178. *The Thermal Decomposition of Oxalates. Part III.*[1] *The Decomposition and Surface Properties of Zinc Oxalate.*

By D. Dollimore and D. Nicholson.

Zinc oxalate dihydrate, when prepared by the conventional method, does not conform exactly to the formula $ZnC_2O_4,2H_2O$, and decomposes in two clearly distinguishable, although not entirely distinct, stages to produce non-porous particles. Evidence for this particulate nature includes nitrogen adsorption isotherms and density measurements. It is suggested that this is consistent with the decomposition kinetics, which are also discussed. When the anhydrous salt is rehydrated and then decomposed, a porous zinc oxalate is obtained with a surface area much larger than that of the non-porous material; an explanation for this behaviour is offered.

In a previous Paper [2] an attempt was made to correlate changes in surface area with the kinetics of thermal decomposition for three compounds, including zinc oxalate dihydrate. In the present Paper the decomposition of this substance is discussed in detail, and the correlation is taken further.

EXPERIMENTAL

Materials and Analysis.—Zinc oxalate dihydrate was prepared by adding pure zinc oxide to a boiling solution of oxalic acid, a method identical with that used to prepare the commercial sample for previously reported work.[1,3]

Thermogravimetric analysis in air gave two plateaux; the first, corresponding to dehydration, occurred between $w = 17.5$ and 17.7 (where w is the percentage loss in weight referred to the initial sample). In a vacuum, however, the plateau occurred at $w = 19.7$ (± 0.2). This supports Robin's statement [4] that complete dehydration does not take place in air.

Analysis of the sample showed that there was an excess (1.7%) of zinc present. The method of preparation suggests that the composition would be: ZnO, 2.1; ZnC_2O_4, 78.2; H_2O, 19.7%; Total 100% (± 0.3). However, X-ray analysis [5] showed no lines corresponding to zinc oxide, and agreed with previous results.[4] It is probable, therefore, that a small amount of basic oxalate is always present and that water in excess of $2H_2O$ is present as adsorbed water.

Decomposition and Nitrogen Adsorption.—Isothermal decompositions were carried out in air, using the apparatus and quantities previously described.[1] The samples were gently tapped down to ensure consistent packing, and then suspended in the furnace after this had been held steady at the required temperature for 3 hr. The loss in weight was plotted against time; reproducibility was better than 1% of w.

Adsorption of nitrogen was carried out in a volumetric apparatus already described.[3] Residues were stored in sealed capsules, and each sample was degassed overnight at room temperature before adsorption measurements were made.

Gravimetric Adsorption Balance.—Water adsorption isotherms were measured with a spiral spring having a sensitivity of approximately 100 cm./g. which supported a narrow-necked spherical glass bulb at its lower end. The balance case was in the form of a condenser 5 ft. in length connected to a vacuum system which included an oil manometer and vapour storage vessel containing deionised distilled water.

Changes in weight were detected by observing the position of the spring with a cathetometer. The springs were calibrated before use; buoyancy effects are negligible for water adsorption in this type of balance.[6] Degassing of the sample prior to adsorption was carried out at $150 \pm 1°$, for up to 18 hr. below 10^{-3} mm. pressure.

[1] Part II, Dollimore, Griffiths, and Nicholson, *J.*, 1963, 2617.
[2] Dollimore D., Dollimore J., and Nicholson, Proc. 4th Internat. Symposium on the Reactivity of Solids (1960), Elsevier, Amsterdam, 1961, p. 627.
[3] Dollimore and Nicholson, *J.*, 1962, 960.
[4] Robin, *Bull. Soc. chim. France*, 1953, 1078.
[5] Dollimore, J., M.Sc. Thesis, London, 1960.
[6] Madeley, Ph.D. Thesis, London, 1957.

RESULTS AND DISCUSSION

Particulate Nature of Residues.—The residues discussed here were obtained from the decomposition of zinc oxalate in air, using a variety of heating times and temperatures. They include an ignition series in which each sample was heated for 30 minutes at a constant temperature, and two isothermal series, at 400 and 420°, in which a batch of samples were placed in a furnace, at the required temperature, and withdrawn one by one after successive time intervals.

