A New Approach to First-Order Chemical Reaction Systems

JAMES WEI and CHARLES D. PRATER
Socony Mobil Oil Company, Paulsboro, New Jersey

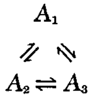
Many chemical reaction systems of interest to chemical engineers can be closely approximated by first-order or pseudo first-order (*1*) reactions. Isomerization reactions and dehydrogenation in an excess of hydrogen are examples. It is well known that even zero- and second-order reactions can be satisfactorily approximated by first-order reactions up to 60% conversion if one is mainly concerned with the changes of compositions vs. reaction time (*2*).

In a system where many chemical reactions occur simultaneously, the set of rate equations obtained are often difficult to solve. Fortunately a linear (first order) set of equations is always solvable in terms of a matrix notation. Matsen and Franklin (*3*) have shown that under special conditions the system can be uncoupled into independent normal modes. It has further been shown that this can always be done (*6*). Far from being merely mathematical symbols used for manipulations the matrix notation leads to a high degree of understanding and insight into the structure of first-order reaction systems; it facilitates intelligent planning of experiments. Furthermore the formulation greatly aids the task of successful simulation of process units.

The important results are given first by the use of a three-component system as an illustration, and the general matrix equations are given later.

THE REACTION PATHS OF FIRST-ORDER SYSTEMS

The set of rate equations for a system of first-order reactions involving three species is (*3, 4*)



$$\begin{tikzcd} & A_1 \arrow[dl, shift left] \arrow[dr, shift left] & \\ A_2 \arrow[ur, shift left] \arrow[rr, shift left] & & A_3 \arrow[ul, shift left] \arrow[ll, shift left] \end{tikzcd}$$

$$\frac{d}{dt} a_1 = -(k_{21} + k_{31})a_1 + k_{12}a_2 + k_{13}a_3$$
$$\frac{d}{dt} a_2 = k_{21}a_1 - (k_{12} + k_{32})a_2 + k_{23}a_3$$
$$\frac{d}{dt} a_3 = k_{31}a_1 + k_{32}a_2 - (k_{13} + k_{23})a_3 \tag{1}$$

where k_{12} is the rate constant of formation of species A_1 from A_2. Many textbooks show that the solution to this set of rate equations is (*3, 4*)

$$a_1(t) = a_1^* + c_{11}e^{-\lambda_1 t} + c_{12}e^{-\lambda_2 t}$$
$$a_2(t) = a_2^* + c_{21}e^{-\lambda_1 t} + c_{22}e^{-\lambda_2 t}$$
$$a_3(t) = a_3^* + c_{31}e^{-\lambda_1 t} + c_{32}e^{-\lambda_2 t} \tag{2}$$

where a_1^* represents the equilibrium concentration of species A_1. The parameters λ are the characteristic decay constants of the system and are functions only of the rate constants k. The constants c depend on the initial values of a_1, a_2, a_3 as well as on the rate constants k.

The characteristic decay constants λ govern the character of the solutions. A negative λ makes the concentration go to infinity and is clearly not physically acceptable. A complex λ will make the composition oscillate about the equilibrium value indefinitely, although with decreasing amplitude as shown in Figure 1*a*. This behavior is not forbidden by thermodynamics, but is forbidden by the statistical mechanical principle of microscopic reversibility (*1*) (*5*). With this principle it may be proven that all λ are real positive numbers (*1*) (*6*), and consequently for a closed first-order system the reaction paths, as shown in Figure 1*b*, do not oscillate.

Many of the important properties of the reaction system may be best demonstrated by composition diagrams in which time appears only as a parameter. For a three-component system the familiar three-phase diagram is shown in Figure 2. Each point of this diagram represents the composition of a mixture. Because of chemical reaction an initial point will move in the diagram with time until it reaches the equilibrium point. In general the path described by the point will be curved, but for first-order reaction systems there are always $(n - 1)$, in this instance two, straight-line reaction paths.

