769. *The Thermal Dissociation of Calcium Hydroxide.*

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Measurements are reported of the equilibrium pressure of the reaction $CaO + H_2O \rightleftharpoons Ca(OH)_2$ which, with those of previous workers, show that it reaches 760 mm. at 512° C, and that the average heat of reaction over the range 300—510° is 24·9 kcal./mole.

THE temperature at which the dissociation pressure of calcium hydroxide reaches 760 mm. has often been measured. Le Chatelier[1] found it to be 450°, Johnston[2] 547°, Drägert[3] 510° (by extrapolation from about 440°), and Tamaru and Siomi[4] 513°. Tamaru and Siomi showed that Johnston's result is too high because he considered dissociation only whereas the reaction $CaO + H_2O \rightleftharpoons Ca(OH)_2$ approaches equilibrium very slowly at low temperatures and measurements should be made from both directions, *i.e.*, dissociation and association. 547° is still widely quoted.[5] We now report attempts to resolve these conflicting results as a preliminary to a study of dissociation of the calcium silicate hydrates.

EXPERIMENTAL

Fig. 1 shows the apparatus, which is similar to that used by Johnston[2] except that the specimen tube is horizontal instead of vertical and there is an additional tap (*F*) which allows moist air to be drawn over the sample for rehydration with a mercury trap which avoids leaving unheated space in which the water vapour could condense, yet keeps the tap cool.

The system is evacuated with tap *F* closed and mercury-sealed. The whole apparatus is then tilted to run mercury from the bulb into the small manometer (*B*); this isolates the specimen and its atmosphere in the part of the apparatus inside the steam-jacket (*C*) but allows the pressure to be measured on the large manometer (*A*), provided that the small manometer is balanced by letting in air at tap (*G*) or adjusting the height of the mercury reservoir. The experiment comprised: (1) preparation of the calcium oxide by decomposing spectroscopically pure calcium carbonate in the apparatus; (2) hydration of the calcium oxide to calcium hydroxide *in situ*; (3) measurements of equilibrium pressure of the reaction between 300° and 510°.

The calcium carbonate was converted into calcium oxide by heating it to 950° and evacuating the apparatus to about 0·05 mm. The small heater (*E*) which was used for this could be interchanged with the main thermostatically controlled heater (*D*), without opening the apparatus to air, by sliding the heaters. The calcium oxide was hydrated by drawing moist carbon dioxide-free air through the apparatus from the tap (*F*). The main heater was wound on a thick copper cylinder, of 18 mm. bore and 43 mm. diameter and 106 mm. long, which just

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[1] Le Chatelier, *Compt. rend.*, 1886, **102**, 1243.

[2] Johnston, *Z. phys. Chem.*, 1908, **62**, 330.

[3] Drägert, Dissertation, Berlin, 1914.

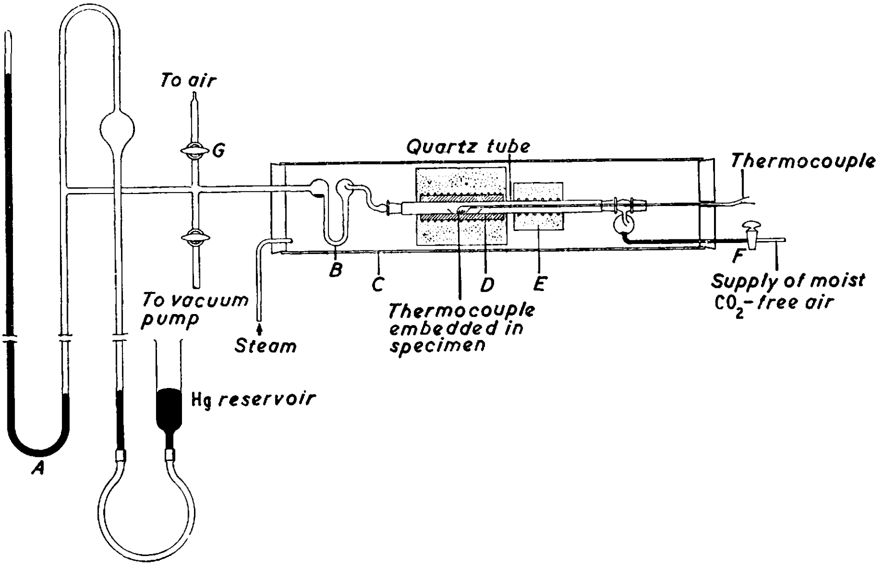
[4] Tamaru and Siomi, *Z. phys. Chem.*, 1932, **161**, *A*, 421.

[5] Lea and Desch, " Chemistry of cement and concrete," Arnold, London, 1956, p. 34; Dreyfus, " La chimie des ciments," Editions Eyrolles, Paris, 1950, Vol. I, p. 68; Kühl, " Zement Chemie," Verlag Technik, Berlin, 1952, Vol. 2, p. 37.

fitted over the quartz tube, and was supplied by a double " Variac " transformer. Temperatures were measured with a Pt/Pt–13%Rh thermocouple of 36 S.W.G. (0·2 mm. diameter) wire which had 15 cm. each side of the hot junction wound into a " coiled coil," about 20 mm. long, embedded in the specimen. The thermocouple was new at the beginning of the experiment; at the end it was checked against a new Pt/Pt–10%Rh couple at the b. p. of benzophenone (305°) and both indicated the same temperature (according to the maker's calibration) to within less than 0·5°.

