Summary

1. The isotherm curves for the system, water-toluene-acetone, have been experimentally determined at three temperatures, 0°, 20° and 30° An apparatus suitable for such determinations is described.
2. Temperature has but little effect on the mutual solubility of the three components.

MADISON, WISCONSIN

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EQUILIBRIA IN SYSTEMS INVOLVING CALCIUM, HYDROGEN AND NITROGEN

BY CHARLES A. KRAUS AND CHARLES B. HURD

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The reactions of the more electropositive elements with hydrogen and with nitrogen and the interaction between the corresponding hydrides and nitrides, as well as the interaction of these compounds with nitrogen and hydrogen, possess considerable interest from the standpoint of the chemistry of nitrogen compounds. Up to the present time the available data are extremely meager. The present investigation was undertaken for the purpose of supplying further data in this field.

1. Action of Ammonia on Calcium and Barium Nitrides

Among the more recent and important investigations may be mentioned that of Mentrel,[1] who studied the reaction, $Ba(NH_2)_2 = Ba_3N_2 + 4NH_3$. He states that this reaction is reversible.

As is well known, calcium amide loses ammonia at higher temperatures and is ultimately converted to the nitride. Experiments were accordingly carried out in which the nitride was subjected to the action of ammonia in order to determine whether this reaction was reversible in the case of calcium.

Calcium amide was first prepared by treating the metal with liquid ammonia in a quartz tube in the presence of a trace of iron oxide, which served as catalyst. After vaporization of the excess ammonia, the resulting hexammoniate[2] was converted to the amide at temperatures slightly above that of the surroundings. The tube containing the amide was connected with a manometer, a vacuum pump, and a source of pure ammonia vapor. In a series of experiments, extending over a period of two months and at temperatures ranging from 200° to 850°, no indication of an equilibrium was observed. At higher temperatures, gradual decomposition of the amide took place with loss of ammonia and in the end there was left behind a yellow, porous material which consisted of calcium nitride.

[1] Mentrel, *Compt. rend.*, **135**, 740 (1902).

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

In view of the statement of Mentrel, the experiment was varied as follows. Ammonia was introduced into the system containing calcium nitride and measurements were made to determine whether any absorption took place either at a given temperature or on passing from higher to lower temperatures. In no case was such an effect observed.

To test these results further, metallic barium was treated in a similar manner. No indications of an equilibrium could be detected. Ammonia continued to be given off until only the nitride remained behind. On introducing ammonia gas into the tube containing the nitride, there was no indication of absorption at temperatures up to 850°.

Barium amide was also formed by passing ammonia over metallic barium. At 60°, a grayish deposit was observed on the surface of the metal which doubtless consisted of the amide. At 290°, this product melted, forming a dark gray liquid. At higher temperatures, this liquid became limpid and boiled vigorously, leaving behind a yellow solid. When this solid cooled, reliquefaction did not take place. This product was undoubtedly barium nitride. Experiments in which this nitride was treated with ammonia vapor gave no indications of reaction.

Our experiments, therefore, fail to confirm the observation of Mentrel and would appear to indicate that, under ordinary conditions, calcium and barium nitrides do not react with ammonia vapor.

2. Action of Nitrogen and Hydrogen on Calcium Hydride and Nitride, Respectively

Gautier[3] studied the action of nitrogen on the hydrides of the metals of the alkaline earths and states that nitrogen may in part replace hydrogen in the hydrides at higher temperatures. Haber and van Oordt[4] studied the action of nitrogen on calcium hydride and of hydrogen on calcium nitride. They state that the final product of the reaction of hydrogen on calcium nitride contains 15 parts of hydride per 100 parts of nitride, while the final product in the reaction of nitrogen with calcium hydride contains 10 parts of hydride per 100 parts of nitride.

Dafert and Miklanz[5] have studied the action of hydrogen on the nitrides and nitrogen on the hydrides of the metals of the alkaline earths, as well as of mixtures of hydrogen and nitrogen on these substances. They have established the existence of compounds corresponding to the formula $M_3N_2H_4$, where M is an alkaline earth metal. The calcium and strontium compounds were obtained in a comparatively pure state. They established the formation of ammonia due to the action of hydrogen on barium nitride or, perhaps, $Ba_3N_2H_4$.

[3] Gautier, *Compt. rend.*, **134**, 1108 (1902).

[4] Haber and van Oordt, *Z. anorg. Chem.*, **44**, 340 (1905).

[5] Dafert and Miklanz, *Monatsh.*, **34**, 1685 (1913).

Calcium hydride was prepared as follows. Calcium in the form of fresh filings was heated in a quartz tube through which purified hydrogen was passed. Reaction was found to take place readily at slightly elevated temperatures. The product first formed appeared somewhat yellow in color and was very brittle. This product was slightly grayish within, due, presumably, to the presence of a small amount of unchanged calcium, as was later confirmed by analysis. The initial product was pulverized and again treated with hydrogen, until a uniformly white product was obtained. This material contained a small amount of calcium oxide which, however, took no part in any subsequent reactions in which the hydride was involved. By rapidly handling it in a dry atmosphere the formation of oxide may be greatly reduced.

