

# Variation of Surface Area During the Thermal Decomposition of Solids

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A brief review is made of the factors which affect the increase and decrease of surface area during the isothermal decomposition of a solid. In order to develop mathematical expressions to describe this process it is assumed (a) that surface area increases linearly with fraction decomposed unless there is a relaxation effect, (b) that relaxation is characterized by a single relaxation time, and (c) that sintering rate is proportional to surface area. It is found that these three assumptions lead to an adequate representation of nearly all the existing data when combined with appropriate expressions for decomposition kinetics. The equations derived are discussed and suggestions made as to suitable methods of testing them.

## 1. INTRODUCTION

The changes of surface area which accompany the thermal decomposition of many solid substances have been studied experimentally for a number of reactions.<sup>1</sup> In many cases these studies comprise surface area measurements made on residues produced after heating the solid for an arbitrary period of time at a series of temperatures. The present work, however, is concerned with the way in which surface area varies with time during isothermal decomposition.

Although the detailed mechanisms responsible for increasing surface area and for sintering are obscure a quantitative formulation of the dependence of surface area on time during thermal decomposition will be of use in interpreting existing data and in the development of future experimental work.

Gregg<sup>2</sup> discussed different possible processes according to whether the formation of the product involves straining due to a rearrangement of the crystal lattice or not. When lattice strain does not occur surface area can increase only if channels are made accessible as in the case of zeolites: this kind of process is not of interest here. The other alternative leads to collapse of the strained product lattice and the formation of micelles. Gregg refers to a product lattice in which atoms occupy the lattice points which they occupied in the reactant as a pseudo lattice and argues that this may not rearrange immediately it is formed; some doubt has been cast on the existence of a pseudo lattice defined in this way.<sup>3</sup>

Surface area changes are complicated by the fact that elevated temperatures encourage sintering so that particles in contact weld together because of the transport of atoms, leading to a reduction of surface area. Three regions of sintering can be distinguished according to the value of the parameter  $T_T$  which is the ratio of the absolute temperature to the absolute melting temperature of the solid. When  $T_T$  is less than about 0.2 adhesion is the main mechanism: from 0.2 to about 0.35 surface diffusion predominates and above 0.5 bulk diffusion is possible.

## 2. FACTORS INFLUENCING SURFACE AREA INCREASE

It is assumed that the above processes, although occurring simultaneously, do not interfere with one another. The assumption is not important with respect to the

measured rate constants but needs careful consideration if these constants are to be related to more fundamental properties of the system.

We consider first the surface area changes which result from the decomposition process, and ignore any sintering. If the initial surface area per gram of the reactant material (denoted by 1) is  $A_i$  and the average number of particles of final product produced (denoted by 2) from each initial particle is  $n_2$ , then we define a maximum attainable surface area  $A_m$  as

$$A_m = n_2^{\frac{1}{2}} \beta A_i, \quad (2.1)$$

where  $\beta$  is a constant defined in the appendix.

In eqn. (2.1) it is assumed that reaction always results in an unstrained product lattice which is formed immediately on decomposition. However, intermediates can exist which have the stoichiometric composition of the product but a distorted crystal lattice.<sup>4, 5</sup> When these intermediates are stable at room temperatures, surface area does not develop to its maximum possible value after a period of heating. The process of surface area development will be one in which nucleation from the strained metastable lattice occurs at a rate  $1/\tau$ , where it is assumed that the delaying process can be associated with a single relaxation time  $\tau$ . The temperature dependence of this quantity would be expected to have the form  $1/\tau = B \exp(-E_s/RT)$ , where  $E_s$  is the strain energy stored in the distorted lattice. Then assuming that each fraction decomposed produces the same number of monodisperse product particles, the area of material 2 contained in 1 g of product at time  $t$  when a fraction  $\alpha$  has decomposed is

