It should be noted that the pressures in Table III are "partial pressures" of carbon dioxide and not total pressure and the experimental data are slightly different from those of Table II. In making this correction we have taken into account the change of vapor pressure of water with total pressure.[14] The agreement is quite remarkable and falls down only at 700 atm. The weak point, assuming for the moment that formula (3) will represent the true course of solubility, is how to select the partial molal volume for the liquid, since usually only values at one atmosphere and one temperature are known. In our case we adjusted the value of $\overline{V}$ until we got a reasonable fit. It clearly shows that even though of interest, a prediction based on such a calculation would be uncertain. Equation 3 brings out the fact mentioned previously that when the gas phase assumes the characteristics of a liquid, the change in $\overline{V}_1^1 - \overline{V}$ will be small and consequently the solubility will be affected by pressure only slightly. Zelvinskii's results[3] were expressed in cc. gas (S. T. P.) per cc. of water. The volume of water was taken at room temperature which we suppose was 20° and we believe he used "partial pressures." In order to compare our low pressure results with those of Zelvinskii we have made the corresponding changes and the two sets are given in Table IV. The agreement is poorer the higher the pressure. At 100° Zelvinskii admits that he could not get reproducible results above 60 atmospheres. In the other instances

(14) See Table II in Wiebe and Gaddy, This Journal, **56**, 76 (1934).

Table IV

"Partial pressure" of CO_2, atm.	Solubility[a] 50°		Solubility[a] 75°		Solubility[a] 100°	
	Our values	Zelvinskii's equation 3	Our values	Zelvinskii's equation 4	Our values	Zelvinskii's equation 5
25	9.74	9.65	6.90	7.10	5.57	5.57
50	17.25	17.35	12.65	12.99	10.35	10.75
75	22.52	23.10	17.09	17.67	14.42	15.51
100	25.62	26.90	20.62	21.14	17.78	19.88

[a] Solubility expressed in cc. gas (S. T. P.) per cc. of water, the latter at 20°.

his experimental fluctuations would explain the discrepancies. He was handicapped in not having a piston gage but had to resort to a roundabout intermittent compressibility measurement to calculate his pressure, using a Bourdon gage in the meantime. Zelvinskii obviously could not anticipate the sudden change in the solubility curve beyond 100 atm. and his equations therefore cannot be used for extrapolation.

We want to thank Mrs. W. E. Deming for helping us in our calculations.

Conclusion

An apparatus for measuring the solubility of carbon dioxide in water has been described.

The solubility of carbon dioxide in water has been measured at 50, 75 and 100° from 25 to 700 atm.

A calculation of the solubilities was made at 75 and 100°, according to the theory of dilute solutions, and agreement was obtained.

Carbon dioxide, like nitrogen, hydrogen and helium, shows a minimum of solubility, though only in the higher pressure range.

The Rate of Formation and the Dissociation of Calcium Hydride

By Warren C. Johnson, Morris F. Stubbs, Albert E. Sidwell and Alphonse Pechukas

A survey of the literature shows a wide variation in the results obtained by several investigators who have studied the reaction between hydrogen and calcium.[1] Although there is no question that a definite compound is formed between these elements, there is considerable uncertainty regarding the conditions for combination. This situation may be attributed to several factors among which are: (1) the variations in the purity

(1) See Remy-Genneté, Ann. chim., [10] **19**, 353 (1933), for earlier references.

of the calcium and of the hydrogen, (2) the form and surface area of the metal and (3) the presence or absence of a film of oxygen or nitrogen or both on the surface.

Metallic calcium which has been exposed to air does not react appreciably with hydrogen at room temperature; but when it is purified by distillation and maintained in a vacuum, it will react slowly with hydrogen at a temperature as low as 0°.[1] Hüttig[1] has observed that calcium is exceedingly active when it is obtained from a liquid ammonia

solution by evaporation of the solvent. It was found to burn rapidly in air and to absorb appreciable amounts of hydrogen at ordinary temperatures.

The activity of calcium obtained from liquid ammonia solution may be explained readily when one considers the condition of the metal in this medium. Kraus[2] has shown that calcium forms a compound with ammonia, the composition of which is represented by $Ca(NH_3)_6$. When the ammonia solution is allowed to evaporate, the first solid phase to appear is the hexammonate. The latter has a high dissociation pressure, even at the boiling point of ammonia; accordingly, it readily decomposes to give ammonia and metallic calcium in a very finely divided state. The alkali metals do not form ammonates with ammonia at temperatures above $-100°$; consequently, alkali metal solutions upon evaporation yield crystals of the metal directly. These crystals are relatively inactive toward hydrogen at ordinary temperatures. Barium and strontium also form hexammonates with ammonia and their behavior is similar to that of calcium.

The dissociation of calcium hydride also has been studied by a number of workers,[3] the results of which have been interpreted in several ways. The conclusions can be digested into the following: (A) calcium hydride dissociates to give calcium and hydrogen

$$CaH_2 = Ca + H_2 \qquad (1)$$
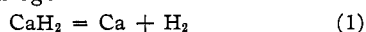
an equilibrium exists among the three constituents, and at a given temperature the equilibrium pressure of the hydrogen is independent of the relative amounts of the solid phases present; (B) the dissociation of the hydride takes place in two steps, one of which involves the formation of a sub-hydride

$$CaH_2 = CaH + 0.5H_2 \qquad (2)$$
$$CaH = Ca + 0.5H_2 \qquad (3)$$
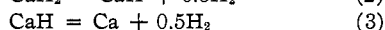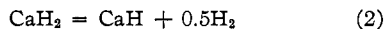
and likewise an equilibrium is assumed to exist among the four constituents with the pressure of the hydrogen being independent of the composition of the solid phases; and (C) calcium hydride and metallic calcium form a series of solid solutions with the dissociation pressure being dependent upon the composition of the condensed mixture.

The widely divergent opinions arising from the results of dissociation measurements may be ex-

(2) Kraus, THIS JOURNAL, **30**, 653 (1908).

(3) See Remy-Genneté, *Ann. chim.*, [10] **19**, 263 (1933), for earlier references.

plained in part by the fact that different procedures have been employed in the experimental studies. However, it appears more significant to us that most of the workers have confined their measurements to rather limited experimental conditions; consequently, their conclusions are based upon results which pertain only to these conditions.

In the present investigation a study is made of the conditions favorable for the formation of calcium hydride by the reaction of hydrogen with different forms of metallic calcium. In the case of the active form of calcium derived from a liquid ammonia solution, the rate of the reaction is studied and an attempt is made to interpret the results from a kinetic standpoint. In addition, a study is made of the dissociation of calcium hydride over a wide range of temperature and in particular of composition of the solid phases. The results which have been obtained support the suggestion of the formation of solid solutions of calcium in calcium hydride and of calcium hydride in calcium. There is no indication of the existence of a sub-hydride of calcium. The results also explain as well as unify those of former workers.

