Perturbation Chromatography in Chemically Reactive Systems

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A one-dimensional column is considered in which a number of chemical reactions with arbitrary kinetics may take place among an arbitrary number of components. Initially, the column is in complete chemical and physical equilibrium. A localized small perturbation is introduced in the column at time $t = 0$. It is shown that, in general, this initial perturbation separates into a definite number of peaks which move with different velocities. Each peak broadens according to an asymptotic relation, depending on a characteristic dispersion coefficient. If n is the number of components, m the number of independent reactions, and σ the number of equations of state to be considered, there are n-m-σ peaks. These peaks do not correspond to single substances as in classical chromatography, but each peak has an eigencomposition. The velocities of the peaks are derived as functions of stoichiometry and equilibrium data. The dispersion coefficients depend, in addition, on the kinetics of the chemical reactions and on the rate of mass transfer. Thus, perturbation chromatography offers a means of determining both equilibrium and rate data. The theory is illustrated by means of two examples.

The term *perturbation chromatography* used in the title of this paper covers a broader class of phenomena than is normally associated with chromatography. A definition will now be given which, at the same time, delimits the scope of this work. Consider the steady flow of a multicomponent fluid over a uniformly distributed fixed adsorbent-catalyst phase. In the initial steady state condition, fluid composition is independent of position and time and determines the concentrations in the fixed phase through various physical and chemical equilibrium relations. At some time zero, the system is perturbed over a small portion of its length by a small change in composition of one of the phases. Perturbation chromatography is the behavior of the system after time zero. The description and use of the set of disturbances which propagates downstream is considered here.

Earlier work in this area is summarized by Collins and Deans (2), who discussed the number and velocity of peaks to be expected under ideal, local equilibrium conditions. In the present work, the equilibrium theory is generalized, and chemical and mass transport kinetics are taken into consideration. The behavior of the set of disturbances resulting from the initial perturbation will be related to the equilibrium composition of both phases, the stoichiometry of the reactions taking place, the chemical and physical equilibrium functions, and the interphase transfer and intraphase chemical reaction rates. These relations can be put to practical use in obtaining unknown equilibrium and rate information from observation of pulse behavior.

The information to be gained is quite general. In particular, no limitation as to number of components or reactions is necessary; the restriction of infinite dilution in a carrier fluid is avoided, and the various equilibrium and rate functions are not required to be linear in concentrations.

In the first part of the paper, general equations are derived and applied to the local equilibrium problem. Peak velocities are obtained for cases in which neither phase, the flowing phase, or both phases are subject to additional restrictions in the form of equations of state. In the second part, the method of moments is applied to the perturbation transport equation to yield first and second moments of peaks. The first moments are related to the velocities of the local equilibrium case; the second moments yield expressions for peak width in terms of equilibrium and rate parameters.

A generalization of a problem studied by Klinkenberg (5) is used to illustrate the methods derived. This problem is particularly suitable, since an analytical asymptotic solution is available for comparison in certain limiting cases. Finally, a numerical example is presented to show the development and asymptotic behavior of peaks after an initial disturbance in the fixed phase.

BASIC EQUATIONS

Standard procedure for applying continuity conditions to a column is to write mass balances for the two phases separately. In the usual chromatographic case, convection and dispersion terms appear in the flowing phase (f) balances but not in those for the fixed phase (s). Here it is very convenient in what follows to have the balances for both phases written as a single vector equation. The transition is accomplished by adopting the following notation.

1. Let $c_1, \ldots c_{nf}$ denote concentrations of the flowing phase species; $c_{nf+1} \ldots c_n$ denote concentrations of the

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fixed phase species. Each component is present in the form of two species; the concentrations thus form a column vector $\mathbf{c}$ with twice as many elements as there are components in the system. In certain limiting cases, the concentration of one or more components may be zero in one or the other of the phases.

2. The transfer of a component from one phase to the other is considered to be a reaction. The stoichiometric coefficients in such mass transfer reactions must take into account the volume fractions of the respective phases.

3. Flowing phase velocity and diffusion coefficients, as well as the phase areas, become particular matrices of order n. The velocity matrix $\mathbf{V}$ is diagonal with v^f as the only nonzero element in positions 1 through n_f. The area matrix $\mathbf{A}$ is also diagonal, the first n_f elements being a^f, while the remaining ones are a^s. Here and later, the superscripts f and s refer to flowing and stationary phases, respectively. The diffusion matrix $\mathbf{D}$ will in general have nonzero elements in the n_f by n_f submatrix referring to the flowing phase, and also in the similar submatrix referring to the fixed phase. In its full form, $\mathbf{D}$ accounts for diffusive coupling among components in the respective phases. If $\mathbf{D}$ is primarily associated with dispersive mechanisms in the flow direction, it will also be diagonal.

With the assumptions of one-dimensional flow at constant pressure, the fundamental balance is

$$\frac{\partial}{\partial t}(\mathbf{Ac}) = -\frac{\partial}{\partial z}(\mathbf{AVc}) + \frac{\partial}{\partial z}\left(\mathbf{AD}\frac{\partial \mathbf{c}}{\partial z}\right) + \mathbf{Ar} \qquad (1)$$

where $\mathbf{r}$ is the vector of source terms, including both interphase transfer and chemical reaction contributions. The units of r_i are moles species i per unit time and volume of the phase to which i belongs.

The source vector $\mathbf{r}$ is expressed in terms of reaction rates through the stoichiometric vectors $\boldsymbol{\nu}^j$, which are of two types, as indicated above. If j refers to a mass transfer reaction, $\boldsymbol{\nu}^j$ will have only two nonzero elements whose ratio is $(-a^f/a^s)$. If j refers to an intraphase chemical reaction, the elements of $\boldsymbol{\nu}^j$ will be stoichiometric coefficients in the usual sense. If the scalar rates are denoted by ρ_j, the column vector $\mathbf{r}$ is given by

$$\mathbf{r} = \sum_{j=1}^{m} \boldsymbol{\nu}^j \rho_j \qquad (2)$$

The summation limit m in Equation (2) is the total number of stoichiometrically independent reactions which occur in the system. This is equivalent to the requirement that the $\boldsymbol{\nu}^j$ be a set of m linearly independent column vectors, which in turn requires that $\mathbf{r}$ vanish if and only if all the ρ_j are zero. A second requirement of $\mathbf{r}$ is intuitively obvious and essential to the proof of necessary mathematical results. It is that any nonzero $\mathbf{r}$ must have at least one positive and one negative element, a corollary of the overall conservation of mass.

To this point, temperature has not been mentioned explicitly. In the one-dimensional formulation, the concentrations of one species in each phase (say c_{n_f} and c_n) can be the enthalpy per unit volume of that phase. Hereafter, temperature will be assumed locally constant, as is the case in the usual chromatographic procedures. Equations of state for one or both phases will then be relations involving concentrations in the usual sense.

As an introduction to the following discussion of particular cases, it should be noted that Equation (1) and specification of the rates ρ_j are not sufficient in general to determine the one-dimensional system, all considerations of boundary and initial conditions aside. The flowing phase velocity v^f and the phase areas are local variables along with the c_i, so that two more (scalar) equations (or restrictions) are required. Three physically appropriate cases are differentiated as follows:

1. Each phase includes a carrier species not counted in $\mathbf{c}$. v^f, a^f, and a^s can be taken as constant without violating total continuity conditions. This case has the simplest mathematical form and will be used as the framework for the examples.

2. The fixed phase includes a carrier (such as the number of solid sites per volume of fixed phase), but the flowing phase does not. An equation of state of the form

$$g^f\,(c_1, \ldots\, c_{n_f}) = 0 \qquad (3a)$$

applies to the flowing phase. The areas a^f and a^s can be considered constant, but the velocity v^f is determined by overall continuity consistent with Equation (3a).

3. Neither phase contains an uncounted carrier. In addition to Equation (3a), a second equation of state applies to the fixed phase; that is

$$g^s\,(c_{n_f+1}, \ldots\, c_n) = 0 \qquad (3b)$$

Both a^f/a^s and v^f are determined locally by these additional restrictions.

The number of equations of state used will be denoted by the symbol σ in the following sections.

LINEARIZATION OF CASE (1), σ=0

As noted in 1 above, $\mathbf{A}$ and $\mathbf{V}$ are constant matrices in this case. Equation (1), after premultiplication by $\mathbf{A}^{-1}$, is

$$\frac{\partial \mathbf{c}}{\partial t} = -\mathbf{V}\frac{\partial \mathbf{c}}{\partial z} + \frac{\partial}{\partial z}\left(\mathbf{D}\frac{\partial \mathbf{c}}{\partial z}\right) + \mathbf{r} \qquad (4)$$

The initial equilibrium state of perturbation chromatography is given by

$$\mathbf{c} = \mathbf{c}^*; \quad \frac{\partial \mathbf{c}^*}{\partial t} = \frac{\partial \mathbf{c}^*}{\partial z} = 0; \quad \mathbf{r}(\mathbf{c}^*) = \mathbf{0} \qquad (5)$$

The (everywhere) small deviation from the equilibrium state after perturbation is

$$\mathbf{x} = \mathbf{c} - \mathbf{c}^* \qquad (6)$$

With the assumption that $\mathbf{D}$ does not depend explicitly on z, Equations (4), (5), and (6) yield

$$\frac{\partial \mathbf{x}}{\partial t} = -\mathbf{V}\frac{\partial \mathbf{x}}{\partial z} + \mathbf{D}\frac{\partial^2 \mathbf{x}}{\partial z^2} + \mathbf{K}\,\mathbf{x} \qquad (7)$$

where

$$\mathbf{K} = \left(\frac{\partial \mathbf{r}}{\partial \mathbf{c}}\right)_{\mathbf{c}=\mathbf{c}^*} \qquad (8)$$

In classical chromatography, where the components do not couple, $\mathbf{K}$ consists of four square matrices of equal order, each of which is diagonal. Here, every element in the n by n matrix $\mathbf{K}$ may be nonzero. Equation (7) is, of course, only first order correct in the small deviation of $\mathbf{x}$. Experimental conditions appropriate to this approximation may always be approached in practice (2).

