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Propagation of Signals of Finite Concentration in Gas Chromatography. I. The Quasi-Ideal Model

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Abstract

A general system of partial differential equations describing the propagation of signals of finite concentrations in a chromatographic column is derived. These equations are related to the mass-balance equations for the solutes and the carrier gas. The model used assumes that there is no temperature or pressure variation at any point in the column when the signal is eluted, and that the equilibrium between stationary and mobile phases is instantaneous. It is shown that this model, which leads to a tractable set of equations, is generally valid. The solution of this system of equations gives new insight into the phenomena which are responsible for the peak deformations and broadening in preparative scale chromatography.

INTRODUCTION

The simplifying assumptions made in linear chromatography, which permit description of the propagation of the conventional analytical peaks at zero concentration in order to account for their usually Gaussian shape and to relate the peak broadening effects to the experimental parameters, are no longer valid when the concentration of the solute in the mobile phase becomes large (*1*).

In a later work we shall show how to calculate the concentration range in which the assumptions of zero concentration chromatography cease to be valid and how to account for the peak deformation and the change in the retention time observed in this range (*2*). In this work we derive and discuss a general system of equations which could account for the important deformations which occur when a signal of finite concentration of any shape is eluted throughout a chromatographic column.

This problem has been studied and discussed many times (*3–7*), but the results previously published have not led to a general quantitative description and discussion of the peak shapes observed in preparative gas chromatography where solute concentrations have to be large. This situation has probably arisen because the point of view of most workers in this field was to consider the effects of large concentration as perturbations to the zero concentration model of propagation, or because of their failure to realize that the effects of diffusion or mass-transfer kinetics are second order compared to the effects originating in the large concentration of solute in the mobile and stationary phases. These are actually first-order effects, as is demonstrated by the fact that the coefficients of the mass-balance equations depend on the concentrations. This is the translation in mathematical terms of the influence of concentrations on flow rate (the *sorption effect*, modifying the overall mass balance in the gas phase) and on the equilibrium constant of dissolution or adsorption (the *isotherm effect*, modifying the mass balance of the solute). Both effects are complex functions of the pressure gradient in the column in gas chromatography, and should be accounted for.

A very broad and deep treatment of the general chromatographic problem at finite concentration has recently been published by Helfferich and Klein (*8*). They covered the field excellently. Many specific cases, however, are not or cannot be solved by their approach, and the problem studied here, the propagation of a one-solute band at finite concentration with a non linear isotherm and a large sorption effect, belongs to that group, although it is a special case of multicomponent chromatography. Unfortunately, the hodographic transform H, used by Helfferich and Klein (*8*), which greatly simplifies the solution of the system of equations describing the propagation and separation of a multicomponent band when the partition coefficients are not independent, is useful only for linear or Langmuir-type isotherms. In the more general case the H-transform cannot be used and one should rely on the characteristics theory as described by Jacob (*9*) or more recently by Aris and Amundson (*10*).

Furthermore, when the mobile phase is a gas, the sorption effect becomes very important and should be accounted for quantitatively. The mathematical difficulties of the problem are then much more important, and it was possible for Helfferich and Klein to explain only in broad terms how the sorption effect modifies the migration of bands when the isotherm is linear (Ref. *8*, pp. 348–350).

This work is thus an attempt to extend the previous work on multicomponent chromatography (*8*) to the general case of gas chromatography where the sorption effect and the effect of a nonlinear isotherm do coexist and simultaneously influence the band migration, sometimes synergistically, sometimes in an antagonistic way. This illustrates the major differences between gas and liquid chromatography, the sorption effect and the mobile phase compressibility being negligible in this later case.

Finally, we have chosen to put the main emphasis on the study of the stability and transformation of shocks or discontinuities as a means of following the change of peaks shape during their migration. The corresponding stability diagram discussed in this work can be considered as the counterpart of the composition grids of Helfferich (*8*) which permits the study of the transformation of the continuous part of the signal.

The rigorous mathematical formulation of the problem would be possible although many difficulties would arise in the significance or even definition of some kinetics parameters. It is well known that a complete solution of this problem at the analytical level has not yet been given, although most of the phenomena seem to be understood and a satisfactory description of the experimental results has been achieved (*1*). The situation is much more complex when the concentration is finite, and before trying to account for the kinetics effects in details, it seemed to us interesting to study quantitatively the first-order effects, and to determine the degree to which they account for the deformation of the peaks which are observed at large concentrations and which cannot be accounted for in kinetic terms only. The complete system of equations is not mathematically tractable. A considerable simplification occurs if the broadening effects of mass-transfer kinetics are neglected, which is another reason to consider only the first-order terms. Finally, the justification of this assumption lies in the high rate of mass transfers under the experimental conditions prevailing in chromatography, so that the first-order effects become the most important at moderate concentrations, as will be shown (*2*), the kinetics effects taking place only to dampen the very steep concentration gradients which would otherwise occur, and thus to "soften the angles."

Such a physicochemical model would be useless if it had no predictive value. Accounting satisfactorily for the first-order effects of concentration in chromatography at finite concentration will lead to a new, more accurate, general method of determining dissolution or adsorption isotherms (*2*). It will give a quantitative method to optimize the productivity of industrial prep-scale chromatographic units (*11*), and it will also allow us the estimation of the range of concentration in which the zero-concentration conventional theory of chromatography is valid, and how deviations from the ideal model can lead to effects which are well known by the analysts but have not yet been explained.

Finally, the justification of our model lies in its success, its mathematical tractability (*12*), the excellent agreement between the concentration profiles obtained from computers and from chromatographs (*11*), and in its other applications (*2*).

We shall first describe the assumptions made in deriving the systems of equations and discuss their justification as well as their conditions and range of validity. Then we shall derive the equations which describe the propagation of continuous parts and of discontinuities.