The constants in Equation (2) depend on the initial composition of the

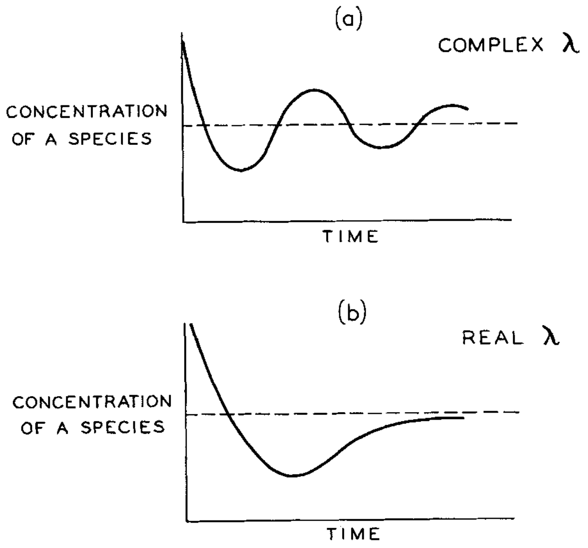


Fig. 1. Concentrations vs. time.

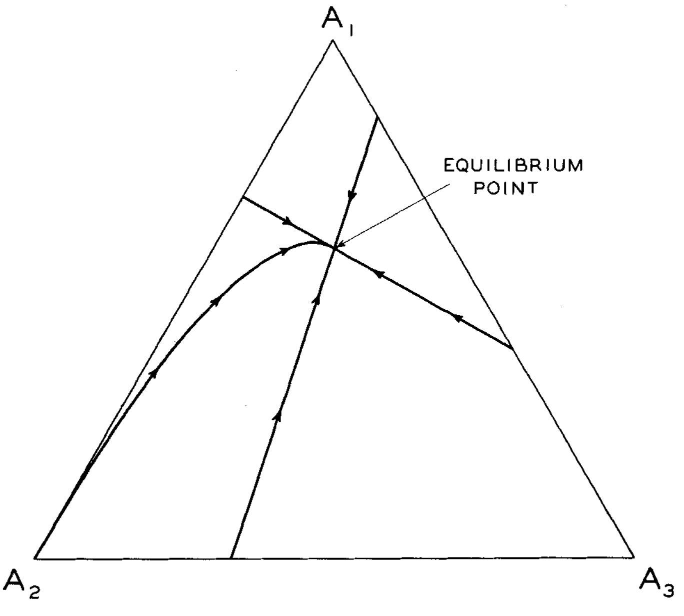


Fig. 2. Reaction paths in the composition plane.

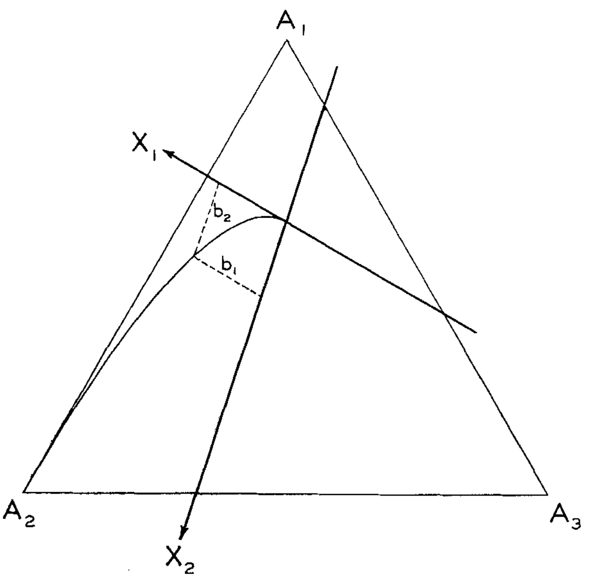


Fig. 3. The oblique axes based on straight-line reaction paths.

mixture. Suppose one could arrange an initial mixture so that all the c's are zero except those related to λ_1; then the reaction path is a straight line where

$$\frac{a_1(t) - a_1^*}{c_{11}} = \frac{a_2(t) - a_2^*}{c_{21}} = \frac{a_3(t) - a_3^*}{c_{31}} = e^{-\lambda_1 t} \qquad (3)$$

Other straight-line reaction paths are obtained by similar arrangement of initial composition so that only the c's related to λ_2 are left. Thus one learns to associate a straight-line reaction path with a particular characteristic decay constant λ.

