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Review

# Non-linear waves in chromatography
# III. Multicomponent Langmuir and Langmuir-like systems

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## Abstract

This third instalment on non-linear waves examines in detail the chromatographic behavior of multicomponent systems whose sorption equilibria are uniformly competitive and without selectivity reversals. This very common class includes systems with multicomponent Langmuir isotherms, but is not restricted to them. An examination of particle velocities and wave velocities leads to a set of rules for what may and may not happen in a column if sorption equilibrium is of this type. As an example, all qualitative features of frontal analysis are deduced without calculation. The arguments also illustrate how, more generally, wave theory can be used to deduce chromatographic behavior from given equilibrium properties. In addition, an easy-to-use mathematical procedure is presented with which column responses in systems with Langmuir sorption isotherms can be calculated. The procedure is based on a transformation of the concentration variables. Compositions of plateau zones between waves, wave velocities, and sharpening criteria are obtained as simple algebraic expressions or conditions in terms of the values of the new variables in only the initial and entering fluids. The new variables are easily transformed back into concentrations where this is desired. Three fully calculated examples of five-component frontal analysis, separation of a three-component mixture by displacement development, and two-component elution from an overloaded column show how analytical solutions can be obtained for many cases of practical interest. As in Part II, the assumptions of ideal chromatography are taken for granted.

*Keywords:* Reviews; Non-linear chromatography; Wave theory; Langmuir and Langmuir-like systems; Multicomponent systems; Adsorption isotherms; Frontal analysis; Displacement chromatography; Coherence theory; Preparative chromatography; Particle velocities; Riemann problems

## Contents

# 1. Introduction

Part I of this series has dealt with fundamental properties of waves in non-linear single-component chromatography [1]. Part II has extended the coverage to multicomponent systems with interactions between the solutes, concentrating on general aspects of wave interference and the concept of coherence [2]. The current, third instalment examines specifically one very common class of systems: those with sorption equilibria obeying the Langmuir equations or behaving in a similar manner. Qualitative rules for chromatographic behavior in such systems are deduced from general considerations of conservation of matter and of the velocities at which solute molecules and their concentrations move through the column. In addition, an easy-to-use mathematical procedure is shown for quantitative calculations of column responses in systems in which the Langmuir equations for sorption equilibrium are an acceptable approximation. Because it is so simple and fast, this procedure also recommends itself for obtaining approximate answers in systems that are merely Langmuir-like.

As in the previous instalments, attention is focused on what will develop in the column locally from given concentrations and concentration gradients, regardless of when and where these conditions exist and how they arose in the first place. Examples then show how this knowledge can be used to deduce column responses under specific initial and entry conditions.

A rudimentary understanding of the fundamentals of waves and wave interferences, discussed in the previous two instalments, will be required for following the presentation here. The most essential concepts and ideas are briefly reviewed in Section 3, and Table 7 provides a "dictionary" of frequently used terms. However, at least a perusal of Part II is recommended in addition. Also, the reader not familiar with the wave-theory picture of frontal analysis, displacement development, and overload

elution may find a review of the respective sections in Part II helpful.

As in Part II and for the same reasons, the assumptions of ideal chromatography are taken for granted. Specifically, they are: local equilibrium between the moving and the stationary phase, ideal plug flow, mass transfer in axial direction by convection only, axially uniform volumetric flow-rate of bulk moving phase, isobaric and isothermal behavior, and absence of chemical reactions that transform solutes (except adsorption or chemisorption). The effects of nonidealities are largely the same as in single-component systems, discussed in Part I, and, in essence and with few exceptions, only make all waves less sharp than ideal theory predicts. In particular, except in extreme cases, they do not alter the general features of the response pattern such as sequence of waves and compositions of zones between the latter, and can usually be accounted for by mere corrections to the results of ideal theory.

Most but not all of the material presented here has been published previously, much of it by other authors, if under different viewpoints. In particular, early work by Glueckauf [3,4] contains solutions for various cases with Langmuir sorption equilibria including two-component elution from an overloaded column. The fundamental studies by Rhee et al. [5,6], as far as they relate to quantitative aspects of chromatography, are essentially confined to Langmuir systems. Also, there is a close analogy in mathematics between $n$-component Langmuir systems and $(n+1)$-component ion-exchange systems with constant separation factors, for which the theory has been worked out in great detail by Helfferich and Klein [7]. The history of these developments has recently been put in perspective by Guiochon and Golshan-Shirazi [8]. The current instalment aims at providing a rounded and reasonably comprehensive picture, and references to earlier work have been chosen to fit this purpose. We apologize to those who may not have received due credit.

## 2. Langmuir and Langmuir-like equilibria

This section explains the types of isotherms to which the current instalment is devoted.

### 2.1. Langmuir isotherms

The Langmuir equations for sorption equilibrium, extended by Markham and Benton [9] to systems with $n$ sorbable solutes, are

$$q_j = \frac{a_j c_j}{1 + \sum_{i=1}^{n} (b_i c_i)} \quad \text{for all } j \qquad \text{(III.1)}$$

(For definitions and explanation of symbols, see Section 10 and Table 7.)

Langmuir [10,11] deduced his equation from kinetic postulates whose rigor is open to question. However, Eqs. (III.1) can instead be derived with a thermodynamic argument (minimum of free energy at equilibrium), showing it to be valid in ideal systems [12,13]. If one takes Langmuir's derivation at face value, all $b_i$ coefficients necessarily are positive, and the additive terms of the denominator acquire physical significance: Each $b_i c_i$ term (as fraction of the total denominator) reflects surface coverage by the respective solute $i$ and so reduces sorption of any solute $j$, and the leading 1 term (also as fraction of the total) represents the extent of still unoccupied surface area. Increased sorption of any one solute discourages further sorption of all because it decreases the still accessible free surface area. Such equilibria are called *competitive*.

It has been argued that Eqs. (III.1) are thermodynamically consistent only if the ratio $b_i/a_i$ of the coefficients is the same for all solutes [14–16]. This conclusion is based on an idealization of the state of adsorbed molecules and implies that the ultimate capacity (loading in moles at fluid-phase concentration extrapolated to infinity) in single-solute systems is the same for all solutes, regardless of their nature and molecular size (for a single solute, Eqs. (III.1) give $q_j = a_j/b_j$ for $c_j \to \infty$). Reality tends to differ, mainly because larger molecules require more space on or in the sorbent. In practice the Langmuir equations can usually be fitted much better to observed equilibria if the coefficient ratios are allowed to differ from one another. Rather than worry about finer points of thermodynamics, the practical chromatographer who wants to stick with the simple Langmuir equations will therefore not hesitate to

work with unequal coefficient ratios, as will be done here.[1]

If thermodynamic consistency is not demanded, Eqs. (III.1) can also be used with negative values of some $b_i$ coefficients [provided $\Sigma(b_i c_i) < 1$ under all conditions, to guarantee that the $q_i$ cannot become negative]. In this way, the equations can be fitted to some "synergistic" sorption equilibria, that is, to equilibria in which sorbed molecules of some solute or solutes encourage rather than discourage additional sorption of others. Here, such cases are not counted as Langmuir or Langmuir-like, although the mathematical transformation in Section 6 Section 7 remains applicable [7].