A MODEL OF PROPAGATION OF SIGNALS OF FINITE CONCENTRATION

Some of the assumptions made in this model have been suggested in previous work (*3–7*). The most important new characteristics of our model are the combination of:

(1) The explicit use of thermodynamic data at equilibrium in the equations. This is especially important in the study of the conditions of stability of the discontinuities and of the temperature influence on these conditions.

(2) The influence of the pressure gradient on the migration and deformation of peaks is introduced and accounted for.

(3) The model makes use of the existence of the stagnant mobile phase (*2*), the fraction of the mobile phase which is inside the support particles. This is important because it allows an accurate definition and choice of the velocities which are involved in the equations.

(4) A double set of equations of mass balance because of the existence of discontinuous solutions to the propagation problem.

General Assumptions

These assumptions regard the behavior of the gas phase, the equilibrium between the two phases, and the temperature.

(1) The gas phase behavior remains ideal both for its compressibility

and for its mixing properties. In addition, the flow rate is always determined by Darcy's law (*13*) applied to the pure carrier gas. The pressure profile is the same whether the column is in steady conditions or during the elution of a large concentration zone.

(2) The mobile and the stationary phases are always in equilibrium. Furthermore, the rate of the axial diffusion is zero and the rate of the radial diffusion is infinite, so the composition of both the gas and liquid phases are constant in a column cross-section.

(3) The column is isotherm. The variation of local temperature when the zone is eluted is neglected.

We shall now discuss the reasons, the range of validity, and the importance of the assumptions before proceeding to the derivation of the equations.

Ideal Behavior of the Gas Phase

The carrier gas has already been assumed to behave ideally in chromatography. It has been shown that even for carbon dioxide this assumption is realistic (*14*), so it seems to be quite valid in our problem, too, especially if it is taken into account that the partial pressure of the solute does not exceed 0.3 bar at the injection in practice (*15*) and that this pressure is reduced as the band spreads. Further corrections should probably be applied, however, for the contribution of gas phase nonideality to the equilibrium constant between both phases.

Flow Rate and Pressure Profiles

It is easy to illustrate the influence of the pressure gradient in the column as follows. If a mixture of carrier gas and solute vapor of constant concentration is steadily fed into a column, as in frontal analysis, an equilibrium is eventually reached between the two phases and there is no more macroscopic exchange of solute between these phases. The situation is then identical to the expansion of the mixture in a tube, from column inlet to outlet pressure, with no change of composition whatsoever. The partial pressure of the solute is proportional to the local pressure, and accordingly its local concentration in the stationary phase decreases in proportion to this pressure. In elution chromatography for a single compound, the partial pressure and concentration can only be lower than the corresponding values in this steady state, and this has important consequences.

The retention of a compound is determined by the ratio between the number of sorbed molecules and the number of molecules in the gas phase at equilibrium in the local conditions. When the isotherm is not linear, this pressure variation directly affects the retention by changing the equilibrium constant. In addition, whether the isotherm is linear or not, there is a second effect of decompression on the gas velocity.

It is necessary to include the pressure gradient in the equations. Unfortunately, it is not possible to do so by referring to some average pressure, as we shall show later that the effect of the pressure gradient is a function of the isotherm itself (*2*). It is not possible to solve the equations derived without some simplification. This is the reason why we shall assume with Haarhoff (*16*) that the pressure profile is unchanged by the elution of a large concentration signal. This assumption is justified by the observation that the local pressure does not vary by more than a few millibars during the elution of a large concentration band (*16*). Mathematically, this means that

$$\partial P/\partial t = 0 \tag{1}$$

whereas $\partial p/\partial z$ and $\partial u/\partial z$ are not zero. The pressure profile is given by integration of Darcy's law:

$$P = P_i^2 - \frac{z}{L}(P_i^2 - P_o^2) \tag{2}$$

where $P(z)$ is the local pressure, P_i and P_o the inlet and outlet pressures, and L the column length (*13*).

We shall also neglect the influence of the solute concentration on the viscosity of the mobile phase. This assumption is valid in elution chromatography where the bands are relatively narrow compared to the column length and the solute concentrations are smaller, but some correction should probably be introduced if the model is to be applied to frontal analysis.

Equilibrium between the Two Phases

It is presently impossible to solve the equations of a model which assumes a finite rate of mass transfer between the two phases. The simpler problem already discussed here is very difficult to solve, and extensive computer time is necessary to obtain actual concentration profiles for given experimental conditions (*11*). Furthermore, because the kinetics of mass transfer is not well understood under the zero concentration assumption, where it plays a major role, it would not be easy to express it mathematically for finite concentrations [for example, should the coupled theory (*1*) be generalized and how?] not even to speak of the problem of making a reasonable estimation of the rate constants necessary for practical applications.

The equilibrium assumption is therefore necessary in order to have a solvable system. Its justification arises from the fact that the effects of diffusion and other kinetic phenomena are second-order sources of band broadening compared to those originating from the finite concentration, as explained above; i.e., the coefficients of the mass-balance equations are function of the concentrations, and thus the first partial derivatives disappear at zero concentration, whereas the equilibrium assumption results, in mathematical terms, in neglecting the second partial derivatives in these equations.

