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Numerical Simulation of Band Propagation in Nonlinear Chromatography

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Abstract

A model for the propagation of a finite concentration zone in a chromatographic column is discussed for the case of a single component sample. This model is based on the modern theory of nonlinear hyperbolic systems of partial differential equations. It accounts for the nonlinear effects due 1) to the thermodynamics of solute–stationary phase equilibrium (i.e., the nonlinearity of the equilibrium isotherm), 2) to the interaction between radial mass transfer and flow velocity (the sorption effect in gas chromatography), and 3) to the pressure gradient along the column (in gas chromatography). Numerical results are obtained by using the Godunov method. The column is divided into a large number of short segments. At each corresponding point a sequence of Riemann problems (a concentration step at each time interval) is solved. The stability of this procedure depends strongly on the ratio *dz*/*dt* of the elementary column segment length to the time interval. The main advantage of this method over previous ones is that it is not necessary to locate the concentration discontinuities for separate computation of their migration. The excellent results of a comparison between the experimental profiles obtained for the elution of large concentration zones of *n*-hexane on graphitized carbon black and the profiles calculated by this method from the isotherm of *n*-hexane determined separately, illustrate the validity of the method and its accuracy.

INTRODUCTION

The theory of the migration of zones in analytical chromatography usually assumes that the concentration of the solute in the mobile phase is negligibly small. This has several major consequences: the flow rate is not perturbed by the presence of the solute, the kinetics of mass transfer is independent of the solute concentration, elution is an isothermal process and, most importantly, the constant of the physicochemical equilibrium of the solute between the mobile and the stationary phases is independent of the concentration of the solute in the mobile phase. Those are the basic assumptions of linear chromatography. From there it is easy to show that the band profile is Gaussian, provided 1) that the kinetics of mass transfer between the two phases is rapid compared to the migration of the zone, 2) that there is no significant amount of high energy sites on the surface of the adsorbent or support, and 3) that the sample injection band is pluglike or at least very narrow compared to the standard deviation of the elution band (*1*). The validity of this conclusion in the general case of analytical chromatography is well supported by experimental results. A Gaussian curve is a good approximation for most band profiles recorded in analytical chromatography, even though in almost all cases the actual profile deviates somewhat from a Gaussian profile due to the serious experimental difficulties encountered when trying to satisfy exactly the three conditions just listed.

When the concentration of the solute increases, however, it is commonly observed that the band profile changes progressively. The peak broadens and becomes more and more unsymmetrical, the retention time of the peak maximum varies, and the need for a more sophisticated theoretical treatment of the band profile arises. The reason of this phenomenon is related to the fact that the concentration of solute in the mobile phase cannot be considered as negligibly small any more. This has several major consequences, the relative importance of which depends on the mode of chromatography used and on the experimental conditions, since the finite concentration of the solute can influence the band profile through different pathways (*2, 3*). The most important ones are the deviation of the equilibrium isotherm from a linear behavior, the difference between the partial molar volumes of the solute in the mobile and stationary phases, the variation of the viscosity of the mobile phase with its composition, the heat absorbed or generated when the solute goes from one phase to the other, and the change in the mass transfer kinetics associated with the variation of concentration during the passage of the zone.

The most important of these phenomena is that, when the sample size is increased and the concentration of the solute in the migrating band becomes large, the equilibrium constant of the solute between the stationary phase and the mobile phase does not remain constant, and the assumption of linear chromatography, i.e., of a linear isotherm, breaks down.

The plot of the concentration of the solute in the stationary phase at equilibrium versus its concentration in the mobile phase, i.e., the equilibrium isotherm, may have one of different shapes. In gas chromatography the solubility of the solute in the liquid phase or the amount of the compound under study adsorbed on the surface of the adsorbent most often increases faster than the partial pressure of the solute in the mobile phase and tends toward infinity when this partial pressure approaches the vapor pressure at the column temperature (*2*). Then the retention of the compound considered increases with increasing concentration: the retention time of most compounds which have a large column capacity factor ($k' > \sim 2$–3) increases with increasing sample size. Other isotherms are possible, of course, including a Langmuir-type isotherm at low concentration followed by capillary condensation in the pore of the adsorbent or support (*2*). Sometimes the solute–solvent miscibility is not complete over some range of mixture composition. Then two phases coexist in that range, and chromatography just does not work in the corresponding conditions.

In liquid chromatography, on the other hand, a Langmuir isotherm, or an isotherm having a similar shape, is very frequent (*4*). In such a case the amount of solute in the stationary phase at equilibrium increases more slowly than the concentration in the mobile phase, and the retention time decreases steadily with increasing sample size. There are examples of the opposite behavior, however. For a number of compounds the amount sorbed on the surface of the stationary phase increases with increasing concentration in the mobile solvent at very low concentrations, then decreases at larger concentrations, and the isotherm experiences an inflection point for some intermediate value of the concentration (*5*). The retention time of such a compound would increase with increasing sample size at low values of the sample size, then go through a minimum and decrease.

At the same time that the retention time varies, the band profile becomes more and more unsymmetrical, the tail becoming steeper and steeper if the retention time increases with increasing sample size; the front becoming steeper and steeper in the opposite case. Large concentration band profiles become complex in the case of isotherms with an inflection point.

Another source of nonlinear behavior of the chromatographic phenomenon and of changes in the band profile is related to the difference in the partial molar volumes of the solute in the mobile and the stationary phases, which gives rise to the so-called sorption effect (*6*), of major importance in gas chromatography, but often close to being insignificant in liquid chromatography. Since in chromatography the flow rate of the mobile phase (pure solvent) at the column inlet is kept constant, the presence of the solute at finite concentration perturbs the flow rate of the mobile phase (solvent + dissolved solute) inside the migrating band. In gas chromatography this effect can become very large if the vapor pressure of the solute is important, since the molar volume of a vapor is several hundred times larger than that of the liquid. Then the flow velocity of the gas phase is much larger inside the band than upstream or downstream, and it increases with increasing solute concentration.

In gas chromatography the sorption effect tends to act in an opposite way to the isotherm effect just described. It gives rise to peaks which have a very sharp front and a quasi-Gaussian tail, as are often seen for compounds with very small retention on open tubular columns ($k' < 0.5$–1) (*7*). For compounds with intermediate retention (k' between ~0.5 and 1.5), it is even possible in certain cases to achieve an almost complete compensation of one effect by the other (*8*). This can be done exactly by adjusting the column average pressure, which determines the extent of the sorption effect but does not influence the isotherm effect (*7*). In liquid–solid chromatography the solute displaces the solvent from the surface of the stationary phase, the solute molecules replacing the solvent molecules, and the difference in volume occupied by the solute and by the displaced solvent is very small, so this effect is rarely significant (*4*).

Other effects are of lesser importance and are often neglected. The variation of the viscosity of the mobile phase with its composition may affect the flow velocity. As long as the composition of the mobile phase is radially homogeneous, it causes but little change in the band profile. In liquid chromatography, however, if the solution of solute becomes much more viscous than the solvent, hydrodynamic instabilities may arise, resulting in "fingering flow" and a dramatic loss of performance. Because of the compressibility of the mobile phase in gas chromatography, the effect of viscosity could be more serious than in liquid chromatography. But organic vapors, even those of compounds with large molecular weights, usually have a small viscosity. If hydrogen or even nitrogen is used as the carrier gas, the change in the viscosity of the gas with composition is small and the effect on the band profile is very small and most probably negligible (*2*).

Another effect of possible importance is the thermal effect. When a solute is sorbed by the stationary phase, i.e., on the band front, some heat is usually generated; this heat is absorbed when the solute returns to the mobile phase, i.e., on the band tail. The band front is in a warm zone and tends to move faster than the center of the band, while the band tail, which is in a cold area, tends to move more slowly. The thermal effect usually tends to broaden the band, at least in gas chromatography. In liquid chromatography it would be conceivable to observe a reversed thermal effect if the passage of the solute from the mobile phase to the stationary phase is an endothermal process. Such a phenomenon has never been reported. This effect should be more important in wide preparative columns, which operate almost adiabatically, than in narrow analytical ones, which operate isothermally. In practice, this effect is neglected; there are no experimental data available to suggest that it is a wrong assumption. It is worth noting, however, that the enthalpy of adsorption in reversed phase liquid chromatography can be very significant, especially for heavy molecular weight solutes such as triglycerides and peptides, and this observation warrants a more thorough investigation.

All these phenomena are known, and most of them have been investigated in some detail. There is no general theory, however, which takes all of the effects of finite concentration into account at the same time. This is probably too difficult to do at present (*9*). A model is not yet available for the prediction of the elution band profile in the case of a large amount of a single compound when the equilibrium isotherm is known. Further advances in preparative chromatography require the development of such models taking into account, minimally, the effects of the equilibrium isotherm and of the sorption phenomenon. The aim of this paper is the presentation of such a model and a discussion of its numerical solution in the simple case of the elution of a single component band in gas chromatography.

The exact prediction of the band profile requires the solution of a system of partial differential equations which are derived by writing the mass balance for the mobile phase and for the solute(s). This system of equations is impossible to solve analytically in the general case and is difficult to study (*10*). An analytical solution is possible only in the case of a linear isotherm, in which case a Gaussian profile is obtained.

A considerable simplification is brought to the problem if we assume that the kinetics of radial mass transfer is infinitely fast while axial diffusion is negligible, i.e., that the column efficiency is infinite. This leads to the model of ideal, nonlinear chromatography. Its properties have been discussed by several authors, notably Jacob (*10–12*), Rhee (*13, 14*), and Aris and Amundson (*15*). Jacob used the method of characteristics to derive a number of important qualitative results regarding the change in the band profile during elution (*16, 17*). A program using this approach has been written and used (*12*). The method, however, is of limited application and very complex. It is possible to show that in certain conditions the system can propagate concentration discontinuities. The program must locate these discontinuities exactly during each loop, as the migration rates of the continuous part of the profile and of the discontinuity do not follow the same equations. Because of the errors introduced, almost half the band area is lost during the calculation, which leaves some doubt regarding the validity of the results.

