

## Studies in the System Calcium Sulphate/Water

### Part 5.—Surface Area and Porosity Changes in the Dehydration of Calcium Sulphate Dihydrate

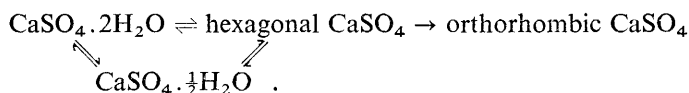
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Changes in surface area and porosity caused by heating calcium sulphate dihydrate have been studied by nitrogen sorption at 77 K, with limited oxygen and argon studies at the same temperature. Hysteresis is observed, mainly in hexagonal  $\text{CaSO}_4$ , but the observed increases in surface area are not accompanied by marked increases in porosity. Sintering, with a consequent reduction in surface area is only observed in orthorhombic  $\text{CaSO}_4$ . The oxygen and argon sorption results are interpreted in the light of previous work.

Calcium sulphate dihydrate decomposes at low temperatures according to the following reaction scheme:<sup>1</sup>



The dihydrate occurs naturally as gypsum, and the hemi-hydrate and hexagonal  $\text{CaSO}_4$  are important as starting materials for gypsum plasters. The conversion of hexagonal to orthorhombic  $\text{CaSO}_4$  (anhydrite) is irreversible, and the presence of anhydrite can have deleterious effects on the properties of plasters.

The kinetics and mechanisms of dehydration of gypsum and hemi-hydrate, and of the rehydration of hexagonal  $\text{CaSO}_4$  have been studied,<sup>2-5</sup> and in the latter case, surface effects are particularly important.

Relatively few studies of the surface properties have been made in view of the technical importance of the changes outlined. Gregg and Willing studied the sorption of oxygen,<sup>6</sup> nitrogen,<sup>6</sup> carbon tetrachloride<sup>7</sup> and water vapour<sup>7</sup> on calcium sulphate dihydrate heated in air. Type II isotherms were obtained in each case, and plots of surface area against reaction temperature showed a double maximum for oxygen, nitrogen and carbon tetrachloride, whereas water sorption showed only a single maximum. The double maximum was assumed to be due to the two stage dehydration of the dihydrate through hemi-hydrate to hexagonal calcium sulphate. Sintering occurred at temperatures above 620 K. A significant result obtained by these authors was that surface areas calculated from oxygen sorption were significantly greater than those calculated from nitrogen sorption. This was assumed to be due to the presence of channels of such a size as to admit oxygen molecules but not nitrogen.

Moloney *et al.* studied the sorption of nitrogen, oxygen and argon and also found that oxygen sorption gave surface areas approximately twice those derived from nitrogen or argon.<sup>8</sup> Surface area against temperature plots obtained by these

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authors gave only single maximum. Ridge and Moloney<sup>9</sup> concluded that sorption of oxygen and nitrogen on calcium sulphate was complex and that surface areas calculated from such measurements were of doubtful significance, although they did not give reasons for this conclusion, and still quoted B.E.T. surface areas. Mercury porosimetry measurements were also quoted as percentage porosity but no pore size distributions were given.<sup>10</sup> Moloney *et al.*<sup>11</sup> obtained evidence for pore sizes varying between 100-1000 Å in the product formed by heating the dihydrate at low temperature.

## EXPERIMENTAL

The starting material used throughout the work was A.R. calcium sulphate dihydrate, which gave an X-ray diffraction pattern in excellent agreement with that published in the A.S.T.M. Index. Reaction products were characterised by X-ray diffraction<sup>12</sup> and d.t.a.<sup>13</sup>

Adsorption and desorption isotherms were determined in an all glass volumetric apparatus,<sup>14</sup> using nitrogen, oxygen and argon as adsorbates at ~77 K. Samples were heated directly on the vacuum frame at temperatures between 300 and 635 K for times varying between 10 min and 2200 h. The sample was weighed immediately after each sorption experiment to determine the extent of decomposition until complete dehydration had occurred.

