179. *The Thermal Decomposition of Oxalates. Part I. The Variation of Surface Area with the Temperature of Treatment in Air.*

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The changes in surface area (measured by volumetric adsorption) which occur when nine heavy-metal oxalates are heated at various temperatures have been determined. Chemical changes are more complex than for carbonates and hydroxides. The first reaction is usually dehydration and is followed by conversion into oxide, and a maximum in the plot of surface area against temperature is usually shown in the latter process. Iron oxalates also show a second maximum which can be attributed to a change from the amorphous to the crystalline form of ferric oxide. Mathematical expressions relating surface area to other parameters are discussed for its increase and for sintering.

THE work described in this paper constitutes a general investigation into the changes in surface area which take place when selected heavy-metal oxalates are decomposed by heat in air. The experimental procedure for decomposition is similar to that used by Gregg [1] in his study of the decomposition of hydroxides and carbonates. The reactions involve a single-stage decomposition of the type, $A(s) \longrightarrow B(s) + C(g)$, whereas for hydrated oxalates decomposition may involve several intermediate stages.

With heavy-metal oxalates possible stages include the formation of an anhydrous oxalate and a transient conversion into metal [2] which in the presence of air will be reoxidised immediately. An intermediate carbonate stage would not be expected to be stable.[3]

As the surface area of a solid depends on its previous history, oxides prepared by decomposing oxalates would differ in their surface properties from similar oxides prepared by thermal decomposition of other oxysalts. It is part of the present study to see if the theories outlined by Gregg [1] for the production of a greater number of product particles from a given number of reactant particles can be extended to the more complicated decomposition processes taking place on the thermal treatment of oxalates in air.

At a given temperature two competing processes contribute to surface-area changes: (1) Those increasing surface area, such as strains resulting from the difference between specific volumes of reactant and solid product, which are opposed by sintering processes which tend to reduce surface area. (2) As the decomposition temperature is raised the second process, which proceeds mainly by diffusion mechanisms,[4] becomes faster and more important. In general, therefore, the lower the temperature of decomposition the greater will be the increase of surface area expected, as sintering will be slow. However, if the reaction is relatively slow it is possible for the strains set up to be dissipated and hence there is no increase in surface area.[5] We have chosen heating times so as to reduce sintering effects to a minimum and enhance those mechanisms which increase the surface area.

EXPERIMENTAL

Materials.—The oxalate samples were either commercial or were prepared by precipitation from solution. Analysis showed that the formula, when given by the manufacturers, was correct within 1%. The aluminium oxalate was described as a basic oxalate but had an approximate formula $Al_2(C_2O_4)_3,4H_2O$. The formulæ given for the other oxalates, which were

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[1] Gregg, *J.*, 1953, 3940.

[2] Robin, *Bull. Soc. chim. France*, 1953, 1078.

[3] Duval, "Inorganic Thermogravimetric Analysis," Elsevier, Amsterdam, pp. 187, 206, 223, 237, 274.

[4] Hüttig, *Kolloid Z.*, 1942, **98**, 6, 263; 1942, **99**, 262.

[5] Dollimore, Dollimore, and Nicholson, 4th Internat. Symposium on the Reactivity of Solids, 1960, Elsevier, Amsterdam, 1961.

all in powdered form are $MC_2O_4,2H_2O$, where M ≡ Mn, Fe, Co, Ni, and Zn, and $Cr_2(C_2O_4)_3,6H_2O$, $Fe_2(C_2O_4)_3,5H_2O$, and $CuC_2O_4,\frac{1}{2}H_2O$. Chromium oxalate was an apparently glassy solid. Attempts to obtain further supplies of ferric oxalate indicated the existence of several hydrated forms. It was successfully prepared in a form corresponding to the formula given, as a crystalline plate-like material with a greenish-yellow appearance.