When nitrogen was passed over the hydride thus obtained, a gain in weight took place. The gain, however, was never found to be equal to the theoretical gain if complete conversion to nitride had taken place. This result was in part due to the fact that, at the temperature of the experiment calcium hydride is appreciably volatile as may be readily shown by heating calcium hydride in a stream of hydrogen.

In view of the uncertainty of the results derived from the weights of the substances involved in the reaction, analyses of the initial and final products were made. For this purpose a special apparatus was devised by means of which the product could be introduced into acidulated water and the amount of hydrogen evolved determined volumetrically.

The analyses of the original calcium hydride formed showed that this product contained over 90% of calcium hydride, CaH_2. The remainder consisted chiefly of calcium oxide, due to the contact of the material with air. When this material was treated with nitrogen, the resulting product was found to contain less than 10% of calcium hydride.

On passing nitrogen over heated calcium, a product was obtained containing less than 6% of unchanged calcium. This material, heated to a very high temperature in hydrogen, increased in content of calcium hydride up to about 16%. Little increase above this percentage could be obtained. The temperatures required were in the neighborhood of 900°, under which conditions calcium hydride is comparatively volatile. At temperatures below 700°, calcium nitride, heated in hydrogen, gained in weight, probably due to the formation of an amide or imide.

3. Equilibrium in the System, Calcium Hydride, Calcium, Hydrogen

Measurements on this equilibrium were first carried out by Moldenhauer and Roll-Hansen[6] who measured the equilibrium pressure of calcium hydride up to 1000°. They concluded that dissociation takes place in two stages according to the equations $CaH_2 = CaH + {}^1/_2H_2$, and CaH

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[6] Moldenhauer and Roll-Hansen, *Z. anorg. Chem.*, **82**, 130 (1913).

$= \mathrm{Ca} + {}^1/_2\mathrm{H}_2$. According to their determinations of the dissociation pressure of the sub-hydride, the equilibrium pressure is approximately ${}^1/_2$ that of the normal hydride. The above equilibrium was measured by Brönsted[7] at lower temperatures and pressures. More recently the same equilibrium has been studied by Ephraim and Michel[8] who virtually repeated the experiments of Moldenhauer and Roll-Hansen with somewhat divergent results. These earlier measurements will be discussed below.

Method and Procedure.—In view of the fact that the true equilibrium in this system may be obscured by certain sources of error, the method employed and the precautions observed will be described below in some detail.

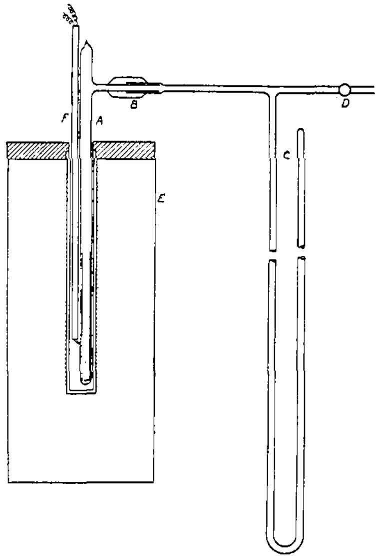

Fig. 1.—Apparatus employed in determining the dissociation pressure of calcium hydride

The hydride was prepared from fresh filings of metallic calcium which were placed in a fused quartz boat in a horizontal Vitreosil tube, which was heated by means of a blast lamp. Pure, dry hydrogen was passed through the tube until tests showed that all air was displaced. The material in the boat was then heated to a moderate red heat, the current of hydrogen being regulated to compensate for the rapid absorption of gas which takes place under these conditions.

If calcium hydride, and to a lesser extent calcium itself, is heated to redness in contact with quartz, a certain amount of reaction takes place between the metal and the silica, wherein calcium oxide and silicon are formed. The reaction products, however, adhere to the walls of the silica boat and, if care is observed to remove the products without disturbing this coat, a pure calcium hydride may be obtained. From the silica boat the calcium hydride was transferred immediately into the measuring apparatus in which the equilibrium pressure of the hydride was determined.

The apparatus employed is shown in outline in Fig. 1.

The hydride was contained in a fused quartz tube A, of approximately 13 mm. internal diameter and 42 cm. length, closed at the bottom by means of a thick plug of fused quartz. The equilibrium chamber was joined to the remainder of the apparatus (constructed of glass) by means of a joint of de Khotinsky cement B.

At C is shown the manometer of the vacuum type. This manometer was checked from time to time against a high vacuum. Connection between the measuring system

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[7] Brönsted, *Z. Elektrochem.*, **20**, 81 (1914).

[8] Ephraim and Michel, *Helvetica Chim. Acta*, **4**, 907 (1921).

and the vacuum pump was made by means of the stopcock D. The equilibrium tube A was heated by means of an electric furnace E.

