648. *The Dehydration of Gypsum. Part IV.* The Heat of Immersion, Heat of Hydration, Specific Gravity, Sedimentation Volume, and Bulk Density of the Dehydration Products.*

By S. J. Gregg and E. G. J. Willing.

The quantities enumerated in the title of this paper have been measured on samples of gypsum dehydrated at a succession of temperatures between 110° and 700°. The heat of immersion, the sedimentation volume, and the "tapped" bulk volume all show one maximum in the region of 180° and another in the region of 300°. The heat of hydration falls monotonously as temperature increases, and probably provides a measure of the proportion of "hemihydrate" lattice present in the solid.

The results in the main substantiate the conclusions drawn from the work of Parts I—III and summarised in Part III.

In Parts I—III, the surface area and the chemical nature, of the product formed by the thermal dehydration of gypsum at a series of temperatures have been studied by means of the adsorption of vapours. In the present work the products have been examined by reference to a number of other properties which might be expected to provide supporting evidence. The heat of immersion (in carbon tetrachloride) should give fairly direct, and the bulk volume and the sedimentation volume rather indirect, information as to the variation of the surface area of the solid; the specific gravity and the heat of hydration should give some information as to the chemical and physicochemical nature of the solid phases present.

Experimental.

Materials.—The gypsum was from the batch used in Parts I—III, and was sieved to 40–80 mesh. The dehydrated samples were prepared on the thermal balance in the manner described in Part I. After calcination, the sample was kept in a desiccator over phosphoric oxide until used. All the determinations on a given sample were carried out within 24 hours of its preparation.

The carbon tetrachloride (May and Baker's; boiling range 76—77·5°) was dried over phosphoric oxide. The methyl alcohol (May and Baker's "Commercial," >99% pure) was dried in a manner similar to that given by Lund and Bjerrum (*Ber.*, 1931, **64**, 210): it was kept over magnesium turnings for several days and was then refluxed for 2—3 hours. It was then distilled and the fraction of b. p. 65—66° was collected. The decalin (B.D.H.) was a mixture of the *cis-* and the *trans-*form; it was purified by shaking it with concentrated sulphuric acid till no further tarry matter was removed, and then shaken with alkali, washed with water, dried ($CaCl_2$ and P_2O_5), and distilled, the fraction of b. p. 182—183° being collected. The ethylbenzene (B.D.H.) was dried over phosphoric oxide.

All the liquids were boiled just before use to expel dissolved air.

Apparatus and Procedure.—Heat of immersion in carbon tetrachloride (H_L, *cal. g.*$^{-1}$). The heat of immersion of a solid in an inert liquid (*i.e.*, one that neither reacts with nor dissolves the solid) is known to give a measure of the surface area of the solid (Bangham and Razouk, *Proc. Roy. Soc.*, 1938, *A*, **166**, 572). Indeed, in those cases where the surface is energetically uniform, H_L is proportional to the surface area S cm.^{2} of a given material; for then $H_L = hS$, where h is the heat of immersion per cm.^{2} of the material. In general, the value of h would vary from one substance to another and also from specimen to specimen of a given substance; the latter variation would arise from difference in pretreatment of the specimens and might be expected to be smaller, as a rule, than the former.

Carbon tetrachloride may be regarded as "inert" towards the dehydration products of gypsum. In the present study the heat of immersion of each sample in carbon tetrachloride was determined by means of a calorimeter of special design, to be described elsewhere by Gregg and Hill. It consists essentially of two cylindrical Dewar flasks (of 300 c.c. capacity), *A* and *B*, set in holes in a large aluminium block. A thermel of 16 thermocouples has its "cold" junctions in flask *A* and its "hot" junctions in flask *B*, each set of junctions being mounted on a copper holder. The sample (previously outgassed at 90°) was contained in a sealed-off bulb, and this was placed in a bulb-holder in flask *B*. Connections for the thermel are taken off to a sensitive galvanometer; and an electrical heating coil is mounted, also in flask *B*, for calibration purposes. Each flask contained 30 c.c. of carbon tetrachloride. After insertion of the bulb with its sample, the calorimeter (which was set in a large air-thermostat) was left overnight to settle down. Next morning, readings of the galvanometer were taken for an hour or so to check that they were nearly or quite constant, and the bulb was then broken by a breaker rod. Readings were continued for a further hour or so, to enable cooling corrections to be made; and finally the electrical calibration was performed. Agreement of duplicates to within 0·02 cal. g.$^{-1}$ was usually obtained. The results are plotted as H_L against temperatures of preparation in Fig. 1 (Curve I).