This has a very important consequence which has not been fully realized yet, although its existence was known before (*8*). It has been understood and used systematically by Jacob for the first time (*9*). This is the appearence and propagation of stable discontinuities (*17*). It is difficult to explain with accuracy this effect which originates from some special properties of the system of equations to which our model leads but is not actually observed, although the very asymmetrical peak profiles observed [for example, with the early peaks in capillary columns (very sharp front and "normal" tail) or with overloaded columns (very sharp front *or* tail)] illustrate pretty well the situation for the analysts (cf. Fig. 1). The system of equations we shall describe has mathematical properties similar to those of the systems describing two much more widely known phenomena which, by analogy, may also illustrate the situation, although

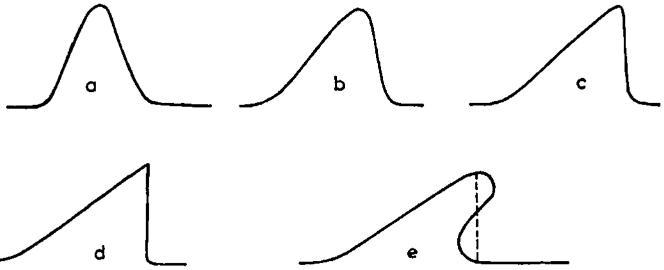

FIG. 1. Origin of discontinuities of concentration in conditions in which the sorption effect, for example, is important. The front of a band initially Gaussian (*a*) of large concentrations becomes steeper and steeper (*b*) until a vertical inflection tangent appears (*c*) which is the origin of a concentration discontinuity (*d*). A peak profile, such as *e*, would be physical nonsense.

care should be taken not to draw the analogy too far. These are the shock waves and the rolling sea waves. A shock wave is a pressure discontinuity which propagates faster than sound; the local compression heats the oscillating medium, and so the waves which would tend to propagate faster than the shock wave enter a region of space where air is cold and are delayed whereas the waves which would tend to propagate slower than the shock wave are in a hot region of space where their speed becomes faster and they join up with the shock, hence its stability. Mathematically, the conditions of stability of these discontinuities are similar; they correspond to the conditions of nonexistence of the characteristics of the system of equations (*8*, *12*, *17*, *18*). The problem of the stability of the concentration discontinuities in finite concentration chromatography can be illustrated by the rolling waves.

In some circumstances, for example, near the seashore, waves develop a rolling form. This phenomenon, which would be impossible if gravity was stronger, arises because, in the conditions prevailing near the beach, the equation describing the continuous profile of the wave propagating along the axis Oz yields three values of the water height in some range of z values.

The system of equations describing the propagation of a concentration profile in chromatography has similar properties, as originally shown by De Vault (*19*) for liquid chromatography (cf. Fig. 1). Clearly however, such a shape is impossible for a concentration profile. De Vault has suggested a solution: to replace the impossible part of the continuous profile obtained as a solution of the standard equations by a vertical line which conserves the profile area (*19*), as shown Fig. 1. A more rigorous solution, more general and satisfactory from the point of view of the physical chemist, is to consider that concentration discontinuities are possible parts of the peak profile and to write the mass-balance equations around them to determine their propagation rate.

A discontinuity appears when an inflection tangent to the profile becomes vertical. Then the discontinuity builds up at the expense of the neighboring continuous profiles until it eventually reduces and disappears if the column is long enough. Because chromatography is essentially a dilution process, the conditions of zero concentration will always prevail at the end and the peak will become Gaussian. A discontinuity can reduce progressively to an inflection point with the vertical tangent and disappear. In some cases it can also collapse as a whole.

It might be argued that discontinuities are mere artifacts introduced only by our unability to tackle them with a more accurate model which incorporates kinetic effects. Although it is true that diffusion relaxes the infinite concentration gradients corresponding to discontinuities, the fundamental effects from which they originate are real. The very steep peak fronts or tails correspond to conditions in which the first-order and the second-order effects compensate, and in which the trend to a steeper profile because of the large concentration effect is compensated for by the dampening effects of diffusion which smoothe the profiles. It is known that in such conditions numerical solutions to systems of partial differential equations have a strong trend toward divergence. So, as long as the peak profile cannot be described by an analytical solution, the study of discontinuities properties and propagation is necessary.

It can also be shown mathematically that (*20*) in the general case where first-order and dispersional effects arise together, some parts of the peak propagate merely by translation, with no change in shape. When dispersional effects tend to zero, these nondeforming parts tend to become vertical. Thus discontinuities in the first-order, nondispersional model can be considered as a limiting case of the general model and should not be regarded as an "artifact."

In summary, our model will require the derivation of two systems of equations, one determining the propagation of the continuous part of the concentration profile and the other determining the propagation of the discontinuities. The study of the interaction between the two systems, i.e., the appearance and disappearance of discontinuities during the propagation of a band, will be an important part of the resolution of the problem.

Radial Equilibrium

The assumption of a zero radial concentration gradient through a chromatographic column is indeed a consequence of the more general equilibrium assumption. Most of the peak broadening in prep-scale columns at very low sample size, when second-order effects are predominant, originates in the radial heterogeneity of the column packing (*21*). More recently, however, columns of large diameter (5 in. to 1 ft) have been reproducibly packed with an efficiency at zero concentration which is of the same order of magnitude as the efficiency of analytical columns (*15*), thus making this assumption quite realistic.

Isothermal Elution of Large Concentration Bands

The elution of a chromatographic band generates a temperature profile which is a function of the concentration profile or, more precisely, of its derivative (although the temperature effect is not proportional to the derivative of the concentration profile). This effect has been studied by Bayer and Hupe and used as the basic principle of a new detector (*22*). More recently, Hupe has studied the temperature signal which appears during the elution of a large concentration band and shown that temperature variations can be as large as 15°C (*23*). This effect, however, is very much dependent on the thermal conductivity of the packing, and it is well known that the thermal conductivity of powders depends greatly on the nature of the surrounding gas. When nitrogen, which was used as the carrier gas by Hupe, is replaced by helium, which is much more interesting as a carrier gas in prep-scale gas chromatography because it leads to larger productivity (*15*), we observed on a 5 in. diameter column a much smaller effect: 1 or 2°C only.