The temperature was measured by means of a platinum-platinum rhodium thermocouple F. The junction of the thermocouple was placed immediately against the quartz tube A at the point where the reacting material was located. The couple was calibrated before the experiments, by means of standard samples of lead, aluminum and copper, and at the end of the experiments it was checked against aluminum and found to have remained constant. The upper end of the furnace was closed by means of a plug of asbestos wool in order to minimize circulation. The temperature at different points within the furnace varied by less than 5°. All temperatures given were measured at the level at which the material was located in the quartz tube. The temperature was maintained constant by means of hand adjustment and ammeter control to within 1° between 600° and 1000°.

The greatest difficulty to be overcome in experiments with calcium hydride in quartz containers is due to the volatility of calcium hydride and its action on the quartz. Since hydrogen is evolved in this reaction, no determination of the equilibrium pressure can be made if the hydride is allowed to come in contact with the quartz container. This difficulty was somewhat troublesome in the earlier experiments and was finally overcome by placing the hydride in a tube constructed of pure iron and contained within the quartz tube A. The iron tube was of sufficient length to prevent the vapor of calcium hydride from coming in contact with the walls of the quartz tube.

The method of carrying out a series of experiments was as follows. Calcium hydride, prepared as described, was quickly mixed with about $^1/_3$ its weight of fresh calcium filings, and placed in the iron tube. This tube was then allowed to slide to the bottom of the quartz tube A, the open upper end of which was then sealed off. The reaction tube was then quickly joined to the manometer system and immediately evacuated. By working rapidly and on days when the humidity was low, little change occurred in the hydride due to the action of moisture.

After exhausting the equilibrium chamber, the electric furnace was placed in position around the quartz tube, the thermocouple was introduced, and the furnace opening was plugged with asbestos wool. The temperature was then raised to approximately 800°, the system remaining attached to the pump. In this way any adsorbed gases were driven off. It was found that a certain amount of hydrogen was always evolved from calcium hydride made as above described, when heated to a temperature of from 300° to 400°. At higher temperatures this excess of hydrogen was reabsorbed by the excess of calcium present.

When all foreign gases had been removed from the system, the furnace was heated to about 970° and the temperature maintained constant. The pressure was then read at intervals until it reached constant value. A small amount of hydrogen was then withdrawn from the system by means of the vacuum pump and pressure readings were again taken until a constant value was reached. In this way equilibrium was approached from both sides.

After carrying out the measurement at a given temperature, the temperature was lowered and again maintained constant and pressure observations were made as before. This procedure was followed until a temperature was reached at which the rate of reaction was so low that measurements could not be made. The rate at which equilibrium is established varies greatly with the temperature. At 900° it was established in about 10 minutes, while at 600° approximately 10 hours was required.

Data.—The results of three independent series of measurements are given in the following table in which are given the temperatures at which

TABLE I

DISSOCIATION PRESSURE OF CALCIUM HYDRIDE AT DIFFERENT TEMPERATURES

Series 1		Series 2		Series 3	
t °C.	$P_{\text{cm. Hg}}$	t °C.	$P_{\text{cm. Hg}}$	t °C.	$P_{\text{cm. Hg}}$
985	57.50	934.7	23.41	978.8	44.08
921	18.26	905.4	14.08	958.2	33.14
892	10.80	864.3	6.79	931.5	22.36
...	...	834	3.76	871.2	8.40
...	...	792	1.52	843.6	4.82
...	...	...	...	769.2	0.93
...	...	...	...	734.0	0.42

the pressure observations were made and the equilibrium pressures in centimeters of mercury as observed.

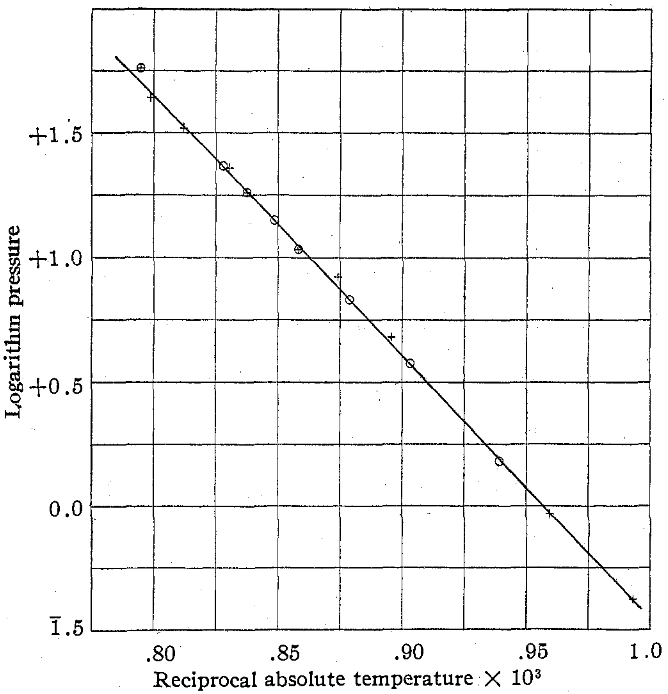

Fig. 2.—The dissociation pressure of calcium hydride as a function of the temperature

The results are shown graphically in Fig. 2, in which values of the logarithms of the pressures are plotted as ordinates against values of the reciprocals of the absolute temperature as abscissas.[9] Points of Series 1

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[9] The tangent to this curve at any point gives the value of H/R, where H is the energy change accompanying the reaction and R is the gas constant. If we write $\Theta = 1/T$, the reciprocal of the absolute temperature, then the differential equation of the curve is $\frac{d \log K_p}{d\Theta} = -\frac{H}{R}$.

are represented by combined crosses and circles, Series 2 by circles, and Series 3 by crosses. It will be observed that the points lie near a curve which closely approximates a straight line.