From the definitions of (2) and (8) it is seen that $\mathbf{K}$ is the sum of m dyads of order n; that is

$$\mathbf{K} = \sum_{j=1}^{m} \boldsymbol{\nu}^j \left(\frac{\partial \rho_j}{\partial \mathbf{c}}\right)_{\mathbf{c}=\mathbf{c}^*} \qquad (9)$$

where the $\partial \rho_j/\partial \mathbf{c}$ are row vectors of order n. If the latter are linearly independent, then the rank of $\mathbf{K}$ is m, a result which is essential to what follows. Hereafter, the symbol d

will be used for the nullity of **K**; that is, $d = n - m$.

Since **K** is of nullity d, there are d constant independent row vectors $\mathbf{s}^j$ such that

$$\mathbf{s}^j\ \mathbf{K} = \mathbf{0} \qquad (10)$$

There is also a direct consequence of the stoichiometry of the reactions. A set of vectors $\mathbf{s}^j$ can be determined from the fact that any vector $\mathbf{s}^j$ is orthogonal to all $\boldsymbol{\nu}^i$. The vectors $\mathbf{s}^j$ can be taken as row vectors of an n by d matrix **S**, so that

$$\mathbf{SK} = 0 \qquad (11)$$

There will be also d constant independent column vectors $\mathbf{e}^i$ such that

$$\mathbf{K}\,\mathbf{e}^i = \mathbf{0} \qquad (12)$$

The vectors $\mathbf{e}^i$ are associated with the equilibrium conditions as follows: Let

$$h_i\ (c_1, c_2, \ldots\ c_n) = 0 \qquad (13)$$

be the conditions of equilibrium for the m stoichiometrically independent reactions. The linearized conditions then are given by

$$\sum_{j=1}^{n} \left(\frac{\partial h_i}{\partial c_j}\right)^* x_j = 0 \qquad (14)$$

The solution set of this can be represented by

$$\mathbf{x}_e = \mathbf{E}\,\mathbf{y} \qquad (15)$$

where **E** is a $d \times m$ matrix, the column vectors of which are $\mathbf{e}^i$, and **y** is a d dimensional column vector. Equation (15) represents all equilibrium states in the neighborhood of the original equilibrium state of the column. Since the rates vanish for equilibrium

$$\mathbf{KE} = 0 \qquad (16)$$

It should be noted that **S** and **E** are not uniquely defined. An **S** matrix premultiplied by a nonsingular $d \times d$ matrix will generate another **S** matrix. Similarly, an **E** matrix postmultiplied by a nonsingular $d \times d$ matrix will generate another **E** matrix. The final results obtained in this work are invariant against the choice of **S** and **E**.

Klinkenberg's Problem

In a recent article, Klinkenberg (*5*) considered the chromatographic flow of components A and B in a carrier gas over a packing which catalyzed the reaction $A \rightleftharpoons B$. He obtained results for the asymptotic velocity and width of the single peak which results from the infinite dilution perturbation with an A-B mixture. His assumption of physical equilibrium between flowing and fixed phases is not required in the method to be used here, so that the results obtained will include Klinkenberg's solution as a special case.

In the following, subscripts 1 through 4 on **x** will refer to A, B in the flowing phase, and A, B in the fixed phase, in that order. The linearized rate expression for the three reactions are

$$\rho_1 = \mathcal{H}_1\ (x_1 - \beta_1 x_3) \quad (A \text{ mass transfer}) \qquad (17a)$$

$$\rho_2 = \mathcal{H}_2\ (x_1 - \beta_2 x_4) \quad (B \text{ mass transfer}) \qquad (17b)$$

$$\rho_3 = \mathcal{H}\ \ (x_3 - \beta\ x_4) \quad (A \rightleftharpoons B \text{ reaction}) \qquad (17c)$$

Equation (17*c*) implies that the reaction occurs in the fixed phase. In Klinkenberg's version, (17*a*) and (17*b*) were assumed to be at equilibrium, that is, $\mathcal{H}_1$ and $\mathcal{H}_2$ very large.

Since $n = 4$, $m = 3$ for this problem, $d = n - m = 1$; the **S** matrix becomes a four-element row vector, one possible form of which is

$$\mathbf{S} = \frac{1}{\gamma}\ [a^f, a^f, a^s, a^s] \qquad (18)$$

The constant γ is used to normalize the produce **SE**. The **E** matrix is a four-element column vector, a version of which is

$$\mathbf{E} = [\beta_1\beta,\ \beta_2,\ \beta,\ 1]^T \qquad (19)$$

Then, if $\mathbf{SE} = 1$, γ is given by

$$\gamma = a^f\ (\beta_1\beta + \beta_2) + a^s\ (\beta + 1) \qquad (20)$$

The **K** matrix is obtained from the $\boldsymbol{\nu}$ vectors

$$\boldsymbol{\nu}^1 = \begin{bmatrix} -1/a^f \\ 0 \\ 1/a^s \\ 0 \end{bmatrix}, \quad \boldsymbol{\nu}^2 = \begin{bmatrix} 0 \\ -1/a^f \\ 0 \\ 1/a^s \end{bmatrix}, \quad \boldsymbol{\nu}^3 = \begin{bmatrix} 0 \\ 0 \\ -1 \\ 1 \end{bmatrix} \qquad (21)$$

and the derivatives of the rates (*17*), according to Equation (9). **K** is given by

$$\mathbf{K} = \begin{bmatrix} -\mathcal{H}_1/a^f & 0 & \mathcal{H}_1\beta_1/a^f & 0 \\ 0 & -\mathcal{H}_2/a^f & 0 & \mathcal{H}_2\beta_2/a^f \\ \mathcal{H}_1/a^s & 0 & -\mathcal{H}_1\beta_1/a^s - \mathcal{H} & \mathcal{H}\beta \\ 0 & \mathcal{H}_2/a^s & \mathcal{H} & -\mathcal{H}_2\beta_2/a^s - \mathcal{H}\beta \end{bmatrix} \qquad (22)$$

Clearly, $\mathbf{SK} = \mathbf{KE} = 0$, as required.

MODIFICATIONS FOR THE $\sigma = 1$ AND $\sigma = 2$ CASES

For the $\sigma = 1$ case, **V** is a variable, while **A** is constant as before. After linearization and premultiplication by $\mathbf{A}^{-1}$, Equation (1) becomes

$$\frac{\partial \mathbf{x}}{\partial t} = -\mathbf{V}^*\frac{\partial \mathbf{x}}{\partial z} + \mathbf{D}\frac{\partial^2 \mathbf{x}}{\partial z^2} - c^*\frac{\partial \mathbf{V}^f}{\partial z} + \mathbf{K}\,\mathbf{x} \qquad (23)$$

where $\mathbf{V}^*$ is the equilibrium velocity matrix with diagonal elements $(v^f)^*$ and 0, the equilibrium velocities of the phases. The local derivative $\partial\mathbf{V}^f/\partial z$ must be such that the flowing phase equation of state, Equation (3*a*), is satisfied.

Let

$$\mathbf{b}^f = \left(\frac{\partial g^f}{\partial \mathbf{c}}\right)_{\mathbf{c}=\mathbf{c}^*} = [b^f{}_1, b^f{}_2, \ldots\ b^f{}_{nf},\ 0, \ldots\ldots, 0] \qquad (24)$$

Then, to first-order terms

$$\mathbf{b}^f\,\mathbf{x} = 0 \qquad (25)$$

For an ideal gas the elements, $b^f{}_1$ to $b^f{}_{nf}$ are equal to unity.

If Equation (23) is premultiplied by $\mathbf{b}^f$, the first three terms vanish, leaving

$$0 = -\mathbf{b}^f\,\mathbf{c}^*\frac{\partial \mathbf{V}^f}{\partial z} + \mathbf{b}^f\,\mathbf{K}\,\mathbf{x} \qquad (26)$$

It is shown elsewhere (*4*) that $\mathbf{b}^f\,\mathbf{c}^* \neq 0$ in any physically reasonable case. Thus

$$\frac{\partial \mathbf{V}^f}{\partial z} = (\mathbf{b}^f\,\mathbf{c}^*)^{-1}\,\mathbf{b}^f\,\mathbf{K}\,\mathbf{x} \qquad (27)$$

which can be substituted into Equation (23), eliminating $\partial\mathbf{V}^f/\partial z$. The result is, after rearrangement and factoring

$$\frac{\partial \mathbf{x}}{\partial t} = -\mathbf{V}^*\frac{\partial \mathbf{x}}{\partial z} + \mathbf{D}\frac{\partial^2 \mathbf{x}}{\partial z^2} + [1 - (\mathbf{b}^f\,\mathbf{c}^*)^{-1}\,\mathbf{c}^*\,\mathbf{b}^f]\,\mathbf{K}\,\mathbf{x} \qquad (28)$$

This is a generalization of the result of Collins (*2*). Since $\mathbf{V}^*$ is the same as **V** in the $\sigma = 0$ case, Equation (28) is identical in form to Equation (7) if $\mathbf{K}^{(1)}$ is defined by

$$\mathbf{K}^{(1)} = [1 - (\mathbf{b}^f \mathbf{c}^*)^{-1} \mathbf{c}^* \mathbf{b}^f] \mathbf{K} \tag{29}$$

The proof that $\mathbf{K}^{(1)}$ is of rank m is given by Klauser (*4*).

