

Intraparticle Diffusion Effects in Complex Systems of First Order Reactions

II. The Influence of Diffusion on the Performance of Chemical Reactors

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Received June 24, 1962

In complex systems of first order reactions within porous catalyst particles in the presence of Fick's law diffusion, the experimental data will always appear to come from a consistent set of rate constants although these constants do not represent the proper rate constants for the chemical process. This fact enables one to use the same methods to compute the performance of various reactor designs both in the presence and absence of intraparticle diffusion effects. Solutions are presented for piston flow and stirred tank reactors in terms of the characteristic species. The results show that diffusion effects will often produce marked changes in product distributions and apparent catalyst selectivity. The apparent sequence of reactions may be extensively modified—some consecutive reactions may even appear to be parallel reactions.

I. INTRODUCTION

Part I of this paper (1) discusses the influence of intraparticle diffusion on systems of coupled first order reactions occurring within a single catalyst particle. Expressions were obtained for the over-all rates of reaction for the entire particle in terms of the concentrations ambient to the particle; these concentrations were considered to be constant over the boundary of the particle. The rates of reaction were shown to be linear functions of the ambient concentrations such that the overall rate of reaction of species A_i per unit volume of catalyst is $\sum_j (k_{ij}^\dagger a_j - k_{ji}^\dagger a_i)$. The constants, k_{ij}^\dagger , are the diffusion-disguised rate constants and are functions only of the intrinsic rate constants k_{ij} , the diffusivities D_i , and the particle geometry; they are independent of the ambient concentrations. Thus the rate of change of the ambient composition vector \mathbf{a} in the presence of intraparticle diffusion effects is given by

$$d\mathbf{a}/dt = -\mathbf{K}^\dagger \mathbf{a} \quad (1)$$

where \mathbf{K}^\dagger is the matrix of diffusion-disguise

rate constants. The ability to characterize the over-all rate of reaction for each particle, in the presence of diffusion effects, by the diffusion-disguised rate constant matrix of Eq. (1) enables us to discuss readily the influence of such diffusion effects on the performance of various types of chemical reactors. The discussion will show that, if diffusion effects are present, marked changes in the product distributions and apparent catalyst selectivity may occur. The apparent sequence of reactions may be extensively modified—some consecutive reactions may even appear to be parallel reactions.

We shall limit our discussion to stirred tank and piston flow reactors. By stirred tank reactors we shall mean a reactor in which the residence times of the molecules in the reactor are distributed exponentially. By a piston flow reactor we shall mean a reactor in which the residence time of every molecule has the same constant value τ . The influence of diffusion on the performance of reactors with other distributions of residence time can be determined by methods described by Wei and Prater (2).

II. THE INFLUENCE OF INTRAPARTICLE DIFFUSION ON THE PERFORMANCE OF PISTON FLOW REACTORS

A. The Integration of the Rate Equations

Equation (1) can be applied to a bed of catalyst particles in a piston flow reactor if the concentrations ambient to a catalyst particle are assumed to be approximately uniform over the distance of a particle diameter. The time variable of Eq. (1) is related to the space variable s , which is measured from the top of the catalyst bed, by $t = s/v$, where v is the linear velocity of flow of the reactants through the packed bed. This gives for Eq. (1)

$$\frac{d\mathbf{a}(s)}{ds} = -\frac{f}{v} \mathbf{K}^\dagger \mathbf{a}(s) \quad (2)$$

where \mathbf{K}^\dagger is the rate constant matrix per unit volume of catalyst and f is the fraction of the bed volume occupied by the catalyst particles. On the other hand, when diffusion effects are absent, the equation that applies is identical to Eq. (2) except that the diffusion-disguised rate constant matrix \mathbf{K}^\dagger is replaced by the true rate constant matrix \mathbf{K} .

The integration of Eq. (2) over the reactor space variable, s , is best accomplished in terms of the characteristic values and vectors of the rate constant matrix \mathbf{K}^\dagger (Wei and Prater, ref. 3). Let \mathbf{X}^\dagger be the matrix of characteristic vectors of the matrix \mathbf{K}^\dagger and $\mathbf{\Lambda}^\dagger$ be the diagonal matrix of characteristic values with elements designated so that $\lambda_1^\dagger = 0 \leq \lambda_2^\dagger \leq \lambda_3^\dagger \leq \dots \leq \lambda_n^\dagger$. According to Eq. (I-32), where I designates Part I of this paper, we have

$$\mathbf{K}^\dagger = \mathbf{X}^\dagger \mathbf{\Lambda}^\dagger (\mathbf{X}^\dagger)^{-1} \quad (3)$$

When diffusion effects are absent, we have the corresponding equation

$$\mathbf{K} = \mathbf{X} \mathbf{\Lambda} \mathbf{X}^{-1} \quad (4)$$

Let $\mathbf{a}(0)$ be the composition vector at $s = 0$; the integral of Eq. (2) is then (4)

$$\mathbf{a}(s) = \mathbf{X}^\dagger \exp(-f\mathbf{\Lambda}^\dagger s/v) (\mathbf{X}^\dagger)^{-1} \mathbf{a}(0) \quad (5)$$

where $\exp(-f\mathbf{\Lambda}^\dagger s/v)$ is a diagonal matrix with diagonal elements $\{1, \exp(-f\lambda_2 s/v), \exp(-f\lambda_3 s/v), \dots, \exp(-f\lambda_n s/v)\}$.