Discussion.—Assuming that hydrogen is the only constituent present in the reaction mixture whose pressure is appreciable, the pressure of the equilibrium mixture may be taken as a measure of the equilibrium constant. This assumption appears justified since no appreciable volatilization of materials was found to occur during the course of the experiments. Since the necessary thermal data for calculating the equilibrium constant at various temperatures are not known, the results obtained may be treated empirically. The best curve that may be drawn through the points deviates from a straight line by less than 1%.

Writing $\log P_{\mathrm{H}_2} = \frac{A}{T} + D$, where A and D are constants, and solving this equation for the values of the constants according to the curve, there is obtained the equation, $\log P_{\mathrm{cm.}} = -\frac{10.66 \times 10^3}{T} + 10.14$. This yields for the energy change accompanying the reaction the value 48400 calories.

Guntz and Bassett[10] have determined the heat of formation of calcium hydride from its elements at ordinary temperatures and found it to be 46200 calories. Brönsted has also determined this quantity and obtained the value 45100 calories. The agreement of these values with that obtained from the curve cannot be looked upon as confirming the correctness of the results, since it is very doubtful that calcium hydride dissociates into hydrogen and metallic calcium. This is indicated, in the first place, by the results of Moldenhauer and Roll-Hansen, although their work is not altogether conclusive. Our own experiments would appear to indicate that metallic calcium could scarcely have been present in these experiments, since, according to Pilling,[11] the vapor pressure of calcium is 0.173 mm. at 700° and 2.0 mm. at 805°, the melting point of calcium, while the boiling point lies at 1240°. With values of the vapor pressure of calcium of this order of magnitude, it is inconceivable that consistent measurements could have been obtained at temperatures approaching 1000°.[12]

The determinations include three points at temperatures below the melting point of metallic calcium. The curve as drawn passes through these points and it does not appear that the precision of the measurements is

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[10] Guntz and Bassett, *Compt. rend.*, **140**, 863 (1905).

[11] Pilling, *Phys. Rev.*, [2] **18**, 362 (1921).

[12] This problem has been further studied by Mr. W. C. Johnson in this Laboratory. The volatility of calcium at temperatures in the neighborhood of 800° was confirmed. Furthermore, unquestioned evidence of the formation of a sub-hydride was obtained. While the normal hydride is white, the sub-hydride is dark gray to black in appearance. It appears to be much less volatile than calcium itself. The details of this work will be published later.

such as to warrant drawing the curve with an inflection point at the melting point. Nevertheless, it would be possible to draw a curve through the points for liquid calcium, which might be in somewhat better agreement with the determinations, by slightly reducing the slope of the curve at the higher temperatures.

The consistency of the results obtained in three independent determinations would appear to indicate that a true equilibrium exists in which calcium hydride and hydrogen are involved. While further evidence is desirable regarding the second solid phase present in the system, there can be little doubt that a sub-hydride exists as Moldenhauer and Roll-Hansen have suggested.

Our results are compared with those of earlier investigators in Fig. 4, in which the upper continuous straight line represents the results of this investigation and is identical with that of Fig. 2. The points determined by Moldenhauer and Roll-Hansen are represented by crosses, those determined by Ephraim and Michel by squares, while a few of the determinations of Brönsted are represented by double circles. The points represented by combined cross and circle, through which a broken line is drawn, represent Moldenhauer and Roll-Hansen's determinations of the sub-hydride equilibrium.

It will be seen that the determinations of Moldenhauer and Roll-Hansen are subject to very large variations. The lowest point falls very nearly on our curve, while at intermediate temperatures the points lie much above our curve. At higher temperatures the curve determined by these investigators again crosses our own and at the highest temperatures lies considerably below it. The determinations of Ephraim and Michel are inconsistent with both our own determinations and those of Moldenhauer and Roll-Hansen. The values determined by Brönsted lie considerably above our curve. An examination of Brönsted's data shows that his curve is markedly concave toward the axis of reciprocal temperatures, indicating, if the results are correct, that the energy change accompanying the formation of the hydride from its elements, or from a lower hydride, diminishes markedly with increasing temperature. Brönsted has proposed an equation for the curve which accounts for his values very satisfactorily on the assumption that, as he states, the sum of the heat capacities of calcium and hydrogen is 4.2 calories greater than that of the hydride. This, however, would correspond to an increase and not a decrease in the value of the energy change with increasing temperature. To account for a decrease, it would be necessary to assume that the heat capacity of the hydride is greater than that of the sum of the constituents from which it is formed, which assumption does not appear probable. As Lewis and Randall have pointed out,[13] at higher temperatures, the difference in the

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[13] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., N. Y., 1923, p. 472.

heat capacities is probably very small, and it is not to be expected that the curve will deviate from a straight line sufficiently to become observable over a temperature interval of a few hundred degrees. Probably the form of the curve as found by Brönsted is due to undetermined sources of experimental error.