## 2.2. Langmuir-like isotherms

In practice, sorption equilibrium behavior often resembles that of Eqs. (III.1), but not closely enough for an acceptable quantitative fit even if the coefficient ratios are allowed to differ from one another. Here, such equilibria will be called "Langmuir-like". To qualify as such, sorption equilibrium must meet two conditions:

- no selectivity reversals,
- increased strength of competition for sorption capacity decreases the distribution coefficients of *all* solutes.

The condition of no selectivity reversals specifies that the sorbent may not prefer a solute $j$ over a solute $k$ at some compositions, but $k$ over $j$ at others. Stronger competition results from either a concentration increase of a solute or replacement of molecules of one solute by those of another that is a stronger competitor. (For mathematical criteria, see Appendix A).

For later deductions, the key property of Langmuir-like sorption equilibria is:

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[1]The Langmuir isotherm becomes deficient at high loading because it does not account for the fact that large molecules fit less well into small patches between other adsorbed molecules. So-called scaled-particle isotherms [16,17] and isotherms based on ideal adsorption theory [16,18,19] include this effect and are thermodynamically consistent, but mathematically more complex. They do not necessarily fit the definition of "Langmuir-like" used here.

- The distribution coefficients $q_j/c_j$ of *all* solutes vary in the same direction, that is, either increase jointly or decrease jointly as the composition of the fluid phase is varied.

This comes about because the changed strength of competition with change in composition affects all solutes in qualitatively the same way.

## 3. Waves, wave interference, velocities, and coherence

This section presents a brief outline of the most essential elements of Parts I and II, to the extent that the material in the current instalment builds on them. The outline should suffice for the reader who only wishes to get a general idea of what may or may not happen in Langmuir or Langmuir-like systems and is content with taking the results of deductions and derivations at face value. However, the reader who desires to follow the deductions and understand how he can use such arguments to derive his own rules for systems with different equilibrium properties will benefit from a study of the previous instalments, especially the sections on velocities (I.2), sharpening behavior of waves (I.4 and I.5), coherence (II.4 and II.5), and wave interference (II.8)[2].

In the context of chromatography, a *wave*[3] is defined as a monotonic variation of solute concentrations (and possibly temperature) in the column. It may be *self-sharpening* or *nonsharpening*. A self-sharpening wave sharpens into, or remains, a so-called *shock*. In contrast, a nonsharpening wave spreads as it travels. Granted the premises of ideal chromatography, shocks are ideally sharp concentration steps (i.e., concentration discontinuities), and the widths of nonsharpening waves increase linearly with traveled distance or elapsed time. Moreover, the sharpening or spreading behavior depends only on the sorption equilibrium properties; this is because

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[2]Sections, tables and figures from Parts I and II of this series are referred to by "I" or "II", followed by the number of the respective item.

[3]Names in earlier sources include boundary, front, mass-transfer zone, and transition.

the simplifying idealizations rule out all other dispersive effects.

In multicomponent systems a wave may be *coherent* or *noncoherent*. If it is noncoherent, the concentration profiles of the different solutes in the wave shift relative to one another, causing the wave to break up into several coherent waves that separate from one another, much as do the peaks in ordinary (linear) analytical chromatography. In contrast, in any coherent wave the profiles of the different solutes advance in perfect synchronization: Concentrations $c_1,..., c_n$ of the different solutes that coexist with one another at the same point in distance and time will travel jointly at the same speed and so remain in one another's company. The wave may sharpen or spread, but will remain a single wave rather than breaking up into several. Coherence or the lack of it is a property of a wave, not of an entire column or effluent history, and relates less to the current state of affairs than to what will happen to the wave on its further travel. Coherence can be viewed as a "stable" condition because any composition variation at the column inlet or in the column, if given enough time and not further disturbed, sorts itself out into a set of coherent waves. If the initial composition of the column is uniform and the composition of the entering fluid remains constant [this is called a *Riemann problem* for short], all waves originate at one and the same distance–time point: the column inlet and start of the operation. In ideal chromatography, all waves then are coherent from the outset. In conventional analytical chromatography (elution development), coherence is attained everywhere when all solute peaks have separated from one another.

In ideal chromatography, the maximum number of coherent waves into which a single noncoherent wave may break up is equal to the number of sorbable solutes (rare exceptions in systems with selectivity reversals are of no interest here).

If the composition of the entering fluid is changed repeatedly or the initial composition of the column was not uniform, faster coherent waves may catch up and interfere with slower ones that were produced earlier at the column inlet or originated farther downstream in the column. Such an interference of two coherent waves produces temporarily a single noncoherent wave, which is subsequently resolved

into new coherent waves: For resolution of a noncoherent wave into coherent ones, it makes no difference whether this occurs at start at the column inlet or at a later time through wave interference farther downstream.

A key argument in the current instalment operates with *particle velocities* and *wave velocities* in the column[4]. The distinction between the two is crucial. The particle velocity of a solute is defined as the average velocity at which molecules of that solute advance in the direction of flow. For a solute $j$ it is given by

$$v_j = \frac{v^\circ}{1 + (\rho/\varepsilon)q_j/c_j} \tag{I.5}$$

Eqs. (I.5) is equivalent to the familiar relationship between retention time $t_R$, column deadtime $t_0$, and capacity factor $k'$ in linear chromatography [20]

$$t_R = t_0(1 + k') \tag{III.2}$$

as is apparent from the fact that $(\rho/\varepsilon)q_j/c_j = k'$ in the linear case and that the velocities $v_j$ and $v^\circ$ are inversely proportional to the retention time $t_R$ and deadtime $t_0$, respectively.

Eqs. (I.5) is readily derived with the argument that the molecules make headway, at the velocity $v^\circ$ of moving-phase flow, only during the fraction of time they spend in that phase rather than on or in the stationary sorbent. This derivation makes clear that the particle velocity is a velocity of an *identifiable object*. In contrast, the wave velocity of a solute – definable only where there is a concentration gradient of that solute – is the velocity at which a given concentration value of that solute advances. For a solute $j$ in a single-component ideal system it is given by

$$v_{c_j} = \frac{v^\circ}{1 + (\rho/\varepsilon)\, dq_j/\, dc_j} \tag{I.4}$$

This equation can be derived from conservation of matter of the solute in a differential cross-sectional volume element of the column (inflow minus outflow equals change in content). The wave velocity is a

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[4]In Ref. [7], written before the notation of wave theory was adopted, the terms species velocity and concentration velocity (or composition velocity) are used.

velocity of *a given value of a dependent variable*, in isothermal chromatography of a concentration or composition. The wave velocity depends on the slope $dq_j/dc_j$ of the isotherm (i.e., of its tangent) at the respective concentration, whereas the particle velocity depends on the slope $q_j/c_j$ of the chord to that point (see Fig. 1); only if the sorption isotherm is linear, so that $dq_j/dc_j = q_j/c_j$, are the two velocities the same.

