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## Rate Tracer Studies of Heterogeneous Catalysis

By

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### Abstract

The employment of transient tracing in which transfer of isotopic species is superposed on a heterogeneous catalytic reaction occurring under steady state conditions is described as rate tracing. Mathematical relationships are developed to show how such use of isotopic tracers is an effective method for determining step velocities and surface concentrations of intermediates in complex heterogeneous catalytic systems.

### Introduction

This paper is a sequel to the note published recently in this Journal, HAPPEL<sup>1)</sup> in which the theory of transient tracing was developed for the model reaction



The same nomenclature will be used here as in the previous note and the numeration of additional equations will follow in order those previously developed. For simplicity it is assumed that a single atom of tracer species is present in each molecule of the components. Extension to cases where more than a single atom is marked or a change occurs in the total number of molecules is straight-forward but will not be carried out here.

The object in this paper is to consider in greater detail the extent to which the parameters involved can be determined by experiments in which tracer concentration is measured as a function of time and to note differences between the treatment for closed and open systems. Since tracer redistribution is linear it is quite generally possible to calculate parameters from observed transient values for tracer concentration in the terminal species alone. In some cases initial tracer concentration in intermediates is desirable. The results are applicable for a variety of systems as well as for the simple example, Eq. (1), which is first considered.

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### Closed Systems

In the previous note the equations for closed systems were given for the case in which the overall reaction is at equilibrium, with the overall velocity  $V=0$ . This is the only case in which the concentration  $C^A$ ,  $C^{A^I}$  and  $C^B$  will strictly remain constant. Let us consider an experiment in which at time  $t=0$  the species A is marked  $z_0^A$  by a step change in concentration in the gas phase. The model equations are assumed to apply so that observation of the course of tracer concentration  $z^A$  with time can be expressed empirically by Eq. (14), which contains the constants  $C_1$ ,  $C_2$ ,  $C_3$ ,  $\lambda_1$  and  $\lambda_2$ . With this information, by means of Eqs. (15) and (16) it is possible to obtain expressions for  $z^{A^I}$  and  $z^B$ . Two relationships are obtained by setting values for  $z_0^{A^I}$  and  $z_0^B$  at  $t=0$  into these expressions. Two additional independent relationships are obtained from the expressions for  $\lambda_1$  and  $\lambda_2$ . Solution of these four equations gives numerical values for the four distinguishable parameter groups, namely

$$\frac{Wv_1}{\beta C^A}; \frac{v_1}{C^{A^I}}; \frac{v_2}{C^{A^I}}; \frac{Wv_2}{\beta C^B}. \quad (18)$$

If we chose to observe the marking  $z^B$  instead of  $z^A$  the same information could be derived, and it would also be possible to initially mark  $z_0^B$  and  $z_0^{A^I}$  with the same result. Observation of the marking of both terminal species will produce more than enough information to uniquely fix the values of the parameter groupings, Expressions (18). The constants  $C_1$ ,  $C_2$  and  $C_3$  are arbitrary in the sense that they depend on initial conditions as well as the parameters. However, when both A and B are marked, these constants can be eliminated to obtain the four constants in Eq. (16), namely  $\lambda_1$ ,  $\lambda_2$  and the two expressions in brackets which are sufficient to fix the values of the four parameter groupings. Note that in this case the initial condition of marking of the intermediate  $z_0^{A^I}$  is not required. In other words the parameter groups are functions of these observed constants. This can be demonstrated by means of the inversion theorem discussed by AMUNDSON<sup>2)</sup> which uses the Jacobian determinant.

If we know the parameter groups in Expression (18), and specify  $W/\beta$  together with either  $C^A$  or  $C^B$ , the values of  $v_1$ ,  $v_2$  and  $C^{A^I}$  can be determined.