The matrix of characteristic vectors \mathbf{X}^\dagger

enables us to shift to a system of characteristic species. This changes the system of highly coupled reactions described by Eq. (2) into a set of independent, irreversible, first order reactions as discussed by Wei and Prater (3) and by Wei (1). Let $\mathbf{b}^\dagger(s)$ be a composition vector in the system of characteristic species obtained from the rate constant matrix \mathbf{K}^\dagger . Then a composition vector $\mathbf{a}(s)$ expressed in the molecular system of species is transformed into the composition vector $\mathbf{b}^\dagger(s)$ expressed in the characteristic system of species by the equation

$$\mathbf{b}^\dagger(s) = (\mathbf{X}^\dagger)^{-1} \mathbf{a}(s) \quad (6)$$

The reverse transformation is given by the equation

$$\mathbf{a}(s) = \mathbf{X}^\dagger \mathbf{b}^\dagger(s) \quad (7)$$

We must emphasize that the composition vectors $\mathbf{b}^\dagger(s)$ and $\mathbf{a}(s)$ represent the same actual composition; it is merely written in different coordinate system. Using Eq. (6) in Eq. (5), we obtain

$$\mathbf{b}^\dagger(s) = \exp(-f\mathbf{\Lambda}^\dagger s/v) \mathbf{b}^\dagger(0) \quad (8)$$

Since the matrix $\exp(-f\mathbf{\Lambda}^\dagger s/v)$ is diagonal, Eq. (8) is equivalent to the set of n independent equations

$$b_i^\dagger(s) = \exp(-f\lambda_i^\dagger s/v) b_i^\dagger(0) \quad (9)$$

which corresponds to complete uncoupling of the system of reactions into independent, irreversible reactions. The parameter, s , can be eliminated from the set of equations (9) to give

$$\frac{b_i^\dagger(s)}{b_i^\dagger(0)} = \left[\frac{b_j^\dagger(s)}{b_j^\dagger(0)} \right]^{\lambda_i/\lambda_j} \quad (10)$$

Equation (10) gives the fraction of the i th characteristic species remaining as a simple power function of the fraction of the j th characteristic species remaining and provides a convenient method for computing the reaction paths in composition space.

Wei and Prater (3) have shown how the characteristic species are related to straight line reaction paths in composition space and how the characteristic vectors that constitute the transformation matrices \mathbf{X} and \mathbf{X}^\dagger can be determined from laboratory measurements of the location of the straight line

reaction paths and the equilibrium composition. The characteristic vectors of the matrices \mathbf{K} and \mathbf{K}^\dagger are not, in general, the same and consequently the set of characteristic species are not identical. Hence, the integration of Eq. (2) for packed bed flow reactors in which intraparticle diffusion effects are unimportant yields a set of equations identical to Eqs. (9) and (10) except that, in general, different characteristic species, denoted by $b_i(s)$, will be obtained with different values of the decay constants, denoted by λ_i . For this case, therefore, we have

$$\mathbf{a}(s) = \mathbf{X} \exp(-\Lambda f s/v) (\mathbf{X})^{-1} \mathbf{a}(0) \quad (5a)$$

$$b_i(s) = \exp(-f \lambda_i s/v) b_i(0) \quad (9a)$$

and

$$\frac{b_i(s)}{b_i(0)} = \left[\frac{b_j(s)}{b_j(0)} \right]^{\lambda_i/\lambda_j} \quad (10a)$$

If the diffusivities of all the molecular species are equal, the transformation matrices \mathbf{X} and \mathbf{X}^\dagger become identical, the matrix Λ^\dagger is equal to $\Lambda \mathbf{n}$ and the matrix \mathbf{K}^\dagger is given by

$$\mathbf{K}^\dagger = \mathbf{X} \Lambda \mathbf{n} \mathbf{X}^{-1} \quad (11)$$

(see Wei, ref. 1). In this case, since the matrices \mathbf{K} and \mathbf{K}^\dagger have the same set of characteristic vectors, they have the same set of characteristic species and consequently the same set of straight line reaction paths. Hence, although diffusion effects do not alter the location of the straight line reaction paths when the diffusivities are all equal, the decay constants λ_i of each characteristic species B_i is reduced by its own effectiveness factor

$$\eta_i = 3\varphi_i^{-2}(\varphi_i \coth \varphi_i - 1) \quad (12)$$

where

$$\varphi_i = R \sqrt{\lambda_i/D} \quad (13)$$

as shown in part one of this paper. Since the larger the value of λ_i the smaller the value of η_i , the effect of diffusion is to reduce the ratio of the larger to the smaller characteristic decay constants. As λ_i increases in value η_i approaches $(3/\varphi_i) = 3 \sqrt{D/R^2 \lambda_i}$, as a limit. This gives us the upper and lower

bounds of the ratio $\lambda_n^\dagger/\lambda_2^\dagger$ in terms of the true decay constants λ_n and λ_2 ; they are

$$\sqrt{\lambda_n/\lambda_2} \leq (\lambda_n \eta_n / \lambda_2 \eta_2 = \lambda_n^\dagger / \lambda_2^\dagger) \leq \lambda_n / \lambda_2 \quad (14)$$

Thus the ratio of the decay constants, $\lambda_n^\dagger/\lambda_2^\dagger$, is reduced to the square root of the true value for the most extreme diffusion effect.