For the $\sigma = 2$ case, both **V** and **A** are local variables. Equation (1) may be linearized and premultiplied by $(\mathbf{A}^*)^{-1}$, with the result

$$\frac{\partial \mathbf{x}}{\partial t} + (\mathbf{A}^*)^{-1} \left[\frac{\partial \mathbf{A}}{\partial t} + \frac{\partial (\mathbf{AV})}{\partial z} \right] \mathbf{c}^* = - \mathbf{V}^* \frac{\partial \mathbf{x}}{\partial z} + \mathbf{D} \frac{\partial^2 \mathbf{x}}{\partial z^2} + \mathbf{K}\,\mathbf{x} \tag{30}$$

where (*) again refers to the equilibrium state. In this case, both Equations (3*a*) and (3*b*) must be satisfied. Equivalent to Equation (24), let

$$\mathbf{b}^s = \left(\frac{\partial g^s}{\partial \mathbf{c}} \right)_{\mathbf{c}=\mathbf{c}^*} = (0, 0, \ldots, 0, b^s{}_{nf+1}, \ldots, b^s{}_n) \tag{31}$$

Since $\mathbf{b}^s\,\mathbf{x} = 0$, and because of the structure of **V** and **A**, premultiplication of Equation (30) by $\mathbf{b}^s$ leads to

$$(a^s)^{-1} \frac{\partial a^s}{\partial t} \mathbf{b}^s \mathbf{c}^* = \mathbf{b}^s \mathbf{K}\,\mathbf{x} \tag{32}$$

Similarly, premultiplication by $\mathbf{b}^f$ gives

$$(a^f)^{-1} \left[\frac{\partial a^f}{\partial t} + \frac{\partial (a^f v^f)}{\partial z} \right] \mathbf{b}^f \mathbf{c}^* = \mathbf{b}^f \mathbf{K}\,\mathbf{x} \tag{33}$$

Since neither $\mathbf{b}^s\,\mathbf{c}^*$ nor $\mathbf{b}^f\,\mathbf{c}^*$ vanishes for normal systems, Equations (32) and (33) can be solved for the components of $(\mathbf{A}^*)^{-1} \left[\frac{\partial \mathbf{A}}{\partial t} + \frac{\partial (\mathbf{AV})}{\partial z} \right]$ in terms of $\mathbf{Kx}$. The results may be substituted into Equation (30) to yield, after terms are collected

$$\frac{\partial \mathbf{x}}{\partial t} = - \mathbf{V}^* \frac{\partial \mathbf{x}}{\partial z} + \mathbf{D} \frac{\partial^2 \mathbf{x}}{\partial z^2} + \mathbf{K}^{(2)}\mathbf{x} \tag{34}$$

where

$$\mathbf{K}^{(2)} = [1 - (\mathbf{b}^f \mathbf{c}^*)^{-1} \mathbf{c}^* \mathbf{b}^f - (\mathbf{b}^s \mathbf{c}^*)^{-1} \mathbf{c}^* \mathbf{b}^s] \mathbf{K} \tag{35}$$

It follows from Equations (34) and (35) that the exact nature of the relation between a^f, a^s, and total cross-section area does not effect perturbation chromatographic results.

Modification of *E* and *S* for $\sigma = 1$ and $\sigma = 2$ Cases

The arguments which lead to the existence of an **E** matrix such that $\mathbf{KE} = 0$ are not changed. The vector of deviations **y** is still d dimensional, but only a $(d - \sigma)$ dimensional subspace is permissible, consistent with Equations (3*b*) and/or (3*a*). The generalization of Equation (16) is then

$$\mathbf{K}^{(\sigma)} \mathbf{E} = 0 \tag{36}$$

There also still exist d constant, linearly independent row vectors $\mathbf{s}^{(\sigma)j}$ which span the left-hand null space of **K**. In the $\sigma = 1$ case, one of these vectors can obviously be taken as $\mathbf{b}^f$, because of Equation (24). In the $\sigma = 2$ case, both $\mathbf{b}^f$ and $\mathbf{b}^s$ are $\mathbf{s}^{(2)}$ vectors and are clearly independent. Other independent $\mathbf{s}^{(\sigma)j}$ can be obtained from the condition

$$\mathbf{s}^{(\sigma)j}\, \boldsymbol{\nu}^{(\sigma)j} = 0 \tag{37}$$

where $\boldsymbol{\nu}^{(\sigma)j}$ is as before [Equation (2) and preceding remarks]. The forms of $\boldsymbol{\nu}^{(1)j}$ and $\boldsymbol{\nu}^{(2)j}$ follow from Equations (29) and (35), respectively:

$$\boldsymbol{\nu}^{(1)j} = \boldsymbol{\nu}^j - (\mathbf{b}^f \mathbf{c}^*)^{-1} \mathbf{b}^f \boldsymbol{\nu}^j \mathbf{c}^* \tag{38a}$$

$$\boldsymbol{\nu}^{(2)j} = \boldsymbol{\nu}^j - (\mathbf{b}^f \mathbf{c}^*)^{-1} \mathbf{b}^f \boldsymbol{\nu}^j \mathbf{c}^* - (\mathbf{b}^s \mathbf{c}^*)^{-1} \mathbf{b}^s \boldsymbol{\nu}^j \mathbf{c}^* \tag{38b}$$

The matrix $\mathbf{S}^{(\sigma)}$ formed from the row vectors $\mathbf{s}^{(\sigma)j}$ then satisfies

$$\mathbf{S}^{(\sigma)} \mathbf{K}^{(\sigma)} = 0 \tag{39}$$

Velocities Associated with an Equilibrium Perturbation

An equilibrium perturbation $\mathbf{x}_e$, as defined by Equation (15), is a solution of a restricted class of problems which may be termed *local equilibrium* or *hyperbolic*. The basic restrictions are that the system can be assumed to be in equilibrium for all z and t and that there are no dispersive mechanisms in the flowing phase ($D = 0$). The appropriate transport equation is

$$\frac{\partial \mathbf{x}_e}{\partial t} = - \mathbf{V}^* \frac{\partial \mathbf{x}_e}{\partial z} + \mathbf{r} \tag{40}$$

The unknown vectors **r** and $\mathbf{x}_e$ must be determined such that Equation (15) is satisfied and

$$\mathbf{Sr} = 0 \tag{41}$$

that is, the stoichiometric restrictions are satisfied. Substitution of $\mathbf{Ey}$ for $\mathbf{X}_e$ and premultiplication by $\mathbf{S}^{(\sigma)}$ yields

$$\mathbf{S}^{(\sigma)}\mathbf{E} \frac{\partial \mathbf{y}}{\partial t} = - \mathbf{S}^{(\sigma)}\mathbf{V}^*\mathbf{E} \frac{\partial \mathbf{y}}{\partial z} \tag{42}$$

It can be shown (*4*) that $\mathbf{S}^{(\sigma)}\mathbf{E}$ is nonsingular, so that

$$\frac{\partial \mathbf{y}}{\partial t} + \mathbf{F} \frac{\partial \mathbf{y}}{\partial z} = 0 \tag{43}$$

where the $(d \times d)$ matrix **F** is given by

$$\mathbf{F} = [\mathbf{S}^{(\sigma)} \mathbf{E}]^{-1} \mathbf{S}^{(\sigma)} \mathbf{V}^* \mathbf{E} \tag{44}$$

For the $\sigma = 0$ case, the eigenvalues of **F** are real with lower bound zero and upper bound v^f [see (*4*)]. It will be assumed for all cases that the eigenvalues are real and distinct.

Let the eigenvalues of **F** be $v_1, v_2, \ldots v_d$, corresponding to a set of normalized left-hand eigenvectors (row) $\mathbf{f}^{lj}$ and right eigenvectors (column) $\mathbf{f}^{ri}$; that is

$$\mathbf{f}^{lj}\,\mathbf{F} = v_j\,\mathbf{f}^{lj} \tag{45}$$

$$\mathbf{F}\,\mathbf{f}^{ri} = v_i\,\mathbf{f}^{ri} \tag{46}$$

and

$$\mathbf{f}^{lj}\,\mathbf{f}^{ri} = \delta_{ij} \tag{47}$$

Then, if η_i is defined by

$$\mathbf{y} = \sum_{i=1}^{d} \mathbf{f}^{ri}\,\eta_i \tag{48}$$

or

$$\eta_i = \mathbf{f}^{li}\,\mathbf{y} \tag{49}$$

premultiplication of Equation (43) by $\mathbf{f}^{li}$ yields

$$\frac{\partial \eta_i}{\partial t} + v_i \frac{\partial \eta_i}{\partial z} = 0 \tag{50}$$

Equation (50) states that certain linear combinations of deviations **x**, defined through Equations (15) and (49), have distinct propagation velocities v_i. An initial perturbation, present in a small interval of the column, will separate into $d(=n - m)$ disturbances. each moving with a characteristic velocity. These correspond to the peaks of the usual chromatographic column in the $\sigma = 0$ case, with the following generalizations: finite concentrations of components other than carrier gas in the equilibrium state, hence a coupling between components not found in infinite dilution chromatography; chemical reactions in either or both phases; general (nonlinear) physical and chemical equilibrium relations.

