Thermochimica Acta, 38 (1980) 1—14
© Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

THE EFFECT OF HEAT TREATMENT ON THE ADSORPTION PROPERTIES OF SOLIDS. I. INTRODUCTION *

DAVID DOLLIMORE

The Chemistry Department, The University of Salford, Salford (Gt. Britain)

(Received 28 September 1979)

ABSTRACT

The use of various parameters calculated from the adsorption isotherm to follow the thermal treatment of solids is outlined. The parameters include the variation in the BET-C constant, the calculation of the apparent pore volume, the average pore radius and the pore size distribution. It is pointed out that the actual character of the adsorption isotherm can be altered by the heat treatment process. Three mechanisms of heat treatment are considered, namely, sintering, gasification of solids, and the thermal decomposition of crystals. The manner in which the specific surface area may be related to these processes is described.

INTRODUCTION

The determination of the adsorption isotherm can be used to evaluate the surface area of the solid under investigation. The adsorption isotherm usually chosen is that of nitrogen gas at -195.8°C. Besides the specific surface area, the adsorption isotherm can be used to calculate the mean pore radius or the pore size distribution and the total volume of the pores. Most adsorption isotherm equations (for example the BET equation [1]) contain an extra parameter (in the BET equation the constant C) which is either a function of the heat of adsorption or the heat of adsorption itself. Because this parameter most often does not give a good value of the heat of adsorption, it remains relatively neglected and the differences ascribed quite reasonably to the method of analysis. The process of heat treatment causes alterations in the surface area which have often been reported [2], and also differences in the other parameters calculated from the adsorption isotherm which are less often reported [3]. These comments refer to physical adsorption — the heat treatment may also cause changes in the catalytic properties of the solid residues.

The heat treatment of solids are generally of two types. In the first the solid is treated at a constant temperature — called here isothermal heat treatment. In the second the solid is treated to a rising temperature programme, usually but not always a linear rise of temperature with time. Properly handled, both heat treatments can be used to provide kinetic and thermodynamic data [4]. These treatments can, however, be interrupted, and the

---

* This and the following paper form the substance of the Mettler Award lecture delivered at the 9th NATAS Conference held in Chicago, 23—26 September 1979.

adsorptive properties of the residues investigated to provide evidence about the changes in the surface during decomposition. However, even if the material does not undergo decomposition, heat treatment can still alter the surface properties by the process of sintering. This is both a time and temperature dependent mechanism and the determination of the surface parameters from the adsorption isotherms can also help in this field [5].

THE ADSORPTION ISOTHERM AND THE BET ANALYSIS

There are five commonly recognised types of adsorption isotherm [6] — three of which exhibit a relatively sharply rising initial portion from which the surface area is calculated. The other two isotherms represent the condition where adsorbate — adsorbate interaction is more important or of the same magnitude as adsorbate — adsorbent interaction. These latter two types cannot be ignored in the context of heat treatment as many heat-treated carbons, and some heat-treated oxides show this kind of isotherm for the adsorption of water vapour [7].

The "traditional" equation used to describe the adsorption isotherm is the BET equation. The relationship is

$$\frac{p}{x(p_0-p)}=\frac{1}{x_mC}+\frac{C-1}{x_mC}\cdot\frac{p}{p_0} \qquad (1)$$

where x is the amount of gas adsorbed at pressure p, x_m is the monolayer coverage and p_0 is the saturated vapour pressure.

The constant C is a function of the heat of adsorption. The two parameters in the BET equation, x_m and C, may then be calculated from the linear plot of $p/x(p_0-p)$ against p/p_0 in the region of $p/p_0 = 0.05 \sim 0.35$. The concept of an actual monolayer existing is however a myth, as it is implicit in the BET theory that no layer (and this includes the monolayer) is complete until the saturated pressure is reached. The method nevertheless produces acceptable values for the monolayer capacity and the specific surface area. The values of C are generally large, but do not produce an acceptable value for the heat of adsorption, although in a series of samples the variation in the value of C will parallel the variation in the heat of adsorption. There are however analytical reasons for suspecting the value of C thus obtained [8]. In the first place, it is a function of the relative pressure $(p/p_0)_m$ at which the statistical monolayer value x_m is located on the adsorption isotherm, being given by