The case for the closed system in which the overall reaction being traced is not equilibrium is more complicated. In place of Eq. (11) we have

$$\frac{d}{dt} \begin{bmatrix} C^A z^A \\ C^{A^I} z^{A^I} \\ C^B z^B \end{bmatrix} = \begin{bmatrix} -\frac{W}{\beta} v_{+1} & \frac{W}{\beta} v_{-1} & 0 \\ v_{+1} & -(v_{+1} + v_{-2}) & v_{-2} \\ 0 & \frac{W}{\beta} v_{+2} & -\frac{Wv_{-2}}{\beta} \end{bmatrix} \begin{bmatrix} z^A \\ z^{A^I} \\ z^B \end{bmatrix}. \quad (19)$$

In deriving Eq. (19) it is assumed that  $V=v_{+1}-v_{-1}=v_{+2}-v_{-2}$  for otherwise the

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characterization of the system would require some knowledge of the kinetics of individual steps. Appropriate simplification consists in taking  $C^{Ai}$  constant, consistent with this assumption. Further simplification is to take  $V$  constant (strictly true for zero order reactions). The concentrations of  $C_A$  and  $C_B$  may then be expressed as

$$C^A = C_0^A - \frac{WV}{\beta} t \quad (20)$$

$$C^B = C_0^B + \frac{WV}{\beta} t \quad (21)$$

The resulting relationships are linear, but not with constant coefficients.

The overall velocities corresponding to Eq. (6) can be determined from the quasi-steady state approximation when  $W/\beta \ll 1$  so that  $(WC^{Ai}/\beta) dz^{Ai}/dt \rightarrow 0$  and

$$-\frac{\beta}{W} \frac{d(C^A z^A)}{dt} = \frac{\beta}{W} \frac{d(C^B z^B)}{dt} = V_{+2}^{1,2} z^A - V_{-2}^{1,2} z^B \quad (22)$$

Graphical determination of  $d(C^A z^A)/dt$  or  $d(C^B z^B)/dt$  will enable direct evaluation of  $V_{\pm 2}^{1,2}$ . This approximation, however, will not enable separate values of  $v_{+1}$  and  $v_{+2}$  to be obtained. The same limitation occurs in the case of open systems as discussed in connection with Eqs. (5) and (6).

### Open Systems

It is not necessary to conduct experiments at equilibrium to describe open systems exactly in terms of linear differential equations with constant coefficients. It is convenient, however, to distinguish two cases for such unsteady state tracing. In the one case at time  $t=0$  a step concentration change could be introduced into the reactor system gases themselves, the same as is done in closed system experiments. In the second case at time  $t=0$  a step tracer concentration change is introduced into the feed stream and maintained. It is useful to consider these cases separately since the respective differential equations are not exactly the same.

For the case in which a tracer concentration change is introduced into the reactor system, in place of Eq. (11) we have a homogeneous system with the matrix  $A$  expressed as

$$A = \begin{bmatrix} -\left(\frac{F_P^A}{\beta C_P^A} + \frac{Wv_{+1}}{\beta C_P^A}\right) & \frac{Wv_{-1}}{\beta C_P^B} & 0 \\ \frac{v_{+1}}{C^{Ai}} & -\frac{(v_{+1} + v_{-2})}{C^{Ai}} & \frac{v_{-2}}{C^{Ai}} \\ 0 & \frac{Wv_{+2}}{\beta C_P^B} & -\left(\frac{F_P^B}{\beta C_P^B} + \frac{Wv_{-2}}{\beta C_P^B}\right) \end{bmatrix} \quad (23)$$

This matrix is not singular as in the case of Eq. (11). This is because the overall material balance is not time independent as in the case of the closed system; see Eq.

