525. *The Dehydration of Gypsum. Part I. A Study of the Thermal Decomposition of Gypsum by the Adsorption of Oxygen and of Nitrogen at* −183°.

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The surface area S (m.^{2} g.$^{-1}$) of gypsum dehydrated at a succession of temperatures between 100° and 700° has been determined by adsorption of nitrogen and of oxygen. There are maxima for S at *ca.* 180° and *ca.* 280°. In the region *ca.* 150° to *ca.* 350° the area calculated from oxygen adsorption is significantly greater than that calculated from nitrogen adsorption—probably owing to the presence of channels large enough to admit oxygen, but too small to admit nitrogen, molecules. Above 400° the " oxygen " and the " nitrogen " areas agree closely.

MORE than a thousand papers have been published on calcium sulphate and its hydrates during the past 50 years : very varied results have been obtained and there is much disagreement as to their interpretation. Since the products of dehydration of the dihydrate are " active " solids, possessing a considerable surface area, it was decided to apply to this problem some of the methods used in investigating such solids. The methods selected in the present study include the measurement of the following : adsorption of vapours (carbon tetrachloride at 25°, nitrogen and oxygen at −183°, water vapour at 25°); heat of immersion in an inert liquid (carbon tetrachloride); specific gravity in various liquids; bulk density; and heat of hydration.

The general line of approach has been to prepare a " calcination series " from gypsum; a series of samples of gypsum was taken and each sample was heated to a particular temperature (different for each sample) for a definite length of time; and the properties listed in the previous paragraph were then measured on each sample. The range of temperature covered was from 100° to 700°, at close intervals—10° or so—at the lower end, and wider ones—100° or so—at the higher end of the range.

In the present paper the adsorption of nitrogen and of oxygen on the samples is reported.

EXPERIMENTAL.

Materials.—The gypsum was part of a large lump of transparent gypsum (often called selenite) purchased from Messrs. George and Becker. It was analysed, with the following results (theoretical values for $CaSO_4,2H_2O$ given in parentheses) : CaO, 32·56 (32·58); MgO, 0·1; Fe_2O_3, Al_2O_3, SiO_2, absent; SO_3, 45·90 (46·50); CO_2, 0·44; moisture, 0·01; total water, 20·60% (20·93%). The lump was broken up, then ground in a mortar, and finally sieved through I.M.M. sieves so as to obtain a number of definite fractions. In some experiments 40—80-mesh, and in others 80—100-mesh, fractions were used.

The nitrogen and oxygen were obtained from commercial cylinders and were dried by passing through drying tubes containing activated alumina and phosphoric oxide. Before being filled, the storage vessels and drying tubes were thoroughly evacuated and then flushed out several times with dry gas. The oxygen is reported to be 99·4—99·7% pure, the chief impurity being argon, and the nitrogen to be *ca.* 99·9% pure, the chief impurity being oxygen (British Oxygen Co., personal communication).

Procedure.—The volumetric apparatus used for the determination of the adsorption isotherms of oxygen and nitrogen is identical with that already described by Gregg and Sing (*J. Phys. Colloid Chem.*, 1951, **55**, 592) with the addition of an oxygen vapour-pressure thermometer. The whole apparatus was enclosed in a constant-temperature chamber kept at 25—25·5°, to within 0·1°. The saturated vapour pressure was read every time an equilibrium point on the isotherm was determined, and it was found to vary by ±1·5 cm. from time to time, corresponding to a temperature variation of only ±0·2°. The vapour-pressure thermometer showed that the temperature of the bath was, in general, 0·2—0·3° higher than the b.p., owing to superheating.

A sample of dehydrated gypsum, 5—6 g., was first prepared by heating the selenite on a thermal balance : this is essentially a crucible hung from the arm of an analytical balance into a furnace maintained at a fixed temperature (for list of references, see Gregg and Winsor, *Analyst*, 1945, **70**, 336). The change in weight on progressive dehydration could thus be followed easily. For samples prepared at temperatures below 300° the heating was continued till the dehydration (to $CaSO_4$) was just complete. At temperatures above this, one hour was used as a standard time; above 300° the time required for decomposition was less than one hour, and became increasingly short as the temperature rose; it would therefore have been difficult at the higher temperatures to arrest the heating when decomposition was

just complete, and it was accordingly deemed more satisfactory to standardise the period of one hour. (Tests, described later, were done to correlate conditions below and above 300° : samples were prepared at 320° and at 404° by heating for different lengths of time between 30 minutes and 24 hours.)