$$(p/p_0)_m=\frac{-1+\sqrt{C}}{C-1}$$

or

$$C=\frac{[1-(p/p_0)_m]^2}{(p/p_0)_m^2} \qquad (2)$$

This produces a very large variation of C with an extremely small variation in $(p/p_0)_m$ in the low pressure region in which $(p/p_0)_m$ is found. Secondly, the two measurements from the BET plot, namely the intercept and the slope, contain two factors, $1/C$ and $(C-1)/C$ and with C large, the first of these appears as nearly zero and the second approximates to unity. Attempts to calculate C from this analytical method are therefore suspect. However, the BET equation can be rearranged to give

$$C = \frac{n(1-X)^2}{X - nX(1-X)} \tag{3}$$

where $n = x/x_m$ and $X = p/p_0$. The constant C may therefore best be calculated by compiling a table of values of C against values of $(p/p_0)_m$ using eqn. (2) and reading off the value of C corresponding to the experimentally determined value of $(p/p_0)_m$. This avoids the analytical errors in determining C mentioned above but conceals the fact that eqn. (3) shows in its application that C is not a constant [9]. This escapes notice in the conventional BET plot because $1/C \to 0$, and $(C-1)/C \triangleq 1$, not just for C being constant and large, but for C being variable and large. The limits set to the BET plot are really expressions of the fact that the equation only really produces a curve describing the adsorption isotherm up to the top limit of $p/p_0 \triangleq 0.35$ and that deviations can often be seen beyond this value. This point regarding the value of C and the application of eqn. (3) on the adsorption isotherms of a series of heat-treated materials is taken up in later parts of this series.

THE CALCULATION OF THE MEAN PORE RADIUS, THE PORE SIZE DISTRIBUTION AND THE TOTAL VOLUME OF THE PORES FROM THE ADSORPTION ISOTHERM

The mean pore radius can be calculated from simple algebra applied to the adsorption isotherm [10]. It can be shown that if the amount adsorbed is expressed as a volume of condensed liquid, then

$$\frac{V_s}{S} = \frac{r}{2} \tag{4}$$

where S is the specific surface area, V_s is the volume of condensed liquid calculated from the amount adsorbed at or near the saturated vapour pressure, and r is the mean pore radius of the pores. It is thus apparent that in the heat treatment of a porous material, or a material likely to produce a porous matrix, the pore volume V_s and the mean pore radius r are useful additional factors to be calculated from the adsorption isotherm. The application of the Kelvin equation, relating the pressure at which condensation occurs on curved surfaces to the radius of curvature, allows a pore size distribution to be compiled for heat-treated materials, which contains more detail than just quoting the mean pore radius [10,11]. The Kelvin equation takes the form

$$\log p/p_0 = \frac{-2\gamma V \cos\theta}{rRT} \tag{5}$$

where γ = surface tension of adsorbate; V = molar volume of the adsorbate; θ = angle of contact; R = the gas constant; and T = the absolute temperature (K). Here p is the pressure at which condensation occurs in pores of radius r.

This equation is usually applied to the Type IV isotherms showing hysteresis and is applied to the desorption branch of the isotherm on the basis of its application to a spherical curved surface. Applied to the adsorption branch where condensation occurs in a cylindrical surface, the equation takes the form

$$\log p/p_0 = \frac{-\gamma V \cos\theta}{rRT} \tag{6}$$

The obstacle to the estimate of $\cos\theta$ is removed by assuming that the adsorbate condenses onto a surface already covered with an adsorbate layer whose amount and thickness is calculated from the BET equation. This assumption implies that $\cos\theta = 1$. This of course neglects the point inherent in the proof of the BET equation that the monolayer is not complete until $p/p_0 = 1$. The ratio x/x_m does not imply the number of layers present; if x_m is the statistical monolayer, then x/x_m is the statistical and not the actual number of layers. It is also inherent in the application of this theory that the porous structure is a series of non-intersecting cylindrical pores. Such a formalised structure is unlikely in the majority of cases, although it remains a useful approximation for comparison purposes. This has prompted the development of the so-called "modelless" method [12] in which the hydraulic radius is estimated, and then an actual pore size distribution calculated upon the assignation of a geometrical structure to the pores. The pore size distribution method in practice leads in the majority of cases to a distribution of pore sizes around a single peak, or a bimodel distribution, but rarely more than this. The information usually quoted from these pore size distributions is usually the value of the radius at these peaks of distribution; less often, the volume contribution at these peak values is quoted. It is worth noting that information of this kind could be gained directly from the adsorption isotherm without reference to the complicated process of pore size distribution. This point will be raised in connection with heat-treated materials in other parts of this series.

