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# Equilibrium in the system calcium, calcium hydride, hydrogen

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# EQUILIBRIUM IN THE SYSTEM

## CALCIUM, CALCIUM HYDRIDE, HYDROGEN

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of Chemistry of Union College in partial
fulfillment of the requirements for the
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Moissan[1] first showed in a qualitative way that hydrogen and calcium form a combination which is very little dissociated below 700° C. He also showed that this compound can be expressed by the chemical formula $CaH_2$ and seemed to be a well defined compound. Gautier[2] makes a statement that calcium hydride begins to dissociate as soon as the hydrides of strontium and barium (about 675° C.) Moldenhauer and Roll-Hansen[3] made a systematic study of the dissociation pressure from 780° C. to 1 027° C. These workers point out that the equilibrium pressures may be masked by the action of the calcium and the calcium hydride on the reaction vessel. Moreover, it is their opinion that the reaction takes place in two steps; namely, $CaH_2$— $CaH$ $/$ 1/2 H, and $CaH$— $Ca$ $/$ 1/2 H. They calculate that the energy change accompanying the dissociation is about the same in each step (21 000 cal.). Bronsted[4] measured the dissociation of the hydride between 650° and 750° C. His work does not substantiate the dissociation's taking place in two steps. Ephraim and Michel[5] repeated the work of Moldenhauer and Roll-Hansen but did not obtain the same results. Kraus and Hurd[6] studied the equilibrium pressures of calcium hydride between 734° C. and 985° C. Three independent measurements were in excellent agreement. It is the opinion of these workers that consistent results could not be obtained if the hydride dissociates into metallic calcium and hydrogen for calcium has a vapor pressure of 2 mm. at its melting point 805° C. Since this metal boils at 1 240° C., the vapor pressure at 1 000° C. must be considerable. They add as a foot-note that W. C. Johnson working in the laboratory of Clark University found unmistakable signs of the subhydride and that its dissociation pressure was

exceedingly low at 790° C. Recently G. F. Huttig[7] and his co-workers have published considerable work on the chemistry of the metallic hydrides. They assert that in the case of calcium $CaH_2$ is an ideal limiting compound toward which all compounds tend as the temperature is lowered. They also make the statement that the dissociation pressure is not only a function of the temperature but also of the gross weight of the solid phase. It is of interest to note that Huttig and Brodkorb[8] say that the reaction between calcium and hydrogen takes place in two stages; the first between 380° C. and 450° C., the second between 550° C. and 600° C. This double reaction is attributed by them to a protective surface covering formed at the lower temperature. Kraus and Hurd who prepared their hydride at about 600° C. remark that upon heating this hydride a certain amount of hydrogen is evolved between 300° and 400° C. which is reabsorbed as the temperature rises.

The present investigation is practically a repetition of the work of Kraus and Hurd. The hydride, however, instead of being formed beforehand and then placed in the measuring system was formed in a pure iron cylinder in the system proper. The cylinder itself which was 1 3/4 inches in length and 4/10 inch in diameter was so constructed that hydrogen could pass readily through the walls. The end was closed by a cap of the same metal which screwed into the body of the cylinder with eight fine threads.

The method of experimentation was as follows:

