Q_t = sludge volumetric flow rate, L^3T^{-1}
S = settling flux = cu, LT^{-1}
S_t = terminal, or no-compression, settling flux = cu_t, LT^{-1}
u = particle settling velocity, relative to G_t, LT^{-1}
u_t = terminal, or no-compression, settling velocity, LT^{-1}
v = particle velocity, relative to the container, LT^{-1}
x = vertical position, L
X = total depth of sediment, L
θ = included angle of cone
ρ_l = liquid density, ML^{-3}
ρ_p = particle density, ML^{-3}
σ = interparticle compressive stress, based on total cross-sectional area, $ML^{-1}T^{-2}$

LITERATURE CITED

Abbott, J., C. Dell, B. Denison, D. Knott and N. W. Hill, "Coal Preparation Plant Effluent Disposal by Means of Deep Cone Thickeners," Paper 20, *6th Int. Coal Prep'n Cong.*, Paris, France (Mar., 1973).

Dahlstrom, D. A., C. F. Cornell, R. C. Emmett and C. E. Silverblatt, "Gravity Sedimentation Operations," pp. 19-44 to 19-57, in Perry and Chilton (1973).

Dell, C. C., and W. T. H. Keleghan, "The Dewatering of Polyclay Suspensions," *Powder Technol.*, **7**, 189 (1973).

Dixon, D. C., "Momentum-Balance Aspects of Free-Settling Theory. I. Batch Thickening," *Sep. Sci.*, **12**, 171 (1977*a*).

Dixon, D. C., "Momentum-Balance Aspects of Free-Settling Theory. II. Continuous, Steady-State Thickening," *ibid.*, 193 (1977*b*).

Dixon, D. C., "Momentum-Balance Aspects of Free-Settling Theory. III. Transient Compression Resistance," *Sep. Sci. Technol.*, **13**, 753 (1978).

Fitch, B., "Sedimentation Process Fundamentals," *Trans. Am. Inst. Min. Engrs.*, **223**, 129 (1962).

Flannery, S. D., "Fluid/Particle Separation by Continuous Thickening," B.E. Thesis, Univ. New South Wales (1978).

Kos, P., "Gravity Thickening of Water-Treatment-Plant Sludges," *J. Am. Water Works Assoc.*, **69**, 272 (1977).

Perry, R. H., and C. H. Chilton, ed., *Chemical Engineers' Handbook*, p. 2-58, McGraw-Hill, New York (1973).

Ralston, A., and H. S. Wilf, *Mathematical Methods for Digital Computers*, Vol. 1, pp. 116-117, Wiley, New York (1960).

Smiles, D. E., "Sedimentation and Self-Weight Filtration in Industrial Slurries," *PACE*, **28**, 13 (1975).

Smiles, D. E., "Sedimentation: Integral Behaviour," *Chem. Eng. Sci.*, **31**, 273 (1976).

Turner, J. P. S., and D. Glasser, "Continuous Thickening in a Pilot Plant," *Ind. Eng. Chem. Fundamentals*, **15**, 23 (1976).

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An Introduction to the Nonlinear Theory of Adsorptive Reactors

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Coupling between transient chemical reaction at equilibrium and a linear and isothermal chromatographic separation is studied when a nonlinear chemical mass action law is assumed to hold between the species. It is shown that the qualitative features of the chromatograms can be predicted by simple algebraic calculations. Two novel properties of the adsorptive (or chromatographic) reactor are demonstrated. The improvement of the theory, with regard to quantitative predictions, is discussed.

SCOPE

An adsorptive or chromatographic reactor is defined as a transient chemical reactor in which the reactants and the products undergo a chemical reaction and a chromatographic separation simultaneously. The coupling between these two physicochemical phenomena gives rise to peculiar behaviors with respect to standard reactors: equilibrated reaction forced to completion, enhancement of selectivity, of chemical reaction rate, etc. Dinwiddie (1966) and Magee (1961) have outlined the potential uses of this reactor in industry. On the other hand, Langer et al. (1972) and Hattori et al. (1968) have pointed out that the chromatographic reactor is a good tool to determine kinetic schemes or to measure kinetic rates with a little amount of reactant. In biochemistry, the method is used to measure association constants of drugs and proteins (see, for example, Oster et al. 1976). In the field of separation science, Shiloh (1966) and Golden et al. (1974) have studied the competition between separation and precipitation, complexation or neutralization in ion exchange columns (see Klein, 1978).

Unfortunately, the analysis of the transient behavior of the reactor needs complicated models. Two kinds of models are found in the literature: complicated models, which account for as many as possible physical processes and require tedious numerical procedures to be solved (Chieh Chu, 1971; Hattori, 1968) and simple models in which simplifying assumptions are made (first-order kinetic in Langer et al., 1972, linear chromatography in Kocirick, 1967, and Villermaux, 1978, instantaneous equilibrium in Magee, 1963, or Gore, 1967, analogy with semibatch reactor in Schweich et al., 1978).

The purpose of this paper is to give a first insight into what we think to be a general method which describes the behavior of the adsorptive reactor when the feed composition change is an instantaneous step function (the case of a feed pulse is not studied). It is assumed that dispersion and mass transfer processes are negligible and that the reaction is at equilibrium at every time and at any point inside the isothermal column. We use the same mathematical method as Tondeur (1969). It is very similar to the method of characteristics used by Rhee (1970 to 78) and to the concept of coherence developed by Helfferich (1967) and Helfferich and Klein (1970). After the development of theory, the transient esterification of acetic acid with ethanol and the dehydrogenation of cyclohexane to benzene are interpreted as illustrative examples.

Some possible generalizations are suggested, especially in the frequent case of nonlinear adsorption isotherms.

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CONCLUSIONS AND SIGNIFICANCE

The proposed model is a unified theoretical framework within which most of the published results on chromatographic reactors can be found when it is assumed that no kinetic rate limitation occurs. The reactor model consists of a set of nonlinear partial differential equations which could be solved by the so-called method of characteristics (Rhee, 1970, 1978; Jeffrey, 1976). We use a simplified approach based on a theorem proved by Lax (1957) which allows us to introduce quickly the concepts of composition space, composition routes and characteristic equation. Then we show that the qualitative features of the reactive chromatograms can be predicted with very simple algebraic calculations which do not require the use of a computer. It is shown that the shape of the chromatograms depends essentially upon the capacity factors of each species and upon the stoichiometric numbers. The influence of the stoichiometric numbers can be drastic, since they can affect the natural elution order of the species in the absence of reaction. This is what we call a chemical pumping effect which allows elution of a highly retained component with the less retained one.

Most of the theoretical concepts introduced in this paper are strikingly similar to those introduced by Helfferich (1967), Helfferich and Klein (1970) with the $H(h)$ function, Klein et al. (1967) and Tondeur and Klein (1967) in multicomponent chromatography, but they have different physical meanings. For instance, we introduce a characteristic or watershed (Helfferich) point which gives rise to a novel property of the adsorptive reactor. For some specified inlet composition changes which always contain all of the reacting species, it is possible to collect a fraction of one pure component at the outlet in spite of the complex composition at the inlet. It seems to us that this peculiar behavior might lead to practical applications. The comparison between theory and experiments shows a good qualitative agreement. On a quantitative point of view, it seems that the assumptions of linear adsorption isotherms and constant velocity in gas-phase reactors are rather coarse, since they do not account for all experimental results. It is also shown how the theory may be extended to Langmuir adsorption isotherms, but no comparison between theory and experiment is made in that case. The specific problems of nonlinear isotherms are summarized and will be treated in a future paper.

STATEMENT OF THE PROBLEM AND BASIC ASSUMPTIONS

We shall deal with the reaction $\sum_i \nu_i P_i \rightleftarrows 0$. The stoichiometric number ν_i is positive (negative) if P_i is a product (reactant). We shall assume that the concentrations obey the mass action law

$$K = \prod_i P_i^{\nu_i} \tag{1}$$

We shall assume furthermore that:

1. The column is isothermal.
2. Dispersion and mass transfer processes are negligible.
3. The fluid velocity is constant. It is thus supposed that physical or chemical expansion of the fluid and sorption effects are unimportant. This assumption is justified for liquid adsorption but rather coarse for gas adsorption.
4. The adsorption isotherms are linear.

These assumptions allow us to write a differential mass balance with respect to the component P_i:

$$u \frac{\partial P_i}{\partial x} + \frac{\partial P_i}{\partial t}(1 + \alpha_i) = \nu_i r = r_i \qquad i = 1 \ldots n \tag{2}$$

r_i is the molar rate of generation ($\nu_i > 0$) or consumption ($\nu_i < 0$) of species P_i. α_i is the capacity factor of component P_i defined as the ratio of the amount Q_i of component i in stationary phase to the amount P_i in the fluid phase. We shall use the apparent velocity of component P_i defined by

$$R_i = \frac{u}{1 + \alpha_i} \tag{3}$$

and we shall assume that the species are indexed, so that

$$R_1 > R_2 > \ldots > R_n$$

When chemical equilibrium is assumed, r is not known, and it must be eliminated from the set of Equations (2). This can be done by a suitable linear combination of these equations two by two and leads to

$$u\left[\nu_j \frac{\partial P_i}{\partial x} - \nu_i \frac{\partial P_j}{\partial t}\right] + \nu_j(1 + \alpha_i)\frac{\partial P_i}{\partial t} - \nu_i(1 + \alpha_j)\frac{\partial P_j}{\partial t} = 0 \tag{4}$$

The $n - 1$ Equations (4) with the mass action law (1) is a set of n equations with n unknowns.