For the $\sigma = 1$ case, the eigenvalue corresponding to one of the eigenvectors is just the flowing phase velocity v^f. This can be seen from the rearranged definition of $\mathbf{F}$ [Equation (44)]:

$$\mathbf{S}^{(1)}\,\mathbf{E}\,\mathbf{F} = \mathbf{S}^{(1)}\,\mathbf{V}^*\,\mathbf{E} \tag{51}$$

One of the row vectors in $\mathbf{S}^{(1)}$ is $\mathbf{b}^f$, as shown above. From the definition of $\mathbf{V}^*$, it follows that

$$\mathbf{b}^f\,\mathbf{E}\,\mathbf{F} = \mathbf{V}^f\,\mathbf{b}^f\,\mathbf{E} \tag{52}$$

Thus, $\mathbf{b}^f\mathbf{E} = \mathbf{f}^{l_1}$, which corresponds then to the eigenvalue $v_1 = v^f$. A nonzero linear combination η_1 of deviations would correspond to perturbation of the equation of state (3*a*); hence, it is not physically realizable. It follows that only $d - 1$ distinct peaks will be observable.

Similarly, it can be shown for the $\sigma = 2$ case that both $\mathbf{b}^f\mathbf{E}$ and $\mathbf{b}^s\mathbf{E}$ correspond to nonexcitable perturbation with eigenvectors v^f and 0, respectively. In general, the number of observable peaks to be expected from a general perturbation is given by

$$d_p = n - m - \sigma \tag{53}$$

This is a generalization of the result of Collins (*2*), who considered the $\sigma = 1$ case.

Peak Velocity in Klinkenberg's Example

Since $d = 1$, $\sigma = 0$ in this example, $\mathbf{F}$ is a scalar, and only one peak is expected. The factor $(\mathbf{SE})^{-1}$ is unity because of the normalization, so that

$$\mathbf{F} = \mathbf{S}\,\mathbf{V}^*\,\mathbf{E} = \frac{v^f\,a^f\,(\beta\beta_1 + \beta_2)}{\gamma} \tag{54}$$

This is in agreement with Klinkenberg's l/μ_t (his notation), where l is column length and μ_t is mean residence time of the single peak.

BASIC CONCEPTS OF THE GENERAL THEORY

In the previous sections the solution of the linearized equations has been given under the assumption that kinetic effects can be disregarded. If kinetic effects are taken into account, complete analytical solutions can be found only in the very simplest cases. Intuitively, it might be expected that these effects have no influence on the qualitative behavior of the column, that is, on the separation of an initial perturbation into a certain number of peaks. However, it is well known that these peaks do not keep their shape but become wider as they move along the column with different velocities.

In order to utilize these characteristics of chromatographic systems, it will be necessary to define quantities such as the velocity and the width of a peak in a way which is both mathematically and experimentally useful. That is, the definitions should allow the calculation of these quantities analytically from the kinetic constants in the basic equations and the experimental determination of the kinetic constants from observations of the response of an actual chromatographic column. This can be achieved by utilization of the moments of the functions $\mathbf{x}(z,t)$ with respect to the coordinate z. This method has been applied frequently in the past in order to analyze simple ($n = 1$ or $n = 2$ and $d = 1$) chromatographic systems (*1*, *3*).

Definitions

It will be necessary first to introduce some definitions. An instrument is a device which measures a linear combination of the perturbation variables x_i. Thus, an instrument is represented by a nonzero, n dimensional row vector $\mathbf{l}$. The response s of the instrument is then given by

$$s(z,t) = \mathbf{l}\,\mathbf{x}(z,t) \tag{55}$$

The response will be called a *signal* if all moments of s exist. That is, s is a signal if

$$\int_{-\infty}^{+\infty} z^j\,s(z,t)\,dz \qquad \text{exist for all } t \text{ and } j = 0, 1, 2, \ldots$$

A signal is defined to be of order ν if

$$\int_{-\infty}^{+\infty} z^j\,s(z,t)\,dz \;\begin{matrix} = 0 & j = 0, 1, \ldots \nu - 1 \\ \neq 0 & j = \nu \end{matrix} \tag{56}$$

A signal of order 0 (that is, a signal with nonvanishing zero moment) is a regular signal. Otherwise it is a singular signal. The center $z^*(t)$ of a signal is defined as

$$\int_{-\infty}^{\infty} (z - z^*)^{\nu+1}\,s(z,t)\,dz = 0 \tag{57}$$

where ν is the order of the signal. Thus, by Equations (56) and (57)

$$z^* = \int_{-\infty}^{+\infty} z^{\nu+1}\,s\,dz/(\nu+1)\int_{-\infty}^{+\infty} z^{\nu}\,s\,dz \tag{58}$$

dz^*/dt is the center velocity of a signal, and

$$v = \lim_{t\to\infty} \frac{dz^*}{dt} \tag{59}$$

is the asymptotic center velocity provided that this limit exists. The variance σ^2 of a regular signal is defined as

$$\sigma^2 = \int_{-\infty}^{+\infty} (z - z^*)^2\,s\,dz \Bigg/ \int_{-\infty}^{+\infty} s\,dz \tag{60}$$

and the dispersion D^* of a regular signal is defined as

$$D^* = \frac{1}{2}\lim_{t\to\infty}\frac{d\sigma^2}{dt} \tag{61}$$

provided that the limit exists.

A chromatographic column will be said to be in a mode if the asymptotic center velocity of the signal is the same for any instrument $\mathbf{l}$. The signal from a column which is in a mode will be called a *peak*, and the asymptotic center velocity of such a signal will be called the *velocity* of the mode or of the peak. It will be shown later that if a column is in a mode, any regular signal has the same dispersion independent of the instrument used to obtain the signal. The dispersion coefficient thus obtained will be called the *dispersion* of the mode or of the peak.

If these definitions are applied to the case where kinetic effects can be ignored, it can be seen that a mode corresponds to a column in which only one "peak" exists. (Quotation marks indicate usage of the concept in its general sense, not in the narrow sense as given above.) There are exactly d different modes (if all modes are counted regardless of their physical excitability) with velocities equal to the eigenvalues of F and with dispersions which are all equal to zero.

The foregoing definitions are useful for the following reasons. In an experimental situation, a "peak" can be easily identified, and measurements can be carried out regardless of the number of other well-separated "peaks" which may be in the column. It is not necessary in an experiment to create a column in which there is only one "peak" and which is otherwise clean. (Theoretically, this would be possible, for instance, by cutting out a section of a column containing only one "peak" and by implanting this section into an otherwise unperturbed column.) The moments of an experimental peak can be determined easily by choosing the limits of integration appropriately. In fact, this amounts to looking at only one part of a recorder chart. The situation is different, however, if the moments are determined from thermodynamic and rate functions by analytical integration. A method of identifying a "one peak" column is needed, since the integrations for calculating the moments must be carried out from $-\infty$ to $+\infty$. The presence of other "peaks," however far away from the one under consideration, would interfere with the determination of the parameters of a particular "peak." A column which is mathematically in a mode as defined above corresponds to a column with only one "peak."

Transformation of the Transport Equation

If kinetic effects can not be disregarded, the linearized equations describing the column become, from Equations (7), (28), (29), (34), and (35)

$$\frac{\partial \mathbf{x}}{\partial t} = \mathbf{K}^{(\sigma)}\mathbf{x} - \mathbf{V}^{*}\frac{\partial \mathbf{x}}{\partial z} + \mathbf{D}\frac{\partial^2 \mathbf{x}}{\partial z^2} \tag{62}$$

Before the moment transformation is applied, it is convenient to take advantage of the singularity of $\mathbf{K}$ by a special linear transformation. The new variable $\boldsymbol{\xi}$ is defined by

$$\mathbf{x} = \mathbf{T}\boldsymbol{\xi}, \quad \boldsymbol{\xi} = \mathbf{T}^{-1}\mathbf{x} \tag{63}$$

Equation (62) then becomes

$$\frac{\partial \boldsymbol{\xi}}{\partial t} = \mathbf{T}^{-1}\mathbf{K}^{(\sigma)}\mathbf{T}\,\boldsymbol{\xi} - \mathbf{T}^{-1}\mathbf{V}^{*}\,\mathbf{T}\frac{\partial \boldsymbol{\xi}}{\partial z} + \mathbf{T}^{-1}\mathbf{D}\,\mathbf{T}\frac{\partial^2 \boldsymbol{\xi}}{\partial z^2} \tag{64}$$

It can be shown that the matrix $\mathbf{T}$ can be determined in such a way that $\mathbf{T}^{-1}\mathbf{K}^{(\sigma)}\mathbf{T}$ becomes a matrix with zeros everywhere except in the lower right-hand corner m by m submatrix. This condition does not determine $\mathbf{T}$ unambiguously. It is convenient to define $\mathbf{T}$ in a standard way as follows: a matrix $\mathbf{E}$ is chosen which satisfies Equation (36); $\mathbf{S}$ is determined such that

$$\mathbf{SE} = 1 \tag{65}$$

which is always possible; and $\mathbf{T}^{-1}$ and $\mathbf{T}$ are then determined such that $\mathbf{S}$ occupies the upper part of $\mathbf{T}^{-1}$, $\mathbf{E}$ occupies the left-hand part of $\mathbf{T}$, and the unit matrix appears in the right-hand lower corner of $\mathbf{T}^{-1}$; that is

$$\mathbf{T}^{-1} = \begin{bmatrix} \mathbf{S} \\ \hdashline \mathbf{E}' \end{bmatrix} \tag{66}$$

$$\mathbf{T} = [\mathbf{E} \;\vdots\; \mathbf{S}'] \tag{67}$$

$$\mathbf{E}' = \left[\begin{array}{c:cccc} & 1 & & & \\ & & 1 & 0 & \\ \mathbf{E}'' & & & 1 & \\ & 0 & & & \ddots \\ & & & & 1 \end{array}\right] \tag{68}$$

It can be seen easily that with this definition $\mathbf{E}''$ and $\mathbf{S}'$ are uniquely defined by the condition that $\mathbf{TT}^{-1} = 1$ and by the condition that $\mathbf{T}$ transforms $\mathbf{K}^{(\sigma)}$ in the desired way.