The value of λ completely describes the behavior of a point on the straight-line reaction path. The larger the λ the faster the point approaches equilibrium. Some straight-line reaction paths are thus traversed faster than others. Let b be the distance between the equilibrium point and a point on a straight line path; then the movement of the point is given by

$$b(t) = b^\circ e^{-\lambda t} \qquad (4)$$

where b° is the initial value of b.

If the straight-line reaction paths themselves are used for a new set of coordinate axes (X_1, X_2) as shown in Figure 3, the infinite number of curved reaction paths can be described in a very compact manner. Any mixture can be decomposed into b_1 part of the component that decays rapidly along X_1 and b_2 part of the component that decays slowly along X_2. Each component decays exponentially according to its own lambda, and the resulting reaction path is given by the curved line in Figure 3 and by the equation

$$b_1 = g b_2^{\lambda_1/\lambda_2} \qquad (5)$$

where g is a constant which depends on the initial values of b_1 and b_2. Equation (5) describes all of the reaction paths and is very important in actual application.

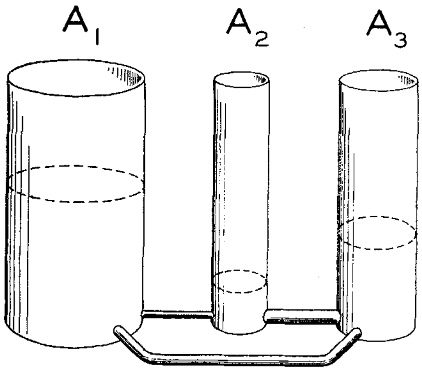


Fig. 4. A hydrodynamic analogy of a coupled system.

This viewpoint provides considerable insight into the reasons for the difficulties with the usual solutions and into the mathematical structure of first-order rate processes. Equation (1) is difficult to solve because the rate of change of a_1 depends on a_1 as well as a_2 and a_3. By decomposing mixtures of components into noninteracting species based on the straight-line reaction paths an equivalent reaction system is obtained where

$$B_1 \rightarrow 0 \leftarrow B_2$$

and B_o, the equilibrium species, does not react. In contrast to the original situation the rate of change of b_1 now depends only on b_1 and not in any way on b_2. The system is thus uncoupled into independent reactions that are easy to handle:

$$\begin{aligned} \frac{d}{dt} b_o &= 0 \\ \frac{d}{dt} b_1 &= -\lambda_1 b_1 \qquad (6) \\ \frac{d}{dt} b_2 &= -\lambda_2 b_2 \end{aligned}$$

A HYDRODYNAMIC ANALOGY

A hydrodynamic analogue for this reaction system can be used as a demonstration model. Consider the three cylinders with cross-sectional areas proportional to a_1^*, a_2^*, and a_3^* as shown in Figure 4. The bottoms of the cylinders are connected by capillary tubes so that the rate of fluid flow between each pair of cylinders is proportional to the differences of heads; the proportionality constants are analogous to the rate constants k. In this model the volume of fluid in cylinder A_1 is analogous to the concentration of species A_1 in a chemical reaction. It is evident that equilibrium thermodynamics determines the cross-sectional areas of the cylinders, and the task of the kineticists is to determine the sizes of the capillary tubes. The volume of fluid a_1 is equal to the cross-sectional area a_1^* times the height h_1. The rate of flow of fluids among the cylinders is given by the highly coupled set of equations

$$\begin{aligned} a_1^* \frac{d}{dt} h_1 &= -(k_{21}a_1^* + k_{31}a_1^*)h_1 + (k_{12}a_2^*)h_2 + (k_{13}a_3^*)h_3 \\ a_2^* \frac{d}{dt} h_2 &= (k_{21}a_1^*)\, h_1 - (k_{12}a_2^* + k_{32}a_2^*)h_2 + (k_{23}a_3^*)h_3 \qquad (7) \\ a_3^* \frac{d}{dt} h_3 &= (k_{31}a_1^*)h_1 + (k_{32}a_2^*)h_2 - (k_{13}a_3^* + h_{23}a_3^*)h_3 \end{aligned}$$

which are analogous to Equation (1). The transformation of the highly coupled system given by Equation (7) into an uncoupled system analogous to Equation (6) is equivalent to changing the hydrodynamic system of Figure 4 into a static cylinder and two unconnected cylinders leaking at the bottom as shown in Figure 5.