Adsorption Isotherms.—Nitrogen isotherms for a range of samples from these three ignition series are reproduced in Fig. 1. These represent all the stages in the decomposition in air and the various conditions under which these stages can be reached. The character-istic values of w are

$$ZnC_2O_4,2H_2O \longrightarrow ZnC_2O_4 \ (w = 17\cdot6); \ ZnC_2O_4 \longrightarrow ZnO \ (w = 55).$$
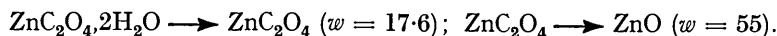
The isotherms are all sigmoid and rise steeply beyond a relative pressure of 0·8; they show no hysteresis up to 0·99 relative pressure. This behaviour indicates that any pores present
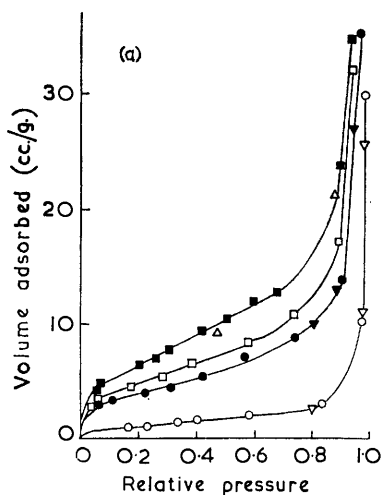

FIG. 1 (a). Nitrogen isotherms at 78°K for residues from samples of zinc oxalate dihydrate heated in air at various tem-peratures for 30 min.

	Adsorption	Desorption
Heated at 200°	□	—
Heated at 300°	■	△
Heated at 450°	●	▼
Heated at 800°	○	△

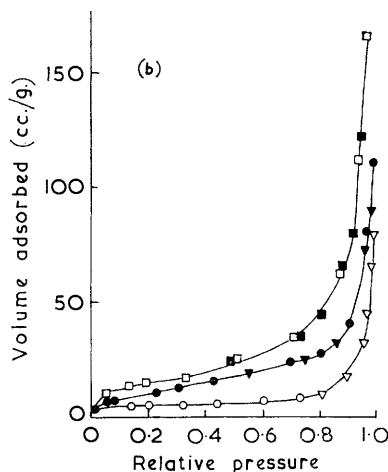FIG. 1 (b). Nitrogen isotherms at 78°K for residues from samples of zinc oxalate dihydrate heated in air at 420°.

	Adsorption	Desorption
Heated for 2 min. at 420° ($w = 13\cdot0$) ...	○	▽
Heated for 7 min. at 420° ($w = 26\cdot8$) ...	●	▼
Heated for 15 min. at 420° ($w = 50\cdot0$) ...	□	■

must be larger than 500 Å and would not be detectable by adsorption methods. The absence of any steeply rising portion in the medium pressure range, characteristic of smaller pores, can be tested by a comparison with the theoretical B.E.T. (Brunauer–Emmett–Teller) adsorption isotherm. This can be written

$$V/V_m = Cx/(1 - x)[1 + (C - 1)x] \tag{1}$$

where V is the volume adsorbed, V_m the volume adsorbed at the monolayer, C the adsorp-tion constant, and x the relative pressure.

H H

Values of C obtained by plotting eqn. (1) as a straight-line relationship range from 100 to 500 for these samples. Eqn. (1) can therefore be written

$$V/V_m = 1/(1 - x)$$

to a good approximation beyond $x = 0.3$. Fig. 2 shows some of the experimental points compared with this isotherm. Only in the case of a sample with a high surface area (350° for 30 minutes, surface area 46 m.²/g.) do these rise more steeply than the theoretical isotherm; in all other cases the absence of substantial interparticle condensation means that the experimental isotherms are more horizontal than the B.E.T. isotherm for intermediate relative pressure ranges. This is compatible with the postulate of non-porosity, and suggests that the surface is more homogeneous than that which is in practice required to obtain a smooth sigmoid isotherm.[7]