Experimental

Purification of Metallic Calcium.—The metallic calcium was obtained from the American Magnesium Corporation. For analysis, it was precipitated as calcium oxalate which was then ignited to the oxide and weighed. *Anal.* Found: Ca, 97.15, 97.19. Qualitative tests showed the presence of small amounts of the chloride, oxide and nitride of the element.

The metal was purified by distillation in a vacuum at high temperatures. For this purpose, a still was used which consisted of a hollow cylinder of Swedish iron, very low in carbon content, about 4 cm. in external diameter and 0.6 cm. wall, as shown in Fig. 1. Approximately 10 g. of calcium is placed in A and then condenser B is immediately screwed in position. The still is inserted in a vertical electric furnace and then evacuated to a pressure of 0.001 mm. A rapid stream of water is allowed to flow through the condenser while the furnace is gradually heated to 750–800°. This temperature is maintained for a couple of hours, with the vacuum pumps in operation, during which time the calcium sublimes to the bottom of the condenser. The furnace is then allowed to cool and the cylinder is filled with butane gas at atmospheric pres-
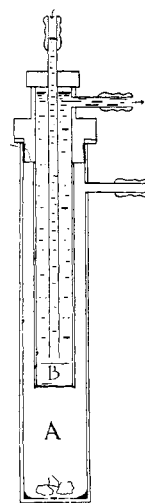

Fig. 1.—Distillation apparatus.

sure. Finally, the condenser is removed so that the calcium may be scraped from the bottom. The metal was found to adsorb oxygen and nitrogen on its surface;[4] hence, to obtain the metal in its most active condition care must be exercised to prevent direct contact with the atmosphere. A second distillation was made in each preparation and several samples were subjected to analysis. *Anal.* Found: Ca, 99.47, 99.54.

Purification of Hydrogen.—Ordinary tank hydrogen was purified by diffusion through a heated palladium tube as described by Kraus and Lucasse.[5]

Preparation of Calcium Hydride at 230–270°.—Metallic calcium, exposed to air or transferred from the still described above in the presence of butane gas, does not react with hydrogen at room temperature. On the other hand, if the distilled metal is kept in a vacuum, it will react with hydrogen slowly at room temperature. Under these conditions the rate of the reaction is too low for the preparation of appreciable amounts of calcium hydride.

A temperature of 230–270° was found very satisfactory for the preparation of calcium hydride. The apparatus used for this purpose is shown in Fig. 2. It consists es-
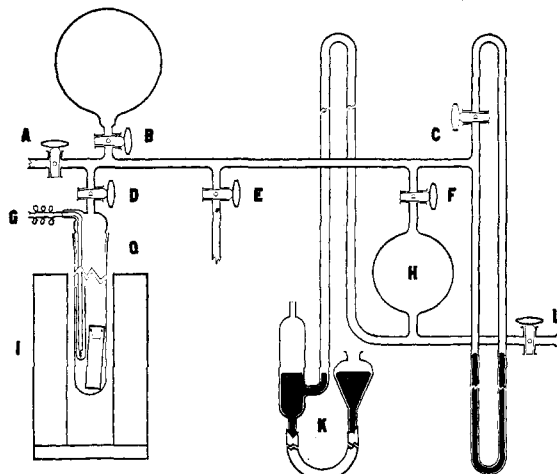

Fig. 2.—Apparatus for preparing calcium hydride and determining its dissociation pressure.

sentially of a storage bulb H for hydrogen, obtained directly from the palladium diffusion tube through L, a quartz reaction chamber Q, a suitable manometer and a means of removing hydrogen from the system. Stopcock A opens into a system comprising a McLeod gage, a mercury vapor pump and an oil pump. Stopcock B leads to a second hydrogen storage bulb, while D opens to the reaction tube which is attached to the system by means of a quartz-Pyrex glass ground joint at Q. Through the upper portion of the ground joint are sealed platinum, platinum-rhodium thermocouple lead wires; they extend below in the reaction tube to a position indicated in the figure. By means of mercury trap K, H may be filled with purified hydrogen at a given pressure.

The furnace I is so constructed as to move freely in a vertical direction between two steel rods. It is heated

electrically and maintained at constant temperature by placing it in series with U. V. 876 ballast tubes.[6] A Leeds and Northrup type K potentiometer was used in measuring the e. m. f. developed by the thermocouple. The thermocouple was calibrated with Bureau of Standards metals at their freezing points. Swedish iron containers were used for the metallic calcium. The walls of these containers varied from 1–1.5 mm. in thickness, while the length was about 5 cm. and the diameter about 1 cm.

In preparing the hydride, about 1 g. of calcium is introduced into the iron tube which is then placed in position in Q. The system is evacuated and when the desired temperature is reached, a known amount of hydrogen is allowed to enter the tube and come in contact with the metallic calcium.[7] With the volume of all flasks and tubes known, the rate as well as the extent of the reaction may be followed by the change in pressure of the hydrogen. The results of a few preparations are given in Table I for both undistilled and distilled calcium. Although only one sample richer than 95% is indicated here after the reaction had proceeded for two hours, by again increasing the pressure of the hydrogen, 99–100%[8] samples were obtained in a relatively short period of time.

TABLE I

THE ACTION OF HYDROGEN ON CALCIUM IN THE REGION OF 250°

Ca, g.	Temp., °C.	Initial press., cm.	5	10	20	30	60	120
			Time in minutes					
			% CaH₂ formed					
A. Undistilled Calcium								
1.1500	250	67.5	6.6	39.8	63.8	72.9	84.9	87.1
0.6379	270	63.1	3.4	12.7	56.6	75.2	85.0	85.5
1.0178	270	87.6	14.8	48.3	74.2	83.5	89.0	90.0
0.7662	270	69.1	26.4	47.6	73.7	85.3	89.0	89.0
B. Distilled Calcium								
1.4265	230	73.6		23.1		63.8		95.3
1.7631	250	85.0	61.1					93.0
0.7531	250	80.0	76.2					93.0
.4544	250	50.0						99.2

Attempts to hydrogenate calcium completely at high temperatures, 650–900°, in a closed iron tube were unsuccessful. Under these conditions, the limit of the reaction was always found at approximately 90%. This point will be discussed later in connection with the dissociation measurements.

The Action of Hydrogen on Active Calcium at Temperatures 0–150° and at High Pressures.—The apparatus used for a study of the rate of the reaction between hydrogen and active calcium at relatively low temperatures and at pressures ranging from 10–90 cm. was essentially that shown in Fig. 3, with the exception that a mercury manometer was used in place of the McLeod gage F. It consists principally of a reaction tube B, a storage bulb for hydrogen G, and a means for maintaining constant temperature in the jacket C. For the latter purpose a liquid of known boiling point is placed in D and allowed to con-

(4) This result substantiates observations made by Remy-Genneté, *cf.* ref. (1).

