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Propagation of Signals of Finite Concentration in Gas Chromatography. II. Study of the Discontinuities and Their Conditions of Stability

Patrick Valentin[a]; Georges Guiochon[b]
[a] CENTRE DE RECHERCHES ELF, SOLAIZE, FRANCE [b] LABORATOIRE DE CHIMIE ANALYTIQUE PHYSIQUE ECOLE POLYTECHNIQUE, PARIS 5ÈME, FRANCE

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Propagation of Signals of Finite Concentration in Gas Chromatography. II. Study of the Discontinuities and Their Conditions of Stability

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PATRICK VALENTIN

CENTRE DE RECHERCHES ELF
69 SOLAIZE, FRANCE

GEORGES GUIOCHON

LABORATOIRE DE CHIMIE ANALYTIQUE PHYSIQUE
ECOLE POLYTECHNIQUE
PARIS 5ÈME, FRANCE

Abstract

The study of a quasi-ideal chromatography model at finite concentration shows the existence of stable discontinuities, resulting either from sorption or isotherm effects. A set of conditions, illustrated in a diagram, determines the conditions of stability of these discontinuities. Solution thermodynamics shows that there exist three possible modes of peak migration. In all cases a progressive variation of the experimental conditions (pressure or temperature of the column) allows passage from one of these modes to another. One of these three possible modes, the double-shock mode, has not been described previously. It is characterized by front and rear stable discontinuities, and its importance rests on the fact that it corresponds to the minimum band broadening. This mode is observed for a column temperature which is near the boiling point of the solute under the average pressure of the carrier gas. The results also show that the derivation of equilibrium isotherms from the deformation of the peaks obtained with large sample sizes is not valid generally.

INTRODUCTION

In a previous paper we discussed a quasi-ideal chromatography model which accounts for the migration of bands of large concentration by assuming that the mobile and stationary phases are always in equilibrium at all points of the column and that the pressure gradient remains unchanged during the elution of a band (*1*). We have shown that the effects of a large solute concentration are first order whereas kinetic effects are second order because the concentration appears in the coefficients of the first partial derivatives in the mass-balance equation whereas the diffusion is introduced only with the second partial derivative (*1*). The solution of a similar model has been previously discussed by Conder and Purnell (*2*) in the special case where the pressure is constant in a column which corresponds to an infinite column permeability. The use of the method of characteristics in this last case has allowed us to refine Haarhoff's theoretical study, to determine precisely the conditions of stability of the discontinuities, to study their interference with the continuous part of the profile (*3*, *4*), and to calculate concentration profiles during the elution in the special case of a linear isotherm (*5*).

Here we will discuss the problems of the stability of the discontinuities and of the deformation of the peaks as related to nonlinear isotherms, together with the effect of column temperature and pressure. The pressure will still be considered as constant. This assumption considerably simplifies the calculations and allows a clearer picture to be presented more easily. It is, unfortunately, less and less realistic because the developments in the packing of large columns lead to the use of finer and finer particles in order to take advantage of the better efficiency available, thus resulting in large pressure drops which can exceed 1 atm for a 1-meter long column (*6*). In another paper we discuss the extension of these results to the case where the pressure gradient is not negligible (*7*).

The complete system was derived in a previous paper (*1*) with the assumption that the pressure profile is unchanged during elution of a band (1). The equations can be simplified by assuming a constant pressure by replacing P and $F = Pu$ by 1 and u, respectively. The system thus obtained is summarized in Table 1 (see Symbols).

We shall first recall briefly the results regarding the migration rate of the continuous profile obtained by integration of Eqs. (1) and (2) and the velocity of the discontinuities (Eq. 4), which have been established previously (*2*–*4*). Then we shall show how the general, mathematical theory of the stability of the discontinuities (*8*) can be applied and combined to the