Bulk volume of a solid. This is the volume V occupied by 1 g. of the solid when it is packed in an arbitrary but standard manner. In general, V is made up of: (*a*) V_a, the volume of the solid material itself; (*b*) V_b, the volume of the macro- and micro-pores in the solid, including those of molecular

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* Part III, preceding paper.

dimensions; and (*c*) V_e, the space between the individual grains (the " voidage "). The aim of the technique used in measuring is to ensure that the variation of V_e shall be as small as possible. The value of V will then give an approximate measure of $(V_a + V_b)$, *i.e.*, of V_b itself, if V_a is known or can be estimated.

In the present study, a portion (*ca.* 3 g.) of the sample which had been previously sieved was weighed into a 10-c.c. measuring cylinder provided with a stop-cock, and was outgassed at 80—90° for 1—2 hours. It was then mechanically tapped for 15 minutes (*ca.* 500 taps) by a device which will be described elsewhere. Duplicates agreed to 1—2%.

In Fig. 1 the results are plotted as V against temperature of preparation (Curve III).

Fig. 1.

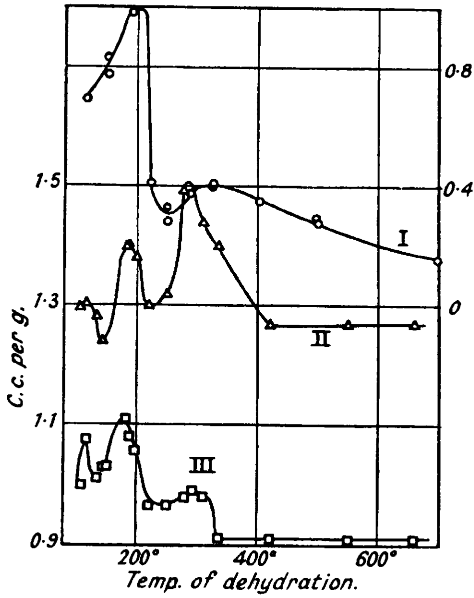


Fig. 2.

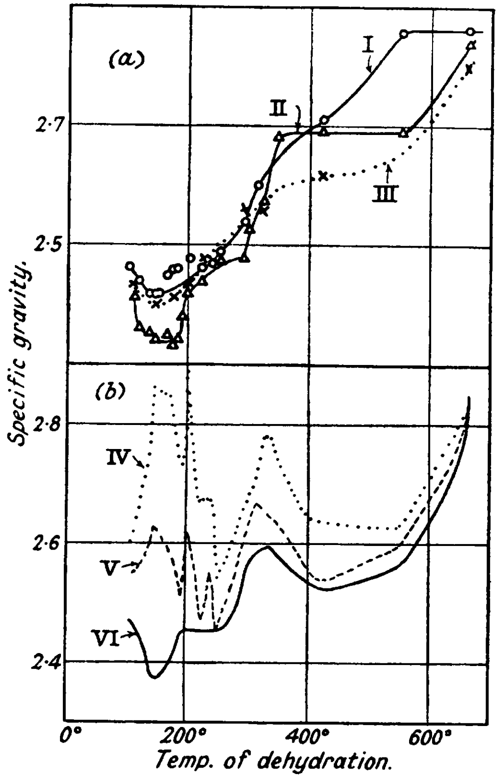


Fig. 1.

Some properties of dehydrated gypsum, plotted against the temperature of dehydration.

I. *Heat of immersion in carbon tetrachloride* (*use right-hand scale*). II. *Sedimentation volume in carbon tetrachloride* (*use left-hand scale*). III. " *Tapped* " *bulk volume* (*use left-hand scale*).

Fig. 2.

The specific gravity (*s.g.*) *of dehydrated gypsum, plotted against the temperature of dehydration.*

I, ○. *s.g. in carbon tetrachloride.* II, △. *s.g. in decalin.* III, ×. *s.g. in ethylbenzene.* IV. *s.g. after immersion for* 24 *hours in methyl alcohol.* V. *s.g. after immersion for* 2 *hours in methyl alcohol.* VI. *s.g. after immersion for* 10 *minutes in methyl alcohol.*