(5) Kraus and Lucasse, THIS JOURNAL, **44**, 1941 (1922).

(6) Jones, *Gen. Elec. Rev.*, **28**, 329 (1925).

(7) In this temperature range, 230–270°, the vapor pressure of metallic calcium is too low for distillation. See Pilling, *Phys. Rev.*, [2] **18**, 362 (1921).

(8) Hereafter the percentage of calcium hydride in a given sample will signify the amount of calcium which has been converted to the hydride on the basis of the formation of CaH₂ in accordance with the equation: Ca + H₂ = CaH₂.

dense in A. H leads to the vacuum pumps as well as to a supply cylinder of liquid ammonia, while I leads to the palladium diffusion tube.
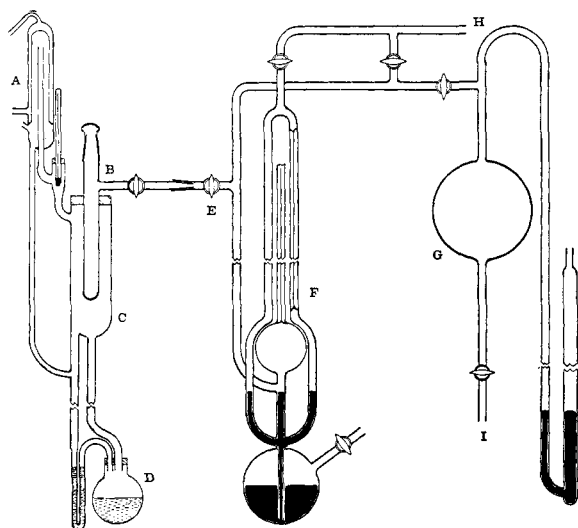

Fig. 3.—Apparatus for studying rate of reaction.

To carry out a series of measurements the entire apparatus is first evacuated. The reaction tube B, which is connected to the vacuum system through a glass-ground joint, is then removed and weighed. It is again attached to the system and a small piece of distilled calcium (0.2–0.3 g.) is dropped into the tube, the glass-ground top being replaced as quickly as possible. The tube is again evacuated and weighed and then liquid ammonia is distilled from the supply tank and condensed on the calcium at −80°. About 5–10 cc. of liquid ammonia is required to ensure complete solution of the calcium. The greater part of the ammonia is then removed at −80° by opening the stopcock E leading to the vacuum pumps. Finally the tube is allowed to warm to room temperature and the last traces of ammonia are pumped out rapidly. This procedure is followed to reduce to a minimum the reaction between ammonia and calcium, $Ca + 2NH_3 = Ca(NH_2)_2 + H_2$. The extent to which this reaction takes place depends upon the length of time the ammonia is allowed to remain in contact with the calcium, the temperature and the presence of impurities in the calcium such as iron and calcium oxide which act as catalysts. Under favorable conditions it was found possible to reduce the formation of calcium amide to 1–2% of the metallic calcium originally used. When the ammonia is removed, about two-thirds of the inside wall of the reaction tube is covered with a layer of finely divided metallic calcium.

Hydrogen gas at a known pressure is permitted to enter the reaction tube from the storage bulb G, and the rate of the reaction is followed by the manometer. At 200° the rate was too high to observe. Some of the results, illustrating typical experiments, are plotted in Fig. 4 with the logarithm of the pressure in cm. as ordinates and the time in hours as abscissas.[9] Experiments 11–12 were carried out at 0° (11 is not shown in the figure since it

(9) These experiments were carried out by Mr. V. B. Henry.

practically coincides with 5); experiments 1–6, at 25°; 7–9 at 100°; and 14–15, at 150°. The last two experiments are not shown in the figure since the rates of the reactions were so high that on the scale of this plot they coincide closely with the pressure axis.

Although the data plotted in Fig. 4 follow a linear relationship in a remarkable manner, nevertheless they show many irregularities at a given temperature. Thus, it is seen that the rate increases markedly as the initial pressure diminishes at a given temperature. This may be explained in part by the fact that different amounts of calcium were used in the series of experiments. In addition, differences in the size of the calcium crystals and the amount of adsorbed gases on their surfaces are undoubtedly more important factors. It is also significant that in all of these experiments a relatively large portion of the metallic calcium is converted to calcium hydride. In several cases as much as 90% of the calcium formed the hydride.
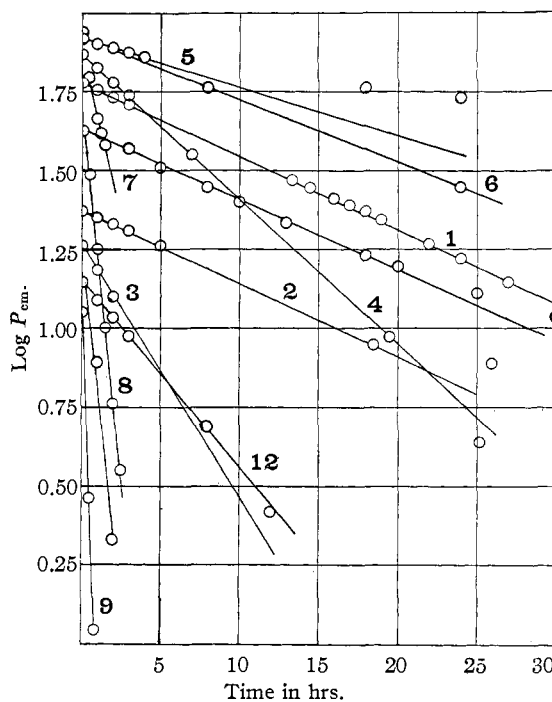

Fig. 4.—Rate of reaction between active calcium and hydrogen at high pressures.

The Rate of the Reaction between Active Calcium and Hydrogen at Low Temperatures and at Low Pressures.— A study of the rate of the reaction at low pressures, 0.1–10 mm., in which process a relatively small amount of the calcium is consumed, gave results consistent with the first order equation but likewise showed the irregularities mentioned above. To avoid these objectionable features it was decided to study the rate for a single sample of calcium over the entire temperature range. In this way a more nearly constant amount of free calcium is maintained and uncertainties due to the preparation of several samples are eliminated.

The apparatus employed is that shown in Fig. 3. A McLeod gage F was designed (volume 50 cc.) to measure

pressures ranging from 0.0001 to 15 mm. The procedure consists in first making a series of measurements with a given sample of calcium (about 0.25 g.) at 25°, then successively at 55, 73 and 100°. Paraffin oil was used as a thermostat at 25°; boiling acetone in flask D, at 55°; carbon tetrachloride, at 73°; and water, at 100°. It was found advisable to maintain the initial pressure at each temperature of the same order of magnitude. In most experiments, the rate was also followed from 100–25° as a check on measurements made by increasing the temperature.