Eqs. (I.4) for the wave velocity is also valid in multicomponent systems, but the stationary-phase concentration $q_j$ of a solute $j$ in these depends not only on the moving-phase concentration $c_j$ of that solute, but on those of all others as well. The derivative $dq_j/dc_j$ thus is not defined as a total derivative. Rather, the ratio of the concomitant variations of $q_j$ and $c_j$ it expresses can in principle assume any value, even if the concentrations of all solutes are given. However, the coherence condition of equal wave velocities of all solutes at the respective point in distance and time allows only certain distinct values (also called *eigenvelocities*). At which of these velocities $v_c$ a given composition $c_1,..., c_n$ in a coherent wave actually travels depends on the nature of the composition variation across the wave (for coherent velocities in Langmuir-like systems, see also next section).

The wave velocity of a shock of a solute $j$ is given by

$$v_{\Delta c_j} = \frac{v^\circ}{1 + (\rho/\epsilon)\Delta q_j/\Delta c_j} \qquad (I.6)$$

where $\Delta$ indicates the difference across the shock.
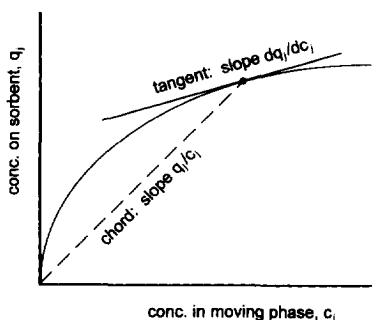


conc. in moving phase, $c_i$

Fig. 1. Single-component isotherm with tangent and chord at given concentration.

Eqs. (I.6) can be derived from conservation of matter for the solute across the traveling shock. If the shock is coherent, the concentrations of all solutes vary stepwise across it, and all these steps advance with the same velocity, $v_\Delta$.

Failure to distinguish between particle and wave velocities quickly leads to paradoxes and contradictions, as a simple example may demonstrate. Consider a coherent wave in a multicomponent system. At any point in distance and time within that wave, the different solutes necessarily have different particle velocities because of their different affinities for the sorbent (the high-affinity solutes spending a greater fraction of time in or on the sorbent and so advancing more slowly). However, if the wave is coherent, the respective composition within the wave advances at one single velocity. If there was no difference between particle and wave velocities, this would be impossible and no wave involving more than one solute could be coherent. In reality, the composition advances at its coherent wave velocity (one of its eigenvelocities), which differs from all the particle velocities of the solutes.

## 4. Rules for coherent waves and patterns: affinity cuts and keys

The present section states rules for what may and may not happen at coherent waves in Langmuir and Langmuir-like systems. These rules allow the essential features of column responses under almost any conditions to be predicted with little or no mathematics, as will be demonstrated with an example in the next section.

Also shown is how the rules can be deduced from considerations of particle and wave velocities, granted Langmuir or Langmuir-like equilibrium and coherent behavior [21]. While not difficult at all, the arguments are somewhat involved and will take time to think through. The reader prepared to accept the rules at face value may skip their deduction without loss in continuity. He may wish to return to it for a deeper understanding of the physical phenomena or if he wants to use the line of argument for deriving his own rules for a system with different sorption equilibrium properties. Mathematical proof for all rules is given in Appendix A.

## 4.1. Rules for coherent waves

Arbitrary composition variations are in general noncoherent. Coherence allows only certain kinds of composition variations across any one wave. The most important rule for Langmuir or Langmuir-like systems describes the properties of these variations.

Consider the solutes ordered, and numbered, in the sequence of decreasing affinity for the sorbent (corresponding to sequence of decreasing capacity factor $k'$ in linear chromatography). In principle, the solutes present at a coherent wave can be divided into two groups: those whose concentrations increase across the wave, and those whose concentrations decrease. If the wave is coherent, the solutes of one group must *all* have higher affinities for the sorbent than do *all* those of the other. In other words, in the affinity sequence the two groups do not overlap. As an example, in a five-component system, the concentrations of solutes 1, 2, and 3 might increase while those of 4 and 5 decrease. In contrast, the wave is necessarily noncoherent if, for example, the concentrations of solutes 1, 2, and 4 increase and those of 3 and 5 decrease.

The rule can be stated more concisely [22]:

- Every coherent wave has an "affinity cut" that divides all solutes into a high-affinity group and a low-affinity group that do not overlap. Across the wave, the concentrations of the members of the two groups vary in opposite directions.

The "cut" can be shown by a vertical line in the list of solutes. For example, for a wave in a five-component system with solutes 1, 2, and 3 in one group and 4 and 5 in the other:

$$\underset{\substack{\text{high—affinity}\\\text{solutes}}}{1\ \ 2\ \ 3}\ \ \Big|\ \ \underset{\substack{\text{low—affinity}\\\text{solutes}}}{4\ \ 5} \qquad (\text{III.3})$$

Such a wave is said to have a 3|4 affinity cut.

The affinity-cut rule must be supplemented to cover cases in which the concentrations of all solutes vary in the same direction:

- Across a coherent wave all concentrations may very in the same direction. In this case, all solutes

should be counted as belonging to the high-affinity group.

That is, the low-affinity group may have no members. For example, in a five-component system a 5|– cut is possible, a –|1 cut is not. The reason for this classification will become apparent later.

For a concise terminology it proves convenient to borrow the concept of keys from distillation. In general, a coherent wave has a *high key* and a *low key*. The keys are solutes which are adjacent in the affinity sequence and whose concentrations vary in opposite directions. In the example III.3 above, solutes 3 and 4 are the high key and low key, respectively. If all concentrations vary in the same direction, the wave has only a high key, no low key.

Additional important general rules are:

- No more than one solute can be absent from one side of a coherent wave while being present on the other. That solute can only be the high key or low key. At one and the same wave, the high key may be absent from one side and the low key from the other.
- The lower the affinity of the keys for the sorbent, the faster is the wave.
- A wave is self-sharpening if the concentrations of the high key are higher on the upstream side than on the downstream side, and is nonsharpening if the opposite is true.

Exceptions to the last rule are possible with isotherm shapes that are unusual in competitive sorption equilibria (isotherms with loci of inflection).

The use of the rules for prediction of response behavior will be illustrated in Section 5, to which the reader can advance without loss in continuity.

## 4.2. Deduction of rules

Consider a multicomponent, coherent wave advancing through the column between plateaus (that is, zones of uniform composition) on its upstream and downstream sides. It is easiest to think of the wave as a shock, but the arguments are equally valid for a diffuse self-sharpening or nonsharpening wave. The first step is to recall that, by virtue of the definition of Langmuir-like equilibrium, the distribu-

tion coefficients $q_i/c_i$ of *all* solutes will be larger on one side of the wave than on the other: larger on the side where competition for sorption capacity is weaker (that strength of competition must be different on the two sides if the wave is coherent is shown farther below). According to Eqs. (I.5), where the distribution coefficients $q_i/c_i$ of the solutes are larger, the particle velocities are lower. Therefore:

Conclusion 1: Each solute's particle velocity is lower on the wave side on which competition for sorption capacity is weaker.

This may be the upstream or downstream side. It is not possible, however, that one solute's particle velocity is higher on the downstream side of the wave while another's is higher on the upstream side.

