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The Relationship Between the Real Time and Selectivity Description of Complex Pseudomonomolecular Kinetic Systems

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For pseudomonomolecular reaction systems in packed bed reactors, an algebraic expression is derived which enables the real time behavior of the reactor to be determined from the known relative rate constant matrix (selectivity) obtained via the Wei–Prater algebraic approach and the real time parameters. A method is developed to experimentally evaluate the real time parameters from packed bed kinetic data (and the known selectivity). A three component example is used to illustrate the relationship between the real time and the selectivity description of the reactor.

NOMENCLATURE

A	cross-sectional area of catalytic bed
A_i	the ith chemical species
a_i	composition of the ith chemical species, moles i/moles reaction mixture
b_i	composition of the ith characteristic species
$b_i(0)$	initial composition of the ith characteristic species
$b_{i,j}$	composition of the ith characteristic species for jth data point
F	moles of reaction mixture per unit time
F_f	molar flow rate
$\mathbf{g}^T$	row vector with typical element g_i
g_i	adsorption isotherm for ith species, atm^{-1}
$\mathbf{I}\dagger$	diagonal matrix defined in conjunction with Eq. (15)
$\mathbf{K}$	intrinsic rate constant matrix
k_{ij}	ijth element of $\mathbf{K}$; rate constant for the reaction $A_j \rightarrow A_i$
M_f	molecular weight of feed (56.1 mass/mole)
P	total pressure (10 atm)
r_i	ith reaction rate, moles i/mass catalyst-time
S^0_{LH}	overall liquid hourly space velocity, volume liquid feed/volume catalyst-time
S_{LH}	liquid hourly space velocity up to any point in catalyst bed, volume liquid feed/volume catalyst up to any z-time
t	real time
$\mathbf{V}$	vector defined in conjunction with Eqs. (15) and (16)
V_i	ith element of $\mathbf{V}$
$V_{i,j}$	ith element of $\mathbf{V}$ for jth data point
$\mathbf{X}$	matrix of characteristic vectors
$\mathbf{X}^{-1}$	inverse of $\mathbf{X}$
x_{ij}	ijth element of $\mathbf{X}$

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y_{ij}	ijth element of $\mathbf{X}^{-1}$
z	distance measured down catalyst bed
z_L	catalyst bed length
$\boldsymbol{\alpha}$	vector of compositions whose components are the a_i
$\boldsymbol{\alpha}(0)$	vector of initial compositions
$\boldsymbol{\beta}$	vector of characteristic compositions whose components are the b_i
$\boldsymbol{\beta}(0)$	vector of initial characteristic compositions
ϵ	volume of voids/volume of reactor
ξ	fictitious, pseudo-distance defined differentially in equation (12)
ξ_j	pseudo-distance for jth data point
ρ_s	mass of catalyst/volume of catalyst (1.2)
ρ_L	mass of liquid feed/volume liquid feed (0.675)
$\boldsymbol{\Theta}$	apparent pseudo-first-order rate constant matrix
$\boldsymbol{\Theta}'$	relative pseudo-first-order rate constant matrix; lmth element unity
$\boldsymbol{\Theta}'_{\mathrm{exp}}$	experimentally determined relative pseudo-first-order rate constant matrix
θ_{ij}	ijth element in $\boldsymbol{\Theta}$; apparent pseudo-first-order rate constant for the reaction $A_j \rightarrow A_i$
θ'_{ij}	ijth element in $\boldsymbol{\Theta}_{\mathrm{exp}'}$, equal to θ_{ij}/λ_m
θ_{lm}	lmth element in $\boldsymbol{\Theta}$; $\boldsymbol{\Theta} = \theta_{lm}\,\boldsymbol{\Theta}'$
θ'_{lm}	lmth element in Θ'_{exp}; $\Theta' = (1/\theta'_{lm})\,\Theta'_{\mathrm{exp}}$
Λ	diagonal matrix whose elements $(-\lambda_i)$ are characteristic values of $\mathbf{K}$
Λ'	diagonal matrix whose ith element is $-\lambda_i/\lambda_m$; mth element unity
$\Lambda\dagger$	diagonal matrix defined in conjunction with Eq. (15)
$\mathrm{EXP}[\Lambda t]$	diagonal matrix whose typical element is $\mathrm{EXP}[-\lambda_i t]$
$\mathrm{EXP}[\Lambda' t]$	diagonal matrix whose typical element is $\mathrm{EXP}[-\lambda'_i t]$
λ_i	eigenvalue of $\mathbf{K}$, nonnegative numbers
λ'_i	λ_i/λ_m
λ_m	mth eigenvalue of $\mathbf{K}$; $\Lambda = \lambda_m \Lambda'$
τ	fictitious, selectivity time scale defined in Eq. (4)
Φ	$(1 + P\mathbf{g}^T\boldsymbol{\alpha})^{-1}$, a function of composition and time that multiplies each rate equation of a pseudomonomolecular system.