A small correction might be necessary for larger diameter columns, but this can be treated as a small perturbation to the isothermal propagation.

Influence of Mass Transfer on Band Propagataion

The material balance equations are usually derived in chemical engineering with the assumption that the gas velocity throughout the column is not affected by mass transfer between stationary and mobile phases. This approximation is justified when these mass transfers are stationary. It would not be valid in chromatography where these transfers are in a transitory state.

The influence of mass transfers on the propagation, the *sorption effect* (*24*), is simple to explain. The carrier gas velocity is larger than the migration rate of a band. Let us consider the volume element of a pure carrier gas which arrives in a region of the column where the solute concentration is not zero. Part of the solute dissolved in the stationary phase vaporizes into the gas phase; its partial molar volume in the gas phase is about 200 times larger than in the solution. The migration rate of the back border of the carrier gas volume is determined by the boundary conditions of the system. Thus the front border accelerates because of this increase in the gas volume (the local pressure does not change appreciably). This explains why, during the migration of a band in certain experimental conditions, the large concentrations tend to migrate faster than the lower concentrations. Because it is impossible for the larger concentrations to leave before the lower ones, the peak profile becomes steeper and a stable discontinuity builds up.

As the peak migration causes a local increase in the gas flow velocity, it is no longer possible to describe the signal propagation by one mass balance equation because this velocity becomes a variable. Such an equation should be written explicitly for the carrier gas and each solute. The solutions of the system will give the concentrations and the velocity profile at any time.

The fact that the concentration profiles of two solutes *and* the velocity profile are given by one common system of equations demonstrates the interaction of the bands of two solutes, at least as long as they are not resolved from each other, when the concentration is large and it is impossible to consider these different phenomena separately (*25*).

Another important consequence of this interaction between concentration and flow velocity deals with the relationship between retention time and retention volume. Because of the sorption effect, the ratio of the retention volume to the retention time for a given mole fraction X is not the outlet carrier gas flow rate, but the actual local flow rate, with the sorption effect included, or its average along the column if the pressure gradient is not negligible. As in most cases the retention time is the observed data, the retention volume, which cannot be derived simply from t_R anymore, loses most of its interest in large concentration chromatography. The retention time, which is easy to measure, has the further advantage of being identical with the residence time as defined in reactor theory in chemical engineering.

Although in practice the sorption effect is important only in gas chromatography, it is general to all types of chromatography. The dissolution of the solute in the stationary phase results in an increase of the volume of this phase and a decrease in the volume of the stagnant mobile phase (*2*), which in turn results in an increase in the apparent rate of migration of the solute. The adsorption itself results in a decrease in the local velocity of the mobile solution. Both of these effects compensate exactly only if the partial molar volumes of the solute are the same in the two phases, otherwise the sorption effect is a function of the difference between these two partial molar volumes. Thus the sorption effect is really important only in gas chromatography where the partial molar volume in the gas phase is about 200 times larger than the partial molar volume of the solute in the solution (or of the adsorbate). One could add that the sorption effect is not restricted to chromatography but is present in any separation process where there is any "radial" mass transfer occurring in a longitudinal flux, such as in distillation and absorption.

We shall now proceed successively to the derivation of the systems of equations describing the propagation of continuous concentration profiles and of concentration discontinuities.

SYSTEM OF EQUATIONS FOR THE PROPAGATION OF CONTINUOUS SIGNALS

We shall assume in this section that all functions are continuous and can be differentiated. This assumption is a very important one and *must* be made because we shall show that we must also consider discontinuous parts in the signal and that these parts obey quite different equations. This is an example of cases where rigorous mathematics is very important in physical chemistry.

We shall use the same packing model as the one used to derive a general theory of chromatography at zero concentration and to unify the theories of packed and capillary columns (*2*). This model distinguishes between two fractions of the mobile phase which act quite differently: the mobile fraction, which is outside the packing particle and possesses all the kinetic moment, and the stagnant fraction, which impregnates the porous particles, is motionless, and is in direct contact with the stationary phase (cf. Fig. 2). Mass transfer between the mobile fraction (which is the only one available for convection) and the stationary phase takes place through the stagnant fraction. The equilibrium constant between these mobile and stagnant phases is unity. An important advantage of this model is to clarify definitions and the choice of the various velocities and the average velocities (*2*).

Mass Balance of the Solute

Let n_A^m be the number of mole of Solute A in the mobile fraction of the gas phase, n_A^s the number of mole in the stagnant fraction, n_A^L the number

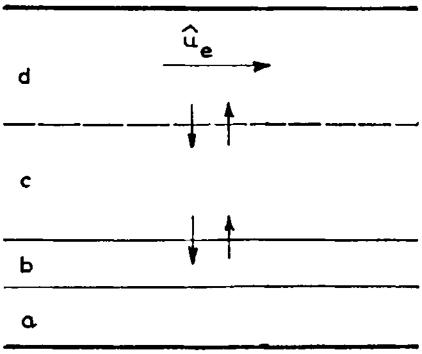

FIG. 2. Scheme of a gas–liquid chromatography column. (*a*) Solid support. (*b*) Stationary liquid phase. (*c*) Stagnant gas phase inside the porous particles of support. (*d*) Mobile gas phase, outside the support particles.

of mole in the stationary phase, and $\hat{u}_e$ the cross-section average, interstitial gas velocity:

$$\hat{u}_e = \frac{Q}{\varepsilon_e A} \tag{3}$$

where Q is the local volume flow rate, A is the column cross-section area, and ε_e is the external porosity (related to the column permeability). V_G is the total volume available to the gas phase in the column, and V_e is the volume available to the mobile fraction. V_e is the extraparticle void volume of the column ($V_e = \varepsilon_e V_c$, where V_c is the total volume of the column, $V_c = AL$).