As soon as possible after preparation, the sample was weighed, with the minimum exposure to air, into the adsorbent bulb. The bulb was then attached to the volumetric apparatus by its ground-glass joint, a heating unit maintained at 85—90° was placed around it, and the sample was out-gassed (by means of a mercury condensation pump, backed by a " Speedivac ") for 2—2½ hours. The heater was then removed, and replaced by a liquid-oxygen bath, the level of the oxygen being kept at a fixed mark.

Fig. 1.

Typical adsorption isotherms of nitrogen at − 183° on gypsum dehydrated at different temperatures T. *Curve I,* T = 190° ; *Curve II,* T = 287° ; *Curve III,* T = 655°.
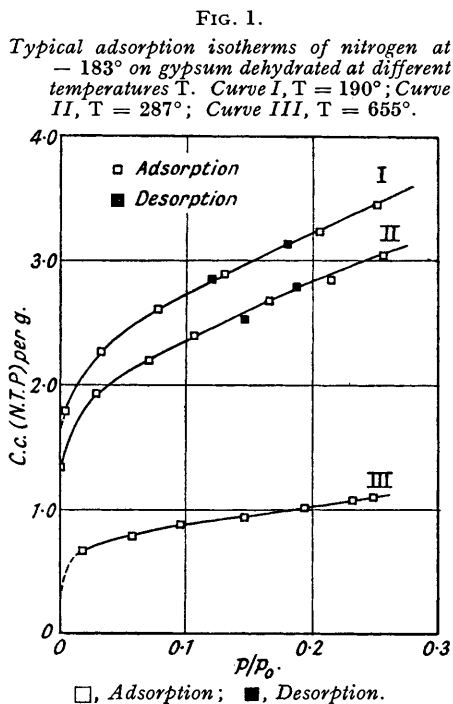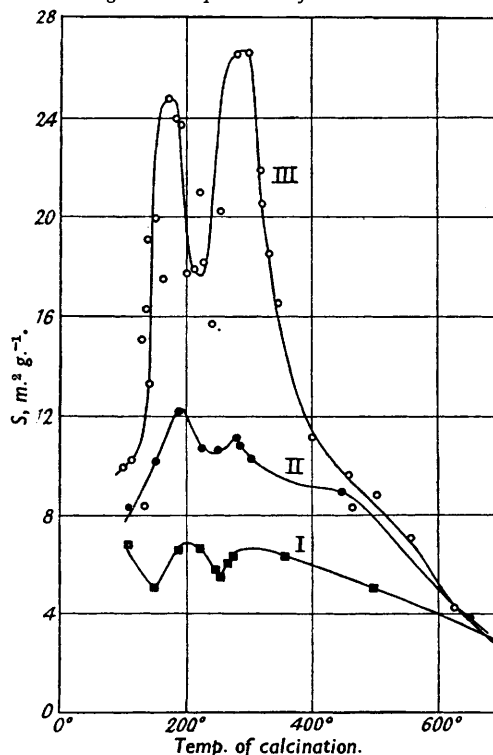

□, Adsorption ; ■, Desorption.

Fig. 2.

Graph of surface area S *of dehydrated gypsum against temperature of calcination.*

(S *was calculated from adsorption isotherms of carbon tetrachloride for Cuve* I, *of nitrogen for Curve* II, *and of oxygen for Curve* III.)

Results.—Nitrogen isotherms. Because of the high value of the saturated vapour pressure of nitrogen at 90·5° K., the highest relative pressure that could be attained with this gas was *ca.* 0·25. Consequently, no complete isotherms were obtainable. The time required for equilibration was less than 15 minutes ; and the isotherms were *reversible, i.e.,* points obtained by withdrawing gas fell on the same curve as those obtained when gas was being added.

Typical isotherms are given in Fig. 1. Because of the restricted range, it is not possible to decide, from a mere inspection of the isotherms themselves, to what type they belong (cf. Brunauer, Deming, Deming, and Teller, *J. Amer. Chem. Soc.,* 1940, **62,** 1723). However, comparison with the two oxygen isotherms, which were carried up to higher relative pressures, leaves little doubt that they are of Type II.

