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RATE EQUATIONS FOR TRACER STUDIES IN RECIRCULATING REACTORS

By

John Happel*

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Abstract

The employment of isotopic tracers is a useful technique for gaining insight into the rate controlling steps of a complex chemical reaction such as is frequently encountered in heterogeneous catalysis. An effective procedure has been to superpose tracer transfer on a reaction which is occurring under steady state conditions. If tracer transfer is employed in this fashion it is often possible to assess the individual step velocities in an assumed reaction mechanism. If transient transfer of tracer is now introduced it is possible in addition to estimate surface concentrations of chemisorbed species.

The purpose of the present paper is to present the mathematical relationships involved when transfer of the tracer is not differential in the investigation. For this purpose a simple example is chosen to illustrate the various possibilities involved.

Introduction

The stoichiometric number concept initiated by Horiuti1) and his colleagues beginning in 1940 has proven to be a powerful tool in study of heterogeneous catalytic reactions2). Marked atoms are employed for the study of reaction mechanisms using two important basic ideas—the stationary state hypothesis and transition state theory. The stationary state assumption, that all intermediates maintain constant concentrations during an experiment, implies that intermediates developed as chemisorbed species will exist only to a negligible extent in the ambient phase. From this it is possible to formulate material balances for isotopic species so that more useful data input is obtainable than from ordinary kinetic experiments where only the overall rate is observed. Transition state theory provides an additional independent relationship for estimation of step velocities from a given mechanistic model.

The use of multiple tracers enables information to be obtained on such complex reactions as isobutane dehydrogenation, sulfur dioxide oxidation and the...
Rate Equations for Tracer Studies in Recirculating Reactors

water gas shift reaction using industrial catalysts. In these cases steady state tracing with differential rates of tracer transfer was employed. Extension of such studies to tracer experiments in which tracer transfer is faster and transient presents additional opportunities and complications. The purpose of this study is to use a simple catalytic reaction system to illustrate the methodology involved in investigations of this type.

Basic Model

Consider the variables involved in the reaction system conducted over a solid catalyst

\[
\begin{align*}
A & \xrightarrow{v_1} \ Al \quad \xrightarrow{v_2} \ B \\
A & \xrightarrow{v_{-1}} \ Al
\end{align*}
\]

(1)

A considerable simplification in mathematical treatment is possible if a rapidly recirculating or stirred tank type of reactor is employed to study such a reaction because concentration gradients in space which are present in tubular reaction systems are avoided. In order for the overall reaction in such a system to maintain a steady state condition it is necessary for feed to be continuously introduced and product to be continuously withdrawn. For such a system the following three differential equations apply, from material balances on species A, B, and Al respectively:

\[
\begin{align*}
\frac{F^i_A z_A^i}{W} - \frac{F^i_B z_B^i}{W} = v_1 z_A^i - v_{-1} z_{Ai} + \frac{\beta}{W} C_{Ai}^A \frac{dz_A^i}{dt} \\
\frac{F^i_A z_A^i}{W} - \frac{F^i_B z_B^i}{W} = - v_2 z_{Ai} + v_{-2} z_B^i + \frac{\beta}{W} C_{Ai}^A \frac{dz_B^i}{dt} \\
-C_{AI}^A \frac{dz_{AI}}{dt} = - v_1 z_A^i + v_{-1} z_{AI} + v_2 z_{AI} - v_{-2} z_B^i
\end{align*}
\]