EXPERIMENTAL DETERMINATION OF STRAIGHT-LINE REACTION PATHS

When the rate constants k are known for a reaction, one can predict the product

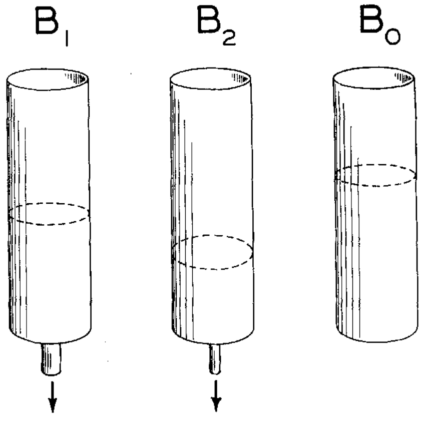


Fig. 5. A hydrodynamic analogy of the equivalent uncoupled system.

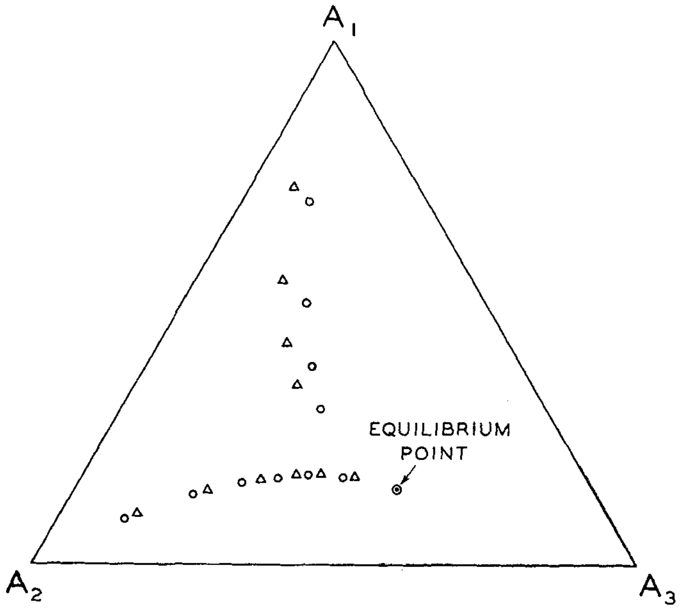


Fig. 6. Product compositions for various reaction times produced by two different sets of rate constants.

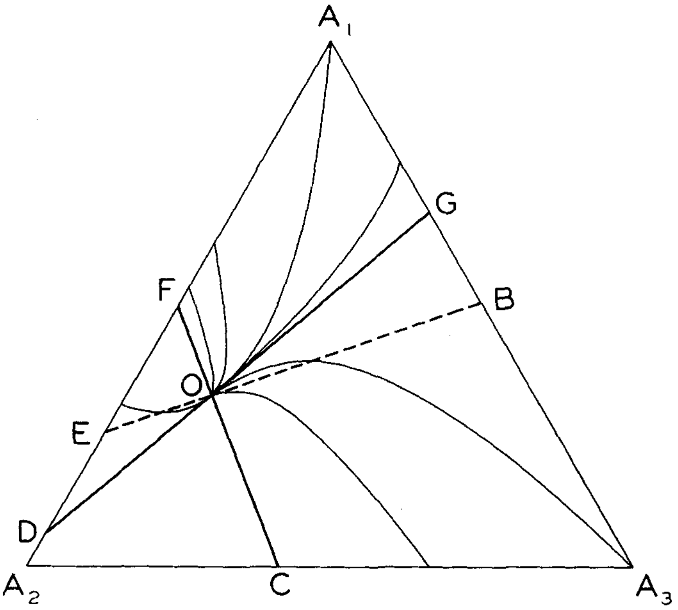


Fig. 8. Reaction paths showing maxima and minima in species A_1.

distribution as a function of reaction time. But usually the k's are not known and must be deduced from kinetic data. The conventional approach is to plot composition vs. time for a set of data and then use a curve-fitting program to obtain the λ's and c's (or k's) as parameters. An analogue computer with an oscilloscope displaying the solutions is particularly convenient for the curve fitting, since direct variations of the values of the k's are easily made. But such curve-fitting techniques are subject to large errors if one is interested in extrapolating to the regions of different initial compositions. Two different sets of k's may fit the same set of reaction data well and yet differ very widely in their predictions of reaction paths in other regions of composition as shown in Figure 6 (*1*).

