647. *The Dehydration of Gypsum. Part III.* A Study of the Process of Dehydration and Rehydration of Gypsum by Adsorption Methods.*

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Samples of gypsum have been dehydrated at a succession of temperatures between 110° and 700°, and the surface area of the product has been estimated by carbon tetrachloride adsorption, both before and after the determination on it of the adsorption isotherm of water vapour at 25°. The surface area is, in general, diminished by the water treatment. In two cases a series of isotherms of carbon tetrachloride and of water vapour were alternately measured, and it was found that treatment by water did not diminish the uptake of *water* in a second run.

Taken together, the results suggest that the maxima at *ca.* 180—190° and at *ca.* 300° in the curve of surface area against temperature, referred to in Part I (Fig. 2), originate in the reactions: gypsum $\longrightarrow$ hemihydrate + water and hemihydrate $\longrightarrow$ anhydrite + water respectively.

As shown in Part II,* the adsorption of carbon tetrachloride can be used to measure the relative (and perhaps absolute) surface area of the dehydration product of gypsum obtained at different temperatures. In the present paper, an experimental study is described in which this adsorption is used to throw light on the chemical and physical changes which occur when gypsum is dehydrated and rehydrated.

EXPERIMENTAL.

Materials.—The gypsum was part of the batch described in Part I; the carbon tetrachloride was purified as described in Part II. The water was ordinary distilled water and had been freed from air by distillation *in vacuo* whilst in the storage section of the apparatus.

Procedure.—The apparatus was that described in Part II, with the addition of a storage system for water and a mercury cut-off for the controlled admission of the water vapour to the sorption balance.

3—4 g. of the dehydrated gypsum (prepared on the thermal balance as described in Part I) were weighed into the platinum bucket of the sorption balance, and an asbestos plug was inserted above the solid to prevent loss by spurting. The outer limb of the balance was placed in position, and the joint waxed over in the manner described in Part II; the sample was then outgassed at a definite temperature (usually between 80° and 90°) till no further loss in weight was registered on the recording drum. The connection to the pump was then closed, and the heating oven replaced by a water-bath kept at 25° ± 0·05°. Admission of vapour began after an hour or so had been allowed for thermal equilibration.

A number of isotherms were determined consecutively on each sample. The general plan was to use carbon tetrachloride adsorption and to follow the change in area produced by water adsorption and desorption on a sample prepared at a given temperature of preparation. The experiments fell into two main groups: in Group *A*, which included most of the samples, three isotherms only were determined on a given sample, *viz.*, carbon tetrachloride followed by water vapour, then again by carbon tetrachloride. In Group *B* a more detailed study with certain individual and typical samples was made, the general idea again being to use carbon tetrachloride isotherms to measure the effect of controlled water treatment, on the area of the sample.

Results.—The carbon tetrachloride isotherms have the general characteristics already described in Part II; equilibration was rapid, the carbon tetrachloride could be completely pumped off at 25°, and all the indications pointed to purely physical adsorption.

With water vapour the isotherm shows quite different characteristics. The curve rises steeply at first, running almost parallel to the adsorption axis, the corresponding pressure being almost too small to be measured accurately (cf. *AB* in Fig. 1). After this initial portion *AB*, the curve bends round sharply, becoming concave to the pressure axis, and gives relatively small increases in adsorption over the pressure range *ca.* $0·1 < p/p_0 < 0·8$; it finally becomes steep again as p/p_0 approaches unity. Except at the higher pressures (where several hours were required) equilibrium was reached within 30 minutes and usually within 5—10 minutes; at pressures above $p/p_0 = 0·8$ it was difficult to reproduce points exactly, presumably owing to slow equilibration. The desorption branch shows peculiar features: usually the isotherm is nearly flat at first, it then falls very steeply, and finally there is another nearly flat portion, the whole giving a stepwise appearance. A second sharp fall occurs at low pressures. Equilibrium at all points on the desorption curve was reached in *ca.* 20 minutes.

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* Part II, *J.*, 1951, 2378.

A portion of the water could not be removed by pumping at 25° even for 12 hours. The amount thus retained (point *D*, Fig. 1) varied from one sample to another according to the temperature of preparation, and always exceeded the uptake at point *B* on the adsorption branch. This " retained " water could be entirely removed by pumping for a few minutes with the sample heated to 85°.