Although the first concern of this investigation was the nature of the residues produced by decomposition in air, it is of interest to know whether the non-porous character of these residues is due to pore blockage by physically sorbed water. To this end a sample
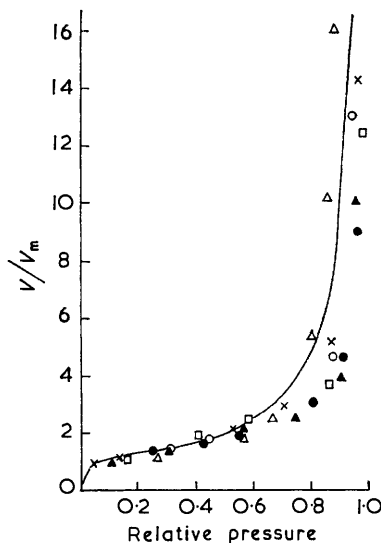

FIG. 2. Comparison of V/V_m with the isotherm $V/V_m = 1(1 - x)$.

Sample heated for: ○ 2 min. at 420° ($w = 13.0$); ● 7 min. at 420° ($w = 26.8$); × 15 min. at 420° ($w = 50.0$); △ 30 min. at 350° ($w = 33.0$); ▲ 30 min. at 450° ($w = 54.5$); □ 30 min. at 800° ($w = 55.0$).

which had decomposed to the anhydrous stage (30 min. at 200°), and one partially decomposed to the oxide stage (30 min. at 350°) were each degassed at 100° for 5—6 hours and the nitrogen adsorption isotherms measured. In each case the characteristic sigmoid isotherm remained unaltered. Of further interest in this respect is the residue from heating for 30 minutes at 800°, for which the value of $w = 55$ suggests that all chemisorbed water has been removed. It is apparent that sintering produced by surface diffusion also results in non-porous products.

A residue prepared by heating the oxalate for 30 minutes at 400° was used as an adsorbent for water. It was degassed for 8 hours to constant weight at 150°. The water vapour adsorption–desorption–adsorption cycle at 20° was completely reversible and gave a sigmoid isotherm, so that retention of water by micropores seems very unlikely.

Density Measurements and Electron Micrographs.—Measurements of the apparent density (β) in carbon tetrachloride and the absolute density (ρ) were made for samples heated at 420°. The absolute density was measured by nitrogen compression at room temperature. The difference $[(1/β) - (1/ρ)]$ then gives a value for the voidage volume per gram (V_v) which is not filled by carbon tetrachloride but is occupied by nitrogen gas. If it is assumed that this volume is entirely due to cyclindrical pores then the approximate value for mean

[7] Halsey, *J. Chem. Phys.*, 1948, **16**, 931.

pore radius is $\bar{r} = 2V_{\mathrm{v}}/S$, where S is the surface area in cm.^{2}/g. Alternatively, if the particles are completely non-porous, the mean particle diameter $\bar{d}$ is $6/\rho S$. Some values of $\bar{d}$ and $\bar{r}$ are listed in Table 1 and $\bar{r}$ is compared with the relative pressure x_{k}, calculated from the Kelvin equation, at which these pores would empty of adsorbed liquid nitrogen. Electron micrographs [5] of samples with a high surface area (46 m.^{2}/g.) showed a large number of very small particles of about $0.01\ \mu$ diameter comparable with the calculated value of $\bar{d}$ for a similar sample (15 minutes' heating at $420°$) given in Table 1. These were accompanied by a few larger masses (up to $1\ \mu$ in diameter) having markedly rough edges which are probably adhering collections of the smaller particles.

<div align="center">TABLE 1.</div>

<div align="center">Particle sizes of residues of $420°$ ignition series from density measurements.</div>

Time of heating (min.)	w	$\bar{r}$	$\bar{d}$	x_{k}
0	0	0·12	12·0	
3	17·3	0·026	2·2	0·957
15	50·1	0·0067	0·022	0·810
20	54·7	0·011	0·036	0·901

It is thus established that in the decomposition of zinc oxalate to the oxide in air non-porous particles are formed. The density and electron micrographs indicate, however, that these non-porous particles adhere lightly together in larger agglomerates, probably owing to the presence of small amounts of water adsorbed on the zinc oxide. These agglomerates remain intact in the presence of carbon tetrachloride, but are separated when nitrogen, and water in the case of the oxide residues, is adsorbed on to them.

