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A CONSIDERATION OF THE ROLE OF SINTERING IN GAS—SOLID INTERACTIONS

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ABSTRACT

An analysis of the role of sintering in gas—solid interactions involving particulate materials is presented. Application of this analysis to decomposition and sintering data for calcium carbonates demonstrates that changes in the porosity caused by sintering proceed at too low a rate to have a significant effect on the decomposition process for this material. For reactions with mass-transport control it is shown that sintering can have a more direct influence on the decomposition rates.

INTRODUCTION

Despite the abundance of thermodynamic and kinetic data on gas—solid interactions, there appears to be a total absence of investigations concerned with concomitant sintering and aggolomeration of reactant or product particulate samples during dissociation or reduction reactions. Such reactions can be represented by the general forms

$$A(s) \rightleftharpoons B(s) + C(g) \qquad (1)$$

and

$$D(s) + E(g) \rightleftharpoons F(s) + G(g) \qquad (2)$$

Examples of these are encountered in the dissociation of metal carbonates and in the reduction of metal oxides by hydrogen, respectively. References have been made regarding the existence [1] and absence [2,3] of sintering in the dissociation of calcium carbonate and in the reduction of iron oxide [4]. In the latter of these reports [4] indirect evidence is presented to substantiate the occurrence of sintering in the reduced iron layer during the reduction reaction. Obviously, changes in the parameters of porosity, particle size, pore size, and surface area resulting from sintering of either the reactant or product layer will alter the kinetics of gas—solid reactions of the types discussed above.

The use of samples in the form of loose powders in gas—solid reactions gives rise to ill-defined physical conditions for the reaction and is likely to be a major source of the controversy concerning the kinetic data. While facilitating the delineation of the prevailing physical conditions, the use of compacted powders does not clarify the picture to a significant extent. In typical experiments, spherical samples of 0.5—1.0 cm diameter are suspended inside a heating zone and monitored gravimetrically as a function of time. Weight loss measurements, sometimes supplemented by interface velocity observations, are used to generate kinetic data for the reactions. For such a sample geometry, in the case of dissociation reactions, the interface moves inwardly from the surface of the sphere. In a typical case of dissociation, e.g. of $CaCO_3$ in accordance with eqn. (1), the resulting calcium oxide is at too low a temperature to sinter during the course of the reaction, however, the decomposing $CaCO_3$ phase is at a temperature over which sintering does occur. Experimental evidence of extensive sintering at temperatures as low as 820°C has been previously reported [5] and recently confirmed [6]. Dissociation experiments have been conducted at temperatures exceeding 900°C for samples with initial porosities as high as 66% (i.e. with a green density of 34%). Thus the calcium carbonate phase will sinter and dissociate simultaneously. In the case of the reduction of iron oxide by hydrogen [4], the average pore size in the resulting iron layer was observed to change during the reaction. Since diffusion of the product gas through the resulting solid layer has been demonstrated to be Knudsen type [7], changes in the pore size will have a direct influence on the flux of this gas and thus reaction rate.

ANALYTICAL TREATMENT

In gas—solid kinetic studies utilizing powder compacts, the rates of reactions have been typically monitored through gravimetric measurements or reaction front velocity determinations. A schematic of a spherical compact geometry is shown in Fig. 1, where r is the instantaneous radius of the reaction interface, and r_0 is the original radius of the unreacted sphere. From mass conservation criteria, the rate of consumption of the reactant is

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -4\pi \rho_m r^2 \frac{\mathrm{d}r}{\mathrm{d}t} \tag{3}$$

where n is the number of moles of the reactant, ρ_m is the molar density of the reactant, r is the radius of the reaction front, and t is time. If we assume that the reaction is chemically controlled, then the rate is directly proportional to the gas pressure, i.e.

$$\frac{\mathrm{d}n}{\mathrm{d}t} = 4\pi r^2 \frac{k_c}{RT}(P_{eq} - P_g) \tag{4}$$

where k_c is the rate constant, P_{eq} is the pressure of the gas in equilibrium with the reactant and product, P_g is the actual pressure of the gas phase, T is the absolute temperature, and R is the gas constant. In the derivation of eqn. (3) the compact is assumed to have a theoretical density. This assump-

