LETTERS TO THE EDITOR

To the Editor:

Kinetics and Thermodynamics

I read the excellent review by Professor Boudart of Benson's "Thermochemical Kinetics" in the *AIChE Journal* **23**, 613 (1977) Professor Boudart called attention to an error in the book which I believe requires additional comment. Not only is Equation 1.3 on p. 2 incorrect but a number of statements which follow are also not true. These statements have an important bearing on the relationship between thermodynamics and reaction kinetics.

On p. 14 of the book it is stated, "We may also note that rate laws, even for very complex processes, can always be written as a product of a kinetic expression (involving rate constants and concentrations) and a thermodynamic expression usually of the form

$$1 - \frac{(P)^p(Q)^q \ldots\ldots}{K_1(A)^a(B^b)\ \ldots\ldots} \quad (1.45)$$

where K_1 is the equilibrium constant for the overall reaction

$$aA + bB + \ldots \overset{1}{\rightleftharpoons} pP + qQ + \ldots\ldots$$

It is this thermodynamic factor which makes the net rate go to zero at equilibrium.

One consequence of this discussion above is that any parameter that does not affect the equilibrium constant but that does affect the kinetic behavior of the system must have an identical effect on both forward and reverse rate constants. This is true, for example, of catalysts, which must speed up the reverse as well as the forward rate by precisely equal factors."

Professor Boudart's comment is consistent with the fact that Equation 1.45 above is incorrectly written. Of importance is also the fact that even if the potential factor, Equation 1.45, is *correctly written* it is *not always* possible for it to be factored from a rate equation. We discussed the conditions for which a potential term can be factored some time ago [R. S. Csuha and J. Happel, *AIChE Journal*, **17**, 927 (1971)]. It is important to establish whether this can be done in order to arrive at a rate equation which will correctly describe behavior as equilibrium is approached.

A unique way to determine whether a given process can be characterized by a rate equation with a factorable potential term consists in measuring forward and reverse velocities of transfer of atomic species by means of tracers. These velocities are related in a simple manner to the potential term in a reaction path for cases where it is possible to factor out the potential term [see J. Happel and R. S. Csuha, *J. Catal.* **20**, 132 (1971); J. Happel, *Catal. Rev.* **6**, 221 (1972)]. Note that for this purpose the forward and backward velocities should be studied not only at equilibrium but over the entire range of conditions under which it is proposed to construct a rate equation; in practical cases at one side of equilibrium.

Since it is possible that the rate controlling step, if indeed one exists, can often change over the concentration range involved in a catalytic conversion, it is desirable to use a procedure like that described above which does not a priori assume that a process can be described by a rate controlling step. Thus the procedure described by Carberry in his recent book [J. J. Carberry "Chemical and Catalytic Reaction Engineering", McGraw-Hill (1976) p. 441] in which the forward rate *at equilibrium* of tracer transfer is measured will not generally provide the required information. The apparent stoichiometric number determined in this fashion will not necessarily remain constant at departure from equilibrium

Neither is the method proposed in the classic text of Denbigh suitable [K. G. Denbigh, "The Principles of Chemical Equilibrium", Cambridge U Press (1955), p. 442] in which he suggests that the measured forward velocity be expressed under initial condition where the quantity of product preser is very small. The forward velocity a equilibrium is approached will often be very substantially influenced by adsorption of product species.

We applied this method of using tracers to the development of rat equations for the dehydrogenation o n-butane [J. Happel and R. S. Atkins *I & EC Fundamentals*, **9**, 11 (1970) J. Happel and M. A. Hnatow, "Advances in Chemistry Series #97, paper #5, p. 92, American Chemical Society (1970)] and found that although the rate could be characterized by a potential factor, the kinetic factor involved was quite complicated. For isobutane dehydrogenation a simpler rate expression with a separable potential term is possible [J. Hoppe, K. Kamholz, D Walsh and V. Strangio, *I & EC Fundamentals*, **12**, 263 (1973]. The development of rate expressions for SO_2 oxidation based on these concepts has also been considered [J. Happel, R. E. Lief and R. Mezaki, *J. Catal.*, **31**, 90 (1973); J. Happel and R. Mezaki, *Chem. Eng. Sci.*, **29**, 1300 (1974)]. It was found that it is not possible to extract a potential term over the complete range of practical interest.

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