INTRODUCTION

A reaction system is monomolecular if the coupling between each pair of species is by first-order reaction only. The kinetics are thus expressed by the linear differential equations:

$$\frac{d\boldsymbol{\alpha}}{dt} = \mathbf{K}\boldsymbol{\alpha}, \tag{1}$$

where $\boldsymbol{\alpha}$ is a vector of compositions and $\mathbf{K}$ the intrinsic rate constant matrix with typical element, k_{ij}, the rate constant for the reaction $A_j \rightarrow A_i$. Pseudomonomolecular systems are reaction systems in which the rates of change of the various species are given by first-order mass action terms, each multiplied by the same function of composition and time. Wei and Prater showed that if certain conditions are fulfilled (5), heterogeneous reactions that take place on a single surface will be pseudomonomolecular. The kinetic rate equations are given by the nonlinear differential equations:

$$\frac{d\boldsymbol{\alpha}}{dt} = \frac{1}{1 + P\mathbf{g}^T\boldsymbol{\alpha}}\,\boldsymbol{\Theta}\boldsymbol{\alpha}, \tag{2}$$

where $\mathbf{\Theta}$ is the pseudomonomolecular rate constant matrix whose typical entry, θ_{ij}, is the pseudo-first-order rate constant for the reaction $A_j \rightarrow A_i$. The term $1/(1 + P\mathbf{g}^T\boldsymbol{\alpha}) \equiv \Phi$ may be identified with the adsorption of the various species on the active sites, with g_i the adsorption isotherm of the ith species and P the total pressure. The θ_{ij} and g_i which appear in $\mathbf{\Theta}$ and $\mathbf{g}^T$, respectively, are complicated functions of the intrinsic rate constants (rate constants undisguised by the adsorption–desorption interactions among gas phase molecules and the catalyst surface) and the thermodynamic adsorption and desorption rate constants; they are considered sufficient to describe the system's kinetic behavior.

The solution of Eq. (2), $\boldsymbol{\alpha}(t)$, expresses the real time behavior of the reaction system; i.e., the correspondence between each composition and the real reaction time, t. All the θ_{ij} and g_i must be known to calculate the reaction time for any composition and conversely, the reaction times must be known for each composition data point to determine the θ_{ij} and g_i experimentally. On the other hand, the selectively behavior; i.e., the composition sequence that is produced from a given initial composition, may be determined without specific knowledge of the g_i and with the rate constant matrix known relative to any one rate constant (Ref. (*4*), see App). Equation (2) is rewritten in terms of the relative pseudo-first-order rate constant matrix, $\mathbf{\Theta}'$:

$$\frac{d\boldsymbol{\alpha}}{dt} = \Phi\theta_{lm}\mathbf{\Theta}'\boldsymbol{\alpha}, \tag{3}$$

where θ_{lm} is the pseudo-first-order rate constant for the reaction $A_m \rightarrow A_l$ and $\Theta = \theta_{lm}\ \Theta'$. A typical element of Θ' is θ_{ij}/θ_{lm} and the lm position is unity. Introduction of a new (fictitious) time scale defined differentially by:

$$d\tau = \frac{1}{1 + P\mathbf{g}^T\boldsymbol{\alpha}}\,\theta_{lm}dt, \tag{4}$$

transforms Eq. (3) into:

$$\frac{d\boldsymbol{\alpha}}{d\tau} = \mathbf{\Theta}'\boldsymbol{\alpha}. \tag{5}$$

The solution of Eq. (5), $\boldsymbol{\alpha}(\tau)$, expresses the selectivity behavior of the reaction system; it is seen that the selectivity behavior is monomolecular with respect to the fictitious selectivity time, τ [compare to Eq. (1)]. Only the relative rate constant matrix, $\mathbf{\Theta}'$, must be known to calculate composition sequences and conversely only experimental composition sequences are necessary to determine $\mathbf{\Theta}'$ experimentally. The apparent physiochemical parameters θ_{lm} and the g_i, which appear implicitly in the selectivity description [Eq. (5)] and explicitly in the real time description [Eq. (2)], are henceforth referred to as the real time parameters. Their evaluation is a necessary prerequisite to knowing the real time behavior.

Wei and Prater (*4*) and Prater *et al.* (*1*) have presented an elegant method of analyzing the kinetics of highly coupled, complex monomolecular and pseudomonomolecular systems. Applications have been confined to determining the relative rate constant matrix, $\mathbf{\Theta}'$, for pseudomonomolecular, solid catalyzed reactions (*2–4*). The experimental determination of $\mathbf{\Theta}'$ is important because it is a measure of the ability of a catalyst to produce a desired product. However, reactor design and reactor modeling demand the calculation of compositions and temperatures as functions of the actual distance down the catalyst bed or the actual residence time of the reactants. Although $\mathbf{\Theta}'$ is sufficient to evaluate a catalyst's ability to produce a desired product, the real time parameters, θ_{lm} and the g_i, are needed (in addition to $\mathbf{\Theta}'$) for the former application.

In this paper, the relationship between the real time behavior and the selectivity behavior is to be studied for a pseudomonomolecular system whose selectivity has been determined via the linear algebraic approach of Wei and Prater. The equations which describe the real time and selectivity kinetics of pseudomonomolecular reaction systems in experimental packed bed reactors are presented. An equation analogous to Eq. (4) is integrated analytically to derive an algebraic relationship between the real time scale, t, and another fictitious time scale, ξ. A method of calculating the real time parameters experimentally is presented and discussed. A three component example is used to illustrate the results quantitatively.

SELECTIVITY BEHAVIOR OF PSEUDOMONOMOLECULAR SYSTEMS IN EXPERIMENTAL, PLUG FLOW, PACKED BED REACTIONS

For the following assumptions:

(i) Plug flow of gas phase,
(ii) Constant cross-sectional area,
(iii) Constant void fraction,
(iv) Isothermal,

a steady state mass balance for the ith species in a differential slab, dz, of reactor is:

$$d(Fa_i) = [\rho_s(1-\epsilon)A\,dz]r_i, \tag{6}$$

where:	a_i	moles i/moles reaction mixture
	r_i	moles i/mass catalyst-time
	ρ_s	mass catalyst/volume catalyst
	F	moles reaction mixture/time
	ϵ	void volume/volume reactor
	A	cross-sectional area of reactor
	z	distance measured down catalyst bed.