(2)  (3)  (4)

where

- \(F^i_A\) = inlet flow rate of feed species i (i = A, B), moles/sec.
- \(F^i_B\) = outlet flow rate of product i (i = A, B), moles/sec.
- \(z_A^i\) = fraction of tracer species in i (i = A, B, Al) in gas phase feed
- \(z_B^i\) = fraction of tracer species in i (i = A, B, Al) in gas phase product
- \(W\) = weight of catalyst in system, g.
- \(v_{\pm i}\) = unidirectional step velocities (i = 1, 2) moles/(sec)(g-catalyst)
- \(\beta\) = volume of dead space (including that in catalyst pores, void and apparatus), cc.
- \(C_{Ai}^A\) = concentration of species i (A, B) in gas phase product (outlet), g-moles/cc.
- \(C_{AI}^A\) = concentration of species Al in solid catalyst, moles/g.
- \(t\) = time, sec.
We wish to employ these equations to determine $v_{\pm 1}$ and $C^M$. It is convenient to accomplish this by a sequential program, first conducting steady state experiments corresponding to $t \to \infty$. Thus if tracer is fed into the system at a constant rate, the overall reaction itself having been first established, the steady state tracer transfer will result in

$$\frac{dz^t}{dt} = \frac{dz^F}{dt} = \frac{dz^M}{dt} = 0 \quad (5)$$

Then equations (2)-(4) reduce to two algebraic equations. At steady state the overall reaction rate $V = v_{+1} - v_{-1} = v_{+2} - v_{-2}$ providing two additional relationships. Thus there are five unknowns, $v_{\pm 1}$, $v_{\pm 2}$ and $z^M$ with only four equations available to solve for them. Sufficient information is available to calculate the overall tracer velocities

$$V_+ = \frac{v_{+1}v_{+2}}{v_{-1} + v_{+2}}; \quad V_- = \frac{v_{-1}v_{-2}}{v_{-1} + v_{+2}} \quad (6)$$

but not the individual $v_{\pm 1,2}$.

For steady state tracing another entirely independent relationship is available from Horiuti's transition state theory:

$$e^{-\theta/RT} = \frac{v_{+1}v_{+2}}{v_{-1}v_{-2}} = \frac{V_+}{V_-} \quad (7)$$

This relationship is not required to determine $V_+$ and $V_-$ for the assumed mechanism, but in an actual case would provide confirmation that the mechanism proposed does indeed involve steps which occur as indicated with stoichiometric numbers equal to unity.

The required additional information can be provided by transient tracing. In such experiments when the overall reaction rate still remains unchanged results can be interpreted by solutions of equations (2)-(4) which provide expressions for $z^t$, $z^F$ and $z^M$ as functions of time. The constant values of $v_{\pm 1,2}$ and $C^M$ will remain unchanged during an experiment. Comparison of observed transients in tracer output with computed ones will enable values of $v_{\pm 1,2}$ and $C^M$ to be selected which result in agreement of theory and experiment.

Equations (2)-(4) are a system of linear ordinary differential equations with constant coefficients which can be solved numerically. Alternatively the response curves of outlet tracer concentration may be conveniently interpreted by means of the moments developed from Laplace transforms of these equations, (Happeu).  

**Closed systems**

It is of interest to examine analytical solutions of the equations which are obtainable for closed systems. In this case there is no feed input or product
removal and the left hand side of equations (2) and (3) will become zero. However, in this case the surface concentrations $C_A$, $C_B$ and $C_{AI}$ will not be constant unless the system is at equilibrium for the overall reaction with $V=0$. In that case

$$v_{+1} = v_{-1} = v_1$$

and

$$v_{+2} = v_{-2} = v_2$$

and equations (2)-(4) reduce to

$$0 = v_1 z^A - v_1 z^{AT} + \frac{\beta}{W} C_A \frac{dz^A}{dt}$$

(8)

$$0 = -v_2 z^M + v_2 z^B + \frac{\beta}{W} C_B \frac{dz^B}{dt}$$

(9)

$$-\frac{C^{AT} dz^{AT}}{dt} = -v_1 z^A + v_1 z^{AT} + v_2 z^M - v_2 z^B$$

(10)

In matrix form

$$\frac{dz}{dt} = AZ$$

(11)