The variables ξ_i have the following physical meaning [see Equations (63) and (66)]. The first d elements of $\boldsymbol{\xi}$ measure the overall stoichiometrical perturbation. If in a fictitious experiment the equilibrium is perturbed without having any transport in the z direction and without adding or removing substance, $\mathbf{Sx} = 0$. Therefore, the first d elements of $\boldsymbol{\xi}$ vanish in this case. The last m elements of $\boldsymbol{\xi}$ measure the displacement from equilibrium. Since each vector in $\mathbf{E}'$ is orthogonal to each vector in $\mathbf{E}$, $\mathbf{E}'$ represents the linearized equilibrium conditions; that is, $\mathbf{E}'\mathbf{x} = 0$ whenever the system is in equilibrium. Thus, the last m elements of $\boldsymbol{\xi}$ are zero in the case of equilibrium.

T Matrix for Klinkenberg's Problem

For Klinkenberg's example, the matrices $\mathbf{T}^{-1}$ and $\mathbf{T}$ are given by

$$\mathbf{T}^{-1} = \begin{bmatrix} a^f/\gamma & a^f/\gamma & a^s/\gamma & a^s/\gamma \\ -\beta_2/\beta\beta_1 & 1 & 0 & 0 \\ -1/\beta_1 & 0 & 1 & 0 \\ -1/\beta\beta_1 & 0 & 0 & 1 \end{bmatrix} \tag{69}$$

$$\mathbf{T} = \begin{bmatrix} \beta\beta_1 & -\mathrm{a}^{\mathrm{f}}\beta\beta_1/\gamma & -\mathrm{a}^{\mathrm{s}}\beta\beta_1\text{-}\gamma & -\mathrm{a}^{\mathrm{s}}\beta\beta_1/\gamma \\ \beta_2 & 1-a^f\beta_2/\gamma & -a^s\beta_2/\gamma & -a^s\beta_2/\gamma \\ \beta & -a^f\beta/\gamma & 1-a^s\beta/\gamma & -a^s\beta/\gamma \\ 1 & -a^f/\gamma & -a^s/\gamma & 1-a^s/\gamma \end{bmatrix} \tag{70}$$

where γ is given by Equation (20).

Transformed K, V, and D Matrices

The following notation will be used for the transformed matrices $\mathbf{K}^{(\sigma)}$, $\mathbf{V}^{*}$, and $\mathbf{D}$:

$$\mathbf{T}^{-1}\mathbf{K}^{(\sigma)}\mathbf{T} = \left[\begin{array}{c:c} \mathbf{0} & \mathbf{0} \\ \hdashline \mathbf{0} & -\mathbf{L} \end{array}\right] \tag{71}$$

$$\mathbf{T}^{-1}\mathbf{V}^{*}\mathbf{T} = \left[\begin{array}{c:c} \mathbf{V}^{(11)} & \mathbf{V}^{(12)} \\ \hdashline \mathbf{V}^{(21)} & \mathbf{V}^{(22)} \end{array}\right] \tag{72}$$

$$\mathbf{T}^{-1}\mathbf{D}\,\mathbf{T} = \left[\begin{array}{c:c} \mathbf{D}^{(11)} & \mathbf{D}^{(12)} \\ \hdashline \mathbf{D}^{(21)} & \mathbf{D}^{(22)} \end{array}\right] \tag{73}$$

In these equations, the matrices on the right-hand sides are all divided such that the upper left-hand corner submatrix is d by d and the lower right-hand corner submatrix is m by m.

From the definition of $\mathbf{F}$, see Equation (44), and from Equations (65), (66), and (72), it follows that

$$\mathbf{V}^{(11)} = \mathbf{F} \tag{74}$$

The symbol $\mathbf{F}$ will be used in what follows instead of $\mathbf{V}^{(11)}$. In numerical calculations it is not necessary to carry out the transformation in Equation (71) in detail in order to obtain $\mathbf{L}$. From Equation (71) it follows that

$$\mathbf{T}^{-1}\mathbf{K}^{(\sigma)} = \left[\begin{array}{c:c} 0 & 0 \\ \hdashline 0 & -\mathbf{L} \end{array}\right]\mathbf{T}^{-1} \tag{75}$$

From this and the form of $\mathbf{T}^{-1}$ [Equations (66) and (68)], it follows that $-\mathbf{L}$ is identical with the lower right-hand corner matrix in the product $\mathbf{T}^{-1}\mathbf{K}^{(\sigma)}$.

For Klinkenberg's example, $\mathbf{L}$ is then easily obtained from Equations (22) and (69):

$$\mathbf{L} = \begin{bmatrix} \mathcal{H}_2/a^f & \beta_2\mathcal{H}_1/\beta a^f & -\mathcal{H}_2\beta_2/a^f \\ 0 & \mathcal{H}_1/a^f + \mathcal{H}_1\beta_1/a^s + \mathcal{H} & -\mathcal{H}\beta \\ -\mathcal{H}_2/a^s & \mathcal{H}_1/\beta a^f - \mathcal{H} & \mathcal{H}_2\beta_2/a^s + \mathcal{H}\beta \end{bmatrix} \tag{76}$$

For this example, the matrices $\mathbf{V}^{(12)}$ and $\mathbf{V}^{(21)}$ are a row and a column vector, respectively. These matrices, which will be needed later, are given by

$$\mathbf{V}^{(12)} = \frac{v^f\,a^f\,a^s}{(\gamma)^2}\,[\beta + 1, \quad -(\beta_2 + \beta\beta_1), \quad -(\beta_2 + \beta\beta_1)] \tag{77}$$

and

$$[\mathbf{V}^{(21)}]^T = -\,v^f\,[0, \ \beta, \ 1] \tag{78}$$

NONEQUILIBRIUM THEORY

The Moment Transformation

In this section, the moments of $\boldsymbol{\xi}$, the transformed perturbation vector, will be calculated as functions of time from Equation (64). The d dimensional column vector $\mathbf{p}^{(\nu)}$ and the m dimensional column vector $\mathbf{q}^{(\nu)}$ are defined as follows:

$$\begin{pmatrix} \mathbf{p}^{(\nu)} \\ \mathbf{q}^{(\nu)} \end{pmatrix} = \frac{(-1)^\nu}{\nu!} \int_{-\infty}^{+\infty} z^\nu \, \boldsymbol{\xi} (z, t) \, dz \qquad (79)$$

$\mathbf{p}^{(\nu)}$ and $\mathbf{q}^{(\nu)}$ are thus functions of time. Differential equations for $\mathbf{p}^{(\nu)}$ and $\mathbf{q}^{(\nu)}$ can be obtained by multiplying Equation (64) by z^ν, by integrating from $z = -\infty$ to $z = +\infty$, and by applying integration by parts to the integrals with integrands

$$z^\nu \frac{\partial \boldsymbol{\xi}}{\partial z} \quad \text{and} \quad z^\nu \frac{\partial^2 \boldsymbol{\xi}}{\partial z^2}$$

Use is made of the fact that for the perturbations considered

$$\lim_{z \to \pm\infty} (z^\nu \boldsymbol{\xi}) = \lim_{z \to \pm\infty} \left(z^\nu \frac{\partial \boldsymbol{\xi}}{\partial z} \right) = 0 \qquad (80)$$

This aspect of the method is well documented in the papers by Aris (*1*) and by Horn (*3*). From the definition (79) and from Equations (71) through (73) and (80), the following set of ordinary differential equations can be derived:

$$\dot{\mathbf{p}}^{(0)} = 0 \qquad (81a)$$

$$\dot{\mathbf{q}}^{(0)} = - \mathbf{L} \, \mathbf{q}^{(0)} \qquad (81b)$$

$$\dot{\mathbf{p}}^{(1)} = - \mathbf{F} \, \mathbf{p}^{(0)} - \mathbf{V}^{(12)} \, \mathbf{q}^{(0)} \qquad (82a)$$

$$\dot{\mathbf{q}}^{(1)} = - \mathbf{L} \, \mathbf{q}^{(1)} - \mathbf{V}^{(21)} \, \mathbf{p}^{(0)} - \mathbf{V}^{(22)} \, \mathbf{q}^{(0)} \qquad (82b)$$

$$\dot{\mathbf{p}}^{(2)} = - \mathbf{F} \, \mathbf{p}^{(1)} - \mathbf{V}^{(12)} \, \mathbf{q}^{(1)} + \mathbf{D}^{(11)} \, \mathbf{p}^{(0)} + \mathbf{D}^{(12)} \, \mathbf{q}^{(0)} \qquad (83a)$$

$$\dot{\mathbf{q}}^{(2)} = - \mathbf{L} \, \mathbf{q}^{(2)} - \mathbf{V}^{(21)} \, \mathbf{p}^{(1)} - \mathbf{V}^{(22)} \, \mathbf{q}^{(1)} + \mathbf{D}^{(21)} \, \mathbf{p}^{(0)} + \mathbf{D}^{(22)} \, \mathbf{q}^{(0)} \qquad (83b)$$

These differential equations can be integrated successively. The integral of (81*a*) is given by

$$\mathbf{p}^{(0)} = \mathbf{b}^{(0)} \qquad (84a)$$

where $\mathbf{b}^{(0)}$ denotes a vector of integration constants. Since L has only eigenvalues with positive real parts (see reference *4*), the integral of (81*b*) is a linear combination of exponentially decreasing functions. Only the asymptotic behavior of the column will be investigated in this paper. It will be seen later that these exponential terms do not contribute to the asymptotic center velocity or to the dispersion. Therefore

$$\mathbf{q}^{(0)} = 0 \qquad (84b)$$

It can be seen that if the exponential terms in $\mathbf{q}^{(0)}$ were carried over to the equations for the higher moments, the only effect would be the generation of other additive decaying exponential terms in the higher moments $\mathbf{p}^{(1)}$, $\mathbf{q}^{(1)}$, $\mathbf{p}^{(2)}$, and $\mathbf{q}^{(2)}$. Equation (84*a*) merely states that an overall mass balance on the column is satisfied at any time and hence gives a trivial physical result. On the other hand, Equation (84*b*) states that if all concentrations are averaged over z, the average concentrations obtained are in equilibrium after a sufficiently long time. This result is nontrivial, since in any real chromatographic column there will always be regions which are not in equilibrium, for example, at the front and the rear of a "peak."

