

LETTER TO THE EDITORS

Recent Papers Concerning Gas-Solid Reactions

In a recent series of papers (1-4) Calvelo and Cunningham, and Mendoza and co-workers developed elegant analytical expressions to describe gas-solid reactions involving porous solids. The attractive feature of this model is that allowance is made for variation of surface area and diffusivity within the solid. It would seem that the model is better than ones (5, 6) which assume constant diffusivity and surface area. It is clearly superior to the conventional "shrinking core" representation (which postulates a sharp reaction boundary and offers little guidance regarding the role played by structural parameters).

While the authors agree that their model is approximate and applicable only for high Thiele moduli, nonetheless they are able to show very pleasing agreement between their predictions and experimental measurements.

The relatively simple mathematical form of the model would render it a very suitable framework for the interpretation of experimental results. The purpose of this letter is to draw attention to several mathematical inconsistencies in the derivation of the model, which would seem to make the final rate expressions of questionable general validity. It is suggested that caution should be exercised in applying these expressions for the interpretation of experimental results.

Reference (2) is the key paper and the principal point of criticism stems from the manipulation of Eq. (21) and from the subsequent use to which these interim results were put.

Integration of Eq. (21) does not yield (22) but rather

$$\frac{dC_A^*}{dz^*} = [(2/(\gamma + 1))mC_A^{*\gamma+1}]^{1/2}. \quad (1)$$

Equation (25) is true only at $z = z_s$ but has been applied at other values of z subsequently [e.g., Eq. (28)].

It is not at all clear that m in Eq. (28) is identical with m in Eq. (21).

The first part of Eq. (40) is inconsistent with Eq. (22) (either in its incorrect form, as given in the paper, or as modified above). If this first part is corrected to the Eq. (22) above, then both sides are functions of z and it is difficult to see how they may be equated to $1/\eta_1$, which is independent of z .

Many other equations [e.g. (41) and (42)] are derived from these erroneous interim results and must therefore be considered suspect.

In view of these apparent errors it is remarkable that the model shows such a good fit with experimental data (4). Furthermore one may question the use of the reaction rate constant of Cannon and Denbigh (7) by the authors in their calculations. In reactions between gases and solids, it is usual to find that the reaction rate "constant" is a function of the physical nature of the surface (e.g., the number of crystal defects). As a consequence, the "constant" is a function of the detailed history (chemical method of preparation, extent of annealing, compacting pressure, etc.) of the solid sample (8, 9) and can be expected to vary greatly between samples prepared under different conditions. The explanation of this second anomaly is that the experiments have been performed under conditions of very high Thiele moduli (and

therefore diffusion control). This is evident from the examination of Fig. 2 in the fourth paper. If the chemical step had presented any resistance to the progress of reaction, there would have been an enormous increase in the rate of reaction with the increase of temperature over the span of 300°C, especially in view of the high activation energy [50 kcal/g mole (7)].

Cunningham and co-workers point out that at very high Thiele moduli the reaction zone narrows to a spherical surface and that the effective diffusivity profiles and surface area profiles become step functions with the step at this surface. The reactant gas concentration takes on a near equilibrium value (zero for irreversible reaction) at this surface. These statements have been verified by the writer in a rigorous numerical solution of the describing equations (10, 11) and may be arrived at by qualitative argument independent of the mathematical development of Cunningham *et al.* Thus, at very high Thiele moduli reactions between gases and porous solids show all the attributes of the *diffusion controlled* moving boundary model (which, of course, is different from the mixed control moving boundary model tested by Cunningham and co-workers). The analytical solution (obtainable in a few elementary steps from the differential equation) is, assuming no boundary layer mass transfer resistance,

$$t = (1 - \epsilon_0) \frac{\rho_m R_0^2}{D_{\text{EffA}}^{\text{D}} C_{\text{Ag}}} \times \left[\frac{1}{2} - \frac{(1-x)^{2/3}}{2} - \frac{x}{3} \right], \quad (2)$$

where ρ_m = true molar density of solid reactant. Unfortunately, the above relationship cannot be directly tested with the data supplied by the authors since they appear to have calculated the wrong diffusivity (that of oxygen in nitrogen instead of the correct diffusivity of oxygen in nitrogen-sulfur dioxide mixture). However, the above relationship means that the ratio of times to achieve a given conversion between experiments is given by

$$\frac{t_1}{t_2} = \frac{D_{\text{EffA}_2}^{\text{D}} C_{\text{Ag}_2}}{D_{\text{EffA}_1}^{\text{D}} C_{\text{Ag}_1}} \quad (3)$$

The figure for the ratio of diffusivities calculated from the diffusivities supplied in the paper should be correct (despite the errors in the diffusivities themselves) being dependent only on ratios of porosities, tortuosity factors, and temperatures (the temperature dependence of all gas diffusivities are about the same at these high temperatures). Table 1 demonstrates how well this relationship is obeyed. The diffusivities used in equation (3) are from those supplied by the authors in Figs. 3-6 of their fourth paper. The experimental ratios t_1/t_2 are from Fig. 2 in that paper.

TABLE 1

Run nos.	t_1/t_2		
	From Eq. (3)	From experiment	
		at 50% conversion	at 80% conversion
I,II	1.11	1.11	1.11
I,III	1.12	1.14	1.15
I,IV	2.01	2.00	2.02

In conclusion, one may say that the model developed by Cunningham and co-workers is excellent in concept, but contains numerous mathematical inconsistencies which render the final rate expressions of problematic usefulness for the purpose of interpreting experimental results.

If the appropriate corrections are made in the interim results, it is questionable whether general analytical solutions would be obtainable. One is therefore led to speculate whether more complex (and hence more realistic) models would provide a more promising pursuit, since numerical methods have to be used in any case.

These investigators have fitted their model to experimental data only in a regime where a much less cumbersome model (a diffusion controlled moving boundary model) may well give equally good results.

Nomenclature as in Ref. (4), unless otherwise indicated.

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