All data were found to agree well with the log p–time plot. Figure 5 shows this relationship for two experiments only. The measurements represented by the upper group of lines were made at initial pressures of hydrogen in the neighborhood of 10 mm., while the lower group of lines represents measurements made at initial pressures of the order of 1 mm.
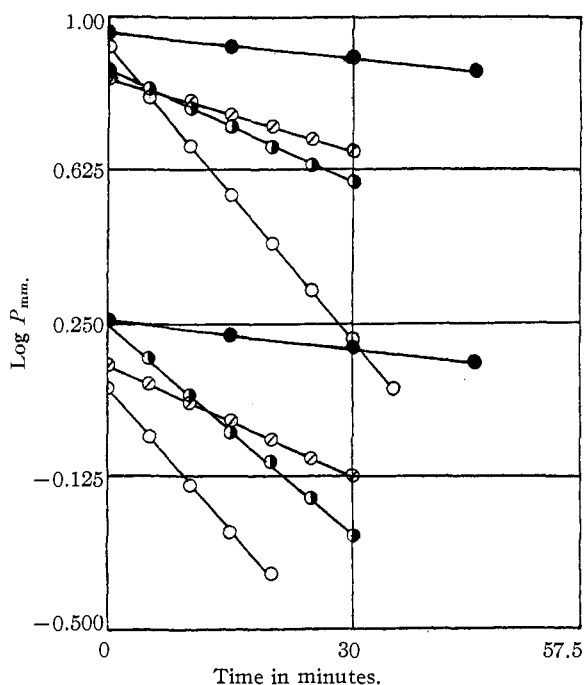

Fig. 5.—Rate of reaction between active calcium and hydrogen at low pressures: ●, 27°, ⊘, 55°, ◑, 73°, ○, 98°.

The Heat of Activation.—Since the slope of the log rate–log p plots for all of the experiments was found to have a value ranging from 0.9 to 1.1, the value of 1.0 was assumed for the order of the reaction. The rate of the reaction of calcium with hydrogen may then be expressed by

$$-\mathrm{d}(H_2)/\mathrm{d}t = K(H_2)$$

or

$$-\mathrm{d}\ln(H_2)/\mathrm{d}t = K$$

assuming the amount of free surface of the calcium to be constant. The Arrhenius equation becomes in this case

$$\mathrm{d}\ln[-(\mathrm{d}\ln p/\mathrm{d}t)]/\mathrm{d}(1/T) = -E/R$$

E is the heat of activation of the reaction and the assumption is made that the volume of the apparatus and the amount of effective surface of the calcium are independent of the temperature. In Fig. 6 the logarithm of the slope of the log p–time isotherms is plotted against $1/T$. K'' is defined as being equal to $-\mathrm{d}\log p/\mathrm{d}t$. The value for the heat of activation is found to be 7700 ± 500 cal./mole.
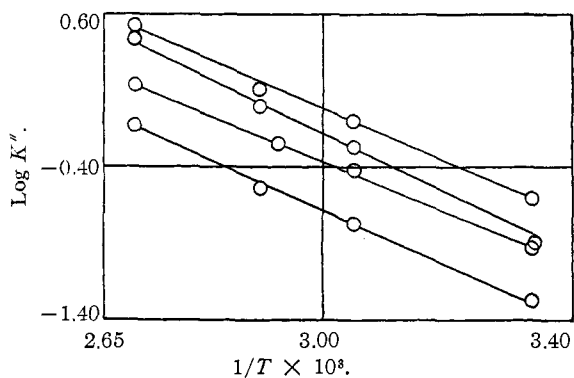

Fig. 6.

Equilibrium Measurements

The apparatus shown in Fig. 2 was used for studying the equilibrium between calcium hydride, calcium and hydrogen. Several experiments were carried out using open iron tubes as containers for the calcium in order to reproduce more closely the conditions employed by several previous investigators. However, reliable data were obtained only by using closed tubes which were suggested by the work of Remy-Genneté.[8] The open tubes previously described were fitted with tapered or threaded plugs after the calcium had been introduced. When heated to a temperature in excess of 600°, hydrogen was free to diffuse through the walls of the tube but the calcium and calcium hydride were confined within. This procedure prevented metallic calcium from coming in contact with the walls of the fused silica tube. In later experiments it was found convenient to drill a small hole in the top of the plug of the tube and to insert in it the thermocouple junction, protected with a thin-walled fused silica tube. This procedure gave a better indication of the temperature of the tube.

The low temperature preparation of the hydride was usually carried out at 250° in an open iron tube as previously described. With a hydride of known composition prepared, the plug of the iron tube and the thermocouple were then fitted in position, the system was evacuated and finally equilibrium measurements were made after temperature control had been established. All equilibrium pressures were obtained by approaching the equilibrium point from both directions; no value was taken until the pressure had remained constant for at least twelve hours and all measurements were repeated several times.

I. **Closed Iron Tube; Addition of Hydrogen to Calcium at High Temperatures.**—Metallic calcium, previously twice distilled, was placed in an iron tube which was then

closed with a plug. After it had been placed in position in the fused silica tube, the entire system was evacuated to a pressure of 10^{-4} mm. and then the furnace was heated to 778°. Hydrogen gas was allowed to enter the system initially at a pressure of 1–1.5 mm., which value is considerably lower than that recorded in the literature for the dissociation pressure of calcium hydride at this temperature. However, the calcium was found to absorb hydrogen readily at these low pressures. By increasing the pressure of the hydrogen in the system a few millimeters, more gas was absorbed and the apparent equilibrium pressure assumed a slightly higher value. This procedure was continued until an approximately 20% hydride was produced. Beyond this point, higher pressures of hydrogen were required for further reaction, but the final equilibrium readings then assumed constant values which were in good agreement with those given by Hurd and Walker and also by Remy-Genneté[3] who worked with mixtures ranging in composition from 20–90% calcium hydride. Although it

was found necessary to increase the hydrogen pressure steadily as the mixture became richer in hydride, at no time was the pressure of the hydrogen in the system greater than the normal equilibrium value below the 20% calcium hydride composition.

Several experiments of this type were carried out at different temperatures. In each instance, hydrogen was absorbed by the calcium at pressures considerably lower than those previously reported. The data are shown in Table II; they represent typical experiments and include only a few of the pressure values for a given temperature. In the actual experiments the measurements were made at small composition intervals. In Fig. 7 the pressure in cm. as ordinates is plotted against the composition in mole per cent. calcium hydride as abscissas. The points are indicated as clear circles.

