KINETICS OF THE DEHYDRATION OF CALCIUM SULPHATE DIHYDRATE IN VACUO*

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When heated, calcium sulphate dihydrate undergoes dehydration as follows: $CaSO_4,2H_2O \rightarrow CaSO_4,\frac{1}{2}H_2O \rightarrow CaSO_4$ (hex).[1,2] (Hexagonal calcium sulphate is formed by the gentle dehydration of calcium sulphate hemihydrate and is sometimes known as soluble anhydrite.) This reaction has been shown to begin at nuclei on the surfaces of single crystals.[3,4] The effects of water vapour on the dehydration have been studied by McAdie,[5] but the kinetics have not been satisfactorily elucidated. This note gives an account of the progress of the dehydration of calcium sulphate dihydrate occurring under the simplest possible conditions, viz. *in vacuo*, where the rate will be determined entirely by processes occurring at the interface between the undecomposed material and the product, and by the diffusion of water through the layer of product.

Experimental

Materials

Reagent grade calcium sulphate dihydrate (composition: CaO, $32 \cdot 6$; SO_3, $46 \cdot 3$; H_2O, $20 \cdot 7$; R_2O_3, $0 \cdot 02$; MgO, $0 \cdot 02$; SiO_2 and insolubles, $0 \cdot 13$; CO_2, $0 \cdot 15$; Na, $0 \cdot 003$; and Cl, $0 \cdot 01\%$) of particle size such as to pass a 52-mesh screen was used.

Procedures

The dehydration of samples $(4 \cdot 5 \pm 0 \cdot 1$ g) was carried out in an all-glass system fitted with a detachable reaction vessel.[2] A movable furnace could be placed around the reaction vessel which could be weighed before and after the experiments. Microscopic examination of the product was carried out with a Vickers projection microscope.

Analysis of Samples

The proportions of the phases in the treated samples were determined by X-ray diffracto-metry using a Siemens generator and diffractometer fitted with a scintillation counter. Hexagonal calcium sulphate and the di- and hemi-hydrates of calcium sulphate could be expected to be present. The compound first named is very hygroscopic[1,2] and is rapidly converted into hemihydrate on exposure to the atmosphere. The following analytical procedure was then adopted: The samples were exposed to the atmosphere for 24 hr to allow hydration of hexagonal calcium sulphate. Lots of 2 g of the product were mixed with $0 \cdot 500$ g powdered silicon[2] and ground by hand for 30 min in a mortar with a pestle. Mechanical grinding was not used as it can result in the formation of hemihydrate from the dihydrate. Flat specimens of uniform packing and density were then prepared and subjected to X-ray diffraction. The peak for the $3 \cdot 79$ Å spacing was used for the

[1] Flörke, O. W., *Neues Jb. Miner. Mh.*, 1952, **84**, 198.

[2] Ridge, M. J., Surkevicius, H., and Goto, M., *Aust. J. Chem.*, 1964, **17**, 1197.

[3] Zolotov, V. A., *Kristallografiya*, 1958, **3**, 237.

[4] Bright, J. E., and Ridge, M. J., *Phil. Mag.*, 1961, **6**, 441.

[5] McAdie, H. G., *Can. J. Chem.*, 1964, **42**, 792.

determination of the dihydrate, and that for the 6·01 Å spacing for the hemihydrate. The means of three measurements were used and the proportions of the two components read off from calibration curves which were virtually linear. The estimated standard deviations of the measurements were 2% for both dihydrate and hemihydrate. The compositions of the original samples were then calculated on the assumptions that hemihydrate contains 6·3% H_2O and was absent from the material in the reaction vessels (see below).

Products of Dehydration in vacuo

Weighed samples of dihydrate were placed in reaction vessels which were then pumped to give black vacua. The temperature was then raised to 85° at which dehydration proceeded at a convenient rate. The treated samples will consist of the original material, if any, and either hexagonal calcium sulphate or calcium sulphate hemihydrate. Analysis by X-ray diffraction showed that the four samples heated longest (viz. for 24, 8, 7, and 6 hr) contained 4, 8, 4, and 18% dihydrate, respectively. The residual water determined from the loss in weight corresponded to 3·01, 6·93, 4·78, and 16·8% of dihydrate from the four samples. It seems clear then that the product of dehydration is best regarded as hexagonal calcium sulphate rather than the hemihydrate.
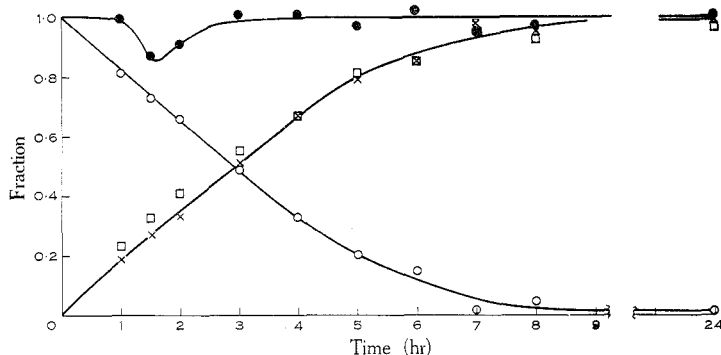