The starting material could not be heated to remove adsorbed gases, so the sample was evacuated at 77 K and flushed with helium several times before measurements were made. Helium was also used to determine dead volumes, and refrigerant temperatures were measured using a nitrogen vapour pressure thermometer.

During measurements of sorption of oxygen and nitrogen on hexagonal  $\text{CaSO}_4$ , the time taken to reach equilibrium was compared.

## RESULTS

### NITROGEN SORPTION

The full adsorption and desorption isotherms (runs 1D-6D) were all of type II in the Brunauer classification.<sup>15</sup> Hysteresis occurred in all samples except the original dihydrate (see fig. 1).

### B.E.T. RESULTS

Runs 1-27 were all carried out in the B.E.T. range ( $0.05 < P/P_0 < 0.35$ ); specific surface areas and *C*-constants for all the runs are given in table 1. Surface areas calculated from adsorption and desorption data are in good agreement and the B.E.T. plots were all linear with good correlation coefficients ( $> 0.99$ ) and low standard deviations.

Fig. 2 shows the effect on surface area of heating at 352 K. Complete dehydration was reached after 100 h at this temperature, while the surface area remained constant up to 250 h, at which time a sample of product rehydrated fully to give  $\beta\text{-CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  as identified by increases in weight, X-ray diffraction and d.t.a. This indicates that only hexagonal  $\text{CaSO}_4$  was present. No evidence for anhydrite (orthorhombic  $\text{CaSO}_4$ ) was obtained under these conditions.

Fig. 3 shows the effect of temperature on surface area; the plots show only a single maximum at ~420 K for a heating time of 240 h. At this point the product was still hexagonal  $\text{CaSO}_4$ . The decrease in surface area at higher temperatures is associated with the formation of anhydrite as identified by X-ray diffraction. The effect of increasing time at constant temperature is to sharpen the maximum.

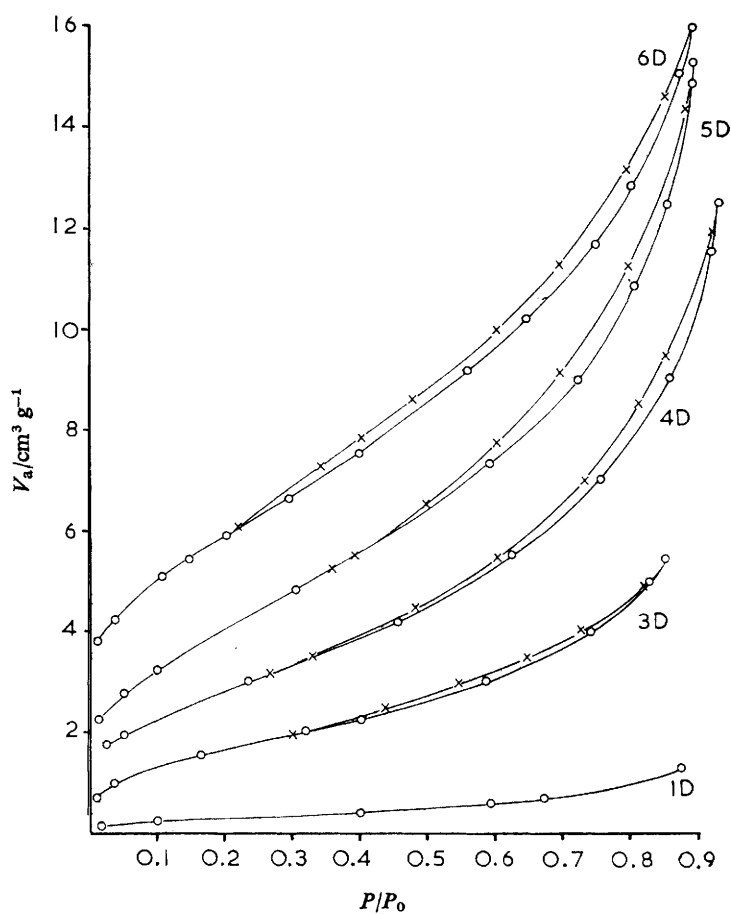


FIG. 1.—Nitrogen sorption isotherms for forms of calcium sulphate: ● adsorption, × desorption. Curve 6D has been raised by 1 unit in  $V_a$ .

