A Dynamic Method for the Study of Heterogeneous Catalytic Kinetics

CARROLL O. BENNETT
University of Connecticut, Storrs, Connecticut

For a trial multistep mechanism for a heterogeneous catalytic reaction, it is suggested that dynamic experiments can be used to calculate the forward and reverse rate constants of individual steps. The experiments consist of the measurement of the composition of the effluent from a continuous stirred-tank catalytic reactor as a function of time as the input composition to the reactor is perturbed. The method of moments is used to obtain the kinetic constants for a trial mechanism from the experimental data.

The difficulty of determining the mechanism of reaction in heterogeneous catalysis is well known. At a given temperature, data on the rate of reaction as a function of composition can often be correlated equally well by equations based on several mechanisms, and the identity of the rate determining step, if any, is difficult to specify. For these reasons rates of catalytic reaction are often empirically expressed as simple n^{th} order equations rather than by the Langmuir-Hinshelwood forms (*3, 18*). A firmer elucidation of the mechanism of reaction usually requires experiments with radioactive tracers or separate adsorption studies. A particularly attractive experimental technique is exemplified by the work of Tamaru (*13, 14*); the amount of adsorption is measured during catalysis.

Additional information on the kinetics of a set of simultaneous reactions can be obtained by unsteady state methods. Eigen and co-workers (*5*) have used relaxation methods to study homogeneous liquid phase reactions. A system at equilibrium is perturbed by a sudden burst of added energy from a high-voltage discharge so that there is a step function increase in the temperature. From the behavior of the system as it reacts toward equilibrium at the new temperature, rate constants in reaction steps can be found. Often the rate determining step in a series of reactions can be deduced by comparing the actual kinetics with those predicted by a mechanism. The temperature or pressure jump required for these studies can also be obtained by shock-tube techniques. Hulburt and Kim (*10*) have suggested that these relaxation methods might be used to add to information on mechanisms in heterogeneous catalysis. Rather than use a temperature jump, it is proposed in this paper that a feed-composition jump from an initial steady state in a continuous flow stirred-tank catalytic reactor (*13*) be used; the pressure and temperature are held constant.

The observation of the response of a flow reactor to a step change in feed composition has been used by Carl Wagner and co-workers (*12*) to investigate mechanisms in heterogeneous vapor phase catalysis. A similar method has recently been used by Hwang (*11*). Hudgins (*9*) has used a sinusoidally varying input concentration to analyze the frequency response of a reactor for the catalytic dehydration of ethanol. All these investigators used conventional tubular reactors, so that the analysis of the data was complicated by nonideal flow and in some cases by diffusional resistances. In this paper it is proposed that a well-stirred reactor be used with small catalyst particles, so that it is not necessary to consider how the input signal travels through the length of a reactor or into catalyst pores.

As an example of a solid-catalyzed gas reaction, let us consider the oxidation of carbon monoxide to carbon dioxide over a solid catalyst.

$$CO + \tfrac{1}{2}\, O_2 \rightarrow CO_2 \tag{1}$$

This reaction may be broken down into the steps

$$CO + V \rightleftarrows CO^* \tag{2}$$

$$\tfrac{1}{2}\, [O_2 + 2V \rightleftarrows 2\ O^*] \tag{3}$$

$$O^* + CO^* \rightleftarrows CO_2^* + V \tag{4}$$

$$CO_2^* \rightleftarrows CO_2 + V \tag{5}$$

In these equations the starred quantities refer to adsorbed species; V is a vacant active site. The ½ before Equation (3) is like a stoichiometric number (*8*); this reaction occurs only one-half as many times as do the other steps.

This mechanism is discussed here only as a reasonable example from among those possible. For instance, the oxygen might react with carbon monoxide to form $CO_3^=$ ions on the catalyst surface (*5, 19*).