TYPE I ADSORPTION ISOTHERMS

In this type of isotherm the amount adsorbed simply rises to a limiting value, usually at a low value of p/p_0 and then remains almost constant for the remainder of the adsorption isotherm. In theory, it is associated with an adsorbed layer one layer thick, but in most physically adsorbed systems it is probably associated with a pore structure where the size of the pores is of the same magnitude as the adsorbate molecule [13]. In this respect it is probably best to adopt the notation of Dubinin [14], namely that the term micropores applies to pores with a diameter less than 20 Å, mesopores with diameters in the range 20—300 Å, and macropores with diameters larger than 300 Å. This type of adsorption isotherm, i.e. Type I, is often found with carbons [7], and the correct interpretation of the adsorption data can be important in following the oxidation of carbon to gaseous products; there is a need to locate the surface where the oxidation process is taking place [15]. An alternative procedure in investigating structures of this type is to look at the adsorption capacity at a p/p_0 value near to saturation for a series of different sized adsorbate molecules and interpreting this in terms of the pore size volume available to the differently sized molecules [13].

CHEMISORPTION AND CATALYSIS

One purpose of heat treatment of solids is to prepare catalysts. The actual activity of the catalyst varies with the heat treatment [16]. Whereas physical adsorption is a process which gives a measure of the overall surface area of the solid, the catalytic process of, for example, cumene cracking on an aluminosilica catalyst can be used to relate this particular activity against the temperature of treatment of the alumino-silicate. Chemisorption of pyridine can be used in the same sense, in this case to determine the activity of the alumino-silicate in terms of acid sites against the heat treatment, and to compare this with the number of hydroxyl sites determined by thermogravimetry. This forms the topic of work reported later in this series. This is simply one illustration of the way in which chemisorption and catalytic processes can be used to judge the activity of a heat-treated oxide and there are many more examples that can be drawn from this field.

HEAT TREATMENT OF SOLIDS THAT SINTER WITHOUT DECOMPOSITION

Materials receiving heat treatment without decomposition undergo a sintering process defined here as an increase in particle size with a decrease in surface area. By following the variation in surface area of, for example, zinc oxide it can readily be shown that the sintering process is a function both of temperature and time [5]. It can be seen from isothermal heating runs that the decrease in surface area occurs towards an equilibrium value determined by the initial physical condition of the oxide and the temperature of the experiment. The process of sintering is to cause a growth in particle size by a mechanism of diffusion. Assuming a constant rate of growth per unit area under isothermal conditions, the sintering process is that of a contracting interface per unit mass of material, involving coalescence of adjacent particles with a decrease in their number. Provided the basic process of diffusion remains the same, the Arrhenius equation can be applied to calculate the activation energy associated with the process. Heating the oxide so that sintering occurs at different temperatures means that the possibility exists that the process of diffusion can alter, and the most obvious change is a change from surface to volume diffusion.

Three processes may be distinguished [17]:

(1) adhesion between particles leading to the formation of siezed joints at points of contact;

(2) surface diffusion, in which coalescence of particles is accelerated by movement of chemical species along the surface; and

(3) bulk diffusion, in which further coalescence is brought about by diffusion of chemical species through the bulk material.

These phenomena occur in the above order as the temperature is increased. Sufficient evidence exists to suggest that the various mechanisms become operative at defined temperatures often expressed as a fraction of the melting point in degrees Kelvin. Thus, if $a = T/T_m$, where T_m = melting point in degrees Kelvin, then surface diffusion occurs in the range $a = 0.33 \sim 0.45$, whilst bulk diffusion is operative beyond $a = 0.5$, often called the Tamman temperature. Adhesion between joints is supposed to take place at much lower temperatures than those indicated above. As most organic compounds have melting points below 300° C, it can be seen that any decomposition processes in organic materials are taking place in a temperature range where bulk diffusion is operative, and in fact many decompositions may be observed to take place either with liquefaction or partial liquefaction. It is this which reduces the adsorptive capacity of solid residues in most organic decompositions to values below the detection limits of the usual adsorption apparatus. It is therefore unusual to find adsorption experiments used to gain information in the decomposition of the usual organic compounds. An exception is the degradation of some polymeric materials to carbons, where large adsorptive capacities may be observed as the amorphous carbon is formed with a progressively rising temperature of reaction.