Surface Measurements and Decomposition Kinetics.—(a) *Dehydration stage.* Isothermal decomposition of zinc oxalate at 200, 258, 312, and $338°$ resulted in a clearly distinguishable break at the end of the dehydration stage. The plots of fraction decomposed (α) against time (t) were sigmoid with a rather rapid induction period, and typical curves for the whole decomposition have been published previously.[2]

The slight induction period is of doubtful significance in this reaction and might be due to temperature variation at the beginning of the reaction. Beyond this point, attempts were made to fit the experimental results to a number of possible kinetic equations. Up to approximately $\alpha = 0.8$ the best fit was obtained for an equation having the general form

$$(1 - \alpha_1) = (1 - kt)^{\mathrm{n}} \qquad (2)$$

where α_1 is the fraction of the hydrate decomposed at time t, and k and n are constants. On differentiation, and substitution of (2), one obtains

$$(1 - \alpha_1)/(\mathrm{d}\alpha_1/\mathrm{d}t) = (-1/kn)(1 - kt) \qquad (3)$$

The value of $\mathrm{d}\alpha_1/\mathrm{d}t$ could be calculated from the α_1 against t data, and the function $(1 - \alpha_1)/(\mathrm{d}\alpha_1/\mathrm{d}t)$ has been plotted against t in Fig. 3(a). Values of n deduced from the slope of the graph in Fig. 3(a) lie between 2.6 and 3.0, so that the behaviour is close to that predicted by Mampel [8] or that from a contracting sphere model in which the interface between hydrate and anhydrous oxalate retreats towards the centre of the particle.

Beyond this point and up to $\alpha_1 = 1.0$, which was taken as the point where $\mathrm{d}w/\mathrm{d}t$ became a minimum and lay between $w = 17.7$ and 20.0, the experimental points fitted the equation

$$\log (1 - \alpha_1) = -kt \qquad (4)$$

This is consistent with a situation in which each of a number of small particles has an equal probability of being dehydrated.

The activation energy for the dehydration reaction was calculated by using the graphs of $(1 - \alpha_1)/n$ against t, and plotting the slope of these lines against $1/T$ (°K) for the three

[8] Mampel, *Z. phys. Chem.*, 1940, *A*, **187**, 43.

lowest temperatures. The resulting straight lines are plotted in Fig. 3(b). The activation energy was only 7 kcal. which is rather low for this type of reaction.[9] This would result if the escape of water vapour were impeded by a thick layer of solid product.

X-Ray photographs and oxalate analysis of samples decomposed in the 400° ignition series indicate that small quantities of zinc oxide are present at an early stage in the reaction and that the two stages of the decomposition are not entirely distinct.
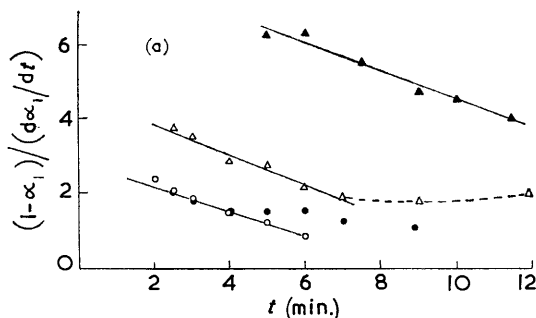

FIG. 3(a). Plot of $(1 - \alpha_1)/(d\alpha_1/dt)$ against t for dehydration of zinc oxalate dihydrate.

○ at 312°, $n = 3$, α_1 between 0·28 and 0·95;
● at 336°, $n = 3$, α_1 between 0·40 and 0·80;
△ at 258°, $n = 2\cdot6$, α_1 between 0·26 and 0·85;
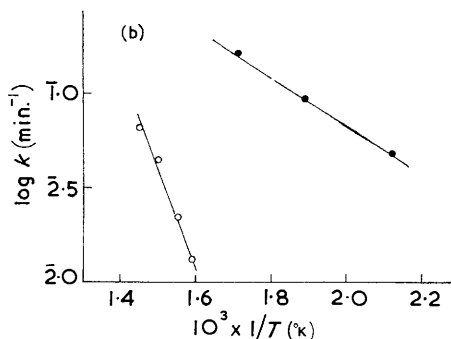▲ at 200°, $n = 2\cdot9$ α_1 between 0·30 and 0·85.