The approach of this paper suggests experimental procedures that lead to an understanding of the behavior of the reacting system and to the evaluation of the rate constants from a minimal amount of experimental data. One first locates the straight-line reaction paths by a series of experiments and then measures the values of the λ's. The values of the k's may then be computed, with a desk calculator, by the formulation which will be given later. In locating the straight-line reaction paths any composition may serve as the first one to be tested experimentally in a reaction and its reaction path to the neighborhood of the equilibrium point recorded in a composition diagram. In general this path will not be a straight line, but it will tell in what direction the straight-line reaction path lies. Since by Equation (5) all reaction paths must become tangent to the slow straight-line path at the equilibrium point, another mixture is prepared having a composition on the tangent, in the neighborhood of the equilibrium point, to the first curved path and its reaction path to the neighborhood of equilibrium determined. If one happens to overshoot the straight-line path, this can be seen readily and corrected since the new reaction path will curve in the opposite direction. It usually takes no more than three tries to locate the straight-line path. The other straight-line path can be located not necessary; when a straight-line path is similarly by drawing tangents to the initial point of a curved reaction path. But this is located in a three-component system, the other straight-line path may be computed without further experimentation. A transformation may be made so that the straight-line paths become perpendicular to each other. This transformation depends only on a knowledge of the position of the equilibrium point and nothing else. When the three-component diagram is distorted so that the lengths of the sides become $\sqrt{1/a_1^* + 1/a_2^*}$, $\sqrt{1/a_2^* + 1/a_3^*}$, and $\sqrt{1/a_3^* + 1/a_1^*}$, then the straight-line reaction paths will be perpendicular and the second path can be located immediately from the first path as shown in Figure 7.

The movement of points on a straight-line path depends on only one of the characteristic decay constants λ, and a plot of log b_i vs. time will give λ_i as the slope. In this approach all data are plotted as straight lines. This is a far easier and more accurate procedure than the determination of the parameters from curved reaction paths by nonlinear curve fitting techniques.

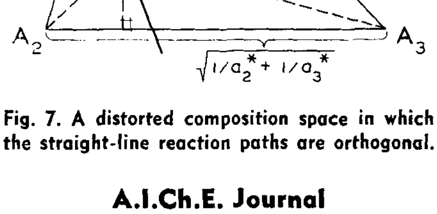


Fig. 7. A distorted composition space in which the straight-line reaction paths are orthogonal.

SOME USEFUL THEOREMS

Many useful properties of this reaction system have been discovered and will appear in a separate publication (*1*). For example in the course of a reaction the concentration of a component may reach a maximum and then decline to the equilibrium point. Since chemical processes usually produce less valuable molecular species along with more valuable ones, it is important to know whether there is a maximum concentration of the more valuable species above the equilibrium value for the overall reaction. Such knowledge is useful in planning optimum operations in a process unit. The three-component diagram of Figure 8 shows a typical example. The dotted line EB is the locus of points for which the rate of change of a_i is zero; hence any reaction path intersecting this line will have an extreme value at the point of intersection. In the diagram DOG and COF are the straight-line reaction paths with the slower and faster rates of decay, respectively. All reaction paths must be tangent to DOG at the equilibrium point 0. Let DOG be the coordinate axis for the amount b_1 and COF be the coordinate axis for the amount b_2. Then from Equation (5)

$$b_2 = g b_1^{\lambda_2/\lambda_1}$$

where $\lambda_2/\lambda_1 > 1$. On the other hand the line EB is given by

$$b_2 = m b_1$$

where m is the slope. Hence for an initial composition in region $COBA_3$ to become tangent to DOG at the equilibrium point, its reaction path must cross the line EB since $\lambda_2/\lambda_1 > 1$. At that point the reaction path has a maximum in the concentration of the species A_1 which is greater than the equilibrium value. By the same argument every composition originating in the region FOE will have a minimum. For the other regions there is neither a maximum nor a minimum; the concentration of A_1 neither overshoots nor undershoots equilibrium.