The experiments of Group *A* will be described first. On each sample there was determined first a carbon tetrachloride isotherm [CCl_4(i)]; the sample was then outgassed at 25°, whereupon the carbon tetrachloride was completely and quickly removed; a water isotherm was then determined [H_2O(i)], and the water was removed by outgassing first at 25° and then at 85°; and finally a second carbon tetrachloride isotherm was determined [CCl_4(ii)]. The water isotherms are shown in Fig. 2; typical carbon tetrachloride isotherms have been given in Part II.

FIG. 1.

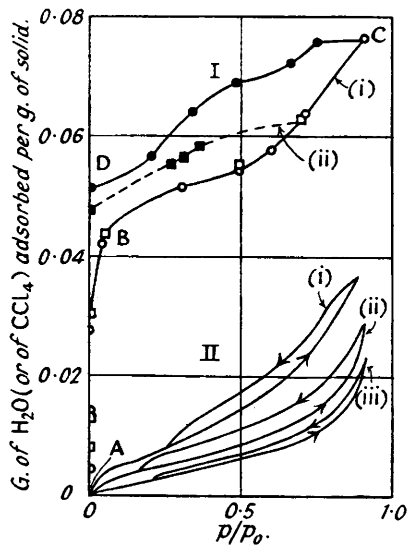

FIG. 2.

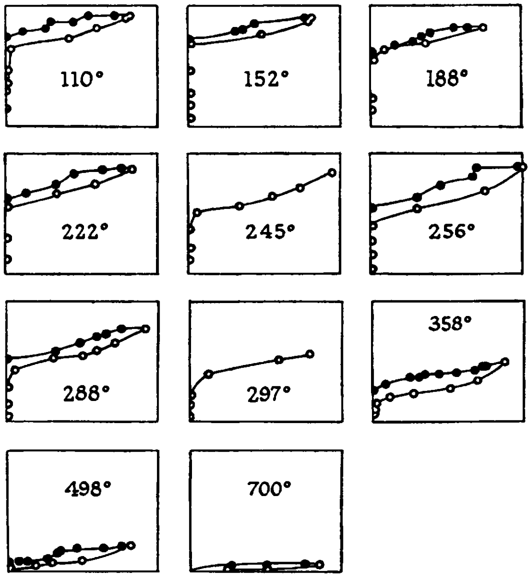

FIG. 1.

Adsorption isotherms of water vapour at 25° *and of carbon tetrachloride at* 25° *on gypsum dehydrated at* 288° (*Expt. B*, 1) : I, H_2O; II, CCl_4.

The isotherms were determined in the order : CCl_4(i); H_2O(i); CCl_4(ii); H_2O(ii); CCl_4(iii).

○, H_2O(i) *adsorption*; ●, H_2O(i) *desorption*. □, H_2O(ii) *adsorption*; ■, H_2O(ii) *desorption*.

FIG. 2.

Adsorption isotherms at 25° *of water vapour on gypsum dehydrated at a series of temperatures* (T). *The value of* T° *is marked on each graph.*

Ordinates : Adsorption, in g. per g. Abscissæ : Relative pressure.

The length of the vertical sides of each rectangle corresponds to 0·01 *g. of water vapour per g. of dehydrated gypsum, and the length of the horizontal sides to a relative pressure of* 1·0 (p/p_0) (p = *equilibrium pressure*, p_0 = *saturated vapour pressure, of water vapour*).

○ *Adsorption.* ● *Desorption.*

On all samples (except those prepared at 500° and upwards) the second carbon tetrachloride isotherm lay below the first, showing that the water treatment had in some way reduced the surface area, *S*. The ratio of the two areas, S_{i}/S_{ii}, was taken as equal to the ratio of the amount of carbon tetrachloride adsorbed on the first and on the second isotherm respectively, at a relative pressure of 0·5. On plotting this ratio against the temperature of preparation, the curve of Fig. 4 was obtained. Typical water isotherms are plotted on a larger scale in Figs. 1 and 3 (Curves I), along with the corresponding carbon tetrachloride isotherms (Curves II).

The second group of experiments, *B*, was now carried out to try to throw some light on the cause of this decrease in area brought about by water treatment.