The method used to solve Equations (4) is based on a mathematical result demonstrated by Lax (1957). Provided that the boundary condition on each P_i is an instantaneous step function at a specified time, the solution of Equations (4) may be expressed as functions of a unique parameter θ which is a function of the variables x and t. This theorem is intimately connected with the so-called method of characteristics in the theory of nonlinear partial differential equations which will not be explicitly referred to in this paper. We shall see, firstly, the use of Lax's theorem in the case of classical linear and ideal adsorption in order to show the main features of the mathematical method and to get some important results which will be used later when chemical reaction and adsorption will be assumed to occur simultaneously.

LINEAR ADSORPTION AND LAX'S THEOREM

The mass balance equations which describe linear adsorption under the assumptions cited in the previous section are:

$$u \frac{\partial P_i}{\partial x} + (1 + \alpha_i)\frac{\partial P_i}{\partial t} = 0 \tag{5}$$

If P_i is a function of the parameter θ, (5) can be written as

$$\left[u \frac{\partial \theta}{\partial x} + (1 + \alpha_i)\frac{\partial \theta}{\partial t}\right]\frac{dP_i}{d\theta} = 0 \tag{6}$$

Equation (6) is equivalent to

$$\frac{dP_i}{d\theta} = 0 \tag{7}$$

or

$$u \frac{\partial \theta}{\partial x} + (1 + \alpha_i)\frac{\partial \theta}{\partial t} = 0 \tag{8}$$

Equation (7) means that a constant P_i is a trivial solution of (5). If P_i is not constant, then (8) must be true. Let us notice that (8) can be written as

$$\left(\frac{dx}{dt}\right)_\theta \frac{\partial \theta}{\partial x} + \frac{\partial \theta}{\partial t} = 0 \tag{9}$$

with

$$\sigma \equiv \left(\frac{dx}{dt}\right)_\theta = R_i \tag{10}$$

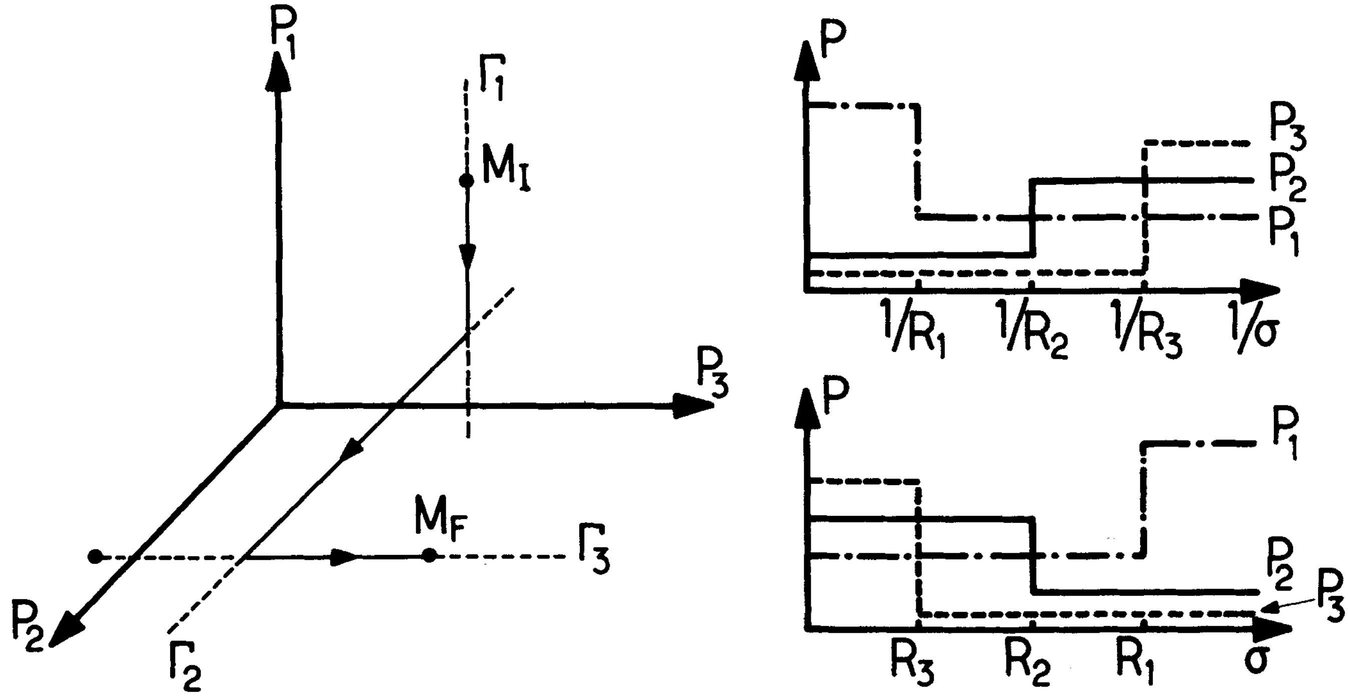

Figure 1. Three-component linear adsorption. Left: composition route in the concentration space consisting of pieces of Γ curves parallel to the axes. Top right: related chromatogram. Bottom right: related profile (P_1: —.—., P_2 ———, P_3 — — — —, arbitrary units).

Equation (10) cannot be true for all i simultaneously. As a consequence, the solution of (6) and hence (5), whatever i, is

$$\sigma = R_i \quad \text{and} \quad P_k = \text{constant for all } k \neq i, \quad i = 1 \ldots n \tag{11}$$

Let us consider now the n dimensional space $\mathcal{P}$ of the concentrations. A given point M in $\mathcal{P}$ is the image of a given composition ($P_1, P_2, \ldots . P_n$). Let M_I be the composition inside the column before the step composition change is applied and M_F the composition inside the column a long time after the step composition change has occurred. M_I and M_F are the compositions on each side of the boundary step function. In order to describe the composition changes along the column axis, Equation (5) must be solved, and hence Equation (11) must be true. Equation (11) defines straight lines parallel to the axes of the space $\mathcal{P}$. Thus the solution of Equation (5) consists in a route from M_I to M_F, in the space $\mathcal{P}$. This route consists of successive pieces of straight lines parallel to the axes. Hence, Equation (11) allows us to know the variations of P_i with respect to P_j. But several routes are possible. Which one is the solution and how to draw a concentration profile (or history) from this composition route? To answer these questions, let us notice that $\theta = \sigma = x/t$ is a peculiar solution of (8). Thus, $P_i(\sigma)$ for a specified t is a concentration profile, and $P_i(1/\sigma)$ for a specified x is a chromatogram. But for times preceding the composition change, P_i is a component of M_I, and for large t it is a component of M_F. Thus, we see that we must go from M_I to M_F with increasing values of t and hence with decreasing values of σ. From (11), σ is constant on the straight line Γ_i, where $\sigma = R_i$. Thus, the composition route from M_I to M_F consists of the ordered succession of pieces of straight lines $\Gamma_1, \Gamma_2, \ldots \Gamma_n$ corresponding to the respective values of σ, $R_1, R_2, \ldots R_n$. We have now a unique composition route along which σ is known. Figure 1 illustrates a composition route in a three-dimensional space and the related concentrations profiles $P_i(\sigma)$ or histories $P_i(1/\sigma)$. Indeed, all these results are easier to get from the theory of linear differential equations, but we are going to see that the method generalizes itself in a very useful way when the reaction is taken into account.

REACTIVE ADSORPTION WITH LINEAR ISOTHERMS

We must solve the set of Equations (4). If we suppose that P_i and P_j are functions of a unique parameter θ, the relationships $\partial P_i/\partial x = dP_i/d\theta \; \partial\theta/\partial x$, $\partial P_i/\partial t = dP_i/d\theta \; \partial\theta/\partial t$ may be substituted in Equation (4). We get an expression similar to (9), which can be written as

$$\left(\frac{dx}{dt}\right)_\theta \equiv \sigma = u \frac{\nu_j \dfrac{dP_i}{d\theta} - \nu_i \dfrac{dP_j}{d\theta}}{\nu_j(1+\alpha_i)\dfrac{dP_i}{d\theta} - \nu_i(1+\alpha_j)\dfrac{dP_j}{d\theta}} \tag{12}$$

Equation (12) is identical to the coherence condition introduced by Helfferich (1967). Moreover, we have

$$\frac{\dfrac{dP_i}{d\theta}}{\dfrac{dP_j}{d\theta}} = \frac{dP_i}{dP_j} \tag{13}$$

Equations (12) and (13) lead to

$$\frac{dP_i}{dP_j} = \frac{\nu_i R_i}{\nu_j R_j} \, \frac{R_j - \sigma}{R_i - \sigma} \tag{14}$$

Let us calculate the total derivative of (1) with respect to P_j. We get

$$\sum_i \frac{\nu_i}{P_i} \frac{dP_i}{dP_j} = 0 \tag{15}$$

Using (14) in (15) we get

$$\sum_i \frac{\nu_i}{P_i} \frac{\nu_i R_i}{\nu_j R_j} \frac{R_j - \sigma}{R_i - \sigma} = 0 \tag{16}$$

Equation (16) is equivalent to

$$G(\sigma) \equiv \sum_i \frac{\nu_i^2 R_i}{P_i} \frac{1}{\sigma - R_i} = 0 \tag{17}$$

Equation (17) is called the characteristic equation of the problem. Let us show now that (17) and (14) define Γ curves in the