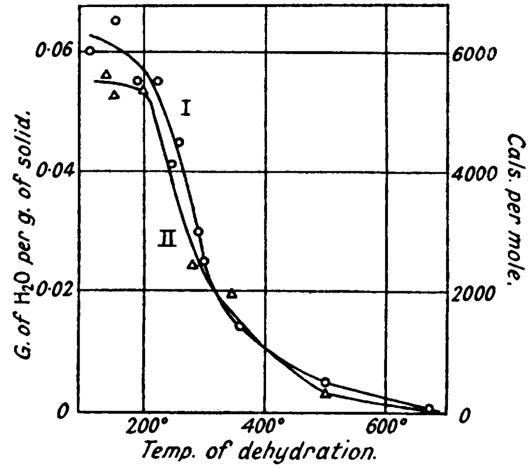
Sedimentation volume in carbon tetrachloride (V_L). The sedimentation volume of a solid in a liquid is the volume occupied by the particles of a suspension after settling (cf. Bloomquist and Shutt, *Ind. Eng. Chem.*, 1940, **32**, 827). It might be expected to run more or less parallel to the bulk volume for a series of related solids (such as a calcination series). Whether V_L depends on the nature of the liquid used is a matter of controversy, but there are good grounds for supposing that it does so depend (cf. Willing, to be published).

The technique of measurement was simple. The weighed sample (*ca.* 3 g.) was introduced into a 10-c.c. measuring cylinder and thoroughly mixed with dry carbon tetrachloride by shaking; after any solids adhering to the walls of the cylinder had been washed down with more carbon tetrachloride, the cylinder was tightly corked, and the solid allowed to settle for 24 hours. The volume could then be read with ease and accuracy. The plot of V_L against temperature of preparation is given in Fig. 1, Curve II.

The specific gravity, ρ, in various liquids. It is well known that the specific gravity of finely divided solids varies according to the liquid in which the solid is immersed for the determination, and various theories have been put forward to account for the effect. The important factors appear to be (*a*) the incomplete penetration of the liquid into the ultrafine pores, and (*b*) the adsorption of the liquid by the solid. Factor (*a*) will tend to *raise* the specific volume, V_ρ $(=1/\rho)$; it will exhibit itself as a " drift," *i.e.*, as a slow increase in specific gravity, or a decrease in specific volume, with time. Factor (*b*) will—by causing the liquid molecules to be more tightly packed at the solid–liquid interface than in the bulk of the liquid—tend to *lower* the specific volume.

The effect of (*b*) will be difficult to predict quantitatively from theoretical considerations, but it will in general be small. Measurements of V_ρ should accordingly throw useful light on the pore structure of the solid; and with liquids whose molecules are large enough to render penetration unimportant, the value of V_ρ should give some information as to the chemical nature of the solid phases present (by comparison with standard values). The experimental method used was similar to that described by Cude and Hulett (*J. Amer. Chem. Soc.*, 1920, **42**, 391). A small soda-glass bulb containing 0·5—1 g. of the sample was outgassed for *ca.* 2 hours at 85°, and weighed in air. The tip was then broken off under the surface of the liquid (by use of a breaking device) and the bulb was weighed under the liquid by suspending it in a sling from the hook of a balance; these weighings were taken after 10 minutes, 2 hours, and 24 hours. Finally, weighings of the empty bulb in air were taken both with and without the tip. From the four weighings the specific gravity of the solid is readily calculated (cf. Gregg and Sing, *J. Phys. Colloid Chem.*, 1951, in the press). Slow penetration effects reveal themselves as a " drift " in the density with time.

FIG. 3.



The " retained " water and the heat of hydration of dehydrated gypsum, plotted against the temperature of dehydration.

Curve I : " Retained " water (use left-hand scale). Curve II : Heat of hydration (use right-hand scale).

The specific gravities of the four liquids were determined by the same method, powdered calcite being used in place of the powder. The results (given as specific gravities referred to water at 4°) are : methyl alcohol, 0·787; carbon tetrachloride, 1·600; decalin, 0·870; ethylbenzene, 0·800 (all at the working temperature of 22·5° ±0·1°).

Results.—With decalin (molar volume 160 c.c.) and with ethylbenzene (molar volume 124 c.c.), no drift in density was noted. With carbon tetrachloride there was a slight drift between 10 minutes and 2 hours, but none between 2 and 24 hours; and with methanol large drifts were obtained (except with the most sintered sample, the 680° one). This would seem to show that there are pores present having a diameter comparable with that of the methyl alcohol molecule, and a few having a diameter of the same order as the carbon tetrachloride molecule. (But the possibility that the drift with methanol is due to slow reaction of the solid with traces of water cannot be entirely ruled out.) The values of ρ with decalin, ethylbenzene, and carbon tetrachloride respectively are plotted against the temperature of preparation in Fig. 2*a*. The methanol results are plotted separately in Fig. 2*b*, and the considerable drift is readily seen. The " 10-minute " value should be the most comparable with the ρ values of other liquids, whether penetration or reaction is the cause of the drift.