Another useful property of the system concerns the interpolation of results. When the behavior of two different initial composition points are known, it is possible to interpolate linearly and obtain the behavior of a mixture of the two. Let mixture R consist of a mixture of $(1 - r)$ part of P and r part of Q; then the points P, Q, and R form a straight line in the composition diagram as shown in Figure 9. As the reaction proceeds, the three points still form a straight line at all other times and the relative distances are unchanged.

THE MATRIX EQUATIONS

The important matrix equations for an n-component system will be given here. Equation (1) may be written as

$$\frac{d}{dt}\begin{bmatrix} a_1 \\ a_2 \\ \cdot \\ \cdot \\ \cdot \\ a_n \end{bmatrix} = \begin{bmatrix} -\sum\limits_{i\neq 1} k_{i1} & k_{12} \cdots & k_{1n} \\ k_{21} & -\sum\limits_{i\neq 2} k_{i2} \cdots & k_{2n} \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ k_{n1} & k_{n2} & -\sum\limits_{i\neq n} k_{in} \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ \cdot \\ \cdot \\ \cdot \\ a_n \end{bmatrix}$$

or

$$\frac{d}{dt} a = K a \qquad (8)$$

The matrix K has the property that the sum of all elements in a column is zero. Without loss of generality one can make $\sum\limits_i a_i = 1$. This system is now formally identical to a continuous Markov process (8). The elements of the matrix K are not independent since the principle of microscopic reversibility (5) requires that at the equilibrium point a^*

$$k_{ij}a_j^* = k_{ji}a_i^* \qquad (9)$$

or

$$KD = S$$

where D is $\{a_1^*, a_2^*, \ldots a_n^*\}$. The matrix $D^{-1/2}\, K D^{1/2} = D^{-1/2}\, S\, D^{-1/2}$ is similar to K and is symmetric; therefore K has only real eigenvalues (9).

For a given initial composition $a(0)$ the solution $a(t)$ is given by *(10)*

$$a(t) = e^{Kt}\, a(0) \qquad (10)$$

where

$$e^{Kt} \equiv I + Kt + K^2t^2/2! + K^3t^3/3! \ \ldots$$

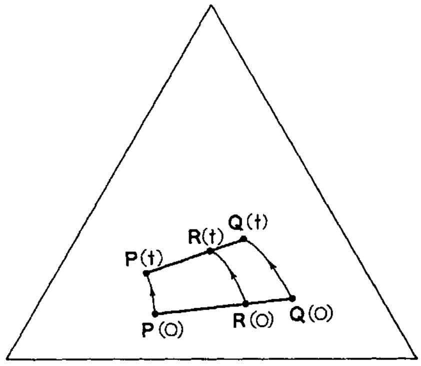


Fig. 9. The interpolation property of a first-order reaction system.

This solution satisfies the initial value, since $a(t)$ reduces to $a(0)$ at time $t = 0$. Substituting this solution in the differential equation one obtains

$$\frac{d}{dt} a(t) = \frac{d}{dt}\left(e^{Kt}\, a(0)\right)$$
$$= Ke^{Kt}\, a(0) = K\, a(t)$$

This form becomes more convenient after K is transformed into a diagonal form by its characteristic vectors. The matrix K possesses n independent column characteristic vectors X_i so that (9)

$$K X_i = \lambda_i X_i \qquad (11)$$

where λ_i is the i^{th} characteristic value, and X_i is the column vector

$$\begin{bmatrix} X_{i1} \\ X_{i2} \\ \cdot \\ \cdot \\ \cdot \\ X_{in} \end{bmatrix}$$

Equation (11) may be written in a compact form

$$K = X\Lambda X^{-1} \qquad (12)$$

where Λ is the diagonal matrix of characteristic values $\{\lambda_o, \lambda_1, \lambda_2 \ldots \lambda_{n-1}\}$ and X is the matrix of column characteristic vectors. $\{X_o, X_1, X_2, \ldots X_{n-1}\}$