Ignition Series.—To determine the variation of surface area with heat treatment, samples were heated in air at a constant temperature for $\frac{1}{2}$ hr. and their surface areas determined. This

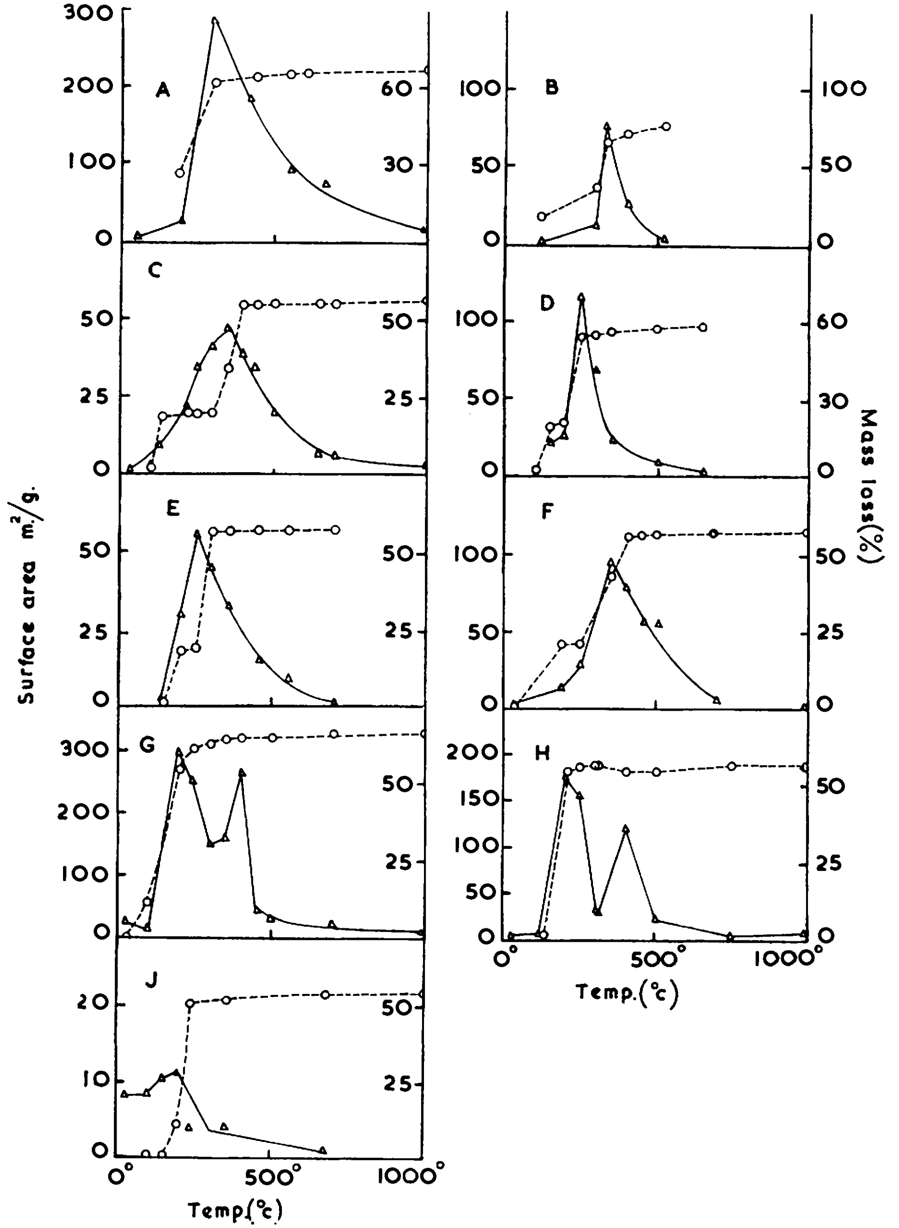

FIG. 1. Thermal treatment of various oxalates. Plots of mass loss and surface area (from nitrogen adsorption) against the temperature of heat treatment.

△ Surface area. ○ Mass loss. Oxalates of (A) Al, (B) Cr(III), (C) Zn, (D) Mn(II), (E) Co(III), (F) Ni, (G) Fe(III), (H) Fe(II), (J) Cu(II).

was repeated at a succession of temperatures, with the time of heating constant. This was sufficient time for the decomposition to occur but kept sintering to a minimum. The samples were heated in fire-clay boats which lost less then 0·001% of their weight in >1 hr. at 1000°.