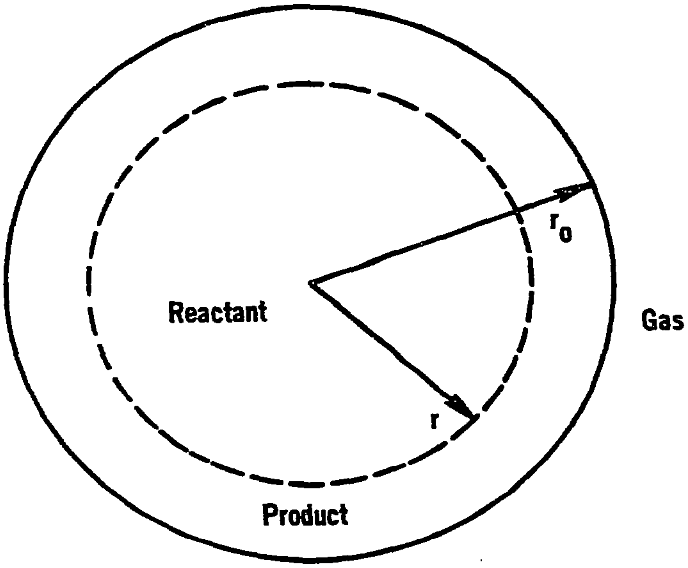


Fig. 1. Geometry of a decomposing spherical sample.

tion is obviously not valid for experimental configurations using compacted powders. Although some compacts are sintered prior to their use in these decomposition reactions, their densities remain less than the theoretical value. Thus for the general case

$$\frac{dr}{dt} = -\tfrac{4}{3}\pi r^3 \left[\frac{d\rho}{dt} + \frac{3}{r}\rho\,\frac{dr}{dt}\right] \tag{5}$$

Combining eqn. (5) with eqn. (4) gives

$$\frac{dr}{dt} = -\frac{1}{\rho}\left\{\frac{k_c}{RT}(P_{eq} - P_g) + \frac{r}{3}\frac{d\rho}{dt}\right\}\,. \tag{6}$$

The solution of eqn. (6) depends on the dependence of ρ on time and on the nature of the kinetically controlling step. As a first solution, we assume ρ to be independent of time. This would be the case where the reactant is not undergoing sintering or is sintering by a surface transport process which does not contribute to densification [8]. Equation (6), therefore, becomes

$$\frac{dr^*}{dt} = -\frac{k_c}{(1-\epsilon)\rho_t RT r_0}[P_{eq} - P_g] \tag{7}$$

where ϵ is the porosity of the reactant, ρ_t is its theoretical density, r^* is the normalized radius r/r_0, and r_0 is the initial radius of the reactant compact. For such a case the dependence of the velocity of the reaction front on pressure is a function of sample porosity, as depicted schematically in Fig. 2. Under isothermal conditions and at constant pressure, the time dependence of the normalized radius is calculated by integrating eqn. (7) with the limits of r^* =

1 at $t = 0$ to r^* at t. The resultant equation is

$$r^* = 1 - \frac{k_c(P_{eq} - P_g)}{(1-\epsilon)\rho_t RTr_0} \cdot t \tag{8}$$

At constant temperature, pressure, and geometry, the relation between r^* and t can be described by a general form

$$r^* = 1 - \frac{K_1}{(1-\epsilon)} \cdot t \tag{9}$$

where K_1 is a time-independent constant whose value is determined by the parameters of eqn. (8). The influence of porosity, ϵ, on the normalized reaction front radius is shown in Fig. 3 for various values of the dimensionless quantity $K_1 t$ ranging from 10^{-2} to 5×10^{-1}. These values essentially cover the entire range of possible real values of r^* and ϵ, although the theoretical limits are $0 \leqslant K_1 t \leqslant 1.0$.

Next we examine the case where $\rho = \rho(t)$. This condition represents a case where sintering is accompanied by densification. For this, the time dependence of density can be obtained from the relationship

$$\left[\frac{\rho - (1-\epsilon_0)\rho_t}{(1-\epsilon_0)\rho_t}\right]^{N/2} = Bt \tag{10}$$

where ϵ_0 is the initial porosity of the reactant, B is a constant containing

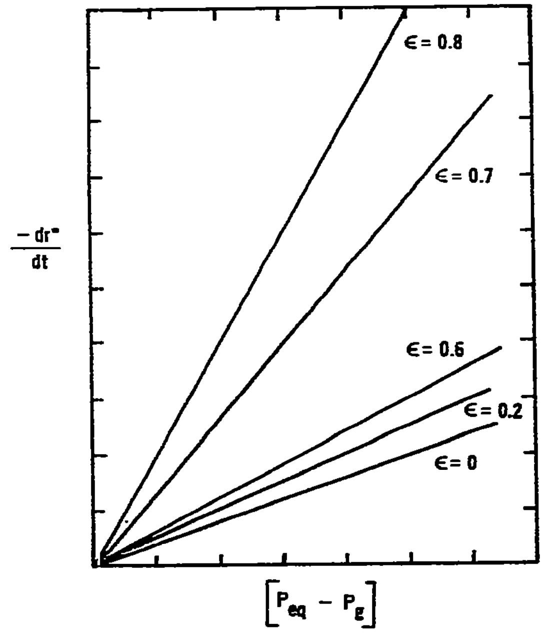


Fig. 2. The dependence of the reaction front velocity on the gas pressure for various sample porosities.