TABLE 1

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

Constant pressure	
F, *X* continuous	*F*, *X* discontinuous
$\frac{\partial X}{\partial t}[1 + k'(1 - X)] = -u\frac{\partial X}{\partial z}$ (1)	$V_{12} = \frac{u_1}{1 + \frac{k_2 - k_1}{X_2 - X_1}(1 - X_2)}$ (4)
$\frac{\partial X}{\partial t}k' = -\frac{\partial u}{\partial z}$ (2)	$V_{12} = \frac{u_2}{1 + \frac{k_2 - k_1}{X_2 - X_1}(1 - X_1)}$ (5)
$k' = k_0'\frac{\gamma_A{}^\infty}{\gamma_A}\frac{1}{1 + X_A{}^L\frac{d\ln\gamma_A}{dX_A{}^L}}\frac{1}{(1 - X_A{}^L)^2}$ (3)	$k_1 = k_0'\frac{P_A{}^0}{P}\gamma_A{}^\infty\frac{X_{A1}{}^L}{1 - X_{A,1}{}^L}$ $k_2 = k_0'\frac{P_A{}^0}{P}\gamma_A{}^\infty\frac{X_{A,2}{}^L}{1 - X_{A,2}{}^L}$ (6)
	$P = 1$ (7)
	$X = \frac{P_A{}^0}{P}X_A{}^L\gamma_A$ (8)
	$\gamma_A = \gamma_A(X_A{}^L)$ (9)
Boundary conditions:	$u(0, t) \equiv u_0$ (10)
	$t = 0 \quad X(z, 0) \equiv 0$ $0 < t \leqslant \tau \quad X(0, t) = X_0(t)$ (11) $t > \tau \quad X(0, t) = 0$

known results of solution thermodynamics. The various possibilities of peak deformation during the elution of bands injected as rectangular zones will then be discussed.

MIGRATION RATES IN CHROMATOGRAPHY AT FINITE CONCENTRATIONS

u is the local apparent transport velocity of an inert compound and is related to the cross-section averaged insterstitial gas velocity ($\hat{u}_e = Q/\varepsilon_e A$, where Q is the volume flow rate of carrier gas, ε_e is the insterstitial porosity, and A is the column cross-section area). In steady-state conditions, u is constant (cf. Eq. 10) and is given by

$$u = u_0 = \hat{u}_e\frac{\varepsilon_e V_c}{V_G} \qquad (12)$$

where V_c is the total volume of the column and V_G the volume available to the gas phase.

During the elution of a large concentration band, the velocity u is no longer constant (*2*) but is given by

$$u = u_0 \exp\left[\int_0^X \frac{k'\,dX}{1 + k'(1 - X)}\right] \tag{13}$$

Any peak profile injected in the column will propagate *and* change shape in the same time. For this reason it is convenient, but not perfectly correct, to speak of the migration rate of a mole fraction X or of its apparent transport velocity v. This velocity is, in fact, the velocity associated to the corresponding characteristic line X = constant (*2*, *4*, *9*). v is given by

$$v = \frac{u}{1 + k'(1 - X)} \tag{14}$$

The residence time of a mole fraction X in the column is

$$t_X = \frac{L}{u_0} \frac{1 + k'(1 - X)}{\exp\left[\int_0^X \frac{k'\,dX}{1 + k'(1 - X)}\right]} \tag{15}$$

This relationship is valid only if there is no discontinuity for the mole fraction X, i.e., for the continuous part of the profile. The speed V_{12} of a discontinuity is related to the apparent transport velocity corresponding to the continuous profile, downstream from the discontinuity, v_1, by the equation

$$\frac{V_{12}}{v_1} = \frac{1 + k_1'(1 - X_1)}{1 + \frac{k_2 - k_1}{X_2 - X_1}(1 - X_2)} \tag{16}$$

In this equation X_1 and X_2 are the mole fractions of the Compound A in the carrier gas immediately upstream and downstream from the discontinuity, respectively, and k_1 and k_2 are the corresponding retardation factors (*1*) given by Eq. (6) (cf. Table 1).

Equations (13) to (16) allow the determination of the progressive deformation of a band of any initial shape during its elution through the column. They can be used to solve numerically all problems of propagation, but they do not lead to a simple study of the effects of various parameters on the peak deformation and broadening. Such a general study is much easier if we consider the properties of stability and propagation of the discontinuities.

THE STABILITY OF CONCENTRATION DISCONTINUITIES

Up to now it has been shown that concentration discontinuities exist and their migration rate has been calculated (Eq. 16). It still remains to be determined when and how they are formed and disappear, since eventually, if the column is long enough, the peak shape will become Gaussian.

The conditions of stability of a discontinuity result immediately from its main property: a discontinuity is a surface perpendicular to the column axis, moving along the column, on which the mole fraction of solute changes abruptly from a given value X_1 downstream of the discontinuity, to another value X_2 upstream of the discontinuity. The rate of migration of the discontinuity itself is determined by the properties of the chromatographic system (Eqs. 4 to 6) and so are the apparent transport velocities of the mole fractions X_1 and X_2 (Eq. 14), so there are three possibilities.