Oxygen isotherms. With two of the samples the measurements were carried up to high relative pressures. The isotherms appeared to be quite definitely of Type II, but presented certain unusual features. The first experiment was carried out on a sample of 40—80 mesh heated for 6 hours at 144°, and the isotherm is shown in Fig. 3 (Curve II). Points 1—4 were determined on the first day ; the time required for equilibration was 1—1½ hours. Overnight some more adsorbate was taken up with a slight reduction in pressure (point 4*a*). On continuation of the admission, points 4*a*—11 fell on a smooth curve. When the system was again left overnight another drift was observed (point 11*a*). The curve was continued on the third day to a relative pressure of 0·98, whereupon withdrawal of gas was begun. As will be seen, a hysteresis loop was obtained, and it did not close even at the lowest pressure reached. It is particularly noteworthy that the small overnight drift (between points 17 and

FIG. 3.

*Adsorption isotherm of oxygen at −183° on gypsum (40—80 mesh) dehydrated for 6 hours at 144°.*
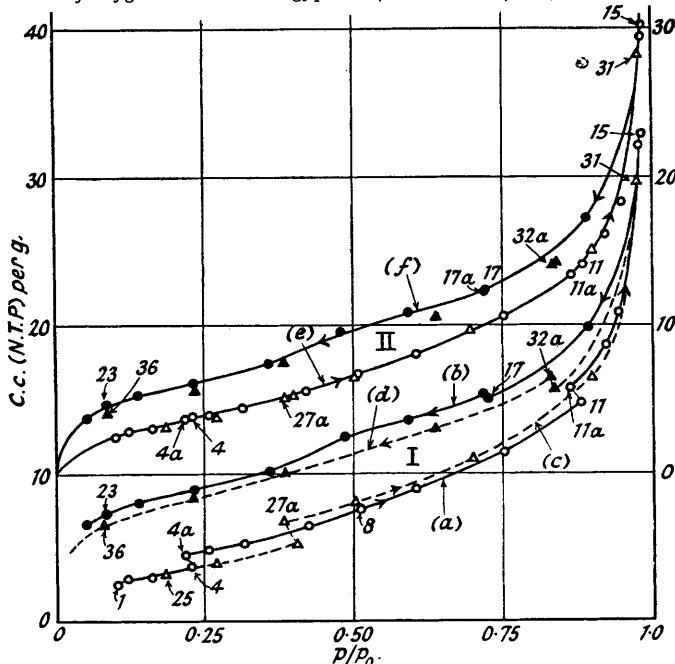
p = equil. pressure of oxygen, p_0 = satd. vapour pressure at −183°. *(The ordinates of isotherm II have all been increased by 10 c.c. g.$^{-1}$.) The experimental points were numbered in the order in which they were determined. The numbers of the points commencing from the origin in each case are : Curve I*a : 1, 2, 3, 4, 4a, 5, 6, 7, 8, 9, 10, 11, 11a, 12, 13, 14, 15; *Curve I*b : 24, 23, 22, 21, 20, 19, 18, 17a, 17, 16; *Curve I*c : 25, 26, 27, 27a, 28, 29, 30, 31; *Curve I*d : 36, 35, 34, 33, 32a, 32, 31; *Curve II*e : 1, 2, 3, 25, 4a, 4, 5, 26, 6, 27a, 27, 7, 28, 8, 9, 29, 10, 11a, 11, 3a, 12, 13, 31, 14, 15; *Curve II*f : 24, 23, 36, 32, 21, 35, 20, 34, 19, 18, 33, 17a, 17, 16.

○ △, *Adsorption* ; ● ▲, *Desorption.*

FIG. 4.

Adsorption isotherm of oxygen at − 183° on gypsum (20—30 mesh) dehydrated for 1 hour at 465°.
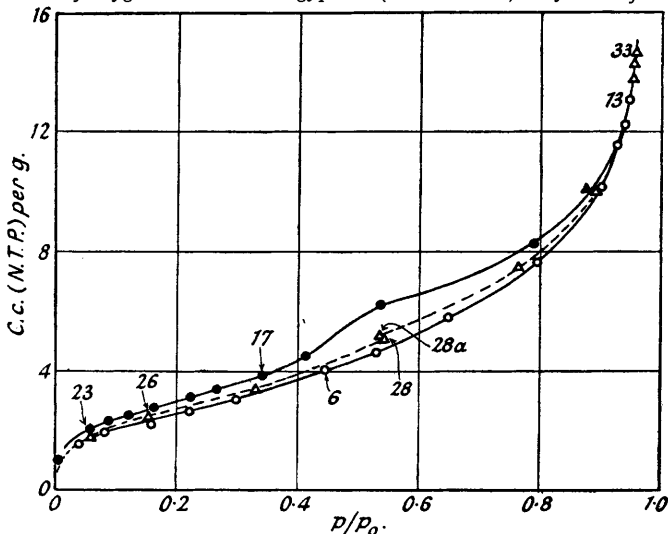
The experimental points were numbered in the order in which they were determined. The numbers of the points, commencing from the origin in each case are : ○, 1—13; ●, 24—14; △, 25—33; ▲, 34.