(17). The transient tracer concentrations can be expressed as previously and shown to be uniquely related to the parameter groupings in Eq. (23). Thus for  $z^A$  and  $z^B$ , we have

$$z^A = C_1 e^{t_1 t} + C_2 e^{t_2 t} + C_3 e^{t_3 t} \quad (24)$$

$$z^B = C_1 A e^{t_1 t} + C_2 B e^{t_2 t} + C_3 C e^{t_3 t} . \quad (25)$$

Experimental data will provide the values of the constants in Eq. (24) or (25). Values for  $\lambda_1$ ,  $\lambda_2$  and  $\lambda_3$  together with the initial concentrations  $z_0^A$ ,  $z_0^{At}$  and  $z_0^B$  provide six relationships. These or the six constants  $A$ ,  $B$ ,  $C$ ,  $\lambda_1$ ,  $\lambda_2$  and  $\lambda_3$  are sufficient to determine the following parameter groups, using numerical computation procedure:

$$\left( \frac{F_P^A}{\beta C_P^A} + \frac{Wv_{+1}}{\beta C_P^A} \right); \frac{Wv_{-1}}{\beta C_P^A}; \frac{v_{+1}}{C^{At}}; \frac{v_{-2}}{C^{At}}; \frac{Wv_{+2}}{\beta C_P^B}; \left( \frac{F_P^B}{\beta C_P^B} + \frac{Wv_{-2}}{\beta C_P^B} \right) . \quad (26)$$

In addition to these groups we know that

$$V = v_{+1} - v_{-1} = v_{+2} - v_{-2}; \frac{F_P^A}{C^A} = \frac{F_P^B}{C^B}; C^A + C^B = \text{constant}.$$

Thus, with a knowledge of  $W/\beta$  and of either  $C_P^A$  or  $C_P^B$  as previously we can determine  $v_{\pm 1}$ ,  $v_{\pm 2}$  and  $C^{At}$ . In addition, if we know  $F_P^A$  or  $F_P^B$ , it is possible to determine  $\beta$  from the tracer experiment.

For the open system case where a step change is introduced into the feed components, we have the non-homogeneous system originally postulated in this study, namely Eqs. (2)~(4). This system may be expressed as discussed, for example, by AMUNDSON<sup>3)</sup> as

$$\frac{dz_P^i}{dt} = A z_P^i + b . \quad (27)$$

The  $A$  matrix in Eq. (27) is the same as that in Eq. (23) and the column vector  $b$  is given by

$$b = \begin{bmatrix} \frac{F_P^A z_F^A}{\beta C_P^A} \\ 0 \\ \frac{F_P^B z_F^B}{\beta C_P^B} \end{bmatrix} . \quad (28)$$

The particular solution corresponds to the values of the tracer at steady state after a long time

$$K = \begin{bmatrix} z_{\infty}^A \\ z_{\infty}^{At} \\ z_{\infty}^B \end{bmatrix} = -A^{-1} b . \quad (29)$$

It is also known that

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$$V = \frac{F_P^A}{W} - \frac{F_P^A}{W} = \frac{F_P^B}{W} - \frac{F_P^B}{W}.$$

However, we do not need to use these relationships to obtain  $A$  because the particular solutions are directly observed. Solutions for Eq. (27) will be of the form:

$$z_P^A = C_1 e^{\lambda_1 t} + C_2 e^{\lambda_2 t} + C_3 e^{\lambda_3 t} + z_{P\infty}^A \quad (30)$$

$$z_P^B = C_1 A e^{\lambda_1 t} + C_2 B e^{\lambda_2 t} + C_3 C e^{\lambda_3 t} + z_{P\infty}^B \quad (31)$$

where the constants  $A$ ,  $B$ ,  $C$ ,  $\lambda_1$ ,  $\lambda_2$  and  $\lambda_3$  will be the same as for the homogenous case corresponding to the same conditions for overall reaction being studied *i. e.*, Eqs. (24) and (25).