Surface-area Measurements.—Nitrogen surface areas were determined by using a volumetric adsorption apparatus.[6] The adsorption was carried out at liquid-nitrogen temperatures and the surface areas were calculated by the B.E.T. method; [7] an area of 16·2 Å^2 was assumed for each nitrogen molecule in the monolayer. The samples were previously degassed under a vacuum at room temperature. Samples were stored after decomposition in sealed tubes to minimise ageing effects.

Results.—The variation in surface area and % mass loss with temperature of treatment is recorded in Fig. 1. All the oxalates gave a surface-area peak at, or immediately before, the position where the decomposition to the oxide was complete. All the resultant oxides then showed progressive sintering, exceptions being the ferrous and ferric oxalate which both showed a second sharp activation peak at 400°.

DISCUSSION

From the results given in Fig. 1 it follows that there is a general pattern of behaviour for the majority of these oxalates, exceptions being ferrous and ferric oxalates.

Dehydration might be expected to produce a surface area maximum when this property is plotted against temperature, as it conforms to the general type of reaction which could show an increase in surface area on thermal decomposition. However, no peaks were observed in this region although there is an increase in surface area which continues into the region where decomposition to the oxide takes place. In two decompositions in which the dehydration was a distinct process, the surface areas increased markedly: zinc oxalate showed an increase from 2·8 to 20·2 m.^{2} g.$^{-1}$ and manganese oxalate one from something less than unity to 22·5 m.^{2} g.$^{-1}$ (these values refer to the anhydrous oxalate content). Sintering of the anhydrous oxalate was not observed. The fact that dehydration occurs at a relatively low temperature would, however, tend to minimise sintering and maintain the surface area at a high value until the oxalate was converted into the oxide.

The production of a surface-area maximum on thermal decomposition of an oxalate to the oxide could result either from an increase in size of the particles, the total number of particles remaining constant, or from an increase in the number of particles resulting in a decrease in their size with a consequent increase in their surface area. The former process is more likely if the molecular volumes of the reactant and product are not too dissimilar. If the difference in molecular volumes is relatively great, then the strain set up within the particles will be sufficient to cause their disruption and an increase in the surface area takes place by the second process.

It can be shown that for the first process

$$V_1/V_2 = (S'_1/S_2')^{1\cdot5}, \qquad (1)$$

where V_1 = molar volume of the oxalate, V_2 = equivalent volume of the oxide, S_1' = surface area of the oxalate, and S_2' = surface area of the oxide, both S's being per g. of oxide.

For the second process

$$V_1/V_2 = (S_1'/S_2')^{1\cdot5}(n'/n)^{0\cdot5}, \qquad (2)$$

where n = number of particles of the oxalate and n' = number of particles of the oxide, present in the volumes considered. It is assumed that in each case all the particles are spherical.

The densities of most oxides are much greater than those of the salts from which they are derived and this would lead to a decrease in surface area if the first process was followed. Table 1 shows that the oxides all had a surface area greater than those of the oxalates from

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[6] Harris and Sing, *J. Appl. Chem.*, 1955, **5**, 223.

[7] Brunauer, Emmett, and Teller, *J. Amer. Chem. Soc.*, 1938, **60**, 309.

which they were derived, so, except perhaps for cupric oxalate, the second process appears to be operative. The densities of only four oxalates are readily available, namely, zinc oxalate (anhydrous and dehydrated), anhydrous manganese and cobalt oxalate, and ferrous oxalate dihydrate. The figures for the ratios V_1/V_2 and $(S_1'/S_2')^{1·5}$ are given in Table 2, these density values having been used in the calculations. This leads to an evaluation of n'/n which shows that the number of oxide particles formed from one of the oxalate particles varies over a very wide range. For zinc oxalate, for instance, $1·05 \times 10^3$ of the $4·80 \times 10^4$ particles of the final product formed from one of the original oxalate particles are, in fact, formed during the dehydration. In general it appears that the greater the ratio V_1/V_2, the greater is the number of particles formed from one of the oxalate. This is in accordance with Gregg's observation[1] that the average number of micelles formed from each crystallite of starting material should increase as the difference

TABLE 1.