Let us examine next what happens to solute molecules when they overtake the wave or are overtaken by it. For that purpose we divide the solutes into "faster" ones whose particle velocities are higher than the velocity of the wave, and "slower" ones whose particle velocities are lower. At each moment in time the wave will be overtaken by the molecules of the faster solutes and will overtake those of the slower solutes. (This is a loose way of speaking; "faster," "slower," "overtaking," etc., are used as though each solute molecule were moving continuously at the solute's particle velocity according to Eqs. (I.5); however, that velocity is averaged over a large number of molecules of the respective solute or a long time span, and in reality each individual molecule alternates between moving at the velocity of moving-phase flow and sitting still, and so may overtake a wave and in the next moment be overtaken by it.)

When "faster" solute molecules overtake the wave, they enter a zone downstream in which competition for sorption capacity is different. If competition in that zone is stronger, they speed up; if competition there is weaker, they slow down [see conclusion (1) above]. Conservation of matter requires the concentration of the solute to decrease when its molecules speed up, and to increase when its molecules slow down. This effect can be rationalized as follows: If the wave is coherent and thus travels "as is", without concentration profiles bulging up or caving in, the flow of any solute relative to the wave (number of molecules that pass per given time span through a given frame of reference that

moves at the velocity of the wave) is the same upstream and downstream of the wave. As a result, where there are fewer solute molecules per centimeter of column, they must advance faster because the number passing through the given frame of reference during the time span must then include some that were farther away at the start of the time span. An analogy that helps to understand this effect is the flow of an incompressible fluid such as water in a pipe: Where the pipe narrows, the velocity of the fluid increases; where it widens, the velocity decreases (see Fig. 2). In that case the reason is that the volumetric flow-rate (volume per unit time passing a given point) is the same everywhere, so that the velocity (volume per unit time and unit cross-sectional area) is inversely proportional to the cross-sectional area. We can conclude:

Conclusion 2: Solutes faster than the wave have lower concentrations on the wave side where competition for sorption capacity is stronger.

The same line of argument can be applied to the solute molecules being overtaken by the wave. Their velocities vary in the opposite manner. What counts for conservation of matter, however, is the velocity *relative to the wave*, and that relative velocity is lower for the molecules of a solute where they are more nearly as fast as the wave. As a result, the concentrations are higher on the upstream side (the side the molecules enter) if competition there is stronger, and are lower on that side if the opposite is true. Thus:

Conclusion 3: Solutes slower than the wave have higher concentrations on the wave side where competition for sorption capacity is stronger.

A comparison of conclusions (2) and (3) above shows:

Conclusion 4: Across any coherent wave, the concentrations of solutes faster and slower than the wave vary in opposite directions.
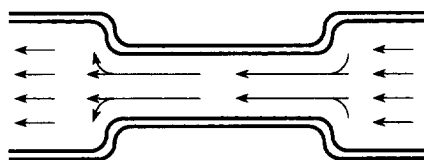


Fig. 2. Flow of incompressible fluid in pipe (schematic). Lengths of arrows characterize velocity of flow.

We can identify the faster and slower solutes by their equilibrium behavior. The stronger the affinity of a solute for the sorbent, the larger is its distribution coefficient $q_i/c_i$ and, according to Eqs. (I.5), the lower is its particle velocity. Thus, all the solutes faster than the wave have lower affinities for the sorbent than do all the solutes slower than the wave. This fact combined with conclusion (4) above yields the affinity cut rule, which was stated before without proof.

The high key is the fastest of the high-affinity solutes, all of which are slower than the wave. Similarly, the low key the slowest of the low-affinity solutes, all of which are faster than the wave. Accordingly:

Conclusion 5: The wave velocity is intermediate between the particle velocities of its high key and low key.

This shows that waves are faster if their keys have lower affinities, as was stated earlier. Moreover, since any given composition $c_1,..., c_n$ can exist in a coherent wave of any affinity cut, it can advance at different velocities (its eigenvelocities), depending on the cut of the wave.

The question remains whether the solutes at a coherent wave can *all* be faster than the wave itself, or *all* be slower. Given Langmuir-like sorption equilibrium, the second possibility exists, the first does not. This can be shown as follows. A solute overtaking the wave either enters a zone with stronger competition, and then must have a higher particle velocity and lower concentration in that zone; or it enters a zone with weaker competition, and then must have a lower particle velocity and higher concentration in that zone. In both cases, the concentrations must be higher where competition is weaker. But this cannot be true for all solutes simultaneously because in a competitive equilibrium, by definition, the strength of competition increases if *all* solute concentrations increase. On the other hand, if all solutes are slower than the wave, their concentrations in the zone with weaker competition must be lower, as is automatically the case if equilibrium is competitive. This proves that the concentrations of all solutes may vary in the same direction, but only if the solutes are slower than the wave and thus all belong to the high- rather than low-affinity group. In terms of keys, a coherent wave across which all

concentrations vary in the same direction has only a high key, no low key; in terms of velocities, the wave may be faster than all solutes, but not slower than all.

Let us now establish which solutes might be absent from one side of a coherent wave while being present on the other. The molecules of such a solute cannot overtake the wave, nor can they be overtaken by it. Consequently, the particle velocity of that solute must equal the wave velocity. (If the wave is diffuse, the particle velocity equals the wave velocity where the concentration of the respective solute becomes infinitesimal.) Since the particle velocities of the solutes differ from one another, this can be true for only one solute on each side of the wave. Moreover, that solute must be the fastest of the high-affinity (slow) group or the slowest of the low-affinity (fast) group, that is, it must be the high key or low key. It is possible, however, that the high key is absent from one side of the wave while the low key is absent from the other. This rule was also stated earlier.

That competition for sorption capacity cannot be equally strong on the two sides of a coherent wave can now be recognized as a consequence of the affinity-cut rule. Competition is necessarily stronger on the side where the concentrations of all high-affinity solutes are higher and those of all low-affinity solutes are lower. Competition can only be equally strong if the two compositions are the same. A single coherent wave (defined as a *monotonic* composition variation) can obviously not exist between equal compositions. However, a coherent *pulse* (consisting of two waves with opposite composition variations) can.

We can now turn to the question under what conditions a plateau between two coherent waves grows in length, or shrinks, or retains its length. Because waves with keys of higher affinities are faster:

• A plateau between two coherent waves grows if the keys of the wave on the downstream side have lower affinities for the sorbent than do those of the wave on the upstream side. The plateau shrinks if the opposite is true.