TABLE II

EQUILIBRIUM PRESSURES AT A SERIES OF COMPOSITIONS
AND TEMPERATURES

A. 0.4745 g. Calcium at 778°

% CaH₂	0.3	0.7	1.7	6.9	10.7	14.6
Press., cm.	0.0	0.1	0.1	0.4	0.6	1.05

% CaH₂	15.5	17.1	19.3	20.2	21.5
Press., cm.	1.10	1.20	1.40	1.41	1.41

B. 2.0376 g. Calcium at 778°

% CaH₂	0.2	0.3	0.6	0.9	1.4	2.5	6.1
Press., cm.	0.0	0.0	0.03	0.05	0.1	0.12	0.25

% CaH₂	8.5	10.8	13.1	19.2	26.4	34.0	48.7
Press., cm.	0.39	0.53	0.90	1.40	1.41	1.41	1.40

C. 0.3035 g. Calcium at 805°

% CaH₂	3.5	6.3	11.5	15.4	21.2	27.3
Press., cm.	0.30	0.50	1.30	2.20	2.84	2.81

% CaH₂	41.2	55.2	68.8	84.2	90.9
Press., cm.	2.81	2.81	2.81	2.90	3.00

D. 0.3035 g. Calcium at 825°

% CaH₂	9.2	13.0	17.0	20.3	25.5	34.6
Press., cm.	1.56	2.20	3.10	3.95	3.95	3.96

E. 0.3035 g. Calcium at 840°

% CaH₂	6.4	9.6	17.4	22.0	32.0	37.4
Press., cm.	1.10	1.90	4.50	5.23	5.24	5.40

F. 0.3035 g. Calcium at 860°

% CaH₂	10.3	14.0	18.0	25.1	30.0
Press., cm.	2.20	4.00	7.00	8.26	8.26

G. 1.7051 g. Calcium at 888°

% CaH₂	11.0	15.0	19.2	24.1	28.0	39.2	78.5
Press., cm.	2.50	5.65	11.75	13.83	13.80	13.82	13.80

H. 0.8491 g. Calcium at 894°

% CaH₂	8.1	14.4	17.0	19.2	25.0
Press., cm.	1.70	5.90	9.78	13.60	14.95

% CaH₂	30.2	34.5	38.8	42.6
Press., cm.	15.40	16.25	17.51	17.51

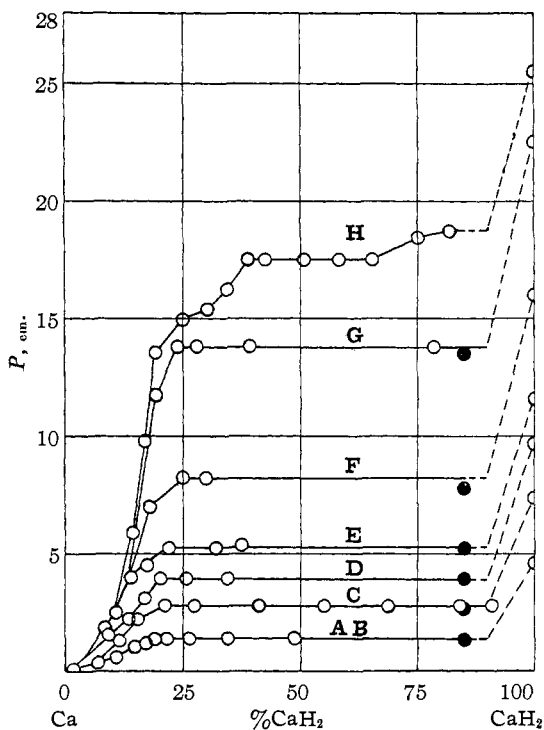| % CaH₂	50.8	58.3	65.2	75.0	82.0
Press., cm.	17.55	17.50	17.55	18.42	19.25

Fig. 7.—Pressure–composition isotherms.

II. Closed Iron Tube; Pure Calcium Hydride at High Temperatures.—It has been shown that hydrogenation of calcium at high temperatures does not produce a hydride richer than approximately 90%, though the hydrogen pressure be increased considerably above that of the normal equilibrium value. On the other hand, 100% samples of the hydride can be prepared by hydrogenation at lower temperatures, 250–300°.

Several such samples were prepared and then

heated to the highest temperature that appeared desirable for a series of measurements, with a large excess of hydrogen present in the gas phase throughout the entire system. This procedure was adopted in order to prevent any dissociation of the hydride which otherwise would occur due to the external volume of the system. When the highest temperature was reached, the pressure of the hydrogen was reduced about 1 cm. by allowing some of the gas to expand into B (Fig. 2), and then the pressure was observed over a period of several hours. This procedure was repeated several times until the hydrogen pressure was observed to increase due to dissociation of a very small amount of the hydride. When the pressure assumed a constant value, equilibrium was considered to have been established. The temperature was then lowered and the same procedure was repeated. In this way, the actual amount of dissociation of the hydride was practically negligible over the entire range of temperature. The results are given in Table III and some of the values are plotted in Fig. 7 as clear half-circles which coincide with the 100% calcium hydride ordinate.

Table III
Dissociation Pressure of Pure Calcium Hydride
A. 99.2% CaH₂

Temp., °C.	894	892	884	880	870	855
Press., cm.	25.31	25.19	21.71	20.93	18.10	14.90
Temp., °C.	848	840	832	823	792	765
Press., cm.	13.20	11.63	10.81	9.71	5.64	3.75

B. 99.7% CaH₂

Temp., °C.	894	885	865	849	838	777	750
Press., cm.	26.15	21.63	16.73	13.91	12.01	4.64	2.90

III. **Closed Iron Tube; 85% Hydride Obtained by Removal of Hydrogen from 100% Hydride.**—After completion of experiments described under II, hydrogen was removed by the vacuum pumps until the composition of the solid phases in each case was approximately 85% calcium hydride. A series of equilibrium measurements was then made with the two samples, over a high and a low temperature range, respectively.

Table IV
Dissociation Pressure of 85% Hydride
A.

Temp., °C.	892	880	860	850
Press., cm.	14.12	11.60	7.80	6.42
Temp., °C.	826	810	790	778
Press., cm.	3.95	2.79	1.87	1.36

B.

Temp., °C.	752	721	689	636
Press., cm.	0.730	0.363	0.155	0.055

For the low temperature measurements a McLeod gage was used to determine the pressure. The data are given in Table IV; the A and B samples refer to those of Table III. Some of the values are plotted in Fig. 7 as solid black circles.

IV. **Closed Iron Tube; Slow Removal of Hydrogen from Rich Hydrides.**—Since it was found impossible to hydrogenate calcium at high temperatures beyond the 90% composition, a study was made of the 90–100% composition range by slowly removing hydrogen from rich samples. For this purpose, hydrides of 96.1 and of 97.1% composition were prepared at 250° and then heated to about 850° in the presence of an excess of hydrogen in order to prevent dissociation. Hydrogen was then removed in small successive amounts so as to reduce the composition of the hydride not more than 1% by each removal. At these intervals the system was allowed to stand for several hours and pressure readings were made when equilibrium apparently had been established. It was found that as the hydrogen was removed the pressure dropped quite slowly at first, then very rapidly and finally assumed a constant value at a composition of about 90%. Further removal of the hydrogen did not change the equilibrium pressure within the limits of errors of the experiments. In one instance the hydrogen was removed until the composition was reduced to 20%. The 90 to 20% range showed no change in the equilibrium pressure. However, it was found impossible to obtain consistent data in the 97 to 90% range; undoubtedly, true equilibrium was not attained in this region.