The (overall) liquid hourly space velocity, S^0_{LH}, defined as the volume of liquid feed per volume of catalyst per unit time, may be used to express the molar feed rate (F_f) of reactants as:

$$F_f = \rho_L(1-\epsilon)Az_LS^0_{LH}/M_f, \tag{7}$$

where:	ρ_L	mass feed/volume feed
	z_L	catalyst bed length
	M_f	mass feed/mole feed (molecular weight).

For a monomolecular or pseudomonomolecular system, the number of moles remain constant and $F_f = F =$ constant. In addition, the liquid hourly space velocity up to any point in the bed, z (volume of liquid feed per volume of catalyst up to z per unit time), may be defined as $S_{LH} \equiv (1-\epsilon)Az_LS^0_{LH}/(1-\epsilon)Az$ or $S_{LH} \equiv S^0_{LH}/(z/z_L)$. In differential form, this relationship becomes:

$$dz = S^0_{LH}z_L\,d\left(\frac{1}{S_{LH}}\right). \tag{8}$$

Substituting Eq. (7) into Eq. (6), rearranging and making use of Eq. (8) yields:

$$\frac{\rho_L}{M_f\rho_s}\frac{da_i}{d(1/S_{LH})} = r_i. \tag{9}$$

It is seen that for the plug flow reactor, the reciprocal space velocity, $1/S_{LH}$, and the distance down the bed, $z = S^0_{LH}z_L(1/S_{LH})$, are interchangeable in expressing the real progress of the reaction. Since $(1/S_{LH})$ has units of time, the real reaction progress in the plug flow reactor described by Eq. (9) may accurately be referred to as real time kinetics. Equation (9) may be written in matrix form for a pseudomonomolecular system:

$$\frac{\rho_L}{M_f\rho_s}\frac{d\boldsymbol{\alpha}}{d(1/S_{LH})} = \frac{1}{1+\mathbf{P}\mathbf{g}^T\boldsymbol{\alpha}}\boldsymbol{\Theta}\boldsymbol{\alpha}. \tag{10}$$

Equation (10) may be written in terms of the relative, pseudo-first-order rate constant matrix, $\boldsymbol{\Theta}'$:

$$\frac{\rho_L}{M_f\rho_s}\frac{d\boldsymbol{\alpha}}{d(1/S_{LH})} = \Phi\theta_{lm}\boldsymbol{\Theta}'\boldsymbol{\alpha}. \tag{11}$$

By introducing a fictional time or pseudodistance, ξ, defined differentially by:

$$\frac{M_f\rho_s}{\rho_L}\theta_{lm}\Phi\,d\left(\frac{1}{S_{LH}}\right) = d\xi, \tag{12}$$

Eq. (11) becomes monomolecular with respect to ξ which will be referred to as the "crazy clock" time:

$$\frac{d\boldsymbol{\alpha}}{d\xi} = \boldsymbol{\Theta}'\boldsymbol{\alpha}. \tag{13}$$

Thus, the real time behavior, $\boldsymbol{\alpha}(1/S_{LH})$, is described by the solution to Eq. (10), the selectivity behavior, $\boldsymbol{\alpha}(\xi)$, by the solution to Eq. (13) and the relationship between the real time behavior, $1/S_{LH}$, and the selectivity behavior, ξ, by the integration of Eq. (12).

THE RELATIONSHIP BETWEEN THE REAL TIME BEHAVIOR AND THE SELECTIVITY BEHAVIOR

The determination of the selectivity behavior ($\boldsymbol{\Theta}'$) of pseudomonomolecular systems via the linear algebraic approach has been summarized in the Appendix. We will assume that the selectivity of the reaction is known; i.e., the characteristic vectors ($\mathbf{X}$) and the relative characteristic values ($\boldsymbol{\Lambda}'$) of $\boldsymbol{\Theta}'$ have been determined experimentally by measuring compositions at various positions along the bed for different (overall) liquid hourly space velocities, S_{LH}^{0}. It is noted once again that the actual position (z or $1/S_{LH}$) corresponding to each composition data point is not necessary to determine the selectivity matrix, $\boldsymbol{\Theta}'$.

The integral of the exponential matrix may be calculated analytically and expressed in compact matrix notation (diagonal matrices can be treated like scalars) to yield:

$$\int_0^{\xi} \text{EXP}[\boldsymbol{\Lambda}'\xi]d\xi = \boldsymbol{\Lambda}\dagger(\mathbf{I}\dagger - \text{EXP}[\boldsymbol{\Lambda}'\xi]), \quad (15)$$

where $\boldsymbol{\Lambda}\dagger$ is a diagonal matrix whose elements are ξ, $1/\lambda_1'$, $1/\lambda_2' \ldots 1 \ldots 1/\lambda_{n-1}'$ and $\mathbf{I}\dagger$ is a diagonal matrix whose elements are $2,1,1 \ldots 1,1$. Note that the mth diagonal element of both $\Lambda\dagger$ and $\boldsymbol{\Lambda}'(\equiv(1/\lambda_m)\boldsymbol{\Lambda})$ is unity. Thus, the real time (or position in the bed), $1/S_{LH}$, which corresponds to any value of the "crazy clock" time, ξ, may be calculated algebraically from Eq. (14) after substitution of Eq. (15):

$$\frac{1}{S_{LH}} = \frac{\rho_L}{M_f\rho_s\theta_{lm}}[\xi + P\mathbf{g}^T\mathbf{X}\boldsymbol{\Lambda}\dagger(\mathbf{I}\dagger - \text{EXP}[\boldsymbol{\Lambda}'\xi])\mathbf{X}^{-1}\boldsymbol{\alpha}(0)]. \quad (16)$$