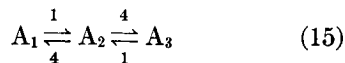
If the diffusivities are not all equal, the matrices \mathbf{K} and \mathbf{K}^\dagger have different characteristic species B_i and B_i^\dagger and transformation matrices \mathbf{X} and \mathbf{X}^\dagger ; hence, the straight line reaction paths are shifted in this case by the presence of diffusion effects. This shift makes the relation between the true and apparent kinetic behavior much more obscure than when all diffusivities are equal. As yet no simple, general, and easy to use relation has been found between the position of the straight line reaction paths and values of the decay constants in the presence of diffusion effects to the positions and values for the true kinetics.

B. The Application of the Method to Typical Examples

We shall use two relatively simple coupled reaction systems to illustrate some of the effects of intraparticle diffusion on the composition sequences and apparent kinetic schemes of piston flow reactors when the diffusivities are all equal. In addition these systems will be used to illustrate the shift of the straight line reaction paths in the presence of diffusion effects when all diffusivities are not equal.

1. A Three-Component Reversible System With Consecutive Reactions

Let us examine a hypothetical system consisting of two consecutive reversible first order reactions;



First let this reaction proceed in a bed of porous catalyst particles in a piston flow reactor under conditions such that the influence of diffusion on the reaction is negligible. The true rate constant matrix \mathbf{K} then applies. The rate constant matrix \mathbf{K} is

transformed to the diagonal form by using Eq. (4);

$$\begin{pmatrix} 1 & -4 & 0 \\ -1 & 8 & -1 \\ 0 & -4 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 1 & 1 \\ 1/4 & 0 & -2 \\ 1 & -1 & 1 \end{pmatrix} \quad (16)$$

\mathbf{K} \mathbf{X}

$$\begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 9 \end{pmatrix} \begin{pmatrix} 4/9 & 4/9 & 4/9 \\ 1/2 & 0 & -1/2 \\ 1/18 & -4/9 & 1/18 \end{pmatrix}$$

$\mathbf{\Lambda}$ \mathbf{X}^{-1}

The matrices \mathbf{X} and \mathbf{X}^{-1} in Eq. (16) were computed by the method given by Wei and Prater (5). Reaction paths for this system can be computed using either Eq. (5a) or, more conveniently, Eq. (10a). Typical reaction paths for this system are shown by the dashed curves of Fig. 1;

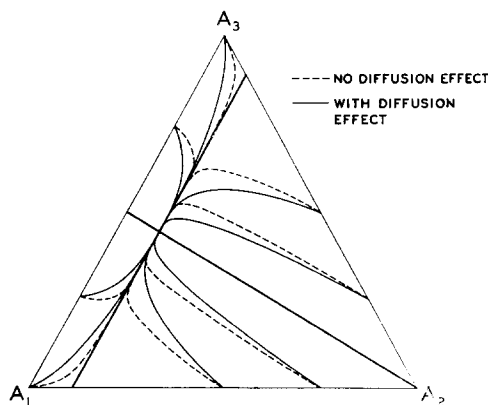


FIG. 1. The effect of diffusion on the reaction paths in an integral reactor.

included among these paths are the two straight line reaction paths shown by the heavy solid lines.

a. Diffusivity effects when all diffusivities are equal. Next let the bed of catalyst be composed of porous catalyst particles with a radius of 1 cm and a diffusivity of 10^{-2} cm²/sec for each reactant. Applying Eqs. (13) and (12) to the values of λ_i from the matrix $\mathbf{\Lambda}$ of Eq. (16), we obtain the values of φ_i , η_i , and λ_i^\dagger given in Table I. The ratio of the decay constants in the absence of diffusion effects is $\lambda_3/\lambda_2 = 9$; for the catalyst particles with $R = 1$ cm and $D_i =$

10^{-2} cm²/sec the ratio has decreased to $\lambda_3^\dagger/\lambda_2^\dagger = 3.22$.