V. **Experiments with Open Iron Tubes.**—Prior to the investigations of Remy-Genneté and of Hurd and Walker open tubes were used as containers for the calcium–calcium hydride mixtures in studying the equilibrium. Brönsted[3] obtained consistent equilibrium values since he confined his measurements to a relatively low temperature range, 641–747°, where the distillation of metallic calcium is inappreciable. Remy-Genneté has pointed out the difficulties which appear when attempts are made to determine the dissociation pressure of calcium hydride in open containers at high temperatures. If an appreciable amount of free calcium is present, either due to the addition of the metal in the preparation of the hydride samples or due to the dissociation of the hydride, it is certain to distill from the container and come in contact with the fused silica or porcelain ves-

sels employed in the experiments. Here the calcium is at a lower temperature and is free to react with hydrogen. The resulting hydride may then react with the silica to produce a calcium silicide and liberate the hydrogen again. In addition, the containers themselves might react directly with calcium hydride to produce calcium silicide or alloys with the liberation of hydrogen gas. Thus, the hydrogen pressure may rise continuously with time, although perhaps slowly, depending upon the volume of the system employed. The extent of distillation of the calcium and the subsequent reaction with the containers will depend greatly upon the composition of the condensed phases.

Several experiments were carried out with open iron tubes using an 85% hydride. No difficulty was found in reproducing the equilibrium measurements of Kraus and Hurd and other investigators, who employed essentially these conditions, provided the measurements were extended over a period of only a few hours and provided the composition of the hydride was not greatly reduced. The distillation of calcium was found to become appreciable after twelve hours at temperatures in excess of 850°.

Experiments with hydrides ranging in composition from 10–50% and in the temperature range of 800–950° showed a large loss of calcium from the open iron tubes. Some of the calcium was found on the walls of the fused silica tube as free metal; some reacted with hydrogen to give calcium hydride on the walls in the cooler regions of the tube, and still another portion of considerable quantity was found in combination with silicon. The latter calcium silicide produced impure silane when placed in dilute hydrochloric acid solution. No reproducible or consistent equilibrium pressures were obtainable.

Experiments with hydrides in the 91–97% composition range in open iron containers at high temperatures showed initially apparent equilibrium pressures which were much higher than those previously reported for poorer hydrides. However, on standing for several days, the pressure was found to increase slowly. When sufficient hydrogen was removed at this point to lower the composition of the condensed mixture below 90%, pressure values were obtained which checked fairly well with those reported above for 85% hydrides. On the other hand, when the latter mixture (below 90%) was allowed to stand for several days, the

pressure of the hydrogen gradually increased again.

VI. Closed Nickel Tube.—Two samples of the hydride (composition 99.9 and 97.2%) were prepared at 250° in a nickel tube. This tube was 1.25 cm. in diameter, 9 cm. in length and had a wall thickness of 0.75 mm. The nickel is permeable to hydrogen at high temperatures but not to calcium and calcium hydride. After the hydride was prepared at 250°, the tube was closed at the top with a tapered plug.

An attempt was made to obtain equilibrium measurements with these two samples at temperatures ranging from 700 to 852°. However, at a given temperature, the pressure was found to increase steadily with time. Thus, the 99.9% hydride at 852° showed a pressure of 12.3 cm. at the end of two hours and 49.3 cm. at eighty-seven hours. The 97.1% sample gave a pressure ranging from 13.7–59.8 cm. over a period of three hundred sixty-one hours. Later examination of the interior of the nickel tube showed it to have suffered considerable deterioration due to reaction with metallic calcium and probably calcium hydride with the formation of alloys. It is evident that as the calcium was consumed by forming an alloy with nickel, hydrogen was liberated. This suggestion conforms to the fact that the hydrogen was not reabsorbed when the temperature of the tube was lowered slowly. However, it is interesting to note that the initial pressures, 12.3 and 13.7 cm., respectively, for these rich hydrides are unusually high.

Heat of Dissociation.—In Fig. 8 the logarithm of the equilibrium pressure is plotted as ordinate against the reciprocal of the absolute temperature as abscissa. Line 2 represents data for pure calcium hydride (Table III). The solid black circles of line 1 correspond to the data of Table IV, a part of which are also shown in Fig. 7. These data are for an 85% hydride obtained by the removal of hydrogen from 100% samples. The clear circles of line 1 represent the pressures corresponding to the flat portions of the curves of Fig. 7. Only a few of these are shown in Fig. 8 since so many of the values coincide with the solid black circles. Circles containing a black lower half are plotted from the data of Remy-Genneté. Only three of these are shown since he worked primarily in a higher temperature range than we employed. Several equilibrium values reported by Hurd and Walker are plotted (line 1) as circles,

left half portion blackened. Most of the data of Brönsted are indicated as circles, right half portion blackened.
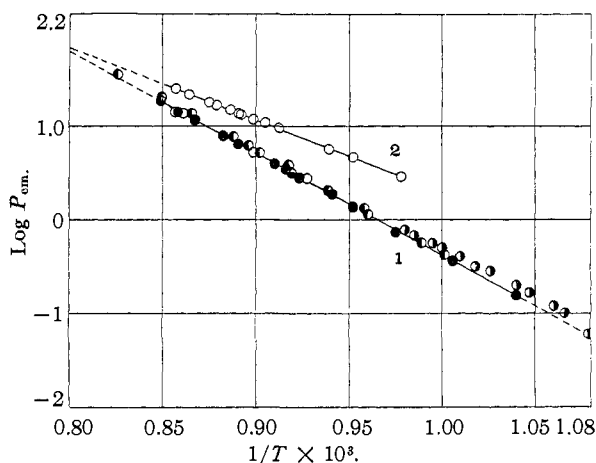

Fig. 8.

From the van't Hoff equation, $d \ln K_p / d(1/T) = -\Delta H/R$, and the slopes of the lines of Fig. 8, we calculate ΔH for line 1 to be 49,700 cal. and for line 2, 35,600 cal. The equations relating the pressure expressed in cm. with the absolute temperature are, respectively

$$\log P_{(cm.)} = -10,870/T + 10.493 \qquad (4)$$
$$\log P_{(cm.)} = -7782/T + 8.070 \qquad (5)$$

Equating $\log P$ in these two equations gives a value for T of 1274 °A. or approximately 1000°. This temperature represents the point of intersection of lines 1 and 2 (extrapolation of dotted lines of Fig. 8). Accordingly, at this temperature the two equilibria become identical.