$$A_2 = A'_m \alpha, \quad (2.2)$$

where  $A'_m$  is given by

$$dA'_m/dt = (1/\tau)(A'_m - A_m),$$

or

$$A'_m/A_m = [1 - \exp(-t/\tau)]. \quad (2.3)$$

Decomposition also removes the reactant so that surface area due to the presence of this material is decreasing. At time  $t$  it will be

$$A_1 = A_i(1 - \alpha). \quad (2.4)$$

The maximum number  $n_2$  of particles which could be formed from one particle of reactant would be expected to depend exponentially on temperature through an expression of the type  $n_2 = B_1 \exp(-\Delta G/RT)$ , and is related to  $A_m$  by eqn. (2.1). Here  $\Delta G$  is the free energy change which accompanies the nucleation and recrystallization process, and  $B_1$  is a pre-exponential factor. If nuclei grow at different rates at different stages in the decomposition the assumption that  $A_2 = A'_m \alpha$  may not be valid.

An alternative means of surface area increase might arise when decomposition proceeds rapidly from nuclei on the surface of small internal pores. The rate of production of gaseous material would then be balanced by its diffusion away through the pores, and if the second process is much slower than the first explosion will occur. Such a mechanism can be responsible for surface area increase when the solid is held together by weak bonds.<sup>6</sup>

### 3. SINTERING

This term is used to refer to a decrease in surface area rather than an increase in density which is customarily measured in studies of the sintering of compacts; and the surface area changes are measured on powdered materials which are not

usually compacted so that opportunities for bulk movement, at least in the early stages of the process, are limited.

The driving force for sintering is excess surface energy over some value which would be attained finally at the temperature under consideration. As surface energy is proportional to surface area then

$$dA/dt = -k_s(A - A_f), \quad (3.1)$$

where  $k_s$  is a constant which depends on  $T$ , and  $A_f$  is the surface area finally attained. Eqn. (3.1) would be expected to apply at least in the temperature region in which surface diffusion is the predominant mechanism. Unfortunately few experimental results are available which are suitable as a test of this assertion. The results <sup>7-9</sup> shown in fig. 1 indicate that eqn. (3.1) can be satisfactory when a reasonable choice of  $A_f$  is made. More complicated relations between  $A$  and  $t$  can be found,<sup>7</sup> and an empirical equation,

$$dA/dt = -k_s A t^{-m}, \quad (3.2)$$

where  $m$  is  $>0$  and  $<1.0$ , has been proposed.<sup>10</sup>

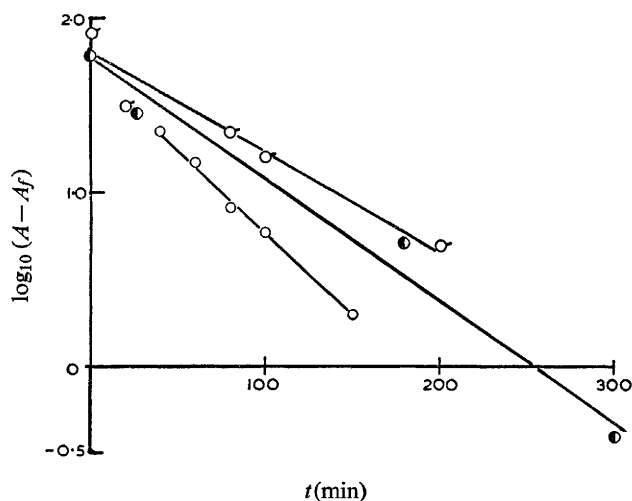


FIG. 1.—The change of surface area with time during the sintering of some oxides. ○, MgO at 550°C (time scale  $\times 0.1$ ) ref. (8); ◻, MgO at 561°C, ref. (7); ●, Fe<sub>2</sub>O<sub>3</sub> at 300°C, ref. (9).

Theoretical models for sintering <sup>11, 12</sup> are highly idealized and are usually difficult to reformulate satisfactorily in terms of surface area. The resulting expressions, involving fractional powers of  $A$ , offer little advantage and lead to equations which are mathematically intractable. As this objection also applies to empirical equations such as (3.2) we adopt eqn. (3.1) as an adequate sintering law.