FIG. 3(b). Activation energies for zinc oxalate decompositions.

● Dehydration stage.
○ Decomposition stage.

(*b*) *Decomposition of the oxalate.* The kinetics of the decomposition of the oxalate have been measured at 355, 372, 392, and 418°. The reaction begins with a slow induction period up to about $\alpha_2 = 0\cdot1$ (where α_2 is the fraction of the oxalate decomposed). This fits the equation $\alpha_2 = k_1 t^n$, with n rising from 1·6 to 1·8 as the temperature falls. These values differ considerably from the value of 4 predicted by Mampel for a nucleation process. Explanation is best sought in terms of an overlap between the two stages resulting from a retention of some water vapour by the dehydrated oxalate. Analysis for oxalate of a residue from the 400° ignition series showed that between $\alpha_2 = 0\cdot05$ and $0\cdot15$ only 90% of the water originally present had been lost.

The intermediate portion of the curve up to approximately $\alpha_1 = 0\cdot6$ follows the law $\alpha_2 = k_2 t$, which has also been found for the vacuum decomposition of this material.[10] The activation energy for this stage was 21 kcal [Fig. 3(b)]. Beyond $\alpha_2 = 0\cdot6$, first-order kinetics were obeyed, as in the dehydration reaction.

It has been shown that the particles produced in the decomposition of the oxalate to the oxide are non-porous. In Table 2 are listed the results of an ignition series at 420°

TABLE 2.

Isothermal ignition series for zinc oxalate at 420°.

| Time of heating (min.)	% Loss in weight (*w*)	Surface area * S (m.²/g.)	Nitrogen density (g./c.c.)	Apparent density in CCl_4 (g./c.c.)	Time of heating (min.)	% Loss in weight (*w*)	Surface area * S (m.²/g.)	Nitrogen density (g./c.c.)	Apparent density in CCl_4 (g./c.c.)
0	0	2·0	2·5	1·9	10	39·5	46·0	—	—
1	3·5	4·4	—	—	15	50·0	51·0	5·0	2·7
2	13·0	13·2	—	—	20	54·7	30·4	5·5	2·9
3	17·3	14·8	1·8	1·3	24	54·8	29·5	—	—
5	21·5	25·0	—	—	30	55·2	25·5	5·5	2·9
7	26·8	39·0	—	—					

* Nitrogen–B.E.T. method used on the assumption that the area of an adsorbed nitrogen molecule in the monolayer is 16·2 Å².

[9] Garner, " Chemistry of the Solid State," Butterworths, London, 1955, p. 220.
[10] Baidins, *Diss. Abs.*, 1958, **19**, 215.

in which samples were removed at different times and the per cent loss in weight, the surface area, and the densities were determined. The changes in surface area follow the same pattern as those discussed previously.[2] There is a gain in the surface area during decomposition such that the surface area is proportional to the loss in weight. This would follow if in unit time the same number of zinc oxide particles are always produced, and is consistent with the explanation of linear kinetics ($\alpha_2 = k_2 t$) for oxalate decomposition offered by Allen and Schaife [11] in terms of the loss of gas from the surface of particles in which the reaction is progressing towards the centre. When log law kinetics take over, the effect of sintering becomes predominant, as here the probability of sintering is proportional to the number of zinc oxide particles already formed (*i.e.*, proportional to α_2), whereas the probability of increasing surface area is related to the probability of decomposition of any remaining particle. The fraction still undecomposed at this stage is $(1 - \alpha_2)$ and the ratio $\alpha_2/(1 - \alpha_2)$ is increasing rapidly. Fig. 4 shows that there is general agreement with these predictions. It would seem that the pseudo-lattice [12] is not sufficiently stable

FIG. 4. Change of surface area for zinc oxalate dihydrate heated at 400 (●) and 420° (○).