With the stirred reactor operating at steady state, let us suppose that the ratio of carbon monoxide to oxygen in the feed is suddenly increased. If Equation (2) is the controlling step, it will take some time for the carbon monoxide and carbon dioxide in the effluent to reach their new steady state values, whereas most of the change in the oxygen concentration will come about more quickly. It should also be evident that the relative rates of four steps cannot be found by measuring three components. Therefore, the present method can distinguish only among the consecutive steps in which the gaseous, measurable components participate. The surface reaction step is not distinguished from the desorption step. An example of a mechanism which might be tested is

$$\tfrac{1}{2}\,[O_2 + 2V \rightleftarrows 2\ O^*] \tag{6}$$

$$CO + O^* \rightleftarrows CO_2^* \tag{7}$$

$$CO_2^* \rightleftarrows CO_2 + V \tag{8}$$

The extent of these three reactions can now be found from the measured concentrations of the three gaseous components as they respond to a step change in the feed to the reactor. The method of obtaining the reaction rate constants and associated relaxation times from the results is described in what follows.

Before proceeding with the description of the way the rates constants can be derived, it is of interest to note that it may sometimes be possible to measure the concentration of one of the adsorbed species in addition to the concentration of the gaseous species. Schönnagel and Wagner (*12*), in studying the catalytic decomposition of formic acid, obtained the adsorbed hydrogen concentration on a palladium catalyst from measurements of the electrical resistance of their catalyst foil. Similarly, Hwang (*11*), who studied the reaction $N_2O + CO \rightleftarrows N_2 + CO_2$ over *n* and *p* types of cobalt ferrite catalysts, measured the thermoelectric power of the catalyst as a function of time, in response to a step change in feed composition. Although not specifically considered, experimentally determined surface concentrations can be used in the analysis to follow as measures of the extent of appropriate steps in a proposed mechanism.

First let us define the relaxation time for the single batch reaction:

$$\sum_{j=1}^{S} \alpha_j A_j = 0 \tag{9}$$

Following Aris (*2*), we define the extent of reaction ξ by

$$c_j = c_{jo} + \alpha_j\ \xi \tag{10}$$

or

$$\xi = \frac{c_j - c_{jo}}{\alpha_j} \tag{11}$$

The rate of reaction is

$$r = \frac{d\xi}{dt} \tag{12}$$

and at equilibrium $r = 0$ and $\xi = \xi_e$. Let

$$X = \xi - \xi_e \tag{13}$$

For a small perturbation from equilibrium ($X << \xi_e$), a McLaurin series gives

$$r = \left(\frac{\partial r}{\partial \xi}\right)_{\xi=\xi_e} X = \beta\ X \tag{14}$$

The conservation equation is now

$$r = \frac{d\xi}{dt} = \frac{dX}{dt} = \beta\ X \tag{15}$$

and

$$X = X_o e^{\beta t} \tag{16}$$

where β must be negative.

For the reaction

$$A_1 + A_2 \rightleftarrows A_3 \tag{17}$$

we can write

$$r = k_1\ c_1\ c_2 - k_1'\ c_3 \tag{18}$$

and

$$\beta = \frac{\partial r}{\partial \xi} = \sum_{j=1}^{S} \frac{\partial r}{\partial c_j}\ \frac{\partial c_j}{\partial \xi} \tag{19}$$

Noting that $\partial c_j/\partial \xi = \alpha_j$ and applying Equation (19) to (18) we get

$$\beta = -\ k_1\ (\bar{c}_1 + \bar{c}_2) - k_1' \tag{20}$$

The quantity β is thus negative, and it is defined as $-1/\tau$, where τ is the relaxation time. The changes in the c_j's are presumed to be small enough so that it is satisfactory to use the average value ($\bar{c}_1 + \bar{c}_2$) in Equation (20). The quantity X follows a first-order decay equation with a time constant τ:

$$X = X_o e^{-t/\tau} \tag{21}$$

For a set of equations

$$\sum_{j=1}^{S} \alpha_{ij}\ A_j = 0 \qquad i = 1, 2, \ldots R \tag{22}$$

an extent of reaction can be defined by

$$c_j = c_{jo} + \sum_{i=1}^{R} \alpha_{ij}\ \xi_i \tag{23}$$

and the conservation equation becomes, in terms of X_i

$$\frac{dX_i}{dt} = \sum_{k=1}^{R} \beta_{ik}\ X_k \tag{24}$$

where

$$\beta_{ik} = \frac{\partial r_i}{\partial \xi_k} = \sum_{j=1}^{S} \alpha_{kj} \frac{\partial r_i}{\partial c_j} \tag{25}$$