#### 4. GENERAL EQUATION FOR SURFACE AREA CHANGE

In general, as  $k_s$  for the product cannot be expected to be the same as  $k_s$  for the reactant, we consider the changes in each material separately. The total surface area per gram of product (containing 1 and 2) at time  $t$  and temperature  $T$  is

$$A(T, t) = A_2 + A_1, \quad (4.1)$$

where  $A_2$  is the total surface area of all the solid 2 particles contained in 1 g of product and  $A_1$  is the same quantity for particles of solid 1. When solid 1 sinters

appreciably  $A_i$  in eqn. (2.4) must be replaced by  $A_i(t)$  which is given by eqn. (3.1) with the boundary condition  $A_i(t) = A_i$ ,  $t = 0$ . Then assuming  $A_f$  for solid 1 = 0,

$$A_i(t) = A_i \exp(-k'_s t), \quad (4.2)$$

where  $k'_s$  is  $k_s$  for solid 1. Using this with eqn. (2.4) gives

$$A_1 = A_i(1-\alpha) \exp(-k'_s t). \quad (4.3)$$

Combining eqn. (3.1) and (2.2) the rate of change of  $A_2$  is

$$\frac{dA_2}{dt} = \frac{d}{dt}(A'_m \alpha) - k_s(A_2 - A_{f_2}), \quad (4.4)$$

which has the solution

$$A_2 = \exp(-k_s t) \int \exp(k_s t) \frac{d(A'_m \alpha)}{dt} dt + C \exp(-k_s t). \quad (4.5)$$

The equations describing decomposition kinetics can be expressed in the form  $(1-\alpha) = f(t)$ ; combining this with (2.3),

$$(d/dt)[A'_m \alpha / A_m] = [1 - \exp(-t/\tau)](-f'(t)) + (1/\tau)[1 - f(t)] \exp(-t/\tau). \quad (4.6)$$

The integration in eqn. (4.5) must in general be performed by parts to give a series in powers of  $t$  which we shall denote by  $\Sigma$ .  $\Sigma$  is conveniently expressed in terms of the integral

$$\begin{aligned} \Sigma_\alpha &= \exp(-k_s t) \int \exp(k_s t) (-f'(t)) dt \\ &= f'(t)/k_s + f''(t)/k_s^2 + f'''(t)/k_s^3 + \dots, \end{aligned}$$

where  $f'(t), f''(t), \dots$ , are successive derivatives of  $f(t)$ . We now divide  $\Sigma$  into two parts, one of which depends on  $\tau$  and one which does not, thus

$$\Sigma = \Sigma_\alpha + \frac{\exp(-t/\tau)[k_s \tau \Sigma_\tau + \alpha]}{(k_s \tau - 1)} \quad (4.7)$$

where  $\Sigma_\tau$  is  $-\Sigma_\alpha$  in which  $k_s$  is replaced by  $(k_s - 1/\tau)$ . When  $t = 0$ ,  $\alpha = 0$  the series reduce to expressions denoted by  $\Sigma^\circ$ ,  $\Sigma_\alpha^\circ$  and  $\Sigma_\tau^\circ$ . Then employing the boundary conditions  $A_2 = 0$ ,  $t = 0$  we obtain

$$\begin{aligned} A_2 &= A_m[\Sigma - \Sigma^\circ \exp(-k_s t)] - A_{f_2} \exp(-k_s t) + A_{f_2} \\ &= A_m[\Sigma_\alpha - \Sigma_\alpha^\circ \exp(-k_s t)] + A_m[\Sigma_\tau \exp(-t/\tau) - \Sigma_\tau^\circ \exp(-k_s t)] \frac{k_s \tau}{k_s \tau - 1} + \\ &\quad \frac{A_m \alpha \exp(-t/\tau)}{(k_s \tau - 1)} - A_{f_2} \exp(-k_s t) + A_{f_2}. \end{aligned} \quad (4.8)$$