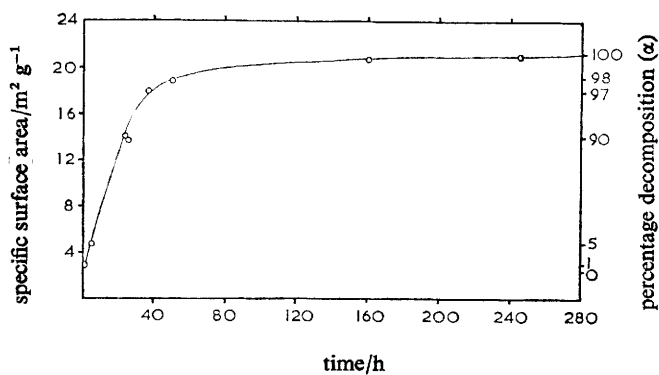


FIG. 2.—Effect of heating time on surface area ( $T = 352\text{ K}$ ).

TABLE 1.—EXPERIMENTAL CONDITIONS AND SURFACE AREA RESULTS FOR HEATED CALCIUM SULPHATE DIHYDRATE

run no.	temp./K	total heating time/h	product	$S_{\text{BET}}/\text{m}^2 \text{ g}^{-1}$	$C_{\text{BET}}$
1D	298	0.17	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	1.1	24.9
1D*				1.0	36.4
2D	298	93	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	1.0	36.0
3D	375	95	trace hex. $\text{CaSO}_4$	6.2	43.3
3D*				8.0	47.0
4D	375	98.5	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ plus hex. $\text{CaSO}_4$	10.8	45.0
4D*				11.2	31.8
5D	375	103.5	hex. $\text{CaSO}_4$	15.3	49.0
5D*				15.4	56.2
6D	375	134	hex. $\text{CaSO}_4$	18.2	67.5
6D				18.9	99.7
1	298	160	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	2.4	9.2
2	352	162		3.0	37.4
3		167		4.8	67.2
4		190	hex. $\text{CaSO}_4$	14.1	80.5
5		214		13.5	127.6
6		249		18.0	69.8
7		299		19.0	84.9
8		458		20.8	85.7
9		704		21.1	101.1
10	375	790		22.2	101.0
11		890		22.3	120.2
12		1103		25.6	97.1
13	395	1139		26.2	75.7
14		1264		27.9	33.2
15	420	1270		29.7	17.5
16		1290	hex. + ortho. $\text{CaSO}_4$	26.9	146.4
17		1334		27.2	88.2
18		1392		28.7	42.8
19	476	1416		28.3	63.8
20		1481	ortho. $\text{CaSO}_4$	28.2	65.3
21		1611		27.4	69.3
22		1851		26.8	70.2
23	553	1854		27.8	63.4
24		1868		24.5	79.1
25		1904		21.4	83.2
26		1954		20.0	48.9
27	587	2213		13.7	98.7

Runs 1D-6D full isotherms, \* desorption. Runs 1-27, B.E.T. range only.

***t*-PLOT RESULTS**

Fig. 4 shows plots of  $V_a/V_m (\propto t)$  against  $P/P_0$  derived from the full isotherm data (runs 1D-6D). At constant  $P/P_0$  there is a steady change in the statistical thickness of the adsorbed layer with heat treatment. Included in the figure are plots of  $V_a/V_m$  calculated from the de Boer<sup>16</sup> and Halsey<sup>17</sup> equations which give convenient