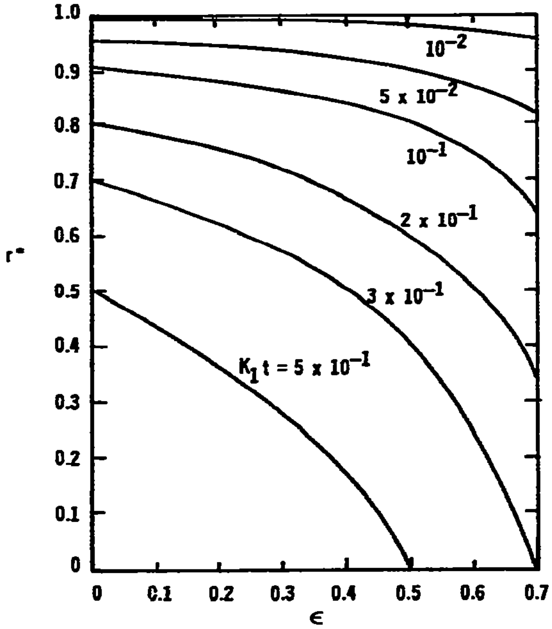


Fig. 3. The influence of porosity on the normalized reaction front radius.

materials property [9], and N is a constant with a value depending on the rate-controlling sintering mechanism [9]. The time dependence of ρ is then determined from eqn. (10) and substituted into eqn. (6), using the normalized radius

$$\frac{\mathrm{d}r^*}{\mathrm{d}t} = -\frac{1}{r_0 \rho}\left\{\frac{k_c}{RT}[P_{\mathrm{eq}} - P_{\mathrm{g}}] + \frac{r}{3}[(1-\epsilon_0)\rho_t B^{2/N}\, t^{(2/N-1)}]\right\} . \tag{11}$$

This equation can be simplified to

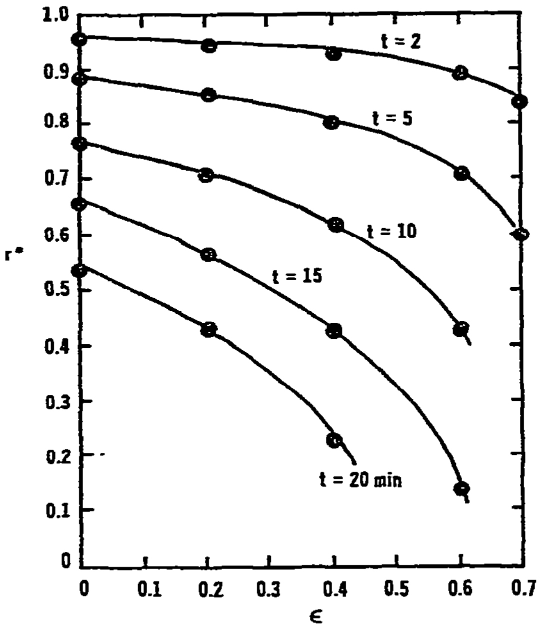
$$\frac{\mathrm{d}r^*}{\mathrm{d}t} = -\frac{1}{(1-\epsilon)}\;[K_1 + K_2 r^* t^{(2/N-1)}] \tag{12}$$

where K_1 is as previously defined and $K_2 = (1-\epsilon_0)B^{2/N}/3$.

DISCUSSION

The validity of the derived relationship of eqn. (8) is based on reactions which are controlled by chemical kinetics and those in which the density of the reactant is independent of time. To evaluate K_1 of eqn. (9) and give absolute values of r^* as a function of time, we examine the results of an investigation by Campbell et al. [7]. These authors investigated r^* vs. t as a function of ϵ for the decomposition of $CaCO_3$ at 900° C. Using these results K_1 values are calculated through eqn. (9) and are reported in Table 1 for various values of r^*. An average K_1 value of 2.3×10^{-2} (min^{-1}) is obtained. With this latter value, the relationship of r^* with ϵ is shown in Fig. 4. These results indicate that at moderate reaction times (~20 min) relatively small changes in the porosity of $CaCO_3$ give rise to significant changes in the reaction front velocity. For example, at $t = 20$ min a change in the porosity from 0.3 to 0.4 leads to a 32.4% increase in the average reaction front velocity.