### Generalization for Open Systems

It is in principle possible by observing the transient marking change for any single terminal species together with initial markings of intermediates or by observing transient marking for both terminal species alone to uniquely determine the parameter groupings for any reversible single path reaction network. There will be a single differential equation for each of the terminal species and intermediates in a given model mechanism. As an example let us consider a slightly more complicated system than previously, corresponding to



The  $A$  matrix corresponding to this system is

$$A = \begin{bmatrix} -\left(\frac{F_P^A}{\beta C_P^A} + \frac{Wv_{+1}}{\beta C_P^A}\right) & \frac{Wv_{-1}}{\beta C_P^A} & 0 & 0 \\ \frac{v_{+1}}{C^{Al}} & -\frac{v_{+1} + v_{-2}}{C^{Al}} & \frac{v_{-2}}{C^{Al}} & 0 \\ 0 & \frac{v_{+2}}{C^{Bl}} & -\frac{v_{+2} - v_{-3}}{C^{Bl}} & \frac{v_{-3}}{C^{Bl}} \\ 0 & 0 & \frac{Wv_{+3}}{\beta C_P^B} & -\left(\frac{F_P^B}{\beta C_P^B} + \frac{Wv_{-3}}{\beta C_P^B}\right) \end{bmatrix}. \quad (33)$$

This matrix contains eight parameter groups, two more than the previous  $3 \times 3$  matrix, corresponding to the two additional parameters required. The equations expressing  $z_P^A$  and  $z_P^B$  will each contain eight constants and we would be able to determine  $v_{\pm 1}$ ,  $v_{\pm 2}$ ,  $v_{\pm 3}$ ,  $C^{Al}$  and  $C^{Bl}$ .

### Irreversible Reactions

An overall reaction is considered irreversible when any one of the steps  $v_{-i}$  is so close to zero that it cannot be determined. For such a system the powerful criterion

developed by HORIUTI<sup>4,5)</sup> connecting thermodynamics to reaction rates of individual steps cannot be used.

The use of transient tracing in a closed system also presents problems because the steady state corresponding to a long time can never be attained without completely reacting the feed component.

Open systems do not present this problem, but observing the marking in reactant species alone will not be sufficient to characterize the system when irreversible steps are present. Thus, considering Eq. (33), if the first step were irreversible with  $v_{-1}=0$ , and an initial marking  $z_0^{A,F}$  were employed the differential equation for  $dz^A/dt$  is uncoupled and  $v_{+1}=V$  alone is determined from transient marking of A tracer. Of course, in this case initial marking of B will not be reflected in transient marking in A.

On the other hand marking  $z_0^{A,F}$  initially and observing the transient marking  $z^B$  will in principle enable all parameters in the system to be determined, even when irreversible steps are involved. If all steps are irreversible, *i. e.*, all  $v_{-i}=0$ ,  $\det(A-\lambda I)=0$  involves only the diagonal and the eigenvalues are all determined directly. In that case, if B is marked at the start, but not A, Al or Bl, we have corresponding to Eq. (33)  $\lambda_i = -F_i^B/\beta C_P$ , which can be evaluated from known information.

### Discussion

Since there exists one differential equation with constant coefficients for each terminal species and each intermediate, it should in principle be possible by marking only one species to resolve complicated networks involving more than two terminal species. From a practical viewpoint it is clear that the closer the unknown parameter is to a given terminal species the more readily it will be determined by marking of that species, unless a very slow or irreversible step intervenes between a reactant and intermediate.

In steady state tracing, as previously discussed by HAPPEL and HNATOW<sup>6)</sup> it is not possible to determine individual step velocities for even the simple sequence, Eq. (11), with one intermediate and two terminal species. Cases involving branching reactions can sometimes be resolved by additional use of HORIUTI's<sup>4,5)</sup> transition state relationships for cases where the reactions are reversible.

HORIUTI's relationships will, of course, also be applicable in the case of transient tracing where reversible reaction systems are involved. In general steady state tracing appears to be of more limited value than transient tracing, since sequences with a number of intermediates can be resolved and concentrations of intermediates determined in the latter case. Numerical implementation of the ideas presented here is discussed in a forthcoming publication, HAPPEL, *et al.*<sup>7)</sup> and applied to the oxidation of carbon monoxide.

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