Combining (4.8) with (4.3) and (4.1),

$$\begin{aligned} \frac{A - A_{f_2}}{A_m} &= \Delta A = [\Sigma_\alpha - \Sigma_\alpha^\circ \exp(-k_s t)] + \\ &\quad \left\{ [\Sigma_\tau \exp(-t/\tau) - \Sigma_\tau^\circ \exp(-k_s t)] \frac{k_s \tau}{(k_s \tau - 1)} + \frac{\alpha \exp(-t/\tau)}{(k_s \tau - 1)} \right\} - \\ &\quad \frac{A_{f_2}}{A_m} \exp(-k_s t) + \frac{A_i}{A_m} (1-\alpha) \exp(-k'_s t). \end{aligned} \quad (4.9)$$

## 5. SURFACE AREA EQUATION WITH DIFFERENT KINETICS

Eqn. (4.9) provides a general expression for surface area per gram as a function of  $t$  or of  $\alpha$ . We now examine the behaviour of  $\Delta A$  predicted by the equation in a more specific manner.

The expressions for reaction kinetics which are given further consideration here are

$$(1-\alpha) = f(t) = (1-kt)^n, \quad n = 1, 2, 3, \quad (5.1)$$

which represents a contracting area or volume model<sup>13</sup> and Erofeyev's equation<sup>14</sup>

$$(1-\alpha) = f(t) = \exp(-kt^n), \quad n = 1, 2, 3, 4, 5. \quad (5.2)$$

Eqn. (5.1) leads to the general expression

$$\Sigma_\alpha - \Sigma_\alpha^\circ \exp(-k_s t) = \sum_{p=1}^{p=n} \frac{n!}{(n-p)!} \left(\frac{k}{k_s}\right)^p (1-kt)^{n-p} - \exp(-k_s t) \sum_{p=1}^{p=n} \frac{n!}{(n-p)!} \left(\frac{k}{k_s}\right)^p. \quad (5.3)$$

When the reaction kinetics are described by eqn. (5.2),  $\Sigma_\alpha$  is more complicated; the results can be expressed in terms of two series which we define as

$$\Sigma a_p = \sum_{p=1}^{\infty} -y^p, \quad \text{where } y = \frac{nkt^{n-1}}{k_s}, \quad y < 1,$$

and

$$\Sigma b_{p-1} = \sum_{p=2}^n (-)^p \frac{n!}{(n-p-1)!} \frac{k}{k_s^p} t^{n-p}.$$

A further  $(n-1)$  infinite series can now be defined in terms of these equations, the  $p^{\text{th}}$  of these being

$$\Sigma A^{p-1} = \frac{\exp(-kt)}{(1+y/k_s)k_s^{p+1}} \left[ \frac{d}{dt} \sum_{A_q^{p-2}=A_1^{p-2}}^{\infty} (-)^p A_q^{p-2} - y^b p - 1 \right], \quad 1 < p < n.$$

The first series when  $p = 1$  is not defined in this way but has the infinite sum  $[(1-y)^{-1} - 1 + y]$ ; hence  $\Sigma A^1$  when  $p = 2$  can be found, and so on. The expression for  $\Sigma_\alpha$  can be written as

$$\Sigma_\alpha = -\exp(-kt^n) \left\{ \Sigma a_p + \sum_{p=2}^n \Sigma A^{p-1} \right\}. \quad (5.4)$$

When  $\alpha \rightarrow 1$  the reaction kinetics of most solid decompositions can usually be adequately described by (5.2) with  $n = 1$ . We then obtain

$$\Sigma_\alpha - \Sigma_\alpha^\circ \exp(-k_s t) = \frac{k/k_s}{(1-k/k_s)} [\exp(-kt) - \exp(-k_s t)], \quad (5.5)$$

which is also given by (5.4) when  $k/k_s$  is  $< 1$  (making  $\Sigma a_p = -y/(1-y)$ ).