This system is readily solved by the matrix method following such references as AMUNDSON. Solving the relationship $(A - \lambda I) = 0$ for $\lambda$ we obtain a cubic characteristic equation which finally reduces to $\lambda = 0$ for one root and for the two others:

$$\lambda = \frac{1}{2} \left[ -\left( \frac{W}{\beta} \frac{v_1}{C_A} + \frac{v_1 + v_2}{C^{AT}} + \frac{Wv_2}{\beta C_B} \right) \right. \pm \sqrt{\left( \frac{Wv_1}{\beta C_A} + \frac{v_1 + v_2}{C^{AT}} + \frac{Wv_2}{\beta C_B} \right)^2 - 4 \left( \frac{W}{\beta} \frac{v_1 v_2}{C_A C^{AT}} + \frac{W^2}{\beta^2} \frac{v_1 + v_2}{C_A C_B} + \frac{W^2}{\beta^2} \frac{v_1 v_2}{C_A C^{AT} C_B} \right)} \left( \frac{v_1 v_2}{Wv_1} + \frac{v_1 + v_2}{v_2} \right) \left( \frac{v_1 v_2}{Wv_1} + \frac{v_1 + v_2}{v_2} \right) \left( \frac{v_1 v_2}{Wv_1} + \frac{v_1 + v_2}{v_2} \right) \end{equation}$$

(13)

It can be shown that these roots are negative so a non-oscillating solution is obtained.

Calling the roots of Equation (13) $\lambda_1$ and $\lambda_2$, we have:

$$z^A = C_1 e^{\lambda_1 t} + C_2 e^{\lambda_2 t} + C_3$$

(14)

$$z^{AT} = C_1 \left( \frac{\beta C_A}{Wv_1} \frac{v_1 + v_2}{v_1} \right) e^{\lambda_1 t} + C_2 \left( \frac{\beta C_A}{Wv_1} \frac{v_1 + v_2}{v_1} \right) e^{\lambda_2 t} + C_3$$

(15)

$$z^B = C_1 \left[ \left( \frac{C^{AT} \lambda_1 + v_1 + v_2}{v_2} \right) \left( \frac{\beta C_A}{Wv_1} \frac{v_1 + v_2}{v_1} \right) \right] e^{\lambda_1 t}$$

$$+ C_2 \left[ \left( \frac{C^{AT} \lambda_2 + v_1 + v_2}{v_2} \right) \left( \frac{\beta C_A}{Wv_1} \frac{v_1 + v_2}{v_1} \right) \right] e^{\lambda_2 t} + C_3$$

(16)
Since in a closed system no tracer is lost, $C_3$ will be the average tracer concentration after a sufficiently long time:

$$C_3 = \langle z_{av} \rangle_{t \rightarrow \infty} = \frac{C^A z_0^A + C^B z_0^B + \frac{W}{\beta} C^M z_0^M}{C^A + C^B + \frac{W}{\beta} C^M}$$

(17)

We can only specify in advance two of the three initial values $z_0^A$, $z_0^M$ and $z_0^B$. The third initial values and the three constants $C_1$, $C_2$ and $C_3$ may then be evaluated from the four equations (14)–(17). Thus a given experiment with arbitrary initial values for all three tracer concentrations will involve discontinuities so that the system will not follow the differential equations postulated over the entire time period.

**Discussion**

This relatively simple example illustrates a procedure for using transient tracing to establish step velocities and surface concentrations in systems involving heterogenous catalysis. The use of a recirculating type reactor not only reduces the problem of concentration and temperature gradients between particles, but corresponds to a system of ordinary rather than partial differential equations.

It should be noted that transient tracing is not needed, if desorption of surface species by inert gas will enable the $z^M$ concentration established by a steady state experiment to be determined. This may not always be possible because changes in catalyst composition may occur during such desorption resulting in more removal of species from the catalyst than corresponds to $C^M$.

It appears that for integral tracer transfer it is simpler to employ an open system in which feed is continuously introduced and product withdrawn than a closed system because steady state conditions for the overall reaction can be achieved and specification of the initial conditions is simplified.

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**References**


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