Discussion

An examination of the data obtained for the rate of the reaction between hydrogen and calcium shows that the rate is greatly dependent upon the method of preparation of the calcium sample. Even in the case of the active form of calcium obtained from liquid ammonia solution it was not found possible to reproduce the surface conditions, although the method of preparation of the samples was standardized to as high a degree as was possible with the apparatus employed. The use of a single sample of calcium over the entire temperature range appears to have been justified, since consistent values were obtained for the heat of activation of the reaction. In a series of eight experiments the heat of activation was found to vary from 7300-8200 cal./mole, the mean of which was found to be 7700 cal./mole.

This value refers to the over-all reaction of hydrogen with calcium, which is independent of the mechanism of the process.

The observed rate of the reaction can be explained by assuming the initial process to be one of adsorption. If Θ_1 is taken as the fractional amount of the surface covered by hydrogen, making use of the equations of the Langmuir adsorption theory, it can readily be shown that

$$\Theta_1 = \frac{b(H_2)}{1 + b(H_2)} \qquad (6)$$

where b is a constant. If it is assumed that the amount of surface covered by the hydrogen is very small, then $b(H_2)$ is small compared with unity and $\Theta_1 = b(H_2)$. Θ_1 is proportional to the rate of the reaction and therefore

$$-d(H_2)/dt = K'\Theta_1 = K'b(H_2) = K(H_2) \qquad (7)$$

If only a small fraction of the adsorbed hydrogen were to react with the calcium, equilibrium would be established readily. Such conditions are in accord with a first order reaction and the results of the rate measurements conform with this conclusion.

On the basis of the straight line relationship found for the plot shown in Fig. 6, it is apparent that the rate of the reaction of hydrogen with calcium at relatively low pressures and temperatures is not predominantly dependent upon a diffusion process. If diffusion were a determining factor, such a consistent relationship would not exist.

The calcium formed from the hexammonate, $Ca(NH_3)_6$, probably appears as exceedingly small crystals. This is in accord with the low value obtained for the heat of activation. In the active form calcium might be found to be an excellent "clean-up" agent for certain gases. The lowest pressure of hydrogen obtained in the experiments of the present investigation was of the order of 0.01 mm. However, it is quite likely that even at this low pressure the calcium would react with hydrogen. The active form of calcium was found to react readily with oxygen at room temperature and at low pressures[10] (1-10 mm.), but the reaction with nitrogen under the same conditions is much slower.

An examination of the curves of Fig. 7 shows that the dissociation pressure of calcium hydride is independent of the composition of the condensed phases within the composition range of approximately 20-90% calcium hydride. On the other

(10) Experiments carried out by Mr. C. Carlson in this Laboratory.

hand, the equilibrium pressure for both poorer and richer hydrides is seen to be dependent upon the composition. Within the 20–90% range the dissociation pressure agrees very well with that found independently by Remy-Genneté and by Hurd and Walker. The agreement with the results of the latter workers is remarkably good. Even the results of some of the earlier workers, who used open containers for the calcium, correspond quite well with those represented by the flat portions of the curves of Fig. 7.

In the 0–20% calcium hydride range the calcium is found to react readily with hydrogen at pressures considerably lower than those represented by the flat portions. This may be explained by the formation of a condensed phase of calcium hydride dissolved in metallic calcium. Upon further addition of hydrogen, the equilibrium pressure remains constant to 90% calcium hydride which result may be interpreted by the formation of a second condensed phase, metallic calcium dissolved in calcium hydride. Beyond 20% calcium hydride, continued addition of hydrogen increases the amount of the second condensed phase, and at a composition of about 90% the calcium hydride poor phase disappears. The constant equilibrium pressure observed in the intermediate composition range strongly indicates the presence of saturated solutions of calcium and calcium hydride in each other.

Although it is not possible to determine the exact compositions of the calcium hydride poor and rich phases at a given temperature by equilibrium pressure measurements, with increasing temperature there appears to be an appreciable increase of the solubility of the two constituents in each other. Thus, at 778° (curve AB, Fig. 7) the flat portion of the curve begins at about 19% CaH_2; the corresponding point shown by curve E, 840°, is at 21% calcium hydride; while in curve F, 860°, it is at 25%; and in curve H, 894°, at 35% calcium hydride. Curve H rises in the 70–85% range, which fact might be interpreted by an increase in the solubility of calcium in calcium hydride at this temperature. Similar data are not available for the rich hydrides at lower temperatures; however, it is evident from curve G that at a temperature as high as 888° the rich hydride phase contains not less than 85% calcium hydride. Curve C shows the corresponding composition to be not less than 91% calcium hydride. As metallic calcium is hydrogenated at higher temperatures,

778° and above, the rate of the reaction decreases rapidly as the 90% composition is reached. Considerable time is also necessary for the attainment of equilibrium. Thus, it is difficult to determine whether the true equilibrium pressure is the same as that represented by the flat portion of the curve or is higher.

Hydrogenation of calcium at the higher temperatures in no case produced a hydride richer than 91%, whereas hydrogenation at 250–300° gave practically 100% samples. It is difficult to account for this difference in behavior but one explanation appears probable. Undoubtedly, no liquid phases are present in the 250–300° range since the melting point of calcium hydride is certainly not less than 1000° and that of metallic calcium has recently been reported as being 848 and 851°.[11] It is quite probable that in the low temperature range the solubility of calcium hydride and metallic calcium in each other is extremely low. Such being the case, here one would expect the solid phases to be essentially pure calcium hydride and metallic calcium. On the contary, as the temperature is increased to 750–800°, the solubility of calcium and calcium hydride in each other would be predicted to increase markedly, and at the same time liquid phases might appear. It is conceivable that the diffusion of hydrogen through the liquid or solid solution phases might be a very slow process. Such an explanation would account for the failure of hydrogenation beyond the 91% calcium hydride composition at high temperatures.

It is interesting to note that all investigators of the dissociation of calcium hydride who employed rich hydrides, 95% calcium hydride or higher, obtained results which appeared to be anomalous when compared with those of other workers using hydrides in the 20–90% range. Such studies have led either to the postulation of the existence of a sub-hydride or to the concept of the presence of poor and rich hydride solid solution phases. Ephriam and Michel, using very pure calcium hydride, concluded that the dissociation pressure is dependent upon the amount of excess calcium present in the condensed phase or phases. They also stated that the condensed phase must have sufficient calcium to correspond to a composition of $CaH_2 \cdot 2Ca$ in order to obtain reproducible equilibrium pressures. Under these conditions

(11) Rinck, Ann. chim., 18, 395 (1932); Hoffman and Schulze, Physik. Z., 36, 453 (1935).

they found pressure values corresponding quite well with those reported by Moldenhauer and Roll-Hansen as representing the dissociation of calcium hydride to the sub-hydride.