The solution at $a(t)$ may be written as

$$a(t) = Xe^{\Lambda t}\, X^{-1}\, a(0)$$

If one defines $b(t)$ as $X^{-1}a(t)$, then the differential Equation (8) becomes

$$\frac{d}{dt} b(t) = \Lambda b(t) \qquad (13)$$

and the solution is

$$b(t) = e^{\Lambda t}\, b(0)$$

or

$$b_i(t) = e^{-\lambda_i t} b_i(0) \qquad (14)$$

The vector X_0 represents the equilibrium species, and $\lambda_o = 0$; $b_o(t) = b_o(0) = 1$; $X_{io} = a_i^*$. By Equation (10) one may write

$$a(t) = X\, b(t) = X_0 + b_1(0)e^{-\lambda_1 t}X_1 + b_2(0)e^{-\lambda_2 t}X_2 + \ldots + b_{n-1}(0)e^{-\lambda_{n-1} t}X_{n-1} \qquad (15)$$

Except for the term X_0 the terms decay to zero as time increases. All the vectors $X_{i\neq 0}$ have the characteristics that $\sum\limits_j X_{ji} = 0$ and can be interpreted as a measure of the internal imbalance or departure from equilibrium.

The set of vectors X_i are mutually orthogonal with respect to the weighing function D^{-1} so that

$$X_i^T\, D^{-1}X_j = 0 \quad (i \neq j) \qquad (16)$$

where X_i^T represents the transpose of X_i. The authors shall first prove that $D^{-1}X_i$ is the left characteristic vector of matrix K

$$(D^{-1}X_i)^T K = \lambda_i (D^{-1}X_i)^T \qquad (17)$$

Since

$$(D^{-1}X_i)^T K = (D^{-1}X_i)^T (SD^{-1})$$

and

$$(D^{-1}X_i)^T S = (SD^{-1}X_i)^T = (KX_i)^T = (\lambda_i X_i)^T = \lambda_i X_i^T$$

one obtains

$$(D^{-1}X_i)^T K = \lambda_i X_i^T D^{-1} = \lambda_i (D^{-1}X_i)^T$$

Since the left and right characteristic vectors of a matrix are orthogonal if they belong to different characteristic values, the theorem is proved.

The reaction paths will now be examined. In Equation (15), if all b's are zero except b_i, then

$$a(t) = X_o + b_i(0)e^{-\lambda_i t}X_i$$

which is obviously a straight line connecting X_o and X_i with t as the parameter. To obtain Equation (5) for the reaction paths one proceeds as follows.

From Equation (14) one has

$$b_i(t) = b_i(0)e^{-\lambda_i t}$$
$$b_j(t) = b_j(0)e^{-\lambda_j t}$$

Eliminating t one finds

$$\frac{1}{\lambda_i} \ln \frac{b_i(t)}{b_i(0)} = -t = \frac{1}{\lambda_j} \ln \frac{b_j(t)}{b_j(0)}, \text{ or}$$

$$b_i(t) = \left[\frac{b_i(0)}{\{b_j(0)\}^{\lambda_i/\lambda_j}}\right] b_j(t)^{\lambda_i/\lambda_j} \qquad (18)$$

The term inside the bracket is a constant and depends only on the initial composition $b(0)$ or $a(0)$.

The interpolation property discussed previously will now be demonstrated. If

$$a^{(3)}(0) = r\, a^{(1)}(0) + (1 - r)\, a^{(2)}(0) \qquad (19)$$

then Equation (10) gives

$$a^{(3)}(t) = e^{Kt} a^{(3)}(0) = e^{Kt}\{r\, a^{(1)}(0) + (1-r)a^{(2)}(0)\} = ra^{(1)}(t) + (1-r)a^{(2)}(t) \qquad (20)$$

which is of the linear form of Equation (19).

SUMMARY AND CONCLUSION

It is possible to uncouple any first-order reaction system into independent reactions. These independent reactions represent straight-line reaction paths and are directly measurable. An expression, in terms of compositions along the straight-line paths, is given for all reaction paths and is useful in the simulation of chemical processes.

