526. *The Dehydration of Gypsum. Part II.* A Study of the Thermal Dehydration of Gypsum by Means of the Adsorption of Carbon Tetrachloride Vapour at 25°.*

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The adsorption of carbon tetrachloride vapour has been measured at 25° on samples of gypsum dehydrated at a succession of temperatures between 100° and 700°. The adsorption isotherms are of B.E.T. Type II with a small value of the parameter c, so the surface area S cannot be determined by application of the B.E.T. procedure. Since, however, all the isotherms can be superposed by adjustment of the scale of the adsorption ordinates, the *relative* values of S can be obtained from adsorption at a given pressure. The curve of S against temperature of preparation resembles those obtained in Part I, from oxygen and nitrogen adsorption, with its maxima now at *ca.* 200° and 300—350°.

In Part I,* the products of the thermal decomposition of gypsum were studied by means of the adsorption of nitrogen and of oxygen. A similar study, by using the adsorption of carbon tetrachloride vapour, is now described.

Experimental.

Materials.—The gypsum was taken from the same lump as that described in Part I. The individual samples were prepared in an exactly similar manner, the range of temperatures being again *ca.* 100—700°, spaced at close intervals at the low-temperature end of the range and at wider ones at the high-temperature end.

The carbon tetrachloride was purified by Fieser's method (" Experiments in Organic Chemistry," 1941, p. 365).

Apparatus.—For the determination of the adsorption, an improved design of the automatically recording sorption balance (Gregg and Wintle, *J. Sci. Instr.*, 1946, **23**, 259) was used. The sample of solid is contained in a bucket, hung in an enclosed space which can be evacuated or can be filled with a known vapour; the change in weight of the solid as it takes up or loses vapour is registered automatically as a function of time, on a revolving drum. The balance case was joined on to a system for the storage of the carbon tetrachloride and its controlled admission to the sorption balance; this system had no taps and the movement of vapour was controlled by suitably raising and lowering mercury levels (cf. Gregg and Sing, *J. Phys. Colloid Chem.*, 1951, **55**, 597). The lubrication of the ground-glass joints on the sorption balance proper was by Dow-Corning High Vacuum Silicone Grease; as an additional precaution the joints were also coated on the outside first with black wax (Edwards's Wax W) and on top of that Everett's No. 1 Hard (m. p. 57°) Vacuum Wax.

Procedure.—The dehydrated gypsum (3—4 g.) was weighed into the bucket of the sorption balance, and an asbestos plug inserted above it to prevent spurting. The outer limb of the balance case was placed in position, and an electric oven maintained at 80—90° put round it. Pumping commenced, and was continued until no further change in weight was recorded on the drum (*ca.* 2 hours). The connection to the pump was then closed by a mercury cut-off and the oven was replaced by a water-bath kept at 25° ± 0·05°. After one hour (for attainment of thermal equilibrium) a charge of carbon tetrachloride was admitted, and the increase in weight registered itself on the recording drum. When the weight had become constant, the pressure p in the dead space was read on a mercury manometer by means of a cathetometer. A series of admissions was made until the pressure reached about 90% of the saturated vapour pressure. Controlled withdrawals were then made in a similar manner, by opening the balance system to the pumps through a mercury cut-off.

Results.—The adsorption isotherms obtained are of B.E.T. Type II, but the initial, steeply rising, portions are so short that they approximate to Type III (Brunauer, Emmett, and Teller, *J. Amer. Chem. Soc.*, 1938, **60**, 309). This implies that the value of the B.E.T. parameter c must be close to unity (cf. Gregg and Jacobs, *Trans. Faraday Soc.*, 1948, **44**, 574); its exact value cannot be determined owing to insufficiency of data at low pressures. (Many points are necessary to determine c when $c \simeq 1$.)