The quantity $\mathbf{X}\boldsymbol{\Lambda}\dagger(\mathbf{I}\dagger - \text{EXP}[\boldsymbol{\Lambda}'\xi])X^{-1}\boldsymbol{\alpha}(0)$ is a vector and will be denoted by $\mathbf{V}[\xi,\boldsymbol{\alpha}(0)]$ with typical element:

$$V_i[\xi,\boldsymbol{\alpha}(0)] = \sum_{j=1}^{n} \{x_{i1}y_{1j}\xi + x_{i2}y_{2j}[\text{EXP}(-\lambda_1'\xi) - 1]/-\lambda_1' + x_{i3}y_{3j} \cdot [\text{EXP}(-\lambda_2'\xi) - 1]/-\lambda_2' + \cdots + x_{in}y_{nj}(\text{EXP}(-\lambda_{n-1}'\xi) - 1]/-\lambda_{n-1}'\}\alpha_j(0),$$

Despite the fact that the compositions, $\boldsymbol{\alpha}$, appear explicitly (in Φ), Eq. (12) can be integrated analytically. Since $\boldsymbol{\alpha}$ is known as a function of ξ [Eq. (A.6)], it may be substituted into Eq. (12). After rearrangement, integration of each side (the constant terms $P\mathbf{g}^T\mathbf{X}$ and $\mathbf{X}^{-1}\ \boldsymbol{\alpha}(0)$ are moved outside the integral), and preserving the matrix order, the following is obtained:

$$\frac{M_f\rho_s\theta_{lm}}{\rho_L}\left(\frac{1}{S_{LH}}\right) = \xi + P\mathbf{g}^T\mathbf{X}\left(\int_0 \text{EXP}[\boldsymbol{\Lambda}'\xi]d\xi\right)\mathbf{X}^{-1}\boldsymbol{\alpha}(0). \quad (14)$$

where x_{ij} are the components of $\mathbf{X}$, y_{ij} the components of $\mathbf{X}^{-1}$ and $-\lambda_i'$ the components of $\boldsymbol{\Lambda}'$. Equation (16) may be written thusly:

$$\frac{1}{S_{LH}} = \frac{\rho_L\xi}{M_f\rho_s}\left(\frac{1}{\theta_{lm}}\right) + \frac{\rho_L P}{M_f\rho_s}\left[\sum_{i=1}^{n} V_i(\xi,\boldsymbol{\alpha}(0))\frac{g_i}{\theta_{lm}}\right]. \quad (17)$$

Since ρ_L, M_f, ρ_s, the V_i and P are known for a given reaction system, the real time behavior ($1/S_{LH}$) may be calculated from the selectivity only after the real time parameters, θ_{lm} and the g_i, are determined experimentally. Conversely, Eq. (17) may be used to experimentally determine the real time parameters. This is possible only if the time course of the experimental data is known. A suitable method is presented and discussed below.

CALCULATION OF THE REAL TIME PARAMETERS g_i AND θ_{lm}

Experimental composition data ($\boldsymbol{\alpha}$) are taken at various positions in the bed ($1/S_{LH}$ or z) and/or for various (overall) liquid hourly space velocities. Thus, $(1/S_{LH}) - \boldsymbol{\alpha}$ pairs are known experimentally, but only the $\boldsymbol{\alpha}$ (composition) data are used to calculate $\mathbf{X}$ and $\boldsymbol{\Lambda}'$ (and thus $\boldsymbol{\Theta}'$). However, if the value of the "crazy clock" time, ξ, corresponding to each $(1/S_{LH}) - \boldsymbol{\alpha}$ pair can be found, then θ_{lm} and the g_i may be calculated via a linear least squares fit of the experimental data to Eq. (17). For any data point (denoted by the subscript j), Eq. (17) becomes:

$$\hat{p}_j = a_{0j}\left(\frac{1}{\theta_{lm}}\right) + a_{1j}\left(\frac{g_1}{\theta_{lm}}\right) + \cdots + a_{nj}\left(\frac{g_n}{\theta_{lm}}\right), \quad (18)$$

where: $\hat{p}_j$ = predicted value of $1/S_{LH}$, using Eq. (17), for the jth data point
$a_{0j} = \rho_L \xi_j / M_f \rho_s$ for the jth data point
$a_{ij} = \rho_L PV_{i,j} / M_f \rho_s$ for the jth data point ($i = 1,2, \ldots n$).

The parameters $1/\theta_{lm}$, g_1/θ_{lm}, . . . g_n/θ_{lm} appear linearly in Eq. (18) and, provided ξ_j can be determined for each of the j data points, they may be obtained via a linear least squares calculation.