## DISCUSSION

Eqn. (5.1) implies the auxiliary condition that  $\alpha = 1.0$  when  $kt = 1.0$ . At times greater than  $1/k$  therefore the only processes which can occur are sintering, producing surface area decrease, and the relaxation process which tends to increase further the surface area. Eqn. (2.2) then becomes  $A_2 = A'_m$ , and after combining with (3.1) and solving, we obtain

$$\Delta A = \frac{\exp(-t/\tau)}{(k_s \tau - 1)} + C \exp(-k_s t). \quad (6.1)$$

The constant  $C$  is found by imposing the boundary condition  $A_2 = A'_2$ ,  $kt = 1.0$  in eqn. (4.9). When the reaction kinetics are described by eqn. (5.2) this situation does not arise because  $\alpha = 1.0$  only when  $kt = \infty$ .

Some of the different types of surface area curve which can be calculated from eqn. (4.9) are illustrated in fig. 2 and 3. In all these examples contracting area kinetics, given by the expression  $(1 - \alpha) = (1 - kt)^2$  are assumed to apply throughout the reaction. Using eqn. (4.9) and (5.3) we then obtain

$$\Delta A = [2x(1 - kt) + 2x^2 - 2x(1 + x) \exp(-k_s t)] - [2xw^2(1 - kt) + 2x^2w^3] \exp(-t/\tau) + 2xw^2(1 + xw) \exp(-k_s t) + \alpha \exp(-t/\tau)/(k_s \tau - 1), \quad (6.2)$$

where  $x = k/k_s$ ,  $w = k_s \tau / (k_s \tau - 1)$  and it is assumed that sintering of solid 1 has a negligible effect on  $\Delta A$ . The choice of a higher value of  $n$  in eqn. (5.1) or (5.2) leads to the same general shapes of curve.

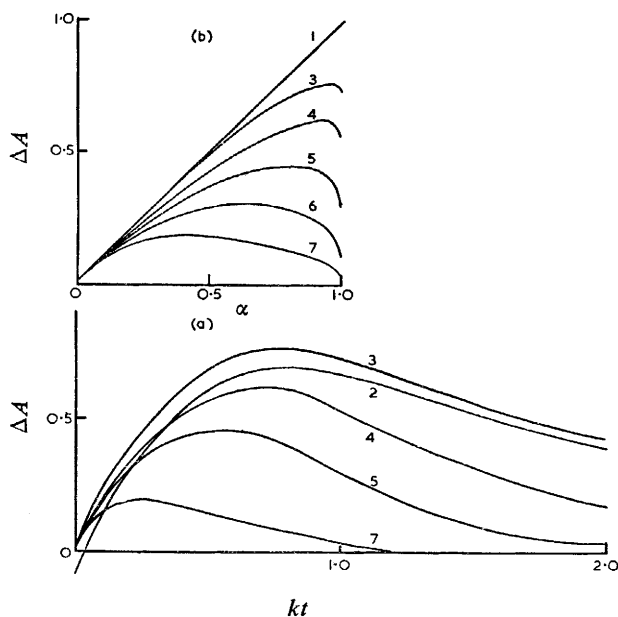


FIG. 2.—Variation of surface area with  $kt$  and  $\alpha$  for contracting area kinetics with  $\tau = 0$ . For curves 1, 3, 4, 5, 6 and 7,  $k/k_s$  has the values  $\infty$ , 2.0, 1.0, 0.5, 0.25 and 0.1 respectively;  $A_i/A_m = 0.01$  and  $A_f/A_m = 0$ . In curve 2,  $A_i/A_m = 0.01$ ,  $A_f/A_m = 0.1$  and  $k/k_s = 2.0$ .

The figures indicate that with a suitable choice of parameters, eqn. (4.9) represents nearly all the surface-area time or surface-area  $\alpha$  curves which have been described.<sup>1, 7-9, 15, 18</sup> An exception is the data of Anderson and Horlock for  $\text{Mg}(\text{OH})_2$  powder<sup>15</sup> where it is probable that surface area changes are considerably influenced by the water vapour evolved during the early stages of the decomposition. Some results for nickel oxalate decomposition are examined below but a rigorous test can only be made when suitable experimental data, which allow an independent assessment of the parameters, are available.

