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Reply to "Comment on 'Theoretical and Experimental Aspects of Surface Diffusion in Porous Catalysts'" by Onno L. J. Gijzeman

We have read the Letter by Dr. O. L. J. Gijzeman (*1*) with interest. There is, in our opinion, a fundamental confusion contained in it, which also reflects a long-standing conceptual problem in several other fields, particularly that of facilitated transport. In fact, in passing from Eqs. (1)–(2) to Eqs. (5)–(6), the Letter (*1*) commits exactly the same error as that found in several early works of facilitated transport (see, for example, Ref. (*2*) for relevant discussions on the subject and additional references). We were perhaps mistakenly hoping that our original paper (*3*) had helped to resolve some of these conceptual difficulties.

Although past and recent experience from the field of facilitated transport suggests that it is probably optimistic to try to clear up such conceptual problems in just a few brief lines, we shall nevertheless attempt once more to do so.

To begin with, we hope that all parties will agree that we should respect the governing equations and that we cannot generally satisfy differential equations of the form $y'' = g(y)$ by simply setting both sides equal to zero. Therefore, the assumption of adsorption–desorption equilibrium, which does not in general satisfy simultaneously the governing equations and the boundary conditions, must be based on some appeal to mathematical or physical approximation. In the present context (with allowance for proper length and/or time scales), the assumption is tantamount to taking D_b and $D_s \rightarrow 0$ in Gijzeman's Eqs. (1) and (2). This is certainly *not* the same as his condition that d^2C/dx^2 and $d^2n/dx^2 \rightarrow 0$ which, while it has the same consequences for (1) and (2), leads erroneously to his Eqs. (5) and (6).

Of course, the equilibrium approximation fails precisely at $x = 0, L$ where terms like $D_s d^2n/dx^2$ are no longer negligible (precisely because d^2n/dx^2 is large, which is contrary to Gijzeman's *Ansatz*.). It is only by reintroducing such terms, in the reaction boundary layers at $x = 0, L$, that one is able to satisfy the no-flux condition $dn/dx = 0$ at $x = 0, L$, which, as Gijzeman correctly surmises, cannot be sustained in the adsorption–desorption equilibrium limit.

This is the essence of the "singular-perturbation" analysis engendered by the neglect of diffusion in the presence of rapid homogeneous reaction and utilized in our original paper (*3*). Similar arguments, of course, apply to the neglect of viscosity in high-speed fluid mechanics or of Planck's constant in the classical limit of quantum mechanics. We hope this citation of other physical examples, rather than distracting from the issue at hand, will serve to illustrate that the conceptual difficulties encountered by Dr. Gijzeman are neither special nor trivial.

REFERENCES

1. Gijzeman, O. L. J., *J. Catal.* **109,** 468 (1988).
2. Goddard, J. D., Schultz, J. S., and Suchdeo, S., *AIChE J.* **20,** 624 (1974).
3. Tsotsis, T. T., Sane, R. C., Webster, I. A., and Goddard, J. D., *J. Catal.* **101,** 416 (1986).

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