The piece of clean calcium metal was placed in the iron cylinder so as to displace all the air possible. The cap was then screwed tightly on the cylinder and placed in the quartz tube C. The quartz tube was connected to the rest of the system by the joint of Khotinsky cement E. The electrically heated furnace B was then
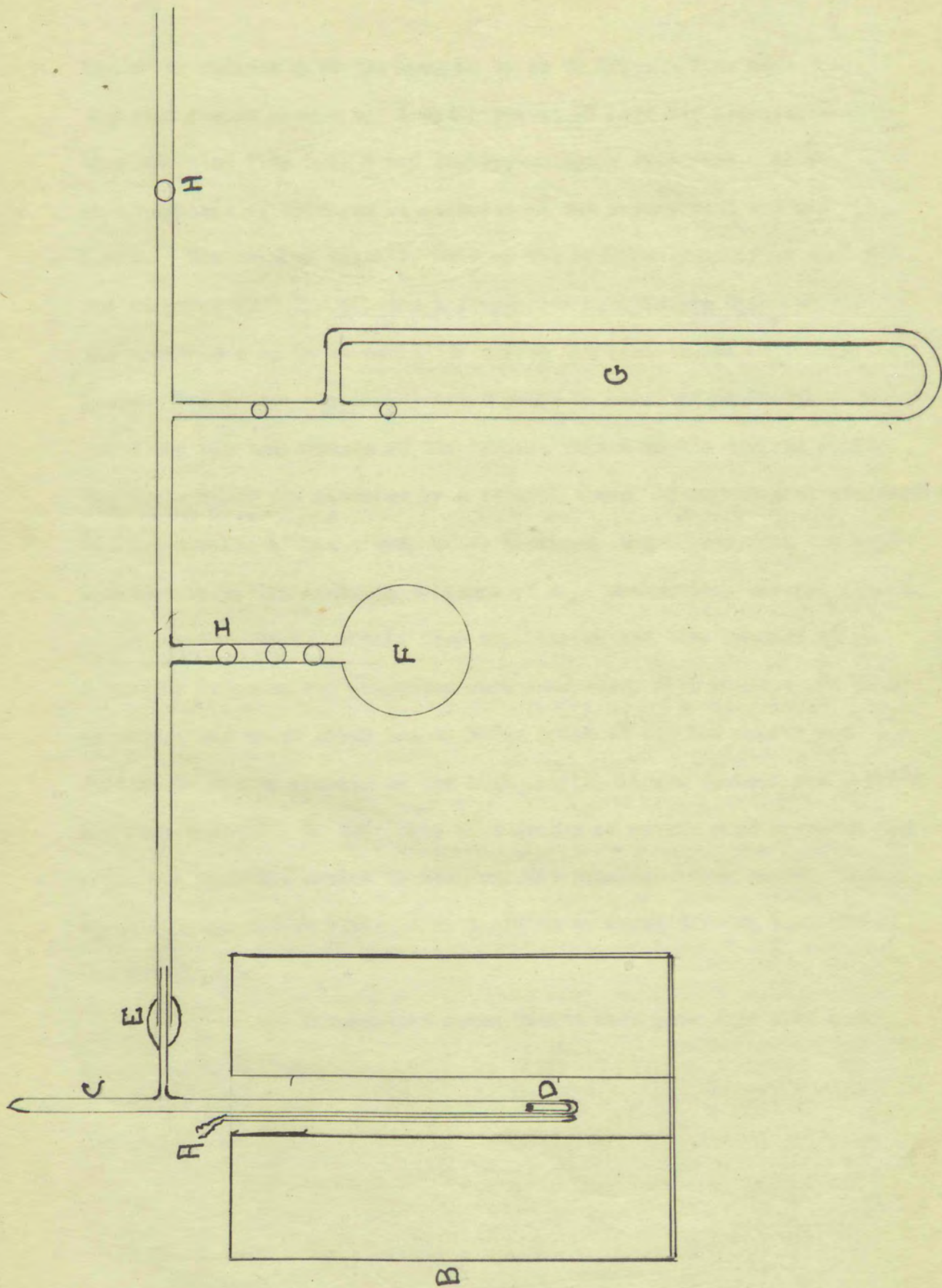
heated to redness with the pump on so as to drive off as much
absorbed gas as possible. A small amount of pure dry hydrogen was
then admitted from bulb F and the system again evacuated. About
an atmosphere of hydrogen as measured on the manometer G was now
let in. The calcium began to take up the hydrogen readily at $450^{\circ}$ C.
and at about $600^{\circ}$ C. All the hydrogen had practically disappeared.
The system was again evacuated to remove the last traces of foreign
gases. The system was now closed tightly by means of stopcocks I
and H and the temperature of the furnace raised to the desired point.
The temperature was measured by a chromel alumel thermo-couple, standardized
against samples of tin, lead, zinc, aluminum, and silver, and was kept
constant to within a degree by means of a potentiometer, ammeter device.

To be certain that equilibrium had been reached at
a certain temperature, pressures were read every five minutes and when
no change was noted after two to three hours at the low points and
fifteen to twenty minutes at the high points, it was assumed equilibrium
had been reached. To test this at a number of points some hydrogen was
withdrawn from the system by the pump and readings taken again. The
same pressure always returned so there is no doubt that an equilibrium
was established.

Two independent measurements were made with different
cylinders as follows:

## DISSOCIATION PRESSURES OF CALCIUM HYDRIDE

### RUN I

| P | log P | $t_c$ | T | $1/T \times 10^4$ |
|---|---|---|---|---|
| 1.12 | .04922 | 780 | 1 053 | 9.496 |
| 4.73 | .67486 | 853 | 1 126 | 8.880 |
| 8.85 | .94694 | 887 | 1 160 | 8.620 |
| 10.79 | 1.03302 | 906 | 1 179 | 8.481 |
| 27.25 | 1.43537 | 955 | 1 228 | 8.143 |
| 42.38 | 1.62716 | 971 | 1 244 | 8.038 |
| 60.90 | 1.78462 | 1 018 | 1 291 | 7.745 |

### RUN II

| P | log P | $t_c$ | T | $1/T \times 10^4$ |
|---|---|---|---|---|
| .85 | -.07007 | 770 | 1 043 | 9.587 |
| 1.88 | .27416 | 809 | 1 082 | 9.242 |
| 4.20 | .62325 | 849 | 1 122 | 8.912 |
| 8.36 | .92221 | 861 | 1 154 | 8.665 |
| 26.73 | 1.42700 | 953 | 1 226 | 8.156 |

