R & D NOTES

Kinetic Behavior of Mixtures with Many First-Order Reactions

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The feed to industrial reactors, in general, consists of many species. For the design and control of these reactors, it is desirable to describe the kinetic behavior of the mixture in terms of concentration of grouped species rather than the concentration of individual species. Many papers dealt with the kinetics of mixtures with many first-order reactions (Wei and Kuo, 1969; Bailey, 1972; Ozawa, 1973; Liu and Lapidus, 1973; Hutchinson and Luss, 1970; Luss and Hutchinson, 1971).

In order to arrive at the general kinetic model, a mixture with many reversible reactions is first considered. Extension of the results to a mixture with many irreversible reactions and to a mixture with a combination of reversible and irreversible reactions follows from the case of reversible reactions by simply setting $k_i^* = 0$ for each species that follows irreversible reaction.

CONCENTRATION OF GROUPED SPECIES AND AN nTH-ORDER DIFFERENTIAL EQUATION

Consider a mixture of n species. If each species in the mixture follows reversible first-order reaction, the concentration of species i is

$$C_i = C_{io}\,[k_i e^{-(k_i + k_i^*)t} + k_i^*]/b_i \qquad (1)$$

$$b_i = k_i + k_i^* \qquad (2)$$

Then, the concentration of the grouped species is

$$C = C_o + \sum_{i=1}^{n} g_i(e^{-b_i t} - 1) \qquad (3)$$

where

$$C = \sum_{i=1}^{n} C_i \qquad (4)$$

$$g_i = C_{io}k_i/b_i \qquad (4a)$$

It can be shown that Equation (3) is the same as the solution of an n^{th}-order differential equation

$$\frac{d^nC}{dt^n} + a_1(T)\frac{d^{n-1}C}{dt^{n-1}} + a_2(T)\frac{d^{n-2}C}{dt^{n-2}} + \dots + a_{n-1}(T)\frac{dC}{dt} + a_n(T)C = Q(T, C_{io}) \qquad (5)$$

if

$$a_1 = \sum_{i=1}^{n} b_i \qquad (6)$$

$$a_2 = \sum_{i=1}^{n-1}\sum_{\substack{j\\ j>i}}^{n} b_i b_j \qquad (7)$$

$$a_n = \prod_{m=1}^{n} b_m \qquad (8)$$

$$Q = a_n\left[C_o - \sum_{i=1}^{n} g_i\right] \qquad (9)$$

The term a_i is the sum of all the possible combination (${}^nC_i$) product terms of rate constants and a function of temperature only.

A WORKING EQUATION AND AN EXAMPLE

To obtain a working equation, Equation (5) is integrated n times with respect to time:

$$a_1\int_o^t C\,dt + a_2\int_o^t\int_o^\tau C\,d\tau dt + \dots + a_n\overset{(n)}{\int_o^t} C\,dt^{(n)} = Qt^n/n! + G_nt^{n-1}/(n-1)! + \dots + G_3t^2/2 + G_2t + (C_o - C) \qquad (10)$$

where

$$G_j = [C^{(j-1)} + a_1C^{(j-2)} + \ldots + a_{j-1}C]|_{t=0} \qquad j = 2, \ldots, n \quad (11)$$

$$C^{(j)} = d^jC/dt^j \quad (12)$$

Equation (10) can be used as a working equation to determine the values of a_i, Q and initial conditions of Equation (5) from experimental data of C vs. time. This will be illustrated by a simple example.