A representative example is given in Fig. 1. The hysteresis loop is typical, and was obtained in all cases except one; it always closed at low pressure. Equilibrium was attained very rapidly, in less than 5 minutes at all points on the adsorption and desorption branches: check readings were sometimes taken by leaving the system for 4 or 5 hours, and in no case was any increase in adsorption registered. This would seem to exclude the possibility of slow penetration into narrow channels, such as might perhaps have been expected. It suggests that any holes left in the solid are either smaller than the diameter of a carbon tetrachloride molecule (*ca.* 5·5 A.) or are considerably larger—*i.e.*, that they are not close to 5 A. in diameter.

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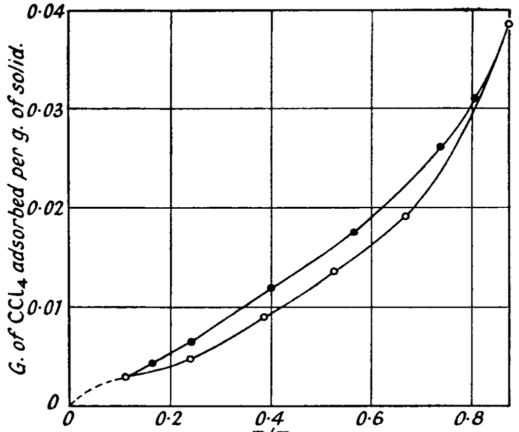
* Part I, preceding paper.

All the carbon tetrachloride could be pumped off at 25° in about an hour, a behaviour characteristic of physical adsorption and showing that chemisorption or penetration into the lattice (*e.g.*, solid solution) is absent. In principle, therefore, the carbon tetrachloride isotherm can be used for the determination of the surface area of the solid.

Calculation of Surface Area S.—It had been hoped that the carbon tetrachloride isotherms would be of B.E.T. Type II with a large value of c (corresponding to a sharp knee at the low-pressure end). It would then have been possible to calculate S with accuracy by the usual B.E.T. procedure; but this procedure is known to fail when $c \bumpeq 1$, as in the present case. However, it fortunately turned out that all the isotherms obtained can be superposed within reasonably close limits, by a mere adjustment of the adsorption ordinates. This implies that the curves are all of the *same shape*. Hence, independently of any particular theory of the isotherm, it is possible to obtain *relative* values of S by taking one of the isotherms as standard, and finding the factor f by which to multiply the ordinates of the others to bring them to coincidence. The point is illustrated by reference to Fig. 2. The factor has there been found by taking the 245° isotherm as standard, and putting $f = 1/x_{0 \cdot 5}$, where $x_{0 \cdot 5}$ is the uptake on any other isotherm when $P = 0{\cdot}5$; the value of the uptake at $P = 0{\cdot}25$ and at $P = 0{\cdot}75$ has then been multiplied by f to get derived adsorptions for each of the other temperatures ($P = p/p_0$, where p_0 = saturated vapour pressure). As will be seen, the points at these last two relative pressures do not diverge by more than $\pm 10\%$ or so compared with the original divergencies of some three-fold.

FIG. 1.

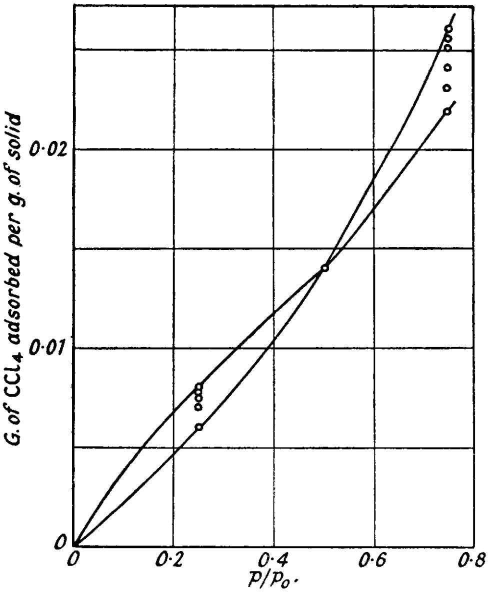
Adsorption isotherm of carbon tetrachloride vapour at 25° on gypsum (80—100 *mesh*) *dehydrated for 2 hours at* 256°.