Some features of the curves in fig. 2 and 3 may be mentioned.

(1)  $\tau = 0$ . All the curves are convex to the  $\Delta A$  axis before the surface area maximum is reached. This maximum occurs before  $\alpha = 1.0$  and its position

depends on the ratio  $k/k_s$ . Even moderate sintering reduces the value of  $\Delta A_{\max}$  (the maximum  $\Delta A$ ) well below  $A_m$ .

(2)  $\tau \neq 0$ . Experimental curves which are concave to the  $\Delta A$  axis indicate that  $\tau \neq 0$ . Such behaviour is strongly marked in the decomposition of  $\text{MgC}_2\text{O}_4$ <sup>16</sup> and is also shown by  $\text{MgCO}_3$ <sup>20</sup> and goethite.<sup>9</sup> On the other hand, it is not necessarily true that  $\Delta A/\alpha$  curves are always concave when  $\tau \neq 0$  (although some flattening does occur).

When  $\tau \neq 0$ ,  $\Delta A_{\max}$  is generally higher for a given  $x$  than for the same  $x$  with  $\tau = 0$ . This is because  $\partial \Delta A / \partial t$  becomes larger at the critical  $kt$  value ( $k\tau$ ) than it would be if  $\tau$  were zero, whilst the counteracting effect, represented by  $k_s$ , remains unaltered.

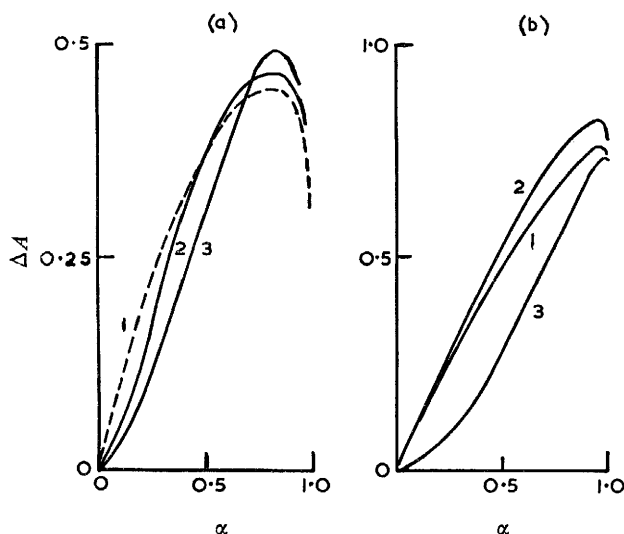


FIG. 3.—Variation of surface area with  $\alpha$ . In 3(a)  $k/k_s = 0.5$  and  $k\tau$  is 0, 0.10 and 0.20 for curves 1, 2 and 3. In 3(b),  $k/k_s = 2.0$  and  $k\tau$  is 0, 0.10 and 0.33 for curves 1, 2 and 3.  $A_i/A_m$  and  $A_f/A_m$  are both zero.

The decomposition of nickel oxalate is a reaction which conforms well to contracting area kinetics<sup>19</sup> and the surface area data for the decomposition of this material in helium are compared in fig. 4 with a curve calculated from eqn. (6.2). Values of  $x$ ,  $k\tau$  and  $A_m$  were calculated by first assuming that  $\tau = 0$  and finding an approximation to  $x$  from the value of  $\partial \Delta A / \partial t$  at the maximum together with (6.2) at this point ( $\Delta A_{\max}$ ,  $\alpha_M$ ). Second approximations to  $x$  and  $A_m$  were then found for a chosen value of  $k\tau$  using ( $\Delta A_{\max}$ ,  $\alpha_M$ ) again and further adjustments made until a satisfactory fit was obtained.