Equation (24) becomes in matrix notation

$$\left\{\frac{dX}{dt}\right\} = [\beta]\ \{X\} \tag{26}$$

Because a given component *j* càn participate in several reactions *i*, the equations are coupled and the relaxation time for a reaction *i* is not apparent. The relaxation times are usually defined (*6*) with respect to the eigenvalues of the matrix $[\beta]$. By a similarity transformation using the modal matrix $[Y]$ the equations in (26) can be uncoupled to give

$$[Y]\left\{\frac{dX}{dt}\right\} = [Y]\ [\beta]\ [Y]^{-1}\ [Y]\ \{X\} \tag{27}$$

or

$$\left\{\frac{dU}{dt}\right\} = \ulcorner\Lambda\lrcorner\ \{U\} \tag{28}$$

where

$$\{U\} = [Y]\ \{X\} \tag{29}$$

and

$$\ulcorner \Lambda \lrcorner = \begin{matrix} \ulcorner -1/\tau_1 & & & \\ & -1/\tau_2 & & \\ & & \ddots & \\ & & & -1/\tau_R \end{matrix} \qquad (30)$$

Equation (28) can be written as

$$\frac{dU_i}{dt} = -\frac{1}{\tau} U_i \quad (i = 1, 2, \ldots R) \qquad (31)$$

with the solutions

$$U_i = U_{io} e^{-t/\tau_i} \qquad (32)$$

This procedure has been given by Eigen (*6*) and by Wei and Prater (*17*). However, the uncoupled equations here lack the usefulness of those treated by Wei and Prater, for there is apparently no comparably elegant way of using the data to find the modal matrix and the eigenvalues of $[\beta]$ when the β_{ij} are unknown. In principle, a batch agitated catalytic reactor such as used by Haag and Pines (*7*) could be used to find the relative rates of the pseudomass action steps by the methods of Wei and Prater. However, the concentrations of adsorbed species (g.-mole/cc. of reactor free volume) are negligibly small in a slowly reacting system containing a low mass of catalyst per unit volume. In such a system the observable components will merely follow the stoichiometry of Equation (17). Because of the experimental difficulty of following the composition history in a batch catalytic reactor, when the relaxation times are only seconds, we consider here a flow system. Although a stirred catalytic reactor does not permit as high a catalyst concentration as a plug-flow reactor, it has two basic advantages: the composition is constant throughout the reactor, so that the composition change from inlet to outlet can be integral; and the fluid dynamics in the reactor are almost independent of rate of throughput.

For a continuous flow stirred-tank catalytic reactor of constant volume, the mass balance on a gaseous component j is

$$V \frac{d\rho_j}{dt} = q_f \rho_{jf} - q\rho_j + V m_j \sum_{i=1}^{R} \alpha_{ij} r_i \qquad (33)$$
$$(j = 1, 2, \ldots S)$$

where the volumetric flow rates q_f and q and the mass concentrations ρ_{jf} and ρ_j are measured at the temperature and pressure in the reactor. When we divide through by the molecular weight m_j, Equation (33) becomes

$$\frac{dc_j}{dt} = \frac{q_f}{V} c_{jf} - \frac{q}{V} c_j + \sum_{i=1}^{R} \alpha_{ij} r_i \qquad (34)$$
$$(j = 1, 2, \ldots S)$$

where $r_i = r_i\,(c_j)$.

The balance on an adsorbed component, including the vacant active sites, is

$$\frac{dc_j^*}{dt} = \sum_{i=1}^{R} \alpha_{ij} r_i \quad (j = S, S+1, \ldots S^*) \qquad (35)$$

When Equation (34) is summed over j, it becomes

$$\left(\sum_{j}^{S} c_j = c = c_f = p/RT \right)$$

$$\frac{c(q_f - q)}{V} + \sum_{i=1}^{R} \bar{\alpha}_i r_i = 0 \qquad (36)$$

where

$$\bar{\alpha}_i = \sum_{j=1}^{S} \alpha_{ij}$$

We must remember that the r_i are not necessarily all equal except at steady state. If Equation (35) is summed over j, including the vacant sites, the right-hand side must be zero. However, if the massless active sites are omitted