TABLE I
VALUES OF φ_i , η_i , AND λ_i^\dagger FOR THE REACTION SCHEME (15) OCCURRING WITHIN CATALYST PARTICLES WITH $R = 1$ CM AND $D_i = 10^{-2}$ CM²/SEC

Index	λ_i	φ_i	η_i	$\lambda_i^\dagger = \lambda_i \eta_i$
1	0	0	1	0
2	1	10	0.27	0.27
3	9	30	0.0967	0.87

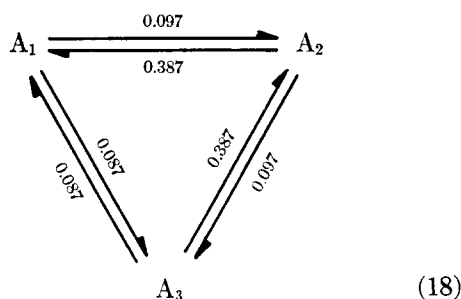
Since for this example the diffusivities of all molecular species A_i are equal, the transformation matrices \mathbf{X} and \mathbf{X}^\dagger are identical, and we can compute the rate constant matrix \mathbf{K}^\dagger using Eq. (3). We have

$$\mathbf{K}^\dagger = \mathbf{X} \mathbf{\Lambda}^\dagger \mathbf{X}^{-1}$$

$$= \begin{pmatrix} 1 & 1 & 1 \\ 1/4 & 0 & -2 \\ 1 & -1 & 1 \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0.27 & 0 \\ 0 & 0 & 0.87 \end{pmatrix} \begin{pmatrix} 4/9 & 4/9 & 4/9 \\ 1/2 & 0 & -1/2 \\ 1/18 & -4/9 & 1/18 \end{pmatrix}$$

$$= \begin{pmatrix} 0.183 & -0.387 & -0.087 \\ -0.097 & 0.774 & -0.097 \\ -0.087 & -0.387 & 0.183 \end{pmatrix} \quad (17)$$

The matrix \mathbf{K}^\dagger of Eq. (17) corresponds to the reaction scheme



A comparison of the values of the rate constants for the true reaction scheme and the scheme given by Eq. (18) shows that the values of the rate constants have been reduced by more than an order of magnitude by intraparticle diffusion. Even more important is the introduction of nonzero values for the rate constants directly connecting the species A_1 and A_3 as seen in scheme (18).

Hence, in the presence of intraparticle diffusion effects the scheme consisting of only consecutive reaction has been modified so as to appear to contain parallel reaction steps from A_1 to A_2 and A_3 .

Typical reaction paths for the diffusion-disguised system given by scheme (18) are computed using either Eq. (5a) or (10a) and are shown by the solid curves in Fig. 1. Since the diffusivities of all species A_i are equal, the actual reaction scheme and the diffusion-disguised scheme both have the same set of straight line reaction paths as shown in Fig. 1. The straight line reaction path with the slowest decay constant is the path parallel to the A_1A_3 side of the reaction triangle. The decrease in the ratio of the largest decay constant to the smallest decay constant, which is caused by the presence of intraparticle diffusion effects, is clearly shown by the decrease in the relative rates of approach of corresponding reaction paths to the straight line reaction path with the slowest decay constant; i.e., except for the initial and final points on corresponding curved reaction paths, the diffusion-modified reaction path always lies nearer the straight line reaction path with the largest decay constant than the corresponding true reaction path. Hence, diffusion effects lead to large changes in catalyst selectivity for many initial compositions.

How extensive is the modification of the kinetic scheme (15) by diffusion effects in the system under discussion can be seen by application of one of the conventional tests used to determine if a reaction is consecutive or parallel. Using the composition along the reaction path determined for an initial composition of pure A_1 , we plot the ratio of the products A_3/A_2 as shown in Fig. 2. The lower curve is obtained for the reaction path corresponding to scheme (15) and has a zero intercept at zero conversion as required by the consecutive reaction A_1 to A_2 to A_3 . The upper curve is obtained for the diffusion-disguised system of scheme (18). The finite intercept at zero conversion indicates a parallel reaction step from A_1 to A_3 . The erroneous conclusion about the true kinetic mechanism can be discovered only by changing the amount of diffusion effect present

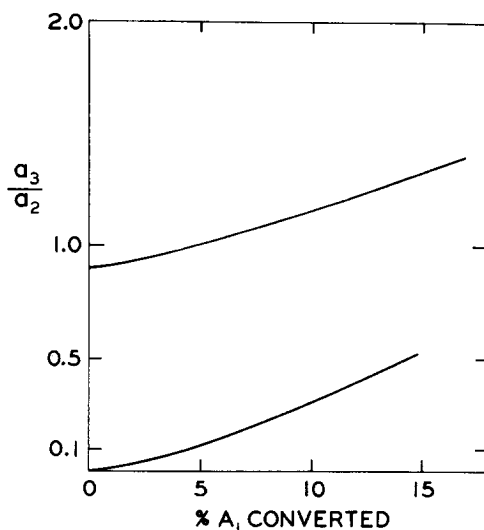


FIG. 2. The effect of diffusion on initial composition ratio.

in the system; this requires a change in some physical parameter of the catalyst such as particle radius or diffusivity.