The mass balance for the solute during the time dt in a fraction of the column of length dz is

$$\frac{\partial n_A{}^m}{\partial t} + \frac{\partial n_A{}^s}{\partial t} + \frac{\partial n_A{}^L}{\partial t} = -\frac{\partial(\hat{u}_e n_A{}^m)}{\partial z} \tag{4}$$

because the contribution of diffusion to the mass flow is neglected. As the various phases are assumed to always be in equilibrium, the total number of solute moles in the gas phase, $n_A{}^G$, is

$$n_A{}^G = n_A{}^m + n_A{}^s = \frac{V_G}{V_e} n_A{}^m \tag{5}$$

since the equilibrium constant between the mobile and stagnant fractions of the gas phase is unity. Combination of Eqs. (4) and (5) gives

$$\frac{\partial n_A{}^G}{\partial t} + \frac{\partial n_A{}^L}{\partial t} = -\frac{\partial}{\partial z}\left(\frac{\hat{u}_e V_e}{V_G} n_A{}^G\right) \tag{6}$$

We shall define a new term which has the dimensions of a velocity by

$$u = \frac{\hat{u}_e V_e}{V_G} \tag{7}$$

We shall give the physical significance of u in the section entitled System of Equations. Taking into account this definition of u, we write Eq. (6) as

$$\frac{\partial n_A{}^G}{\partial t}(1 + k') = -\frac{\partial(u n_A{}^G)}{\partial z} \tag{8}$$

with

$$k' = \left(\frac{\partial n_A{}^L}{\partial t}\right)_z \bigg/ \left(\frac{\partial n_A{}^G}{\partial t}\right)_z \tag{9}$$

This definition of k' is justified because of its properties as we shall demonstrate. As discussed above, we shall assume that $n_A{}^L$ is a function of P and $n_A{}^G$ only; not an explicit function of time and the abscissa (equilibrium assumption). We shall also assume that the local pressure is not a function of time.

Then

$$\left(\frac{\partial n_A{}^L}{\partial t}\right)_z = \left(\frac{\partial n_A{}^L}{\partial n_A{}^G}\right)_z \left(\frac{\partial n_A{}^G}{\partial t}\right)_z = \left(\frac{\partial n_A{}^L}{\partial n_A{}^G}\right)_p \left(\frac{\partial n_A{}^G}{\partial t}\right)_z \tag{10}$$

and

$$k' = \left(\frac{\partial n_A{}^L}{\partial n_A{}^G}\right)_p \tag{11}$$

k' as defined by Eq. (9) is a function of the equilibrium isotherm of Solute A between the gas and stationary phases. This is a generalization of the conventional definition of the column capacity factor to the case of nonlinear isotherms. We shall later study the properties of k' as defined by Eq. (11).

It should be noted that this definition of k' is quite general and is not restricted to the ideal gas phase. In fact, when, as is done below, the gas phase is assumed to be ideal, the p subscript can be dropped and the partial differential Eq. (11) becomes a simple differential one.

In this case the equation of state of an ideal gas can be written

$$n_A{}^G = \frac{V_G X_A{}^G P}{RT} = \frac{V_G X P}{RT} \tag{12}$$

where P is a function of z but not of t.

The mass-balance equation of the solute (cf. Eq. 8) then becomes

$$P\frac{\partial X}{\partial t}(1 + k') = -\frac{\partial(uPX)}{\partial z} \tag{13}$$

Note that Pu is not constant in Eq. (13), as in analytical chromatography, since the solute vapor contributes appreciably to the local velocity.

Mass Balance of the Carrier Gas

Because the carrier gas is not dissolved in the stationary phase, the mass balance of the carrier gas can be derived from Eq. (13) when X is replaced by $(1 - X)$ and k' by 0:

$$-P\frac{\partial X}{\partial t} = -\frac{\partial[uP(1 - X)]}{\partial z} \tag{14}$$

System of Equations

There are three unknowns (u, P, X) which are functions of two variables (z and t). The three partial differential equations are Eqs. (2), (13), and (14). A complete definition of the problem also involves Eq. (11), the equation of the isotherm, and the shape of the band at the inlet of the column (boundary condition).

A more general form of the system, simpler to use, can be obtained. Let

$$F = uP \tag{15}$$

F is proportional to the local, apparent molar flux of gas per unit surface area of the column cross section. Addition of Eqs. (13) and (14) gives

$$P\frac{\partial X}{\partial t}k' = -\frac{\partial F}{\partial z} \tag{16}$$

Multiplication of Eq. (15) by X and subtraction from Eq. (13) gives

$$P\frac{\partial X}{\partial t}[1 + k'(1 - X)] = -F\frac{\partial X}{\partial z} \tag{17}$$

At this stage, the physical meaning of u can be assessed as follows: taking $k' = 0$ (inert sample) in Eq. 17, one finds

$$\frac{\partial X}{\partial t} = -u\frac{\partial X}{\partial z}$$

From a known property of partial differentials, this can be rewritten as

$$\left(\frac{\partial z}{\partial t}\right)_X = u$$

The left-hand side of this equation can be identified with the apparent speed of propagation of the constant molar fraction X.

Thus u is the local apparent transport velocity of an inert peak. It must be emphasized that u is not solely determined by the flow characteristics, as shown by Eq. (7), which means that deriving Eq. (8) directly by mass balance would not have been correct because the right-hand side of Eq. (8) has no real convective meaning.