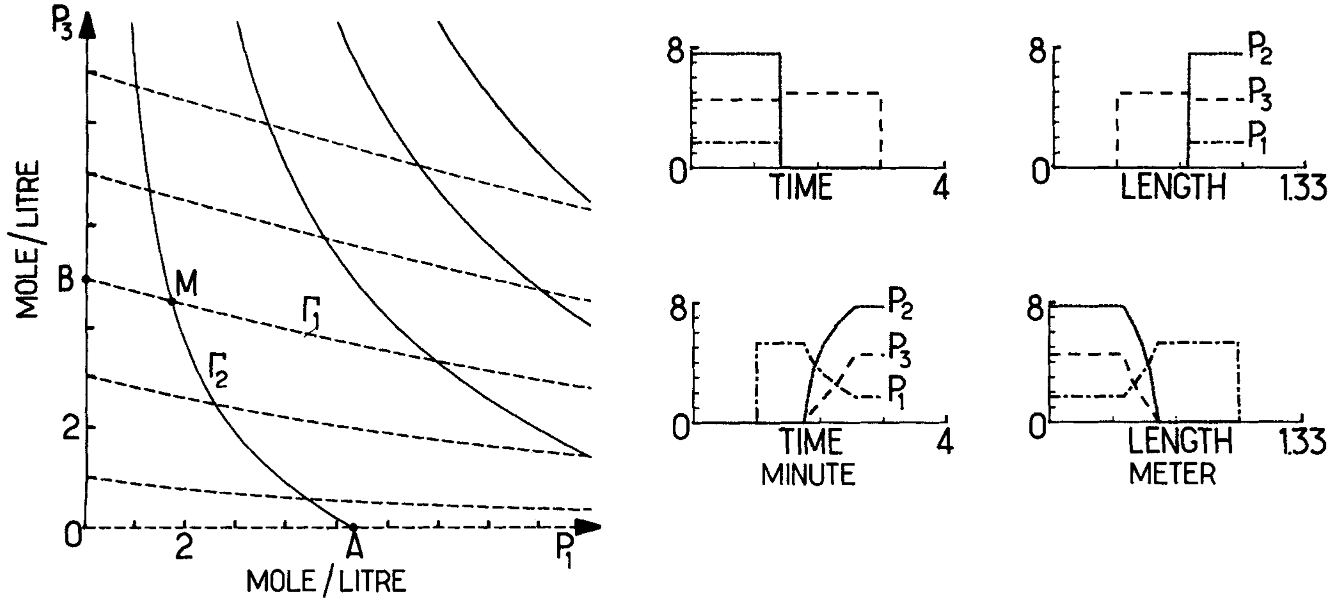

Figure 2. Reactive adsorption: $P_2 \rightleftarrows P_1 + P_3$. Left: projections of the Γ curves on the $P_1 - P_3$ plane. Two-step composition changes are considered. The negative step from M to O, with the route MBO, gives the chromatograms and the profiles of the top right; the positive step from O to M, with the route OAM, gives the chromatograms and the profiles of the bottom right. In the case of the negative step, the fronts are very sharp, but they are not shocks. It is because the Γ_1 curves are almost straight lines. From Equation (14), if Γ is a straight line, dP_3/dP_1 = constant, and hence σ is constant. ($R_1 = 1, R_2 = 0.66, R_3 = 0.33, K = 1$ mole/l. Composition at M: $P_1 = 2$ mole/l. $P_2 = 9$ mole/l. $P_3 = 4.5$ mole/l.)

$n - 1$ dimensional space $\mathscr{P}_K$ of the compositions which obey the mass action law. At a given starting point M_0, $G(\sigma) = 0$ is solved with respect to σ. The solution is used in Equation (14) to get a new point, $M_0 + dM_0$. If we repeat this iterative process, we can draw as many Γ curves emanating from M_0 as there are different roots of $G(\sigma) = 0$. Finally, we obtain a grid of Γ curves in $\mathscr{P}_K$. As previously, we call Γ_k the curve constructed with σ_k. Let us list three important properties of $G(\sigma)$ and Γ_k:

1. $G(\sigma) = 0$ has $n - 1$ roots σ_k such that $R_k \geq \sigma_k \geq R_{k+1} \cdot G(\sigma)$ is a monotonic decreasing function of σ and has n poles $\sigma = R_i$. Hence, $G(\sigma)$ has $n - 1$ roots between the poles.
2. At a given point, the Γ_k curves are generally distinct. From 1, the roots σ_k are distinct (except some double roots), and hence Equation (14) defines different directions.
3. The Γ_k curves pertaining to a category k do not intersect. If it were not so, at a given point M_0, Equation (14) would have several values for a unique value of σ_k, which is impossible.

Now, if we give ourselves an initial state M_I of the column and a desired final state M_F related to a composition step at the inlet of the column, the solution of Equations (4) is a composition route consisting of a succession of Γ_k curves with decreasing values of σ from M_I to M_F. The reasoning which leads to this result is similar to what we have followed in the case of nonreactive adsorption.

Now let us focus our attention on a very important problem, the solution of which gives the main features of the grid of Γ curves. Which one of the Γ curves allows the concentrations of a reactant (P_i or P_j) and a product (P_j or P_i) to vanish at a point M_0 of the space $\mathscr{P}_K$? Let us notice that, at the point M_0, the reaction can no longer proceed, since a product and a reactant are missing. Hence, if P_k varies along Γ curves, provided that $P_i = P_j = 0$, no reaction occurs, and, as shown above, these Γ curves are straight lines parallel to the axes P_k with $k = 1$ to n except $k = i$ and j. There are $n - 2$ such lines, and hence the reactive Γ curve ending at M_0 is unique, since $n - 1$ Γ curves pass at M_0 [some exceptions exist when $G(\sigma) = 0$ has a double root]. The answer to the previous question is given by the following theorem of vanishing species which is briefly proven in the appendix. Provided that $i > j$, the unique Γ curve along which P_i and P_j (such that $\nu_i \nu_j < 0$) vanish at a point M_0 is:

1. Γ_{i-1} if $\nu_i(\nu_i + \nu_j) > 0$.
2. Γ_j if $\nu_i(\nu_i + \nu_j) < 0$.
3. $\Gamma_k, i - 1 \geq k \geq j$ if $\nu_i + \nu_j = 0$. The value of k is given by the position of σ with respect to R_k, where σ is solution of

$$K = \left(\frac{\nu_i R_i}{\nu_j R_j} \frac{R_j - \sigma}{R_i - \sigma}\right)^{\nu i} \prod_{l \neq i, j} P_l^{\nu l} \quad \text{at} \quad M_0$$

We shall not deal with the problem of more than two vanishing species, although this case may be encountered in some applications. Before dealing with illustrative examples, let us consider the analogy between our theory and the theory of nonlinear chromatography. In Helfferich and Klein (1970), Tondeur (1969) and Rhee (1978), characteristic equations composed of a sum of hyperbolic terms can be found together with the homographic dependence of dP_i/dP_j on σ. In spite of the curious and unexplained identity in these mathematical structures, we cannot use the results of these authors since the dependence of $G(\sigma)$ and dP_i/dP_j on the concentrations are different. In the case of constant separation factors, Helfferich introduced the $H(h)$ function. When one or more concentrations go to zero, the $H(h)$ function has trivial roots which give the nature of the Γ curves (composition path after Helfferich) on the borders of the composition space as our vanishing species theorem does. In the case of nonconstant separation factors, Tondeur (1970) gave some rules which contain, once more, our theorem.

Now let us illustrate all these results on simple examples. Consider the stoichiometric relationship

$$P_2 \rightleftarrows P_1 + P_3$$

Here, the reactant is eluted between the two products in the absence of reaction. Let us assume that the initial state inside the column is a point M, where no concentration is zero, and that we want to go to a final state located at the origin of the space $\mathscr{P}_K$. On an experimental point of view, the constant composition feed relative to M is stopped at $t = 0$, and only pure solvent is fed into the column. The previous theoretical results tell us that we must go from M to 0, in the space $\mathscr{P}_K$, along a route consisting of a piece of Γ_1 curve and then a piece of Γ_2 curve. Now let us show that the qualitative description of the behavior of the step composition change does not require the integration of Equation (14). Let us look at the diagram on the left of Figure 2. A point B where P_1 and P_2 vanish is obviously on the P_3 axis. Let $i = 2$ and $j = 1$. The vanishing species theorem tells us that P_1 and P_2 vanish along a Γ_k curve with $k = 1$, since

$$\nu_i + \nu_j = 1 - 1 = 0 \quad i - 1 = 1, \quad j = 1$$
$$\text{and} \quad i - 1 \leq k \leq j$$

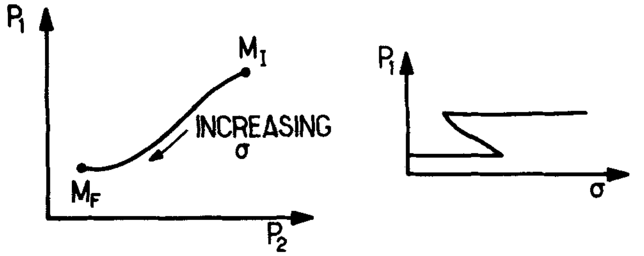

Figure 3. Example of nonphysical profile. The path consists of the oriented Γ curve from M_I to M_F along which σ increases. The related profile is a multivalued function of σ and has no physical meaning (arbitrary units).