The *first moments* $\mathbf{p}^{(1)}$ and $\mathbf{q}^{(1)}$ now can be derived by putting the result of (84) into (82) and by integrating the equations obtained. The result is given by

$$\mathbf{p}^{(1)} = - \mathbf{F} \, \mathbf{b}^{(0)} \, t + \mathbf{b}^{(1)} \qquad (85a)$$

$$\mathbf{q}^{(1)} = - \mathbf{L}^{-1} \, \mathbf{V}^{(21)} \, \mathbf{b}^{(0)} \qquad (85b)$$

where $\mathbf{b}^{(1)}$ is a vector of integration constants. Exponentially decreasing terms are omitted in Equations (85). Similarly, the result

$$\begin{aligned} \mathbf{p}^{(2)} = {} & \mathbf{F}^2 \, \mathbf{b}^{(0)} \, t^2/2 \\ & + [- \mathbf{F} \, \mathbf{b}^{(1)} + \mathbf{V}^{(12)} \, \mathbf{L}^{-1} \, \mathbf{V}^{(21)} \, \mathbf{b}^{(0)} + \mathbf{D}^{(11)} \, \mathbf{b}^{(0)}] t + \mathbf{b}^{(2)} \end{aligned} \qquad (86a)$$

$$\begin{aligned} \mathbf{q}^{(2)} = {} & \mathbf{L}^{-1} \, \mathbf{V}^{(21)} \, \mathbf{F} \, \mathbf{b}^{(0)} \, t - \mathbf{L}^{-1} \, \mathbf{V}^{(21)} \, \mathbf{b}^{(1)} \\ & + \mathbf{L}^{-1} \, \mathbf{V}^{(22)} \, \mathbf{L}^{-1} \, \mathbf{V}^{(21)} \, \mathbf{b}^{(0)} + \mathbf{L}^{-1} \, \mathbf{D}^{(21)} \, \mathbf{b}^{(0)} \\ & - \mathbf{L}^{-2} \, \mathbf{V}^{(21)} \, \mathbf{F} \, \mathbf{b}^{(0)} \end{aligned} \qquad (86b)$$

can be obtained for the asymptotic values of $\mathbf{p}^{(2)}$ and $\mathbf{q}^{(2)}$. $\mathbf{b}^{(2)}$ is a vector of integration constants.

Moments in a Moving Coordinate System

A coordinate system is now considered which moves along the column with velocity v. The coordinate $\bar{z}$ in this system is related to z by

$$\bar{z} = z - vt \qquad (87)$$

The moments in the moving system are $\bar{\mathbf{p}}^{(\nu)}$ and $\bar{\mathbf{q}}^{(\nu)}$ and can be calculated easily from the moments in the stationary system by using (79) and the definition

$$\begin{pmatrix} \bar{\mathbf{p}}^{(\nu)} \\ \bar{\mathbf{q}}^{(\nu)} \end{pmatrix} = \frac{(-1)^\nu}{\nu!} \int_{-\infty}^{+\infty} (z - vt)^\nu \, \xi(z, t) \, dz \qquad (88)$$

From this and from Equations (81) through (83) it follows that

$$\bar{\mathbf{p}}^{(0)} = \mathbf{b}^{(0)} \qquad (89a)$$

$$\bar{\mathbf{q}}^{(0)} = 0 \qquad (89b)$$

$$\bar{\mathbf{p}}^{(1)} = [v \, \mathbf{b}^{(0)} - \mathbf{F} \, \mathbf{b}^{(0)}] \, t + \mathbf{b}^{(1)} \qquad (90a)$$

$$\bar{\mathbf{q}}^{(1)} = - \mathbf{L}^{-1} \, \mathbf{V}^{(21)} \, \mathbf{b}^{(0)} \qquad (90b)$$

$$\begin{aligned} \bar{\mathbf{p}}^{(2)} = {} & [v^2 \, \mathbf{b}^{(0)} - 2 \, v \, \mathbf{F} \, \mathbf{b}^{(0)} + \mathbf{F}^2 \, \mathbf{b}^{(0)}] \, t^2/2 \\ & + [v \, \mathbf{b}^{(1)} - \mathbf{F} \, \mathbf{b}^{(1)} + \mathbf{V}^{(12)} \, \mathbf{L}^{-1} \, \mathbf{V}^{(21)} \, \mathbf{b}^{(0)} \\ & + \mathbf{D}^{(11)} \, \mathbf{b}^{(0)}] \, t + \mathbf{b}^{(2)} \end{aligned} \qquad (91a)$$

$$\begin{aligned} \bar{\mathbf{q}}^{(2)} = {} & - \mathbf{L}^{-1} \, \mathbf{V}^{(21)} \, [v \, \mathbf{b}^{(0)} - \mathbf{F} \, \mathbf{b}^{(0)}] \, t \\ & + [\mathbf{L}^{-1} \, \mathbf{V}^{(22)} \, \mathbf{L}^{-1} \, \mathbf{V}^{(21)} + \mathbf{L}^{-1} \mathbf{D}^{(21)} \\ & - \mathbf{L}^{-1} \, \mathbf{V}^{(21)} - \mathbf{L}^{-2} \, \mathbf{V}^{(21)} \, \mathbf{F}] \, \mathbf{b}^{(0)} \end{aligned} \qquad (91b)$$

Peak Velocities

Suppose the column is in a mode with velocity v. Then the asymptotic center velocity in the moving coordinate system must vanish identically, since all components must have asymptotic zero center velocity by the definition of a mode. That is, the coefficient vector of t in Equation (90*a*) must be zero. Therefore, the following holds: (*a*) If the column is in a mode, $\mathbf{b}^{(0)}$ is a right-hand eigenvector of $\mathbf{F}$, and the velocity of the mode is the respective eigenvalue of $\mathbf{F}$.

As has been explained before, the experimental identification of a mode is simple, since a mode corresponds to a well-separated "peak" in the column. Thus, the result is obtained that the asymptotic velocities of the "peaks" are independent of kinetic effects. The result in (a) is identical with the result of the equilibrium theory.

From the definition of $\mathbf{T}$ in Equation (67) and from Equation (79) for $\nu = 0$, it follows that $\mathbf{E}\mathbf{f}^{ri}$ is proportional to the z averaged perturbation $\mathbf{x}$ in the "peak" corresponding to mode i. Thus, $\mathbf{E}\mathbf{f}^{ri}$ can be called an *eigencomposition.* If the initial perturbation has this z averaged composition (or a composition stoichiometrically equivalent to it), only "peak" i will be nonsingular. All other "peaks" are singular with respect to all instruments $\mathbf{l}$. From this fact, the eigencomposition can be determined experimentally by using noncalibrated instruments, that is, linear instruments with unknown sensitivities to individual components.

Dispersion and Shift

Next it is assumed that the column is in the i^{th} mode corresponding to the i^{th} right-hand eigenvector $\mathbf{f}^{ri}$, of $\mathbf{F}$. It can be seen that in this case the term t^2 in (91*a*) and the term in t in (91*b*) disappear. The vector $\mathbf{b}^{(1)}$ pertains to an interesting phenomenon which will be called the *shift.* Assume for the moment that $\mathbf{b}^{(1)}$ be proportional to $\mathbf{f}^{ri}$, in which case it would be proportional to $\mathbf{b}^{(0)}$. (This is never true in the presence of kinetic effects other than longitudinal mixing.) That is, the stoichiometric variables in a peak would have the same center. In general, this is not the case, since the components in the moving phase are ahead of the components in the stationary phase if there is no equilibrium. (The simplest example is given by $\sigma = 0, n = 2, d = 1$.) In other words, the centers of the stoichiometric variables are shifted relative to one another owing to the kinetic effects. The shift will correspond to that part of $\mathbf{b}^{(1)}$ which is orthogonal to $\mathbf{f}^{ri}$. It is obvious that $\mathbf{b}^{(1)}$ for the i^{th} mode can be determined only up to a vector proportional to $\mathbf{f}^{ri}$, since the property of a column to be in a mode remains unaltered if all perturbations are shifted by a time constant distance in the z direction. Such an operation corresponds to adding a multiple of $\mathbf{f}^{ri}$ to Equation (90*a*).