Determination of *k*′

If the gas phase is ideal, the partition equilibrium of A between the solutions and the gas phase is given by the conventional thermodynamic relationship

$$PX/P_A^0 = \gamma_A X_A^L = Y \tag{18}$$

where P_A^0 is the vapor pressure of the solute, γ_A is its activity coefficient in the solution, X_A^L is its mole fraction in solution, and Y is its activity in both phases. γ_A is a function of X_A^L.

k' should be related to X in order for the system of Eqs. (2), (16), (17), and (11) to be self-consistent. An analytical explicit relationship is possible only if γ_A is constant (linear isotherm). Otherwise, even the simplest conventional relationship between γ_A and X_A^L is too complex to allow the derivation of an explicit relationship, and only a numerical solution is possible.

Combination of Eqs. (11), (12), and (18) gives

$$k' = \frac{RT}{PV_G}\frac{\partial n_A^L}{\partial X} = \frac{RT}{P_A^0 V_G}\frac{\partial n_A^L}{\partial Y} \tag{19}$$

The number of mole of solute in the solution is

$$n_A^L = \frac{m_L}{M_L}\frac{X_A^L}{1 - X_A^L} \tag{20}$$

where m_L and M_L are the mass of stationary phase in the column and its molecular weight, respectively. Differentiation of Eq. (20) and its combination with Eq. (19) gives

$$k' = \frac{RT}{P_A^0 V_G}\frac{m_L}{M_L}\frac{1}{(1 - X_A^L)^2}\frac{dX_A^L}{dY} \tag{21}$$

This equation is similar to the one used by Helfferich (*7*) although the effects of the pressure gradient have been neglected in his work. This was a satisfactory approximation because Helfferich was interested in ion-exchange chromatography, where the pressure effects on compressibility and the solubility of liquids are indeed negligible, but this would not be acceptable in gas chromatography.

It should also be noted that Eq. (21) is valid only for an ideal gas phase. If it is not the case, a correct expression can be derived from Eq. (11) if the function $n_A^L(P, n_A^G)$ is known.

Differentiation of Eq. (18) and its combination with Eq. (21) gives

$$k' = k_0' \frac{\gamma^{\infty}}{\gamma_A} \frac{1}{1 + X_A^L \, \partial \ln \gamma_A / \partial X_A^L} \frac{1}{(1 - X_A^L)^2} \tag{22}$$

where

$$k_0' = \frac{RT}{P_A^0 \gamma^{\infty} V_G} \frac{m_L}{M_L} \tag{23}$$

is the conventional value of the column capacity factor at zero concentration and γ_A^{∞} is the activity coefficient at infinite dilution.

Properties of *k*′

It is clear from Eq. (22) that k_0' is the limit of k' when X_A^L becomes infinitely small.

Equation (21) also shows that the variation of k' with X_A^L results from the superposition of two effects, the isotherm effect or deviation from Henry's law, which is accounted for by the differential term

$$dX_A^L/dY$$

and the effect of the variation of the volume of the solution, which introduces the term $1/(1 - X_A^L)^2$.

This last effect is important since, when the volume of solution increases as the solute concentration increases, a given change in the intermolecular forces per unit volume (dX_A^L/dY) is obtained only if a larger number of solute molecules is dissolved.

We shall now study the variations of k' near $X_A^L = 0$ (dilute solution). The variations of $1/k'$ with X_A^L is represented by the variations of

$$\Delta = \frac{dY}{dX_A^L}(1 - X_A^L)^2 \tag{24}$$

Differentiation of Eq. (24) gives

$$\Delta' = (1 - X_A^L)(Y''(1 - X_A^L) - 2Y') \tag{25}$$

Y' is always larger than 0.5 if the stationary phase is not a polymeric material (*26*). Y'' may be positive and is generally smaller than unity. Consequently, Δ' is most often negative and k' increases with increasing X_A^L (and X). The result is the same if the stationary phase is a polymer. To show this, a relationship similar to Eq. (22) using the volume fraction ϕ_A^L

instead of the mole fraction is derived. In fact, if γ_A is considered as a function of $\phi_A{}^L$, this equation is obtained by replacing $X_A{}^L$ in Eq. (22) by $\phi_A{}^L$. The variations of $1/k'$ with $\phi_A{}^L$ thus depend on the sign of

$$\Delta' = (1 - \phi_A{}^L)(Y''(1 - \phi_A{}^L) - 2Y') \tag{26}$$

where Y is now a function of ϕ_A. It is shown in thermodynamics that for solutions having the same dissolution enthalpy, the derivatives $\partial Y/\partial\phi_A{}^L$ and $\partial^2 Y/(\partial\phi_A{}^L)^2$, when the solute and solvent molar volumes are very different, are nearly equal to the derivatives $dY/dX_A{}^L$ and $d^2Y/(dX_A{}^L)^2$ when solute and solvent molar volumes are similar.

So in gas–liquid chromatography, where k' is an increasing function of X, the large concentrations will seem to be retained more than the low concentrations, resulting in a leading peak with a very sharp tail when the isotherm effect is important. The isotherm effect and the sorption effect are then antagonistic.

This interesting fact can be used to find an optimum temperature in preparative gas–liquid chromatography or to measure the isotherm curvature (PLT method) (*2*).

This can be illustrated in the special case where Henry's law remains valid in a large range of concentrations. Then

$$\gamma_A = \gamma_A{}^\infty = \text{constant} \tag{27}$$

and

$$k' = k_0' \frac{1}{(1 - X_A{}^L)^2} \tag{28}$$

or

$$k' = k_0' \frac{1}{\left(1 - \dfrac{PX}{P_A{}^0\gamma_A{}^\infty}\right)^2} \tag{29}$$

Equation (29) shows that the usual statement that k' may increase or decrease with increasing X and, accordingly, that the peak will have a rear or frontal discontinuity is wrong, as was noted by Stock (*27*). k' increases with increasing X whatever the activity coefficient of A in the solution, except, perhaps, for solutes with extremely unusual thermodynamic properties, but we have not found an example of this.