Surface areas of products of thermal decomposition of oxalates referred to unit weight of oxide content.

Oxalate	Temp. (°c)	Weight loss (%)	Type of material *	Surface area per g. of material	Surface area (S') per g. of oxide
Al	Room	Nil	HA	1·0	3·8
	200°	26·0	HA–HO	25·9	73·3
	300	61·0	HO	28·6	426·8
Cr	120	17·2	HA–A	<1	<2·6
	300	36·6	A	10·5	20·8
	330	65·6	O	76·0	81·8
Zn	100	0·3	HA	2·2	5·1
	220	19·1	A	20·2	38·1
	350	33·0	A–O	46·0	71·7
	400	54·0	O	38·0	40·7
Mn	100	1·5	HA	<1	<2·3
	150	18·2	A	21·2	40·7
	195	20·8	A	25·2	46·8
	250	54·4	O	115·0	123·0
Co	Room	Nil	HA	<1	<2·38
	200°	17·2	A	28·4	53·5
	250	18·5	A–O	55·0	102·0
Ni.....................	Room	Nil	HA	<1	<2·5
	250	21·2	A	28·0	54·0
	350	42·0	A–O	95·0	134·8
Fe(III)	Room	Nil	HA	9	26·2
	150	10·3	A	4·1	10·7
	200	53·0	A–O	290	397·4
	300	63·8	O	149	157·2
	400	64·1	O	263	275·4
Fe(II)	Room	Nil	HA	<1	<2·25
	120	0·7	HA	4·2	9·4
	200	54·0	A–O	175·2	181·4
	300	58·0	O	30·2	28·6
	400	55·5	O	117	117·2
Cu(II)	100	0·9	H	8	16·0
	200	9	A–O	11	20·2

* O, Oxide; H, hydrated; A, anhydrous salt; HA, hydrated salt.
Oxides considered as reference materials: Al_2O_3, Cr_2O_3, Mn_3O_4, ZnO, NiO, Co_3O_4, Fe_2O_3, CuO.

TABLE 2.

Estimate of number of product particles formed from a single particle of original oxalate.

Metal	Diff. in sp. volume	V_1/V_2	$(S'_1/S'_2)^{1·5}$	n'/n	Metal	Diff. in sp. volume	V_1/V_2	$(S'_1/S'_2)^{1·5}$	n'/n
Fe	0·2478	5·178	0·0118	$1·93 \times 10^5$	Mn	0·2055	3·746	0·1901	$3·87 \times 10^2$
Zn	0·2076	4·97	0·0227	$4·80 \times 10^4$	Co	0·1664	3·69	0·3791	$9·47 \times 10$

in specific volume increases. Such calculations must remain only useful approximations until the porosity of the samples is established.

The first peak in the decomposition of ferrous and ferric oxalate is apparently due to increases in the surface area of the oxide by the mechanism governing equation 2. The second peak does not correspond to any chemical change. If it is accepted that an increase in surface area under thermal treatment results from a strain mechanism, then it can be argued that the second peak must result from some transition in the oxide that takes place above 300°. The second maximum could be due to a change from an amorphous to a crystalline form of ferric oxide which is variously quoted [8] as taking place within the range 380—538°. The transformation is stated to be accompanied by a " glow phenomenon " and to produce an ordered aggregate of microcrystals.[9] This would agree with an exothermic peak at 380° noted by Ugai [10] in a differential thermal analysis of ferrous oxalate. Gheith [11] has noted a similar peak in the region 310—400° for the change from an amorphous form to hæmatite, and has used *X*-ray measurements as confirmatory evidence.