The simplest expression for the variation of surface area in the region where diffusion is to be expected [18,19] is

$$\frac{dS_t}{dt} = -k_s(S_t - S_f) \tag{7}$$

for an isothermal experiment, where S_t is the surface area at any time t and S_f is the surface area at $t = \infty$, when the rate has diminished to zero, and k_s is a rate constant. Hence

$$\ln(S_t - S_f) = -k_s\,t + \text{const.} \tag{8}$$

It has been shown that an expression of this kind applies to the sintering of zinc oxide [5] and in further parts of this series it will be shown that it also applies to other oxide systems. Actually, most sintering data have been expressed in terms of the alteration of particle size or the increase in size of the junction between the particles. In order to compare observations on particle size with those on surface area, the relationships $D = 3/Sp$ can be used, where D = equivalent particle diameter, S = specific surface area and p = oxide density. In this way, plots of the variation of particle size may be constructed from surface area observations and the data used to test sintering expressions put forward in terms of these properties. Thus the expression put forward by Lee and Paravano [20] when expressed in terms of surface area changes takes the form

$$\ln(S_t - S_f) + \frac{\ln(S_t + S_f)}{(S_t S_f)^2} = \text{const.}\ t + \text{const.} \tag{9}$$

This has an extra term when compared with eqn. (8). The two are, however, compatible, for it can be shown experimentally [5] that

$$\frac{\ln(S_t + S_f)}{(S_t S_f)^2} = \text{const.}\ \ln(S_t - S_f) \tag{10}$$

In the relatively few experimental systems where the temperature range spans both the regions where surface diffusion processes take place, it can be seen that each region is characterised by its own energy of activation [21].

THE VARIATION OF SURFACE AREA IN GASIFICATION REACTIONS

The situation is simplified here because for the gasification process

A + gas → gaseous products

the surface area of the solid residue may represent the reaction interface.

The traditional isothermal treatment may be considered. If α represents the fraction decomposed, and t the time, then for a zero-order reaction

$$\frac{d\alpha}{dt} = k \tag{11}$$

and

$$\alpha = kt + C \tag{12}$$

so that plots of α vs. t should be linear.

If the reaction is first order

$$\frac{d\alpha}{dt} = k(1 - \alpha) \tag{13}$$

and

$$\log(1 - \alpha) = kt + C \tag{14}$$

then plots of $\log(1 - \alpha)$ vs. t and values of $d\alpha/dt(1 - \alpha)$ should be constant.

For second or higher orders

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \tag{15}$$

where $n \geqslant 2$, therefore

$$t = \frac{1}{k(n-1)}\,\frac{1}{(1-\alpha)^{n-1}} + \text{const.} \tag{16}$$

and plots of t vs. $1/(1 - \alpha)^{n-1}$ should be linear. If the rate-controlling step is to be the chemical reaction between the solid and the gas at the surface of the solid, then the above expressions must be related to the geometry of the interface to make sense. There are several simple models.

Model 1

Consider a system of n spherical impervious particles. On the assumption of a constant rate unit of surface area, then the weight loss W is given by

$$W = pn(\tfrac{4}{3}\pi r^3 - \tfrac{4}{3}\pi(r - tx)^3) \tag{17}$$

where p = density of solid; r = original radius of particles; x = depth of surface gasefied per unit time; and t = time in secs (or whatever unit is convenient).

This is usually expressed in terms of fraction decomposed when

$$\alpha = \frac{r^3 - (r - tx)^3}{r^3}$$

$$= 1 - \frac{(r - tx)^3}{r^3}$$

$$= \frac{tx}{r^3}(3r^2 - 3txr + t^2x^2) \tag{18}$$

and

$$(1 - \alpha)^{1/3} = \frac{r - tx}{r}$$

$$= 1 - \frac{tx}{r} \tag{19}$$

which is usual "contracting sphere" law [4].

The expansion for $\mathrm{d}\alpha/\mathrm{d}t$ is

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{3x}{r}\left(1 - \frac{tx}{r}\right)^2 \tag{20}$$

or

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)^{1/2} = C - C\frac{tx}{r} \tag{21}$$

where $C = \left(\frac{3x}{r}\right)^{1/2}$

which could be used for identification purposes. However, the first-order test is that $\mathrm{d}\alpha/\mathrm{d}t(1 - \alpha)$ should be constant, but in this case is given by

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t(1 - \alpha)} = \frac{3x}{(r - tx)} \tag{22}$$

Nevertheless, if terms in x^2 or greater powers of x are ignored, then

$$\alpha = At \tag{23}$$

where $A = 3x/r$.

