

stationary phase and of the alcohols during the passage of the alcohols through the column. To substantiate this tentative explanation the nitrogen leaving a column which had not been charged with sample was passed through an aqueous solution of morpholine overnight. The solution was concentrated under reduced pressure and analysed by paper chromatography². One single spot of formic acid was found on the finished chromatogram.

Whether the unexpected, and somewhat disquieting results of these experiments were caused by our experimental technique which, however, does not show any uncommon aspects, or by any of the particular samples of support or stationary phase (both obtained from well-known manufacturers in the field) has still to be established. Using another brand of fire-brick support or employing hydrogen as the carrier gas gave the same results. If the phenomenon should thus prove to occur more generally, a warning seems appropriate since the occurrence of ester formations on some types of gas-liquid chromatography columns may occasionally lead to the identification of compounds in complex mixtures of isolated volatiles which are, in fact, not present in the original sample.

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¹ Corse, J., and Dimick, K. P., "Flavor Research and Food Acceptance", p. 302 (New York and London, 1958).

² Osteux, R., Guillaume, J., and Laturaze, J., *J. Chromat.*, **1**, 70 (1958).

Transition of Calcium Sulphate Hemihydrate to Insoluble Anhydrite

RECENTLY Powell¹ directed attention to the fact that for calcium sulphate hemihydrate the rate of transition of soluble anhydrite to insoluble anhydrite was greater in the α - than in the β -form. Similar phenomena were observed in our experiments².

Hemihydrate was heated at temperatures ranging from 120° C. to 170° C. for various periods of time in a thermo-balance, and then kept in air for more than a week. The quantity of insoluble anhydrite formed from the soluble form was estimated from the weight increment due to the natural rehydration of the untransformed soluble material on leaving it exposed to the air. Fig. 1 shows the results obtained for heating at 170° C. The ordinate represents the weight percentage of the insoluble anhydrite and the abscissa the time of heating at 170° C. after dehydration was complete. The following kinds of hemihydrate were examined.

A. Hemihydrate prepared by heating a kind of gypsum, a by-product in the manufacture of salt, in an autoclave; granular crystals about 30 μ across.

B. Ordinary plaster of Paris prepared by heating the same material as in *A* in air; fine crystals with shapes difficult to determine under the microscope.

C. A kind of plaster of Paris manufactured commercially; the crystal state is similar to *B*.

D and *E.* Hemihydrate prepared by heating the dihydrate obtained by setting *B* or *C* in an autoclave; fine and rather needle-like crystals about 1 μ in width.

Afterwards, another series of measurements was made on hemihydrate *F*. The procedure was almost the same as above except that a smaller sample was used and the thermo-balance had a flat tray in order to

make samples more sensitive to heat. The results obtained are shown in Fig. 1 by broken lines. Curves *F-R* and *F-S* correspond to rapid heating, taking about 5 minutes from 80 to 170° C. and to slow heating taking about 65 minutes, while about 60 minutes were required in the previous measurements. The curve *F-G* indicates the case of heating fine powder of hemihydrate *F*, ground in a mortar, under the same condition as *F-R*.

F. Hemihydrate prepared by heating natural lump gypsum which consists of fine crystals in an autoclave; granular crystals somewhat larger than *A*.

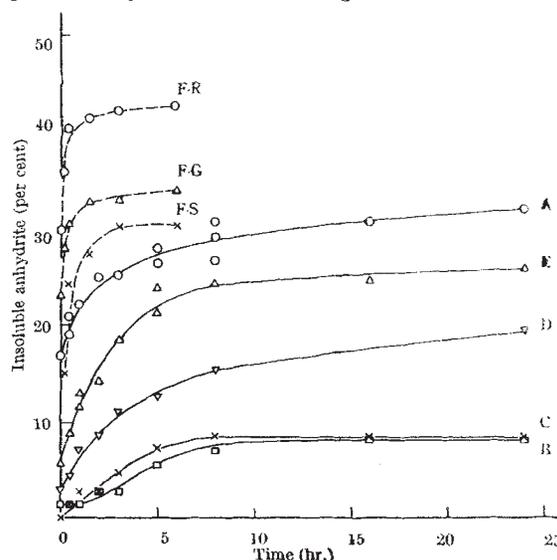


Fig. 1 shows that the hemihydrates prepared in an autoclave form insoluble anhydrite faster than ordinary plaster of Paris. This result agrees with that of Powell. However, there are considerable differences in the rate of formation among the various kinds of hemihydrate prepared in an autoclave. In addition, the rate decreases when fine powder is used or when the rate of heating up to 170° C. is lowered. From these results, it seems that the rate should be considered in connexion not only with the types of hemihydrate, which are assorted mainly with the methods of preparation, but also with the crystal size or faults as described by Buerger³.

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¹ Powell, D. A., *Nature*, **182**, 792 (1958).

² Mitsuki, C., and Kita, M., *Reports Gov. Ind. Res. Inst., Nagoya*, **9**, 413 (1955).

³ Buerger, M. J., "Phase Transformation in Solids" 206 (Wiley, New York, 1951).

Reduction of the Fe₂O₃⁺ Ion at the Dropping Mercury Electrode

THE technique of capacity flow¹, admirably adapted to the study of transient compounds, demands complete homogeneity of the contents of the reaction cell, in contradistinction to the technique of polarography, which depends on there being a concentration polarization. Exploratory experiments showed, however, that the two techniques could be combined, and adequate polarograms obtained, in solutions stirred by rapid