$$\frac{dc^*}{dt} = \sum_{i=1}^{R} \bar{\alpha}_i^* \, r_i \qquad (37)$$

where

$$\bar{\alpha}_i^* = \sum_{j=S+1}^{S^*-1} \alpha_{ij}$$

At steady state, for consecutive steps, the r_i are all equal, and $dc^*/dt = 0$. Also, Equation (34) becomes

$$\frac{q_f c_{jf} - q_s c_{js}}{V} + \bar{\alpha}_j r_s = 0 \qquad (38)$$

and Equation (36) becomes

$$\frac{q_f c - qc}{V} + \bar{\alpha} \; r_s = 0 \qquad (39)$$

where

$$\bar{\alpha}_j = \sum_{i=1}^{R} \alpha_{ij} \qquad (40)$$

and

$$\bar{\alpha} = \sum_{i=1}^{R} \bar{\alpha}_i = \sum_{j=1}^{S} \bar{\alpha}_j \qquad (41)$$

The unsteady state behavior is to be generated in the reactor by a step change from c_{jf}^o to a new c_{jf}, which will eventually cause the concentration in the reactor to change from c_{jo} to c_{js}. These four compositions are measurable quantities. The step change will be small enough so that $c_j - c_{js}$ is much less than c_j, permitting a linearization of the problem by considering the c_j to remain approximately constant as $c_j - c_{js}$ changes from $c_{jo} - c_{js}$ to zero. The resulting simplification of the problem contributes to the method to be developed for finding the rate constants of the individual steps in the catalytic sequence. This linearization also depends on the existence of a relatively small variation in q. It may be necessary with certain reactions for which $\bar{\alpha}_i \neq 0$ to include inert gas in the feed so that q does not change excessively in going from q_o to q_s.

It will be convenient to reduce the number of compositions variables by defining an extent of each reaction, ξ_i. Aris' definition (*2*) is modified for the present problem to give

$$c_j = \frac{q_f}{q} c_{jf} + \sum_{i=1}^{R} \alpha_{ij} \, \xi_i + \Delta c_j \, \zeta \qquad (42)$$
$$j = 1, 2, \ldots S$$

where

$$\zeta = e^{-t/\theta}; \; \theta = V/q \qquad (43)$$

and

$$\Delta c_j = (c_{jf}^o - c_{jf}) \frac{q_f}{q} \qquad (44)$$

For the adsorbed components we define ξ_i by

$$c_j = c_j^o + \sum_{i=1}^{R} \alpha_{ij} \xi_i \quad (j = S+1, S+2, \ldots S^*) \qquad (44a)$$

Equation (42) is formed so that the extent ξ_i is corrected for the mixing effect in the stirred reactor and for the change in volume caused by the reaction. At $t = 0$, Equation (42) gives

$$c_{jo} = \frac{q_f}{q_o} c_{jf}^{o} + \sum_{i=1}^{R} \alpha_{ij}\, \xi_{io} \qquad (45)$$

corresponding to steady state before the step change. As $t \to \infty$

$$c_{js} = \frac{q_f}{q_s} c_{jf} + \sum_{i=1}^{R} \alpha_{ij}\, \xi_{is} \qquad (46)$$

Equation (42) is now substituted into Equation (34) to yield

$$\sum_{i=1}^{R} \alpha_{ij} \frac{d\xi_i}{dt} + \Delta c_j \frac{d\zeta}{dt} = -\frac{\bar{q}}{V} \sum_{i=1}^{R} \alpha_{ij}\xi_i - \frac{\bar{q}}{V} \Delta c_j \zeta + \sum_{i=1}^{R} \alpha_{ij} r_i \qquad (47)$$

In obtaining this equation it has been presumed that the change in q is small so that a term in dq/dt is omitted; $\bar{q}$ is the average of q_{so} and q_s. In view of the definition of ζ, Equation (47) can be simplified to

$$\sum_{i=1}^{R} \alpha_{ij} \frac{d\xi_i}{dt} + \frac{1}{\theta} \sum_{i=1}^{R} \alpha_{ij}\xi_i - \sum_{i=1}^{R} \alpha_{ij} r_i = 0 \qquad (48)$$