An instrument $\mathbf{l}$ measuring the vector $\mathbf{x}$ corresponds by (63) to an instrument $\boldsymbol{\lambda}$ measuring the vector $\boldsymbol{\xi}$, where

$$\boldsymbol{\lambda} = \mathbf{l}\,\mathbf{T} \tag{92}$$

The first d elements in $\boldsymbol{\lambda}$ will be combined to form a row vector $\boldsymbol{\tau}$, and the last m elements in $\boldsymbol{\lambda}$ will be combined to form a row vector $\boldsymbol{\mu}$. Thus

$$\boldsymbol{\lambda} = (\boldsymbol{\tau}, \boldsymbol{\mu}) \tag{93}$$

Assume that the column is in its i^{th} mode and that $\boldsymbol{\tau}$ is given by

$$\boldsymbol{\tau} = \mathbf{f}^{lj} \qquad j \neq i \tag{94}$$

The peak observed by this instrument is then singular, since its zero moment vanishes because of (a) and because of the orthogonality of $\mathbf{f}^{lj}$ and $\mathbf{f}^{ri}$ $(i \neq j)$. The velocity of this singular peak is then determined by the product of $\mathbf{f}^{lj}$ and the coefficient of t in Equation (91*a*). Since the column is in a mode, this velocity must vanish in the coordinate system which moves with the velocity of the mode, so that the following holds: (b) If the column is in the i^{th} mode, the coefficient vector of t in Equation (91*a*) is orthogonal to all $\mathbf{f}^{lj}$ $(j \neq i)$; that is

$$(v_i - v_j)\mathbf{f}^{lj}\,\mathbf{b}^{(1)} + \mathbf{f}^{lj}\,[\mathbf{V}^{(12)}\,\mathbf{L}^{-1}\,\mathbf{V}^{(21)} + \mathbf{D}^{(11)}]\,\mathbf{f}^{ri} = 0 \tag{95}$$

This coefficient vector must be proportional to $\mathbf{f}^{ri}$.

With this equation, all the products $\mathbf{f}^{lj}\,\mathbf{b}^{(1)}$ can be determined (since $v_i \neq v_j$ for $i \neq j$ by assumption), so that $\mathbf{b}^{(1)}$ is determined up to an arbitrary multiple of $\mathbf{f}^{ri}$. The magnitudes $\mathbf{f}^{lj}\,\mathbf{b}^{(1)}$ can also be determined experimentally. Unfortunately, this is only possible if the coefficients of the analytical devices used are known (the devices must be calibrated). It will be seen that other parameters of the "peaks," namely, the dispersion coefficients, can be determined experimentally by uncalibrated devices. There are, however, only $d - \sigma$ observable dispersion coefficients, whereas the number of shift parameters is much larger.

A nonsingular peak will be observed in the i^{th} mode if in the representation

$$\boldsymbol{\tau} = \sum_{j=1}^{d} \alpha_j\,\mathbf{f}^{lj} \tag{96}$$

the coefficient α_i is nonzero, and if $\mathbf{b}^{(0)}$ is a nonzero multiple of $\mathbf{f}^{ri}$. It follows then from the definition of the dispersion coefficient D^*, Equations (60) and (61), and from (b) that D_i^* for the i^{th} mode is given by

$$D_i^* = \mathbf{f}^{li}\,[\mathbf{V}^{(12)}\,\mathbf{L}^{-1}\,\mathbf{V}^{(21)} + \mathbf{D}^{(11)}]\,\mathbf{f}^{ri} \tag{97}$$

D_i^* is independent of $\boldsymbol{\lambda}$ or $\mathbf{l}$; that is, the dispersion is independent of the instrument used. By Equation (97), D_i^* can be calculated analytically from the thermodynamic and kinetic data of the system. It also can be found experimentally by observing the increase of width with time of a separated peak. For the experimental determination of D^*, the only requirement is an analytical device which responds linearly. It is not necessary to know quantitatively how the response is related to the concentrations in the mixture analyzed (uncalibrated instrument).

EXAMPLES

Dispersion for Klinkenberg's Example

For Klinkenberg's problem, $\mathbf{L}$ is given by Equation (76). From this and Equation (20) it follows that

$$\text{Det}\ \mathbf{L} = \gamma\,\mathcal{H}\,\mathcal{H}_1\,\mathcal{H}_2/(a^f)^2\,a^s \tag{98}$$

Those elements of $\mathbf{L}^{-1}$ which are needed for calculating the dispersion coefficient, reduced according to

$$\mathbf{M} = \mathbf{L}^{-1}\ \text{Det}\ \mathbf{L} \tag{99}$$

are given by

$$M_{12} = \frac{\beta_2\mathcal{H}_1}{\beta\,a^f}\left(\frac{\mathcal{H}_2\beta_2}{a^s} + \mathcal{H}\beta\right) + \frac{\mathcal{H}_2\beta_2}{a^f}\left(-\frac{\mathcal{H}_1}{\beta\,a^s} + \mathcal{H}\right) \tag{100a}$$

$$M_{13} = -\frac{\beta_2\mathcal{H}_1\mathcal{H}}{a^f} + \frac{\beta_2\mathcal{H}_2}{a^s}\left(\frac{\mathcal{H}_1}{a^f} + \frac{\beta_1\mathcal{H}_1}{a^s} + \mathcal{H}\right) \tag{100b}$$

$$M_{22} = M_{23} = \frac{\beta\mathcal{H}_2\mathcal{H}}{a^f} \tag{100c}$$

$$M_{32} = \frac{\mathcal{H}_2}{a^f}\left(-\frac{\mathcal{H}_1}{\beta\,a^f} + \mathcal{H}\right) - \frac{\beta_2\mathcal{H}_1\mathcal{H}_2}{a^f a^s} \tag{100d}$$

$$M_{33} = \frac{\mathcal{H}_2}{a^f}\left(\frac{\mathcal{H}_1}{a^f} + \frac{\beta_1\mathcal{H}_1}{a^s} + \mathcal{H}\right) \tag{100e}$$

Since $d = 1$, the vectors $\mathbf{f}^{li}$ and $\mathbf{f}^{ri}$ in Equation (97) become scalars and can be set equal to unity. $\mathbf{V}^{(12)}$ and $\mathbf{V}^{(21)}$ are given by Equations (77) and (78). From Equations (77), (78), and (97) to (100), it follows that

$$D^* = \frac{(v^f)^2(a^f)^2(a^s)^2}{\gamma^3}\left[\frac{\beta_1\beta(1+\beta)^2}{\mathcal{H}_1} + \frac{\beta_2(1+\beta)^2}{\mathcal{H}_2} + \frac{\beta(\beta_1-\beta_2)^2}{a^s\mathcal{H}}\right] \tag{101}$$

If there is physical equilibrium, $\mathcal{H}_1 \to \infty$, $\mathcal{H}_2 \to \infty$, and Equation (101) becomes

$$D^* = \frac{(v^f)^2(a^f)^2\,a^s}{\gamma^3}\ \frac{\beta(\beta_1-\beta_2)^2}{\mathcal{H}} \tag{102}$$

Equation (102) agrees exactly with Klinkenberg's result, which was obtained by a completely different method applicable only to this particular case. Note that Equation (25) in Klinkenberg's paper contains a typographical error. The term $k_A\,K_B$ in the numerator under the square root should be replaced by $k_A\,K_B\,F_{II}$, all Klinkenberg's

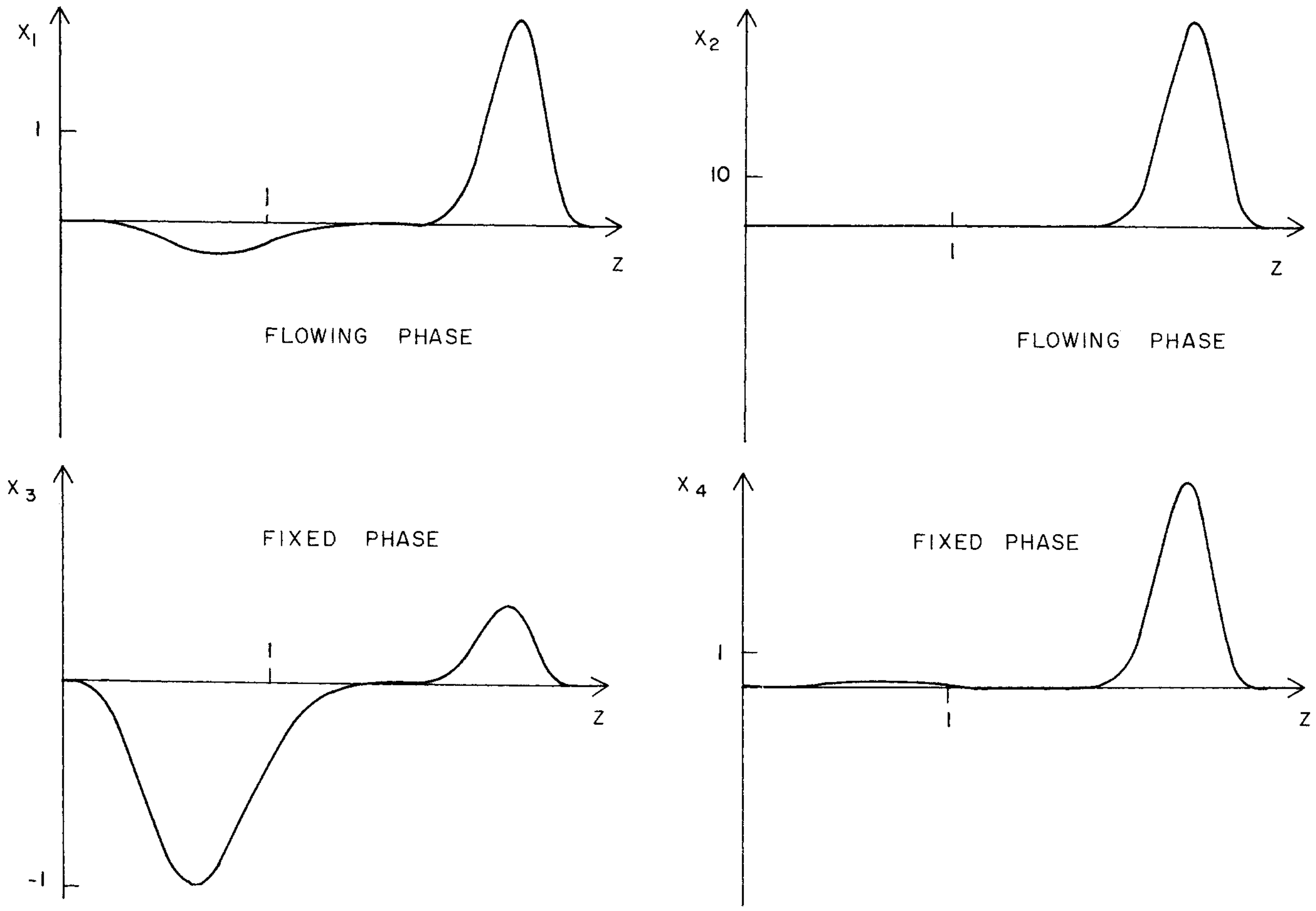

Fig. 1. Perturbation profiles for $d = 2$ at $t = 5.12$.

notation. It can be seen that for $\beta_1 = \beta_2$, the dispersion vanishes. In this case, the perturbations are such that the system always remains in chemical equilibrium, and, therefore, the kinetic effects do not matter.

