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LETTER TO THE EDITORS

Regarding Some Criticisms About Recent Papers on Gas–Solid Reactions

In a recent letter to the Editor, J. W. Evans has pointed out the existence of "several mathematical inconsistencies" in the derivation of a model of diffusion and reaction under effective diffusivity and surface area profiles (*1*), "which would seem to make the final rate expressions of questionable general validity."

Secondly, Evans questioned the application of the developed model to fit experimental data of zinc sulfide oxidation (*2*) arguing that a "much less cumbersome model (a diffusion controlled moving boundary model) may well give equally good results."

The purpose of this letter is to show that the mathematical development of the questioned model is correct and that our results of zinc sulfide oxidation do not correspond to a diffusion controlled moving boundary model, but to a reaction in the asymptotic zone of the effectiveness factor which takes place predominantly in the internal surface area of the solid.

In the following paragraphs we are going to answer Evans' queries in the same order as they appeared in his letter to the Editor.

1. There are not mathematical inconsistencies.

2. Equation 22 in Ref. (*1*) is absolutely correct. The misunderstanding probably arises from the lack of an explicit definition of m; nevertheless, below Eq. 6 it is quoted that: "m is a generalized Thiele modulus which can be calculated by the method proposed by Bischoff" (*3*); this definition also agrees with those of Petersen (*4*) and Aris (*5*):

$$m = L\left[\frac{\gamma+1}{2}\,\frac{k' a_{i0} c_{A_s}{}^{\gamma-1}}{D_{Ae}}\right]^{0.5}. \qquad (1)$$

Anyway, we must accept there is an easily detectable typing error in Eq. (21) which must read as follows:

$$\frac{d^2 c_A{}^*}{dz^{*2}} = \frac{2}{\gamma+1}\, m^2 c_A{}^{*\gamma}. \qquad (2)$$

3. Equation 25 is based on the assumption that C_B profiles are repeated as time elapses, so:

$$\frac{\partial C_B}{\partial t} + \frac{dz_s}{dt}\,\frac{dC_B}{dz} = 0 \qquad (3)$$

By introducing Eq. (3) of reference (*1*) into Eq. (3) of this letter Eq. (25) is readily obtained.

4. m is the same in the whole paper.

5. Equation (40) was obtained for $\gamma = 1$ [as had been pointed out below Eq. (35)]. In addition, there is a lack of the s subscript in the $dc_A{}^*/dz^*$ of Eq. (40) to indicate the effectiveness factor is calculated, as usually, from the gradient at the interface.

6. Since, the preceding answers show that the only errors were two of typing, we want to point out that the mathematical development is correct.

So far, this answers the questions about Ref. (*1*). We will refer now to paper (*2*).

7. The method of calculation used in the zinc sulfide oxidation is described in detail in Ref. (*2*). It shows that when we applied the criterion of validity of the moving boundary model (*6*) our system did not check it.

TABLE 1

Run	t_1/t_2 from Evans' Eq. (3)	t_1/t_2 from experiments			
		$X_B = 0.2$	$X_B = 0.3$	$X_B = 0.4$	$X_B = 0.5$
I/II	1.11	1.50	1.25	1.15	1.11
I/III	1.12	1.50	1.25	1.15	1.14
I/IV	2.01	3.00	2.50	2.00	2.00

8. Furthermore, the said criterion states that a high Thiele modulus is not the only condition to achieve the moving boundary model.

9. Nevertheless, we calculated conversion as a function of time assuming the moving boundary hypothesis [Figs. 3–6 in Ref. (*2*)]. The so calculated conversion-time relationship differed very much from the observed one as was pointed out in Ref. (*2*). On the other hand, the use of the reaction rate constant and effective diffusivity with the moving boundary model hypothesis led to a chemically controlled reaction, namely, the calculated concentration gradient in the ash layer was negligible (only in run IV, c_A began to fall). So Eq. (2) of Evans' letter cannot be used. Furthermore, if we try to fit Evans' Eq. (2) to our data, a variable effective diffusivity is needed. Obviously this cannot be explained in terms of an error in the calculation of the effective diffusivity.

10. By applying our model of diffusion and simultaneous reaction under effective diffusivity and surface area profiles we calculated the number of moles of A consumed per unit time on the external surface area and on the internal one. From these results we observed the reaction took place mostly on the internal surface area of the solid. This means the surface area on which the reaction takes place is very much higher than that for the moving boundary model. Consequently, oxygen demand becomes sufficiently high so as to develop a significant concentration gradient in the ash layer. For example, for run III, $c_{As}/c_{Ae} = 0.35$ for $X_B = 0.18$ and $c_{As}/c_{Ae} = 0.06$ for $X_B = 0.79$. This may explain why our data fit Eq. (3) of Evans for high conversions leading him to an erroneous conclusion. However, if we extend the calculation of Evans (see Table 1 in his letter) for lower conversions we obtain Table 1 of this letter.

Table 1 shows that Eq. (3) of Evans only fits for $X_B > 0.4$ when the ash layer is thick enough to develop a significant concentration gradient through it. For lower conversions Eq. (3) does not hold. Anyway, we emphasize again the accomplishment of Eq. (3) does not mean Eq. (2) holds.

11. In addition, as reaction took place mostly in the internal surface area of the solid and in the asymptotic zone of the effectiveness factor the rate of the process was proportional to $(k')^{1/2}$. Evans questioned the use of the reaction rate constant of Cannon and Denbigh (*7*) because it is a function of the detailed history of the solid. It is evident that an error due to the use of that constant will be greatly decreased—if it exists—since it appears as $(k')^{1/2}$.

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