Hence, a Γ_1 reacting curve ends at B while the P_3 axis is a Γ_2 curve, since the Γ curves pertain to different categories at a given point. Thus the Γ_1 curve emanating from M ends at a point B on the P_3 axis and the route MBO consists of a piece of Γ_1 and then a piece of Γ_2, and it is the solution. Moreover, along MB we have

$$\frac{dP_3}{dP_1} = \frac{R_3}{R_1} \frac{R_1 - \sigma_1}{R_3 - \sigma_1} < 0 \quad \text{since} \quad R_1 \geq \sigma_1 \geq R_2 \geq R_3$$

The images of this route in terms of concentration profiles or histories are given in the top right of Figure 2. Along MB, P_1 and P_2 go simultaneously to zero while P_3 slightly increases. Then P_3 remains constant (commutation from Γ_1 to Γ_2 at B) and then vanishes abruptly as it does in nonreactive linear chromatography (Γ_2 path along BO). It must be noticed that fixed points in the $\mathcal{P}_K$ space correspond to plateaus in the concentration profiles and conversely that the paths from one point to the other are represented by concentration changes in the profiles.

In most cases, the properties of the roots of $G(\sigma) = 0$, Equation (14), and the vanishing species theorem are sufficient to predict the qualitative features of the concentration profiles. Indeed, the quantitative behavior requires a numerical solution of (14) and (17) to be known. For example, the numerical solution gives the projections of the Γ curves in the plane $P_1 - P_3$ as shown on the left of Figure 2 (P_2 is deduced from the knowledge of P_1 and P_3 by the mass action law). It can be seen that the unique route MBO is consistent with what has been said previously about the properties of the chromatograms. If we assume that the initial state is O and the final state is M, the same reasoning applies. P_2 and P_3 vanish on a Γ_2 curve at A, where the P_1 axis is a Γ_1 curve. Hence the route is OAM, and it gives the profiles and histories shown on the bottom right of Figure 2.

In this peculiar example, it can be shown that σ decreases along the routes MBO and OAM. Unfortunately, this is not a general result. The order of the Γ curves insures that σ decreases when a jump from a Γ_k to a Γ_{k+1} curve occurs at a specified point, but nothing is said about the decreasing behavior of σ along a specified Γ curve. For instance, let us consider a piece of Γ curve between M_I and M_F along which σ increases from M_I to M_F. The related profile is shown on Figure 3. It is clear that it has no physical meaning. This is a classical situation in nonlinear chromatography. The nonphysical profile must be replaced by a shock (discontinuous and stable profile) which is not a solution of the differential mass balance Equations (4) but a solution of mass balance equations in terms of finite differences. Let ΔP_i be the difference of the concentrations of P_i on each side of the shock, and let us assume that the shock travels a distance dx along the column axis during a time dt. The hypothetical chemical entity $\nu_j P_i - \nu_i P_j$ is neither consumed nor produced by the reaction, and the classical mass balance equation across a shock in the absence of chemical reaction can be applied:

$$u\left(\nu_j \frac{\Delta P_i}{dx} - \nu_i \frac{\Delta P_j}{dx} \right) + \nu_j(1 + \alpha_i) \frac{\Delta P_i}{dt} - \nu_i(1 + \alpha_j) \frac{\Delta P_j}{dt} = 0 \qquad (18)$$

Let $\sigma_D \equiv dx/dt$ be the velocity of the shock. Equation (18) leads to

$$\nu_j \Delta P_i - \nu_i \Delta P_j + \sigma_D \left[\nu_j \frac{\Delta P_i}{R_i} - \nu_i \frac{\Delta P_j}{R_j} \right] = 0 \qquad (19)$$

or

$$\frac{\Delta P_i}{\Delta P_j} = \frac{\nu_i R_i}{\nu_j R_j} \, \frac{R_j - \sigma_D}{R_i - \sigma_D} \qquad (20)$$

A striking analogy can be seen between Equations (20) and (14). If we write the mass action law on each side of the shock, we get

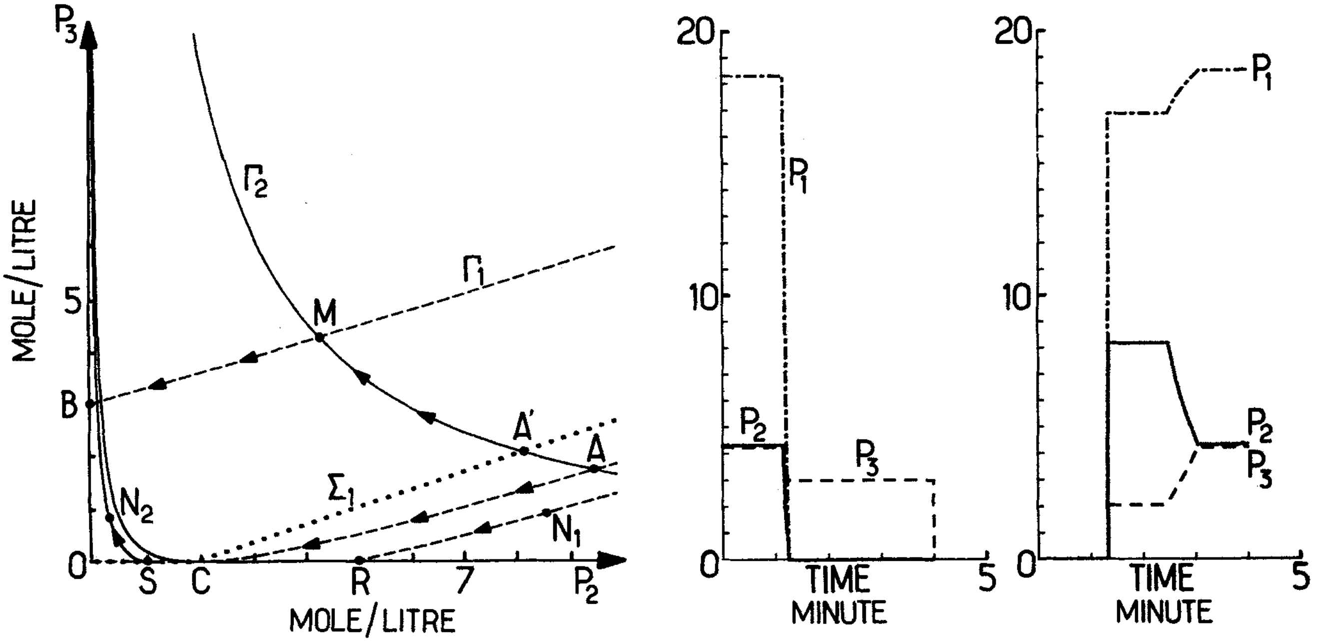

Figure 4. Reactive adsorption: $P_1 \rightleftarrows P_2 + P_3$. Left: projection of the Γ curves on the $P_2 - P_3$ plane. The arrows point toward the direction of decreasing σ. The route MBO gives the chromatogram of the middle of the figure. The route OCAM is irrelevant, since σ increases along OA. Instead, a shock is created, and it is represented by the Σ_1 curve from O to A'. The true route is OA'M, and the related chromatogram is given at the right of the figure. The route N_1RCSN_2 is discussed on Figure 5 (R_1 = 1. R_2 = 0.5. R_3 = 0.25. K = 1 mole/l.)

$$\Delta[\prod_i P_i^{\nu_i}] \equiv \prod_i (P_i + \Delta P_i)^{\nu_i} - \prod_i P_i^{\nu_i} = 0$$

$$\text{or} \quad K = \prod_i P_i^{\nu_i} = \prod_i (P_i + \Delta P_i)^{\nu_i} \qquad (21)$$

Equation (21) is the same formula as (15) expressed in terms of finite differences. Equations (20) and (21) allow us to draw in the $\mathscr{P}_K$ space a grid of Σ curves emanating from a given point. It is important to note that this grid depends upon the given starting point. This is not the case for the Γ curves which are defined by differential equations. Hence, if a shock is involved in the composition route, the Σ curves must be constructed according to the peculiar point at which the shock appears. In other words, the Σ curves depend upon the peculiar step composition change applied to the inlet of the column.