Equation (A.4), in component form, with ξ replacing t and λ_i' replacing λ_i is:

$$b_i = b_i(0)\text{EXP}[-\lambda_i'\xi], \quad (19)$$

which may be solved quite easily for ξ:

$$\xi = \frac{1}{\lambda_i'} \ln\left(\frac{b_i}{b_i(0)}\right). \quad (20)$$

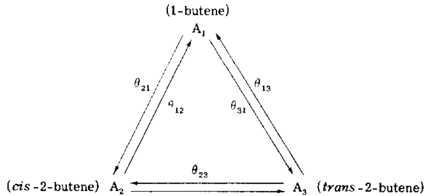
For any (real) composition data point, $\boldsymbol{\alpha}_j$ (with corresponding $1/S_{LH}$ value), $\mathbf{b}_j$ may be calculated using the already determined $\mathbf{X}$; i.e., $\mathbf{b}_j = \mathbf{X}^{-1}\boldsymbol{\alpha}_j$. Likewise, for the initial characteristic composition, $\mathbf{b}(0) = X^{-1}\boldsymbol{\alpha}(0)$. Equation (20) may be written for the jth data point:

$$\xi_j = \frac{1}{\lambda_i'} \ln\left(\frac{b_{i,j}}{b_i(0)}\right). \quad (21)$$

For every data point, Eq. (21) is used [for any i, provided $b_{i,j}$ and $b_i(0)$ have the same sign] to calculate ξ_j, and the resulting $\xi_j - (1/S_{LH})$ pairs used in conjunction with Eq. (18) to calculate the real time parameters. The procedure may be repeated at different temperatures to obtain the temperature coefficients.

DISCUSSION

An example, based on the selectivity results reported by Wei and Prater (*7*) for the interconversion of 1-butene, *cis*-2-butene and *trans*-2-butene, is to be discussed. The reaction scheme is:



Typical reaction paths are shown in Fig. 1 for three different initial compositions; they were calculated using Eq. (A.6) with the $\mathbf{X}$ and $\boldsymbol{\Lambda}'$ matrices used in the original Wei–Prater article. The "crazy clock" time, ξ, is a parameter on the reaction paths, increasing from zero at the initial compositions to larger and larger values as the reaction paths approach the equilibrium point, E. Thus, ξ is a relative measure of the extent of the reaction. "Experimental" real time data were generated by assuming the following values of the real time parameters:

$$g_1 = 5 \text{ atm}^{-1},$$
$$g_2 = 2 \text{ atm}^{-1},$$
$$g_3 = 1 \text{ atm}^{-1},$$
$$\theta_{lm} = \theta_{13} = 0.515 \text{ (moles reaction mixture)/(mass catalyst-hr)}$$

Typical values for the physical parameters (M_f, ρ_s, etc.) appear in the table of nomenclature. No particular significance should be placed on the assumed magnitudes of the real time and physical parameters; they were chosen rather arbitrarily for the purpose of illustration.

Equation (17) predicts that provided $\mathbf{g}^T \neq \mathbf{0}$, each initial composition will yield a distinct $(1/S_{LH})$–ξ curve. Figure 2 is a plot of the "experimental" $1/S_{LH}$ vs ξ data, calculated from Eq. (17), for the three initial compositions whose reaction paths appear in Fig. 1. For $\mathbf{g}^T = \mathbf{0}$ (no adsorption, desorption effects and consequently the apparent pseudo-first-order rate constants are the intrinsic first-order rate constants) a single straight line results for all initial compositions. This line appears as the dashed line on Fig. 2; its analytic expression is derived directly from Eq. (16) by setting $\mathbf{g}^T = \mathbf{0}$.

The plots on Fig. 2 show very little curvature other than at small values of the reaction extent, ξ. We see that despite the extreme nonlinear functionality between $1/S_{LH}$ and ξ, expressed explicitly in Eq. (17), our example illustrates that it is possible for experimental $1/S_{LH}$ vs ξ plots to yield curves which are almost linear. In