Then

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A \tag{24}$$

and

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t(1 - \alpha)} = \frac{A}{(1 - At)} \tag{25}$$

which satisfies the zero-order reaction. This approximation is only true when

$r >> tx$, so that it appears either in the initial stages of the reaction or for very large spherical particles. Other shaped particles, i.e. cubic shapes, can be treated in a similar manner.

Model 2

Consider a system consisting of a single matrix with large pores running through it. The pores must be sufficiently large to present no diffusional problems. Let the initial radius of the pores be r and their total length L. Both these terms could probably be calculated from other data (e.g. the adsorption isotherm on the original material), then

$$\alpha = \frac{(\rho\pi(r + tx)^2 L - \rho\pi r^2 L)}{W_0}$$

$$= \frac{\rho\pi L}{W_0} \cdot tx(2r + tx) \qquad (26)$$

where W_0 = initial weight of sample.

Writing $A = \rho\pi L/W_0$

then

$$\alpha = Atx(2r + tx)$$

$$= 2Axr + Ax^2t^2 \qquad (27)$$

Similarly,

$$\frac{d\alpha}{dt} = 2Axr + 2Ax^2t$$

$$= 2Ax(r + xt) \qquad (28)$$

and

$$\frac{d\alpha}{dt(1 - \alpha)} = \frac{2Ax(r + xt)}{1 - Atx(2r + xt)} \qquad (29)$$

Some simplification can be achieved if $R >> xt$, when

$$\alpha = 2Atxr \qquad (30)$$

$$\frac{d\alpha}{dt} = 2Axr \qquad (31)$$

and

$$\frac{d\alpha}{dt(1 - \alpha)} = \frac{2Axr}{1 - 2Atxr} \qquad (32)$$

This should hold when very large pores are present, or in initial stages of reaction. In any case, towards the end of the reaction the geometrical system upon which this is based would no longer hold; so in many cases plots of $\alpha \sim t$ should be linear and $d\alpha/dt$ should be constant.

Model 3

An even simpler system is to assume that the surface area remains constant. There is evidence available that suggests that this is true in some systems after about 5% burn-off; then

$$\alpha = Sxt\rho \tag{33}$$

where S is the specific surface area

$$\frac{d\alpha}{dt} = Sx\rho \tag{34}$$

and

$$\frac{d\alpha}{dt(1-\alpha)} = \frac{Sx\rho}{1-Sxt\rho} \tag{35}$$

Geometrical models can be fitted to this set of conditions, e.g. a material consisting of large flat plates where the principal reaction interface involved was the two flat faces of the plate.

The interesting point arising from all these models is that although the corresponding form of the burn-off process can be seen in the analogous experimental determinations of $\alpha = f(t)$ and $d\alpha/dt$ or $d\alpha/dt(1-\alpha)$ as a function of time, the reaction interface involved is not necessarily the surface area determined from the adsorption isotherm. The kinetic data can be converted into reaction interface data using the Polanyi—Wigner expression [22] in the form

$$-\frac{dz}{dt} = N_0 \nu \, e^{-E/RT}$$

$$= \left(\frac{r\rho N}{M}\right) \nu \, e^{-E/RT} \tag{36}$$

where N_0 = number of molecules per cm^2, ν = frequency of vibration of atoms in the solid lattice $\simeq 10^{13}$ sec^{-1}; r = distance between atoms in the solid lattice; M = atomic weight; ρ = density; N = Avogadro's Number; and $-dz/dt$ = number of molecules decomposing sec^{-1} cm^{-2}.

This would produce a value of x used in all the kinetic expressions and allow plots of the variation in reaction interface area to be plotted against the measured variation in specific surface area from adsorption experiments. This will be done in later papers in this series.