For a mixture of three species, Equation (10) can be written, after integration

$$\begin{aligned} a_1(f_1 + I_1 + Jt) &+ a_2(f_2 + I_1t + Jt^2/2 + I_2) \\ &+ a_3(f_3 + I_1t^2/2 + Jt^3/6 + I_2t + I_3) \\ &= Qt^3/6 + G_3t^2/2 + G_2t + (C_o - C) \end{aligned} \quad (13)$$

where f_i is the exponential terms in Equation (3) integrated i times and then evaluated at time t, I_i is the value of f_i at time zero, and J is the constant term in Equation (3); that is, $J = C_o - \sum_i g_i$. For the equality of Equation (13) to hold at time much greater than 1, where the exponential terms vanish

$$\begin{aligned} Q &= a_3J && \text{for } t^3 \text{ term} \\ G_3 &= a_2J + a_3I_1 && \text{for } t^2 \text{ term} \\ G_2 &= a_1J + a_2I_1 + a_3I_2 && \text{for } t \text{ term} \end{aligned} \quad (14)$$

Making use of equalities of Equation (14) in Equation (10) for a mixture of three species, we get

$$a_1\left(\int_o^t C\,dt - Jt\right) + a_2\left(\int_o^t\int_o^\tau C\,d\tau dt - I_1t - Jt^2/2\right) + a_3\left(\int_o^{t\,(3)} C\,dt - I_2t - I_1t^2/2 - Jt^3/6\right) = C_o - C \quad (15)$$

Each term in Equation (15) approaches a constant value of I_i as time approaches infinity or when the exponential terms vanish. To determine I_1 and J, the concentration of grouped species is integrated, and the integrated value is plotted against time until it becomes a straight line. The slope of the line is J, and the intercept is I_1. To determine I_2, the second term in Equation (15) with the exclusion of a_2 is computed until it reaches a constant value, which is I_2. One may note that I_1 and J are known by now. Having obtained all the unknowns in Equation (15), except for a_i, we can now select the parameters that best fit the quantity $(C_o - C)$. Once the parameters a_i are determined, the values of Q, G_2, and G_3 can be determined from Equation (14) and the initial conditions of the differential Equation (5) from the definition of G_i [Equation (11)]. Numerical results of a simple example given above are shown in Table 1. To obtain the results, the concentration of grouped species was first computed according to the equation given in Table 1 for C. Based on the computed concentration, the procedures outlined above were followed to arrive at the identification results. Real values of the parameters can also be calculated from the equation in Table 1.

TABLE 1. COMPARISON OF PARAMETERS, REAL VS. IDENTIFICATION RESULTS

	a_1	a_2	a_3	$dC/dt\|_{t=o}$	$d^2C/dt^2\|_{t=o}$	Q
Real	3.50	3.50	1.00	−4.10	6.85	0
Identification results	3.58	3.67	1.07	−4.13	6.98	0.0

$$C = 0.6e^{-t} - e^{-0.5t} - 1.5e^{-2t}$$

CONCLUDING REMARKS

In the present work, a general purpose kinetic model for mixtures with many first-order reactions has been developed. It has been shown that the behavior of grouped concentration of n species corresponds to that of a single dependent variable of an n^{th}-order differential equation. The effect of temperature on the reactions is represented by constant coefficients of the differential equation. From the experimental data on the grouped concentration, the parameters a_i, Q, and the initial conditions of Equation (5) can be determined as illustrated by an example. The step by step identification procedures are such that eventually only the parameters a_i are involved in fitting experimental data, reducing the number of parameters to be determined from $2n$ to n in the final step [for instance, Equation (15) for a mixture of three species].

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NOTATION

$a_i(T)$ = i^{th} constant coefficient in a differential equation
b_i = quantity defined by Equation (2)
$C(t)$ = concentration of all the species combined at time t
$C_i(t)$ = concentration of species i at time t
C_{io} = concentration of species i at time zero
C_o = value of C at time zero
f = symbol used for a functional relationship
f_i = exponential terms in Equation (3) integrated i times and then evaluated at time t
g_i = quantity defined by Equation (4*a*)
$G_i(C_{io}, T)$ = integration constants in Equation (11)
I_i = value of f_i at time zero
J = constant terms in Equation (3)
k_i^* = rate constant of i^{th} species associated with product in reversible reaction
k_i = rate constant of i^{th} species
n = total number of species in a mixture or n^{th} species
$Q(C_{io}, T)$ = quantity defined in Equation (9)
t = time
T = temperature
$\int_o^{t\,(n)}$ = symbol used for integrating n times with respect to time

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