Heat of hydration. Since anhydrite does not react with water in a reasonable space of time, it was thought likely that measurement of the heat evolved when the sample is mixed with excess of water would give an indication of the hemihydrate content of the sample.

For the experimental determination an improved form of ice calorimeter was used, details of which will be published elsewhere. The sample in its bulb was broken under the surface of water by a breaking-rod. Readings of the mercury in the capillary of the calorimeter were then taken every few minutes. Unfortunately, owing to lack of time, duplicates could not be obtained except in two cases, where they agreed to within *ca.* 0·3 cal. g.$^{-1}$. (For most samples the heat of hydration was some 40 cal. g.$^{-1}$.)

The rate of evolution of heat was rapid at first but after 20 minutes it had decreased greatly and after 2 hours was very small; accordingly, it was decided to take the heat evolved in the first 2 hours as the heat of hydration.

The results, calculated as calories per mole of $CaSO_4$, are plotted against temperature of preparation in Fig. 3 (Curve II). In the same diagram are plotted the values of the amount of " retained " water determined in Part III (Figs. 1 and 3), which, it was suggested, is a measure of the hemihydrate content of the sample. As will be seen, the two curves agree remarkably closely (with proper adjustment of the scales of ordinates); and this supports the hypothesis that both the retained water content and the heat of hydration are measures of the hemihydrate content of a sample.

Discussion.

The heat of immersion, the sedimentation volume, and the bulk volume, when plotted against temperature of calcination, all show one maximum at about 180° and another in the region of 300°. These results are in substantial agreement with those of Parts I, II, and III, and they indicate a maximum " activity " in samples prepared at those temperatures. From the very nature of the sedimentation volume and of the bulk volume, one would not expect their curves to coincide in detail with that of surface area against temperature; for, though in general V_L and V both increase with increasing S, exact proportionality would certainly not be expected.

At first sight, one might perhaps expect such coincidence for the heat of immersion curve, since H_L is a direct measure of S. However, as already indicated, the proportionality constant h (— heat of immersion per cm.^{2} of surface) will most probably differ for the anhydrite and the hemihydrate lattice, and will also vary for a given lattice according to the temperature of preparation. Unfortunately, it is not easy to predict even the sense of the variation of h, much less its absolute magnitude for any one sample. One must rest content with noting that the order of magnitude of the values in the following table for the heat evolved per cm.^{2} are reasonable by comparison with those obtained with other solids; *e.g.*, barium sulphate and titanium dioxide in carbon tetrachloride give h as 220 and 240 erg cm.$^{-2}$, respectively, according to Harkins and Boyd (*J. Amer. Chem. Soc.*, 1942, **64**, 1190). (The values in the table have been calculated from the experimental heat of immersion, on the assumption that the areas calculated from the nitrogen isotherms in Part I are correct.)

Heat of immersion per cm.^{2} (h) *of the products obtained by dehydrating gypsum at various temperatures.*

Temp.	116°	152°	188°	222°	250°	287°	325°	400°	500°	700°
h (ergs cm.$^{-2}$)	347	330	330	159	117	138	167	146	134	268

The results for specific gravity are somewhat inconclusive. In the region of 150—180° there is a minimum in the specific gravity determined in carbon tetrachloride, in decalin, in ethylbenzene, and in methyl alcohol (" 10-minutes "), and this would correspond to a maximum in the specific volume of the solid; and this in turn would seem to correspond to the maximum in the surface area, S, determined by adsorption (Parts I and II), and in the sedimentation volume, V_L, the bulk volume, V, and the heat of immersion, H_L (this Part). It is difficult to formulate any detailed interpretation of the numerical values of the minimum density, however, for not only does ρ differ according to the liquid used, but there is wide variation in the values quoted in the literature for $CaSO_4,0{\cdot}5H_2O$ (whence ρ for the dehydrated hemihydrate would have to be calculated). This latter circumstance no doubt arises from the considerable sensitivity of the specific gravity of hemihydrate to conditions of preparation. There is no second maximum in ρ corresponding to the maxima found in S, V_L, V, and H_L, in the region of 300°.

It is of interest that the value of ρ for the 680° sample, *viz.* 2·8—2·86, is not far from the standard value for anhydrite (2·92), and the fall in ρ in Fig. 2*a* as temperature increases from 200° to 680° is not incompatible with the view put forward in Part III that over this range the content of anhydrite is growing at the expense of the content of dehydrated hemihydrate. The presence of the flat portion of the graphs II and III of Fig. 2*a* taken together with the data for methyl alcohol in Fig. 2*b*, suggest that the detailed interpretation is likely to be a complex one, however.

This work was carried out at University College, Exeter.

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[*Received, June 6th*, **1951**.]