Since $\bar{\alpha}_j$ is not identically zero, we obtain from this expression

$$\frac{d\xi_i}{dt} + \frac{\xi_i}{\theta} - r_i = 0 \qquad (49)$$

At steady state we have

$$\frac{\xi_{is}}{\theta} - r_{is} = 0 \qquad (50)$$

so that

$$\frac{dZ_i}{dt} + \frac{Z_i}{\theta} - (r_i - r_{is}) = 0 \qquad (51)$$

where

$$Z_i = \xi_i - \xi_{is} \qquad (52)$$

For $Z_i << \xi_i$, we expand r_i around r_{is} by a Taylor series:

$$r_i - r_{is} = \sum_{k=1}^{R} \frac{\partial r_i}{\partial \xi_k} Z_k + \frac{\partial r_i}{\partial \zeta} \zeta \qquad (53)$$

$$\frac{\partial r_i}{\partial \xi_k} = \sum_{j=1}^{S^*} \frac{\partial c_j}{\partial \xi_k} \frac{\partial r_i}{\partial c_j} = \sum_{j=1}^{S^*} \alpha_{kj} \frac{\partial r_i}{\partial c_j} \qquad (54)$$

$$\frac{\partial r_i}{\partial \zeta} = \sum_{j=1}^{S^*} \frac{\partial r_i}{\partial \zeta} \frac{\partial r_i}{\partial c_j} = \sum_{j=1}^{S^*} \Delta c_j \frac{\partial r_i}{\partial c_j} \qquad (55)$$

In Equation (55), $\Delta c_j = 0$ for $j > S$.

Now B_{ik} and C_i are defined so that

$$B_{ik} = \frac{\partial r_i}{\partial \xi_k} = \sum_{j=1}^{S^*} \alpha_{kj} \frac{\partial r_i}{\partial c_j} \qquad (56)$$

and

$$C_i = \frac{\partial r_i}{\partial \zeta} = \sum_{j=1}^{S^*} \Delta c_j \frac{\partial r_i}{\partial c_j} \qquad (57)$$

Equation (51) then becomes

$$\frac{dZ_i}{dt} + \frac{Z_i}{\theta} - \sum_{k=1}^{R} [B_{ik} Z_k + \delta_{ik} C_k \zeta] = 0 \qquad (58)$$

It is evident from Equations (56) and (57) that the B_{ik} and C_i are related. By using these equations, we change Equation (58) to

$$\frac{dZ_i}{dt} + \frac{Z_i}{\theta} - \sum_{j=1}^{S^*} \frac{\partial r_i}{\partial c_j} \sum_{k=1}^{R} (\alpha_{kj} Z_k + \delta_{kj} \Delta c_k\, \zeta) = 0 \qquad (59)$$

Let us define D_{ij} as an element in the matrix of coefficients $\partial r_i/\partial c_j$, and E_j by

$$E_j = \sum_{k=1}^{R} (\alpha_{kj}\, Z_k + \delta_{kj}\, \Delta c_k\, e^{-t/\theta}) \qquad (60)$$

Then E_j is an experimentally known function of time, and we want to solve for the quantities D_{ij} in the equation

$$\frac{dZ_i}{dt} + \frac{Z_i}{\theta} = \sum_{j=1}^{S^*} D_{ij} E_j \qquad (61)$$

The values of the D_{ij}, which are independent of time, can be found by using the methods of moments (*4*, *16*). Equation (61) can be put in the form

$$\int_{Z_{io}}^{0} dZ_i + \frac{1}{\theta} \int_0^\infty Z_i dt = \sum_{j=1}^{S^*} D_{ij} \int_0^\infty E_j dt \qquad (62)$$

or

$$-Z_{io} + \frac{M_i^{(o)}}{\theta} = \sum_{j=1}^{S^*} D_{ij}\, N_j^{(o)} \qquad (63)$$

where $M_i^{(o)}$ is the zeroth moment of Z_i and $N_j^{(o)}$ is the zeroth moment of E_j. The Laplace transform of (61) is

$$s \int_0^\infty e^{-st}\, Z_i dt - Z_{io} + \frac{1}{\theta} \int_0^\infty e^{-st}\, Z_i dt = \sum_{j=1}^{S^*} D_{ij} \int_0^\infty e^{-st} E_j dt \qquad (64)$$