The broken line passing through the points represented by combined cross and circle represents Moldenhauer and Roll-Hansen's determinations of the equilibrium pressure of the sub-hydride. While these points lie consistently on a straight line, the curve passing through the points intersects our curve for the dissociation of the normal hydride and would also intersect a curve drawn through the points determined by Moldenhauer and Roll-Hansen for the same equilibrium. This throws doubt on the interpretation of the observed results. Subsequent measurements in this Laboratory, referred to in a preceding footnote, indicate that the dissociation pressure of the sub-hydride is exceedingly low, if measurable, at a temperature of 790°. While a sub-hydride in all probability exists, it must be assumed that any measurements of its dissociation pressure cannot be relied upon at the present time. Metallic calcium is so volatile at the temperatures in question that erroneous results may easily be obtained, due to the fact that the metal distils from the hotter to the cooler portions of the tube, under which conditions the normal hydride may conceivably be formed, yielding pressures commensurable with, but lower than those of the normal hydride at the true temperature.

4. Equilibrium in the System, Calcium Nitride, Calcium, Nitrogen

The nitrides of the metals of the alkaline earths possess a much greater stability than the corresponding hydrides. The formation of the nitrides through the action of nitrogen on the metals, however, takes place much less readily than does the corresponding formation of the hydrides. Moissan[14] has studied the formation of nitrides from the elements, as well as the rate of formation and the influence of impurities.

The formation of barium nitride from barium and ammonia with the intermediate formation of barium amide has been studied by Mentrel.[15] He showed that the nitride vaporizes appreciably at 1000°, but apparently exhibits no marked dissociation at that temperature. He also determined the heat of formation of barium nitride. Gautier[3] has observed that the nitrides of barium, calcium, and strontium are dissociated to a much smaller extent than are the corresponding hydrides.

The heat of formation of calcium nitride has been determined by Guntz and Bassett,[10] who obtained the value 112,200 calories per mole. This is comparable with the heat of formation of some of the more stable com-

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[14] Moissan, *Compt. rend.*, **127,** 496 (1898); *Ann. chim. phys.*, **18,** 289 (1899).

[15] Mentrel, *Dissertation,* Nancy, 1902; *Chem. Zentr.*, **1903,** I, 276.

pounds of calcium, and indicates that the stability of the nitride is relatively high.

In addition to the above-mentioned methods of preparing the nitrides, some others, less common, have been employed. Thus Ellis[16] heated the oxide of the metal with magnesium in an atmosphere of nitrogen, while Wolk[17] heated barium amalgam in nitrogen.

The formations of the nitrides of barium, strontium and calcium have also been studied by Dafert and Miklanz.[5]

Previous investigations have indicated that the nitrides are extremely stable substances, but no data are available as to the temperature at which the dissociation pressure might become appreciable. In view of the volatility of the nitrides, as well as of the metals themselves, it appeared impracticable to study these systems at temperatures much above 1000°, and accordingly little hope was entertained that accurate measurements might be obtained on the dissociation pressure of the nitrides. Nevertheless, it appeared of interest to study the order of magnitude of the dissociation pressures in these regions if possible.

Method and Apparatus.—The apparatus at first employed was similar to that used in the determination of the dissociation pressure of calcium hydride, shown in Fig. 1.

Calcium nitride, prepared from calcium filings, was mixed with about half its weight of fresh calcium filings and placed in an iron tube which was introduced into the quartz tube A. Although this was heated to over 1000°, no pressure could be observed on an ordinary vacuum manometer. The apparatus was accordingly modified so that the pressures could be read by means of a sensitive McLeod gage. With this gage, pressures could be accurately read between 0.1 and 0.001 cm. of mercury, and lower pressures could be approximated within 1×10^{-5} to 5×10^{-5} cm., depending upon the value of the pressure.

It was soon found, with the use of this gage, that the apparatus employed was not sufficiently tight to maintain the necessary high vacua. Accordingly, a mercury trap was introduced into the system between the apparatus and the stopcock connecting the apparatus with the vacuum pump. This trap was constructed in the form of a Y, the lower branch of which was connected with a mercury reservoir, by the elevation of which the connection between the apparatus and the stopcock could be closed.

It was found, as a result of experiment, that the tube A, which had originally been constructed of Vitreosil, was not sufficiently tight to permit accurate measurements to be made. Accordingly, it was replaced by a tube constructed of clear quartz. With this alteration, the system remained sufficiently tight to allow such measurements to be made. In the course of 72 hours, the pressure change observed amounted to 8×10^{-5} cm. The residual pressure in the system was measured before and after each series of observations at a temperature of 850°. The following values were obtained; before the first series, 6×10^{-5} cm.; between the first and second, 7×10^{-5} cm.; between the second and third, 8×10^{-6} cm.; and at the end of the third, 11×10^{-5} cm. The last pressure was measured at 950°. It was assumed that the true pressure of the nitrogen could be obtained by subtracting the pressure of the residual gases from the observed

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[16] Ellis, *Chem. Zentr.*, 1909, I, 900.