If $\mathcal{H} \to 0$, the dispersion approaches infinity by Equation (102). On the other hand, if $\mathcal{H}$ is set equal to zero in the original formulation of the problem, and then the problem is treated as one with $n = 2$, $m = 0$, there will be two peaks ($d = 2$), the dispersions of which are determined by the physical rate processes. If there is physical equilibrium, the dispersion of those peaks is, of course, zero. The different results obtained for the two problems (defined by $n = 2$, $m = 1$, $\mathcal{H} \to 0$, and $n = 2$, $m = 0$, respectively) are not contradictory. In the first case, if $\mathcal{H} \to 0$, the time required to approach the asymptotic solution becomes larger and larger. If $\mathcal{H} \neq 0$ but is very small, the one peak with very large dispersion of the former problem would eventually be approached, while the solution of the second problem would give a good approximation to the transition period. As already noted by Klinkenberg, in this case there would be two peaks at the start which later merge into one very broad peak.

TABLE 1

t	dz^*/dt	$(\frac{1}{2})\,(d\sigma^2/dt)$	
0.04	0.398	1.62	10^{-3}
0.08	0.325	4.61	10^{-3}
0.16	0.253	8.55	10^{-3}
0.32	0.181	12.3	10^{-3}
0.64	0.142	12.8	10^{-3}
1.28	0.134	12.2	10^{-3}
2.56	0.134	12.2	10^{-3}
5.12	0.134	12.2	10^{-3}

A Numerical Example for $d = 2$

How peaks separate and approach an asymptotic velocity and rate of spreading can be seen if the partial differential Equation (62) is integrated numerically. This has been done (4) for a case with $n = 4$, $m = 2$, $\sigma = 0$, $d = 2$. The matrices $\mathbf{K}^{(0)}$, $\mathbf{V}^*$, and $\mathbf{D}$ for this example are given by

$$\mathbf{K}^{(0)} = \begin{bmatrix} -6 & 0 & +2.5 & +2 \\ 0 & -3 & +2.5 & +17.5 \\ +6 & 0 & -2.5 & -2 \\ 0 & +3 & -2.5 & -17.5 \end{bmatrix} \tag{103}$$

$$\mathbf{V}^* = \begin{bmatrix} 0.5 & 0 & 0 & 0 \\ 0 & 0.5 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \tag{104}$$

$$\mathbf{D} = 0 \tag{105}$$

In this example there are no chemical reactions but only physical exchange processes. The example differs, however, from ordinary chromatography in that the two substances couple with each other, and therefore peaks are produced which do not correspond to the pure substances. There would be no coupling if the nonzero elements K_{14}, K_{23}, K_{34}, and K_{43} were replaced by zeros, in which case the transport of each substance could be described independently. The partial differential Equation (62) was integrated numerically by a special method which allows doubling of the time increment at each step (*4*). Figure 1 shows the result of the integration at $t = 5.12$ and for an initial perturbation of x_2 only in a very small interval at $z = 0$.

It should be noted that the ordinate scales are different for all four graphs. Two peaks develop in this column, and it can be seen that, owing to the coupling, both peaks contain the perturbations of both substances (equivalent to four components) even though only one substance was introduced in the column at $t = 0$. In this example x_i denotes the perturbation of the concentration in a system which is originally in equilibrium and for which the equilibrium conditions are nonlinear. In such a case, of course, there is no restriction on the sign of x_i. If x_i is negative, the concentration of the respective component is reduced in the peak. Since in the problem in question no substance 1 was introduced originally into the system (x_1 and x_3 are unperturbed originally), the integral perturbation of substance 1 (sum of the integrals over x_1 and x_3 in this case) must be zero. Qualitatively, this means that if x_1 and x_3 are positive in the faster peak, they must be negative in the slower peak (see Figure 1). The numerical results show that the peaks in the moving phase are ahead of those in the stationary phase (that is, there is a shift), but this phenomenon is almost unnoticeable in the figure.

From the $\mathbf{K}^{(0)}$ and the $\mathbf{V}^*$ matrix given by Equations (103) and (104), the velocities and dispersion coefficients of the peaks can be calculated. The results are given by

$$v_1 = 0.4274 \qquad v_2 = 0.1340$$

$$D_1^* = 2.838 \times 10^{-3} \quad D_2^* = 12.00 \times 10^{-3}$$

The magnitudes

$$\frac{dz^*}{dt} \quad \text{and} \quad \frac{1}{2}\frac{d\sigma^2}{dt}$$

were estimated from the results of the numerical integration by calculating z^* and σ^2 for the peaks at each time step and by dividing the increase of these values per step by the corresponding time interval. Results are given in Table 1 for the second peak. The values in the second column are very sensitive to the discretization error of the numerical integration. This source of error is very likely the cause for the slight discrepancy between the last of those values and the value calculated analytically.

NOTATION

$\mathbf{A}$ = area matrix
a^f = flowing phase area, element of A
a^s = stationary phase area, element of A
$\mathbf{b}^f$ = linearized derivative vector of g^f
$\mathbf{b}^s$ = linearized derivative vector of g^s
$\mathbf{b}^{(i)}$ = vector of integration constants for the i^{th} moment
$\mathbf{c}$ = concentration vector, moles/volume. appropriate phase
$\mathbf{D}$ = diffusion matrix
d_p = number of physically observable peaks
d = $n - m$, the nullity of K
D^* = dispersion coefficient
$\mathbf{E}$ = $d \times n$ equilibrium matrix
$\mathbf{E}'$ = $n \times m$ submatrix of T^{-1}, Equation (66)
$\mathbf{E}''$ = $d \times m$ submatrix of E', Equation (68)
$\mathbf{e}^{(i)}$ = i^{th} column vector in E, $i = 1, \ldots d$
$\mathbf{F}$ = $d \times d$ velocity matrix, Equation (44)
$\mathbf{f}^{li}$ = i^{th} left-hand eigenvector (row) of F, $i = 1, \ldots d$
$\mathbf{f}^{ri}$ = i^{th} right-hand eigenvector (column) of F, $i = 1, \ldots . d$
g^f = flowing phase equation of state function
g^s = stationary phase equation of state function
h_i = i^{th} equilibrium function, $i = 1, \ldots . m$
$\mathbf{K}$ = linearized rate matrix, $n \times n$
$\mathbf{l}$ = instrument, operating on $\mathbf{x}$ to give a signal s
$\mathbf{L}$ = $m \times m$ submatrix of $T^{-1}KT$, Equation (71)
m = number of stoichiometrically independent reactions, including mass transfer
n = total number of components, counting each substance twice if it is in both phases
n_f = number of components in flowing phase
$\mathbf{p}^{(\nu)}$ = d subvector of ν^{th} moment of $\boldsymbol{\xi}$, Equation (79)
$\mathbf{q}^{(\nu)}$ = m subvector of ν^{th} moment of $\boldsymbol{\xi}$, Equation (79)
$\mathbf{r}$ = rate vector, Equation (2)
$\mathbf{S}$ = $n \times d$ stoichiometric matrix
s = signal
$\mathbf{s}^{(j)}$ = j^{th} row vector in S
$\mathbf{T}$ = $n \times n$ transformation matrix, Equation (67)
t = time
$\mathbf{V}$ = velocity matrix
v = peak velocity
v_i = i^{th} eigenvalue of F
v^f = flowing phase velocity
$\mathbf{x}$ = concentration perturbation vector
$\mathbf{y}$ = d column vector of independent equilibrium perturbations
z = distance in flow direction

Greek Letters

α_j = coefficients in Equation (96)
β_i = equilibrium constants in Equation (17) and others, Klinkenberg's example
γ = normalizing factor, Equation (20)
δ_{ij} = Kronecker delta
η_i = combination of perturbations defined by Equation (49)
$\boldsymbol{\lambda}$ = transformed instrument, defined by Equation (92)
$\boldsymbol{\mu}$ = m subvector of $\boldsymbol{\lambda}$, Equation (93)
$\boldsymbol{\nu}^{(i)}$ = i^{th} stoichiometric vector, with units depending on whether (i) refers to an interphase reaction or to an intraphase reaction
ν = moment number
$\boldsymbol{\xi}$ = transformed perturbation vector, Equation (63)
ρ_j = j^{th} reaction rate, with units depending on whether the reaction is inter- or intraphase
σ = number of equations of state for a case
$\boldsymbol{\tau}$ = d subvector of $\boldsymbol{\lambda}$, Equation (93)

Superscripts

f = flow phase
s = stationary phase
$*$ = original equilibrium state before perturbation
σ = number of equations of state (0, 1, or 2)
ν = moment number

Subscripts

e = equilibrium state
p = peaks

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