THE VARIATION OF SURFACE AREA IN THE THERMAL DECOMPOSITION OF OXYSALT SYSTEMS

The general reaction to be considered here is

$$A(s) \rightarrow B(s) + \text{gaseous products}$$

Here A could be an oxysalt such as a carbonate, and B a product oxide, whilst the gaseous product would be carbon dioxide. Not all such decompositions are so simple and the possibility of reaction with the atmosphere must always be examined [23]. The situation is complicated by the fact that the reaction interface is not necessarily the surface area, as a layer of oxide product is built up covering the reaction interface as the process of decomposition continues. Other complicating factors are the real consideration that must be given to diffusion problems as the product gas must diffuse away from the reaction interface through a layer of product oxide, and further complications are the change in volume, due to differences in density between oxysalts and their corresponding oxides causing a distortion of the geometrical system, and finally a break-up of particles under the strain imposed upon them by this process [24]. This break-up of the particles means that the particle radius will diminish with an increase in the number of particles in the system, resulting in an observed increase in specific surface area as determined by adsorption. This is opposed by the sintering processes discussed earlier [17]. There is thus an increase in surface area followed by a diminution. The maximum surface area recorded coincides with the point where the strain cannot be contained within the original lattice structure, but it does not necessarily coincide with the completion of the chemical reaction. The treatment correlating the kinetics with this kind of change in the surface area has been set out in a general fashion [18] but may be cited here for a specific kinetic behaviour [19].

Let the surface area due to the activation, S_a, be proportional to the fraction decomposed, i.e.

$$S_a = k_1 a \qquad (37)$$

Suppose in the decomposition the contracting sphere equation holds of the type

$$1 - (1 - \alpha)^{1/3} = k_2 t \qquad (38)$$

which rearranges to

$$\alpha = 1 - (1 - k_2 T)^3 \qquad (39)$$

then

$$S_a = k_1[1 - (1 - k_2 t)^3]$$

$$= k_1 k_2 t(3 - 3k_2 t + k_2^2 t^2) \qquad (40)$$

Differentiating

$$\frac{dS_a}{dt} = k_1 k_2 (3 - 6k_2 t + 3k_2^2 t^2)$$

$$= 3k_1 k_2 (1 - k_2 t)^2 \qquad (41)$$

Let the sintering be described by

$$\frac{dS_s}{dt} = -k_4 S \qquad (42)$$

(this is one of the simplest expressions, and the other more complicated equations may be used instead).

The overall rate of change of surface area is then

$$\frac{dS}{dt} = 3k_1k_2(1 - k_2t)^2 - k_4S$$

$$= A(1 - Bt)^2 - CS \tag{43}$$

where A, B and C are substituted for the various functions of k to simplify the expression. Rearrangement gives

$$\frac{dS}{dt} + CS = A(1 - Bt)^2 \tag{44}$$

The corresponding expression after integration takes the form

$$S = A'[E - Ft + Gt^2] + \text{const.} \tag{45}$$

where A', E, F and G are substituted for various functions of k to simplify the expression.

In addition, the combination of density and surface area data provides an illustration of the effect of increase in the number of particles brought about by the activation process. If the original salt consists of n particles mole^{-1} with a molar volume and molar surface area of V_1 and S_1 then

$$V_1 = \frac{M_1}{\rho_1} = \tfrac{4}{3}\pi n_1 r_1^3 \tag{46}$$

where M_1 = gram molecular weight; ρ_1 = density; and r_1 = the average radius of the particles.

The molar surface area of the original unreacted material can be expressed by

$$S_1 = s_1M_1 = 4\pi n_1 r_1^2 \tag{47}$$

where s_1 = the experimental surface area in m^2 g^{-1}.

It therefore follows that

$$r_1 = \frac{3V_1}{s_1} \tag{48}$$

and

$$r_1 = \left(\frac{s_1}{4\pi n_1}\right)^{1/2} \tag{49}$$

In the decomposition process the oxysalt produces n_2 particles mole^{-1} with a molar volume and molar surface area of V_2 and S_2, respectively. As before

$$V_2 = \frac{M_2}{\rho_2} = \tfrac{4}{3}\pi n_2 r_2^3 \tag{50}$$

and

$$S_2 = s_2M_2 = 4\pi n_2 r_2^2 \tag{51}$$

where M_2 = the effective molecular weight of partially decomposed reacted material; S_2 = the experimental surface area in $m^2\ g^{-1}$; ρ_2 = density; and r_2 = average radius of the particles.