Now let us study the example (Figure 4):

$$P_1 \rightleftarrows P_2 + P_3$$

Here the reactant is first eluted, and then the products are eluted. The vanishing species theorem tells us that P_1 and P_2 vanish on a Γ_1 curve, and hence the P_3 axis is a Γ_2 curve. On the other hand, when P_1 and P_3 vanish on the P_2 axis, we have

$$i = 3, \quad j = 1 \quad \nu_i + \nu_j = 0$$

From the third part of the vanishing species theorem, P_2 and P_3 vanish along a Γ_k curve with $2 \leq k \leq 1$. This means that either Γ_1 or Γ_2 ends on the P_2 axis, according to the value of σ solution of $K = -P_2R_3(R_1-\sigma)/R_1(R_3-\sigma)$. If P_2 is small enough, σ must be close to R_3 and $\sigma - \sigma_2$. The Γ curve along which P_1 and P_3 vanish is a Γ_2 curve, and the P_2 axis near the origin is a Γ_1 curve. At the point C on the P_2 axis, where $\sigma_2 = R_2$ [the location of C is given by $K = -P_2R_3(R_1-R_2)/R_1(R_3-R_2)$], the P_2 axis becomes a Γ_2 curve. But along the P_2 axis, σ is constant since it accounts for nonreactive chromatography. Hence, at C, we must have $\sigma_1 = \sigma_2 = R_2$. We shall call such a point C a characteristic or watershed point (after Helfferich); it is a peculiar point at which $G(\sigma) = 0$ has a double root $\sigma_{k-1} = \sigma_k = R_k$. We shall see later the importance of this point. If we solve Equations (14) and (17), we can draw the projections of the Γ curves in the $P_2 - P_3$ plane as shown on Figure 4. From Equations (14) and (17), it can be shown by straightforward but tedious calculations that the Γ curves have no inflection point, and d^2P_3/dP_2^2 is positive. But we have

$$\frac{d^2P_3}{dP_2^2} = \frac{R_3}{R_2}\,\frac{R_2 - R_3}{(R_3 - \sigma)^2}\,\frac{d\sigma}{dP_2} > 0 \quad \text{and} \quad R_2 > R_3 \quad (22)$$

Hence

$$\frac{d\sigma}{dP_2} > 0 \quad \text{along every } \Gamma \text{ curve} \qquad (23)$$

Equation (23) allows us to draw on Figure 4 the arrows pointing toward the direction of decreasing σ. If the step composition change involves a path in the direction of the arrows, the solution is valid. On the contrary, if a path is in the opposite direction of the arrows, the continuous mass balance equations do not hold, and the Γ curve must be replaced by a Σ curve accounting for a shock. Now let us deal with the composition route originating at M and ending at the origin. Along MBO, σ decreases and the chromatograms are those of the middle of Figure 4. The case of a positive step composition change giving a route from O to M is more complicated. At a first glance, OCAM seems to be a possible route. Unfortunately, σ increases from O to A, and thus a shock is involved. The Γ_1 curve emanating from O must be replaced by a Σ_1 curve emanating from (or ending at) the origin. It gives the route OA'M which is composed of a shock on OA' and a spreading transition on A'M. (In this example, the Σ_1 curve emanating from the origin has a common segment with the P_2 axis along OC.) The related chromatogram is given on the right of Figure 4. Now let us look at the peculiar behavior of the Γ curves due to the characteristic point C. Let us assume that the initial state is N_1 and the final state is N_2. The only possible route is N_1RCSN_2. It is surprising to see that four pieces of Γ curves are needed, and moreover that a jump from a Γ_2 to a Γ_1 is involved at C. This last fact is not contradictory with what has been said previously because along SCR, σ remains constant (hence does not increase). The related chromatogram, shown on Figure 5, has a curious property. Although the initial and final states do not involve zero concentrations, P_1 and P_2 vanish during a finite time. Tondeur (1970) showed a similar behavior in ion exchange governed by mass action equilibria with affinity inversions, and it has been also pointed out in the competiton between a concentration and a thermal wave in adiabatic nonlinear chromatography (Rhee, 1970; Sweed, 1978). With a suitable recycle system, it would probably be possible to feed the reactor with a mixture of the three species and to collect pure P_2.

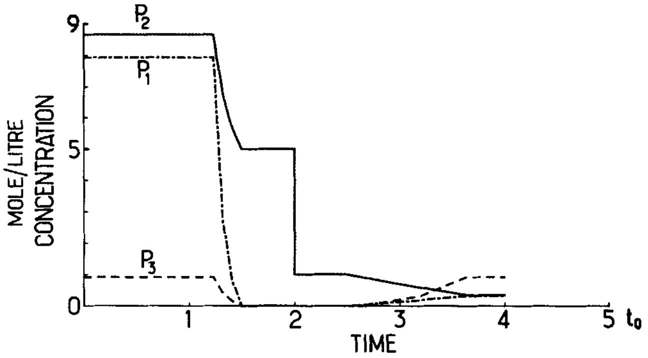

Figure 5. The composition route from N_1 to N_2 (see Figure 4) implies a subroute on the P_2 axis along which P_3 and P_1 are zero. Hence from $t = 1.5$ to $t = 2.5$, pure P_2 is eluted, although the column is fed with the three species. A suitable recycle system at the outlet of the column would allow one to collect pure P_2 and to recycle a part or the whole of P_1 and P_3 effluent in the feed stream. This is a new property of the adsorptive reactor which has never been pointed out earlier. (Concentrations in mole/liter, time normalized by the retention time of an unretained solute.)

EXPERIMENTAL CONFIRMATIONS AND SHORTCOMINGS OF THE THEORY

We have studied the esterification reaction of acetic acid by ethanol catalyzed by a cation exchange resin (SPC 118 Bayer) carried out in a liquid solid chromatographic reactor at 50°C. The main features of the experiments are described in a recent paper by Sardin and Villermaux (1979). In order to illustrate our theory, we chose an experiment in which the column is fed with a solution of ethanol (C = 1.4 mole/l) and water (C = 1.0 mole/l) in dioxane. At time $t = 0$, a positive step of acetic acid is performed while the composition of the feed with respect to water and ethanol is kept constant. The effluent is sampled by a fraction collector, and the composition is analyzed by gas chromatography. The results are shown on Figure 6. The concentration of water was found to be nearly independent of time because its retention time is very high. It will be supposed that it is actually constant. The adsorption process is slightly nonlinear, and we choose average values for the capacity factors of each species (ethanol $\alpha = 1.3$ between 1.5 and .5 moles/l, acetic acid $\alpha = 0.0$, ethyl acetate $\alpha \sim 0.1$). As the concentration of water is constant, the apparent stoichiometric relationship is ethanol + acetic acid ⇄ ethyl acetate, $K = 2$/concentration of water. With the previous notations, it is written as

$$P_3 + P_1 \rightleftarrows P_2$$

The projections of the Γ curves in the $P_3 - P_1$ plane are shown on Figure 7. The route consisting of Γ curves from M_I to M_F is irrelevant, since σ increases. Hence, two shocks are involved. They are the images of two Σ curves in Figure 7 which are very close to the Γ curves. These Σ curves give the discontinuous profiles on Figure 6 which are in pretty good agreement with the experimental curves if it is kept in mind that the dispersive and mass transfer processes are neglected in our theory. Nevertheless, the shape of the ethanol steps is not satisfactory. This may be explained by the nonlinear isotherm of this component and by the chemical kinetic limitation which is revealed by the apparent thermodynamic equilibrium constant in the final state which is found to be 2 instead of 4 at 50°C. On the other hand,

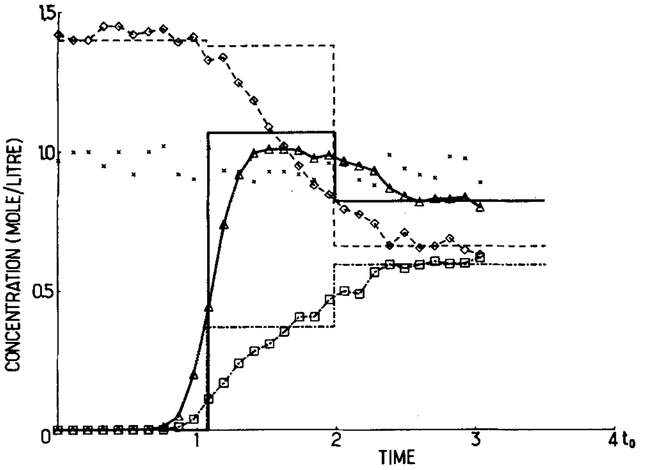

Figure 6. Esterification of acetic acid (□ —.—.— □) by ethanol (◇ — — — — ◇) to ethyl acetate (△ . . . . △) and water (X X X). The concentration of water is independent of time (~ .95 mole/l). The experimental chromatograms are interpreted by two successive shocks which are in pretty good agreement with the experimental data points except for ethanol. The theory accounts for the overshoot of ethyl acetate. The theoretical curves are only a sketch of the reality, since the dispersive and kinetic processes round off the sharp fronts, but the qualitative features of the chromatograms are good (time is normalized by the retention time of acetic acid).

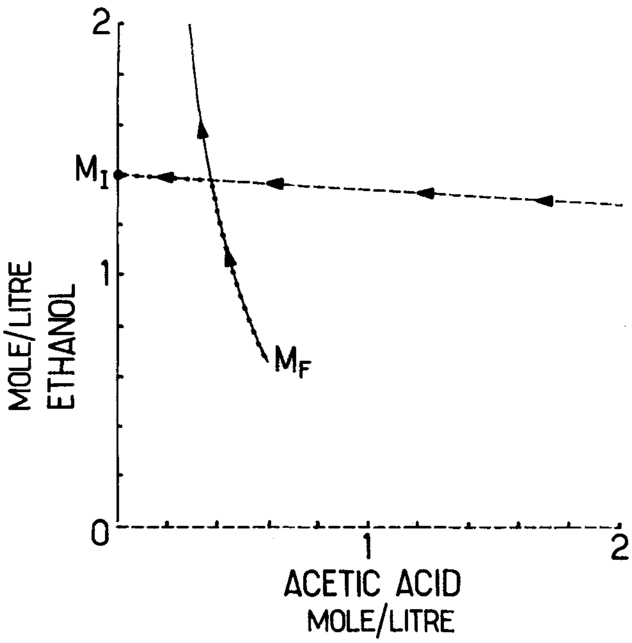

Figure 7. Projections of the Γ curves in the plane acetic acid—ethanol. From M_I to M_F, σ increases and Σ curves (. . . .) must be considered instead of Γ curves (— — — — or ————). In this case they are very close to the Γ curves. (The arrows point toward the direction of decreasing σ, concentrations in mole/liter.)

the theory takes into account the overshoot of ethyl acetate which proves that the model is a good one, at least from a qualitative point of view.