For example, a plateau between a wave with 3|4

Table 1
Properties of coherent waves and plateaus between coherent waves in $n$-component Langmuir-like systems (solutes numbered in sequence of decreasing affinity for sorbent)

|  | Slowest wave | Second-slowest wave | Third-slowest wave | General wave | Fastest wave |
|---|---|---|---|---|---|
| **Waves** | | | | | |
| Affinity cut (high key\|low key) | 1\|2 | 2\|3 | 3\|4 | $k\|k=1$ | $n\|-$ |
| High-affinity group | Solute 1 | Solutes 1,2 | Solutes 1,2,3 | Solutes $1,...,k$ | All solutes |
| Low-affinity group | Solutes 2,3,...,$n$ | Solutes 3,4,...,$n$ | Solutes 4,...,$n$ | Solutes $k+1,...,n$ | None |
| Possible concentration variations across self-sharpening wave in direction of flow[a] | | | | | |
| Decrease | Solute 1 | Solutes 1,2 | Solutes 1,2,3 | Solutes $1,...,k$ | All solutes |
| Increase | Solutes 2,3,...,$n$ | Solutes 3,4,...,$n$ | Solutes 4,...,$n$ | Solute $k=1,...,n$ | None |
| Possible concentration variations across nonsharpening wave in direction of flow* | | | | | |
| Decrease | Solutes 2,3,...,$n$ | Solutes 3,4,...,$n$ | Solute 4,...,$n$ | Solute $k=1,...,n$ | None |
| Increase | Solute 1 | Solutes 1,2 | Solutes 1,2,3 | Solutes $1,...,k$ | All solutes |
| Coherent velocity, $v_c$ | $v_1 \leq v_c \leq v_2$ | $v_2 \leq v_c \leq v_3$ | $v_3 \leq v_c \leq v_4$ | $v_k \leq v_c \leq v_{k-1}$ | $v_c \geq v_n$ |
| Solutes that may be absent from one side while present on other (but not both from same side) | Solutes 1,2 | Solutes 2,3 | Solutes 3,4 | Solutes $k,k=1$ | Solute $n$ |
| **Plateaus** | | | | | |
| Plateau between coherent waves | Grows if keys of upstream wave have higher affinities for sorbent than do those of downstream wave | | | | |
|  | Retains length if between diffuse waves of same affinity cut | | | | |
|  | Shrinks under all other circumstances | | | | |

[a] Exceptions to sharpening behavior are possible if sorption equilibrium is other than "normal".

cut upstream and one with 4|5 cut downstream grows; a plateau between a wave with 3|4 cut upstream and one with 1|2 cut downstream shrinks. Also:

- A plateau between coherent waves of the same affinity cut retains its length if both waves are diffuse, and shrinks if either or both waves are shocks.

The shrinking is a result of the fact that the velocity of a coherent shock is necessarily higher than the wave velocity of the composition on its downstream side, and lower than that of the composition on its upstream side (the resulting tendency of the tail to catch up with the head is what makes the wave sharpen into a shock or maintain that sharpness). Note that a plateau may travel with constant length between two waves of the same affinity cut even if both waves are self-sharpening; in that case it does so as long as the waves are still diffuse at least in their portions bordering the

plateau. The plateau begins to shrink only when at least one wave has sharpened into a shock in that portion.

For ease of reference the most important properties of coherent waves in Langmuir and Langmuir-like systems are summarized in Table 1[5].

### 4.3. Non-Langmuir equilibria

The method of deducing properties of coherent waves from a comparison of particle velocities and wave velocities is not restricted to Langmuir-like systems. The unambiguous classification into high- and low-affinity groups of solutes slower and faster

[5]The rules for affinity cuts and sequence of waves of common origin are in part equivalent to empirical rules developed by Vermeulen and co-workers for ion exchange from results of numerical calculations ("alphabet rule," "slope rule," etc.) [23–25]. Those rules, however, had no explanation in physics, addressed only Riemann problems in ion exchange with constant selectivity coefficients, and originally lacked the caveat that they are not necessarily valid unless selectivity reversals are excluded.

than the wave, respectively, is always possible, regardless of the nature of sorption equilibrium. However, without the guarantee that all distribution coefficients increase or decrease jointly, there may be non-conformist solutes with opposite behavior, even if equilibrium is competitive in that it obeys condition (III.55). The affinity cut rule can then no longer be relied upon because the concentration of any such maverick varies like those of the members of the other affinity group. Moreover, a solute may act as maverick at some waves, but not at others.

## 5. Example: deduction of frontal analysis pattern

The application of the rules deduced in the previous section may be illustrated with the example of frontal analysis (see also Part II, Sections II.2 and II.7). As will be seen, in a case as simple as this, all qualitative features of the pattern can be predicted with the rules alone, without need for any calculation. On purpose, a case for which the response pattern is well known has been chosen, so that the rules can be seen to lead to predictions fully in accordance with established behavior. For clarity, the arguments are carried through for just five components, but the extension to any larger or smaller number of solutes is obvious.

In frontal analysis the entering fluid contains all solutes, the column initially contains none. The initial composition of the column is uniform and the composition of the entering fluid is kept constant. All waves therefore originate at one distance–time point – start of operation and entry to column – and fan out as they travel with different velocities (see Fig. 3). There is no wave interference, and all waves are coherent from the start. At all times, faster waves are downstream of slower ones.

With five solutes, a pattern generated by a single starting variation may have as many as five waves. Any wave that is slower than another must have keys of lower affinities than the other, otherwise the waves would not become separated by plateaus that grow in length. Accordingly, the five possible waves, in the sequence from slowest to fastest, must have the cuts $1|2$, $2|3$, $3|4$, $4|5$, and $5|-$, there being no cuts other than these five. The possibility that one or
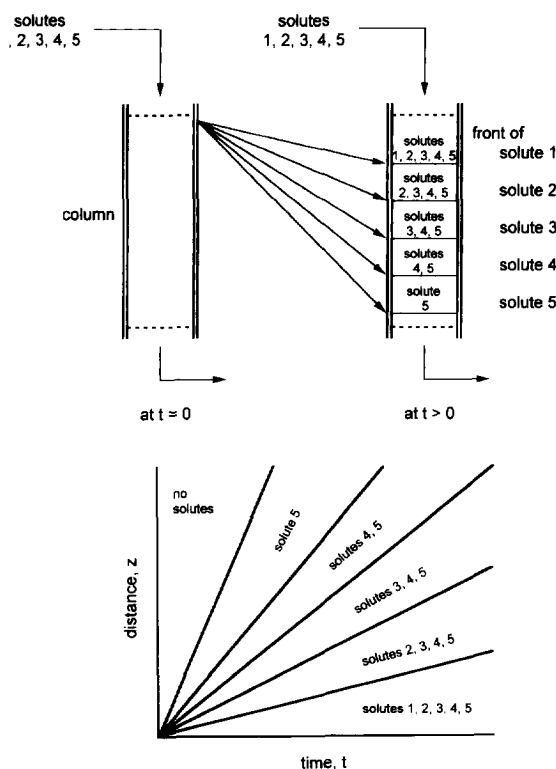


Fig. 3. Frontal analysis: operating procedure (top) and distance–time diagram with wave trajectories (bottom).

several of the five waves are missing will be ruled out later.

Solute 1 is present in the entering fluid, but absent from the column initially, so there must be at least one wave at which that solute is present on the upstream side but absent from the downstream side. This can only be a wave at which it is a key, and that is so only at the wave with $1|2$ cut, the slowest wave. Solute 1, absent from the downstream side of that wave and not a key at any faster wave, must then be absent from the rest of the pattern. Solute 2 is likewise present in the entering fluid, but absent from the column initially, and so must also be present on the upstream side but absent from the downstream side of at least one wave and be a key at that wave. In principle, this could be the wave with $1|2$ cut or the wave with $2|3$ cut. Here, however, it can only be the latter because solutes 1 and 2 cannot both be absent from the same side of the same wave while being present on the other side. Not being a key at

any faster wave, solute 2 must be absent from anywhere downstream of that wave with 2|3 cut. By the same argument, solutes 3, 4, and 5 are seen to be present on the upstream sides and absent from the downstream sides of the waves with 3|4, 4|5, and 5|– cuts, respectively, and absent anywhere farther downstream. Five waves are needed, one for each solute to be the high key, so none of the five possible waves can be missing.