Rhee derived the solution of the Riemann problem (i.e., frontal analysis response) in the case of a Langmuir isotherm (*14*). In spite of the generality of this type of isotherm in chromatographic systems, there are a number of cases where the method is not applicable, most notably the case of a rectangular injection. Aris and Amundson (*15*) described in great detail the method of characteristics for the solution of this type of systems of partial differential equations, and gave a number of applications in chromatography.

We discuss here the theoretical background of a numerical solution of the system of partial differential equations which describes the migration of a single component band (*18*). This work is based on recent developments made in the study of nonlinear hyperbolic systems of partial differential equations and especially on the work of Godunov (*19*). Since we must write separately the mass balance of each compound in the chemical system, the system of partial differential equations corresponding to the separation of a mixture contains one equation for each component of the mixture and one for the solvent. Then the present approach is not directly applicable, but the very simple algorithm obtained for the calculation of the profiles solution of the system of two partial differential equations in the case of a single compound can most probably be extended to the solution of a system of three partial differential equations, in the case of a two-component mixture, as suggested by results obtained in another area by Kvaalen et al. (*20*).

On the other hand, this numerical solution has the advantage of approaching the physical solution satisfactorily. The concentration discontinuities appear, build up, and/or disappear in a natural way. It is not necessary to carry out a special calculation to locate them. Furthermore, this solution gives the elution profile corresponding to any injection profile. In this way it is more general than the solution of the Riemann problem, since it can predict the profile of a zone of any finite width and profile at injection. It must also be emphasized that the method is applicable to any isotherm defined through an equation or a table.

The flow velocity varies during the elution of a band, especially in gas chromatography. The general algorithm can be adapted to take that effect into account and to calculate the flow velocity profile which accompanies the elution of a large concentration band.

Finally, the method is applied to the calculation of the elution profiles of *n*-hexane on graphitized carbon black, a system which corresponds to an isotherm with an inflection tangent (*21*). The results of the prediction are compared to some experimental data.

I. THE CHROMATOGRAPHIC MODEL

We use the model described and discussed by Valentin which accounts for the migration and transformation of the large concentration band of a single, pure compound along a chromatographic column (*2*, *22*). The main assumptions of this model are the following:

(1) The column is supposed to be radially homogeneous, and so is the input profile. Therefore the problem is monodimensional. The only variables are the abscissa along the column and the time.
(2) Gases follow ideal gas laws for compressibility and mixing.
(3) Liquids are not compressible.
(4) Darcy's law is valid in the range of flow velocity investigated. The column permeability is constant, independent of the abscissa.
(5) The local pressure is constant during an experiment, i.e., depends on the abscisa, not on the time, even during the passage of a large concentration band.
(6) The carrier gas is not sorbed by the stationary phase (in gas chromatography).

(7) Temperature is constant during an experiment, independent of the position or the time.

(8) Mass and heat energy exchanges between the mobile and the stationary phases are infinitely fast. The two phases are constantly at thermal and composition equilibrium.

(9) Axial diffusion proceeds at a negligible speed.

Combination of Assumptions 8 and 9 results in an infinite efficiency of the column. In this model, band broadening results only from the combination of the nonlinear effects taking place during the elution, which are the phenomenon studied here, and of rounding errors arising from the large number of numerical operations which have to be carried out. As discussed later, these errors may be used to simulate the effect of finite column efficiency.

The mass balance for a Compound A in the column may be written:

$$\frac{d}{dt}(N_M^A + N_S^A) = -\frac{d}{dz}(uN_M^A) \tag{1}$$

where the subscripts S and M stand for stationary and mobile phase, respectively; the variables are the time t and the abscissa along the column z; N_M^A and N_S^A are the number of moles of Compound A per unit length of column (concentration in a monodimensional model) in the mobile phase and in the stationary phase at equilibrium, respectively; and u is the local velocity of the mobile phase.

The unknowns are the local mobile phase velocity u and the values of N_M^A and N_S^A for each Compound A. N_M^A and N_S^A are not independent; they are related by the equilibrium isotherm.

Equation (1) is valid for the solutes as well as for the mobile phase.

In the case where there are a number n of solutes in the original sample, they compete for access to the stationary phase and the composition of the sorbed material is given by a set of equations usually referred to as "the mixed isotherm:"

$$N_S^i = k^i(N_M^1, N_M^2, N_M^3, \ldots, N_M^i, \ldots, N_M^n) \tag{2}$$

where i (between 1 and n) stands for the ith component of the mixture, and k^i is a function of the composition of the mobile phase.

For gas chromatography the carrier gas is not sorbed by the mobile phase (Assumption 6), and the last equation, which expresses the equilibrium of the mobile phase, is

$$N_S^{n+1} = 0 \tag{3}$$

In liquid chromatography the mobile phase is sorbed by the stationary phase, and an equation similar to Eq. (2) applies for the mobile phase.

II. APPLICATION TO GAS CHROMATOGRAPHY

The mole fraction of each compound is related to the local pressure and to the number of moles per unit column length by the following equation (Assumption 2):

$$N_G^i = \lambda p X_i \tag{4}$$

where λ is a proportionality coefficient which depends on the column characteristics and its temperature, but which will otherwise be constant and is the same for all compounds. Combination of Eqs. (1), (2), and (4) gives

$$\frac{d}{dz}(upX_i) + \frac{d}{dt}[pX_i + k^i(pX_1, pX_2, \ldots, pX_n)] = 0 \tag{5}$$

There are n equations similar to Eq. (5), one for each compound in the original sample. In addition, there is a similar equation for the carrier gas:

$$\frac{d}{dz}\left[up\left(1 - \sum_{i=1}^{n} X_i\right)\right] + \frac{d}{dt}\left[p\left(1 - \sum_{i=1}^{n} X_i\right)\right] = 0 \tag{6}$$

It is more practical, however, to use instead of Eq. (6) the sum of all Eqs. (5) (i.e., for each of the n compounds) and of Eq. (6). This is the total mass balance equation of the column:

$$\frac{d}{dz}(up) + \frac{d}{dt}\left[p + \sum_{i=1}^{n} k^i(pX_1, pX_2, \ldots, pX_n)\right] = 0 \tag{7}$$

In Eq. (7) the product up is proportional to the molar flow rate of the mobile phase through the column.

The local pressure is derived from Darcy's law, assuming that the local velocity remains constant during the elution of a compound. Then the pressure profile is given by the conventional equation (*23*)

$$p(z) = \sqrt{P^2 - \frac{z}{L}(P^2 - 1)}$$

where P is the inlet to outlet pressure ratio, in practice equal to the absolute value of the inlet pressure, and L is the column length.

As a consequence of Assumption 5, that the partial differential of the local pressure by respect to time is zero, we can rewrite the above equations and obtain the final system of partial differential equations:

$$\text{(I)}\quad \left| \begin{array}{ll} \frac{d}{dz}(FX_i) + \frac{d}{dt}[pX_i + k^i(pX_1, pX_2, \ldots, pX_n)] = 0 & (9) \\ \frac{d}{dz}(F) + \frac{d}{dt}\left\{\sum_{i=1}^{n} k^i(pX_1, pX_2, \ldots, pX_n)\right\} = 0 & (10) \end{array} \right.$$

The unknowns in Eqs. (9)–(10) are the total flow rate F and the flow rates of each of the compounds, F_i.

III. MATHEMATICAL PROPERTIES OF THE SYSTEM OF EQUATIONS

The equations leading to the System I of partial differential equations (Eqs. 9 and 10) have been derived with the assumption that all functions (i.e., the N_i's, X_i's, F_i's) can be differentiated as often as necessary. It can be shown, however, that the concept of solution of such a system can be extended to discontinuous functions (cf. Section VI, the Appendix, and Ref. *24*). Then System I of Eqs. (9)–(10) also contains implicitly the usual equations written for the propagation of discontinuities (*10, 11*). This is due to the conservative properties of this system of equations.

The system of partial differential Eqs. (9)–(10) is a hyperbolic system of nonlinear equations. It is not written in the classical way used by mathematicians, however. The variables z and t have been exchanged. To chemists this may seem of little importance, but this exchange creates some uncomfortable, awkward, and sometimes difficult situations when the classical theories of partial differential equations are applied to our system (*15*). The physical significance of the functions involved is changed, often reversed. The designation of symbols is ambiguous: the classical theory of nonlinear hyperbolic systems has been derived mostly for the solution of hydrodynamic problems. The longitudinal gradient of flux becomes a time gradient of accumulation (the increase of the amount of solute contained in a column section). Worse, the velocity of the classical theory (*dz*/*dt*) becomes here the reverse of velocity (*dt*/*dz*). We call it the retention ratio (in s/cm).

An important consequence of this nonclassical character of the chromatographic system of partial differential equations is that the most appropriate vectorial space for a discussion of the properties of the solution of the system is a $(n + 1)$ dimensional *flow rate space* (where the coordinates of the vectors are the flow rates of each component of the studied mixture and the total flow rate) and not the corresponding *amount space* (where the vector coordinates are the amount of each chemical species involved) or concentration space. Physically, this means that if the amount of each component is known at each location, there is still one degree of indetermination, the mobile phase flow velocity. If the flow rates of each component and the total flow rate are known, the system is entirely determined, including the local composition (*22*).

IV. THE BOUNDARY CONDITIONS

We know the initial conditions of the system, i.e., the value of the unknowns at the time origin, and the amounts injected, i.e., the value of the unknowns at the column inlet. In other words, because the unknowns are the flow rates, $FX_i(z,t)$, we know all the $FX_i(z,0)$ (usually 0, except for the mobile phase) and the $FX_i(0,t)$ (usually 0 for the solutes and FT for the carrier gas, except during injection).

These are not the conventional boundary conditions of a system of partial differential equations (cf. Fig. 1). This is related to the fact that only the upper right quadrant of the (z,t) plane has a physical meaning in the case of the chromatographic problem. It is possible, however, to transform the problem into a standard Cauchy problem, because all the eigenvalues of the system are positive (cf. Section VI). Information transfer in a chromatographic column flows exclusively toward increasing time.