The method is tedious and, as it requires the adjustment of three parameters does not provide a rigorous test of these equations. It is carried out here merely to demonstrate that experimental results can be adequately represented. A better test of the theory can only be made when  $k$ ,  $k_s$  and  $A_m$  can be estimated independently. Also, the assumption that contracting area kinetics apply throughout the reaction is an approximation, and other kinetic equations apply equally well or better to this reaction.<sup>20</sup>

The quantities  $A_m$  and  $\tau$  are the most difficult to estimate independently. An approximation to  $A_m$  could perhaps be found from electron microscope data by



assuming that  $A_m$  is the surface area per gram which would be given by the smallest particles produced. Alternatively it is possible in some cases to find  $A_m$  from a tangent to the  $\Delta A$  against  $\alpha$  curve at  $\alpha = 0$ . Even small changes in  $\tau$  reflect considerable changes in  $A_m$ .

The equations discussed here provide a starting point for a quantitative analysis of the problem of surface area change during decomposition. No account has been taken of effects such as particle size distribution or the influence of escaping gas on sintering.

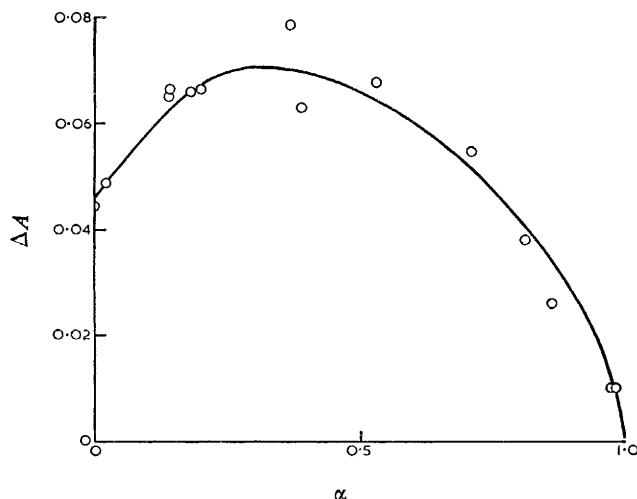


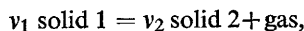
FIG. 4.—Variation of surface area with  $\alpha$ . Solid line calculated for  $n = 2$ ,  $k/k_s = 0.024$ ,  $k\tau = 0.30$ . Points are for the decomposition of nickel oxalate in He taken from ref. (16).  $\odot$ ,  $A_i = 50 \text{ m}^2 \text{ g}^{-1}$ ,  $A_m$  calculated as  $1050 \text{ m}^2 \text{ g}^{-1}$ ;  $\square$ ,  $A_i = 70 \text{ m}^2 \text{ g}^{-1}$ ,  $A_m$  calculated as  $1680 \text{ m}^2 \text{ g}^{-1}$ .

Within these limits, however, an adequate representation of experimental data can be made providing the effect of relaxation is included. Conversely it should be possible to predict the degree of dispersion which would result from a given heat treatment once the values of the relevant activation energies have been established.

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## APPENDIX

We consider the reaction



and write the molecular mass of  $v_1$  mole of solid 1 as  $M_1$  and  $v_2$  mole of solid 2 as  $M_2$ . In solid 1 there will be  $n_1$  particles in 1 g initially, i.e.,

$$n_1 = \gamma_{1,3} v_1^3 / \rho_1, \quad (\text{A1})$$

where  $\gamma_{1,3}$  is a three-dimensional shape factor and  $v_1$  a mean dimension;  $\rho_1$  is the density of solid 1. The area of 1 g of solid 1 is initially

$$A_i = n_1 \gamma_{1,2} v_1^2, \quad (\text{A2})$$

where  $\gamma_{1,2}$  is a two-dimensional shape factor.