(1) The migration rate V_{12} of the discontinuity is larger than the apparent transport velocity of X_1 *and* smaller than the apparent velocity of X_2:

$$v_1 < V_{12} < v_2 \tag{17}$$

As v_1 is smaller than v_2, the mole fraction X_2 tends to outrun the mole fraction X_1, thus creating a rolling wave profile; either X_2 would roll over X_1 if $X_2 > X_1$ or dig under it if $X_2 < X_1$. This is absolutely impossible, as previously shown (*1*), and so the discontinuity is stable. Of course, this does not prevent X_1 and X_2 to change progressively as a result of the interaction between the continuous and discontinuous parts of the profile, but the discontinuity itself remains stable as long as Condition (17) is fulfilled. We shall refer to it as a "shock," by obvious analogy to a shock wave.

(2) The migration rate of the discontinuity is smaller than the apparent transport velocities of *both* X_1 and X_2:

$$V_{12} < v_1 \quad \text{and} \quad V_{12} < v_2 \tag{18a}$$

There is a trend to build up the discontinuity from the rear or upstream and to destroy it from downstream. Again, the discontinuity is stable if $v_1 < v_2$, but we shall consider a stable discontinuity fulfilling Condition (18) as partly stable.

TABLE 2

Stability Conditions of Concentration Discontinuities

$V_{12}/v_1 \geq 1$	and	$V_{12}/v_2 \leq 1$	stable shocks discontinuities
$V_{12}/v_1 \geq 1$	and	$V_{12}/v_2 \geq 1$	partly stable discontinuities
$V_{12}/v_1 \leq 1$	and	$V_{12}/v_2 \leq 1$	
$V_{12}/v_1 \leq 1$	and	$V_{12}/v_2 \geq 1$	unstable discontinuities

There is a symmetrical case with

$$V_{12} > v_1 \qquad \text{and} \qquad V_{12} > v_2 \tag{18b}$$

which has similar properties.

(3) The last possibility is

$$v_1 > V_{12} > v_2 \tag{19}$$

where the discontinuity is not stable. An unstable discontinuity can either collapse at once or disappear progressively, $|X_2 - X_1|$ decreasing to zero by continuous changes of both X_1 and X_2, depending on the chromatographic conditions.

Conditions (17) to (19) can be written with the use of V_{12}/v_1 and V_{12}/v_2 only, ratios which are given by Eq. (16). These conditions are summarized in Table 2.

THE STABILITY DIAGRAM

Conditions such as those given in Eqs. (17) to (19) or in Table 2 define regions in the X_1, X_2 plane in which shocks can or cannot exist. This geometrical construction, which illustrates the conditions of stability of the discontinuities, is their stability diagram. This diagram is very useful because it will allow us to describe the progressive deformation of a peak and the appearance and disappearance of the discontinuities.

The diagram is limited to a square since both X_1 and X_2 are by definition smaller than unity. In addition, they should be smaller than

$$X_m = \frac{P_A{}^0}{P} \tag{20}$$

whenever the column temperature is smaller than the boiling point of Compound A under the column pressure P. X_m will be the upper limit of X_1 and X_2.

A point on the X_1, X_2 diagram (cf. Fig. 1) represents a discontinuity between mole fractions X_1 (downstream) and X_2 (upstream). This point

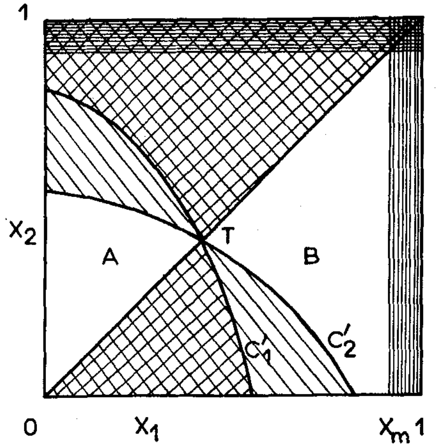

FIG. 1. Stability diagram with one transition point, T. The column temperature is slightly lower than the boiling point so the region $X_i > X_m$ is impossible. To satisfy Condition 21 (stability of the corresponding discontinuity), a point above the bisector ($X_2 > X_1$) should be below C_1'; accordingly, images below the bisector and above C_1' fulfill that condition too. The same is true for Condition 22 and C_2'. Region A corresponds to stable discontinuities at the front edge of the peak ($X_2 > X_1$) while Region B corresponds to stable discontinuities at the rear part of the peak.

is the image of the discontinuity. If the point is above the bisector, the discontinuity is on the leading part of the peak ($X_2 > X_1$); if the point is below the bisector, the corresponding discontinuity is on the peak tail ($X_2 < X_1$).