b. Diffusion effects when all diffusivities are not equal. When the diffusivities are not all equal the transformation matrix \mathbf{X}^\dagger is not identical with the transformation matrix \mathbf{X} and the computation becomes more lengthy. Let us examine the computation for the same system as above except that the catalyst diffusivity constant for the molecular species A_3 is reduced to 10^{-3} cm²/sec with the diffusivity constants for the species A_1 and A_2 remaining at 10^{-2} cm²/sec. In order to make the computation, we need to transform the matrix $\mathbf{D}^{-1}\mathbf{K}$ into its diagonal form by means of Eq. (I-13). In order to use this equation, we need to compute the transformation matrix \mathbf{Y} , which is composed of the characteristic vectors of the matrix $\mathbf{D}^{-1}\mathbf{K}$; these characteristic vectors can be computed by the method described by Wei and Prater (5). Using the matrix \mathbf{Y} determined by this method in Eq. (I-13), we obtain

$$10^2 \begin{pmatrix} 1 & -4 & 0 \\ -1 & 8 & -1 \\ 0 & -40 & 10 \end{pmatrix} = \mathbf{D}^{-1}\mathbf{K}$$

$$\begin{pmatrix} 1 & 1 & 1 \\ 0.250 & -0.620 & -3.63 \\ 1 & -3.802 & 26.30 \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 348 & 0 \\ 0 & 0 & 1552 \end{pmatrix} \begin{matrix} \\ \\ \varphi^2/R^2 \end{matrix}$$

$$\mathbf{Y} \begin{pmatrix} 0.741 & 0.741 & 0.074 \\ 0.251 & -0.622 & -0.095 \\ 0.008 & -0.118 & 0.021 \end{pmatrix} \quad (19)$$

$$\mathbf{Y}^{-1}$$

The matrix φ^2/R^2 in Eq. (19) gives 0, 18.6, and 39.4 for the values of φ_1 , φ_2 , and φ_3 , respectively. These values are used in Eq. (12) to calculate the values of η_i ; they are $\eta_1 = 1$, $\eta_2 = 0.153$, and $\eta_3 = 0.074$. Using these values in Eq. (I-32), we obtain for the diffusion-disguised rate constant matrix \mathbf{K}^\dagger

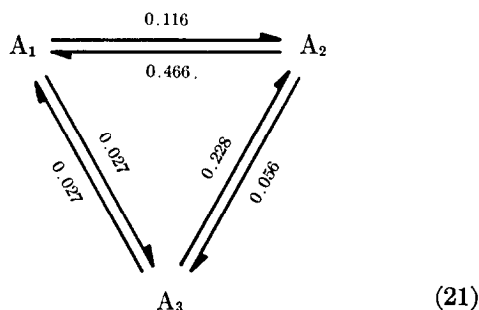
$$\mathbf{K}^\dagger = [\mathbf{D}\mathbf{Y}][(\mathbf{K}\mathbf{1}/R^2)\varphi^2\mathbf{n}\mathbf{Y}^{-1}]$$

$$= \begin{pmatrix} 1 & 1 & 1 \\ 0.25 & -0.62 & -3.63 \\ 0.10 & -0.38 & 2.63 \end{pmatrix}$$

$$= \begin{pmatrix} 0 & 0 & 0 \\ 0.134 & -0.331 & -0.051 \\ 0.009 & -0.135 & 0.024 \end{pmatrix}$$

$$= \begin{pmatrix} 0.143 & -0.466 & -0.027 \\ -0.116 & 0.695 & -0.056 \\ -0.027 & -0.228 & 0.083 \end{pmatrix} \quad (20)$$

Thus the diffusion-disguised form of the kinetic scheme (15) for the above case is



The transformation matrix \mathbf{X}^\dagger is computed from the matrix \mathbf{K}^\dagger (Wei and Prater, ref. 5) so that Eq. (3) may be used to convert \mathbf{K} into a diagonal form; we have

$$\mathbf{\Lambda}^\dagger = (\mathbf{X}^\dagger)^{-1}\mathbf{K}^\dagger\mathbf{X}^\dagger \quad (22)$$

$$\mathbf{\Lambda}^\dagger = \begin{pmatrix} 0.444 & 0.444 & 0.444 \\ 0.447 & 0.170 & -0.489 \\ 0.109 & -0.615 & 0.045 \end{pmatrix}$$

$$\begin{pmatrix} 0.143 & -0.466 & -0.027 \\ -0.116 & 0.695 & -0.056 \\ -0.027 & -0.228 & 0.083 \end{pmatrix}$$

$$\begin{pmatrix} 1 & 1 & 1 \\ 0.25 & 0.096 & -1.419 \\ 1 & -1.096 & 0.419 \end{pmatrix}$$

$$= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0.128 & 0 \\ 0 & 0 & 0.793 \end{pmatrix} \quad (23)$$

Typical reaction paths are computed for this system using Eq. (5a) or (10a); these are shown in Fig. 3 by the solid curves. The

