2. The rate of decomposition of the hydrogen peroxide by hydrochloric acid was examined over the whole range of possible concentrations. For any given concentration of hydrogen peroxide below 100% a "critical concentration" of hydrochloric acid was found below which the rate of decomposition was monomolecular, the acid concentration remaining unchanged, and above which chlorine was liberated to an extent such that the liberated oxygen swept the chlorine out of the reaction mixture. The relationship between acid concentration and velocity constant was determined and it was suggested that the rate constant was proportional to $(1-\alpha)$ multiplied by the acid concentration, where α is the dissociation of the acid calculated from conductivity data.

3. The mechanism of the reaction involved may possibly be represented by the formation of a complex, $H_2O_2.HCl$, which breaks down into hypochlorous acid and water. This is followed by a reaction between hypochlorous acid and hydrogen peroxide, and above the critical concentrations by the liberation of chlorine due to the displacement of the equilibrium among hypochlorous acid, hydrochloric acid and chlorine.

4. Similar experiments were carried out with hydrobromic acid, analogous results were obtained and the same explanation was advanced. The rates of reaction were found to be considerably greater than in the case of hydrochloric acid, and bromine was liberated at far lower concentrations due to this greater rate and to the smaller extent to which bromine is hydrolyzed.

5. The decomposition of the hydrogen peroxide by the halogens is due to the hydrolysis of the latter, the resulting oxy-acid causing the decomposition of the peroxide accompanied by the formation of the halogen hydride.

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THE HYDRATES OF LIME

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An exhaustive study of the literature on the system, calcium oxide plus water, shows many discrepancies as to the compounds capable of existing in such a system. Following a suggestion of the National Lime Association, the present study was undertaken to determine whether there was any other hydrate than the well-known monohydrate $Ca(OH)_2$, or $CaO.H_2O$.

Review of the Literature

Karcz[1] claims to have prepared a white granular powder of the formula $CaO.2H_2O$, by digesting calcium oxide with water for several days at 60°. He also gives data on

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[1] Karcz, *Chem.-Ztg.*, **22**, 38 (1898).

drying at various temperatures and shows the transition point of $CaO.2H_2O$ to $CaO.H_2O$ to be about 60°, although the compound $CaO.2H_2O$ loses some water at temperatures lower than 60° in dry air. He concludes, therefore, that calcium oxide forms an unstable hydrate with two molecules of water.

Herzfeld[2] also reports the existence of such a hydrate, but his analytical data show that the hydrate, if formed, might have been partially decomposed at ordinary temperature before the water content was determined.

The solubility data given by Herzfeld seem to indicate the possible existence of a higher hydrate than $CaO.H_2O$. If the solubility of calcium oxide as determined by Herzfeld is plotted against temperature (Fig. 1), the curve shows a break at approximately 60°, indicating a transition point. For this case, $CaO.2H_2O$ would be stable below 60°, and $CaO.H_2O$ above that temperature.

Selivanov[3] states that calcium hydroxide adsorbs considerable water but forms no definite hydrate, and that the amount of this adsorption depends upon the amorphous state of the hydroxide. He found that the amount of water adsorbed was far less than that corresponding to the formula $CaO.2H_2O$ both when amorphous $CaO.H_2O$ was exposed to water vapor and also when $CaO.H_2O$ was precipitated from an aqueous solution.

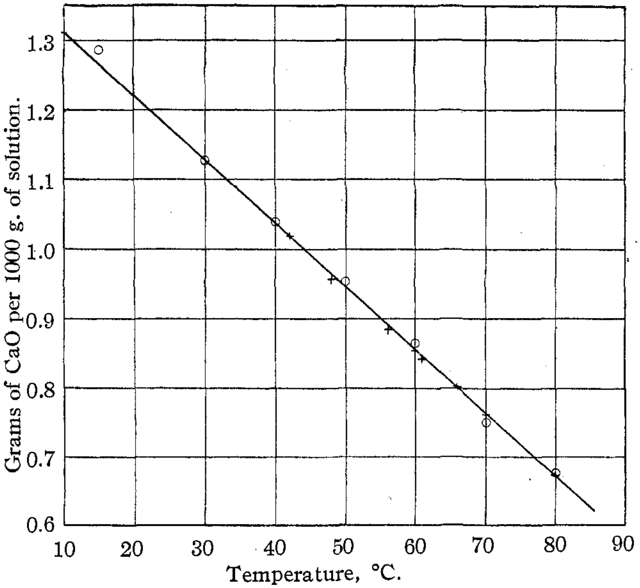

Fig. 1.—Solubility of calcium oxide in water. Circles, Herzfeld's data; crosses, authors' data.