Let us now consider the example of the dehydrogenation of cyclohexane to benzene carried out in a 1 m length stainless steel tube packed with a 0.3% platinum catalyst on alumina which acts as a chromatographic adsorbent. The effluents are analyzed by continuous mass spectrometry which gives the chromatograms of each species in the mixture. A detailed description of the apparatus is given in a paper by Schweich and Villermaux (1979). The experiment consists of a positive step followed by a negative step of cyclohexane in pure nitrogen at 220°C. The experimental curves are shown on Figure 9. In this case, two assumptions of the theory are not true: the adsorption isotherm of benzene is not linear and the volumetric flow rate varies along the column axis as a consequence of the chemical expansion. It is obvious that a quantitative interpretation of the experiment in terms of the theory would be suspect. However, we may choose average values of the capacity factor (hydrogen $\alpha = 0$, cyclohexane $\alpha = 3.85$, benzene $\alpha \sim 10.7$). This example

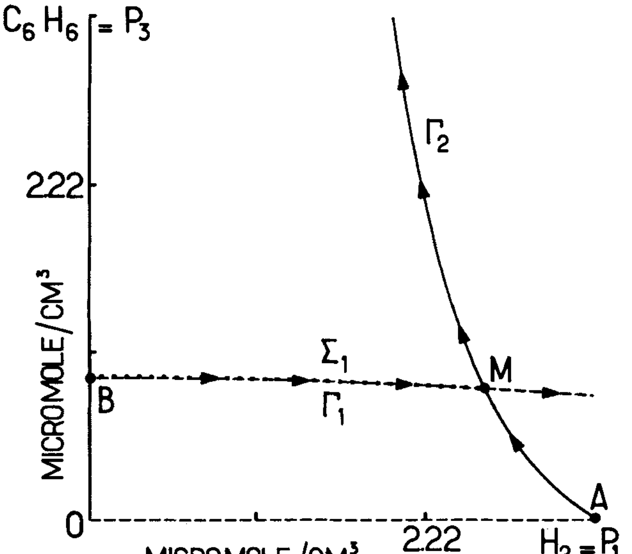

Figure 8. Projections of the Γ curves in the plane H_2–C_6H_6 for the dehydrogenation of cyclohexane to benzene. The unit of concentration is the micromole per cubic centimeter. (The arrows point toward the direction of decreasing σ.)

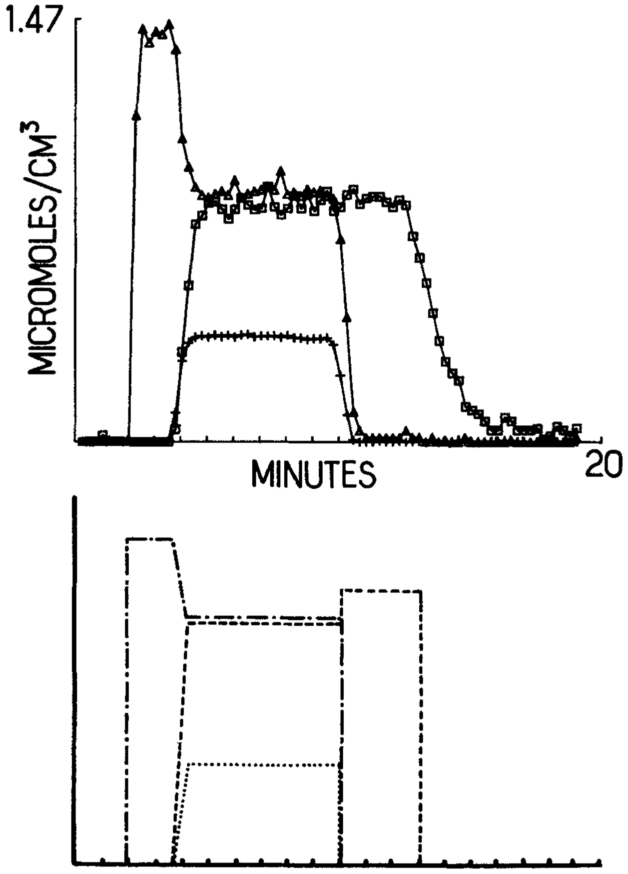

Figure 9. Cyclohexane (exp + ——— +, theory . . . .) dehydrogenation to benzene (exp □ ——— □, theory — — —) and hydrogen (exp △ ———△, theory —.—.—) carried out at 220°C on a platinum on alumina catalyst. The prediction of the theory is qualitatively good except for the height of the hydrogen peak and the tail of benzene. (Same scale for the two figures. H_2 is divided by 3.)

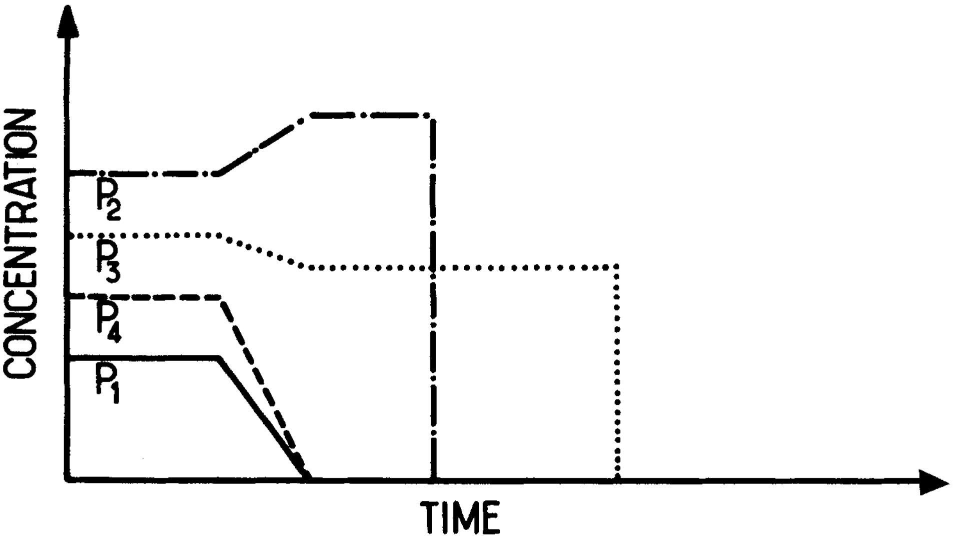

Figure 10. Reaction $P_1 + P_2 \rightleftarrows P_3 + P_4$. Peculiar composition change showing the possibility to elute the most retained solute P_4 together with the less retained one P_1. This chromatogram is predicted from the vanishing species theorem and Equation (14) only (arbitrary units).

gives an illustration of the second part of the vanishing species theorem. With the previous notation, the stoichiometric relationship is

$$P_2 \rightleftarrows P_3 + 3P_1$$

$$P_2 = C_6H_{12}, \quad P_3 = C_6H_6, \quad P_1 = H_2$$

When P_2 and P_1 vanish, $\nu_i(\nu_i + \nu_j) = -1\,(-1 + 3)$ is negative. Thus, P_2 and P_1 vanish along a Γ_1 curve. The projection of the Γ curves on the $P_3 - P_1$ plane is shown on Figure 8. Once more the arrows point toward the direction of decreasing σ. The positive step is accounted for by the route OAM along which σ decreases. The negative step is not represented by Γ curves, since σ would increase along the Γ_1 curve emanating at M. Hence a shock is involved. It is accounted for by the Σ_1 curve which is very close to the Γ_1 curve. This route gives the theoretical chromatogram of Figure 9. As the time at which the experiment begins is not known, the theoretical curves are located in such a way that the second transition is in good agreement with the experimental one. The prediction of the theory is in good agreement with the experiment for the positive step except for the height of the hydrogen peak. For the negative step, the nonlinear adsorption isotherm of the benzene erases the overshoot and induces a tail in place of an abrupt concentration change which would account for linear adsorption. In the next section we shall summarize the problems, the solutions of which would improve the quantitative predictions of the theory.

DISCUSSION

We have shown that the vanishing species theorem allows us to predict the order of elution of the species in simple cases. Moreover it gives, together with Equation (14), the shape of the chromatograms. The nature of the transitions (shock or spreading transition) is much more difficult to determine. Tedious calculations or numerical integration procedures are needed. Fortunately, the nature of the transitions does not affect the elution order of the species, and hence the vanishing species theorem may give useful information.

Let us give the general procedure which must be followed to get the qualitative shape of the chromatograms:

1. Find all the pairs (P_iP_j) of one reactant and one product and calculate $\nu_i(\nu_i + \nu_j)$.
2. If $\nu_i(\nu_i + \nu_j) > 0$ (< 0), $\Gamma_{i-1}(\Gamma_j)$ is the Γ curve along which P_i and P_j vanish simultaneously. All the other Γ curves are straight lines at this point.
3. If $\nu_i + \nu_j = 0$, calculate σ solution of

$$K = \left(\frac{\nu_i R_i}{\nu_j R_j}\,\frac{R_j + \sigma}{R_i - \sigma}\right)^{\nu_i} \prod_{l \neq i,j} P_l^{\nu_l}$$

If $R_k \geq \sigma \geq R_{k+1}$ then $\sigma = \sigma_k$ and P_i and P_j vanish along a Γ_k curve. The characteristic or watershed loci are determined by the previous relationship with $\sigma = R_k$, $(k = j$ to $i - 1)$.