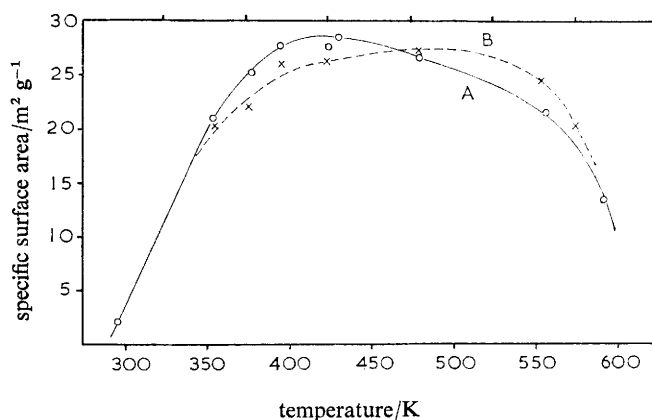


FIG. 3.—Effect of temperature on surface area. Curve A:  $\sim 240$  h at each temperature, curve B:  $\sim 120$  h at each temperature.

analytical representations of the statistical layer thickness on non-porous solids.<sup>18</sup> It is obvious that the calcium sulphate data do not fall on a common curve nor do they agree particularly well with the calculated curves except for sample 6D which lies close to the Halsey curve at high relative pressures.

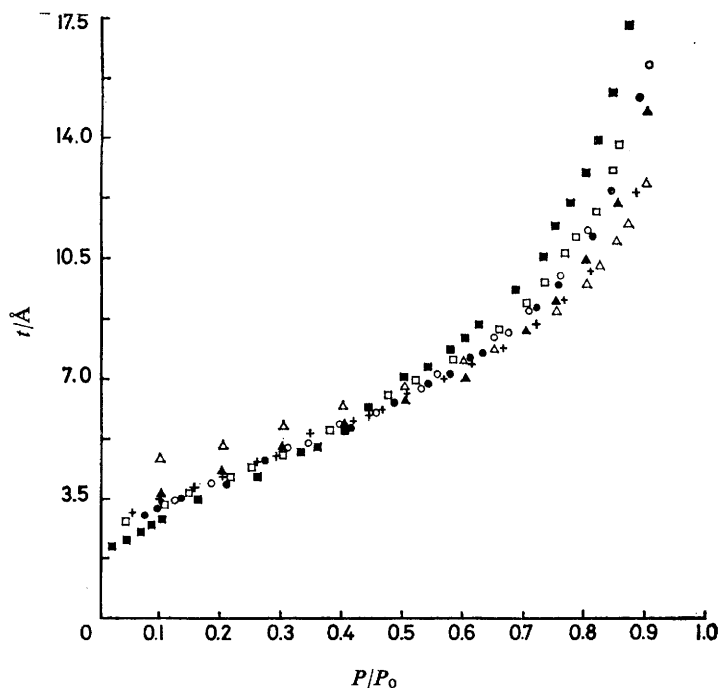


FIG. 4.—Comparison of experimental and calculated thickness of sorbed layer. ■ Sample 1D, ● Sample 5D, □ Sample 3D, + Sample 6D, ○ Sample 4D. △ calculated from Halsey's equation; ▲ calculated from de Boer's equation.

## PORE-SIZE DISTRIBUTIONS

Desorption data have been used to calculate distributions, by the methods of Pierce<sup>19, 20</sup> and Brunauer.<sup>21-23</sup> Fig. 5 shows some pore-size distributions calculated for sample 6D. Table 2 gives maximum pore-radii and cumulative surface areas based on the two calculations. Thinning corrections were obtained from changes in the  $V_a/V_m$  values.

