Application of the Method of Moments to Rate Tracer Studies of Heterogeneous Catalysis

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Recently Happel and Hnatow (1973) discussed a methodology for using tracers which has been successfully employed for the determination of rate controlling steps for several industrially important catalytic processes. In this technique a reaction is maintained at steady state conditions and rate traced by steady passage of isotope. By rate tracing is meant the use of tracers to study transfer of atomic species from one reactant or product molecule to others rather than the more common application of tracers in which distribution of traced species in the molecules themselves is involved. By employing a recirculating, gradientless reactor system it is not necessary to integrate the rate equations for either the overall reaction studied or the tracer rates involved. This has the advantage that it is not necessary to assume any special form of rate equation for the steps involved. In these studies both multiple levels and multiple tracers were employed to resolve the step velocities of complex reaction networks.

It appears that extension to experiments in which unsteady state rate tracing is employed will considerably extend the usefulness of the method by enabling predictions of the relative abundance of surface species involved to be made in addition to the step velocities which sometimes are not determined by steady state tracing. It should then be possible to test the applicability of various rate equations as regards such common postulates as uniformity of catalyst surface and accessability of catalyst sites. It is the purpose of this note to show how the method of moments can be conveniently applied for this purpose.

A model catalytic reaction is taken as a paradigm for illustrating the method. Consider the reaction

$$A \underset{v_{-1}}{\overset{v_{+1}}{\rightleftharpoons}} Al \underset{v_{-2}}{\overset{v_{+2}}{\rightleftharpoons}} B \qquad (1)$$

Assume that a steady state reaction is being conducted in a gradientless reactor with feed being introduced and product withdrawn continuously. For this system at a given time $t = 0$ we will introduce a pulse which produces a concentration of tracer in one of the species (A in this case) in the reactor. We wish to employ the response curves of tracer in the product stream to predict the concentration of component A on the catalyst surface C^{Al} and the step velocities $v_{\pm 1,2}$.

Material balances for the atomic tracer species transfer are as follows:

$$\frac{\beta}{W} C^A \frac{dz^A}{dt} + v_{+1} z^A - v_{-1} z^{Al} = -\frac{F^A z^A}{W} \qquad (1)$$

$$\frac{\beta}{W} C^B \frac{dz^B}{dt} - v_{+2} z^{Al} + v_{-2} z^B = -\frac{F^B z^B}{W} \qquad (2)$$

$$C^{Al} \frac{dz^{Al}}{dt} - v_{+1} z^A + v_{-1} z^{Al} + v_{+2} z^{Al} - v_{-2} z^B = 0 \qquad (3)$$

The boundary conditions are

$$\text{at} \quad t = 0 \quad z^{Al} = z^B = 0; \quad z^A = z_0{}^A$$

$$\text{at} \quad t = \infty \quad z^A = z^{Al} = z^B = 0$$

z^A, z^{Al} and z^B are unknown functions of t

Taking the Laplace transforms of Equations (1) to (3), we have

$$\frac{\beta}{W} C^A s \,\bar{z}^A(s) - \frac{\beta}{W} C^A z_0{}^A + v_{+1} \bar{z}^A(s) - v_{-1} \overline{z^{Al}}(s) = -\frac{F^A \overline{z^A}(s)}{W} \qquad (4)$$

$$\frac{\beta}{W} C^B s \,\overline{z^B}(s) - v_{+2} \overline{z^{Al}}(s) + v_{-2} \overline{z^B}(s) = -\frac{F^B}{W} \overline{z^B}(s) \qquad (5)$$

$$C^{Al} s \,\overline{z^{Al}}(s) - v_{+1} \overline{z^A}(s) + v_{-1} \overline{z^{Al}}(s) \quad v_{+2} \overline{z^{Al}}(s) - v_{-2} \overline{z^B}(s) = 0 \qquad (6)$$

These three simultaneous equations may be solved for $\overline{z^A}(s), \overline{z^{Al}}(s), \overline{z^B}(s)$. Thus

$$\overline{z^A}(s) = \frac{\frac{\beta}{W} C^A z_0{}^A}{\frac{\beta}{W} C^A s + v_{+1} - \dfrac{v_{-1} v_{+2}}{C^{Al} s + v_{-1} + v_{+2} - \dfrac{v_{-2} v_{-1}}{\frac{\beta}{W} C^B s + v_{-2} + \frac{F^B}{W}}} + \frac{F^A}{W}} \qquad (7)$$

with similar expressions for $\overline{z^{Al}}(s)$ and $\overline{z^B}(s)$.