4. Draw qualitatively the Γ_k curves emanating from the regions where P_i and $P_j = 0$ according to the three preceding steps. Along these Γ_k curves, the increasing behavior of P_r with respect to P_s is known from

$$\frac{dP_r}{dP_s} = \frac{\nu_r R_r}{\nu_s R_s}\,\frac{R_s - \sigma_k}{R_r - \sigma_k}$$

the sign of which depends only on k, r and s.

5. Deduce from the grid of Γ curves drawn in step 4 the shape of the chromatograms assuming spreading transitions.
6. If necessary, solve numerically Equations (14) and (17) to get quantitative predictions and locate the shocks.

In some cases, this procedure is not required to find out the properties of the reactor with respect to the chemical reaction. Let us take the following example which illustrates what we call the chemical pumping effect:

$$P_1 + P_2 \rightleftarrows P_3 + P_4$$

From the third case of the vanishing species theorem, it is deduced that P_1 and P_4, the least and the most retained species, vanish along either Γ_1, Γ_2 or Γ_3. Hence, there exists a region in the space $\mathscr{P}_K$ in which P_1 and P_4 vanish along a Γ_1 curve. Let M_I be an initial state in this region, and let us assume that we want to go to a final state located at the origin of $\mathscr{P}_K$. The route consists of a piece of Γ_1 along which P_1 and P_4 vanish, followed by a piece of Γ_2 and Γ_3 curves along which nonreactive adsorption takes place. The chromatogram is thus as shown on Figure 10 (it is supposed that there are no shocks). The important result is that P_4 is eluted together with P_1, in spite of the fact that it is the most retained component. Indeed, if M_I is chosen in another region than the previous one, P_4 may be eluted later. This peculiar behavior of the adsorptive reactor is due to the relative influence of the chromatographic properties of the species and of the stoichiometric numbers. The influence of the latter can be very important. Let us take $\nu_4 = 0.5$ in the preceding stoichiometric relationship. When P_1 and P_4 vanish, $\nu_i(\nu_i + \nu_j) = \nu_4(\nu_1 + \nu_4) = 0.5(-1 + 0.5) = -0.25$. We are in the second case of the vanishing species theorem, and hence P_1 and P_4 vanish always along a Γ_1 curve and whatever M_I the chemical pumping effect occurs. It must be noticed that this effect is strictly analogous to the selectivity reversal which was dealt with in ion exchange accompanied by chemical reaction, by Golden et al. (1974). This behavior may be of some interest in practical separations, especially those for which P_3 and P_4 are separated with difficulty. Probably other peculiar properties of the chromatographic reactor could be discovered by the mean of the vanishing species theorem.

It has been clearly shown, especially with the experimental examples, that the theory is good from a qualitative point of view but sometimes fails in the quantitative predictions which highly depend on the assumptions made throughout this paper. For example, what happens when dispersive and mass transfer processes, kinetic rate limitations, nonlinear isotherms, velocity variations due to chemical expansion, or finite pulse injection are considered?

It is beyond the scope of this introductory paper to give complete answers to these questions, as far as they are known. We shall only outline the theoretical considerations in which further progress is required. Firstly, dispersive and kinetic processes (mass transfer or slight reaction rate limitation) do not affect to a high extent the spreading transitions. On the other hand, the shocks are spread (see Figure 6). The method developed by Rhee et al. (1971, 1972) can be applied in such problems even for the part played by the reaction rate. It seems theoretically possible to measure reaction rate constants from the broadening of the shocks, but the results will probably be falsified by the broadening effects of dispersive and mass transfer processes. The case of a finite pulse injection is more complicated, since two successive concentration changes are involved, and hence Lax's theorem cannot be used when interferences between transitions occur. The mathematical method of characteristics must be used to get further analytical results (see, for example, Jeffrey, 1976). As in multicomponent chromatography (Helfferich and Klein, 1970; Rhee, 1978), the interference between two shocks or a shock and a spreading transition may probably be described by an analytical method. On the other hand, the interference between spreading transitions requires a numerical method. It seems to us that if an h transformation, analogous to that introduced by Helfferich (1967), exists, this problem probably has an analytical solution.

It would be of interest to find some analytical results concerning the pulse injection of a reactant undergoing a reversible decomposition reaction, since it would give the best design of a chromatographic reactor that would force the reaction to completion.

The problem of variable velocity is even more complicated, since Equations (2) are no longer valid and must be replaced by

$$P_i \frac{\partial u}{\partial x} + u \frac{\partial P_i}{\partial x} + \frac{\partial P_i}{\partial t}(1 + \alpha_i) = \nu_i r \qquad (24)$$

together with a relationship governing the flow (Darcy's law, for example). We cannot find methods other than numerical procedures to solve Equation (24). It may be that some experimental results suggest simplifying assumptions such that $P_i\, \partial u/\partial x$ is small as compared to the other terms.

The problem of nonlinear isotherms is easier to handle. Firstly, let us see when the linear isotherm assumption fails. When the reactor is used as an analytical tool, it is probably possible to find physical conditions for which the assumption is true. If the reactor is used as a production tool, and if the species are in a sufficiently small amount, as for instance in rare earth processing, it is true again. But if a large amount of reactants (or a small amount of adsorbant) are required as a consequence of economic considerations, the adsorption isotherms will become nonlinear, and the theory can no longer predict even the shape of the chromatograms. This phenomenon is surely the explanation for the shape of the benzene vanishing step in Figure 9. This is evidenced by the work of Wetherhold et al. (1974) who studied the hydrolysis of methyl formate. Our theory allows us to locate the transitions in good agreement with their experimental curves, but we could never find the overshoot they observed on the methanol chromatogram. Their model, assuming Freundlich isotherms, accounts for this overshoot. Let us show briefly how the theory may be adapted to nonlinear isotherms, assuming an adsorption of Langmuir type:

$$Q_i = \alpha_i \frac{P_i}{D},\ D = 1 + \sum_i a_i P_i\ (a_i \text{ proportional to } \alpha_i) \qquad (25)$$

Using Lax's theorem, we find instead of Equations (14) and (17)

$$\frac{dP_i}{dP_j} = \frac{\nu_i R_i}{\nu_j R_j}\, \frac{R_j - \sigma}{R_i - \sigma} - \frac{R_i \sigma}{R_i - \sigma}\, \frac{\nu_j Q_i - \nu_i Q_j}{\nu_j u D} X$$

$$X = \sum_i \frac{\nu_i R_i}{\nu_j R_j}\, \frac{R_j - \sigma}{R_i - \sigma}\, a_i \Bigg/ \left[1 + \sum_i \frac{R_i \sigma}{R_i - \sigma}\, \frac{\nu_j Q_i - \nu_i Q_j}{\nu_j u D}\, a_i\right] \qquad (26)$$

$$R_i = \frac{u}{1 + \dfrac{Q_i}{P_i}}$$

$$G(\sigma) \equiv \sum_k \frac{\nu_k}{P_k} \left[\frac{\nu_k R_k}{R_k - \sigma} - \frac{\sigma}{uD} \sum_i \frac{R_i R_k}{(R_i - \sigma)(R_k - \sigma)}\, a_i(\nu_i Q_k - \nu_k Q_i) \right] = 0 \qquad (27)$$

The proof is given in the Appendix. The Γ curves can be drawn from Equations (26) and (27), but no qualitative features of the chromatograms can be known, since the three properties of the Γ curves and $G(\sigma)$ together with the vanishing species theorem are no longer valid. We are presently working on this subject, and we are trying to find a general theorem in the case of nonlinear isotherms which will give, without any numerical procedure, the shape of the chromatograms. Some preliminary results are already available and will be the subject of future papers.

NOTATION

$G(\sigma)$ = characteristic equation
K = chemical equilibrium constant
$M_{I,F,0}$ = points in the spaces $\mathcal{P}$ and $\mathcal{P}_K$
P_i = component i or concentration of component i in the fluid phase
$\mathcal{P}$ = space of concentrations
$\mathcal{P}_k$ = space of the concentrations which obey the mass action law
Q_i = amount of component i in the stationary phase in equilibrium with P_i
R_i = apparent velocity of component i
$r_i = \nu_i r$ = rate of generation of species i
t = time
u = carrier fluid velocity
x = length

Greek Letters

α_i = capacity factor of the adsorbent with respect to component i
Γ_i = composition path
ν_i = stoichiometric number
σ_i = root of the characteristic equation
σ_D = velocity of a shock
Σ_i = composition path of a shock
θ = parameter along the composition paths

LITERATURE CITED

Chieh, Chu, and L. C. Tsang, "Behavior of a Chromatographic Reactor," *Ind. Eng. Chem. Proc. Design Develop.*, **10**, No. 1 (1971).

Dinwiddie, *U.S. Patent 3,243,472* (1966).

Golden, F. M., K. I. Shiloh, G. Klein and T. Vermeulen, "Theory of

Ion-Complexing Effects in Ion-Exchange Column Performance," *J. Phys. Chem.*, **78**, 926 (1974).

Gore, G. E., "Performance of Chromatographic Reactors in Cyclic Operations," *Ind. Eng. Chem. Proc. Design Develop.*, **6**, No. 1, 10 (1967).

Hattori, T., and Y. Murakami, "Study on Pulse Reaction Technique. I. Theoretical Study," *J. Catalysis*, **10**, 114 (1968).

Helfferich, F., "Multicomponent Ion Exchange in Fixed Beds," *Ind. Eng. Chem. Fundamentals*, 6, 362 (1967).