Hüttig and Brodkorb state that the formula CaH_2 represents an ideal limiting composition which is never realized experimentally. They also found very high dissociation pressures when rich hydrides (97% calcium hydride) were used. They concluded that upon the removal of hydrogen a single phase, poorer in hydrogen than CaH_2, is first formed which later separates slowly into two phases, one richer and one poorer in hydrogen. The richer phase was thought to be nearly pure calcium hydride and the poorer one, not metallic calcium but a phase which holds hydrogen more firmly than does calcium hydride.

Kassner and Stempel worked with a hydride which was at least 97% calcium hydride and were even able to obtain it in the form of water clear crystals. The results of these workers again show unusually high dissociation pressures. On the basis of the rather consistent results found by other workers for the poorer hydrides they concluded that their measurements were in reality to be considered as representing the dissociation of pure calcium hydride to the sub-hydride and hydrogen, and that previous workers had not measured the dissociation pressure of this equilibrium but of another, namely, the dissociation of the sub-hydride to metallic calcium and hydrogen. Kassner and Stempel did not find it possible to pass from one equilibrium to another by the addition or removal of hydrogen as the case might be. However, they did find that when metallic calcium is added to pure calcium hydride at a given temperature, the dissociation pressure of the mixture is much lower and, in fact, corresponds closely to that reported by previous workers using partially hydrogenated calcium samples.

The use of open containers in the 95–100% range is not as objectionable as it first appears. Here there is not an appreciable amount of calcium in a condition to distill unless the external volume of the apparatus should be large. On this basis it is difficult to explain the unusually high pressures obtained by Kassner and Stempel for 97–100% hydrides, unless their measurements were extended over a considerable period of time. Their values are approximately twice as great as those of the present study. Aside from this fact it is significant that the rich hydrides always give

higher equilibrium pressures than do the poorer ones, regardless of the use of open or closed containers. We feel that by using the closed container most of the objectionable experimental features are eliminated. In addition, the data as represented by line 2 (Fig. 8) show a linear relation to exist in the plot of log P against $1/T$. Such a relationship would not be expected if the experimental errors were large or if equilibrium were not attained.

Evidently, equation (1) does not represent the dissociation process for pure calcium hydride; instead, the following would be more correct

$$CaH_2 = \text{Solution (rich in } CaH_2) + H_2 \qquad (8)$$
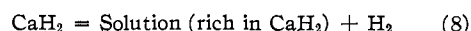
Accordingly, the concentration of the calcium dissolved in calcium hydride is a determining factor in the magnitude of the dissociation pressure. It might be stated that perhaps a very small amount of dissociation of pure calcium hydride would cause a considerable lowering of the dissociation pressure. However, the evidence which is available does not support this statement. In the first place, the data for the dissociation of pure calcium hydride were obtained with samples hydrogenated to the extent of 99.2 and 99.7%. The two samples gave essentially the same pressure values, though they differed in composition by 0.5%. In addition, experiments concerned with the slow removal of hydrogen from two samples, 96.1 and 97.1%, showed initially a slow decrease in the equilibrium pressure.

The dissociation of pure calcium hydride, in accordance with equation (8), produces a single condensed phase. Further removal of hydrogen merely decreases the hydrogen content of this phase until the 90% composition is reached. At this point a second condensed phase appears and the equilibrium may be expressed as follows

$$\text{Solution (rich in } CaH_2) = \text{Solution (poor in } CaH_2) + H_2 \qquad (9)$$
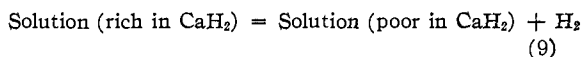
These two condensed phases are in equilibrium with each other until a composition of approximately 20% is reached. Below this composition the rich hydride phase disappears and a single poor hydride phase remains.

We find that upon extrapolation lines 1 and 2 (Fig. 8) intersect at a temperature of about 1000°. One might conclude that 1000° represents the lowest temperature for the existence of a single phase, undoubtedly liquid. Here calcium and calcium hydride would be considered as being

completely miscible with each other. Experiments on the addition of hydrogen to calcium at 1000° were not attempted. Early in the investigation it was found that above 900° there is a slight but appreciable reaction of the hydride with the iron container. However, by working rapidly in this high temperature range, it might be possible to obtain some information relative to the nature of the phases present in the different composition ranges. In addition, a study of the melting point diagram of the system would aid in the clarification of some of these points.

The results of the present investigation lend no support to the postulation of the existence of a sub-hydride of calcium. If such a hydride were to exist, one would expect a discontinuity to appear in the dissociation pressure in the neighborhood of a composition of 50% calcium hydride. It appears that the formation of solutions of either solid or liquid phases, in a large part has been responsible for the interpretation which has been given by some workers for the existence of a sub-hydride.

Making use of equations (8) and (9) and of the intrepretation which has been given for the dissociation process in the different composition ranges, one readily may explain the results of most of the investigators of the calcium hydride equilibrium. While in some cases the actual values of the dissociation pressure may be in error, due primarily to the use of open containers for the metal–hydride mixtures, in the main the essential conclusions formulated by these investigators are in accord with the results of the present study.

Similar studies have been carried out in this Laboratory with lithium hydride.[12] The results lead to conclusions quite analogous to those proposed for the calcium hydride dissociation. At 700° lithium hydride is soluble in metallic lithium to the extent of about 20%, whereas the solubility

(12) L. Hill, Ph.D. Dissertation, University of Chicago, March, 1938.

of lithium in lithium hydride does not exceed 5%. One may well question the interpretation which has been given for the dissociation of all of the alkali and alkaline earth metal hydrides. In each case the accepted viewpoint has been the dissociation of the hydride to free metal and hydrogen, in which process the dissociation pressure is considered to be independent of the composition of the condensed phases.

Summary

The reaction between hydrogen and several forms of metallic calcium has been studied at a series of temperatures and of pressures.

The rate of the reaction between hydrogen and active calcium, as obtained from liquid ammonia solution, is found to be proportional to the pressure of the hydrogen. The heat of activation of the reaction is 7700 ± 500 cal./mole.

Conditions are described for the preparation of pure calcium and its hydride.

The dissociation of calcium hydride has been studied over the entire composition range and in the temperature interval 640–894°.

Pure calcium hydride is found to have a much higher dissociation pressure than partially hydrogenated calcium samples.

Upon the removal of hydrogen from pure calcium hydride, a hydride rich solution phase first appears which subsequently produces a hydride poor phase. Within the range of saturation the dissociation pressure is found to be constant at a given temperature. As hydrogen is removed from the poor hydride phase the equilibrium pressure is found to decrease.

No evidence is forthcoming to support the existence of a sub-hydride of calcium.

It is suggested that the equilibria involving the dissociation of all of the alkali and alkaline earth metal hydrides may be quite analogous to that found for calcium hydride.