V. THE SORPTION EFFECT

In gas chromatography it is not possible to consider the local gas velocity as time-independent during the passage of a migrating zone. The gas velocity depends on the composition of the gas phase, which itself depends on the mass transfers between mobile and stationary phases. First pointed out by Bosanquet and Morgan (*25*), this effect has been thoroughly discussed by Golay (*26*), Peterson and Helfferich (*27*), Haarhof and Van der Linde (*28*), and Jacob and Guiochon (*3*, *10*).

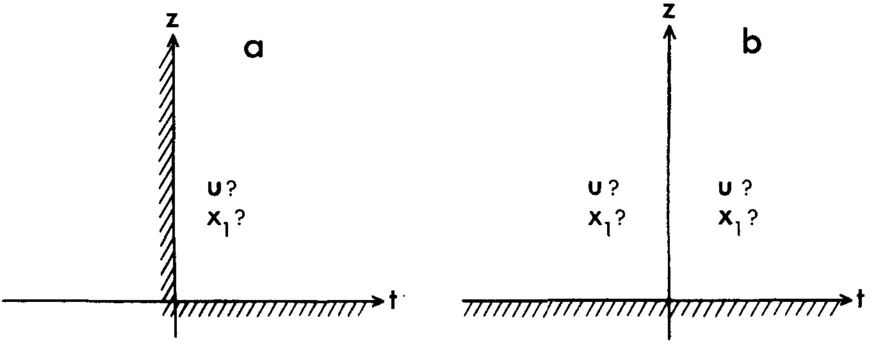


FIG. 1. Boundary conditions of the chromatography problem (a) and the classical Cauchy problem (b). For the chromatographic problem only $t > 0$ matters, and we know the conditions at $z = 0$ (injection profile $u_0(t)$) and at $t = 0$ (the column is empty, $F_i = 0$ except for the mobile phase).

The mass flow rate of carrier gas sent to the column is kept constant by the flow rate controller. The addition of solute vapor to the gas phase increases the local velocity. The passage of this vapor to the stationary phase is tantamount to its disappearance, from a volumetric point of view, since the density of the liquid, whether pure, sorbed on the surface of an adsorbent, or dissolved in the stationary solvent, is about 200 times larger than the density of the vapor.

As a consequence, when dealing with gas chromatographic problems, we may not simplify System I by assuming the flow rate to be constant and by taking F off the differential operator. In liquid chromatography, the solute displaces the solvent when it is sorbed. Neglecting the sorption effect will have no significant effect on the accuracy of the predictions in most cases unless there is a significant difference between the volume occupied by the sorbed solute and the corresponding volume of displaced solvent.

VI. NONLINEAR HYPERBOLIC SYSTEMS

Let w be the vector of coordinates $(FX_1, FX_2, \ldots, FX_i, \ldots, FX_n)$ in the n-dimensional space. The system of equations becomes

$$\frac{dw}{dz} + \frac{d}{dt}[H(w)] = \frac{dw}{dz} + D_wH(w)\frac{dw}{dt} = 0 \qquad (11)$$

$$w(0,t) = W_0(t) \qquad (12)$$

with

$$H(w) = \begin{vmatrix} pX_1 + k^1(pX_1, pX_2, \ldots, pX_i, \ldots, pX_n) \\ pX_2 + k^2(pX_1, pX_2, \ldots, pX_i, \ldots, pX_n) \\ \vdots \\ pX_i + k^i(pX_1, pX_2, \ldots, pX_i, \ldots, pX_n) \\ \vdots \\ pX_n + k^n(pX_1, pX_2, \ldots, pX_i, \ldots, pX_n) \\ \sum_{i=1}^{n} k^i(pX_1, pX_2, \ldots, pX_i, \ldots, pX_n) \end{vmatrix} \tag{13}$$

$D_wH(w)$ stands for the matrice obtained by differentiation of the matrice $H(w)$ in respect to each of the coordinates of w.

A system of partial differential equations such as the one studied here is called hyperbolic if the eigenvalues of the matrice $D_wH(w)$ are real for any vector w. If these eigenvalues are real and all different, the system is called strictly hyperbolic.

For example, in the case of a single solute, the system of partial differential equations becomes

$$\frac{d}{dz}\begin{vmatrix} FX \\ F \end{vmatrix} + \frac{d}{dt}\begin{vmatrix} pX + k(pX) \\ k(pX) \end{vmatrix} = \begin{vmatrix} 0 \\ 0 \end{vmatrix} \tag{14}$$

The eigenvalues of $D_wH(w)$ are 0 and $[1 + (1 - X)k']/u$, and the system is strictly hyperbolic.

As a consequence of this property, it has been shown that the information propagates at a finite velocity, i.e., in the case of the chromatographic system at a finite value of the retention ratio (see Section III). If the initial condition, i.e., $F(0,t)$, is zero for all values of time outside a finite interval (which corresponds to the injection of a finite sample plug), the same property is true for the function $F(z,t)$ for any other value of z (see Fig. 2). A sample plug will propagate along the column and elute within a finite time, leaving the column in the same condition as it was before the injection. This property should be expected from a satisfactory model of chromatography.

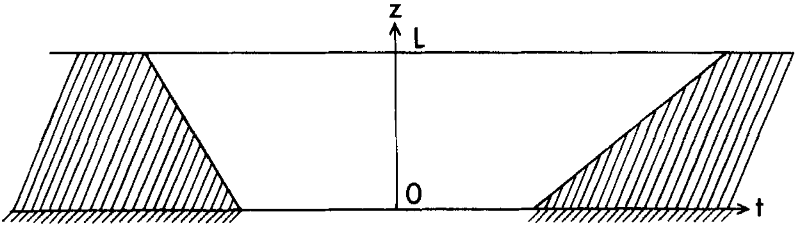


FIG. 2. Propagation of a solution, i.e., a band profile, along the column. The boundary condition is zero except in a limited time interval at the column inlet ($z = 0$). The solution is zero, except on a limited time interval at any position along the column. Hence, the migration of the zone takes a finite time, at least within the framework of the ideal model. Diffusion will smooth the profile and give it a quasi-Gaussian tail. The solution is zero in all the hatched areas. The boundary condition in zero on the hatched part of the time axis.

Except for the theory of characteristics (*10*), directly derived from the case of linear hyperbolic systems, the theory of nonlinear hyperbolic systems of partial differential equations is in most part very recent and still very incomplete (*29, 30*). There is no general result on the existence of solutions nor, of course, any general result on the convergence of algorithms permitting the calculation of approximate solutions. This is related to the unfortunate property of these systems that they do not necessarily have a regular solution, even for very regular initial functions. Singularities may appear for any positive value of z, depending on the initial function (boundary condition).

It is about as difficult to understand the physical significance of the appearance of singularities in the solution of the system as it is to account for this phenomenon (*2*). A more detailed discussion, leading to the concept of weak solution and of mathematical entropy, can be found in Ref. *24*. Some explanations are also presented in the Appendix.

VII. METHODS OF NUMERICAL SOLUTIONS

The methods based on the utilization of characteristics which are usually simple and accurate become impractical as soon as a discontinuity arises, which is the normal case in ideal nonlinear chromatography. Thus, we shall apply methods using a finite differential approach.

The general principle of these methods consists of a discretization of the plane $z > 0$, i.e., a space increment, δz, and a time increment, δt, are chosen and a network of points with coordinates $i\delta t$ and $k\delta z$ is created

(Fig. 3). A recurrence process permits the calculation of an approximate value of the solution at the points on $z = n\delta z$ from the points on the previous line ($z = (n - 1)\delta z$). The solution will be assumed to be constant on the time interval $|i\delta t - (i + 1)\delta t|$. Let $u(n,i)$ be the value of the function calculated for the step $n\delta z$ and the interval $|i\delta t - (i + 1)\delta t|$.

The calculation begins by the discretization (cf. Fig. 4) of the initial condition u_0; for example, by writing

$$u_i = \frac{1}{\delta t} \int_{i\delta t}^{(i+1)\delta t} u_0(t)dt \tag{15}$$

There exist a number of different methods to write the iteration process. The Lax-Friedrich relationship was the first to be suggested for the numerical solution of nonlinear hyperbolic systems (*29*):

$$\frac{u_i^{n+1} - \dfrac{u_{i+1} + u_{i-1}}{2}}{\delta z} = \frac{f(u_{i+1}^n) - f(u_{i-1}^n)}{2\delta t} \tag{16}$$

The advantage of this method is that it does favor one direction of propagation, in agreement with our understanding of the physical problem.

A. Condition of Stability

Consideration of the "propagation velocity" (i.e., the retention ratio) gives a necessary condition for the stability of the calculation. As noted

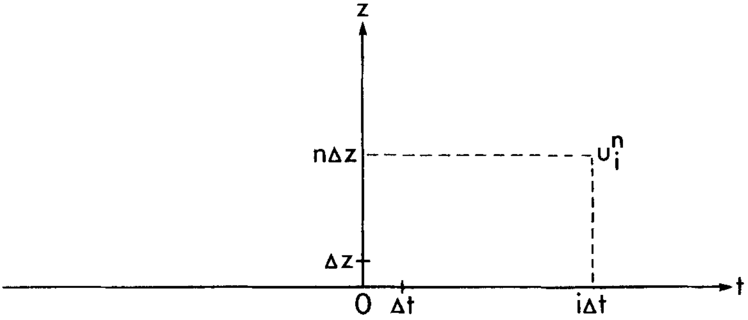


FIG. 3. Networking of the *t,z* plane for the calculation of the solutions of the system of partial differential equations.