The fine particles of oxide eventually formed in these decompositions would be immediately subject to sintering, the extent of which depends on the mechanism of diffusion. This is stated by Hüttig [4] to depend on the ratio of the temperature to the melting point of the oxide (T_m, in °K). Thus copper oxide (m. p. 1026°C) would be subjected to surface diffusion at 159°C (0·3 × m. p. in °K), and the oxide would be sintering rapidly as it is formed. The Tammann temperature at 648°C produces a bulk diffusion process which is shown by the fact that the oxide is a solidified " melt " after ½ hour at 1000°. The ratio T_p/T_m gives information on the type of diffusion to be expected at the temperature (T_p) at which the maximum surface area is observed (all units in °K). The values in Table 3 show that, in all cases except copper, this ratio is smaller than 0·33, which is the temperature above which surface diffusion produces sintering.[12]

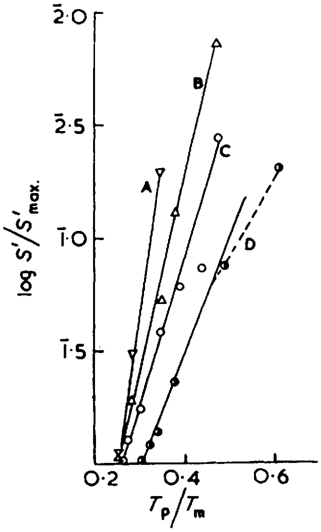

FIG. 2. Logarithmic relation between surface area and temperature of treatment for the sintering of oxides.
A, Cr_2O_3. B, Mn_3O_4. C, Co_3O_4. D, ZnO.

These thermal decomposition experiments were continued into the range where no further decomposition took place but sintering only occurred. Boswell and Iler [13] were

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[8] Gmelin, " Handbuch der anorganischen Chemie," Eisen, Teil B, Verlag Chemie, Berlin, 1930, p. 131.

[9] Boehm and Jantsch, *Coll. Czech. Chem. Comm.*, 1951, **15**, 708.

[10] Ugai, *Zhur. obschei Khim.*, 1954, **24**, 1315.

[11] Gheith, *Amer. J. Sci.*, 1952, **250**, 677; *Diss. Abs.*, 1952, **12**, 199.

[12] Jones, *Metal Treatment*, 1946, **13**, 265.

[13] Boswell and Iler, *J. Amer. Chem. Soc.*, 1936, **58**, 924.

TABLE 3.

T_p/T_m values at the maximum surface area of the oxide formed from the decomposition of oxalates.

Metal	Oxide formed	$S'_{max.}$ (m.^{2}/g.)	T_p (°K)	T_m (°K) of oxides in lit.[c]	T_p/T_m
Al	Al_2O_3	426·8	573	2283—2323°	0·247—0·251
Fe(III)	Fe_2O_3	397·4	473	1640—1863	0·254—0·288
Fe(II)	Fe_2O_3	181·4	473		
Ni	NiO	134·8	623	2230—2263	0·275—0·279
Mn	Mn_3O_4	123	523	1833—1978	0·264—0·285
	MnO [a]			1923—2058	0·255—0·272
Co	Co_3O_4	102·0	523	—	—
	CoO [b]	81·8	623	2263—2598	0·240—0·275
Zn	ZnO	71·7	623	2073—2248	0·277—0·301
Cu	CuO	20·2	473	1299—1609	0·294—0·364

[a] Value for MnO quoted because Duval [3] indicates that this is an intermediate product formed before formation of Mn_3O_4. [b] Value of CoO quoted as Co_3O_4 is converted into this at 900°. [c] Landolt-Bornstein, " Physikalish-Chemische Tabellen," Verlag Julius Springer, Berlin, 1927, Table 83; " Handbook of Chemistry and Physics," ed. C. D. Hodgman, Chemical Rubber Publ. Co., Cleveland, Ohio, 42nd edn., 1960—1961, pp. 516—686; U.S. Atomic Energy Report ANL-5750.

able to show that $\log D = kT + C$ described the behaviour of nickel oxide at various temperatures (T), where D is the number of nickel atoms across one edge of a nickel oxide lattice, and effectively measures the extent of sintering. If the ratio $S'/S'_{max.}$ represents the ratio of the surface area at absolute temperature T to the maximum surface area, and T_m is the melting point of the oxide in the same units, then by analogy $\log (S'/S'_{max.})$ should represent the extent of sintering and the graph of $\log (S'/S'_{max.})$ against T/T_m should be linear. The systems reported in this paper do show this linear relation (Fig. 2).

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