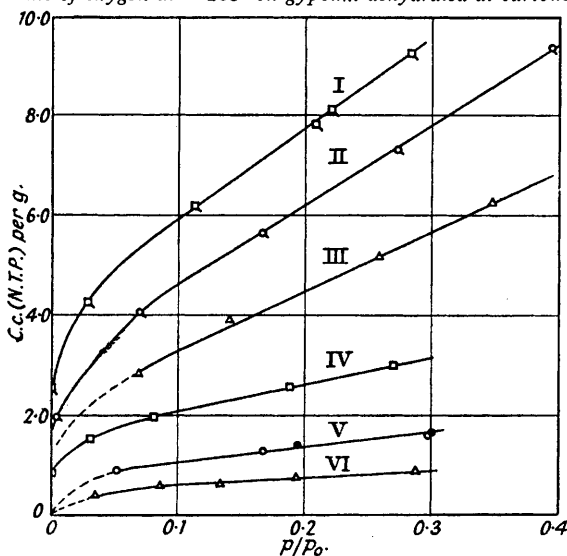○ △, *Adsorption* ; ● ▲, *Desorption.*

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17a) led to an *increase* in the amount adsorbed; this is opposite to the behaviour normally encountered in adsorption work, where the amount adsorbed *decreases* if the system is left overnight at any point on the desorption branch.

If the overnight drifts are subtracted from all subsequent adsorption and desorption points, the smooth isotherm (Fig. 3, Curve II) is obtained. A second experiment showed that the *adsorption* branch could be reproduced, but not the desorption branch (see points 25—36).

The second isotherm was measured on a sample prepared by heating 20—30-mesh gypsum at 465° for one hour. The whole isotherm was determined in one run, so as to avoid overnight drifts. The appearance of the isotherm (Fig. 4) suggests that a slow drift was, nevertheless, present the whole of the time; and that, although in the interval between successive points the drift was too small to affect the smoothness of the curve, yet the cumulative effect prevented the loop from closing near point 16. The near-parallelism of the curves between points 2—6 and 17—23, and the shape of the hysteresis loop, lend some support to the suggestion. The difference in the adsorption values at any given pressure, between the two nearly parallel portions of the curves (2—6 and 17—23), would then give a measure of the drift.

FIG. 5.

Adsorption isotherms of oxygen at −183° *on gypsum dehydrated at various temperatures* T.

I, T = 299°; *II*, T = 254°; *III*, T = 345°; *IV*, T = 505°; *V*, T = 630°; *VI*, T = 700°.

△, ○, □, ◖, ◗, Adsorption; ●, Desorption.

A second experiment was done on the same sample, but the system was now left overnight after point 28 (Fig. 4). The uptake increased, giving point 28a. On allowance being made for this drift as before, the subsequent adsorption points fitted the curve of the first run extremely well. (The desorption curve had to be abandoned at point 34, owing to an accident.)

In view of the large amount of labour involved, the main set of isotherms (36 in number) was not taken beyond a partial pressure of *ca.* 0·35, so that the measurements were confined to the range where the B.E.T. equation is known to hold for Type II isotherms. Some typical results are shown in Fig. 5. With samples prepared below 500° some hysteresis was always obtained; but with samples prepared above 500° the curves were quite reversible, and no overnight drifts were noted.

With samples prepared below *ca.* 250°, equilibration frequently required some 2—3 hours; but the change in adsorption after the first hour was so small that the difference in the surface area obtained by taking the reading after 1 hour, instead of after 2—3 hours, was inappreciable. Accordingly, one hour was fixed as the arbitrary time for each point. (With samples prepared at 500° and above, equilibrium was reached in *ca.* 15 minutes.)