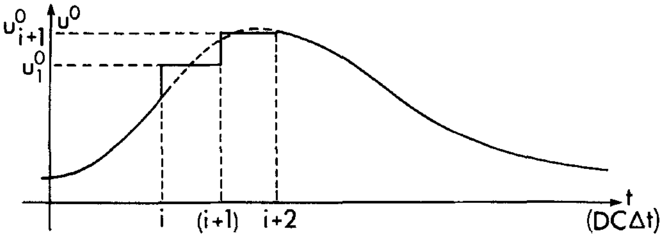


FIG. 4. Discretization of the boundary condition, i.e., the injection profile. The figure shows how Eq. (15) is used to calculate F_{0i}, i.e., to discretize the mass flow rate of Compound i at the column inlet.

above, a characteristic of nonlinear, hyperbolic systems of partial differential equations is the existence of a finite retention ratio. If u_0, the initial function (injection band profile), is zero everywhere outside a certain time interval $|a–b|$ (which is, of course, the proper way to carry out an injection in chromatography), the entropic solution (*24*) at the point of abscissa z differs from zero only in the time interval $|(a - Mz) - (b + Mz)|$, with M given by the relationship:

$$M = \operatorname*{Sup}_{u \in R} \operatorname*{Max}_{k \in [1,n]} |\lambda_k(u)| \tag{17}$$

Furthermore, the numerical value of the retention ratio corresponding to the single step process described above (cf. Eq. 16) is $\delta t/\delta z$. There will be a loss of information if this numerical value of the retention ratio is smaller than the actual retention ratio of the initial condition (cf. Fig. 5). The calculated solution will be zero inside the hatched area, whereas it should be different from zero. To avoid this difficulty, the following condition, called the Courant-Friedrichs-Lewy condition (CFL), must be fulfilled (*31*):

$$\frac{\delta z}{\delta t} \operatorname*{Sup}_{(u \in R,\, k \in [1,n])} |\lambda_k(u)| \leqslant 1 \tag{18}$$

For example, for the simplest case of a nonlinear hyperbolic equation (*24*):

$$\text{(II)} \quad \left|\begin{array}{ll} \dfrac{du}{dz} + \dfrac{d}{dt}(f(u)) = 0 & \text{(19a)} \\[2ex] u(0,t) = u_0(t) & \text{(19b)} \\[2ex] t \in R,\ z > 0 & \text{(19c)} \end{array}\right.$$

the condition becomes:

$$\frac{\delta z}{\delta t} \sup_{y \in R} |f'(y)| \leqslant 1 \tag{20}$$

B. The Godunov Method

We shall make use here of the Godunov method (*19*) which derives from the following observation: at the point $n\delta z$ of the network (cf. Fig. 6 and Section VII), we have an approximate solution made of a number of constant segments and separated by steps. We know how to derive an approximate solution of the Riemann problem of the system of Eqs. (11)–(13), i.e., to solve this system for the following initial function:

$$\left| \begin{array}{ll} u^0(t) = u^- & t < 0 \\ & \\ u^0(t) = u^+ & t > 0 \end{array} \right. \tag{21}$$

Thus we solve a series of local Riemann problems for the System I (Eqs. 9 and 10 or 11 to 13) at the points $n\delta z$ and we combine these solutions to obtain an approximate solution at point $(n + 1)\delta z$. At each point $\{i\delta t, n\delta z\}$ the Riemann problem is solved; let $w^n_{i+1/2}$ be the solution on the vertical line AB (cf. Fig. 7). Because of the homogeneity of both Eq. (11) and the initial condition, the solution of the Riemann problem is constant on any straight line going through the point at which the initial function is discontinuous.

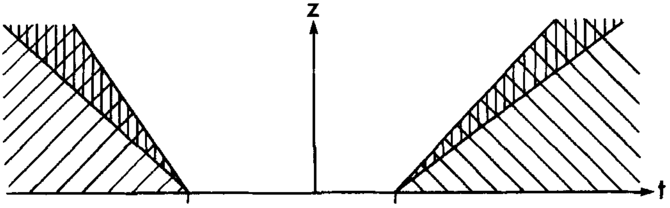


FIG. 5. Condition of stability of the numerical method. The numerical solution is zero in the two hatched area. However, the actual solution of the problem is not zero in the vertically hatched areas.

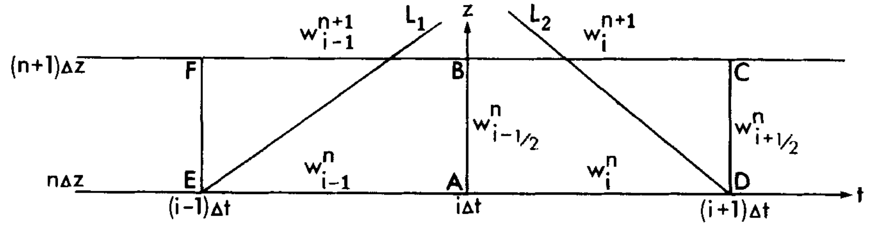


FIG. 6. Godunov procedure for the calculation of a solution of the system of partial differential equations by solving a series of Riemann problems for every value of *i*. See explanations in text.

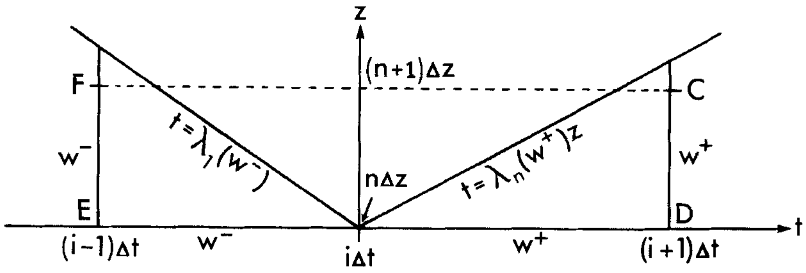


FIG. 7. Derivation of the Courant-Friedrichs-Lewy condition.

Integration of Eq. (11) on (ABCD) gives

$$\iint_{\mathrm{ABCD}} \frac{dw}{dz} + \frac{d}{dt} H(w) = 0 \tag{22}$$

or

$$w_i^{n+1} = w_i^n - Q[H(w_{i+1/2}^n) - H(w_{i-1/2}^n)] \tag{23}$$

This, however, assumes that the value of $w_{i+1/2}^n$ is not perturbed by the neighbor Riemann problems. The solution of the Riemann problem is constant under the straight lines which have a slope λ_1 for $x < 0$ and λ_n for $x > 0$. Accordingly, if δz is small enough and the straight lines going through the point $\{i\delta t, n\delta z\}$ with slopes $\lambda_1(w_{i+1}^n)$ and $\lambda_p(w_i^n)$ do not cut the vertical segments EF and DC, respectively, the Eq. (23) is valid. This may be written as follows:

$$\delta z \lambda_i(w_{i-1}^n) \leqslant \delta t$$

$$\delta z \lambda_p(w_i^n) \leqslant \delta t \tag{24}$$

These two conditions are verified if the CFL condition is satisfied.

C. Convergence of the Godunov Method

There are few general results available regarding the existence of a solution and the convergence of the approach described here. In the case of the simple Eq. (19), it has been shown that there is one single solution and that the method converges toward it (*19*, *32*, *33*). Results regarding more complex functions are still incomplete. Lax and Wendroff (*34*) have shown that if a conservative algorithm converges, it tends toward a weak solution of System (11) (*25*). Furthermore, if a discrete entropy relationship is valid at each step of the calculation (*34*), the limit function is an entropic solution of the system (*25*).

Finally, in the case of the Godunov method, the discrete entropy condition (*24*) is always verified; if the method converges, it is toward an (the?) entropic solution. This does not prove, however, either the existence of that solution or the convergence of the series of solutions calculated by this method.

The main drawback of methods like the present one is that they are of the first order, i.e., that the error made at each passage from $n\delta z$ to $(n + 1)\delta z$ is of the same order as δz (*35*). Thus, these methods will tend to dampen discontinuities. There are methods of the second order used for the solution of linear, hyperbolic problems. Unfortunately, they give rise to strong oscillations in the neighborhood of discontinuities. One possible refinement to the numerical solution of the chromatographic problem would be the use of a method which would be second order almost everywhere, except close to discontinuities, where it would be first order (*32*).

D. Antidiffuse Method

The general principle of this method is to start from a good first-order method and to modify it in the regions where the solution is regular, i.e., far from discontinuities, to obtain a more accurate, second-order method.

The first-order method will be Godunov's method, as described in the previous sections and in Eq. (24). The second-order method used was a Lax-Wendroff method, using a two-term expansion of $w_i^{(n+1)}$, assumed to be a regular function of w_j^n. The quasi-second-order method is obtained by testing for each value of i whether a concentration discontinuity is near; for example, by checking whether the solution calculated at point n tends to oscillate. If it does, the Lax-Wendroff method is used instead of the Godunov one. It has been shown (*32*) that this type of method converges toward the entropic solution in the case of the simplest hyperbolic equation (Eq. 19). In this case, however, the condition of stability is twice as stringent as the Courant-Friedrich-Lewy condition written above for the Godunov method.

Since the antediffuse method did not give any improvement over the simpler Godunov method, we do not give any detail on its application here. They can be found elsewhere (*18*).

VIII. THE CHROMATOGRAPHIC SYSTEM FOR THE ONE COMPONENT SAMPLE

The system of partial differential equations describing the elution of a large concentration band of a pure compound in gas chromatography is given by Eq. (14). The local flow rate of mobile phase, F, is proportional to the product pu. Accordingly, the differential matrice associated with $H(w)$ is

$$D_w(H) = \begin{vmatrix} \frac{P}{F}(1 + k'(PX)) & -\frac{PX}{F}(1 + k'(PX)) \\ \frac{P}{F}k'(PX) & -\frac{PX}{F}k'(PX) \end{vmatrix} \tag{25}$$

The eigenvalues of this matrice are:

$$\lambda_1 = 0 \tag{26}$$

$$\lambda_2 = \frac{1 + (1 - X)k'(PX)}{u} \tag{27}$$

The system is strictly hyperbolic, and the associated eigenvectors are

$$w_1 = \begin{vmatrix} FX \\ F \end{vmatrix}, \quad w_2 = \begin{vmatrix} 1 + k'(PX) \\ k'(PX) \end{vmatrix} \tag{28}$$

The results of the study of the second vector field depend on the nature and shape of the isotherm. This study requires an estimate of the expression $D_w\lambda_2 w_2$ (*35*), which is equal to

$$D_w\lambda_2 w_2 = (P/F^2)[1 + (1 - X)k'][P(1 - X)k'' - 2k'] \qquad (29)$$

A detailed study of the Riemann problem requires the determination of the roots of the term $[P(1 - X)k' - 2k']$. The design of the Godunov method, however, can be simply made from the following observations.