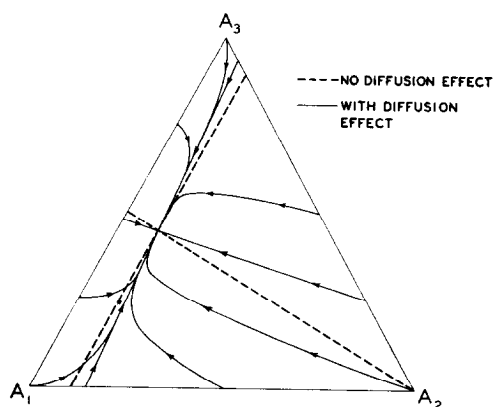
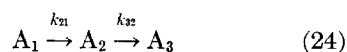


FIG. 3. The effect of diffusion in a system where the diffusivities of the molecular species are not equal.

straight line reaction paths for the true kinetic scheme (15) are shown by the dashed lines. We see that, when the diffusivities are not all equal, the presence of diffusion effects shifts the positions of the straight line reaction paths. Also, the selectivity is again greatly altered for many initial compositions as shown by a comparison of the true and diffusion disguised reaction paths obtained for an initial composition of pure A_2 .

2. A Three-Component Irreversible System with Consecutive Reactions

The three-component irreversible system



is sufficiently simple so that explicit expressions can be obtained for k_{ij}^\dagger in terms of the

true rate constants k_{mn} and the diffusivities and D_i . We have

$$\begin{aligned} \mathbf{D}^{-1}\mathbf{K} &= \begin{pmatrix} k_{21}/D_1 & 0 & 0 \\ -k_{21}/D_2 & k_{32}/D_2 & 0 \\ 0 & -k_{32}/D_3 & 0 \end{pmatrix} \\ &= \mathbf{Y}(\varphi^2/R^2)\mathbf{Y}^{-1} \\ &= \begin{pmatrix} 0 & \frac{k_{32}}{k_{21}} - \frac{D_2}{D_1} & 0 \\ 0 & 1 & 1 \\ 1 & \frac{-k_{32}D_1}{k_{21}D_3} & \frac{-D_2}{D_3} \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 \\ 0 & \frac{k_{21}}{D_2} & 0 \\ 0 & 0 & \frac{k_{32}}{D_2} \end{pmatrix} \\ &= \begin{pmatrix} \frac{D_1}{D_3} & \frac{D_2}{D_3} & 1 \\ \left[\frac{k_{32}}{k_{21}} \frac{D_2}{D_1}\right]^{-1} & 0 & 0 \\ -\left[\frac{k_{32}}{k_{21}} \frac{D_2}{D_1}\right]^{-1} & 1 & 0 \end{pmatrix} \quad (25) \end{aligned}$$

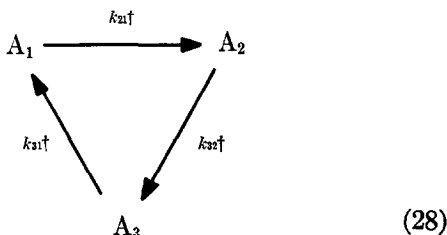
Hence,

$$\begin{aligned} \varphi_1 &= 0 \\ \varphi_2 &= R \sqrt{k_{21}/D_1} \\ \varphi_3 &= R \sqrt{k_{32}/D_2} \end{aligned} \quad (26)$$

The values of η_i are given by Eq. 12. Hence, using Eq. (I-32), we have

$$\mathbf{K}^\dagger = \begin{pmatrix} k_{21}\eta_2 & 0 & 0 \\ -k_{21}\eta_2 \frac{1 - (\varphi_3/\varphi_2)^2(\eta_3/\eta_2)}{1 - (\varphi_3/\varphi_2)^2} & k_{32}\eta_3 & 0 \\ -k_{21}\eta_2 \frac{1 - (\eta_3/\eta_2)}{1 - (\varphi_2/\varphi_3)^2} & -k_{32}\eta_3 & 0 \end{pmatrix} \quad (27)$$

Thus the diffusion-disguised reaction scheme becomes



where

$$\begin{aligned} k_{21}^\dagger &= k_{21}\eta_2 \frac{1 - (\varphi_3/\varphi_2)^2(\eta_3/\eta_2)}{1 - (\varphi_3/\varphi_2)^2} \\ k_{32}^\dagger &= k_{32}\eta_3 \end{aligned}$$

$$k_{31}^\dagger = k_{21}\eta_2 \frac{1 - (\eta_3/\eta_2)}{1 - (\varphi_2/\varphi_3)^2}$$

Let us compare the diffusion-disguised scheme (28) with the true reaction scheme (24) for a catalyst bed in a piston flow reactor when $k_2 = 1 \text{ sec}^{-1}$, $k_{32} = 2 \text{ sec}^{-1}$, $D_1 = 2 \times 10^{-2} \text{ cm}^2/\text{sec}$, $D_2 = 1 \times 10^{-2} \text{ cm}^2/\text{sec}$ and $R = 1 \text{ cm}$. For this case, we have

$$\begin{aligned} \Lambda &= \mathbf{X}^{-1}\mathbf{K}\mathbf{X} = \\ &= \begin{pmatrix} 1 & 1 & 1 \\ 1 & 0 & 0 \\ -1 & 1 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ -1 & 2 & 0 \\ 0 & -2 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 & 0 \\ 0 & 1 & 1 \\ 1 & -2 & -1 \end{pmatrix} \\ &= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \quad (29) \end{aligned}$$