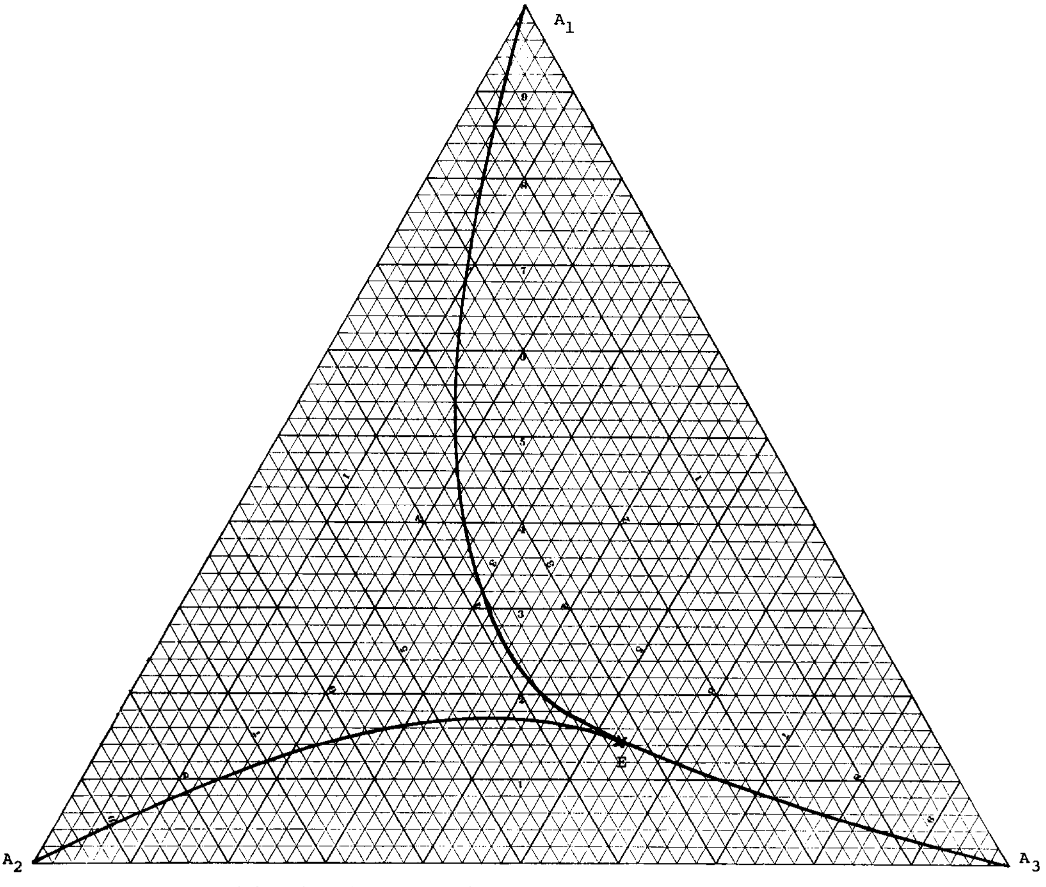


FIG. 1. Selectivity of the interconversion of 1-butene, *cis*-2-butene and *trans*-2-butene.

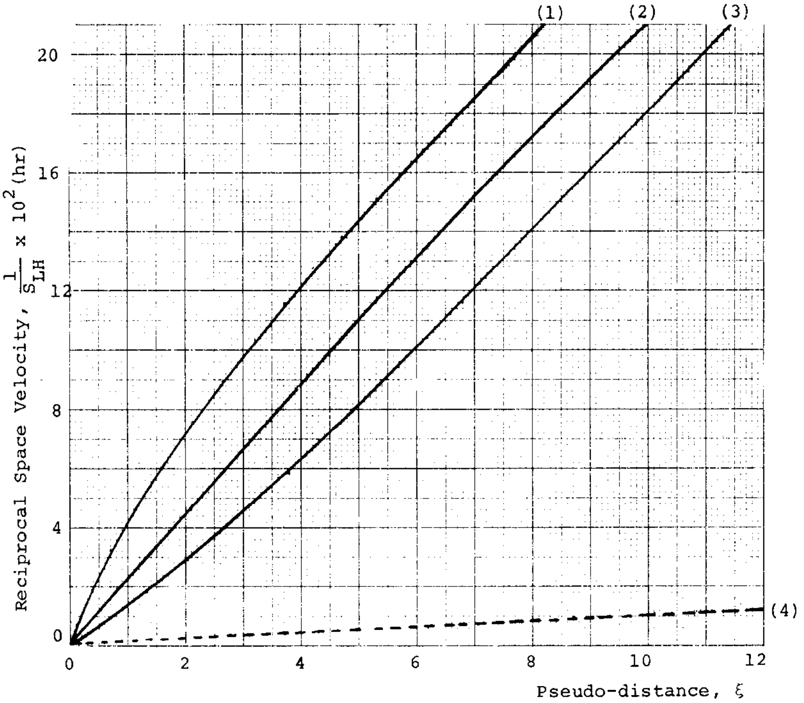


FIG. 2. Reciprocal space velocity vs pseudodistance for various initial concentrations. (1) Pure A_1; (2) pure a_2; (3) pure A_3; (4) all $g_i \equiv 0$.

general, the curvature will depend upon the magnitude of the individual specie's adsorption–desorption activity and the relative degree to which the specie are present along the experimental reaction path (which of course ultimately depends upon the initial compositions and the selectivity). However, as long as one or all of the g_i in $\mathbf{g}^T$ are *not* zero, the "almost" linear curves will be distinct and different for each initial composition. Only when the experimental results for various initial compositions are coincident can adsorption–desorption effects be correctly disregarded. Finally, the results suggest that widely different initial compositions should be run to make certain that despite scatter in the experimental results, distinct curves are still observable.

Since a distinct $(1/S_{LH})$-ξ curve exists for each initial composition, a different $1/S_{LH}$ (and for the same volume of liquid feed, a different amount of catalyst) is required for the reaction to proceed to a given extent, ξ. The adsorption–desorption effects decrease the reaction rates depending upon the magnitudes of the various adsorption isotherms, g_i [see Eq. (10)]. Consequently, a relatively smaller increment of composition, $d\boldsymbol{\alpha}$, results for each increment of catalyst bed, $d(1/S_{LH})$; i.e., to attain a given extent of reaction, more catalyst is necessary. This is illustrated in Fig. 2: the broken line (no adsorption–desorption effects) is lower than the other curves and consequently, the $1/S_{LH}$ corresponding to $\mathbf{g}^T = \mathbf{0}$ is smaller at every ξ, with the difference increasing with extent of reaction, ξ. For $\mathbf{g}^T = \mathbf{0}$, the amount of catalyst necessary to achieve a given reaction extent is the same for any initial composition.

When adsorption–desorption effects are present, the most catalyst is required for those initial compositions whose reaction paths contain large amounts of the specie which are adsorbed the strongest (large g_i) and the least catalyst is necessary for those initial compositions whose reaction paths contain the least amount of these specie. This is confirmed in Fig. 2. Curve 1, corresponding to a feed of pure A_1 and whose reaction path contains relatively large amounts of A_1 (g_1, the adsorption isotherm of species A_1 is largest) requires the most catalyst for given extent. On the other hand, curve 3, corresponding to a feed of pure A_3 and whose reaction path contains relatively large amounts of A_3 (g_3 is the smallest adsorption isotherm) but relatively small amounts of A_1, requires the least catalyst for given extent.