In order to assess the role of sintering in the decomposition of calcium carbonate, the magnitude of densification due to sintering for this compound must be determined. The results of a recent investigation [6] of the sintering of $CaCO_3$ compacts at 700° C in 1 atm of CO_2 showed that the rate of densification of this compound at this temperature is slow. Over a 24 h period the change in porosity is less than 3%. In terms of the results shown in Fig. 4, this means that for a 30 min sintering the change in ϵ is approximately 8×10^{-3}. Since these sintering time data were obtained at 700° C and the data of Fig. 4 are based on experiments conducted at 900° C, we can, as a rough estimate assume that $\Delta\epsilon$ at 900° C is an order of magnitude larger than at the lower temperature, i.e. $\Delta\epsilon = 0.08$. This change in ϵ is too small to have a significant effect on the values of r^* and hence the rate of decomposition of the carbonate. These expectations are supported by experimental observations on the decomposition behavior of unsintered compacts of $CaCO_3$ and compacts which have been sintered at 700° C for up to 25 h. These results are depicted in Fig. 5 as the fraction of $CaCO_3$ converted (α) per second vs. time in hours at 700° C. The conclusion is that the sintering process of $CaCO_3$ is too slow to have a significant influence on the rate of decomposi-



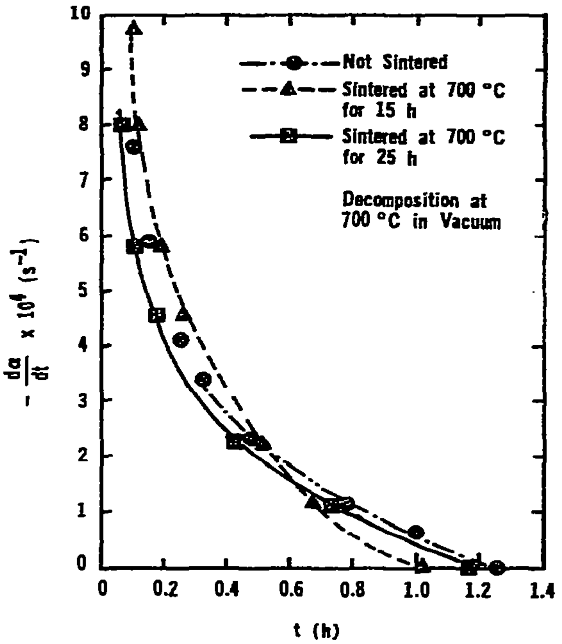


Fig. 4. The normalized reaction front radius as a function of porosity for $CaCO_3$ decomposition at 900°C.

Fig. 5. The influence of sintering on the decomposition rates of $CaCO_3$ at 700°C.

TABLE 1

Calculated K_1 values for the decomposition of calcium carbonate [a]

r^*	ϵ	t (min)	$K_1 \times 10^2$ (min^{-1})
0.0	0.33	28.0	2.4
	0.51	14.0	3.5
	0.66	12.0	2.8
0.50	0.33	18.5	1.8
	0.51	10.5	2.3
	0.66	8.0	2.1
0.67	0.33	12.5	1.8
	0.51	7.0	2.3
	0.66	6.0	1.9
0.79	0.33	8.0	1.8
	0.51	4.0	2.6
	0.66	3.0	2.4
			Ave. 2.3

[a] Kinetic data from ref. 7.

tion. This conclusion refers to the influence of sintering on the porosity in a kinetically controlled decomposition.

For mass-transport controlled reactions, however, changes in the pore size and shape distributions can have an influence on the reaction kinetics even if the overall porosity is essentially constant. Such changes can occur during the surface-transport controlled mechanisms of sintering [8]. In the case of the decomposition of $CaCO_3$, the product oxide is at too low a temperature (during typical decomposition experiments) to sinter and hence no changes in the pore distributions are anticipated. However, as pointed out earlier, changes in the kinetics of reduction of FeO have been attributed to changes in the pore size of the resulting iron layer. Although in principle the treatment for such a case is provided by eqn. (11), the analytical solution is not simple.

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REFERENCES

1 D. Beruto and A.W. Searcy, Nature (London), 263 (1976) 221.
2 R. Barker, J. Appl. Chem. Biotechnol., 23 (1973) 733.
3 R. Barker, J. Appl. Chem. Biotechnol., 24 (1974) 221.
4 N.W. Warner, in A.W. Hills (Ed.), Heat and Mass Transfer in Process Metallurgy, Institute of Mining and Metallurgy, London, 1967, p. 73.
5 A.W. Hills, Chem. Eng. Sci., 23 (1968) 297.
6 E. Fuss and Z.A. Munir, unpublished work.
7 F.R. Campbell, A.W.D. Hills and A. Paulin, Chem. Eng. Sci., 25 (1970) 929.
8 R.M. German and Z.A. Munir, Metall. Trans., 6B (1975) 289.
9 G.C. Kuczynski, Trans. AIME, 185 (1949) 169.