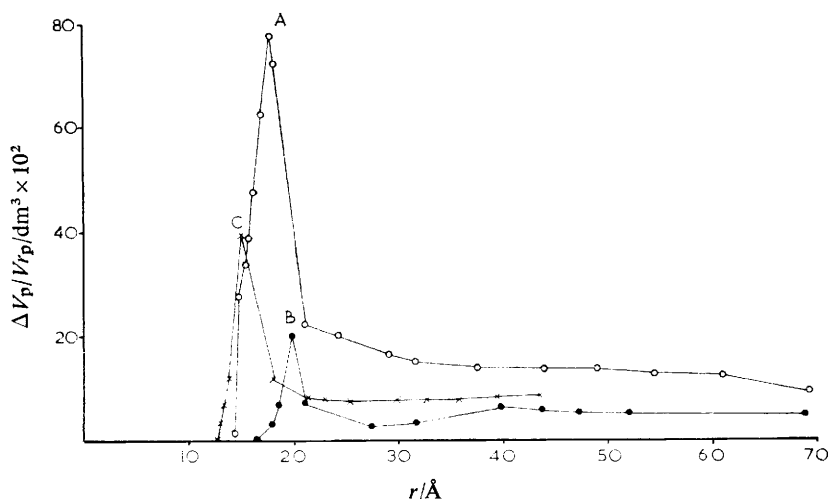


FIG. 5.—Pore size distributions for sample 6D. Curve A: Pierce calculation, curve B: Brunauer cylindrical pores, curve C: Brunauer, spherical pores.

TABLE 2.—COMPARISON OF CUMULATIVE SURFACE AREAS AND PORE SIZE MAXIMA

compound	$S_{BET}/m^2\ g^{-1}$		Pierce		Brunauer "Modelless"	
	ads.	des.	$r/\text{\AA}$	$S/m^2\ g^{-1}$	$r^*/\text{\AA}$	$S/m^2\ g^{-1}$
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (1D)	1.1	1.0	22	0.8	7.8	1.1
mainly $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (3D)	6.2	8.0	22	4.9	5.4	5.4
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ + hex. $\text{CaSO}_4$ (4D)	10.8	11.2	19	8.2	6.8	10.0
mainly hex. $\text{CaSO}_4$ (5D)	15.3	15.4	19	10.9	5.7	12.8
hexagonal $\text{CaSO}_4$ (6D)	18.2	18.9	18	10.3	7.1	10.3

\* core radii

TABLE 3.—ARGON SORPTION DATA COMPARED WITH NITROGEN DATA

compound and sample number	$S_{BET}/m^2\ g^{-1}$ adsorption			$S_{BET}/m^2\ g^{-1}$ desorption		
	nitrogen	liquid A <sup>a</sup>	solid A <sup>b</sup>	nitrogen	liquid A	solid A
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (1D)	1.1	0.7	0.7	1.0	0.7	0.7
hexagonal $\text{CaSO}_4$ (9)	21.1	17.3	16.1	21.1	18.6	17.2
hexagonal $\text{CaSO}_4$ (10)	22.2	17.4	16.2	22.2	17.4	16.2
hexagonal $\text{CaSO}_4$ (12)	25.6	16.9	15.6	—	—	—
hexagonal $\text{CaSO}_4$ (14)	27.9	17.7	16.4	—	—	—
orthorhombic (26)	20.0	14.7	13.6	—	—	—
orthorhombic (27)	13.7	10.5	9.7	—	—	—

<sup>a</sup>  $\rho_{\text{liq}} = 1.402\ \text{g dm}^{-3}$ ,  $A_m = 13.8\ \text{\AA}^2$ ; <sup>b</sup>  $\rho_{\text{solid}} = 1.65\ \text{g dm}^{-3}$ ,  $A_m = 12.8\ \text{\AA}^2$

## ARGON SORPTION

Adsorption and desorption runs were carried out using argon at 77 K. All isotherms were of type II. Surface areas are given in table 3 and compared with those derived from nitrogen sorption. Two sets of argon values are quoted, based on the liquid and solid densities.<sup>24</sup>

## COMPARISON OF SORPTION RATES

Fig. 6 compares the rates of sorption of oxygen and nitrogen for a sample of hexagonal  $\text{CaSO}_4$ . Sorption of nitrogen is time dependent after an initial rapid stage.