Aris and Amundson (1973) discuss the Laplace transform as a moment-generating function. Butt (1962) has discussed its application to kinetics of homogeneous reactions. For our present purpose only the zeroth and first moments are involved and may be expressed as follows:

$$M_0 = \lim_{s \to 0} \bar{f}(s) \qquad (8)$$

$$M_1 = -\lim_{s\to 0}\frac{d\bar{f}(s)}{ds} \qquad (9)$$

Application of Equation (8) gives the zeroth moments from the transform, Equation (7),

$$M_{0zA} = \frac{\dfrac{\beta}{W} C^A z_0{}^A}{v_{+1} - \dfrac{v_{-1}v_{+1}}{v_{-1} + v_{+2} - \dfrac{v_{-2}v_{+2}}{v_{-2} + \dfrac{F^B}{W}}} + \dfrac{F^A}{W}} \qquad (10)$$

with similar expressions for M_{0zAl} and M_{0zB}. Two of these moments are directly obtained from the tracer data, namely M_{0zA} and M_{0zB}. Either of these zeroth moments or steady state tracing data enable

$$V_+{}^{1,2} = \frac{v_{+1}v_{+2}}{v_{-1} + v_{+2}}; \quad V_-{}^{1,2} = \frac{v_{-1}v_{-2}}{v_{-1} + v_{+2}} \qquad (11)$$

to be determined. Equations (11) are not independent. It is known that

$$V = v_{+1} - v_{-1}; \quad V - v_{+2} - v_{-2}; \quad V = V_+{}^{1,2} - V_-{}^{1,2} \qquad (12)$$

These relationships together provide only three independent equations, insufficient to determine the four unknown velocities $v_{\pm 1,2}$. Happel and Hnatow (1973) stated incorrectly that $v_{\pm i}$ in a similar case could be obtained by steady state tracing. M_{0zAl} cannot be observed conveniently without special examination of the catalyst during the experiment. Observation of the first moments M_{1zA} and M_{1zB} is needed for the two additional relationships necessary to determine $v_{\pm 1,2}$ as well as C^{Al}.

Application of Equation (9) after obtaining $d\,\overline{z^A}(s)/ds$ from Equation (7) gives one of these, the first moment:

$$M_{1zA} = \left\{ \frac{\dfrac{\beta}{W} C^A z_0{}^A}{\left[v_{+1} - \dfrac{v_{-1}v_{+1}}{v_{-1} + v_{+2} - \dfrac{v_{-2}v_{+2}}{v_{-2} + \dfrac{F^B}{W}}} + \dfrac{F^A}{W} \right]^2} \right\}$$

$$\times \left\{ \frac{\beta}{W} C^A + \left[\frac{v_{-1}v_{+1}}{\left[v_{-1} + v_{+2} - \dfrac{v_{-2}v_{+2}}{v_{-2} + \dfrac{F^B}{W}} \right]^2} \right] \left[C^{Al} + \frac{\dfrac{\beta}{W} C^B v_{-2}v_{+2}}{\left(v_{-2} + \dfrac{F^B}{W} \right)^2} \right] \right\} \qquad (13)$$

with a similar expression for M_{1zB}.

These expressions can be simplified to some extent by incorporating expressions for $V_\pm{}^{1,2}$ and the zeroth moments. If it can be assumed that the surface species can be desorbed by an inert gas without altering catalyst composition, C^{Al} can be independently determined and then either M_{1zA} or M_{1zB} serves to establish the step velocities $v_{\pm 1,2}$.

DISCUSSION

The method developed is applicable to situations in which the catalyst particles are small enough or temperatures are low enough to ensure high effectiveness factors with small intraparticle diffusion or temperature gradients. The use of a recirculating reactor instead of a fixed bed enables the problem of interparticle diffusion to be avoided.

It should be noted that desorption of surface species by inert gas could also enable z^{Al} to be determined. Then $v_{\pm 1,2}$ could be calculated without the need for transient tracing. Determination of C^{Al} and z^{Al} in this fashion is often not desirable because of changes in catalyst composition introduced by reducing the partial pressures of all ambient reacting species to zero.

Application to more complicated systems is straightforward since in all cases tracer transfer results in systems of simultaneous linear equations regardless of the kinetics of the reaction steps themselves. Indeed in many cases $v_{\pm i}$ can be calculated from steady state tracing experiments alone, simplifying the application of the first moments in calculating surface concentration of adsorbed species. The method may also find application in homogeneous reaction systems where the quasi steady state assumption is applicable and to enzyme catalyzed reactions as well as noncatalyzed solid-fluid reaction systems.

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NOTATION

A^l = refers to species A adsorbed on the catalyst
C^{Al} = concentration of species Al on solid catalysts, g moles/g
C^i = concentration of species i, ($i = A, B$) in gas phase in the reaction system, g moles/cc
F^i = outlet flow rate of product i ($i = A, B$), g moles/s
$\mathcal{L}[f(t)] = \bar{f}(s)$ = Laplace transform ($f(t) = z^i(t)$; $i = A, Al, B$)
M_{0zi} = zeroth moment of the species z^i ($i = A, Al, B$)
M_{1zi} = first moment of the species z^i ($i = A, Al, B$)
t = time, s
$v_{\pm i}$ = unidirectional step velocities ($i = 1, 2$) moles/(s) (g catalyst)
V = overall reaction rate, g moles/(s) (g catalyst)
$V_\pm{}^{1,2}$ = overall unidirectional tracer velocities given in Equation (11) g atoms/(s) (g catalyst)
W = weight of catalyst in system, g
z^i = fraction of component i that contains tracer (under the simplifying assumption of a single atom of tracer species per molecule of i) ($i = A, Al, B$)
β = volume of dead space (including that in catalyst pores, voids and apparatus), cc

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