Fig. 1.—Fractions of calcium sulphate dihydrate and hexagonal calcium sulphate in samples of dihydrate held *in vacuo* at 85° for various periods. □, Hexagonal calcium sulphate from the loss in weight (α_W). ×, Hexagonal calcium sulphate from X-ray diffractometry (α_X). ○, Calcium sulphate dihydrate from X-ray diffractometry. ●, Sums of the fractions of calcium sulphate dihydrate and of hexagonal calcium sulphate determined by X-ray diffractometry.

Kinetics of the Reaction

Figure 1 shows the fractions transformed, α_W and α_X, determined from the loss in weight and X-ray analyses respectively, and the fraction of residual dihydrate for samples heated at 85° for periods up to 24 hr. The sums of the independent determinations by X-ray diffractometry of hexagonal calcium sulphate and the dihydrate are also shown, and it is seen that there seems to be a marked minimum just before the reaction begins to slow down appreciably. This effect has been observed before[6] in the transformation of hexagonal to orthorhombic calcium sulphate at

[6] Goto, M., Molony, B., and Ridge, M. J., *J. chem. Soc.* (*A*), 1966, 9.

temperatures above 200°, in which case it was attributed to a deterioration in crystallinity as a result of the phase change followed by an improvement due to sintering. In view of the low temperature in the present case the mobility leading to sintering probably results from the presence of water vapour which is in the process of being disengaged from the system.[6,7]

The values of α_w agree with those of α_x reasonably well, although there is a systematic deviation in the region of the minimum in the sums of the components as determined by X-ray diffraction.

The partly transformed grains of dihydrate were found by microscopy to be covered with a layer of product. As the grains were approximately equiaxial and dehydration appeared to proceed by an interface moving through the microcrystals, "diminishing sphere" kinetics[8] should be applicable. This treatment leads to the equation

$$A - B(1-\alpha)^{\frac{1}{3}} = kt \tag{1}$$

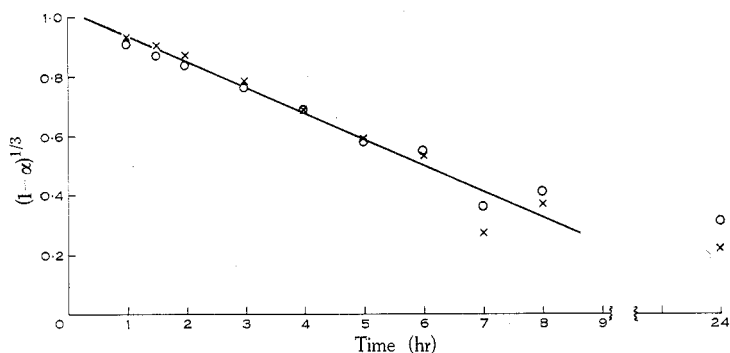where A, B, k are constants and α is the fraction transformed at time t.

Fig. 2.— $(1-\alpha)^{\frac{1}{3}}$ plotted against time for the results shown in Fig. 1. × Calculated from the fraction of hexagonal calcium sulphate found by X-ray diffractometry. ○ Calculated from the loss in weight. The least square line for the gravimetric results is shown.

Figure 2 shows $(1-\alpha)^{\frac{1}{3}}$ plotted against time for the values of α_w and α_x shown in Figure 1. The least square line for α_w is drawn, the correlation coefficient being -0.969. It is seen that the experimental results accord well with the diminishing sphere model. However, it was found that if $(1-\alpha)^{\frac{1}{2}}$ was plotted against time the results conformed to a straight line equally well, the correlation coefficient being -0.983. Kinetic equations with half powers may be derived from the "diminishing plate" model,[8] which cannot be applied in this case as the reaction has been found (see above) not to take place in the appropriate fashion. These results form another example of the extent to which formal kinetics cannot be used alone to distinguish between possible mechanisms of chemical reactions (cf.[9]).

[7] Ridge, M. J., Molony, B., and Boell, G. R., J. chem. Soc. (A), 1967, 594.

[8] Gregg, S. J., "The Surface Chemistry of Solids." (Chapman & Hall: London 1961.)

[9] Ridge, M. J., Trans. Faraday Soc., 1956, 52, 1; Mulcahy, M. F. R., and Ridge, M. J., Trans. Faraday Soc., 1953, 49, 1297.