The limit of Equation (64) as $s \to 0$ is the same as Equation (63). To take advantage of higher moments, we differentiate Equation (64) with respect to s to give

$$s \int_0^\infty (-t) e^{-st}\, Z_i dt + \int_0^\infty e^{-st}\, Z_i dt + \frac{1}{\theta} \int_0^\infty (-t)\, e^{-st}\, Z_i dt = \sum_{j=1}^{S^*} D_{ij} \int_0^\infty (-t) e^{-st}\, E_j dt \qquad (65)$$

Taking the limit as $s \to 0$, we get

$$\int_0^\infty Z_i dt - \frac{1}{\theta} \int_0^\infty t\, Z_i dt = -\sum_{j=1}^{S^*} D_{ij} \int_0^\infty t\, E_j dt \qquad (66)$$

or

$$M_i^{(0)} - \frac{M_i^{(1)}}{\theta} = -\sum_{j=1}^{S^*} D_{ij} N_j^{(1)} \qquad (67)$$

where $M_i^{(1)}$ and $N_j^{(1)}$ are defined as the first moments of Z_i and E_j. A second differentiation of Equation (64) gives

$$s \int_0^\infty t^2\, e^{-st}\, Z_i dt - \int_0^\infty t\, e^{-st}\, Z_i dt - \int_0^\infty t\, e^{-st}\, Z_i dt + \frac{1}{\theta} \int_0^\infty t^2\, e^{-st}\, Z_i dt = \sum_{j=1}^{S^*} D_{ij} \int_0^\infty t^2\, e^{-st}\, E_j dt \qquad (68)$$

As s goes to zero, this becomes

$$-2\, M_i^{(1)} + \frac{M_i^{(2)}}{\theta} = \sum_{j=1}^{S^*} D_{ij}\, N_j^{(2)} \qquad (69)$$

Equations (63), (67), and (69) can be written together as

$$
\begin{aligned}
\sum_{j=1}^{S^*} D_{ij}\, N_j^{(0)} &= \frac{M_i^{(0)}}{\theta} - Z_{io} \\
\sum_{j=1}^{S^*} D_{ij}\, N_j^{(1)} &= \frac{M_i^{(1)}}{\theta} - M_i^{(0)} \qquad (70) \\
\sum_{j=1}^{S^*} D_{ij}\, N_j^{(2)} &= \frac{M_i^{(2)}}{\theta} - 2M_i^{(1)}
\end{aligned}
$$

From these nine linear equations we can find the values of nine of the D_{ij}. Reference to Equations (6) to (8) shows that of the eighteen possible D_{ij} ($R = 3$, $S^* = 6$) nine are zero. A little thought will show that other three-step mechanisms for the reaction will also result in only nine nonzero D_{ij}. For some mechanisms, especially simpler ones, there are additional relations among the D_{ij}. Rather than continue with a general notation, it is clearer to complete the solution for the D_{ij} in terms of Equations (6) to (8). We identify the components as follows:

Component	j
O_2	1
CO	2
CO_2	$3 = S$
O^*	4
CO_2^*	$5 = S^* - 1$
V	$6 = S^*$

For the index i, 1 refers to Equation (6), 2 to (7), and 3 to (8), so that $R = 3$. The rate equations are

$$r_1 = k_1 c_1 c_6^2 - k'_1 c_4^2 \qquad (71)$$

$$r_2 = k_2 c_2 c_4 - k'_2 c_5 \qquad (72)$$

$$r_3 = k_3 c_5 - k'_3 c_3 c_6 \qquad (73)$$

From these equations is found

$$D_{ij} = \frac{\partial r_i}{\partial c_j} = \begin{bmatrix} k_1\bar{c}_6^2 & 0 & 0 & -2k'_1\bar{c}_4 & 0 & 2k_1\bar{c}_1\bar{c}_6 \\ 0 & k_2\bar{c}_4 & 0 & k_2\bar{c}_2 & -k'_2 & 0 \\ 0 & 0 & -k'_3 c_6 & 0 & k_3 & -k'_3\bar{c}_3 \end{bmatrix} \qquad (74)$$