Estimation of the Surface Area S.—Since the isotherms both of oxygen and of nitrogen may be taken as Type II, it is possible to estimate the surface area of the solid by means of the B.E.T. procedure (Brunauer, Emmett, and Teller, *J. Amer. Chem. Soc.*, 1938, **60**, 309). Accordingly, the quantity $p/v(p_0 - p)$ was plotted against p/p_0, and good straight lines were obtained over the range $0·05 < p/p_0 < 0·30$ for oxygen, and $0·05 < p/p_0 < 0·25$ for nitrogen. From the intercept $1/v_m c$ and the slope $(c - 1)/v_m c$, values for v_m and c were obtained (v = volume of oxygen or of nitrogen adsorbed at pressure p, reduced to N.T.P.; v_m = volume required to fill a completed monolayer on the solid; c is a constant of the B.E.T. equation given by $c = e^{(E_1 - \lambda)/RT}$, where E_1 is the heat of adsorption in the first molecular layer, λ is the latent heat of condensation, and R and T have their usual meanings. To calculate S

from v_m, a value had to be assumed for the cross-sectional area A_0 of the molecules of the adsorbate; the figures here taken were $A_0 = 14\cdot1$ A.² for oxygen, and $A_0 = 17\cdot0$ A.² for nitrogen (cf. Emmett and Brunauer, *J. Amer. Chem. Soc.*, 1937, **59**, 1553).

In Fig. 2 the area S is plotted against the temperature of preparation (Curve II for nitrogen, Curve III for oxygen). As will be seen, the areas from the nitrogen are much smaller than those from the oxygen data over the range 150—350°, whereas from 400° upwards there is close agreement. The oxygen curves show pronounced maxima in the regions of 180° and 280°; maxima occur in the nitrogen curves also at about the same temperatures, but they are much less pronounced.

The effect on S of varying the time of heating was studied at two temperatures by reference to the oxygen isotherms. At 404° the effect is small : samples prepared by heating for ½ hour, 1 hour, and 24 hours had surface areas of 11·1, 11·2, and 10·2 m.² g.⁻¹, respectively. At 320° the effect was more marked, successive experiments with times of 1 hour, 1 hour, ¾ hour, ¾ hour, and 24 hours giving areas of 20·5, 21·8, 13·7, 17·2, and 13·8 m.² g.⁻¹, respectively. Reference to Curve III of Fig. 2 will show that 320° is on a steeply falling branch of the curve of temperature against area, where one would expect an unusually marked dependence of area on the conditions of preparation, including the time of heating. One is justified in concluding that the general shape of the curves of Fig. 2 would not be significantly different had one been able to prepare all the samples, at temperatures above as well as below 300°, by heating " just to decomposition."

Discussion.—According to a principle due to Hedvall (*Chem. Review*, 1934, **15**, 139), a solid is brought into a more active condition by the occurrence of a phase change, which loosens the lattice (" Auflockerung "). An " active " solid is one which dissolves in solvents, or reacts more rapidly than the corresponding solid in its ordinary condition. The activity may be due to lattice strain, or to the presence of a large area, or to both.

In systems such as the present one, the phase change which brings about activation is a thermal decomposition. Acting in the opposite sense is the process of *sintering*; understood in its broadest sense, this term implies any process whereby the sample of solid tends towards a state with no strain and with a minimal surface area. The process is most probably complex, and comprises a number of distinct mechanisms; but in general it will be accelerated by a rise in temperature. Hence, as soon as a larger area is produced by thermal decomposition, it will begin to diminish because of sintering. Since the two processes—activation and sintering— will in general have different characteristics and different temperature coefficients, the occurrence of a maximum in S at a particular temperature is understood.

Evidence is presented in later parts of this series that the phase change responsible for the first maximum at 180° is Gypsum $\longrightarrow$ Hemihydrate + Water, and for the second Hemi-hydrate $\longrightarrow$ Anhydrite + Water.

The difference in the values of S obtained by oxygen and by nitrogen adsorption respectively is believed to originate in the sizes of the channels which are formed during the dehydration; since the oxygen molecule is smaller ($A_0 = 14\cdot1$ A.²) it can penetrate into pores from which the nitrogen molecule ($A_0 = 17\cdot0$ A.²) is excluded. This view is consistent with (*a*) the longer time for equilibration with oxygen, and (*b*) the peculiar hysteresis in which, it will be recalled, the amount adsorbed *increased* if the system was left overnight even on the *desorption* branch. If this explanation is correct, it will be inferred from Curves II and III of Fig. 2 that the area of the walls of these finer pores is very considerable, being of the same order as the area accessible to the nitrogen molecules only. The results with carbon tetrachloride as adsorbate, reported in Part II, are in conformity with this explanation.

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