The e.m.f. of the thermocouple was measured with a slidewire potentiometer. The galvanometer used with this controlled the temperature: by means of a photocell and semi-silvered mirror inside the galvanometer the light spot operated a relay, switching between two selected values of heating current for each temperature. These values were adjusted to give a temperature cycle of amplitude not more than 1° C and period 3½—4 min. The heat capacity of the copper block resulted in an effectively sinusoidal time–temperature curve for the specimen.

FIG. 1. *Apparatus for measurement of dissociation pressure.*



A cathetometer was used to measure pressure difference on the manometer (*A*) and to check the levels of the manometer (*B*).

Method.—After preliminary preparation and hydration of the calcium oxide specimen the apparatus was evacuated rapidly to 0·1 mm. or less and the temperature of both specimen and steam-jacket raised to *ca.* 100° to desorb gases from the glassware. After mercury was tilted into the manometer (*B*) pumping was continued for ½ hr., and if no difference in level could then be detected in (*B*) the experiment proceeded. The temperature of the specimen was raised until a small pressure difference appeared, and the potentiometer-controller was then set to maintain this temperature and the small manometer arms balanced by stopping the vacuum pump, admitting a little air, and adjusting the height of the large mercury reservoir. The pressure was then read on the large manometer. The pressures were balanced and measured until equilibrium was reached. This took several hours or even days for the lower temperatures but a sample which had undergone several dehydration–hydration cycles reached equilibrium much more rapidly. After a series of measurements had been made, the apparatus was left with moist

	Temp. (°K)	Pressure (mm.)		Temp. (°K)	Pressure (mm.)		Temp. (°K)	Pressure (mm.)
(D)	635°	19·0	(D)	683°	81·7	(E)	754°	418·0
(A)	635	24·0	(D)	707	140·0	(E)	767·5	548·0
(D)	665	50·5	(A)	707	143·5	(E)	772	630·0
(A)	680	75·6	(D)	731	241·0	(E)	776·5	671·0
(D)	681	79·7	(A)	731	246·8			

(D) Dissociation, (A) association, (E) equilibrium.

carbon dioxide-free air flowing over the specimen. Opening tap (*F*) allowed the mercury to flow back from the small manometer into the bulb. A water-pump in place of the vacuum-pump provided a small steady flow of air through the apparatus.

Results.—Measurements were repeated from both directions—asssociation and dissociation—for eight temperatures in the region 350—500° c. The results are shown in the Table and Fig. 2. Fig. 2 shows log p plotted against the reciprocal of absolute temperature T in accordance with the van't Hoff equation $\log_e K_p = -\Delta H/\boldsymbol{R}T +$ constant, from which the temperature at which the equilibrium pressure is 760 mm. is 511° c.

The standard deviation (parallel to the $1/T$ axis) of the points about the line corresponds, at 760 mm., to about ±3·0° (it is only ±1·0° at the lower temperatures owing to the reciprocal temperature scale). A similar calculation was made on Tamaru and Siomi's results which showed only 1·8° standard deviation at 760 mm.

The errors are probably in the temperature rather than the pressure measurements. Although particular care was taken to immerse the thermocouple in the specimen, the reading is unlikely to be more accurate than ±1·0°. The cycling of the temperature due to the thermostat may also be responsible for a further error of about 1·0°. Errors in pressure measurement are most likely to be due to sticking of the mercury in the small manometer or differences in meniscus on a rising and a falling column; this was not more than 0·25 mm., which corresponds to a temperature error of less than 0·2° at 511° c. As Tamaru and Siomi used a weighing method their thermocouple was not immersed in the specimen, but they used a closed-end furnace which probably gave more stable conditions; they regarded their temperatures as accurate to ±1·0°.

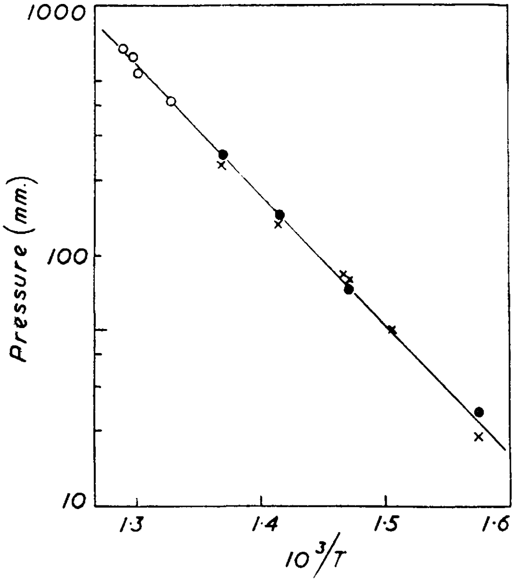


FIG. 2. *Relation between* log p *and temperature.*
× Dissociation, ● association, ○ equilibrium.

The average heat of reaction (ΔH) for the temperature range 300—510° c was also calculated from the slope of the line in Fig. 2, and was found to be 24·9 kcal./mole.

The results of this investigation confirm Tamaru and Siomi's work and suggest that a figure of 512° would be the best estimate of the dissociation temperature of calcium hydroxide. The figure of 547° should definitely be rejected.

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