The inequalities given in Table 2 define regions of the plane which are above or below the two curves of the equations

$$\frac{V_{12}}{v_1} = 1 \quad \text{or} \quad \frac{1 + k_1'(1 - X_1)}{1 + \dfrac{k_2 - k_1}{X_2 - X_1}(1 - X_2)} - 1 = 0 \tag{21}$$

$$\frac{V_{12}}{v_2} = 1 \quad \text{or} \quad \frac{1 + k_2'(1 - X_2)}{1 + \dfrac{k_2 - k_1}{X_2 - X_1}(1 - X_1)} - 1 = 0 \tag{22}$$

Equation (22) is derived from Eq. (21) by exchanging X_1 and X_2 so the two curves C_1 and C_2 are symmetrical in respect to the bisector. Once these curves are drawn, the regions of stability of the discontinuities are determined from the sign of the left-hand side of Eqs. (21) and (22).

A shock can either originate in the shape of the injection band (in the case of a rectangular injection there are front and a rear discontinuities initially) or appear some time during elution when Condition (17) is fulfilled. Such a shock will appear on one side of the peak, usually at a point where $X \neq 0$. The image of the newly appearing discontinuity is on the bisector. This line is thus a natural border of the stability regions.

It can be shown that both curves C_1 (Eq. 21) and C_2 (Eq. 22) can be decomposed into the bisector and another curve, C_1' or C_2'. Eq. (21), for example, can be written as

$$(X_2 - X_1)f(X_1, X_2) = 0 \tag{23}$$

An example of a stability diagram is shown in Fig. 1 for a case where $X_m < 1$ and where the curves C_1 and C_2 intersect the bisector at one point T.

The discontinuity is stable if the left-hand side of Eq. (23) is positive. Consequently, the first condition for the stability of the discontinuities is that $f(X_1, X_2) > 0$ above the bisector $(X_2 > X_1)$ and $f(X_1, X_2) < 0$ below the bisector. It has been arbitrarily assumed in Fig. 1 that $f(X_1, X_2) > 0$ above the curve C_1'. The regions where this condition is not fulfilled are hatched vertically (Fig. 1). We then proceed in the same way with Eq. (22) and curve C_2'.

The use of such a diagram to describe the progressive deformation of a peak during its elution is complicated and will be described later, after the properties of C_1' and C_2' and the significance of the point T are discussed. To illustrate the possibilities of the method, however, we shall describe here (cf. Fig. 2) the elution of a band injected as a rectangular pulse, where the stability diagram (Fig. 2a) is very simple, the curves C_1 and C_2 are limited to the bisector, and the discontinuities are stable for $X_2 > X_1$ only. The physical conditions leading to such a diagram will be discussed in the next section.

The rectangular injection pulse has two shocks, A and A′ (Fig. 2*b*). These shocks are represented by their images A and A′ on the diagram, respectively. The front shock (Point A) is not stable in the case selected since its image is in a hatched area. It will collapse at once and be replaced by a continuous profile. The shock in A′ is stable; this shock will keep the same amplitude as long as the plateau is not destroyed, the peak being transformed into BB′ (Fig. 2*c*). When the continuous profile begins to interfere with the shock, its height decreases progressively (profile CC′, Fig. 2*d*). The image of that shock moves from A′ toward the origin. The

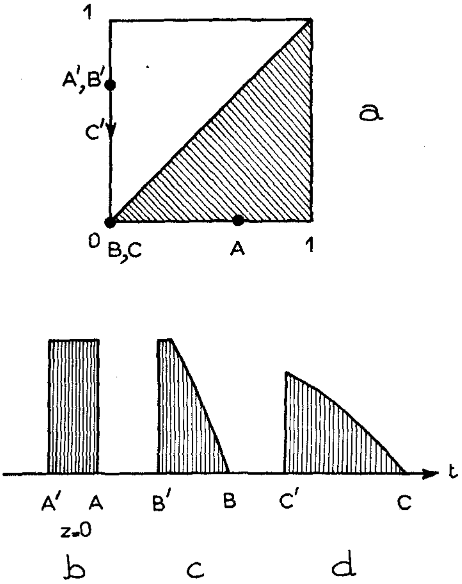

FIG. 2. Propagation of a rectangular injection in the case of a linear isotherm ($X_m > 1$, sorption effect). (*a*) Stability diagram. Stable discontinuities can be found only at the front of the peak. The corresponding points are above the bisector. (*b*) The injection. The two discontinuities are shown by A and A′. Profiles BB′ and CC′ are observed after migration of the band along the column.

area of the different profiles are the same (conservation of mass) if care is taken for the variation of the gas phase velocity.