Helfferich, F. and G. Klein, "Multicomponent Chromatography. Theory of Interference," *Chromatographic Science Series*, Vol. 4, Marcel Dekker, New York (1970).

Jeffrey, A., "Quasilinear Hyperbolic Systems and Waves," *Research Notes in Mathematics*, Pitman (1976).

Klein, G., "Ion Exchange Accompanied by a Chemical Reaction," in *Percolation Processes, Theory and Applications*, NATO Advanced Study Institute, Portugal (July, 1978).

Klein, G., D. Tondeur and T. Vermeulen, "Multicomponent Ion Exchange in Fixed Beds," *Ind. Eng. Chem.*, **6**, 339 (1967).

Kocirik, M., "A Contribution to the Theory of Chromatography. Linear Non-Equilibrium with a Chemical Reaction of the First Order," *J. Chrom.*, **30**, 459 (1967).

Langer, S. H. and J. E. Patton, "A Gas Chromatographic Reactor Study of the Kinetics of Dicyclopentadiene Dissociation," *J. Phys. Chem.*, **76**, No. 15, 2159 (1972).

Lax, P. D., *Comm. Pure Appl. Math.*, **10**, 537 (1957).

Magee, E. M., *Canadian Patent 631,882* (1961).

Magee, E. M., "The Course of a Reaction in a Chromatographic Column," *Ind. Eng. Chem. Fundamentals*, **2**, No. 1 (1963).

Oster, Y. T., Keresztes-Nagy, R. F. Mais, J. Becktel and J. F. Zaroslinski, "Effect of Temperature on Binding of Warfarin by Human Serum Albumin," *J. Pharm. Sci.*, **65**, No. 11, 1673 (1976).

Rhee, H. K., and N. R. Amundson, "An Analysis of an Adiabatic Adsorption Column: Part I. Theoretical Development," *Chem. Eng. J.*, **1**, 241 (1970).

Rhee, H. K., N. R. Amundson, and B. J. Bodin, "A Study of the Shock Layer in Equilibrium Exchange Systems," *Chem. Eng. Sci.*, **26**, 1571 (1971).

Rhee, H. K., and N. R. Amundson, "A Study of Shock Layer in Nonequilibrium Exchange Systems," *ibid.*, **27**, 199 (1972).

Rhee, H. K., "Equilibrium Theory of Multicomponent Chromatography," in *Percolation Processes, Theory and Applications*, NATO Advanced Study Institute, Portugal (July, 1978).

Sardin, M., and J. Villermaux, "Esterification Catalysée par une Resine Echangeuse de Cations dans un Reacteur Chromatographique," *Nouv. J. Chimie*, 3, 4, 255 (1979).

Schweich, D., and J. Villermaux, "The Chromatographic Reactor. A New Theoretical Approach," *Ind. Eng. Chem. Fundamentals*, **17**, 1 (1978).

Schweich, D., and J. Villermaux, "Measurement of Chemical Equilibrium Constants by Continuous Mass Spectrometry of Transient Compositions at the Outlet of a Pulsed Reactor," *Anal. Chem.*, **51**, 77 (1979).

Shiloh, K. I., M.S. thesis, Univ. Calif., Berkeley (1966).

Sweed, N. H., "Nonisothermal and Nonequilibrium Fixed Bed Sorption," in *Percolation Processes, Theory and Applications*, NATO Advanced Study Institute, Portugal (July, 1978).

Tondeur, D., Thèse d'université Nancy, France (1969).

Tondeur, D., and G. Klein, "Multicomponent Ion Exchange in Fixed Beds. Constant Separation Factor Equilibrium," *Ind. Eng. Chem.*, **6**, 351 (1967).

Tondeur, D., "Theory of Ion Exchange Columns," *Chem. Eng. J.*, **1**, 337 (1970).

Villermaux, J., "The Chromatographic Reactor," in *Percolation Processes, Theory and Applications*, NATO Advanced Study Institute, Portugal (July, 1978).

Wetherhold, R. G., E. H. Wissler, and R. P. Bischoff, "An Experimental and Computational Study of the Hydrolysis of Methyl Formate in a Chromatographic Reactor," *Adv. Chem. Ser.*, **133**, 181 (1974).

APPENDIX: PROOF OF THE THEOREM OF VANISHING SPECIES

Let M_0 be a point where $P_i = P_j = 0$ with $\nu_i\nu_j < 0$. At M_0 there are $n - 2$ Γ curves accounting for nonreactive adsorption and only one, say Γ_k relative to the reaction. When P_i and P_j go to zero along Γ_k, we have

$$\frac{P_i}{P_j} \to \frac{dP_i}{dP_i} = \frac{\nu_i R_i}{\nu_j R_j}\,\frac{R_j - \sigma_k}{R_i - \sigma_k} \quad \text{(valid in the neighborhood of } M_0) \tag{A1}$$

P_i/P_j is positive, ν_i/ν_j is negative, and then at any point of Γ_k close to M_0, we must have $R_i \leq \sigma_k \leq R_j$. Hence, some of the nonreactive Γ curves must satisfy

$$\sigma_1 = R_1, \quad \sigma_2 = R_2, \ldots\ldots, \sigma_{j-1} = R_{j-1} \tag{A2}$$

$$\sigma_{n-1} = R_n, \ldots\ldots\ \sigma_i = R_{i+1} \tag{A3}$$

Within $[R_j, R_i]$ we may have either $\sigma_l = R_l$ or $\sigma_l = R_{l-1}$, depending on the value of l with respect to k. k is such that $i - 1 \geq k \geq j$ from (A2) and (A3). Now assume that ν_i and $\nu_i + \nu_j$ are positive. From the mass action law we have

$$K = \left(\frac{P_i}{P_j}\right)^{\nu_i} P_j^{\nu_i+\nu_j} \prod_{l \neq i,j} P_l^{\nu_l} \tag{A4}$$

Since P_j goes to zero, P_i/P_j goes to infinity. The result is true again if ν_i and $\nu_i + \nu_j$ are negative. From (A1), σ_k goes to R_i. But only σ_{i-1} and σ_i can go to R_i. As $\sigma_i = R_{i+1}$, we must have $k = i - 1$, and the first part of the theorem is proved. The same reasoning is valid to prove the second part; *in this case,* $\nu_i(\nu_i + \nu_j) < 0$ *implies* $\sigma_k \to R_j$ *since* $P_i/P_j \to 0$, and $k = j$ is the unique solution. To prove the third part, let us combine (A4) with (A1) when $\nu_i + \nu_j = 0$:

$$K = \left[\frac{\nu_i R_i}{\nu_j R_j}\,\frac{R_j - \sigma_k}{R_i - \sigma_k}\right]^{\nu_i} \prod_{l \neq i,j} P_l^{\nu_l} \tag{A5}$$

The value of σ_k depends upon the P_l components ($l \neq i,j$) of M_0 which are arbitrary. Hence, σ_k may take any value between R_j and R_i, since $(R_j - \sigma_k)/(R_i - \sigma_k)$ is a monotonic function of σ_k. This means that every Γ_k curve for which $i - 1 \leq k \leq j$ is a possible way for P_i and P_j to vanish.

This proof could be extended to the case of nonlinear isotherms provided that the characteristic equation of the multicomponent chromatoghaphic process is known. If ω_k is the root of this nonreactive characteristic equation, the comparison between σ_k and ω_k would give rise to the theorem for the peculiar case of isotherms which have been considered.

Proof of Equations (25) and (26)

Using the same way leading to (12), we get

$$\left(\frac{dx}{dt}\right)_\theta \equiv \sigma$$

$$= u\,\frac{\nu_j \dfrac{dP_i}{d\theta} - \nu_i \dfrac{dP_j}{d\theta}}{\nu_j \dfrac{dP_i}{d\theta} - \nu_i \dfrac{dP_j}{d\theta} + \nu_j \dfrac{dQ_i}{d\theta} - \nu_i \dfrac{dQ_j}{d\theta}} \tag{A6}$$

with $Q_i = \alpha_i P_i/D$ and $R_i = u/(1 + Q_i/P_i)$ and using P_j as the parameter:

$$\frac{dP_i}{dP_j} = \frac{\nu_i R_i}{\nu_j R_j}\,\frac{R_j - \sigma}{R_i - \sigma} - \frac{R_i \sigma}{R_i - \sigma}\,\frac{\nu_j Q_i - \nu_i Q_j}{\nu_j u D}\,\frac{dD}{dP_j} \tag{A7}$$

Equation (A7) is not similar to (14), since $dD/dP_j = \sum_i a_i\, dP_i/dP_j$. Let us write (A7) as

$$\frac{dP_i}{dP_j} = A_{ij} + B_{ij}\frac{dD}{dP_j} \tag{A8}$$

If we multiply (A8) by a_i and sum with respect to i, we get

$$\frac{dD}{dP_j} = \sum_i a_i \frac{dP_i}{dP_j} = \sum_i a_i A_{ij} + \frac{dD}{dP_j}\sum_i a_i B_{ij} \tag{A9}$$

Hence

$$\frac{dD}{dP_j} = \sum_i \frac{\nu_i R_i}{\nu_j R_j}\,\frac{R_j - \sigma}{R_i - \sigma}\,a_i \Bigg/ \left[1 + \sum_i \frac{R_i \sigma}{R_i - \sigma}\,\frac{\nu_j Q_i - \nu_i Q_j}{\nu_j u D}\,a_i\right] \tag{A10}$$

Equations (A10) and (A8) give Equation (25). To get Equation (26), we use Equation (15) together with Equation (25).

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