[17] Wolk, *ibid.*, 1910, II, 1442.

total pressure. In general, the final rather than the initial pressure was assumed to give more nearly the correct value.

In carrying out a series of measurements, the furnace was slowly brought to a temperature of 1050°, and then allowed to cool slowly. The temperature and pressure were read at intervals. It was observed, during the first series, that a small amount of calcium had distilled into a region slightly above the point where the quartz tube extended out of the furnace. It was impossible to avoid this difficulty, but by working as indicated the effect was minimized as much as possible. The distillation of the calcium or some other product from the warmer to the cooler portion of the tube, however, may have had an appreciable influence on the measurements, since the equilibrium as measured may not have been that of the hottest portion of the tube, where the temperature was read. In the initial experiments, where the distillation process had not proceeded far, this factor was perhaps of little influence; but in succeeding experiments with the same sample of material the pressures as measured were doubtless somewhat lower than the true ones.

The results of three series of measurements made with the same sample are given in Table II. The results of the first run are undoubtedly more reliable than the succeeding ones, in view of the distillation of the calcium from the hotter to the cooler portions of the tube, as just mentioned. In the first column is given the temperature on the centigrade scale and in the second column the observed pressure. In the third column, in the

Table II

Dissociation Pressure of Calcium Nitride

Series 1

t °C.	$P_{\text{cm. Hg}} \times 10^4$ Obs.	Corr.	Calc.	t °C.	$P_{\text{cm. Hg}} \times 10^4$ Obs.	Corr.	Calc.
958	1.0	0.3	0.23	1030	3.3	2.6	2.95
969	1.0	0.3	0.36	1032	4.3	3.6	3.16
987	1.6	0.9	0.69	1033	3.7	3.0	3.27
1011	2.2	1.5	1.56	1034	4.0	3.3	3.37
1012	2.5	1.8	1.62	1039	4.4	3.7	3.96
1014	2.7	2.0	1.73	1043	4.8	4.1	4.52
1019	2.9	2.2	2.05	1045	5.4	4.7	4.82
1020	2.8	2.1	2.12	1045	5.4	4.7	4.82
1020	2.8	2.1	2.12	1047	5.9	5.2	5.15
1022	3.0	2.3	2.27	1049	6.2	5.5	5.48
1028	3.6	2.9	2.77				

Series 2

t °C.	$P_{\text{cm.}} \times 10^4$ obs.	t °C.	$P_{\text{cm.}} \times 10^4$ obs.
965	0.9	1040	4.1
1016	2.4	1042	4.0
999	1.8	1040	3.9
1020	2.5	1026	2.5
1029	3.2	1007	2.0

Series 3

t °C.	$P_{\text{cm.}} \times 10^4$ obs.	t °C.	$P_{\text{cm.}} \times 10^4$ obs
949	0.8	1046	4.1
985	1.4	1042	3.9
1007	1.7	1037	3.1
1020	2.4	1004	1.5
1030	3.1	978	1.1

first series of experiments, is given the observed pressure, corrected for the pressure of the residual gas, here assumed to be 7×10^{-5} cm.; and in the last column is given the calculated pressure according to an empirical equation.

If the logarithms of the pressures are plotted against the reciprocals of the absolute temperatures, the points should lie approximately on a straight line if the pressures measured represent true equilibrium pressures. When the observed pressures are plotted in this way, it is found that a curve results which is markedly convex toward the axis of reciprocal temperatures. When, however, the corrected pressures are similarly plotted, the points lie upon a straight line within the limits of the experimental error. The curves obtained for the three series of measurements do not coincide, although they run parallel with one another. Apparently, in succeeding experiments, the curves are displaced toward lower temperatures. This is doubtless due to the distillation of material from the hotter to the cooler portions of the tube, the temperature of the equilibrium mixture thus being lower than the temperature as measured.

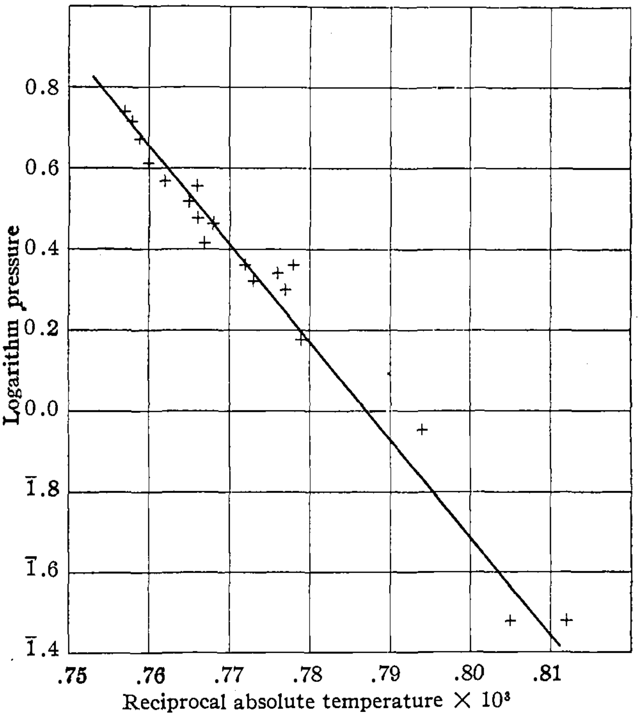

Fig. 3.—The dissociation pressure of calcium nitride as a function of the temperature