In diagrams such as the one shown in Fig. 2(*a*), only one shock can take place, either at the front or the rear part of the peak profile. In more complex situations, such as that represented by Fig. 1, two shocks are possible, one on each side of the profile.

We shall now discuss the various properties of the stability diagram.

Equation of C_1'

k' is given by Eq. 3 (Table 1), and k_1 and k_2 by Eq. (6). Then Eq. (21) becomes

$$(1 - X_1)(1 - X_2^L) - (1 - X_2)(1 - X_1^L) \times \frac{X_2^L - X_1^L}{X_2 - X_1}\frac{P^0}{P}\gamma_1\left(1 + X_1^L\frac{d\ln\gamma_1}{dX^L}\right) = 0 \qquad (24)$$

This equation cannot be solved in X_1 or X_2 in the general case, but once the isotherm (Eq. 9) is given, it is possible to solve it numerically.

In the case of an ideal solution ($\gamma_A \equiv 1$), Eq. (24) becomes:

$$(X_2 - X_1)\left(\frac{P_A{}^0}{P} - 1\right) = 0 \tag{25}$$

Then C_1' (and C_2') does not exist and only the bisector is a boundary in the stability diagram. Three cases are possible.

(1) $P_A{}^0 > P$ (the column pressure P is usually taken as unity). Then Condition (17) is fulfilled for $X_2 > X_1$, and discontinuities are stable when the corresponding point is above the bisector (cf. Fig. 2). The sorption effect dominates, and shocks appear at the front of the peak.

(2) $P_A{}^0 < P$. Then Condition (17) is fulfilled for $X_1 < X_2$, and discontinuities are stable when the corresponding point is below the bisector. In this case shock can appear only at the rear edge of the peak. The isotherm effect is dominating.

(3) $P_A{}^0 = P$. Then Eq. (24) is always satisfied, and so

$$v_1 = v_2 = V_{12}$$

All existing discontinuities are stable, and a rectangular injection will propagate without deformation.

This result is very important. It shows that at a column temperature equal to the boiling point of the substance at the column pressure, the peak broadening will result only from the second-order kinetic terms, while the effects of a finite concentration will tend to stabilize the injection profile and will add no contribution of their own to the broadening. A similar result is obtained with a nonideal solution following Henry's law ($\gamma = \gamma^\infty = $ constant). Then Eq. (23) becomes

$$(X_2 - X_1)\left(\frac{\gamma P_A{}^0}{P} - 1\right) = 0 \tag{26}$$

This time the double-shock propagation mode is obtained for $\gamma P_A{}^0 = P$. It again corresponds to conditions in which the peak broadening is minimum and the peak symmetry maximum. It should be noted, however, that it is quite improbable that a solution could follow Henry's law up to such a large mole fraction.

Effect of Pressure and Temperature on the Stability Diagram

As shown by Eq. (23) the influence of temperature and pressure on the boundaries of the stability diagram results from the variation of the activity coefficient and the vapor pressure. The activity coefficient varies only slightly with temperature, and its change in the 20 to 50°C range around the boiling point of the studied compound will be negligible compared to that of the vapor pressure except in very unusual cases; for example, when the retention process is a complexation reaction or when very strong polar interactions take place in solution. Then it is probable that the solution will be very far from ideal and that injection of large sample with high partial pressures will not be possible.

Practically all the effects of temperature and pressure are described by the variations of the dimentionless parameter X_m (cf. Eq. 20).

Transition Point

As explained above, when a discontinuity appears on the side of a continuous profile, its image is on the bisector. The discontinuity cannot usually appear on either side of the peak. It will appear on the peak tail if $dv/dX < 0$, v being the apparent transport velocity of the mole fraction X (cf. Eq. 14) because then Condition (17) can be satisfied only when $X_1 > X_2$. If $dv/dX > 0$, the discontinuity will appear on the front side, since Condition (17) can then be fulfilled only if $X_1 < X_2$. Only if $dV/dX = 0$ can the shock appear on either side of the peak. The corresponding point is a transition point. From Eqs. (13) and (14) the coordinates of the transition points are given by

$$2k' - (1 - X)\frac{dk'}{dX} = 0 \tag{27}$$

These points are also the intersection between the bisector and the curves C_1' and C_2' as can be seen directly by letting $X_2 = X_1 + dX$ and expanding Eq. (21) into powers of dX. This is, of course, because transition points which correspond to the origin of a shock either at the front or the rear side of a peak, are on the boundary of two stability regions.