Tschoumanoff[4] digested a constant amount of calcium oxide with increasing amounts of water and found that increasingly large amounts of water remained with the hydrated lime after drying in carbon dioxide-free air at 112–115°.

Bourdakoff,[5] however, points out that Tschoumanoff's conclusions are in conflict with the phase rule, and must be due to unsatisfactory methods of experimentation.

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[2] Herzfeld, *Z. Rubenzuck. Ind.*, **1897**, 818.

[3] Selivanov, *J. Russ. Phys. Chem. Soc.*, **44**, 1797 (1912).

[4] Tschoumanoff, *ibid.*, **44**, 201 (1912).

[5] Bourdakoff, *ibid.*, **44**, 1325 (1912).

He also gives some data on the absorption of water by calcium hydroxide and considers it as adsorption rather than the formation of a hydrate. He states that calcium hydroxide separates from water at room temperature as $CaO.H_2O$, crystalline and entirely non-hygroscopic.

Experimental Work

It is seen from the above review that no definite conclusion can be drawn as to the existence of a dihydrate of calcium oxide. The work on this problem proceeded in two directions; first, attempts to prepare the dihydrate by various methods, and when these proved unsuccessful, the redetermination of the solubility curve of calcium hydroxide.

Attempts to Prepare the Dihydrate of Lime.—The references mentioned above point to the possible existence of a dihydrate stable below 60°. The following methods of preparation of dihydrates were followed: (a) evaporation of lime water at 30°, both under a vacuum and in dry air; (b) precipitation of calcium hydrate from calcium salt solutions with potassium hydroxide; (c) long contact of hydrated lime with water at 55°.

In all cases, both analysis and microscopic examination showed no evidence of another compound than $CaO.H_2O$, with, in some cases, 4–7% of adsorbed moisture. The crystals, more or less well-formed according to the methods used, were always the hexagonal prisms with or without pinacoïds, the same form as reported by Bourdakoff for the monohydrate.

Determination of Solubility of Calcium Oxide in Water.—Since the work described above showed no indication of the existence of the compound $CaO.2H_2O$, and since Herzfeld's solubility curve as shown in the literature is one of the strongest indications in favor of the existence of this compound, the solubility curve was redetermined.

Seidell[6] in his book on "Solubilities" gives a table of the solubility of calcium oxide from 0° to 100°, which is an average of the determinations of various experimenters. An examination of the original data shows discrepancies often as high as 5% among the different determinations. One of the experimenters points out that the possible cause of the error is the slow rate of solution of calcium oxide, and the fact that on increasing the temperature its solution often remains supersaturated. Therefore, the method used here was to approach the equilibrium from both the supersaturated and undersaturated sides.

The excess of lime was allowed to settle and the clear solution pumped off and titrated with acid using phenolphthalein as an indicator. These results plotted against temperature give a straight line from 10° to 80° (Fig. 1), showing no indication of a break at 60°. Two determinations at about 60° were made where Herzfeld showed his high point and both

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[6] A. Seidell, "Solubilities of Inorganic and Organic Compounds," D. Van Nostrand Co., 1919.

these points fell on the straight line. This shows definitely that no dihydrate exists between 10° and 80°.[7]

TABLE I

SOLUBILITY OF CALCIUM OXIDE IN WATER

Cc. of 0.1580 *N* hydrochloric acid used; 98.8 cc. of lime water titrated

Temp. °C.	From super-saturated side Cc.	From under-saturated side Cc.	Solubility in g. of CaO per 1000 g. of solution
10	...	29.31	1.310
42	22.72	22.69	1.018
48	21.20	21.20	0.957
56	19.52	19.51	.884
60	18.86	18.82	.855
61	18.56	18.54	.842
66	17.61	17.60	.802
70	16.76	16.72	.762
80	14.74	14.70	.673

Summary

1. The literature shows some evidence of the existence of a dihydrate of calcium oxide, $CaO.2H_2O$, stable below 60°.

2. Attempts have been made to prepare this compound by evaporation of a lime water solution at low temperatures, by precipitation from a dilute calcium salt solution, and by agitation of calcium hydroxide with water. In each case, however, the monohydrate $CaO.H_2O$ has been obtained, containing only 7% or less adsorbed water when in a finely divided condition.

3. The solubility curve for calcium oxide in water has been redetermined and shows definitely that no dihydrate exists.

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[7] Selivanov [*Z. anorg. Chem.*, **85**, 329 (1914)] reports the formation of a higher hydrate of lime, $2CaO, 3H_2O$, on melting the cryohydrate. This compound decomposes completely above 0°.