Equation (26) gives $\varphi_1 = 0$, $\varphi_2 = 7.07$, and $\varphi_3 = 14.14$. Using Eq. (12), we obtain $\eta_1 = 1$, $\eta_2 = 0.364$, and $\eta_3 = 0.197$. The value of \mathbf{K}^\dagger may now be computed from Eq. (27); we have

$$\mathbf{K}^\dagger = \begin{pmatrix} 0.365 & 0 & 0 \\ -0.141 & 0.394 & 0 \\ -0.224 & -0.394 & 0 \end{pmatrix} \quad (30)$$

The matrices \mathbf{X}^\dagger and $(\mathbf{X}^\dagger)^{-1}$ are computed by the method of Wei and Prater (5) and applied to the matrix \mathbf{K}^\dagger to obtain Λ^\dagger ;

$$\begin{aligned} \Lambda^\dagger &= (\mathbf{X}^\dagger)^{-1}\mathbf{K}^\dagger\mathbf{X}^\dagger = \begin{pmatrix} 1 & 1 & 1 \\ 1 & 0 & 0 \\ -4.86 & 1 & 0 \end{pmatrix} \\ &= \begin{pmatrix} 0.365 & 0 & 0 \\ -0.141 & 0.394 & 0 \\ -0.224 & -0.394 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 & 0 \\ 0 & 4.86 & 1 \\ 1 & -5.86 & -1 \end{pmatrix} \\ &= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0.365 & 0 \\ 0 & 0 & 0.394 \end{pmatrix} \quad (31) \end{aligned}$$

The values of λ_i from Eq. (29) and λ_i^\dagger from Eq. (31) are used to compute the reaction paths for the true and the diffusion-disguised scheme. Typical reaction paths are shown in Fig. 4. Again it is seen that, when the diffusivities are not equal, the straight line reaction paths are shifted. Some reaction paths are not greatly affected by dif-

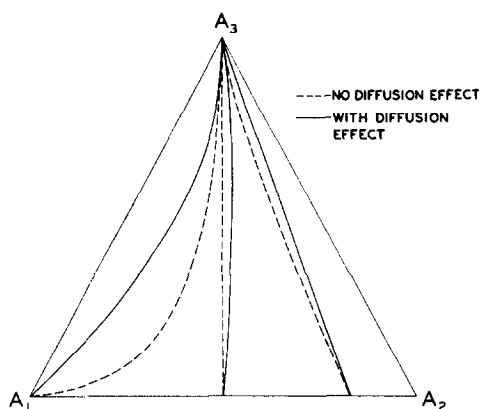


FIG. 4. The effect of diffusion on the reaction paths in an irreversible reaction system.

fusion, but others (such as for an initial composition of pure A_1) are considerably shifted.

III. THE INFLUENCE OF INTRAPARTICLE DIFFUSION ON THE PERFORMANCE OF STIRRED TANK REACTORS

Only a short discussion, sufficient to illustrate the formal inclusion of intraparticle diffusion in the equations for stirred tank reactors, will be given for coupled systems of first order reactions. A detailed comparison of piston flow and stirred tank reactors is given by Wei and Prater (2). Consider the steady state operation of a continuously stirred tank reactor with a volume V . Let the fractional volume occupied by the catalyst be f , and the volumetric flow rate of fresh reactants into and products out of the tank be V/θ , where θ is the average residence time of a molecule in the tank. Equation (1) shows that the rate equation for each catalyst particle has the same form in both the presence and absence of diffusion effects; the true rate constant matrix \mathbf{K} is merely replaced by the diffusion-disguised rate constant matrix \mathbf{K}^\dagger . Hence, the usual set of algebraic equations hold for the stirred tank reactor when diffusion effects are present; the true rate constants are merely replaced by the diffusion-disguised rate constants. These equations, written in matrix form, are

$$(V/\theta)(\mathbf{a}^\circ - \mathbf{a}_0) - fV\mathbf{K}^\dagger\mathbf{a}_0 = 0 \quad (32)$$

where the inlet composition is designated by the vector \mathbf{a}° , and the outlet composition

by the vector \mathbf{a}_0 . Solving Eq. (32) for the outlet composition vector, we have

$$\mathbf{a}_0 = (\mathbf{I} + f\theta\mathbf{K}^\dagger)^{-1}\mathbf{a}^\circ \quad (33)$$