The determination of the transition points is made from Eq. (27) which can be written as

$$2 - (1 - X)\frac{d}{dX}(\ln k') = 0 \tag{28}$$

In a previous paper (Ref. 1, Eq. 21) it was shown that

$$k' = k_0'\gamma_A^\infty \frac{dX_A^L}{dY} \frac{1}{(1 - X_A^L)^2} \tag{29}$$

This equation leads to Eq. (3). Combining Eqs. (28) and (29) gives

$$2X_m(1 - X^L)\left(\frac{dY}{dX^L}\right)^2 - (1 - X)\left[2\frac{dY}{dX^L} - (1 - X^L)\frac{d^2Y}{(dX^L)^2}\right] = 0 \tag{30}$$

The roots of this equation can be calculated if we know the isotherm equation (Eq. 9) because Eq. (8) may be written as

$$Y = X/X_m = \gamma X^L \tag{31}$$

Transition Range

This is the range of X_m values in which there is at least one transition point on the stability diagram. The favorable temperature range is the one in which it is possible to operate the column so that there is a transition point on the stability diagram of a given compound. It depends on the transition range and the pressure range in which it is possible to operate the column. It is interesting to determine the transition range because then it is possible to find operating conditions of the column (temperature, pressure, sample size) which ensure minimum peak broadening. Then the effect of a large sample concentration, far from contributing to an increase in peak broadening, will tend to reduce it because of the stabilizing effect of the shocks, which works against the kinetics sources of peak broadening.

For an ideal solution the transition range is limited to one value $X_m = 1$. For all solutions this value belongs to the transition range since Eq. (30) is valid for $X_m = 1$ and $X^L = Y = 1$.

It is also interesting to determine whether the origin can be a transition point. The corresponding value of X_m is

$$X_m^* = \frac{2Y'(0) - Y''(0)}{2[Y'(0)]^2} \tag{32}$$

where Y' and Y'' stand for dY/dX^L and $d^2Y/(dX^L)^2$. Values of X_m immediately lower than X_m^* do not belong to the transition range which is, in practice, limited to the range $|X_m^* - 1|$. The determination of the sign of the left-hand side of Eq. (30) and consequently of dv/dX has two possibilities.

(1) If $X_m < X_m^*$, $dv/dX < 0$ around the origin. Only shocks at the rear side of the peak are possible for low solute concentrations. The isotherm effect is dominating even at low concentrations. There is no transition point, the isotherm effect is the most important at all concentrations, and shocks are only possible at the rear front.

(2) If $X_m > X_m^*$, $dv/dX > 0$ around the origin. At low concentrations only shocks at the front side of the peak are possible, but in most cases of actual solutions there is a transition point at which dv/dX becomes negative if $X_m < 1$. So the sorption effect dominates at low concentrations with a front shock while the isotherm effect dominates at high concentrations with a rear shock. If $X_m > 1$, there is no transition point and the sorption effect always dominates.

Operating conditions resulting in $X_m = X_m^*$ are called limit transition conditions. They can be determined directly by plotting the variation of retention times with sample size at various temperatures (*7*).

These conditions of X_m result in conditions on the column temperature, which also depends on the column pressure (cf. Eq. 20).

Examples of Propagation

The results of the previous discussion permit a simple qualitative description of the deformation of large concentration bands through a chromatographic column.

If there is no transition point, the propagation is very simple as shown already in Fig. 2 (sorption effect). The propagation in the case of a dominating isotherm effect is shown in Fig. 3. The situation is more complex if there is a transition point.

Then the apparent transport velocity v of a mole fraction X first increases with increasing X (sorption effect), goes through a maximum (transition point), and decreases with a further increase of X (isotherm effect). Figure 4 shows such a stability diagram (Fig. 4*a*) and the profile corresponding to various steps in the propagation of a rectangular injection (Fig. 4*b* to 4*h*). These profiles can be determined either by computer calculation using Eqs. (13) to (16), or by a graphic method when the velocity profile $v(X)$ is known. The area of the profile is not constant because the local fluid velocity changes with X (cf. Eq. 13), and only $\int_0^\infty Xu\,dt$ is constant. The arrows give the direction of movement of the shocks in their displacement relative to the mass center of the band. Consequently,