○ *adsorption*; ● *desorption.*

FIG. 2.

Superposition of the adsorption isotherms of carbon tetrachloride vapour at 25° *on samples of gypsum dehydrated at various temperatures. The isotherms were brought to coincidence at* $p/p_0 = 0{\cdot}5$ *by adjustment of the scale of ordinates.*



At $p/p_0 = 0{\cdot}25$, *the points* (*reading downwards*) *refer to the samples dehydrated at the following temperatures:* 110°, 188°, 222°, *and* 288°; 358°, 297°; 152°, 245°; 498°, 700°; 256°; *and at* $p/p_0 = 0{\cdot}75$, *at the following temperatures*: 152° *and* 245°; 288° *and* 358°; 110°, 188°, 250°, *and* 256°; 700°; 222°; 498°.

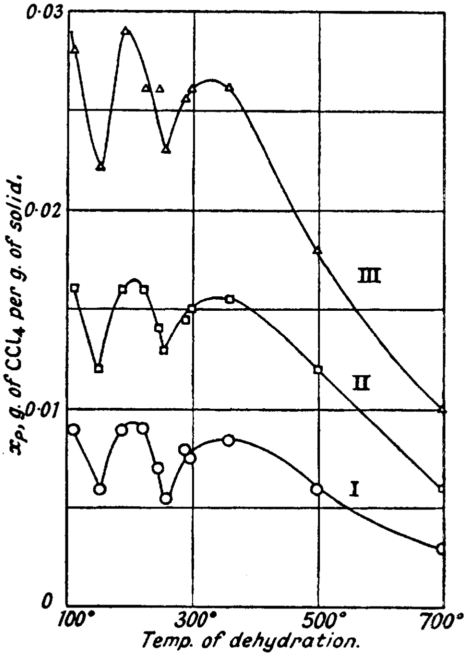
Alternatively expressed, one may take the value of the carbon tetrachloride adsorption, say x_p, of a sample at a given value of P, as proportional to S. In Fig. 3, x_p has been plotted against the temperature of preparation for $P = 0{\cdot}25$, $P = 0{\cdot}5$, and $P = 0{\cdot}75$. The three curves so obtained are of the same shape and they all show maxima at *ca.* 200° and at 300—350°. (The points were not sufficiently close together to give better precision than this).

To obtain absolute values of S from the carbon tetrachloride isotherms it is only necessary to know the absolute area for one sample, and the others can then be calculated thence by comparison of the uptakes at a given pressure, as just explained. The 700° was taken as the reference sample, and the area given by the nitrogen and the oxygen isotherms is assumed correct; this sample has been selected as being the most sintered and accordingly the most free from fine pores—which might, for example, exclude the carbon tetrachloride molecule. The curve of (absolute) S against temperature of preparation, thus obtained, is given in Fig. 2 of Part I, along with that calculated from the oxygen and the nitrogen isotherms.

Discussion.—From Fig. 2 of Part I, it will be seen that the maxima in the curve derived from carbon tetrachloride do not quite coincide with those from the oxygen- and the nitrogen-adsorption data; the difference may well originate in the difference in molecular size between carbon tetrachloride and the other two gases: since the carbon tetrachloride molecule is larger than the others it would be excluded from pores which are open to them. This suggestion is consistent with the lower value of S obtained from carbon tetrachloride adsorption.

FIG. 3.

Plot of x_p *against the temperature of dehydration of the gypsum.*



(x_p = *amount of* CCl_4 *adsorbed by the sample, at relative pressure* P.) *Curve I,* $P = 0{\cdot}25$; *Curve II,* $P = 0{\cdot}50$; *Curve III,* $P = 0{\cdot}75$.

The origin of the maxima is believed to be the same as that of the nitrogen and oxygen curves: the lower-temperature maximum is due to the reaction Gypsum ⟶ Hemihydrate + Water, and the higher-temperature one to Hemihydrate ⟶ Anhydrite + Water. The detailed evidence for this view will be presented in Part III.

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