The situation is different in gas–solid chromatography because the curvature of the isotherm in the low concentration range is much larger. In most cases, such as for a Langmuir isotherm, k' will decrease with increasing X, and the sorption and isotherm effects will act in the same direction.

It should be noted, too, that k' is a function of the local pressure P, although this is not explicit in Eq. (22), because an analytical expression of k' can be given only as a function of $X_A{}^L$. But $X_A{}^L$ is a function of Y and consequently of PX, through the equation of the isotherm (Eq. 18). Thus k' increases with P at constant X, which is the mathematical translation of the well-known fact that the solubility of a vapor increases with its partial pressure in the gas phase.

Equation (22) shows that k' can be considered as a constant only under conditions in which $X_A{}^L$ is very small. From Eq. (18), this is possible only if X is very small, which is the usual field of analytical applications, or if one of the two conditions is satisfied:

$$P_A{}^0 \gg P$$

or

$$\gamma_A \gg 1 \tag{30}$$

In both cases the corresponding compound is weakly retained, and this observation is of limited use in practice.

Maximum Range of Concentration in Preparative Gas Chromatography

It has been shown that practically the most important source of limitation of the partial pressure of the sample at injection is overflooding of the column by the solution of sample in the stationary phase (*2*) due to swelling of the solution outside the porous particles. In practice this prevents to use partial pressures larger than some fraction of the inlet pressure (*15*); this effect is quite general.

There is another source of limitation which might be important in particular cases, especially when exotic stationary phases are used for their unusual specificity. Equation (21) shows that k' becomes infinite if $dY/dX_A{}^L = 0$, which is the situation arising whenever there is separation of the solutions by demixing into two phases of the solution of Compound A in the stationary phase. In this case the two solutions are in epuilibrium with a gas phase of well-defined composition. No separation can be achieved under such circumstances because chromatography proceeds only as long as there is a well-defined relationship between the composition of the gas phase and the overall composition of the liquid phase. When there is separation, the composition of each phase is constant, and only the ratio of the amounts of the two phases changes.

This limitation of the partial pressure of the sample at injection, which apparently has not yet been observed, illustrates the analogy between chromatography and extractive distillation when the same limit is observed.

SYSTEM OF EQUATIONS FOR THE PROPAGATION OF DISCONTINUITIES

The equations derived above are not valid for a concentration discontinuity if one occurs in the signal. To derive the equations of the propagation of such a discontinuity, the mass balance of Solute A is written for an infinitely small volume of the column which includes the discontinuity (*9*, *17*, *18*, *28*).

In the section on general assumptions we explained that we assumed that the pressure profile is not modified during the elution of a large concentration band and that it remains the same as the one given by Eq. (2) and derived from Darcy's law:

$$u = -w\frac{\partial P}{\partial z} \tag{31}$$

where w is a proportionality constant.

Equation (31) allows discontinuities of the gas flow velocity with a continuous pressure which may be differentiated at any point of the column.

From a theoretical and experimental study of pressure fluctuations, Haarhoff (*16*) has, during the elution of large concentration bands, reached conclusions opposite to those of a paper by Scott (*29*), i.e., that there is no pressure discontinuity. It seems certain that this is a good approximation of the experimental facts.

Mass Balance Equations

Let V_{12} be the migration rate of a discontinuity which separates the column between two volumes, the downstream one, in which all parameters are denoted by the subscript 1, and the upstream one, for the parameters of which the subscript 2 is used (cf. Fig. 3). The solute mass balance gives

$$-V_{12}[(n_{A_1}{}^G - n_{A_2}{}^G) + (n_{A_1}{}^L - n_{A_2}{}^L)] = -(u_1 n_{A_1}{}^G - u_2 n_{A_2}{}^G) \tag{32}$$

Since the carrier gas is ideal, Eq. (32) may be written

$$-V_{12}\left[X_1\left(1 + \frac{n_{A_1}{}^L}{n_{A_1}{}^G}\right) - X_2\left(1 + \frac{n_{A_2}{}^L}{n_{A_2}{}^G}\right)\right] = -u_1 X_1 + u_2 X_2 \tag{33}$$

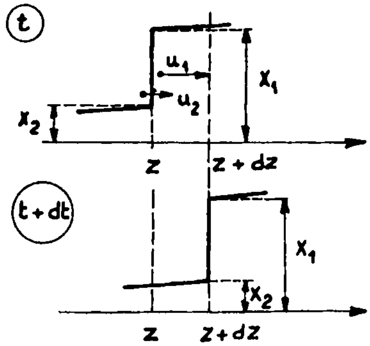

FIG. 3. Mass balance around a shock wave u_2 and u_1 are the speed of the gas phase upstream and downstream, respectively, of the discontinuity. Due to the sorption effect, there is a discontinuity in the speed of the mole fraction discontinuity. X_1 and X_2 are the mole fractions in the gas phase, and $V_{12} = dz/dt$ is the apparent migration rate of the discontinuity.

with $X_1 = X_{A_1}{}^G$ and $X_2 = X_{A_2}{}^G$, analogous to Eq. (12).

Let

$$k_1 = X_1 \frac{n_{A_1}{}^L}{n_{A_1}{}^G} \tag{34}$$

k_1 is the retardation factor downstream from the discontinuity, with its analog k_2 upstream.

The propagation rate of the discontinuity is then described by the mass balance equation for the solute, which becomes

$$-V_{12}(X_1 - X_2 + k_1 - k_2) = -u_1 X_1 + u_2 X_2 \tag{35}$$

and the mass balance equation for the carrier gas, which is obtained from Eq. (35) where $k_1 = k_2 = 0$, and replacing X_1 by $1 - X_1$ and X_2 by $1 - X_2$:

$$-V_{12}(X_2 - X_1) = -u_1(1 - X_1) + u_2(1 - X_2) \tag{36}$$

Equations (35) and (36) can be rearranged by elimination of either u_1 or u_2:

$$V_{12} = \frac{u_1}{1 + \dfrac{k_1 - k_2}{X_1 - X_2}(1 - X_2)} = \frac{u_2}{1 + \dfrac{k_1 - k_2}{X_1 - X_2}(1 - X_1)} \tag{37}$$

The retardation factor is given by Eq. (34). We shall now study this factor.