Again, it follows that

$$r_2 = \frac{3V_2}{S_2} \tag{52}$$

and

$$r_2 = \left(\frac{S_2}{4\pi n_2}\right)^{1/2} \tag{53}$$

The ratio of these two radii is given by

$$\frac{r_1}{r_2} = \frac{V_1 S_2}{V_2 S_1} \tag{54}$$

or

$$\frac{r_1}{r_2} = \left(\frac{S_1 n_2}{S_2 n_1}\right)^{1/2} \tag{55}$$

and

$$\frac{V_1}{V_2} = \left(\frac{S_1}{S_2}\right)^{3/2}\left(\frac{n_2}{n_1}\right)^{1/2} \tag{56}$$

If the number of particles remains the same

$$\frac{V_1}{V_2} = \left(\frac{S_1}{S_2}\right)^{3/2} \tag{57}$$

but the thermal data shows this latter result is rarely found and more often $n_2 > n_1$.

If the molecular weight of the original reactant material is designated as M_1 and of the final product as M_3, then the "effective" molecular weight of the partially reacted material M_2 can be estimated by use of the relationship

$$M_2 = (1 - \alpha) M_1 + \alpha M_3 \tag{58}$$

where α = fraction decomposed. Thus the molar surface area of the partially reacted material is given by

$$S_2 = s_2 \{(1 - \alpha) M_1 + \alpha M_3\} \tag{59}$$

This allows the variation of the ratio of particles (n_2/n_1) to be followed during the course of either an isothermal decomposition or a TG experiment.

CONCLUSION

It can be seen that in the course of a decomposition, the nature of the adsorption isotherm may be altered either by a change in the porous structure or by an alteration in the value of C in the description of the analysis by the BET equation. The values of the mean pore radius, the total pore volume and, in particular, the estimate of the specific surface area can be used to explain the processes of thermal decomposition. This can be used to follow the mechanism of sintering, the gasification reactions of the type A(s) + gas → gaseous products and decompositions of oxysalts of the type A(s) → B(s) → gaseous products.

REFERENCES

1 S. Brunauer, P.H. Emmett and E. Teller, J. Am. Chem. Soc., 60 (1938) 309.
2 See S.J. Gregg, The Surface Chemistry of Solids, Chapman and Hall, London, 1961.
3 R.Sh. Mikhail, D. Dollimore, A.M. Kamel and N.R. El-Nazer, J. Appl. Chem. Biotech., 23 (1973) 431.
4 See C.J. Keattch and D. Dollimore, An Introduction to Thermogravimetry, Heyden, London, 1975.
5 D. Dollimore and P. Spooner, Trans. Faraday Soc., 67 (1971) 2750.
6 S. Brunauer, L.S. Deming, W.S. Deming and E. Teller, J. Am. Chem. Soc., 62 (1940) 1723.
7 A.N. Ainscough, D. Dollimore and G.R. Heal, Carbon, 11 (1973) 189.
8 D. Dollimore, J. Oil Colour Chem. Assoc., 54 (1971) 616.
9 D. Dollimore and P. Spooner, J. Appl. Chem. Biotech., 24 (1974) 35.
10 S.J. Gregg and K.S.W. Sing, Adsorption, Surface Area and Porosity, Academic Press, New York, 1967.
11 D. Dollimore and G.R. Heal, J. Appl. Chem., 14 (1964) 109.
12 S. Brunauer, R.Sh. Mikhail and E.E. Bodor, J. Colloid Interface Sci., 24 (1967) 451.
13 D. Dollimore and G.R. Heal, Trans. Faraday Soc., 59 (1963) 2386.
14 M.M. Dubinin, J. Colloid Interface Sci., 2 (1967) 487.
15 D. Dollimore and A. Turner, Trans. Faraday Soc., 66 (1970) 2655.
16 D. Dollimore and K.H. Tonge, J. Chem. Soc. B, (1967) 1380
17 S.J. Gregg, J. Chem. Soc., (1953) 3940.
18 D. Nicholson, Trans. Faraday Soc., 61 (1965) 990.
19 D. Dollimore and D. Tinsley, J. Chem. Soc. A, (1971) 3043.
20 V.J. Lee and G. Paravano, J. Appl. Phys., 30 (1959) 1735.
21 D. Dollimore and T.E. Jones, J. Appl. Chem. Biotech., 23 (1973) 29.
22 M. Polanyi and E. Wigner, Z. Phys. Chem., Abt. A, 139 (1929) 439.
23 D. Dollimore and D.L. Griffiths, J. Therm. Anal., 2 (1970) 229.
24 D. Dollimore and D. Nicholson, J. Chem. Soc., (1962) 960.