region.

Temp.	250°	300°	315°
p mm. (60 mole % NaH) *	1.00	10.5	19.5
p mm. (<0.3 mole % NaH)	0.97	9.7	18.6

* Calculation from equation (1).

The results confirm that the pressure changes only slightly over the much wider composition range that is covered by the plateau at these lower temperatures.

Non-equilibrium Systems.—Freshly prepared sodium hydride was heated in an evacuated vessel at temperatures within the range 100–150°. The decomposition rates (Fig. 4) are constant at any one temperature, but vary considerably with change in temperature, and the pressures measured within the two-hour period increase to values that are up to fifty times those corresponding to the plateau pressure. Under these conditions, the forward reaction ($\text{NaH} \rightarrow \text{Na} + \frac{1}{2}\text{H}_2$) only is occurring; the appropriate rate constants k_f are given in Table 3.

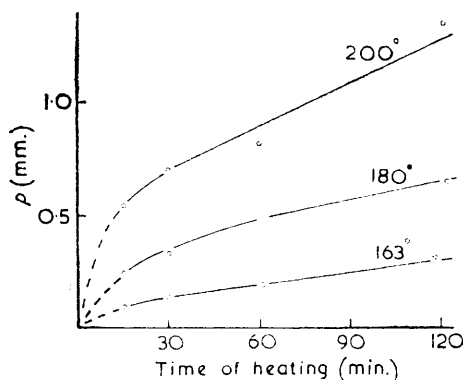
TABLE 3.

Rate constants (k) and equilibrium constants (K) for the thermal dissociation of sodium hydride.

$10^3/T$ (°K)	$k_f \times 10^3$ (mole fraction NaH decomposing per sec.)	$K \times 10^4$	$k_b \times 10^4$
2.65	0.73	1.99	0.366
2.53	3.35	4.67	0.716
2.46	8.81	7.85	1.12
2.39	32.6	12.4	2.62

In a plot of $\log_{10} k_f$ against $1/T$, the first three points (Table 3) lie exactly on a straight line, the slope of which gives a value of the activation energy for the forward reaction, $E_f = 24.9$ kcal./mole. The fourth point lies a little off the line; it was not used in the

FIG. 5. Variation in dissociation rates at 150–200°. (Experimental conditions as in Fig. 4.)



calculation of E_f , since only two determinations were made at short heating times, and 145° is approaching the temperature for which the pressure-time relation is not linear (Fig. 5). Since $\Delta H = E_f - E_b$, the activation energy for the back-reaction (*i.e.*, formation of sodium hydride from the elements) is 11.0 kcal./mole. Alternatively, if we assume the

activities of sodium hydride and sodium to be unity, and the activity of hydrogen as equal to the pressure in view of the low pressure involved, then the equilibrium constant $K = p^{\frac{1}{2}}$ where p is the dissociation pressure given by equation (1). Values of K (p being expressed in atmospheres) are given in Table 3. Furthermore, if it is assumed that the formation and decomposition of sodium hydride involve the same mechanisms (at least so far as the rate-determining steps are concerned), then $K = k_i/k_b$, where k_b is the rate constant for the back reaction. A plot of k_b against $1/T$ gives the value $E_b = 11.1$ kcal./mole.

As temperature is increased above about 150° , the initial rate of decomposition of the hydride continues to increase rapidly, but at any one temperature the decomposition rate becomes slower on continued heating (Fig. 5). The shape of these curves will be due, to some extent, to the diminishing quantity of sodium hydride present in the sample as decomposition proceeds. To assess the significance of this factor, a series of experiments was carried out in which a fresh sample of pure sodium hydride was heated for varying periods at 167° . From the quantity of hydrogen produced, it was possible to determine the extent of decomposition at the end of each experiment. In each case, the measured pressure was

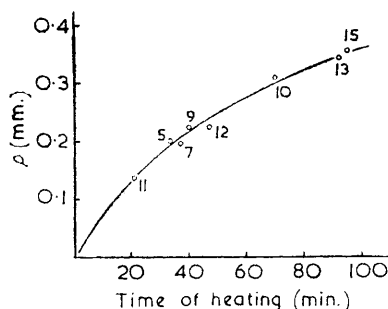


Fig. 6. Dissociation pressures of sodium hydride at 167° , corrected for variation in composition.

(Initially 0.0222 g. NaH, vessel volume 545 ml.)

Expt. No.....	5	9	10	11	12	13	14	15
Mole % NaH in sample at end of each experiment	96.6	93.0	91.7	91.2	90.4	89.1	88.4	87.1

(Intermediate experiments involved other temperatures, but the hydrogen evolution is allowed for in calculating composition.)

then corrected to allow for this decomposition, assuming that under standard conditions the pressure would be proportional to the quantity of hydride available. The results (Fig. 6) lie close to a smooth curve rather than a straight line, so that some factor other than changes of composition in the sample is responsible for the variation in decomposition rates. The back-reaction of hydrogen with sodium may begin to be significant at these pressures. On the other hand, we may also regard the pressures shown in Fig. 6 as being produced by a constant quantity of sodium hydride that has an increasing number of sodium atoms dispersed throughout its lattice. The attraction of Na^+ for H^- ions is the main factor in determining the lattice energy, and the presence of Na atoms may also help to retain H^- in the lattice. In the low-temperature experiments (Fig. 4), the quantity of sodium in the lattice is insufficient to influence the linear pressure-time relation.

Transition from Non-equilibrium to Plateau Pressures.—Figs. 4–6 have illustrated the behaviour of sodium hydride/sodium systems in the γ composition range (Fig. 1) represented by sodium hydride that is decomposed to a small extent. If hydrogen is withdrawn progressively from sodium hydride, a stage is reached at which the hydrogen pressure produced under standard conditions falls rapidly. A series of identical experiments was carried out in which the sample was heated at 200° for 30 minutes, the dissociation pressure measured, the vessel evacuated, and the process repeated. The pressures obtained

TABLE 4.

Pressures developed in identical successive experiments (initially 0.0222 g. NaH, vessel volume 545 ml.).

Pressure (mm.) after 30 min. heating at 200°	0.96	0.90	0.64	0.31	0.26	0.17	0.09	0.07	0.05
Mole % NaH in sample after each expt.	82.8	77.4	74.7	67.0	66.1	64.2	62.0	61.1	60.0

during the first 15% of decomposition were consistently high, but then fell rapidly in successive experiments (Table 4) to a value corresponding to the plateau pressure. Thereafter, the pressure values were reproducible and independent of the time of heating, and were established within 15 minutes. The sharp decrease in the rate of hydrogen evolution occurs as the composition passes from the γ into the β range, *i.e.*, through point B (Fig. 1) and semi-quantitative experiments at other temperatures have shown that the behaviour illustrated in Table 4 is a characteristic property of sodium hydride.

The compositions corresponding to both the plateau limits A and B (Fig. 1) vary with temperature, and are being determined in separate investigations.

The authors are grateful to the United Kingdom Atomic Energy Authority for financial assistance.

THE UNIVERSITY, NOTTINGHAM.

[Received, February 5th, 1964.]