A refers to $\alpha_1 = 1.0$, $\alpha_2 = 0$, B to $\alpha_2 = 0.6$, and C to $\alpha_2 = 1.0$.
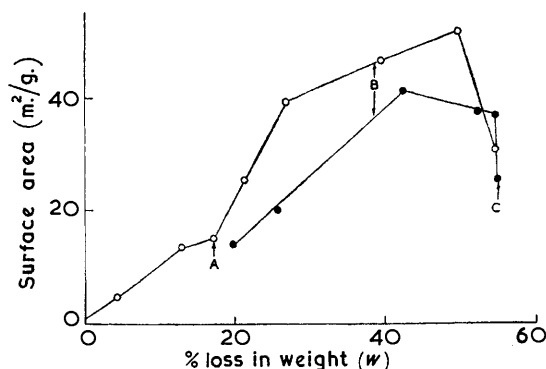
to exist for any appreciable length of time, and the fact that sintering takes precedence at quite an early stage in the reaction even before the log law is obeyed supports this contention.

Adsorption of Water on Anhydrous Zinc Oxalate.—Anhydrous zinc oxalate was prepared by heating three batches of the original material in air for 30 minutes at 200°, the mean loss in weight being 17.5%. Small samples for adsorption were then chosen from this residue. Before adsorption the dehydration process was completed by heating at 150° under a vacuum until constant weight was attained ($w = 19.7$).

The adsorption isotherms for water at 20 and 25° (Fig. 5) are similar to the sigmoid isotherms for non-porous substances. Comparison with the theoretical B.E.T. isotherm, however, shows that the uptake of water vapour beyond $x = 0.15$ to 0.20 is considerably higher than that expected. At a relative pressure of 0.992 the 0.25 g./g. of water taken up is equivalent to 20% by weight of water in the hydrated substance, and is comparable with the water content of 19.7% in the original material. It appears, therefore, that rehydration is taking place at these temperatures, and that the dehydrated oxalate is able to take up more than the original amount of water present.

When an attempt was made to desorb water from sample A, which had taken up 0.226 g./g. at $x = 0.816$, it was found that it could be removed only very slowly and 0.210 g./g. still remained at a pressure of $x = 0.114$ after a total desorption time of 45 hours. The sample was finally opened to a vacuum at 25°, and the rate of loss of water was 0.003 g./hr. The final 0.18 g./g. of adsorbed water was removed by degassing at 150°. On rehydrating at 20° this sample took up a much greater quantity of water than the original dehydrated sample, and the isotherm shows a distinct break from the usual path at a

[11] Allen and Schaife, *J. Phys. Chem.*, 1954, **58**, 667.
[12] Gregg, *J.*, 1953, 3940.

relative pressure of 0·40.   Calculation of the surface area by the " point B " method from this isotherm gave ~140 m.²/g.

Two experiments were carried out at 20°, in which the sample was exposed to water vapour at constant relative pressure.   The uptake of water obeyed the $t^{\frac{1}{2}}$ diffusion law (Fig. 6), indicating that rehydration rather than adsorption was taking place.[13]

In order to investigate the effect of this dehydration–rehydration cycle on surface properties a dehydrated oxalate having a surface area of 28·7 m.²/g. was evacuated and
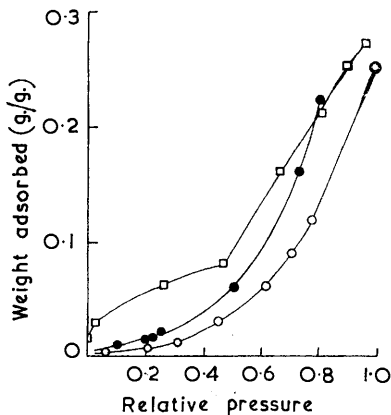
FIG. 5.   Adsorption of water vapour on anhydrous zinc oxalate.

Sample A: ● adsorption at 25°;   □ re-adsorption at 20°.
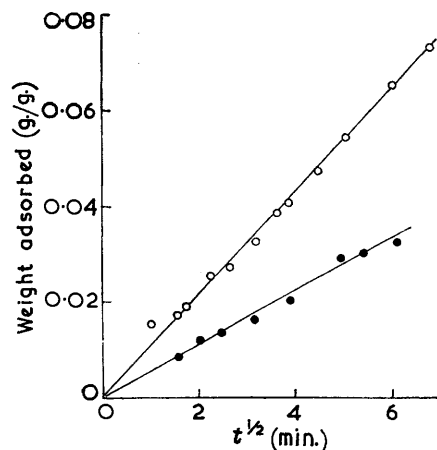Sample B: ○ adsorption at 20°.