A. The Riemann Problem

The situation is described in Fig. 8. The value of the solution is:

w^- in Area 1 of Fig. 8

w^1 in Area 2 of Fig. 8

w^+ in Area 4 of Fig. 8

In Area 3 there is a succession of simple two-waves, either discontinuities or expansion waves, i.e., parts of solutions which are regular with respect to the variable t/z (cf. Section III, above). w^1 is determined as follows: w^1 is on the same first class integral curve as w^-, and it is possible to go from w^1 to w^+ along one (or several, depending on the sign of $[P(1 - x)k'' - 2k']$) acceptable two-wave(s). This solution does exist if w^- and w^+ are close and if $[P(1 - X)k'' - 2k']$ is not zero close to w^- or w^+.

The critical point, however, is that in all cases this value w^1 is constant on the vertical line $k = 0$ and satisfies the Rankine-Hugoniot relationship

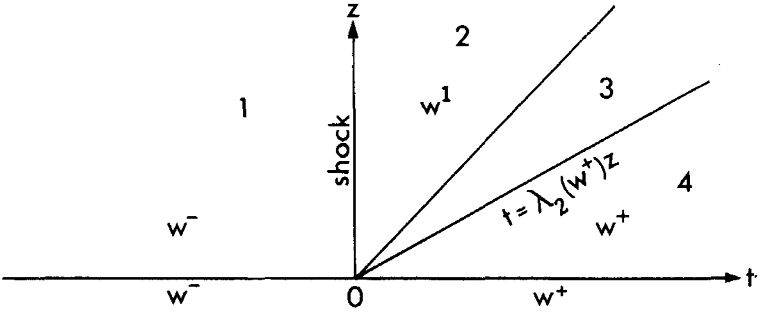


FIG. 8. Solution of the Riemann problem and construction of the Godunov algorithm.

$$[H(w^1) - H(w^-)] = 0[w^1 - w^-] \tag{30}$$

or

$$H(w^1) = H(w^-) \tag{31}$$

The first class integral curves are characterized by $X = Cte$. Finally, although we do not know w^1 exactly, we do know $H(w^1)$, which is the only function through which w^1 is used in the Godunov method.

B. Condition of Stability

The CFL condition is especially simple to write, and also to fulfill, in this case, since one of the eigenvalues is zero. It comes:

$$\frac{\delta z}{\delta t} \sup_{w \in R^2} \lambda_2(w) \leqslant 1 \tag{32}$$

or, after taking the largest possible values for each of the terms involved,

$$\frac{\delta z}{\delta t} = Q \leqslant \frac{u_{\min}}{1 + k'_{\max}} \tag{33}$$

where $u_{\min}$ is the smallest possible flow velocity during the experiment, i.e., the migration velocity of an unretained compound (column length divided by the time hold-up and corrected for the decompression effect, Ref. *23*), and $k'_{\max}$ is the maximum slope of the isotherm. This takes into account the variation of the mobile phase velocity during the passage of the band (cf. the sorption effect, Section V).

C. Boundary Conditions

We now transform the chromatographic system into one which has standard boundary conditions.

Since the system of partial differential equations is hyperbolic, the propagation of the bands takes place at finite retention ratio, i.e., there is a finite value of time T such that the output of the column at time $t + T$ does not depend on the initial state of the system at any time prior to t (cf.

Section III). Thus, it is possible to study the behavior of the system by assuming a constant initial condition.

The eigenvalues of the matrice $D_wH(w)$ being positive or zero, the solution of the system with the standard boundary conditions (see Fig. 1) is equal to the constant initial input for $(t < 0, z > 0)$ and to the solution of our experimental problem for $(t > 0, z > 0)$. In practice it is useless to calculate the values of u_i^n for $i < 0$ $(t < 0, z > 0)$, since they are constant.

D. The Godunov Algorithm for Gas Chromatography

From what has been said before, the iteration equation for the calculation of the solution at stage n is

$$w_i^{n+1} = w_i^n - \frac{\delta z}{\delta t}\,[H(w_i^n) - H(w_{i-1}^n)] \tag{34}$$

In gas chromatography, however, the local pressure depends on the abscissa, which we have neglected so far. To take it into account, we may merely write in the above equation that p is equal to pn, a function of $n\delta z$ derived from Eq. (8). The final form of the iteration loop is thus

$$(G)\left|\begin{array}{lr} (FX^G)_i^{n+1} = FX_i^n - Q[(P^nX_i^n + k(P^nX_i^n)) - (P^nX_{i-1}^n + k(P^nX_{i-1}^n))] & \\ & (35) \\ (F^G)_i^{n+1} = F_i^n - Q[k(P^nX_i^n) - k(P^nX_{i-1}^n)] & (36) \\ P^n = \sqrt{P^2 - \dfrac{n\delta z}{L}(P^2 - 1)} & (37) \end{array}\right.$$

This set of equations, G, is the set of formulas used to write the basic loop of our program.

IX. APPLICATION

Using the algorithms just discussed, we have written a program which permits the derivation of a numerical solution of the system of partial differential equations describing the migration of the zone of a pure compound through a chromatographic column. The equilibrium isotherm of the compound considered must be known and made available to the program under a suitable form to allow the calculation of the amount of solute sorbed as a function of the concentration in the mobile phase. This program permits the prediction of the elution profile of the zone corresponding to any input function.

In this paper we compare the predictions of the model with experimental results obtained for the injection of narrow, rectangular plugs of *n*-hexane on graphitized carbon black.

In a previous paper we described the determination of the adsorption isotherm of *n*-hexane on graphitized carbon black at 100°C (*5*) using the step and pulse method. The elution profiles of large sample size bands were recorded with the same equipment.

From the isotherm obtained previously and using our program, we calculated the band profiles of these large samples of *n*-hexane with the following assumptions. The inlet carrier gas flow rate is kept constant during the experiment, and the solute concentration in the mobile phase entering the column is zero for t negative. At time $t = 0$ the input concentration becomes equal to x_0 and remains constant until $t = t_0$. Then it becomes zero again and remains so until the end of the calculation.

Calculations have been made with two programs, one using the Godunov algorithm and the other one the antediffuse Lax-Wendroff/Godunov algorithm. The latter did not give any significant improvement in the band profiles over the results obtained with the Godunov method, and because it is more complex and takes a much longer time to run, the antediffuse algorithm was abandonned and is not discussed in detail here.

In all cases the numerical retention ratio $\delta t/\delta z$ was kept constant during the whole calculation. The CFL condition was always satisfied, except for one calculation.

X. RESULTS AND DISCUSSIONS

Figure 9 shows the profiles recorded following the injection of four samples of increasing sizes (5.6, 87, 245, and 360 μg, respectively, Fig. 9a) and the profiles resulting from the calculations performed on the same sample amounts (Fig. 9b). All the profiles have been plotted on the same scale. The concentration of *n*-hexane in the 800-μL (NTP) gas plugs injected was 0.18, 2.8, 8.0, and 11.7%, respectively. Details on the calibration of the detector which is required in these experiments are given elsewhere (*5*). Figure 10 (a to d) permits a more precise comparison between the experimental and the predicted profiles obtained in each case. In Figs. 11(a) and 11(b) the calculated flow rate and concentration

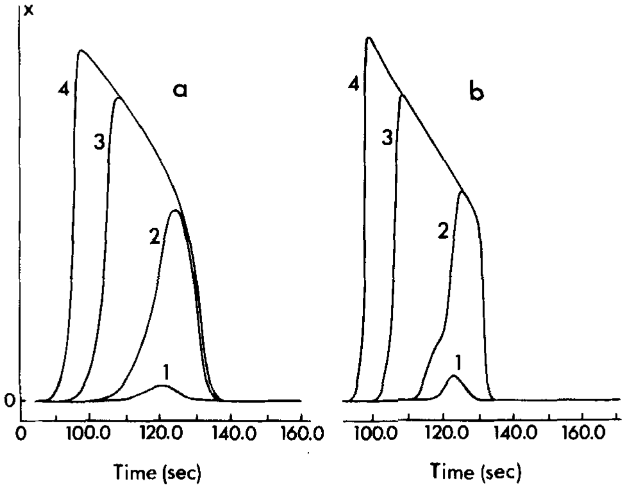


FIG. 9. Comparison between experimental and calculated band profiles. Ordinate: *n*-hexane partial pressure in the eluent, arbitrary unit. (a): Experimental results. Column: 50 cm long, 2.1 mm i.d., packed with 1.51 g Carbopack C,HT (Supelco). Temperature: 100°C. Carrier gas flow velocity: 17.7 cm/s. Inlet to outlet pressure ratio: 1.60. Sample: 500 μL of a nitrogen/*n*-hexane vapor mixture. Sample size: 1, 5.6 μg; 2, 87 μg; 3, 245 μg; 4, 360 μg. Samples are injected as vapor diluted in nitrogen. (b): Calculated profiles, corresponding to the same sample sizes as the experimental profiles in Fig. 9(a).

profiles are shown for the first (5.6 μg) and the third (245 μg) samples, respectively. Figures 12(a) and 12(b) illustate the progressive change in profile during the migration of the 245-μg band inside the column. Since each profile in these two figures is an instantaneous photograph of the band profile inside the column, the profile asymmetry is opposite to the one observed in Figs. 9 and 10, which represent elution profiles, at column exit. The part of the profile the closest to the column exit is the first one to get out. Figure 13 shows the influence of the pressure gradient in gas chromatography. Finally, Fig. 14 shows what may happen when the Courant-Friedrichs-Lewy condition is not satisfied.