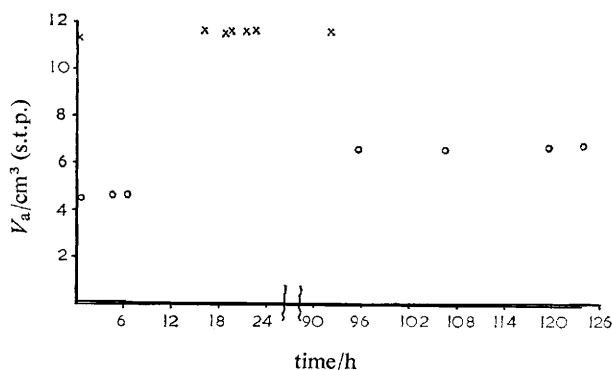


FIG. 6.—Comparison of sorption rates, × oxygen, ○ nitrogen.

## DISCUSSION

## VARIATION OF SURFACE AREA WITH TEMPERATURE

The increase in surface area shown in fig. 2 is caused by the conversion of dihydrate to hexagonal  $\text{CaSO}_4$ , which involves a radical change in crystal structure. A smaller increase in surface area is produced when the transition to orthorhombic  $\text{CaSO}_4$  occurs. It is only after this is formed completely that reduction in surface area occurs, presumably due to sintering. The double maximum observed by Gregg and Willing<sup>6, 7</sup> is a consequence of their sample treatment, since it has been shown that under dry conditions or vacuum a single stage conversion to hexagonal  $\text{CaSO}_4$  occurs. It is only after this is formed completely that reduction in surface area occurs.<sup>2</sup> Only in moist atmospheres does the reaction proceed via the hemi-hydrate which on decomposition gives rise to a second maximum in the surface area plot.

It is apparent from the early runs that some changes occur on evacuating  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  at room temperature. There is an initial reduction in surface area ( $1.1$  to  $1.0 \text{ m}^2 \text{ g}^{-1}$ ) which may not be significant, but at longer times an increase to  $2.4 \text{ m}^2 \text{ g}^{-1}$  is observed which indicates that some decomposition had probably occurred.

## t-PLOTS

The variations in statistical thickness of the adsorbed nitrogen layer shown in fig. 4 indicate that there are changes in either porosity or surface energy of the sorbent, or both. In general, increasing porosity would be characterised by positive deviations in  $t$  as  $P/P_0$  increases. The order of increasing thickness shown in fig. 4 is not compatible with the hysteresis shown in fig. 1. This suggests that changes in porosity

do not account for the trends shown in fig. 4. Changes in  $C_{\text{BET}}$  given in table 1 suggest that there is an increase in the energy of sorption and therefore in the surface energy of the sorbent. However, a simple increase in  $C_{\text{BET}}$  would not cause the complexity shown in fig. 4, since changes in  $C$  only have a slight effect on the slope of the  $t$ -plot, particularly at low relative pressures.<sup>25</sup>

#### PORE-SIZE DISTRIBUTIONS

Fig. 1 shows that the hysteresis loops in samples 3D-6D are narrow and that the starting material (1D) shows no detectable hysteresis. Any pore-size distribution can be regarded as the difference between the experimental  $t$ -curve and that from a non-porous material, *e.g.* one as described by the de Boer or Halsey equations. It can be seen from fig. 4 that this difference is very small and it therefore follows that the cumulative pore volumes will be very small and the calculated pore sizes will be uncertain. However the distributions for all samples (except 1D) showed a maximum at  $\sim 20 \text{ \AA}$  radius.

It is often assumed that the increases in surface area obtained in thermal decomposition reactions are due to increases in porosity. Although some increases in porosity obviously occur in this case, as shown in table 2, a considerable proportion of the increase must be due to fragmentation of the starting material. This is indicated in table 4 by the increasing discrepancy between the total surface area,  $S_{\text{BET}}$ , and the surface area in pores. The proportion of total surface in pores decreases with heating time, and for sample 6D can be as low at 50 % depending on the pore model chosen.