FIG. 6.   Adsorption of water on anhydrous zinc oxalate at constant relative pressures at 20°.
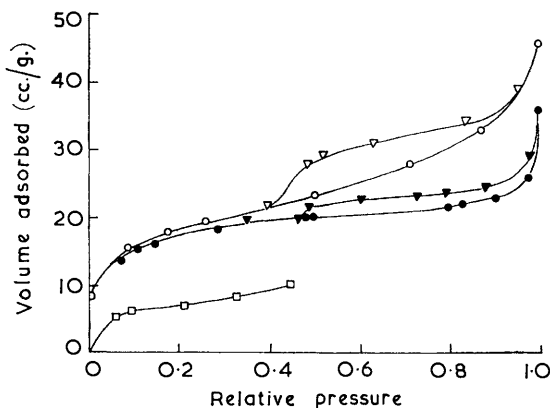
● Relative pressure = 0·773.
○ Relative pressure = 1·000.

FIG. 7.   Nitrogen isotherms at 78°K for specially treated zinc oxalate.

	Adsorption	Desorption
Original sample ...	□	—
First cycle	○	▽
Second cycle	●	▼

exposed to water vapour at 25° for 18 hours.   The amount of water vapour taken up was equivalent to 31·5% of the total weight compared with 19·7% for the original sample; thus water in excess to the extent of approximately one molecule per molecule of oxalate had been taken up.   This was then dehydrated at 150° under a vacuum for 3 hours, and all the water was lost.   A nitrogen isotherm (Fig. 7) at liquid-nitrogen temperatures showed marked hysteresis, and the surface area had increased to 65·5 m.²/g.

A second cycle of rehydration and vacuum decomposition was carried out in an identical fashion, and the lower isotherm in Fig. 7 was obtained; the surface area at this stage was 64·8 m.²/g.   Argon adsorption isotherms at liquid-nitrogen and liquid-oxygen

[13] Barrer and McLeod, *Trans. Faraday Soc.*, 1954, **50**, 980; 1955, **51**, 1290.

temperatures showed similar characteristics of porous materials but the loop closed at a relative pressure of 0·25 for the first temperature and at $x = 0·5$ for the second temperature.

The large increase in surface area and the introduction of a porous type of structure was not observed when the original oxalate was decomposed under a vacuum at 150° for 3 hours; the surface area in this case was 32·2 m.^{2}/g., which was higher than normal for decomposition to the anhydrous stage in air. The isotherm, however, was sigmoid and reversible without hysteresis.

The general form of the isotherm in Fig. 7 has been associated by several workers [14] with slit capillaries having parallel sides, resulting from plate-like particles held apart in some way. An estimate of the width of such slits can be made from the value of the relative pressure at the steepest part of the desorption loop using the Kelvin equation, and assuming that the lateral dimensions of the plates are much larger than the slit width. Inspection of the nitrogen isotherms in Fig. 7 suggests that the values for the separation of the plates are ∼36—38 Å.

The results show clearly that the solid has developed pores as a result of dehydration and subsequent rehydration. The uptake of water exceeds that required for hydration to the dihydrate. It is possible that this excess water would be in the form of a saturated solution of the oxalate, as its immediate environment would consist of zinc oxalate particles only. On evacuation, the physically adsorbed water would be removed first, depositing primary particles from the solution between the larger undissolved particles. It can be postulated from the shape of the isotherm that further decomposition results in a collapse to plate-like particles which are cemented together by the particles deposited from solution. A similar theory of cementation has been used to explain the increase in strength of calcium carbonate compacts which have been saturated with water.[15]

THE DEPARTMENT OF CHEMISTRY, ROYAL COLLEGE OF ADVANCED TECHNOLOGY,
SALFORD 5, LANCS.   [*Received, May* 14*th*, 1963.]

[14] De Boer, *Proc.* 10th Symposium of the Colston Research Society, Butterworths, London, 1958, p. 68.
[15] Dollimore and Gregg, *Trans. Brit. Ceram. Soc.*, 1955, **54**, 262.