The first observation is that the model accounts very well for the experimental phenomena. The predicted and observed band profiles are very close (see Figs. 9 and 10); the retention times (corresponding to the elution of the concentration maxima), the appearance of a sharp bend on the tail part of the profiles at high concentrations, the existence and the time of appearance of the abrupt concentration variations are well accounted for.

The second observation is that agreement between predicted and

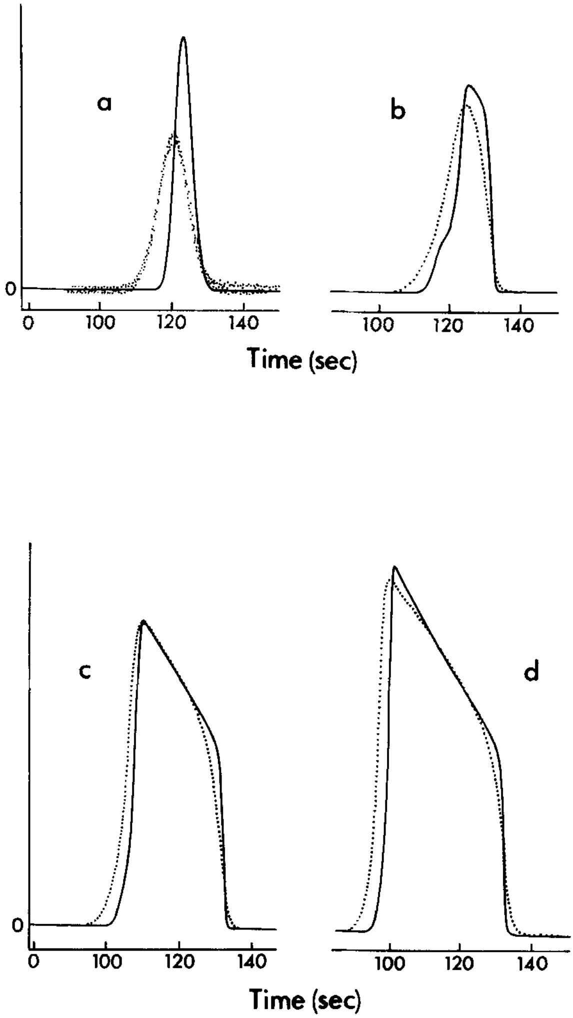


FIG. 10. Comparison between experimental and calculated band profiles. The dotted lines are experimental profiles; the dots represent data points as acquired by the computer. The solid lines represent the calculated profiles. (a): Sample size: 5.6 μg. (b): Sample size: 87 μg. (c): Sample size: 245 μg. (d): Sample size: 360 μg.

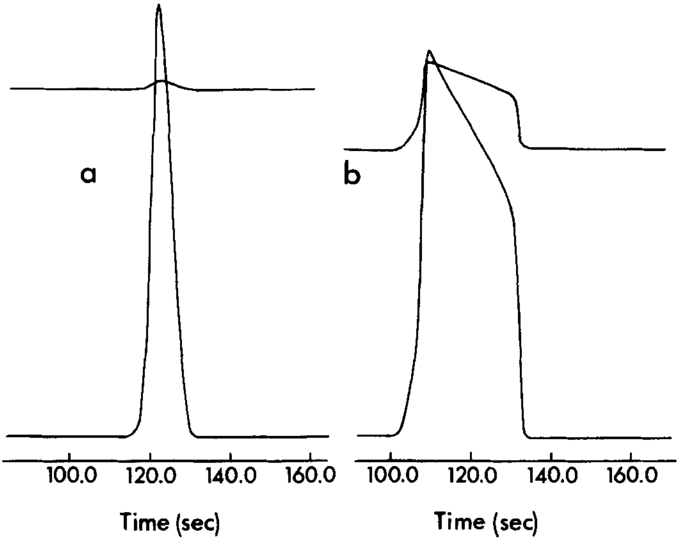
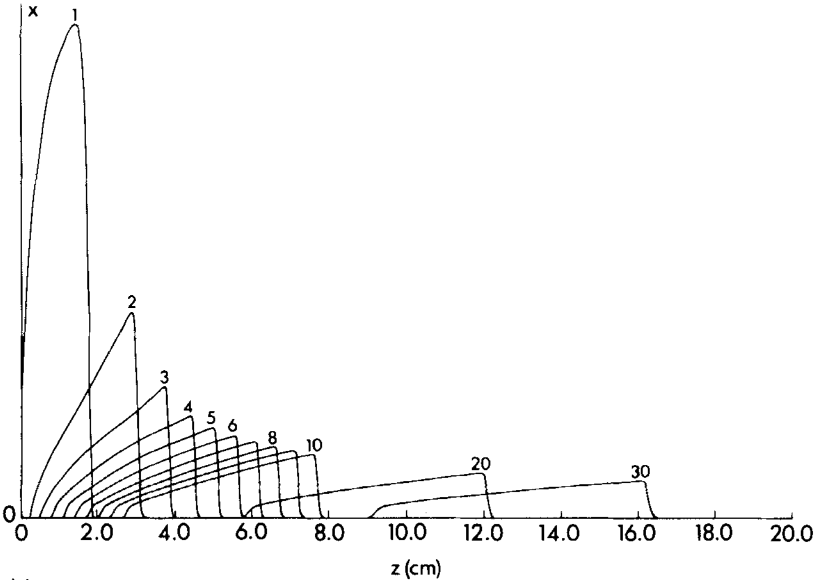
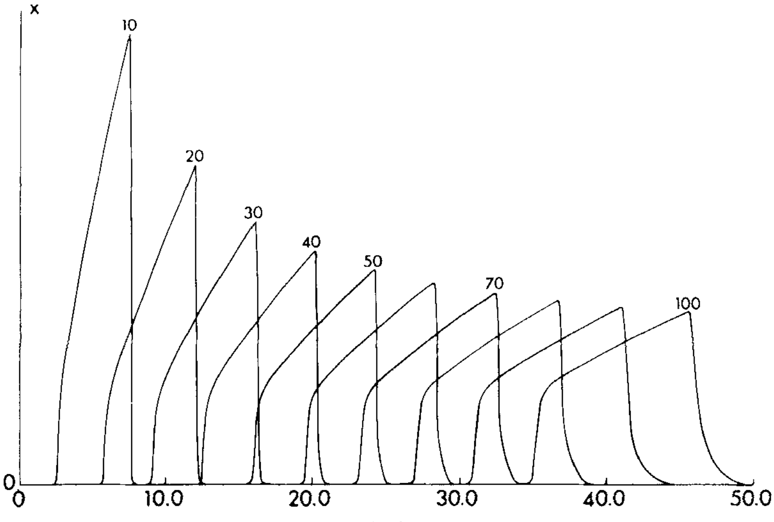


FIG. 11. Variation of the carrier gas velocity during the elution of a large concentration band. Calculated flow velocity profiles and concentration profiles (arbitrary units). Sample sizes: (a) 5.6 μg *n*-hexane vapor; (b) 245 μg *n*-hexane vapor. The initial flow velocity is 17.699 cm/s. The maximum velocity is 17.70 cm/s in the first case and 17.76 cm/s in the second case. These variations (0.33 and 0.35%, respectively) are too small to be detectable in practice.

experimental results improves with increasing concentration (see Figs. 10a to d), which is to be expected from a model which neglects the second-order effects (mass transfer kinetics) and puts the emphasis on the first-order effects (thermodynamics, i.e., nonlinear behavior of the equilibrium isotherm and sorption effect). Significantly, the major difference between the predicted and the observed profiles lies in the fact that calculated profiles are steeper than experimental ones, i.e., correspond to a larger column efficiency. The peak recorded for a very small sample size is significantly broader (1.8 times) than the peak calculated, which corresponds to a 3.3 times less efficient column. The origin of the sharpness of the simulated profiles is found in our original assumption that the contribution of resistance to mass transfer to band broadening is negligible. There is some smoothness, however, in these profiles which do not show the sharp concentration discontinuities predicted by ideal, nonlinear chromatography. The reason is to be found in the "numerical diffusion," the errors made in the millions of individual calculations which result in a band profile. By adjusting the space increment, δz, properly (δt is selected to satisfy the CFL condition), it might be possible



(a)



(b)

FIG. 12(a). Progressive change of the band profile during its elution through the column. Calculated profiles at different times represent the concentration distribution of the solute along the column. Sample size: 245 μg. The profile asymmetry of a space profile is the reverse of the asymmetry of a time profile (i.e., an elution chromatogram as in Figs. 9 and 10), since the farther down the column a molecule is at a given time, the sooner afterwards it exists. Time between 1 and 30 s after injection of the sample. The number on each curve is the time in seconds.

FIG. 12(b). As in Fig. 11(a), but time between 10 and 100 s after injection of the sample.

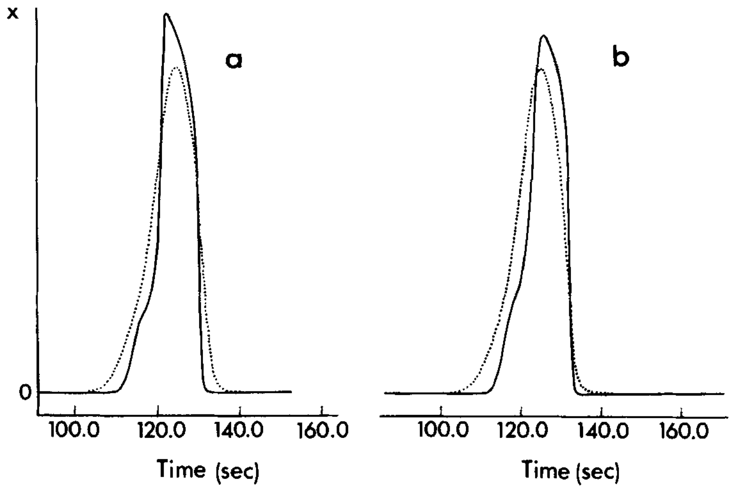


FIG. 13. Influence of the pressure profile of the carrier gas along the column on the elution profile of a finite concentration band in gas chromatography. (a): Profile calculated with the assumption of a constant pressure equal to the average column pressure (P_0/j, where j is the James and Martin pressure correction factor). (b): Profile calculated with the assumption of a classical pressure profile given by Eq. (8) and unperturbed by the migration of the large concentration band.

to fine tune the "numerical diffusion" and use it to replace the apparent diffusion, better known in chromatography by its avatar, the column HETP (*37*).