Using Eq. (3) in Eq. (33), we have

$$\begin{aligned} \mathbf{a}_0 &= [\mathbf{I} + f\theta\mathbf{X}^\dagger\mathbf{\Lambda}^\dagger(\mathbf{X}^\dagger)^{-1}]^{-1}\mathbf{a}^\circ \\ &= \{\mathbf{X}^\dagger[\mathbf{I} + f\theta\mathbf{\Lambda}^\dagger](\mathbf{X}^\dagger)^{-1}\}^{-1}\mathbf{a}^\circ \end{aligned} \quad (34)$$

since $\mathbf{I} = \mathbf{X}^\dagger\mathbf{I}(\mathbf{X}^\dagger)^{-1}$. The inverse of the product of matrices is the product of the inverse of the individual matrices taken in reverse order; hence

$$\mathbf{a}_0 = \mathbf{X}^\dagger[\mathbf{I} + f\theta\mathbf{\Lambda}^\dagger]^{-1}(\mathbf{X}^\dagger)^{-1}\mathbf{a}^\circ \quad (35)$$

When the diffusivities are all equal, we have $\mathbf{X}^\dagger = \mathbf{X}$ and $\mathbf{\Lambda}^\dagger = \mathbf{\Lambda}n$. For this special case Eq. (35) becomes

$$\mathbf{a}_0 = \mathbf{X}[\mathbf{I} + f\theta\mathbf{\Lambda}n]^{-1}\mathbf{X}^{-1}\mathbf{a}^\circ \quad (36)$$

Let us compare Eqs. (35) and (36) with the equations for the composition at the outlet of the piston flow reactor. Let s_0 be the length of the piston flow reactor; then the composition at the outlet, as a function of the inlet composition $\mathbf{a}(0)$, is obtained from Eq. (5). We have

$$\mathbf{a}(s_0) = \mathbf{X}^\dagger \exp(-f\mathbf{\Lambda}^\dagger s_0/v)(\mathbf{X}^\dagger)^{-1}\mathbf{a}(0) \quad (35a)$$

and for the case of equal diffusivities

$$\mathbf{a}(s_0) = \mathbf{X} \exp(-f\mathbf{\Lambda}ns_0/v)\mathbf{X}^{-1} \quad (36a)$$

They differ in that the inverse of the matrices $(\mathbf{I} + f\theta\mathbf{\Lambda}^\dagger)$ and $(\mathbf{I} + f\theta\mathbf{\Lambda}n)$ replace the matrices of exponentials shown in Eqs. (35a) and (36a), respectively.

Let us now examine the reaction rate expression for the stirred tank reactor. In terms of the outlet concentrations, which are also the ambient concentrations within the reactor, the reaction rate expressions are given by

$$d\mathbf{a}/dt = -f\theta\mathbf{K}^\dagger\mathbf{a}_0 = -f\theta\mathbf{X}^\dagger\mathbf{\Lambda}^\dagger(\mathbf{X}^\dagger)^{-1}\mathbf{a}_0 \quad (37)$$

Using Eq. (35) in Eq. (37) we obtain the rate expression in terms of the inlet concentration;

$$d\mathbf{a}/dt = -f\theta\mathbf{X}^\dagger\mathbf{\Lambda}^\dagger[\mathbf{I} + f\theta\mathbf{\Lambda}^\dagger]^{-1}(\mathbf{X}^\dagger)^{-1}\mathbf{a}^\circ \quad (38)$$

When all diffusivities are equal, Eq. (38) becomes

$$d\mathbf{a}/dt = -f\theta\mathbf{X}\Lambda\mathbf{n}[\mathbf{I} + f\theta\Lambda\mathbf{n}]^{-1}\mathbf{X}^{-1}\mathbf{a}^\circ \quad (39)$$

If we define an over-all effectiveness matrix, $\mathbf{n}^* = \mathbf{n}(\mathbf{I} + f\theta\Lambda\mathbf{n})^{-1}$ that includes both diffusion effects and the influence of mixing losses, Eq. (39) becomes

$$d\mathbf{a}/dt = -f\theta\mathbf{X}\Lambda\mathbf{n}^*\mathbf{X}^{-1}\mathbf{a}^\circ \quad (40)$$

The element η_i^* of the matrix \mathbf{n}^* is given by

$$\eta_i^* = [(1/\eta_i) + f\theta\lambda_i]^{-1} \quad (41)$$

When the residence time, θ , approaches zero, $\mathbf{a}_0 \rightarrow \mathbf{a}^\circ$ and the terms $f\theta\lambda_i$ in Eq. (41) approach zero. Hence, $\mathbf{n}^* = \mathbf{n}$; this corresponds to pure diffusion effects in a differential reactor. When the residence time approaches infinity, equilibrium is substan-

tially reached in the tank and $\mathbf{n}^* \rightarrow 0$ since $f\theta\lambda_i$ becomes infinite. When $\mathbf{n} = \mathbf{I}$ and $f\theta\Lambda$ remains finite, diffusion effects are absent. Then we have a case of pure inlet mixing loss, and $\mathbf{n}^* = (\mathbf{I} + f\theta\Lambda)^{-1}$ (6). When $\mathbf{n} \rightarrow 0$, we have maximum diffusion effects and $\eta_i^* \rightarrow 3/\varphi_i$.

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