The area required to produce 1 g of solid 2 is  $A_i M_1/M_2$ . If  $n_2$  particles are produced from one particle of solid 1 then the number produced when the initial area is  $A_i M_1/M_2$  is

$$n_1 n_2 \frac{M_1}{M_2} = n_2 \frac{M_1}{M_2} \frac{\gamma_{1,3} v_1^3}{\rho_1}. \quad (\text{A3})$$

The maximum surface area which could be produced from 1 g of solid 2 is thus

$$A_m = n_1 n_2 (M_1/M_2) \gamma_{2,2} v_2^2, \quad (\text{A4})$$

where the meaning of  $\gamma_{2,2}$  and  $v_2$  are analogous with those above for solid 1.

The number of particles in 1 g of 2 is

$$n_1 n_2 M_1/M_2 = \gamma_{2,3} v_2^3/\rho_2. \quad (\text{A5})$$

Equating (A3) and (A5) we have

$$\frac{v_1}{v_2} = \left[ \frac{\rho_1 \gamma_{2,3}}{\rho_2 \gamma_{1,3}} n_2 \frac{M_2}{M_1} \right]^{\frac{1}{3}}, \quad (\text{A6})$$

and from (A2) and (A4)

$$\frac{v_1}{v_2} = \left[ \frac{A_i \gamma_{2,2}}{A_m \gamma_{1,2}} n_2 \frac{M_1}{M_2} \right]^{\frac{1}{2}}. \quad (\text{A7})$$

Equating (A6) and (A7) gives

$$A_m = n_2^{\frac{1}{2}} \left[ \left( \frac{M_1}{M_2} \right)^{\frac{1}{2}} \left( \frac{\rho_2 \gamma_{1,3}}{\rho_1 \gamma_{2,3}} \right)^{\frac{1}{2}} \frac{\gamma_{2,2}}{\gamma_{1,2}} \right] A_i. \quad (\text{A8})$$

The quantity in square brackets is given the symbol  $\beta$  in the text.

<sup>1</sup> for a review of some of this work, see Gregg, *Surface Chemistry of Solids* (Chapman Hall, 1962).

<sup>2</sup> Gregg, *J. Chem. Soc.*, 1953, 3940.

<sup>3</sup> Goodman, *Proc. Roy. Soc. A*, 1958, **247**, 346.

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<sup>5</sup> Frost, Breck, Clayton, Ruddock and Miller, *Can. J. Chem.*, 1957, **35**, 1446.

<sup>6</sup> Gregg and Packer, *J. Chem. Soc.*, 1954, 3887.

<sup>7</sup> Gregg, Packer and Wheatley, *J. Chem. Soc.*, 1955, 46.

<sup>8</sup> Zhbroya, Sinitsyna and Roginskii, *Proc. Acad. Sci. U.S.S.R.*, 1958, **147**, 57.

<sup>9</sup> Razouk and Mikhail, *Adv. Chem. Series*, 1961, no. 33, 42.

<sup>10</sup> Rhines, *Agglomeration* (Interscience, 1962).

<sup>11</sup> Coble, *J. Appl. Physics*, 1961, **32**, 787, 793.

<sup>12</sup> McKenzie and Shuttleworth, *Proc. Phys. Soc. B*, 1949, **360**, 833.

<sup>13</sup> Jacobs and Tompkins, *Chemistry of the Solid State* (Butterworths, 1955).

<sup>14</sup> Erofeev, *C.R. Acad. Sci. U.S.S.R.*, 1946, **52**, 511.

<sup>15</sup> Anderson and Horlock, *Trans. Faraday Soc.*, 1962, **58**, 1993.

<sup>16</sup> Danes and Novakova, *Coll. Czech. Chem. Comm.*, 1960, **25**, 2477; 1962, **27**, 1105.

<sup>17</sup> Dollimore and Nicholson, *J. Chem. Soc.*, 1964, 908.

<sup>18</sup> Glasson, *J. Appl. Chem.*, 1961, **11**, 201; 1963, **13**, 111.

<sup>19</sup> Dollimore and Broadbent, private communication.

<sup>20</sup> Jacobs and Kureishy, *Trans. Faraday Soc.*, 1962, **58**, 551.