The final observation is the occurrence of a hump on the front side of the peaks, especially important on the second profile but noticeable also on the two largest ones. This hump is an artefact which originates in the method we used for the derivation of the isotherm representation (*5*). We have not used one of the conventional equations for this isotherm, because they give the concentration in the mobile phase or the vapor pressure at equilibrium as a function of the amount sorbed and they cannot be solved analytically for the amount sorbed, which is necessary for the program. We have preferred to interpolate the data by fitting them on a cubic spline (i.e., a French curve). Although this function is known to give excellent results within the range of the measurements carried out, the spline introduces spurious oscillations outside this range, in its immediate vicinity (cf. Ref. *5*, Fig. 2), making the extrapolation of this function ill-advised. To avoid the consequences of these oscillations, we have assumed the isotherm to be linear at very small concentrations, replacing the spline by a tangent in the range of partial pressures below

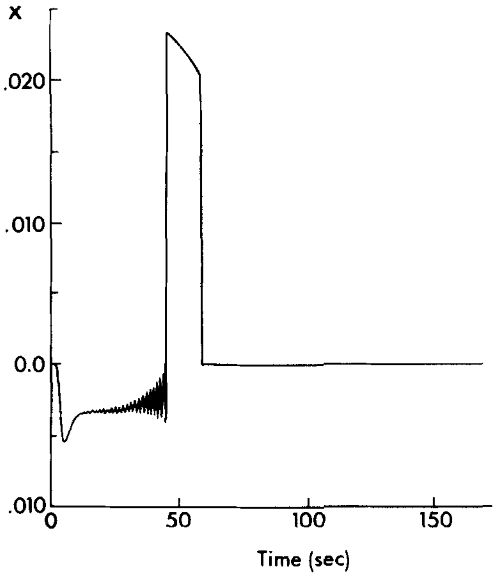


FIG. 14. Example of a concentration profile obtained with an incorrect value of the ratio *dz*/*dt*, not satisfying the Courant-Friedrichs-Lewy condition.

the smallest one experimentally accessible with accuracy. This creates a discontinuity in the second derivative of the isotherm. The result is the hump, which occurs at the same concentration as this discontinuity.

Also noteworthy is the way the tail parts of the experimental profiles corresponding to the three large sample sizes (overloaded column) are barely distinguishable from each other (see Fig. 9a). This fact demonstrates the validity of the concept of an association between a concentration and a velocity (i.e., the retention ratio of the corresponding characteristic line). It also verifies that the correct relationship has been established between the peak profile and the shape of the isotherm: the sharp bend in the tail part of the last two experimental profiles, corresponding to the two largest samples, corresponds to the inflection point of the isotherm, takes place at the same solute concentration, and disappears when the band maximum falls below that concentration. All these features of the experimental profiles (see Fig. 9a) can be found on the calculated profiles 2 to 4 (Fig. 9b), as well as on the different profiles of the band inside the column (Figs. 12a and 12b); they are merely enhanced by the larger efficiency.

Figures 12(a) and 12(b) also illustrate the very rapid decrease, a near collapse, of the band maximum at the beginning of its migration, associated with a rapid increase in the band width. This explains why the massive column overloading, which almost always takes place at injection, generally results in a modest band asymmetry: the nonlinear region of the isotherm is sampled by the band for only a very short part of its migration along the column. It will be noted again in these figures how the sharp bend in the tail of the profiles forms early (it is obvious in Fig. 11a at the 2nd second) and remains stable. It is the diffusion-smoothed discontinuity corresponding to the inflection point of the isotherm. This in turn corresponds to a maximum in $k'(C)$ at the largest retention ratio that a concentration may experience in the column (*8*).

Figures 11(a) and 11(b) show the flow velocity profiles in two cases, a quasi-analytical sample (5.6 μg) and a large one (245 μg). The variation of the flow velocity during the elution of a band, even a large one (Fig. 11b), is relatively small: for a concentration step at the column inlet of 8% during 1.2 s (injection of a 800-μL (NTP) gas sample in a 2.1-mm i.d. column, with a flow rate of 36 mL/min), the maximum velocity change is 0.35%, which is probably too small to be measured, even with a precise flow meter.

Finally, comparison between Figs. 13(a) and 13(b) shows that in gas chromatography it is important to take the pressure gradient into account. The band profile calculated on the assumption that the pressure is constant and equal to the column average pressure results in a predicted band profile which is markedly farther from the experimental one than the profile calculated using Eq. (8) to account for the pressure variation along the column, and this in spite of the fact that both programs take the sorption effect into account in exactly the same way.

Figure 14 illustrates the importance of satisfying the CFL condition in order to achieve acceptable results when operating the program. The profile in this figure bears no resemblance to any chromatographic profile. It does not even have a physical sense, since it incorporates sections where the solute concentration is negative.

XI. CONCLUSION

The numerical solution of the nonlinear, hyperbolic system of partial differential equations which describes the migration of a large concentration band along a chromatographic column has been proven to give satisfactory results in spite of the necessity of neglecting the diffusion term in order to obtain an equation system which can be programmed. The band profiles calculated are in good agreement with those determined experimentally, except for the fact that the sides of the profiles predicted are quite a bit steeper than the sides of the profiles recorded experimentally, at least in our case. This is due to the assumption of a very large column efficiency (the model assumes an infinite efficiency, but the program requires several millions calculations, resulting in numerical smoothing). In the present program there is no way to account for a variation in the column efficiency.

The use of the program written to apply this method of numerical solution permits a detailed study of the various parameters involved in the control of a band profile:

> The nature of the isotherm. It is especially easy to change it since the amount sorbed in the stationary phase (i.e., either dissolved or adsorbed) is calculated using a subroutine of the main program. Any isotherm given as an analytical expression, such as a Langmuir isotherm, is easy to include. Difficulties may arise in the use of experimental adsorption data, depending on the method used to fit these data, but there are many numerical solutions to these problems.
>
> The injection profile. Plug injection of large samples is a physical impossibility. A rectangular injection profile would be ideal, but this can never be achieved in practice. Discretization of a complex injection profile is not difficult to achieve, however. These data are injected in the calculation through another subroutine which makes them easy to change.
>
> The column parameters, describing its design (length, phase ratio) or its operation (flow velocity, inlet pressure in GC). They are easy to modify because they are entered as data in the program. The present program does not permit any adjustment of column efficiency, which is its most significant drawback.

Work is in progress to exploit the potentialities of this powerful tool to study the performance of heavily loaded chromatographic columns in more detail (*37*).

APPENDIX

Singularities in the Solution of the System

The nonlinear hyperbolic system of partial differential equations that describes the behavior of a large concentration band in a chromatographic column can propagate discontinuities, as in many other similar systems (*38*). For example, the system describing the propagation of sounds in air can propagate shock waves. In the case of chromatography, the origin and properties of these discontinuities have been recognized by De Vault (*39*) and discussed by Jacob et al. (*40*) and by Rhee and Amundson (*41*). They are related to the fact that a velocity can be associated with a concentration. If the "velocity of the concentration" increases with increasing solute concentration in the mobile phase, as is the case with a Langmuir-type isotherm, the large concentrations (i.e., the top of the peak profile) tend to pass the small concentrations (i.e., the peak base). De Vault recognized that this is an impossible situation (*39*): it is not possible to have three different values of the concentration at the same point of the column. Instead, a stable vertical front appears and grows. This is a concentration discontinuity. The theory of characteristics explains the appearance, growth, decay, and collapse of these discontinuities (*40*). It is much more difficult, however, to account for their behavior quantitatively during the numerical solution of the problem (*42*). We now present a few explanations on the mathematical background of the problem.

We shall discuss only the simplest case of a single nonlinear, hyperbolic partial differential equation:

$$\left|\begin{array}{l} \dfrac{du}{dz} + \dfrac{d}{dt}(f(u)) = 0 \\[2ex] u(0,t) = u_0(t), \qquad t \in R, z > 0 \end{array}\right. \tag{1a}$$

where the matrice D_wH reduces to the scalar number $f'(u)$, so the problem is always strictly hyperbolic.

There is an important family of curves in the half-plane $(z,t,\ z > 0)$ which is defined by

$$\left|\begin{array}{l} dt/dz = f'[u(t(z),z)] \\[2ex] t(0) = t_0 \end{array}\right. \tag{2a}$$

These curves are called characteristic lines or characteristics of the problem. It is easy to show that along these lines the following relationship applies:

$$\frac{d}{dz}[u(t(z),z)] = \frac{du}{dz} + f'(u)\frac{du}{dt} = 0 \tag{3a}$$

and thus

$$u(t(z),z) = u_0(t_0) \tag{4a}$$

and

$$dt/dz = f'(u_0(t_0)) \tag{5a}$$

The curves we are considering, defined by Eqs. (2a), are straight lines. It is often (and rather loosely) said that the initial condition propagates along the characteristics (*40*). The solution can be derived numerically in a very straightforward and easy way as long as the characteristic lines issued from two different points of the boundary profile ("injection profile") do not intersect, and for all values of time before such an intersection takes place. As soon as two characteristic lines intersect, a regular solution to the system cannot exist any longer. For example, the Burgers equation belongs to the family defined by Eq. (1a) with

$$f(u) = u^2/2 \tag{6a}$$

For this equation the characteristic line from the point $(t_0,0)$ is given by

$$t = u_0(t_0)z + t_0 \tag{7a}$$

With $u_0(t) = t$ as a boundary condition, the characteristics are represented in Fig. 15 and the classical solution is

$$u(t,z) = \frac{t}{1 + z} \tag{8a}$$

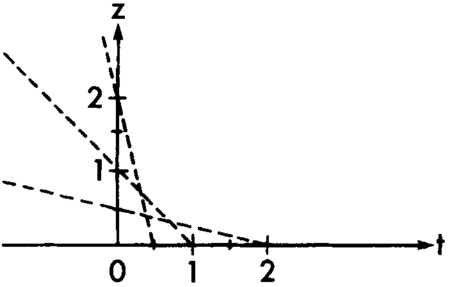


FIG. 15. Characteristic lines of the Burgers equation.