Experiment B, 1. The sample was prepared by heating gypsum for 75 minutes at 288°. The following isotherms were determined in succession : CCl_4(i)–outgas at 25°–H_2O(i)–outgas at 25°, then 85°–CCl_4(ii)–outgas at 25°–H_2O(ii)–outgas at 25°–CCl_4(iii)–outgas at 25° then 85°. The results are given in Fig. 1. The first three runs correspond to those of Group *A*; and CCl_4(ii) lies, as expected, below CCl_4(i). The second water isotherm [H_2O(ii)] was carried up to a water content only slightly exceeding that retained at point *D* of the first run [H_2O(i)]. The solid was now outgassed at 25° so that the retained water was not removed, and a carbon tetrachloride isotherm [CCl_4(iii)] was immediately determined. As will be seen, this last isotherm runs below both CCl_4(i) and CCl_4(ii), showing that the water treatment has still further reduced the surface area. The "retained" water was removable, in the usual way, by pumping at 85°.

Experiment B, 2. The sample was prepared by heating gypsum for 2 hours at 256°. The following isotherms were determined: CCl_4(i)–outgas at 25°–H_2O(i*a*), to point *F*–outgas at 25°–CCl_4(ii)–outgas at 25°–H_2O(i*b*) from *F* onwards–outgas at 25°–CCl_4(iii)–outgas at 25° then 85°–CCl_4(iv)–outgas at 25°–H_2O(ii).

FIG. 3.

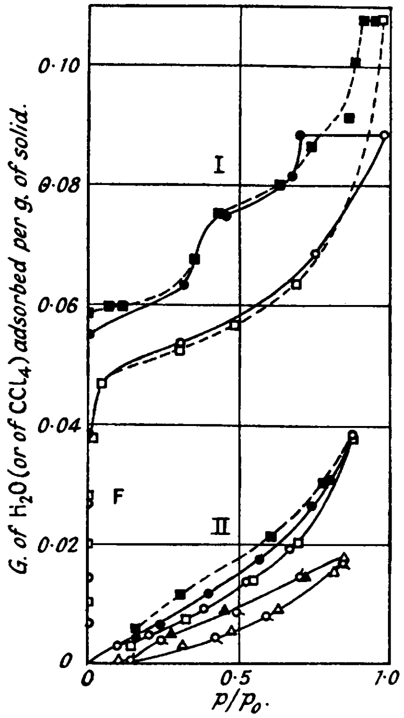

FIG. 4.

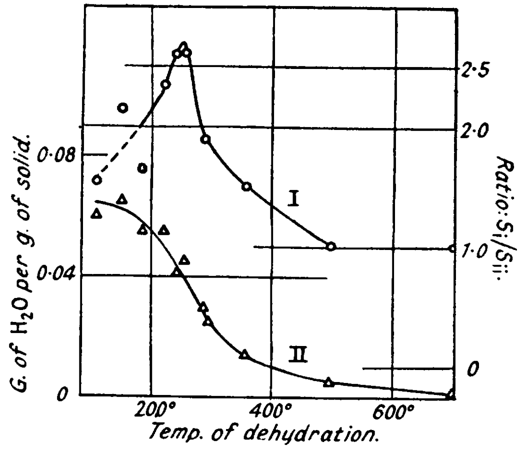

FIG. 3.

Adsorption isotherms of water vapour at 25° *and of carbon tetrachloride at* 25° *on gypsum dehydrated at* 256° (*Expt. B,* 2).

The isotherms were determined in the order: CCl_4(i); H_2O(ia) *to point* F; CCl_4(ii); H_2O(ib) *from* F *onwards*; CCl_4(iii); CCl_4(iv); H_2O(ii).

○, ● H_2O(i); □, ■ H_2O(ii); ○, ○, ●, ● CCl_4(iii); △, ▲ CCl_4(iv).
○, ● CCl_4(i); □, ■ CCl_4(ii);

FIG. 4.

Curves for properties of gypsum dehydrated at a series of temperatures.

I. *The ratio* S_i/S_{ii} (S_i = *surface area before,* S_{ii} = *surface area after, exposure to water vapour*). *Use right-hand ordinates.*

II. *The amount,* x_{AB}, *of water adsorbed up to a point corresponding to point* B *of Fig.* 1. *Use left-hand ordinates.*

The results are given in Fig. 3. The first carbon tetrachloride isotherm [CCl_4(i)] was of the usual type In the first water isotherm the measurements were taken up only to point *F* on the initial steep portion *AB*; on outgassing at 25°, *no* water was lost, strongly suggesting that it is held by chemisorption or by chemical combination. Continuing from *F*, the carbon tetrachloride isotherm [CCl_4(ii)] obtained had an adsorption branch which coincided within experimental limits with that of CCl_4(i). [The *desorption* branch differed from CCl_4(i) for a reason which is not apparent.] It seems then that the water present has no effect on the magnitude or the nature of the surface area of the solid; this means that the water cannot be adsorbed on the surface of the solid, for the carbon tetrachloride would then either have to compete with it for room, or else would be adsorbed on top of the water layer; in either of these cases the carbon tetrachloride isotherm would be modified. One infers therefore that the water has entered the bulk of the solid, presumably by chemical combination, and has left the surface unchanged.