Determination of the Retardation Factor

A relationship can be derived between k_1 (or k_2) and the column capacity factor k'. From Eq. (34):

$$k_1 = X_1 \frac{n_{A_1}{}^L}{n_{A_1}{}^G} = \frac{X_1}{n_{A_1}{}^G} \int_0^{n_{A_1}{}^G} \left(\frac{\partial n_{A_1}{}^L}{\partial n_{A_1}{}^G}\right)_p dn = \int_0^{X_1} \left(\frac{\partial n_{A_1}{}^L}{\partial n_{A_1}{}^G}\right)_p dX \tag{38}$$

Combination with Eq. (11) gives

$$k_1 = \int_0^{X_1} k' \, dX \tag{39}$$

Integration of Eq. (22), or combination of Eqs. (12), (20), (23), and (34) gives

$$k_1 = k_0' \frac{P_A{}^0 \gamma_A{}^\infty}{P} \frac{X_{A_1}{}^L}{1 - X_{A_1}{}^L} \tag{40}$$

Equations (37) and (40) permit the numerical calculation of the propagation of discontinuities in any case.

Boundary Conditions

To achieve a complete definition of the problem, the boundary conditions should be given for the integration of the system of equations. These boundary conditions deal with the carrier gas flow and the band injection.

There are two ways of defining the flow rate. First, give the inlet and outlet pressures which correspond experimentally to a control of the inlet pressure [$P(z = 0, t) = P_i$]; second, give the inlet flow rate and the outlet pressure which corresponds to a control of the carrier gas flow rate [$F(0, t) = F_0$ = constant]. The outlet pressure remains constant in both cases [$P(L, t) = P_0$].

These two conditions are equivalent if we assume that the pressure profile does not change during the elution of a peak; then Darcy's law relates the inlet and outlet pressures to the flow rate. We shall use the second conditions [$F(0, t) = F_0$; $P(L, t) = P_0$] since we have chosen F as our main variable.

The boundary conditions regarding the mole fraction are those of elution chromatography:

$$\begin{array}{ll} t = 0 & X(z, 0) = 0 \\ 0 < t \le \xi & X(0, t) = X_0(t) \\ t > \xi & X(0, t) = 0 \end{array} \tag{41}$$

and corresponds to the injection of a band profile which is determined by the variation of the mole fraction X_0 during time ξ.

CONCLUSION

We have designed a model of quasi-ideal chromatography to study the effects of large concentration on the deformation and broadening of bands in gas chromatography, with the basic assumptions that the gas and liquid phases are always in equilibrium and that the pressure profile is not changed during the elution of a zone. This model is described by a set of partial differential equations, algebraic equations, and boundary conditions which are summarized in Table 1.

This system has no analytical solution. Furthermore, the coefficients of the partial differential equations are functions of the local pressure and consequently depend on the abscissa, so the method of characteristics which is valid for a pressure constant in the whole column (*9*, *12*, *18*), cannot be applied without approximations. This method has been very

TABLE 1

Mathematical Translation of the Quasi-Ideal Model of Gas Chromatography at Finite Concentration

F, X continuous	F, X discontinuous
$P\frac{\partial X}{\partial t}[1 + k'(1 - X)] = -F\frac{\partial X}{\partial z}$	$V_{12} = \frac{u_1}{1 + \frac{k_2 - k_1}{X_2 - X_1}(1 - X_2)}$
$P\frac{\partial X}{\partial t}k' = -\frac{\partial F}{\partial z}$	$V_{12} = \frac{u_2}{1 + \frac{k_2 - k_1}{X_2 - X_1}(1 - X_1)}$
$k' = k'_0\frac{\gamma_A{}^\infty}{\gamma_A}\frac{1}{1 + X_A{}^L\frac{d\ln\gamma_A}{dX_A{}^L}}\frac{1}{(1 - X_A{}^L)^2}$	$k_1 = k'_0\frac{P_A{}^0\gamma_A{}^\infty}{P}\frac{X_{A1}{}^L}{1 - X_{A1}{}^L}$
	$k_2 = k'_0\frac{P_A{}^0\gamma_A{}^\infty}{P}\frac{X_{A2}{}^L}{1 - X_{A2}{}^L}$
$P = \sqrt{P_i{}^2 - \frac{z}{L}(p_i{}^2 - P_0{}^2)}$ (pressure profile)	
$X = \frac{P_A{}^0}{P}X_A{}^L\gamma_A$	
$\gamma_A = \gamma_A(X_A{}^L)$ (isotherm)	
Boundary conditions: $u(0, t) \equiv u_0$	
$t = 0$ $X(z, 0) \equiv 0$	
$0 < t \leq \zeta$ $X(0, t) = X(t)$	
$t > \xi$ $X(0, t) = 0$	

useful for solving the simpler problem in which the pressure is constant all along the column, for calculating the peak profiles during the elution of bands of compounds with linear isotherms (cf. Eqs. 27–29), and for studying their deformation (*11*).

The assumption of a negligible pressure gradient is not very realistic, however, because relatively fine particles have to be used to pack the columns to enhance the kinetics of mass transfer, and this results in pressure drops in excess of 1 atm. Experiments show that such pressure gradients have a strong influence on the band shape and thus should be taken into account (*15*).

We shall study the solution of the system when the pressure gradient is different from zero in another work (*30*).

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