Once the real time parameters are determined via a linear least squares fit of the "experimental" data (such as those shown in Fig. 2) to Eq. (17), the $(1/S_{LH})$-ξ transformation [Eq. (17)] and the reaction paths [Eq. (A.6)] may be combined to determine the actual progress of the reaction in the catalyst bed. Figure 3 is a cross plot of the $1/S_{LH}$ vs ξ transformation and the reaction path for an initial composition of pure A_2. For any "crazy clock" time or reaction extent, ξ, the composition and the reciprocal space velocity, $1/S_{LH}$, may be determined. This can also be done analytically by direct calculation using Eqs. (A.6) and (17). For a given overall liquid hourly space velocity (S_{LH}^0) and catalyst bed length (z_L), the actual position in the bed (z) is determined by integration of Eq. (8):

$$z = S_{LH}^0 z_L \left(\frac{1}{S_{LH}}\right). \tag{22}$$

Thus, once the real time parameters are known, the actual position in the bed corresponding to any composition can be determined algebraically and analytically using Eqs. (A.6), (17) and (22). The $(1/S_{LH}) - \xi$ transformation and subsequent

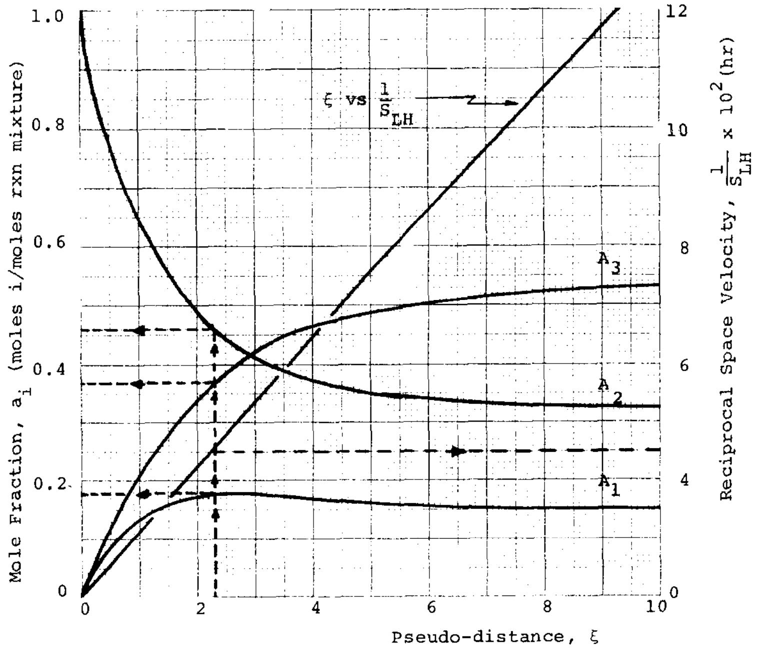


FIG. 3. The interrelationship between the real time and selectivity descriptions for an initial concentration of pure A_2.

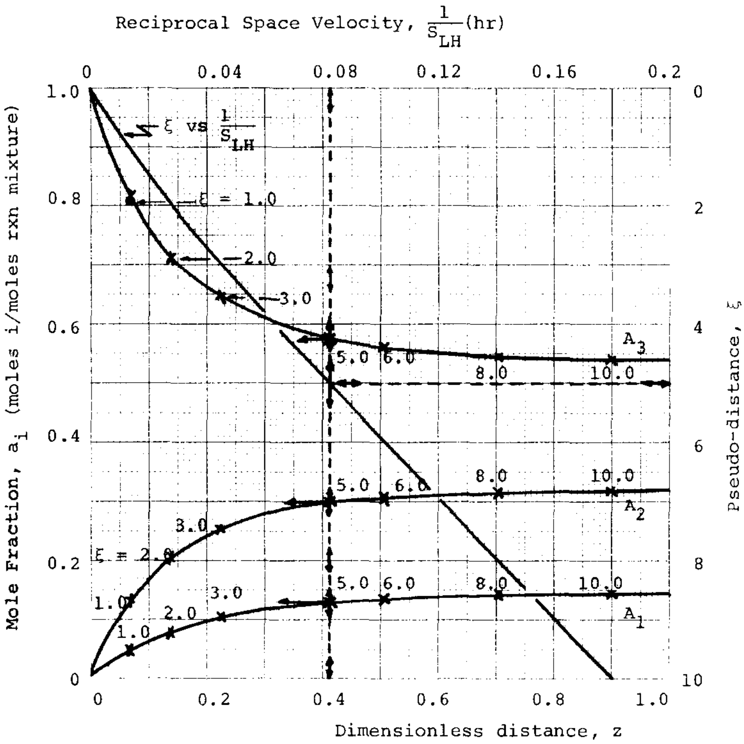


FIG. 4. The real time solution compared to the $(1/S_{LH})$–ξ solution, with $S^0_{LH} = 5.0$ cc/cc-hr.

integration has led to an *analytic* solution to the nonlinear differential equations in Eq. (10).

To illustrate this point further, Eq. (10) was solved numerically using a Runge-Kutta integration routine, for an initial composition of pure A_3. The results are plotted on Fig. 4 as composition (α) vs dimensionless distance (z) and via Eq. (22) vs $1/S_{LH}$; they are shown by the smooth curves. The $(1/S_{LH})$–ξ transformation was calculated using Eq. (17) and plotted. Values of α were calculated via Eq. (A.6) for $0 \leq \xi \leq 10$ and these results also appear in Fig. 4 ("X" symbols). It is seen that the results are entirely consistent and in fact identical.