In Fig. 3 the logarithms of the corrected pressures for the first series of experiments are plotted as ordinates against the reciprocals of the absolute temperatures as abscissas. As may be seen from the plot, the points lie upon a straight line within the limits of the experimental error. The greatest deviations are observed at relatively low pressures, where the precision of the measurements is lowest. For the three points at the lowest pressures, the deviations reach a value of approximately 25%. For the remaining points, the deviations do not exceed 10% and for the most part are less than 5%. Considering the values of the pressures and the conditions under which the experiments were carried out, it would seem that, at the higher pressures and temperatures, the agreement is reasonably satisfactory. The straight line as drawn on the plot corresponds to the equation, $\log P_{\text{cm.}} = -\frac{24.36 \times 10^3}{T} + 15.166$. This yields for H, the energy change of the reaction per mole of nitrogen, the value 113,250 calories, which corresponds very closely with the heat of formation of calcium nitride as determined by Guntz and Bassett. It is doubtful, however, whether this agreement can be looked upon as a confirmation of the results obtained, inasmuch as it is extremely doubtful that metallic calcium is here involved in the equilibrium. At the temperatures in question and with the low pressures existing in the apparatus, any free calcium present must have vaporized into the cooler portions of the tube, probably to regions where the temperature would be little in excess of 700° or 750°. The fact that a fairly good agreement is obtained among the different points of a given series would appear to indicate the existence of a definite equilibrium and it is possible that, in the case of calcium nitride, a sub-nitride may be formed corresponding somewhat to the sub-hydride, as pointed out in the preceding section. In any case it may be concluded that calcium nitride is an extremely stable compound.

5. Equilibrium in the System Calcium, Hydrogen, Nitrogen, Calcium Nitride, Calcium Hydride, and Reaction Products

The results presented in Section 2 indicate that reaction takes place between hydrogen and calcium nitride and between nitrogen and calcium hydride. It was, therefore, decided to determine, if possible, whether equilibria exist in the system composed of calcium hydride, calcium, calcium nitride and hydrogen.

The apparatus employed was similar to that shown in Fig. 1, except that a side tube of quartz was connected to the tube A and provided with a small heating furnace. A palladium tube was introduced, closed at the end and sealed through a glass tube by means of a short length of platinum tubing. The end of the palladium tube was placed within 2.5 cm. of the tube A within the auxiliary furnace. The glass tube, into which the palladium tube was sealed, was connected with a manometer and a source of hydrogen. When the palladium tube was heated by means of the auxiliary furnace, diffusion of hydrogen took place, either into or out of the system, depending upon the pressure. If any gas other than hydrogen were present in the reaction tube, its partial pressure could be determined by comparing the pressures indicated by the manometer connected to the reaction tube A and that attached to the palladium diffusion tube. Both the original reaction tube and the diffusion tube were provided with connections to sources of hydrogen and of vacuum.

A freshly prepared mixture of calcium hydride, calcium nitride, and calcium filings was introduced into an iron tube which was then sealed into the reaction tube A. The ingredients were quickly mixed before introduction into A and the subsequent operations were carried out as quickly as possible in order to minimize the influence of the atmosphere.

After introduction of the materials into the reaction tube the system was heated and pumped out, after which the equilibrium pressures were measured at a series of temperatures. The following values were obtained.

TABLE III

DISSOCIATION PRESSURES IN A MIXTURE OF CALCIUM HYDRIDE, NITRIDE AND CALCIUM

t °C	1008.1	969.3	882.1	812.5
$P_{\text{cm. Hg}}$	45.70	23.80	6.26	1.51

The gas present was evidently pure hydrogen, since the pressure readings on the two manometers were equal. Equilibrium was established very quickly and was approached from both sides, so that there can be no question but that the pressures read represented equilibrium pressures.

After the above series of readings had been made, the temperature was kept at 870° for several days and hydrogen was removed several times a day. After some days it was observed that the pressure was falling slowly from a value of 4 cm., although no hydrogen was being removed at the time. This continued until the pressure became so low that it could not be read on the manometers. When the temperature was raised to 1030°, no indication of evolution of gas was observed.

On readmitting hydrogen into the system through the palladium tube, rapid absorption took place. Unfortunately, it was found necessary to discontinue the investigation at this point.