At each wave the high key was seen to be present on the upstream side but absent from the downstream side, and to be the only member of the high-affinity group. The rules require the concentrations of all members of the other, low-affinity group to vary in the opposite direction, that is, to be higher on the downstream side than on the upstream side. In other words, at each wave, the solutes that are present on both sides must have higher concentrations on the downstream side than on the upstream side.

Lastly, because at each wave the concentration of the high key is higher on the upstream side than on the downstream side, all waves normally are shocks.

This example illustrates how practical conclusions can be arrived at and qualitative features of column responses be deduced with the rules for coherent waves alone, with no need for any calculation. It is not always possible, however, to arrive in this way at a picture as complete as that shown here for frontal analysis. Of course, the frontal analysis pattern is familiar to anyone working with nonlinear multicomponent chromatography, so the principal value of its deduction here is not in confirming the known but, rather, in establishing the conditions under which it arises; this makes it possible to identify what kind of deviations will occur under what conditions if equilibrium is not Langmuir-like.

## 6. Mathematics of Langmuir systems: the $h$-transformation

The quantitative calculation of column responses in multicomponent systems by conventional methods under initial and entry conditions of any complexity is so lengthy and cumbersome that it requires a fairly powerful computer or work station. However, if the Langmuir Eqs. (III.1) is an acceptable approximation

to sorption equilibrium, even complicated cases can be calculated with relative ease by hand or on a pocket calculator. Analytical solutions can be given for all cases with uniform initial and constant entry conditions (i.e., Riemann problems) and some others notably including elution of a binary mixture under conditions of concentration and volume overload. The procedure is applicable regardless of whether or not the $b_i/a_i$ coefficient ratio is the same for all solutes, and even to equilibria in which some $b_i$ coefficients are negative, provided only that Eqs. (III.1) are acceptable.

What mainly makes calculations of column responses in the conventional manner so lengthy is the fact that the concentrations of all solutes vary across each wave. Even in a case as simple as frontal analysis, the compositions between the different waves are unknown and must be calculated step by step before emergence times of waves can be determined. The mathematics become very much simpler with a non-linear transformation of the concentrations $c_1,..., c_n$ into new dependent variables $h_1,..., h_n$ that are the roots of a simple polynomial [26]. For short, they will be called roots from here on. The roots cannot be identified one-on-one with individual components or properties. Rather, a variation of only one concentration changes all roots, and a variation of only one root changes all concentrations. The principle of the transformation and the general aspects of column behavior in terms of the roots are outlined in the present section. The relevant equations are shown in the next section and are illustrated with three sample cases calculated step by step in Section 8. A brief history of the transformation, widely applicable also in many other fields, is given in Appendix B.

The most important properties of the new variables are:

• Only one root $h_i$ varies across any coherent wave

and, with the roots numbered $h_1$, $h_2$,..., $h_n$ from smallest to largest and the solutes numbered in the order of decreasing affinity for the sorbent:

• The index of the root that varies across a coherent wave corresponds to the high key of the wave.

For instance, the root that varies across a wave with $1|2$ cut is $h_1$ ; in general, that which varies across a wave with $j|j+1$ cut is $h_j$ .

For any system with uniform initial and constant entry conditions, as in frontal analysis, the result is that the compositions of all intermediate plateaus between the waves can be written down immediately in terms of only the roots of the initial composition of the column, $h_i{}^\circ$, and of the composition of the entering fluid, $h_i'$. For instance, for a five-component system and with waves and plateaus numbered from column inlet to outlet, the roots sets of the various plateaus are:

| | | | | | |
|---|---|---|---|---|---|
| entering fluid: | $h_1'$ | $h_2'$ | $h_3'$ | $h_4'$ | $h_5'$ |
| wave 1 (high key 1) | | | | | |
| plateau 2: | $h_1{}^\circ$ | $h_2'$ | $h_3'$ | $h_4'$ | $h_5'$ |
| wave 2 (high key 2) | | | | | |
| plateau 3: | $h_1{}^\circ$ | $h_2{}^\circ$ | $h_3'$ | $h_4'$ | $h_5'$ |
| wave 3 (high key 3) | | | | | | (III.4) |
| plateau 4: | $h_1{}^\circ$ | $h_2{}^\circ$ | $h_3{}^\circ$ | $h_4'$ | $h_5'$ |
| wave 4 (high key 4) | | | | | |
| plateau 5: | $h_1{}^\circ$ | $h_2{}^\circ$ | $h_3{}^\circ$ | $h_4{}^\circ$ | $h_5'$ |
| wave 5 (high key 5) | | | | | |
| initial fluid: | $h_1{}^\circ$ | $h_2{}^\circ$ | $h_3{}^\circ$ | $h_4{}^\circ$ | $h_5{}^\circ$ |

This can be shown as follows: Across the slowest wave, whose high key is solute 1, only $h_1$ varies. Accordingly, in plateau 2 downstream of that wave all other roots still have the same values as in the entering fluid. Moreover, $h_1$ can vary across no other wave, and so must change across the slowest wave all the way from its value $h_1'$ in the entering fluid to its value $h_1{}^\circ$ in the initial fluid. By the same token, across the second, next faster wave, only $h_2$ varies, and must do so all the way from $h_2'$ to $h_2{}^\circ$. Applying that reasoning to all waves and roots one obtains the compositions of the intermediate plateaus shown in the pattern (III.4) above.

Not only the composition of intermediate plateaus, but also the velocities of coherent shocks and wave velocities of compositions in diffuse coherent waves are given by very simple algebraic expressions in terms of the local values of the roots, as will be seen in the next section. This allows column responses even under fairly complex initial and entry conditions to be calculated with relative ease.

Lastly, whether a coherent wave is self-sharpening or nonsharpening can be seen immediately from the behavior of its varying root [see criterion (III.22) in the next section]:

• A coherent wave is self-sharpening if the root that varies across it has a higher value on the upstream side than on the downstream side, and is nonsharpening if the opposite is true.

### 6.1. h-Transformation and composition path grids

The $h$-transformation makes working with composition path grids as described in Part II superfluous. However, to illustrate the connection between the two methods, Fig. 4 shows a conventional path grid for a two-component Langmuir system and the corresponding transformed grid with the roots $h_1$ and $h_2$ instead of the concentrations $c_1$ and $c_2$ as the coordinates. Upon transformation, the paths become parallel to the axes by virtue of the property that only one root varies across any coherent wave; the watershed point $W$ on the $c_1$ axis becomes a corner of the diagram, and the "fast"-path portion of the $c_1$ axis (above $W$) becomes the top border of the diagram so that $c_2 = 0$ along both the left and top axes ($h_2 = 1/a_2$ along the left axis, $h_1 = 1/a_2$ along the top axis). In $n$-component systems the geometry of the transformed path grid is so that all paths of any one family are parallel to one of the $n$ axes: The transformation has "orthogonalized" the grid.
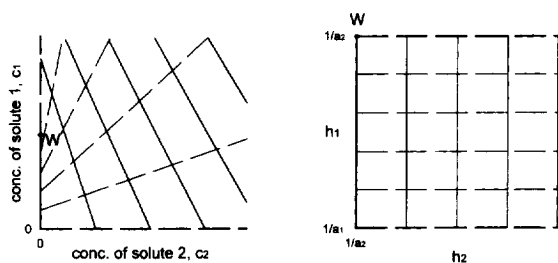


Fig. 4. $h$-Transformation: conventional two-component composition path grid with concentrations as coordinates (left) and transformed grid with roots as coordinates (right).