The Equations (70) can now be written as

$$\begin{bmatrix}
N_1^{(0)} & N_4^{(0)} & N_6^{(0)} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & N_2^{(0)} & N_4^{(0)} & N_5^{(0)} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & N_3^{(0)} & N_5^{(0)} & N_6^{(0)} \\
N_1^{(1)} & N_4^{(1)} & N_6^{(1)} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & N_2^{(1)} & N_4^{(1)} & N_5^{(1)} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & N_3^{(1)} & N_5^{(1)} & N_6^{(1)} \\
N_1^{(2)} & N_4^{(2)} & N_6^{(2)} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & N_2^{(2)} & N_4^{(2)} & N_5^{(2)} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & N_3^{(2)} & N_5^{(2)} & N_6^{(2)}
\end{bmatrix}
\begin{Bmatrix} D_{11} \\ D_{14} \\ D_{16} \\ D_{22} \\ D_{24} \\ D_{25} \\ D_{33} \\ D_{35} \\ D_{36} \end{Bmatrix}
=
\begin{Bmatrix}
M_1^{(0)}/\theta - Z_{10} \\
M_2^{(0)}/\theta - Z_{20} \\
M_3^{(0)}/\theta - Z_{30} \\
M_1^{(1)}/\theta - M_1^{(0)} \\
M_2^{(1)}/\theta - M_2^{(0)} \\
M_3^{(1)}/\theta - M_3^{(0)} \\
M_1^{(2)}/\theta - 2M_1^{(1)} \\
M_2^{(2)}/\theta - 2M_2^{(1)} \\
M_3^{(2)}/\theta - 2M_3^{(1)}
\end{Bmatrix} \qquad (75)$$

When the values of D_{ij} have been found from the solution (*1*) of this set of linear equations, Equation (74) permits the calculation of the six reaction rate constants and the values of $\bar{c}_4$ and $\bar{c}_6$. The value of $\bar{c}_5$ can be found from Equation (72), for example, applied to data from the steady state measurements. We define $\bar{r} = (r_{so} + r_s)/2$, and then

$$\bar{r} = k_2\bar{c}_2\bar{c}_4 - k'_2\bar{c}_5 \qquad (76)$$

In view of the level of experimental uncertainty common in kinetic studies, it may not be practical to calculate as many as nine constants from experimental results on most systems. For example, it may appear from a qualitative study of experimental results, or from dynamic studies of the type described by Tamaru (*14*), that the step represented by Equation (8) is very rapid. Then the proposed mechanism would be represented by

$$\tfrac{1}{2}\,[O_2 + 2V \rightleftarrows 2O^*] \qquad (6)$$

$$CO + O^* \rightleftarrows CO_2 + V \qquad (77)$$

Here there would be four reaction rate constants and two surface concentrations to determine, and Equations (74) and (75) would be altered accordingly.

The rate of flow to the reactor can be changed so that a new set of D_{ij} can be found at a different value of ξ_s. Equation (74) then permits a test of the mechanism, for the rate constants should remain constant. Other consecutive three-step mechanisms can be tested against the data so that the most plausible one can be determined. A similar procedure could be aged for trial two-step mechanisms like that represented by Equations (6) and (77).

The nature of the backmixed reactor is such that the relaxation time of the slowest step in the series is of the same order as the residence time θ. The latter can be measured by a tracer experiment (*13*). However, the relaxation times of the other steps in the catalytic sequence may be so much less than θ that their rate constants cannot be determined. Equation (75) then could not be solved, and it would be necessary to shorten the proposed mechanism to fewer steps, as already mentioned.

A given composition, and thus r_s, can be obtained at lower values of θ and ξ_s by feeding to the reactor a partially converted mixture rather than a mixture of the reactants only. This procedure should permit the detection of the more rapid steps in the mechanism. Of course, if θ is reduced too much, the slowest (rate controlling) step may not be affected by the step change in feed composition.

The procedure which has been described here, along with the usual methods of applying the Langmuir-Hinshelwood equations to the analysis of steady state data (*2*, pp. 116-122) has the defect of requiring the calculation of six to nine constants from the data. It should not be viewed as a replacement for other ways of studying mechanisms, but as an added method, to be used as the very least along with steady state measurements. It would probably require kinetic data of usual precision to apply the dynamic method to anything more complicated than two-step mechanisms. Nevertheless, it can be said in favor the proposed analysis that in a sense the Z_i vs. time curves provide a very large number of points. These short experiments can easily be repeated many times so that good statistical reliability can be obtained, and the method of moments takes advantage of the inherent reliability of integrated data over differentiated data.