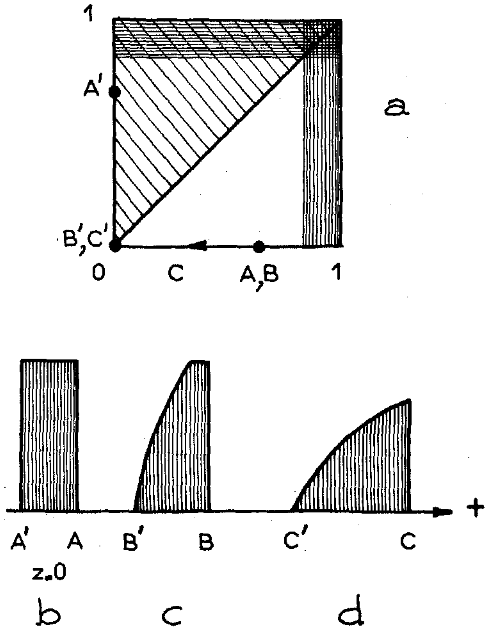

FIG. 3. Propagation of a rectangular injection in the case of a linear isotherm ($X_m < 1$, isotherm effect). (*a*) Stability diagram. A shock can exist only on the back side of the peak. (*b*) Injection profile. (*c*) and (*d*) Profiles obtained after migration along the column.

the construction of the shock suggested by De Vault (*10*), which is exact in liquid chromatography, is incorrect in gas chromatography.

The rectangular injection (Fig. 4*b*) introduces two shocks, a front one (A) and a rear one (A′). The corresponding points on Fig. 4(*a*) show that the second one is stable, but not the first one. Only the shock represented by Point B (Fig. 4*a*) can be stable at the front of a peak, so the injection profile is rapidly transformed into the profile shown in Fig. 4(*c*): the front and rear shocks are represented by Points B and A′ (Fig. 4*a*), and a continuous profile appears on the front side *above* Shock B. The distance between the two shocks, each of which is traveling at constant speed, increases progressively until the plateau disappears. Then the height of the rear shock begins to decrease progressively, the corresponding point moving from A′ to C′. The corresponding shock accelerates while it decreases, but its speed remains smaller than that of the front shock. The band

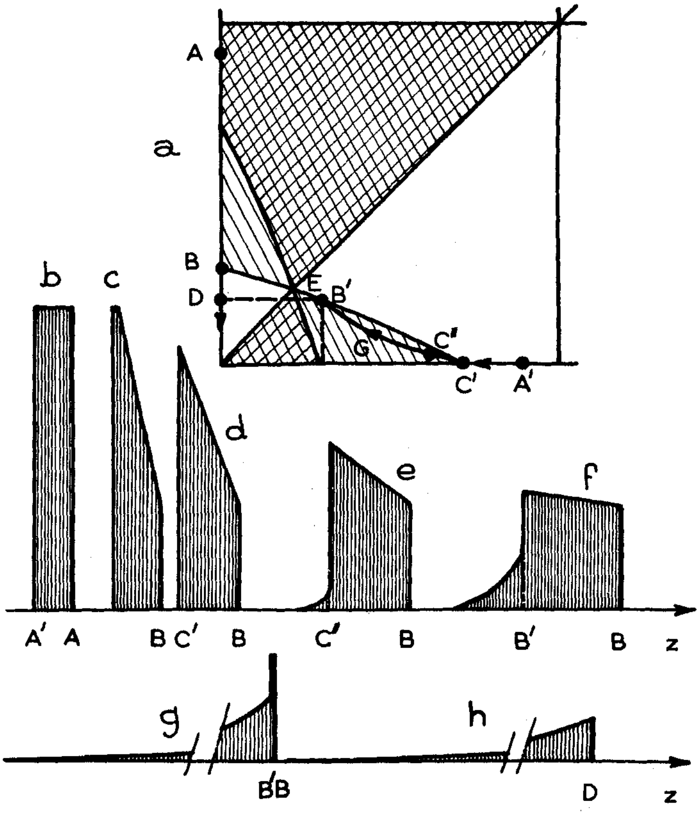

FIG. 4. Propagation of a rectangular injection in the case of a complex stability diagram. (*a*) Stability diagram. (*b*) to (*f*) Profiles corresponding to various steps in the elution (see text).

broadens (Fig. 4*d*). When the rear shock image comes to C′, this shock becomes a partly stable discontinuity (cf. Eq. 18). Its trajectory is given as Line G on Fig. 4(*a*). Its speed increases, but a tail with a continuous profile appears at its base behind it (cf. Fig. 4*e*). The image of the front shock remains in B. Usually the Line G intersects C_1' in D′, which is the image of a stable shock. This shock is faster than the front shock which always has its image in B (Fig. 4*f*). The tail behind the rear shock increases while the distance between the two shocks decreases progressively until they meet. Their images remain in B and B′ all this time (Fig. 4*g*). The rear shock then disappears suddenly while the image of the front shock goes from B to D (Fig. 4*a*). Then only the front shock is stable and its height decreases progressively as the peak moves further along the column (Fig. 4*h*).