## 7. Equations of the $h$-transformation

This section and the next show the equations of the $h$-transformation and their application to sample cases. They are intended for the reader who wishes to work with the transformation on his own problems, and can be skipped without loss in continuity. The general equations for $n$-component systems may look formidable to the non-mathematician, but are easy to apply. However, since many practical problems involve no more than two components, the simple forms to which the equations reduce in that case are also shown.

Prerequisite for the use of the transformation is the validity of the Langmuir Eqs. (III.1) with constant $a_i$ and $b_i$ coefficients. The coefficient ratios $b_i/a_i$ need not be equal. Moreover, $b_i$ coefficients may be negative, but some roots may then become imaginary under some conditions, causing complications (for a procedure of working with imaginary roots, see Schlögl [27]).

### 7.1. Transformation of concentrations into roots and vice versa[6]

In an $n$-component system the $n$ transformed variables $h_i$ are obtained as the $n$ roots of a polynomial called the $H$ function (hyperplane function):

$$\sum_{i=1}^{n} \left( \frac{b_i c_i}{a_i h - 1} \right) - 1 = 0 \qquad \text{(III.5)}$$

The reverse transformation from roots to concentrations is

$$c_j = \frac{\prod_{i=1}^{n}(a_j h_i - 1)}{b_j \prod_{\substack{i=1 \\ i \neq j}}^{n}(a_j/a_i - 1)} \quad \text{for all } j \qquad \text{(III.6)}$$

For two-component systems the equations reduce to

---

[6]The equations in this section are not identical with those given in the Helfferich–Klein adaptation of the transformation for ion exchange to Langmuir-type sorption [7]. The roots differ by a constant factor. For Langmuir systems the procedure shown here is more convenient.

$$\frac{b_1 c_1}{a_1 h - 1} + \frac{b_2 c_2}{a_2 h - 1} - 1 = 0 \qquad \text{(III.7)}$$

and

$$c_1 = \frac{(a_1 h_1 - 1)(a_1 h_2 - 1)}{b_1(a_1/a_2 - 1)}, \quad c_2$$

$$= \frac{(a_2 h_1 - 1)(a_2 h_2 - 1)}{b_2(a_2/a_1 - 1)} \qquad \text{(III.8)}$$

Lastly, for only a single component $j$:

$$h = (1 + b_j c_j)/a_j \qquad \text{(III.9)}$$

The roots of Eqs. (III.5) are in the intervals

$$1/a_1 < h_1 < 1/a_2 < h_2 < \cdots < 1/a_n < h_n \qquad \text{(III.10)}$$

(for two-component systems, $1/a_1 < h_1 < 1/a_2 < h_2$). Within each interval the left-hand side of Eqs. (III.5) (the $H$ function) is monotonic, making it easy to obtain the roots even with only a pocket calculator. As an example, the plot of the $H$ function for a three-component case is shown in Fig. 5.

Full sets of all $n$ roots are needed even where one or several solutes are absent from the respective portion of the column. If a solute $k$ is absent, the $c_k$ term of the $H$ function is zero, so that Eqs. (III.5) has one root less. The existing roots are then numbered according to their intervals in condition (III.10), and the missing root is equated to the reciprocal, $1/a_k$, of the $a_i$ coefficient of the absent solute. If several solutes are absent, this same procedure is applied to each.

Equations can also be given for transforming stationary-phase concentrations $q_j$ into roots and vice versa [7]. However, it is usually more convenient to
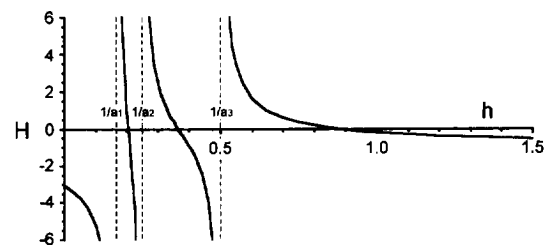


Fig. 5. $H$ function (left-hand side of Eqs. (III.5) plotted vs $h$) for three-component composition with $c_1 = 1.5$, $c_2 = 1.2$, $c_3 = 1.4$, $a_1 = 6.0$, $a_2 = 4.0$, $a_3 = 2.0$, $b_1 = 0.75$, $b_2 = 0.5$, $b_2 = 0.25$ (all in arbitrary consistent units).

interconvert the $q_j$ and $c_j$ with the Langmuir Eqs. (III.1) and their inverse

$$c_j = \frac{(1/a_j)q_j}{1 - \sum\limits_{i=1}^{n} [(b_i/a_i)q_i]} \quad \text{for all } j \qquad \text{(III.11)}$$

### 7.2. Wave velocities[7]

As explained in Section 4, a given composition $c_1,...,\ c_n$ within a diffuse coherent wave can move with different wave velocities (eigenvelocities), depending on the affinity cut of the wave. For each possible cut there is one such velocity, which is intermediate between the particle velocities of the high and low keys. In a wave with $k|k+1$ cut, the varying root is $h_k$ and the coherent velocities $(v_c)_k$ of the compositions are

wave with varying $h_k$:    $(v_c)_k$

$$= \frac{v^\circ}{1 + \dfrac{\rho}{\epsilon} \left[ h_k \prod\limits_{i=1}^{n} (a_i h_i) \right]^{-1}} \qquad \text{(III.12)}$$

This equation gives the wave velocity of a composition with value $h_k$ of the varying root within the wave. As the root value varies across the wave, so does the wave velocity. (Note that all roots other than $h_k$ remain constant across the wave.)

For a coherent shock with varying $h_k$ the velocity is

shock with varying $h_k$:    $(v_\Delta)_k$

$$= \frac{v^\circ}{1 + \dfrac{\rho}{\epsilon} \left[ h_k' h_k'' \prod\limits_{i=1}^{n} a_i \prod\limits_{\substack{i=1 \\ i \neq k}}^{n} h_i \right]^{-1}} \qquad \text{(III.13)}$$

where primes and double primes refer to the com-

positions on the upstream and downstream sides of the wave, respectively. (Note that all roots other than $h_k$ remain constant across the shock.)