NOTATION

A_i = the i^{th} chemical species
B_j = the j^{th} characteristic species
a_i = concentration of species A_i, mole/volume
b_j = concentration of species B_j, mole/volume
c_{ij} = constants in Equation (2), mole/volume
h_i = height of fluid in column A_i, length
k_{ij} = kinetic rate constant from species A_j to A_i, 1/time
t = time
λ_i = characteristic decay constant, 1/time

Vectors

a = composition expressing concentration of A species
b = composition expressing concentration of B species
X_i = characteristic vector of matrix K

Matrices

D = diagonal matrix of equilibrium composition
K = rate constants
S = a symmetric matrix
X = matrix of characteristic vectors of K
Λ = diagonal matrix of characteristic values

Superscripts and subscripts

$*$ = equilibrium value
o = initial value
T = transpose of a vector or matrix

LITERATURE CITED

1. Wei, James, and C. D. Prater, "Advances in Catalysis," Vol. 13, Academic Press, New York (1962).
2. Prater, C. D., and R. M. Lago, *ibid.*, Vol. 8 (1956).
3. Matsen, F. A., and J. L. Franklin, *J. Am. Chem. Soc.*, **72**, 3337 (1950).
4. Frost, A. A., and R. G. Pearson, "Kinetics and Mechanism," Wiley, New York (1953).
5. Onsager, Lars, *Phys. Rev.*, **37**, 405 (1931).
6. Jost, Wilhelm, *Z. Naturforsch.*, **2a**, 159 (1947).
7. Feller, William, "An Introduction to Probability Theory and Its Applications," Vol. 1, Wiley, New York (1957).
8. Bellman, Richard, "Introduction to Matrix Analysis," McGraw-Hill, New York (1960).
9. Birkhoff, Garrett, and S. MacLane, "A Survey of Modern Algebra," MacMillan, New York (1957).
10. Lefschetz, Solomon, "Differential Equations," Interscience, New York (1957).

Manuscript received December 30, 1961; revision received May 14, 1962; paper accepted May 16, 1962. Paper presented at A.I.Ch.E. New Orleans meeting.

Pressure Drops in the Flow of Gases Through Packed and Distended Beds of Spherical Particles

CHARLES A. WENTZ, JR., and GEORGE THODOS
The Technological Institute, Northwestern University, Evanston, Illinois

Pressure drop measurements were made across packed and distended beds having five layers of smooth plastic spheres, 1.23 in. in diameter, arranged in cubic, body-centered cubic, and face-centered cubic orientations of void fractions varying from 0.354 to 0.882. The distended beds were prepared by separating the spheres with permanently attached short lengths of fine rigid wire. Friction factors were calculated from the overall pressure drop measurements with the Ergun equation and were plotted against the corresponding modified Reynolds number which ranged from 2,550 to 64,900. A single relationship resulted for both types of beds which is independent of the geometric orientation and void fraction of the spheres of the bed.

To eliminate entrance and exit effects of the air flowing through the bed pressure drop measurements were also made across the middle layer of each distended bed. Again a single relationship between the corresponding friction factors and modified Reynolds number was obtained which is independent of the geometric orientation and void fraction of the bed.

From the two relationships between friction factors and modified Reynolds number the ratio f'_k/f_k for a packed or distended bed having five layers of spheres is 1.13. This ratio should decrease with increasing number of layers of spheres and approach the limiting value of 1 when the number of layers becomes very large.

Packed columns of granular solids are widely used in many mass and heat transfer operations such as extraction and distillation. Measurements of pressure drops for the flow of gases through packed beds have been made by many investigators (*1, 2, 3, 4, 5, 6, 8*), and relationships between the pressure drop and the Reynolds number have been developed.

Recently McConnachie (*7*) has investigated heat, mass, and momentum transfer for the flow of air past spheres arranged in a body-centered cubic orientation and held apart in space by short lengths of fine rigid wire to produce distended fixed beds having void fractions comparable to those of fluidized beds. Although he conducted pressure drop measurements, experimental limitations did not permit accurate comparisons between the resulting values and corresponding measurements for packed beds. Therefore an attempt has been made in the present study to investigate the effect of the geometric orientation of the particles of the bed on the pressure drop and to determine if the existing relationships between the pressure drop and Reynolds number for packed beds can be extended to distended beds.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

The experimental apparatus included a vertical wind tunnel, 14 in. in diameter