

Transformation of the α - and β -Forms of Calcium Sulphate Hemihydrate to Insoluble Anhydrite

ALTHOUGH there is no difference between the X-ray diffraction patterns of α - and β -calcium sulphate hemihydrate¹, differences have been reported for density, specific heat and the heat of formation². I have shown that the dehydration of each form to soluble anhydrite proceeds at about the same rate, but that the rate of transformation of soluble to insoluble anhydrite is much greater for the α -form. This is of importance in the examination of gypsum plasters, which may contain one or both of these forms according to the method of manufacture. The difference between the α - and β -forms is demonstrated here by simultaneous differential thermal and thermogravimetric analyses³, and by determining the rate of the phase transformation at a static temperature.

Samples of α -hemihydrate were prepared by heating a pure precipitated gypsum in concentrated nitric acid¹, in a saturated steam atmosphere², and in a concentrated solution of magnesium sulphate⁴. Samples of β -hemihydrate were prepared by calcining the same gypsum in open dishes in an air oven at 150°, 200° and 240° C. The differential thermal curve for α -hemihydrate (Fig. 1, curve *a*) indicates the rapid formation of insoluble anhydrite by a sharp exothermic peak at 255° C. The form of the curve was the same for a large number of samples prepared by the methods outlined above. Although in some instances a reduction in the size of the exothermic peak was noted, the claim by Budnikov and Kosyreva⁵, that the differential thermal curve for α -hemihydrate shows no exothermic effect, is not in agreement with my results. The simultaneous thermogravimetric curve showed that the water content of the sample was about 0.1 per cent when the exothermic reaction commenced, and X-ray examination of the sample heated to 290° C. (the end of the exotherm) showed that it contained about 60 per cent insoluble anhydrite. Further conversion of the α -soluble anhydrite to insoluble anhydrite took place slowly between 290° and 550° C., with a loss of about 0.05 per cent of water. The β -hemihydrate behaves differently. The differential thermal curve (Fig. 1, curve *b*) indicates a gradual transformation to insoluble anhydrite commencing at about 300° C. The simultaneous thermogravimetric curve indicates that at 300° C. (the beginning of the exotherm) the water content was reduced to about 0.2 per cent, and X-ray examination of the sample heated to 500° C. (the end of the

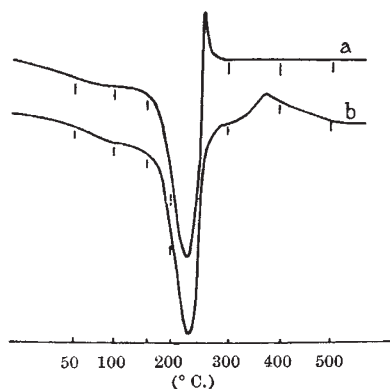


Fig. 1. Differential thermal analysis curves for calcium sulphate hemihydrate. *a*, α -form; *b*, β -form

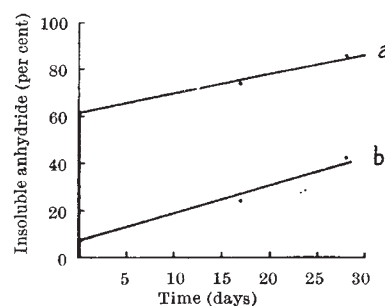


Fig. 2. Rate of formation of insoluble anhydrite from calcium sulphate hemihydrate at 200° C. *a*, α -form; *b*, β -form

exotherm) showed that it was almost pure insoluble anhydrite. By comparison, it should be noted that in the decomposition of the α -hemihydrate a small amount of soluble anhydrite still remained at 500° C.

In a mixture containing α - and β -hemihydrate the exothermic peak of the α -form is often not visible on the differential thermal curve because it is masked by the endotherm of the β -form, which is not complete until about 300° C.; but the form of the curve is still different and the area of the exothermic peak due to the β -form is significant. It is reduced to about half its normal size in a mixture of equal parts of α - and β -hemihydrates, and can therefore give an indication of the proportion of each form present. The area of each exothermic peak of β -hemihydrate was not appreciably different for samples prepared by heating at 150° C. for 4 hr., at 200° C. for 1 hr., and at 240° C. for 45 min.

The phenomena observed under dynamic heating conditions were also observed at a static temperature of 200° C. Fig. 2 shows that initially the rate of transformation of the α -form to insoluble anhydrite is about eight times greater than that for the β -form, but thereafter the rate decreases to about half that of the β -form.

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² Kelley, K. K., Southard, J. C., and Anderson, C. T., U.S. Bur. Mines Tech. Paper 625 (1941).

³ Powell, D. A., *J. Sci. Instr.*, **34**, 225 (1957).

⁴ Schoch, E. P., and Cunningham, W. A., *Trans. Amer. Inst. Chem. Eng.*, **37**, 1 (1941).

⁵ Budnikov, P. P., and Kosyreva, Z. S., *Voprosy Petrograf. i Minera Akad. Nauk S.S.S.R.*, **2**, 342 (1953). (*Chem. Abstr.*, **48**, 13314a (1954).)

Estimation of Strontium in Biological Materials by means of a Flame Spectrophotometer

PREVIOUS attempts to determine the strontium content of biological materials by spectrochemical methods have not been entirely satisfactory, and in at least one investigation¹ the method was abandoned in favour of neutron activation analysis. With recent improvements in the performance of flame spectrophotometers which have been described by various authors² methods have been evolved for the