OBSERVATIONS OF THE REACTION BETWEEN CALCIUM SULPHATE HEMIHYDRATE AND DEUTERIUM OXIDE

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Goto and Ridge[1] have described the hydration of calcium sulphate hemihydrate by liquid water in terms of the solution of the hemihydrate, and heterogeneous nucleation of crystals of the less soluble dihydrate the growth of which is fed by the diffusion of calcium and sulphate ions through the aqueous phase. On this basis the extent of hydration in concentrated pastes can be accounted for over almost the entire course of the reaction. Nevertheless, it is sometimes held that the hydration of hemihydrate under the conditions in question takes place by a solid state reaction (see[2] for example). With a view to supporting further a mechanism based on recrystallization, the reaction has been carried out with deuterium oxide in order to detect the extent to which the water in the hemihydrate is liberated from the lattice at any stage.

Flakes of gypsum (taken from high-grade natural crystals found at Gol Gol, N.S.W.) were heated at 80° for 10 hr in a vessel continuously evacuated by a rotary pump. The product (largely hexagonal calcium sulphate which is often called "soluble anhydrite") could be exposed to the atmosphere to bring about hydration to the hemihydrate. About 5 hr was necessary to bring about conversion and the extent of dehydration and rehydration was followed by weighing the sample.

Samples converted partly or completely into hemihydrate were placed in a glass vessel of about 20 ml capacity, connected to a vacuum system by a tap. Deuterium oxide was admitted in amount nearly 70% in excess of that required for the hydration to dihydrate. The vessel was then closed and the system let stand for 18 hr, at the end of which time hydration could be expected to be complete.[1] The tap to the vacuum system was then opened and excess liquid allowed to distil into a trap cooled by liquid nitrogen. The distillate will not be pure deuterium oxide but will contain water to the extent that calcium sulphate hemihydrate has dissolved in it.

The molar fraction of H_2O in the extracted liquid was measured by a gas chromatographic device. The mixture was passed through a column of powdered zinc at 340°. Here reduction to H_2, HD, and D_2 took place. This was done as no chromatographic column that can effectively separate D_2O from H_2O seems to be

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[1] Goto, M., and Ridge, M. J., *Aust. J. Chem.*, 1965, **18**, 769.

[2] Eipeltauer, E., *Zem.-Kalk-Gips*, 1963, **16**, 9.

available. However, D_2 can be separated from HD and H_2 by a column of colloidal Al_2O_3 and $Fe(OH)_3$ at the temperature of liquid nitrogen.[3] Here satisfactory separation of H_2, HD, and D_2 was obtained by adjusting the rate of flow, D_2 being detained the longest and H_2 the least. Tests with artificial mixtures showed that the ratio $H_2O/(H_2O+D_2O)$ could be determined to within $\pm3\%$.

The fractions of H_2, HD, and D_2 in order were then passed through a column of CuO at 300° and were oxidized to H_2O, HDO, and D_2O respectively. Their molecular proportions were measured from their thermal conductivities as determined by a thermal conductivity cell of a type commonly used as a gas chromatographic detector.

Calcium sulphate hemihydrate is sparingly soluble[4] and only a small fraction of the sample will dissolve in the quantity of deuterium oxide added. Consequently any substantial contamination of the deuterium oxide must be due to hemihydrate having passed through the aqueous phase to get to the growing crystals of dihydrate or to the water having diffused from the hemihydrate into liquid. The extent of the latter process is not likely to be appreciable in view of the low decomposition pressure of hemihydrate of stoicheiometric composition.[5]

TABLE 1

DEHYDRATION OF GYPSUM AND THE REHYDRATION OF THE PRODUCT BY DEUTERIUM OXIDE

| | Run 1 | | Run 2 | |
	Obs.	Theor.	Obs.	Theor.
Weight sample (g)	0·2160		0·1974	
Weight of product of dehydration (g)	0·1774	0·1707	0·1627	0·1560
Weight after rehydration by water vapour[a] (g)	0·1850	0·1822	b	b
Weight D_2O added (g)	0·0510		0·0553	
Excess D_2O (i.e. residue after 18 hr) (g)	0·0180	0·0163	0·0185	0·0161
$H_2O/(H_2O+D_2O)$ (molar fraction of H_2O)	0·240	0·2376[c]	0·112	0·119[c]

[a] Product assumed to be $CaSO_4,H_2O$.

[b] Not rehydrated.

[c] Assuming that all water is free to move about.

The results from two runs are given in Table 1 and it is seen that after hydration is complete the molar fraction of H_2O in the residual aqueous phase is very close to that of the overall system at the beginning of each experiment. This is strong support for the view that the hydration of calcium sulphate hemihydrate takes place by a "through solution" mechanism rather than by a solid state reaction.

[3] Moore, W. R., and Ward, H. R., *J. phys. Chem.*, 1960, **64**, 832.

[4] Kelley, K. K., Southard, J. C., and Anderson, C. T., Tech. Pap. Bur. Mines, Wash., 1941, No. 625.

[5] Razouk, R. I., Salem, A. Sh., and Mikhail, R. Sh., *J. phys. Chem.*, 1960, **64**, 1350.