After completion of the carbon tetrachloride run and outgassing at 25°, point *F* was again reached; the water isotherm was continued [H_2O(*ib*)] and it was of the usual type. On the conclusion of the water run, the sample was outgassed at 25° so as not to remove the " retained " water; the ensuing carbon tetrachloride isotherm [CCl_4(iii)] was lower than both CCl_4(i) and CCl_4(ii), showing that the water treatment, when carried beyond *F*, *had* diminished the surface area. At the conclusion of this isotherm the sample was evacuated at 25° to get rid of all the carbon tetrachloride, and then at 85° to remove retained water. A carbon tetrachloride isotherm determined immediately afterwards [CCl_4(iv)] was identical with CCl_4(iii). Thus the diminution in area, brought about by water treatment beyond *F*, is not affected by the presence or absence of " retained " water. The shape of *BC* is similar to that of a Type II isotherm; but the shape of *CD* and the decrease obtained in *S* suggest that something other than mere physical adsorption of water vapour has occurred along *BCD*.

The final water isotherm [H_2O(ii)] now determined agreed fairly closely with the first water isotherm. The first water treatment, then, did not bring about a significant modification of the solid with regard to its subsequent powers of adsorbing water.

Experiment B, 3. The sample was prepared by heating gypsum at 700° for 1 hour. The following four isotherms were determined in succession: CCl_4(i)–outgas at 25°–H_2O(i)–outgas at 25°–CCl_4(ii)–outgas at 25°, then 85°–CCl_4(iii). The first two isotherms were of the usual shape, though the adsorption was in each case small, consistently with a highly calcined sample. There was a small, but not negligible, retention of water on outgassing at 25° after H_2O(i). The carbon tetrachloride isotherm determined with the water present [CCl_4(ii)] and the one obtained after its removal [CCl_4(iii)] agreed closely, confirming that retained water does not significantly alter the surface area of the sample.

DISCUSSION.

From an examination of the experimental data obtained in the course of the present research (Parts I—IV) it is concluded that *within the range of temperature studied*, viz., 100—700°, *and under the conditions of preparation already described* (*i.e.*, dehydration " in air " on the thermal balance), the only lattices to be considered are: (*a*) The *gypsum* lattice (cf. Wells, " Structural Inorganic Chemistry," 1945, 370). (*b*) The *hemihydrate* lattice: this has a zeolitic type of structure such that water molecules can enter and leave it without destroying the lattice (cf. Caspari, *Proc. Roy. Soc.*, 1936, *A*, **155**, 41; Feitknecht, *Helv. Chim. Acta*, 1931, **14**, 89); according to Bunn (*J. Sci. Instr.*, 1941, **18**, 70), this zeolite structure is able to persist up to a water content corresponding to $CaSO_4,0{\cdot}67H_2O$. (*c*) The *anhydrite* lattice—an ionic lattice (Caspari, *loc. cit.*).

It is now postulated that a sample obtained by thermal dehydration of gypsum at a given temperature consists of a mixture of lattices (*b*) and (*c*). The proportion of (*c*) increases as the temperature of preparation increases, but even at 500—600° there is still some of (*b*) left. This has also been inferred by Newman and Wells from *X*-ray data (*J. Res. Nat. Bur. Stand.*, 1938, **20**, 825). Since within the range of temperature considered all samples are completely dehydrated, the (*b*) content will represent hemihydrate completely denuded of its water.

An attempt will now be made to justify the hypothesis by reference to the experimental facts adduced in the present paper.