An experimental application of the method is being planned and will be reported later. The use of a pulse input is also being considered.

NOTATION

A_j = chemical symbol of j^{th} component
B_{ik} = $\partial r_i/\partial \xi_k$, sec.$^{-1}$
C_i = $\partial r_i/\partial \zeta$, g. mole/(cc.)(sec.)
c_j = concentration of j, g. mole/cc.
c_{jo} = c_j at $t = 0$
c_{jf} = c_j of feed to reactor
c_j^* = concentration of adsorbed species, g.-mole/cc. of of void volume
c = molal density, g.-mole/cc.
c_{js} = c_j as $t \to \infty$
c_{jf}^o = c_{jf} before step change $(t < 0)$
c_j^o = reference concentration of adsorbed species, g.-mole/cc.
D_{ij} = $\partial r_i/\partial c_j$, sec.$^{-1}$
E_j = $\sum_{k=1}^{R} (\alpha_{kj} Z_k + \delta_{kj} \Delta c_k \ e^{-t/\theta})$, g.-mole/cc.
k_1, k_2, etc. = reaction rate constants, suitable units
m_j = molecular weight of j, g./g.-mole
$M_i^{(0)} = \int_0^\infty Z_i dt$, zeroth moment of Z_i
$M_i^{(1)} = \int_0^\infty t \ Z_i dt$, first moment of Z_i
$M_i^{(n)} = \int_0^\infty t^n \ Z_i dt$, n^{th} moment of Z_i
$N_j^{(n)} = \int_0^\infty t^n \ E_j dt$, n^{th} moment of E_j
$N_j^{(1)} = \int_0^\infty t \ E_j dt$, first moment of E_j
$N_j^{(0)} = \int_0^\infty E_j dt$, zeroth moment of E_j
p = pressure, atm.
q = volumetric flow rate from reactor, cc./sec.
q_f = q of feed to reactor
q_o = q at $t = 0$
q_s = q as $t \to \infty$
r = rate of reaction, g.-mole/(cc.)(sec.)
r_i = rate of i^{th} reaction, g.-mole/(cc.)(sec.)
R = gas constant, (cc.)(atm.)/(g.-mole)(°K.)
R = number of consecutive reaction steps
r_{is} = $r_s = r$ as $t \to \infty$
S = number of gaseous components
S^* = number of gaseous plus adsorbed components plus vacancies
T = temperature, °K.
t = time, sec.
$\{U\}$ = $[Y]\{X\}$, transformed perturbation vector, g.-mole/cc.
V = void volume of reactor, cc.
X = $\xi - \xi_e$, g.-mole/cc.
X_o = $\xi_o - \xi_e$
Z_i = $\xi_i - \xi_{is}$

Greek Letters

α_j = stoichiometric coefficient of j^{th} component
$\bar{\alpha}_i = \sum_{j=1}^{S} \alpha_{ij}$
$\bar{\alpha}_i^* = \sum_{j=S+1}^{S^*-1} \alpha_{ij}$
$\bar{\alpha}_j = \sum_{i=1}^{R} \alpha_{ij}$
$\bar{\alpha} = \sum_{j=1}^{S} \bar{\alpha}_j$
α_{ij} = α of j in i^{th} reaction
β = $\partial r/\partial \xi$, sec.$^{-1}$
β_{ik} = $\partial r_i/\partial \xi_k$
δ_{ij} = Kronecker delta, $= 1$ for $i = j$; $= 0$ for $i \neq j$
Δc_j = $c_{jf}^o - c_{jf}$
ζ = $e^{-t/\theta}$
θ = V/q = residence time, sec.
$\ulcorner \Lambda \lrcorner$ = $[Y]\ [\beta]\ [Y^{-1}]$, diagonal matrix of eigenvalues of $[\beta]$, sec.$^{-1}$
ξ = extent of reaction, g.-mole/cc.
ξ_e = ξ at equilibrium
ξ_i = extent of i^{th} reaction, g.-mole/cc.
ξ_{is} = ξ_i as $t \to \infty$
ρ_j = concentration of j, g./cc.
ρ_{jf} = ρ_j of feed
τ = relaxation time, sec.

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