Single-crystal X-ray diffraction evidence lends support to the suggestion of fragmentation. Work by Gay,<sup>26</sup> Richards<sup>27</sup> and Satava and Baldrian<sup>28</sup> indicates that a pseudomorphous oriented aggregate of equiaxed hemi-hydrate crystals some  $10^{-3}$ - $10^{-4}$  cm in diameter results from dehydration. These have good fibre texture in which the (001) axis of the hemi-hydrate coincides with the  $c$ -axis of the original dihydrate. The orientation of the hemi-hydrate is random in the other two directions. On rehydration, an aggregate of dihydrate crystals results with a fibre texture parallel to the original  $c$ -axis. A similar oriented growth of hexagonal  $\text{CaSO}_4$  results on further dehydration of the hemi-hydrate.

#### ARGON AND OXYGEN SORPTION

The results given in table 3 show that the surface areas measured by argon sorption are all lower than those measured by nitrogen, which are in turn approximately half those measured by oxygen (table 5). This is in line with previous work.

The work by Moloney<sup>10</sup> was carried out at a sorption temperature of 90 K, and it was argued that at this temperature oxygen had a smaller cross-sectional area ( $14.1 \text{ \AA}^2$ ) than had argon ( $14.4 \text{ \AA}^2$ ) or nitrogen at 77 K ( $16.2 \text{ \AA}^2$ ). This gave rise

TABLE 4.—COMPARISON OF SURFACE AREA DATA, VARIOUS MODELS  
(DESORPTION DATA)

sample	$S_{\text{BET}}$	Pierce	"Brunauer"			
			modelless	parallel plate	cylinder	sphere
1D	1.0	0.8	1.1	0.2	0.6	1.1
3D	8.0	4.9	5.4	1.7	3.9	6.1
4D	11.2	8.16	10.0	2.4	5.5	8.3
5D	15.4	10.9	12.8	3.3	8.0	12.6
6D	18.9	10.3	10.3	3.9	9.5	15.5



to greater penetration of oxygen into smaller pores, which was measured as doubled surface area. This interpretation did not suggest why the small difference in cross-sectional area between oxygen and argon gave such large differences in area. At the temperature used in the present work, 77 K, argon has a smaller cross-sectional area than oxygen,  $13.8 \text{ \AA}^2$  or  $12.8 \text{ \AA}^2$ , depending on the use of the liquid or solid density in the calculation.<sup>29</sup> For a simple sorption process it might be expected that the reduced cross-sectional area for argon at lower temperatures should lead to greater penetration into pores and a greater measured surface area. This does not happen and it seems therefore that the process is not simple. An alternative explanation is suggested by fig. 6 in which the sorption of oxygen is rapid, while that of nitrogen occurs in a rapid stage followed by a slower one. The rapid stage is one of normal

TABLE 5.—COMPARISON OF RESULTS FROM OXYGEN AND NITROGEN SORPTION

sorbate	nitrogen	oxygen
$S_{\text{BET}}/\text{m}^2 \text{ g}^{-1}$	24.60	53.74
$C_{\text{BET}}$	41.2	164.0
$V_{\text{m}}/10^{-3} \text{ dm}^3 \text{ g}^{-1}$	5.65	14.69

sorption on freely accessible surface, while the slow stage is one of activated entry into small pores, probably by end-on penetration. The pores must be of dimensions such that the slightly smaller oxygen molecule can enter easily, but the nitrogen molecule only with difficulty. The critical dimensions are  $\sim 3 \text{ \AA}$  for the nitrogen molecule and  $2.8 \text{ \AA}$  for oxygen and the pores must be of similar dimensions. Hexagonal  $\text{CaSO}_4$  has empty channels some  $5 \text{ \AA}$  in diameter<sup>12</sup> which contain water in hemi-hydrate and differential penetration by nitrogen and oxygen would seem possible. Ridge and Moloney found that the doubled oxygen surface area was reduced to that measured by nitrogen when hexagonal  $\text{CaSO}_4$  was exposed to water vapour and then degassed at 373 K for 8 h. This treatment produces stoichiometric hemi-hydrate in which the channels are filled with water molecules and therefore cannot be available to oxygen.

We thank Dr. M. J. Jaycock for much helpful discussion and criticism during the course of the work.

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