We deal first with the initial steep portion (*AB*): it has been seen that water cannot be present on the surface, and that it must have entered the bulk solid without affecting its area. This is reasonably explained by supposing that along *AB* the hemihydrate is taking up its zeolitic water. The amount of this water gradually falls as the temperature of preparation is increased (Fig. 4, Curve II). On proceeding with the isotherm beyond point *B*, the following characteristics are noted: (i) the adsorption branch *BC* resembles an ordinary B.E.T. Type II isotherm (Brunauer, Deming, Deming, and Teller, *J. Amer. Chem. Soc.*, 1940, **62**, 1723); (ii) the desorption branch is more or less step-like; (iii) some of the water is " retained " at the conclusion of the desorption branch and can only be removed at 80—90°; (iv) the surface area is decreased after adsorption and consequent desorption of water beyond point *B*.

Fact (i) indicates that the primary process occurring along *BC* is physical adsorption. To account for fact (iii) one postulates that a secondary chemical process occurs at the same time as (and more slowly than) the physical adsorption; this is supported by the step-like form of the desorption branch *CD* [fact (ii)]. Furthermore, this chemical change must be such as to decrease the internal area of the sample [fact (iv)], yet it is unable to exert any effect on the process occurring along *AB*, already referred to. The most likely explanation seems to be this: the hemihydrate formed along *AB* physically adsorbs some water [fact (i)], which then in part combines to form dihydrate [fact (ii)]. The formation of dihydrate at crystallite boundaries could cement neighbouring crystallites together in such a way as to seal off portions of the surface of the crystallites so that carbon tetrachloride molecules could no longer reach them. On desorption the cementing effect would remain, but the lattice channels through which *water* molecules are able to enter and leave would be unaffected.

The first, very sharp step on the desorption branch may originate in the dissociation $CaSO_4,2H_2O \rightleftarrows CaSO_4,\frac{1}{2}H_2O + 1\frac{1}{2}H_2O$, in which equilibrium has not been properly attained (for if it had been attained, the step would be absolutely vertical). The second sharp fall is difficult to explain.

The anhydrite present does not seem to be affected by the water treatment: in a repeat run the height *AB* was not increased, nor was the shape of the branch *BC* noticeably altered. If the anhydrite were to react with water during the water treatment represented by *BCD*, giving hemihydrate or gypsum, then in the repeat run the amount of hemihydrate would be increased and the curve *BCD* correspondingly raised.

It now remains to discuss the way in which the proportions of the different solids vary with the temperature of preparation. For this, reference must be made to the curves of surface area against temperature of preparation, given in Part I (Fig. 2). With nitrogen and with carbon tetrachloride there is a maximum at 180—190°, and a very flat maximum at 280—450°; and with oxygen a similar maximum at 180—190° and a much sharper one at *ca.* 300°. The results of Parts III and IV suggest that the first maximum corresponds to the phase change involved in the reaction gypsum ⟶ hemihydrate + water. The second, very flat, maximum is believed to originate in the reaction hemihydrate ⟶ anhydrite + water, together with the sintering of the anhydrite formed. As judged from Fig. 4, some hemihydrate persists up to *ca.* 500°. From 500° to 700°, sintering of the anhydrite predominates.

The variation of the heights x_{AB} and x_{AD} with the temperature of calcination may now be re-examined. The former quantity is plotted against temperature in Fig. 4. Between 100° and 230°, x_{AB} is fairly close to the value required for the composition of the hemihydrate, $CaSO_4,\frac{1}{2}H_2O$. This supports the view already put forward that over the temperature range of 100—230° the product of dehydration consists almost entirely of the hemihydrate denuded of its water. The fall in x_{AB} setting in at about 230° denotes a decreasing proportion of hemihydrate, and with it a corresponding increase in the proportion of anhydrite. The data for the change in surface area brought about by water treatment, also plotted in Fig. 4 (Curve I), are in substantial agreement with this interpretation. Below 230° the curve is irregular, but above it there is close correlation between the curve showing the ratio S_i/S_{ii} and the curve for x_{AB} (Curve II, cf. also Part IV, Fig. 3). This is to be expected from the postulate that the anhydrite is inert and that it is only the (dehydrated) hemihydrate that reacts with water. (The iregularity below 230° is probably due to the fact that the water isotherms were taken up to various pressures and for various times; thus the extent of the cementing process would vary from experiment to experiment, so that successive experiments are not strictly comparable in this regard; this effect would, of course, diminish as the content of the hemihydrate decreased.)

The fact that *D* lies above *B* suggests that the entry of water into the lattice, although rapid at first, becomes slower as the process nears completion, *i.e.*, whilst the branch *BCD* is being traced out. This deceleration would come about if, for example, there were parts nearly sealed off by anhydrite, so that penetration there would be slow.

The work was carried out at University College, Exeter.

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