It should be pointed out that Figs. 4(*b*) to 4(*h*) are band profiles inside the column. Chromatograms usually are the variation of solute concentration in the gas phase at the column outlet and have the opposite shape.

The second-order sources of peak broadening (mass-transfer kinetics and diffusion) hide some of these effects by relaxing the infinite concentration gradients which correspond to the shocks. For example, the shock crash pictured in Fig. 4(*g*) cannot be observed experimentally, and many of the phenomena described here have not been previously described in gas–liquid chromatography.

CONCLUSION

In gas–liquid chromatography the sorption and isotherm effects operate in opposite directions; sorption effects tend to give peaks with sharp fronts, and isotherm effects lead to peaks with sharp tails. The relative importance of these opposite trends and the final form of the elution band depend on the isotherm and on the temperature. The temperature largely determines whether the sorption or the isotherm effect will dominate. k' decreases exponentially with increasing temperature, while X_m increases exponentially. On the other hand, the sorption effect is practically independent of the temperature and will eventually dominate when the temperature is high enough.

At temperatures around the boiling point under the column pressure, two shocks at the front and back side of the peak are possible. This elution mode, which has not yet been described, is very important because it corresponds to optimum conditions in preparative scale gas chromatography (*6*).

The results of this work cast considerable doubt on the validity of methods for the determination of solubility isotherms which use the peak profiles. As shown by the example discussed by Fig. 4, the elution of a peak in the transition range can be very complicated, and it is not possible to derive the parameters of the isotherm from the chromatogram obtained by frontal analysis or by the elution of a large sample by a numerical calculation of the signal propagation and optimization of these parameters to give the best fit to the experimental results. If one shock is stable during the elution of the band, the opposite side of the band profile could be used. If there are two shocks, only the continuous part of the profile *between* the two shocks can be used. The tail of the peaks in Figs. 4(*g*) and 4(*h*) cannot be used because it results from the degradation of a shock. This selection of the right parts of the profile to use is made all the more difficult by the effects of diffusion and kinetics which dampen the shocks.

Finally, these results should be corrected to take into account the effect of the pressure gradient. As soon as the pressure drop is no longer negligible, there is a local stability diagram which changes progressively along the column. This problem will be discussed in a later paper where it will be shown that if the effect of the pressure gradient is quantitatively of great import, the qualitative and descriptive results discussed above remain fully valid (*7*).

SYMBOLS

F	mass flow velocity of the mobile phase (Pu) in moles/sec
k'	column capacity factor ($\partial n^L/\partial n^G$)
k_0'	column capacity factor at infinite dilution (zero sample size)
k_1', k_2'	column capacity factors downstream and upstream of a discontinuity
k	retardation factor ($k = Xn^L/n^G$)
k_1, k_2	retardation factors downstream and upstream of a discontinuity
L	column length
n^L, n^G	number of moles of solute in the liquid phase and gas phase at equilibrium
P	column pressure
P^0	vapor pressure of the solute studied
t	time
t_X	residence time of the mole fraction X
u	local apparent transport velocity of an inert compound
u_0	carrier gas flow velocity at column inlet
$\hat{u}_e$	cross section averaged interstitial gas velocity
V	volume
V_c	geometrical volume of the column
V_G	volume available to the gas phase
v	apparent transport velocity of the mole fraction X
v_1, v_2	apparent transport velocities of solute downstream and upstream of a discontinuity
v_{12}	velocity of a discontinuity
X	mole fraction in the gas phase
X_1, X_2	mole fractions in the gas phase downstream and upstream of a discontinuity
X_m	maximum mole fraction of compound in the gas phase (P^0/P)

$X_m{}^*$	limit transition mole fraction
X^L	mole fraction of solute in the solution
Y	activity of solute
Y', Y''	first and second derivative of activity by respect to X^L
z	abscissa along the column
ε_e	interstitial porosity of the packing
γ	activity coefficient in solution
γ^∞	activity coefficient at infinite dilution
τ	injection time width

Subscript

1	Refers to the gas phase downstream of a discontinuity
2	Refers to the gas phase upstream of a discontinuity
12	Refers to the discontinuity

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