The results are shown graphically in Fig. 4, in which the logarithms of the observed pressures are plotted as ordinates against the reciprocals of the absolute temperatures as abscissas. The points are represented as circles and a continuous straight line is drawn through them. The consistency of the values obtained would appear to indicate that a true equilibrium of some kind was measured. It will be noted that the curve is very nearly parallel with that of the calcium hydride equilibrium, which is represented by the upper continuous straight line. It is possible that a portion of the calcium distilled from the hotter to the cooler portions of the tube and that the equilibrium represents the equilibrium of calcium hydride, the temperature being in error, due to the distillation effect. This would not, however, account for the rapid absorption of hydrogen in the later stages of the experiment. Furthermore, a consistent series of pressure readings extending over a considerable period of time would not be expected under these conditions.

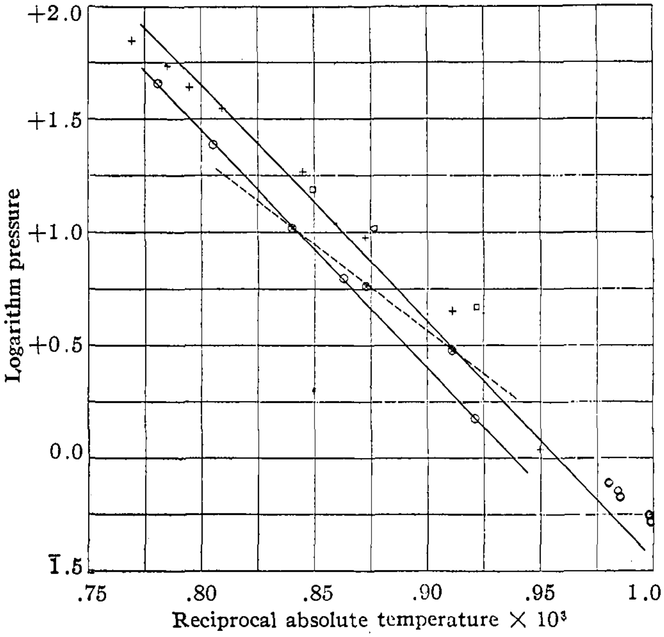

Fig. 4.—Comparison of data of various observers

Summary

The action of ammonia on calcium and barium nitrides has been investigated. Contrary to the statement of Mentrel, no indications of absorption of ammonia by these nitrides could be observed.

Calcium hydride, treated with nitrogen, yields an end product containing less than 10% of hydrogen, and calcium nitride treated with hydrogen yields a product containing approximately 16% of hydrogen.

The dissociation pressure of calcium hydride has been measured at a series of temperatures. The results indicate the existence of a definite equilibrium involving hydrogen and calcium hydride. The third phase is uncertain, but the conditions of the experiment together with the observations of earlier investigators render it probable that a sub-hydride of calcium exists. The results obtained are compared with those of earlier investigators.

An attempt has been made to measure the dissociation pressure of calcium nitride at temperatures somewhat above 1000°. Reproducible pressure readings were obtained of the order of magnitude of 0.3–5.5 $\times 10^{-4}$ cm. The results are consistent with an energy change accompanying the reaction of 113,250 calories, which agrees well with the heat of formation of calcium nitride at ordinary temperatures, as determined by Guntz and Bassett. It is pointed out that in all probability calcium could not have been present as a third phase in this equilibrium.

In a system consisting initially of a mixture of calcium, calcium nitride and calcium hydride, an equilibrium was found to exist at temperatures in the neighborhood of 1000°. Only hydrogen was present in the vapor phase. After continued heating at 870°, the hydrogen was ultimately completely absorbed.

WORCESTER, MASSACHUSETTS

[CONTRIBUTION FROM THE DIVISION OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

A PHOTOCHEMICAL STUDY OF ACETYL-CHLORO-AMINOBENZENE[1]

BY J. H. MATHEWS AND R. V. WILLIAMSON

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In connection with a series of investigations which were being carried out in this Laboratory, there was needed a light sensitive compound whose changes could be easily and accurately followed. The compound, acetyl-chloro-aminobenzene, appeared to be one that might serve the purposes for which these compounds were wanted.

Blanksma[2] appears to be the first to have noted that the compound was sensitive to light and he stated, "The reaction is much accelerated by light and it appears to be a general rule that the radicals Br, Cl, NO_2, NO and O attached to nitrogen, change places, under the influence of sunlight, with an H atom in the nucleus."

Chattaway and Orton also made some velocity measurements on the transformation of the compound in sunlight.[3] But there appears to have been no study made of the effect of light on the transformation of the compound under conditions such that the light intensity and conditions of the experiments were under control. Therefore, the present investigation was undertaken for the purpose of obtaining velocity measurements under conditions which could be duplicated.

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[1] This paper constitutes the major part of a thesis submitted by R. V. Williamson in partial fulfilment of the requirements for the degree of Master of Science at the University of Wisconsin.

[2] Blanksma, *J. Chem. Soc.*, **82**, 646 (1902); *Rec. trav. chim.*, **21**, 290 (1902).

[3] Chattaway and Orton, *Proc. Chem. Soc.*, **18**, 200 (1902).