Upon examining the quartz tube after each run it
was found that Ca or CaH$_2$ or both had escaped from the cylinder and
attacked the tube. In the first run the fault was blamed on the
threads which were not cut very deeply; in the second run the cylinder
used had a better thread and the substance or substances attacking the
tube must have escaped through the walls of the cylinder itself. In
the second run at about 960° C. a mild explosion was heard and the
manometer began to show increased pressure immediately. It was thought
at first that this was caused by a break but the system showed no leak
after standing all night. It was concluded then that enough pressure
must have developed in the cylinder to make minute cracks in the thin
cylinder wall. Some interesting results might be obtained by making
the cylinder longer and narrower so that the cap might be welded and
at the same time leave plenty of room for expansion of the hydride.

Reciprocal Absolute Temperature × 10⁴
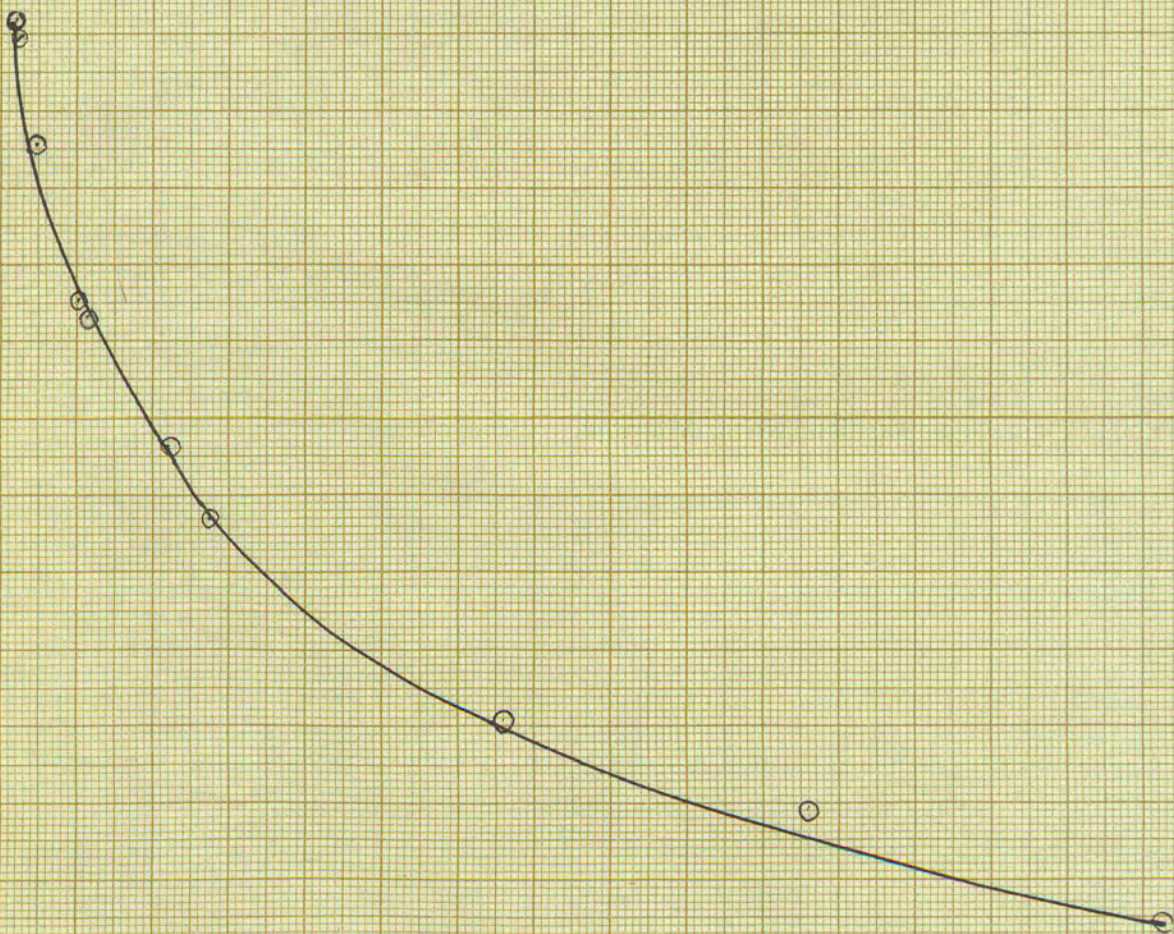
Logarithm Pressure
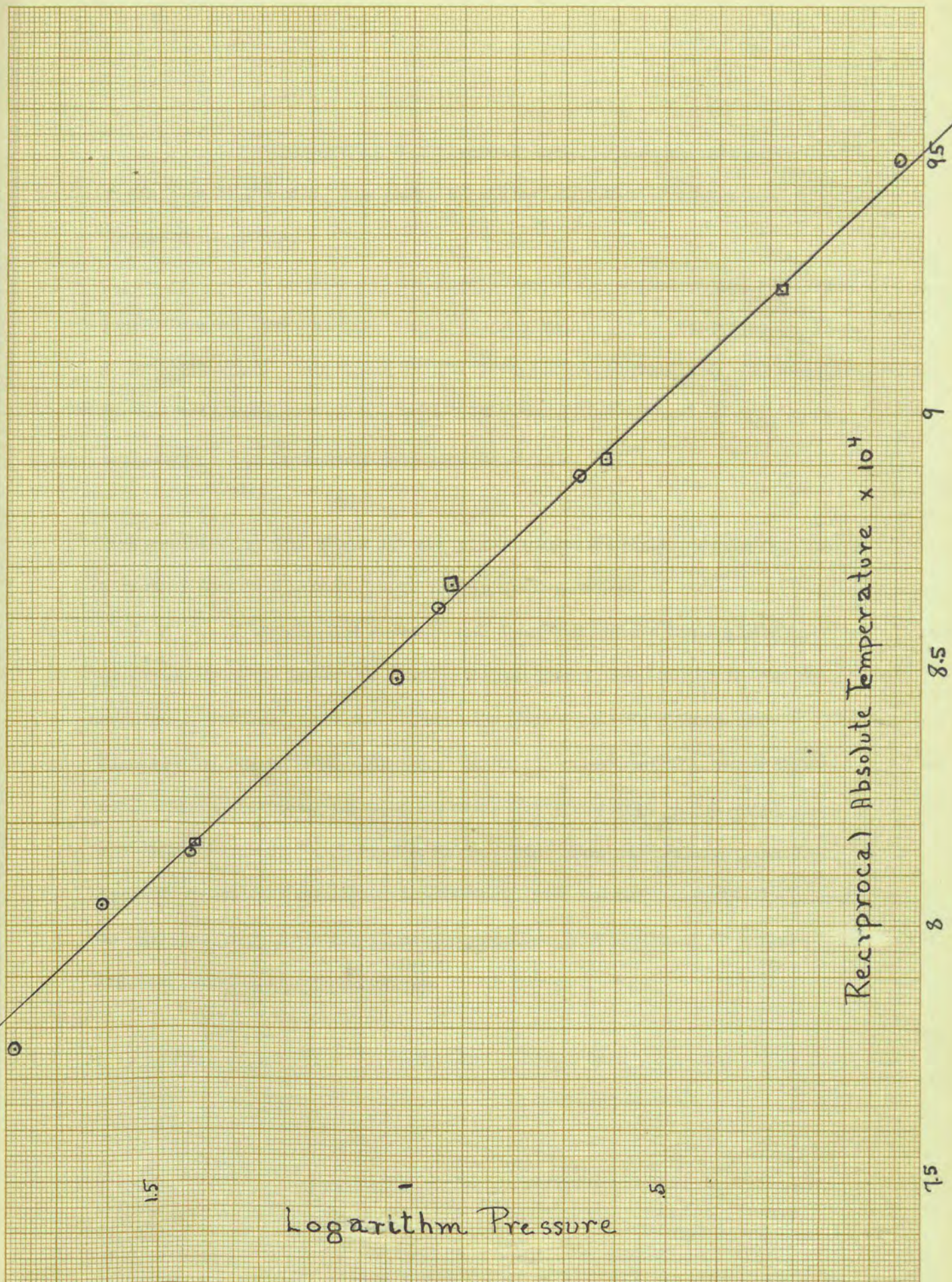
The plot of the pressure against the temperature gives a smooth curve, the slope of which indicates the pressure, temperature change.

The plot of the logarithm of the pressure against the reciprocal of the absolute temperature gives a curve which approximates a straight line. The slope of the line is proportional to the change in the heat contents of the reacting substances. Treating the curve empirically the following equation is found:

$$\log P_{cm} = -\frac{10\ 450}{T} + 9.95$$

The quotient of the slope of the curve times the proportionality factor -4.5787 gives 47 800 calories, the heat of reaction.

Guntz and Basset[9] and Brousted have determined this quantity at room temperature, the former giving the value 46 200 cal. and the latter 45 100 cal. Kraus and Hurd from the dissociation equilibrium obtained 48 400 cal. Although these results check fairly well, the uncertainty of what constitutes the second solid phase does not allow confident statements to be made. The discrepancies in the results of the various investigators may well be due as Huttig suggests to the fact that the dissociation pressure is a function of other factors besides the temperature.

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