With $u_0(t) = -t_2$, on the other hand, the characteristics from the points $(-t_0,0)$ and $(t_0,0)$, respectively, intersect on the y axis ($t = 0$) and there exists no positive value of z, z_a, such that a classical solution is defined for values of z smaller than z_a.

Weak Solutions of a System of Partial Differential Equations

It becomes necessary to extend the concept of solution of a system of partial differential equations and accept discontinuous solutions. This is done by looking for solutions in the framework of the distribution theory. A function u will be a *weak solution* of the system of partial differential equations if

$$\int_0^{+\infty}\int_{-\infty}^{+\infty}\left[w\,\frac{d\Phi}{dz} + H(w)\,\frac{d\Phi}{dt}\right]dtdz - \int_{-}^{+} w_0\Phi(0,t)dt = 0 \qquad (9a)$$

for any vectorial function Φ of Class C.

Whenever u can be differentiated, we find the original system of equations by part integration of Eq. (9a). On the other hand, let us assume that u is a solution of Eq. (9a) and of Class $C1$ except on Curve C of equation $t = s(z)$. For an open ω of the plane (z,t) containing an arc of C, we define ω^+ and ω^- as shown in Fig. 16 and C^- and C^+ as the part of the border of ω^- and ω^+ which are inside ω. Let w^- and w^+ be the limits of w along the curve, on each respective side. If ϕ is supported in ω, we have

$$\int_0^{+}\int_{-}^{+}\left[w\,\frac{d}{dz} + H(w)\,\frac{d}{dt}\right]dtdz = 0 \qquad (10a)$$

If we integrate by parts in ω^- and ω^+, respectively, since w is regular in these two areas, and if we call $\nu^+ = (\nu z^+,\nu t^+)$ the external normal to w^+ (see Fig. 16), we obtain:

$$\iint_\Omega -\left[\frac{dw}{dz} + \frac{d}{dt}H(w)\right]\phi dtdz + \oint_{C^+}\{w^-\nu_z^- + H(w^-)\nu_t^-\}\phi d\nu$$
$$+ \oint_{C^+}\{w^+\nu_z^+ + H(w^+)\nu_t^+\}\phi d\nu = 0 \qquad (11a)$$

Since this relationship must be valid for any function ϕ with support in ω, we must have

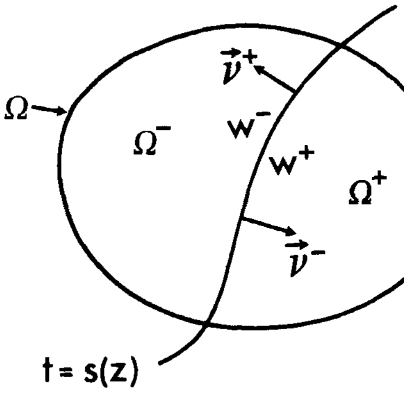


FIG. 16. Definition of the "weak solutions" of a nonlinear, hyperbolic partial differential equation.

$$\frac{dw}{dz} + \frac{d}{dt} H(w) = 0 \qquad (12a)$$

in ω^- and in ω^+ and

$$(w^+ - w^-)v_z^+ + (H(w^+) - H(w^-))v_t^+ = 0 \qquad (13a)$$

As the Curve C has been defined by $t = s(z)$, Eq. (13a) becomes

$$H(w^+) - H(w^-) = s'(z)(w^+ - w^-) \qquad (14a)$$

and $s'(z)$ is the retention ratio of the discontinuity (or shock, by analogy to aerodynamics). Equation (14a) is called the Rankine Hugoniot relationship. It is a necessary and sufficient condition for a function satisfying Eq. (1a), except on a discontinuity line such as C, to be a weak solution of the system. It is interesting to observe that this relationship appears as a natural consequence of the definition of the weak solution (Eq. 9a), while its addition to the system of partial differential equations of chromatography was quite arbitrary (*40*).

New difficulties arise, however, because now a nonlinear hyperbolic partial differential equation may have an infinity of weak solutions, which is not satisfactory. For example, the Burgers equation (Eq. 6a), with an initial condition equal to 0 ($u(0,t) = 0$), has an obvious classical solution, the null function, $u(z,t) = 0$. The following solution, however, is defined for any t_0 and for $a > 0$:

$$
\begin{aligned}
&-\infty < t < t_0 - \frac{a}{2}z, && u(z,t) = 0\\
&t_0 - \frac{a}{2}z < t < t_0, && u(z,t) = -a\\
&t_0 < t < t_0 + \frac{a}{2}z, && u(z,t) = a\\
&t_0 + \frac{a}{2}z < t < +\infty, && u(z,t) = 0
\end{aligned}
\tag{15a}
$$

is an acceptable weak solution. Since it is a classical solution everywhere, it is continuous, while the Rankine Hugoniot relationship is verified along the discontinuities.

The concept of mathematical entropy is introduced to solve this difficulty (*44*).

Mathematical Entropy

We introduce a constraint to limit the number of possible solutions of the system. A function ϕ is called the mathematical entropy of the system of partial differential equations if there exists a function ψ such that

$$\psi' = \phi' D_w H \tag{16a}$$

ψ is called the entropy flux. In fact, due to the exchange between time and space which occurs in the chromatographic system of equations, compared to the classical hyperbolic system, ψ is the time gradient of entropy accumulation.

If a regular solution of the system does exist, then by multiplying it on the left side of $\phi'(w)$, we obtain:

$$\frac{d\phi(w)}{dz} + \frac{d\psi(w)}{dt} = 0 \tag{17a}$$

This is not true, however, if w is not regular. We can then select the entropic solution of the system by requiring that

$$\frac{d\phi(w)}{dz} + \frac{d\psi(w)}{dt} < 0 \tag{18a}$$

for any convex entropy of the system (*44*).

Another definition of the entropic solution is to consider that it is the limit of the solution of systems which include a vanishingly small diffusion term, i.e., it is the limit of the solution of

$$\frac{dw}{dz} + \frac{d}{dt}[H(w)] = \varepsilon \frac{d^2w}{dt^2} \tag{19a}$$

when ε tends toward 0. Equation (19a) has a single, regular solution. The diffusion term has a smoothing, regularizing effect. Furthermore, if ϕ is a convex entropy of the system, we have, for any positive value of ε,

$$\frac{d\phi(w\varepsilon)}{dz} + \frac{d\psi(w\varepsilon)}{dt} < 0 \tag{20a}$$

The limit solution, if it exists, should satisfy Condition (18a). The definition and the procedure make sense since the diffusion term does exist in the original model of chromatography, where it accounts for the resistance to mass transfer and the axial molecular diffusion, but it has been dropped for the sake of simplification and because it is small compared to the other terms.

A detailed study of the diffusional term has been published by Rhee et al. as part of their investigation of the solution of the Riemann problem (*41*). Finally, another method for the selection of the proper solution, due to Lax (*45*), consists in the interdiction of certain types of discontinuity. This was the first method used. It is rather practical and it is the one selected for this work.

The Lax Condition

A shock is "acceptable" if there are no characteristics exiting from it. More precisely, a discontinuity is called a k-shock if the characteristic lines of the kth family enter in the discontinuity while the characteristic lines of the other families do not encounter it. Here are the consequences.

Let w be a weak solution of the equation system, continuous everywhere except along a shock curve C ($t = s(z)$). It is a k-shock curve if the following two relationships are verified along the curve:

$$\lambda_k(w^-) > s'(z) > \lambda_k(w^+) \tag{21a}$$

and

$$\lambda_{k-1}(w^-) < s'(z) < \lambda_{k+1}(w^+) \tag{22a}$$

Once the eigenvalues of the system are arranged in increasing order, $\lambda_k(w(z,t))$ is the retention ratio of the kth characteristics going through the point (z,t), and $s'(z)$ is the retention ratio of the shock at the point $(z,s(z))$.

There are other ways to select the acceptable shocks (*46*, *47*), but the general theory is still quite incomplete. It is possible to demonstrate that these different conditions are equivalent only in particular cases. The following results summarize the present state of development of the theory of nonlinear hyperbolic partial differential equations applicable to the chromatographic model.

In the case of a single equation, all the entropic criteria have been shown to be equivalent. An entropic solution does exist and is unique for all finite boundary condition, u_0 (*48*, *49*). This case is of no importance to us, however. It describes the propagation of the front of a pure gas or vapor which is suddenly introduced into an empty column where it is sorbed. There should be no carrier, so this model cannot describe any chromatographic problem.

In the case of a two-equation problem, Di Perna has shown the existence of a solution for some specific systems and for a finite boundary condition (*50*). A system of two partial differential equations describes the behavior of a single solute in chromatography. It permits the prediction of the band profiles in nonlinear chromatography (largely overloaded columns) and in frontal analysis or of the migration rate of system peaks, but always for a pure compound and a pure mobile phase.

In the case of three-equation or larger systems there is a demonstration of the existence of an entropic solution, after Lax, for a finite and nearly constant boundary condition. It is based on a discretization of the condition and a study of the interactions between discontinuities (*51*). Three-equation systems permit the study of the separation between two compounds in chromatography, provided the ternary sorption isotherm is known, the study of frontal analysis with a mixed mobile phase and the study of other chromatographic problems of similar complexity. It seems that they are the most important in practice. Although chromatography is often used to separate more complex mixtures, the prediction of the band profiles during the separation of a binary mixture would permit detailed studies on the optimization of the experimental conditions for maximum yield, maximum production, or minimum cost which would lead to general conclusions valid to the case of the separation of more complex mixtures.

In spite of the difficulty of the problem and the uncertain nature of the theoretical ground where we have to venture, it seems that such a result is not beyond our reach.

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