CONCLUSIONS

The kinetics of a pseudomonomolecular system in a plug flow, isothermal packed bed reactor are given by the nonlinear differential equations in Eq. (10). For the known selectivity determined via the method of Wei and Prater (*4*), an algebraic relationship between the reciprocal space velocity (or distance into the catalyst bed) and the fictitious selectivity distance has been derived analytically in terms of the real time parameters [Eq. (17)]. A method is described which enables the real time parameters to be found via a linear least squares fit of the composition–space velocity data. Once the real time parameters are determined, the compositions at any distance into the catalyst bed may be calculated analytically from the derived algebraic relationships.

With the selectivity and the real time parameters known, the solution of the nonlinear differential equations in Eq. (10) [i.e., $\alpha(z)$] is available in analytic form [Eqs. (A.6), (17) and (22)]. This is possible because the transformation of independent variables defined differentially in Eq. (12) can be integrated analytically to obtain the algebraic $(1/S_{LH})$-ξ relationship in Eq. (17). The purpose of this paper has been to describe this transformation and how it leads to a relatively simple method to experimentally determine real time parameters from known selectivity.

APPENDIX: SELECTIVITY VIA THE LINEAR ALGEBRAIC APPROACH

For a monomolecular system Wei and Prater (*4*) show that the linear, nonsingular transformation,

$$\boldsymbol{\alpha} = \mathbf{X}\boldsymbol{\beta}, \qquad \text{(A.1)}$$

exists and relates the (measurable) $\boldsymbol{\alpha}$ compositions to the new (characteristic) compositions, $\boldsymbol{\beta}$. The characteristic vectors (eigenvectors) of **K** are the columns of the constant matrix, **X**. The characteristic vectors and the characteristic values, λ_i, (eigenvalues) of **K** are distinct and the similarity transformation,

$$\mathbf{X}^{-1}\mathbf{K}\mathbf{X} = \Lambda = \text{diagonal matrix whose elements are } (\lambda_0, -\lambda_1, \ldots -\lambda_{n-1}), \lambda_0 = 0, \qquad \text{(A.2)}$$

exists. The matrix Λ is a diagonal matrix whose nonzero elements are the eigenvalues of **K**. Equations (A.1) and (A.2) transform Eq. (1) into the following, uncoupled system:

$$\frac{d\boldsymbol{\beta}}{dt} = \Lambda\boldsymbol{\beta}. \qquad \text{(A.3)}$$

The characteristic values, λ_i, are thus the rate constants in the characteristic system. The solution of Eq. (A.3) is:

$$\boldsymbol{\beta}(t) = \text{EXP}(\Lambda t)\boldsymbol{\beta}(0), \qquad \text{(A.4)}$$

where $\text{EXP}(\Lambda t)$ is a diagonal matrix with typical diagonal element $\text{EXP}(-\lambda_i t)$. Because the law of conservation of mass must hold for the $\boldsymbol{\beta}$ system, one characteristic rate constant (λ_0) must be zero. Substitution of Eq. (A.1) into Eq. (A.4) yields the expression for the reaction paths in the $\boldsymbol{\alpha}$ system:

$$\boldsymbol{\alpha}(t) = \mathbf{X}\ \text{EXP}(\Lambda t)\ \mathbf{X}^{-1}\boldsymbol{\alpha}(0). \qquad \text{(A.5)}$$

Wei and Prater present methods of evaluating the characteristic matrix, **X**, from experimental measurements. With **X** known the characteristic compositions for the measured $\boldsymbol{\alpha}$ data are generated (via $\mathbf{X}^{-1}\boldsymbol{\alpha}$) and because the $\boldsymbol{\beta}$ system is uncoupled, the characteristic rate constants (λ_i) are determined easily. With both **X** and Λ known, **K** may be calculated from Eq. (A.2), $\mathbf{K} = \mathbf{X}\Lambda\mathbf{X}^{-1}$.

Equation (13) shows that the selectivity of a pseudomonomolecular system is monomolecular with respect to ξ and is thus amenable to the above formulation. For these systems, instead of Λ, the *relative* characteristic rate constant matrix, $\Lambda'[= (1/\lambda_m)\Lambda]$ is determined, where a typical element of Λ' is $-\lambda_i/\lambda_m$ and the *m*th diagonal element is unity. The experimentally determined relative pseudo-first-order rate constant matrix, Θ'_{exp}, is calculated from Λ' and **X** by $\Theta'_{\text{exp}} = \mathbf{X}\Lambda'\mathbf{X}^{-1}$. A typical element of Θ'_{exp} is $\theta'_{ij} = \theta_{ij}/\lambda_m$; in general the *lm* element of Θ'_{exp} is *not* unity and Θ'_{exp} is not the relative selectivity matrix designated Θ'. However, dividing each element of Θ'_{exp} by θ'_{lm} (i.e., making the *lm* element of Θ'_{exp} unity) generates Θ'. The reaction paths may be calculated via:

$$\boldsymbol{\alpha}(\xi) = \mathbf{X}\ \text{EXP}[\Lambda'\xi]\mathbf{X}^{-1}\boldsymbol{\alpha}(0), \qquad \text{(A.6)}$$

where $\text{EXP}[\Lambda'\xi]$ is a diagonal matrix with typical diagonal element $\text{EXP}[(-\lambda_i/\lambda_m)\xi]$. In this case, the pseudodistance ξ appears as a parameter on the reaction path.

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