For two-component systems, Eqs. (III.12) and Eqs. (III.13) reduce to

wave with    $(v_c)_1$
varying $h_k$:

$$= \frac{v^\circ}{1 + \dfrac{\rho/\epsilon}{a_1 a_2 h_1^2 h_2}}, \quad \begin{array}{l}\text{wave with} \quad (v_c)_2 \\ \text{varying } h_2:\end{array}$$

$$= \frac{v^\circ}{1 + \dfrac{\rho/\epsilon}{a_1 a_2 h_1 h_2^2}} \qquad \text{(III.14)}$$

shock with    $(v_\Delta)_1$
varying $h_1$:

$$= \frac{v^\circ}{1 + \dfrac{\rho/\epsilon}{a_1 a_2 h_1' h_1'' h_2}}, \quad \begin{array}{l}\text{shock with} \quad (v_\Delta)_2 \\ \text{varying } h_2:\end{array}$$

$$= \frac{v^\circ}{1 + \dfrac{\rho/\epsilon}{a_1 a_2 h_1 h_2' h_2''}} \qquad \text{(III.15)}$$

Eqs. (III.12) to Eqs. (III.15) give the real linear velocities, $v$, that is, distance advanced per unit of real time $t$. In practice it is more convenient, however, to work with 'adjusted' velocities, $u$, which are distance advanced per unit of adjusted time $\tau$. The adjusted time is defined as

$$\tau \equiv t - z/v^\circ \qquad \text{(III.16)}$$

At any distance $z$ from the column inlet the adjusted time clock starts ticking when a non-adsorbed marker injected at $t=0$ would pass that spot, that is, when the fluid initially in the column void upstream of the location $z$ has been displaced. (The procedure is commonly used in gas chromatography, where adjusted retention times or volumes are measured from the emergence of an air peak.) Fig. 6 illustrates the relationship between the $t$ and $\tau$ scales. The adjusted velocities corresponding to the real ones in Eqs. (III.12) to Eqs. (III.15) are as follows. For $n$-component systems:

---

[7]The equations in this series have been formulated in terms linear velocities (distance per unit time) because these are easiest to visualize. They could equally well have been cast in terms of cumulative effluent volume instead of time, and column volume upstream (distance from inlet multiplied by cross-sectional area) instead of distance, as often done in theory of chromatography [28,29]. At the expense of being more abstract, those variables lead to slightly simpler algebra and make it easier to accommodate some complications such as variations of the volumetric flow-rate or column diameter.
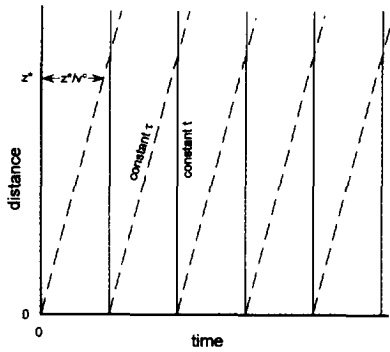
Fig. 6. Scales of real time $t$ and adjusted time $\tau$. At any distance $z^*$ from column inlet, adjusted time is shorter by time span $z^*/v^\circ$ required to displace fluid from interstitial void upstream.

diffuse wave with varying $h_k$: $(u_c)_k$

$$= v^\circ(\epsilon/\rho)h_k \prod_{i=1}^{n} (a_i h_i) \qquad \text{(III.17)}$$

shock with varying $h_k$: $(u_\Delta)_k$

$$= v^\circ(\epsilon/\rho)h_k'h_k'' \prod_{i=1}^{n} a_i \prod_{\substack{i=1 \\ i \neq k}}^{n} h_i \qquad \text{(III.18)}$$

and for two-component systems:

diffuse wave with varying $h_1$: $(u_c)_1$

$$= v^\circ(\epsilon/\rho)a_1 a_2 h_1^2 h_2 \qquad \text{(III.19)}$$

diffuse wave with varying $h_2$: $(u_c)_2$

$$= v^\circ(\epsilon/\rho)a_1 a_2 h_1 h_2^2$$

shock with varying $h_1$: $(u_\Delta)_1 = v^\circ(\epsilon/\rho)a_1 a_2 h_1' h_1'' h_2$

$$\qquad \text{(III.20)}$$

shock with varying $h_2$: $(u_\Delta)_2 = v^\circ(\epsilon/\rho)a_1 a_2 h_1 h_2' h_2''$

Moreover, there is a simple relationship between the adjusted velocity $(u_c)_k$ of a composition in a coherent wave with varying root $h_k$ and the adjusted particle velocities $u_j$ of the solutes at that composition:

$$u_j = (u_c)_k/a_j h_k \qquad \text{for all } j \text{ and } k \qquad \text{(III.21)}$$

## 7.3. Sharpening behavior

A wave sharpens if its tail runs faster than its head, and spreads if the opposite is true. As Eqs. (III.17) or Eqs. (III.19) show, the wave velocity in a diffuse coherent wave increases with the value of the varying root. Accordingly, a simple inspection of the values of that root suffices to determine the sharpening behavior. For a wave with varying root $h_k$:

$$\begin{aligned} \text{self} - \text{sharpening} \quad &\text{if} \quad h_k' > h_k'' \\ \text{nonsharpening} \quad &\text{if} \quad h_k' < h_k'' \end{aligned} \qquad \text{(III.22)}$$

Here, as before, primes and double primes refer to the upstream and downstream sides of the wave, respectively. For example, in any Riemann problem [see pattern (III.4)] the sharpening behavior of each wave is immediately apparent from the root values of the initial and entering fluids: The wave with varying $h_k$ is a shock if $h_k'$ is larger than $h_k^\circ$, and is diffuse if the opposite is true.

## 7.4. Noncoherent waves

The calculation of the development of a noncoherent diffuse wave requires numerical integration over distance and time. This integration is much simpler and faster with the roots instead of the concentrations as dependent variables. This is because Eqs. (III.17), if read as the velocity at which a given value of the root $h_k$ advances, is valid even if the wave is noncoherent. The equation can be rearranged to [30]

$$(\partial h_k/\partial \tau)_z = - h_k \prod_{i=1}^{n} (a_i h_i)(\partial h_k/\partial z)_\tau \qquad \text{for all } k$$

The variation of a root with time depends only on the gradient of that root and the local values of all roots, not on the gradients of the other roots, whereas the change of a concentration with time depends on all local concentration values and gradients. Moreover, in interference of two coherent waves, a common occurrence, all concentrations vary, but only two roots do; as a result, the number of simultaneous equations to be integrated is lower if roots rather than concentrations are used as the dependent variables.

### 7.5. Linear chromatography as limiting case

The mathematics in terms of the $h_i$ contains linear chromatography as the limiting case of infinite dilution or vanishing $b_i$ coefficients. If all $b_i c_i$ terms in Eqs. (III.1) and Eqs. (III.5) become vanishingly small, the $q_j$ approach proportionality to the respective $c_j$ and all root values $h_j$ approach the reciprocals of the respective $a_j$ coefficients:

$$q_j \to a_j c_j \quad j = 1,...,n$$
$$h_j \to 1/a_j \quad j = 1,...,n \quad \text{if all } b_i c_i \to 0$$

Any coherent wave now is only a vanishingly small variation of a root. Under these conditions, Eqs. (III.12) and Eqs. (III.13) for the wave and shock velocities, respectively, reduce to

$$(v_c)_j, (v_\Delta)_j \to \frac{v^\circ}{1 + (\rho/\epsilon)q_j/c_j} \quad \text{if all } b_i c_i \to 0$$

$$(v_c)_j, (v_\Delta)_j \to \frac{v^\circ}{1 + (\rho/\epsilon)q_j/c_j} \quad \text{if all } b_i c_i \to 0$$

and so become equal to the particle velocity, given by Eqs. (I.5), whose equivalence to the retention equation Eqs. (III.2) of linear chromatography was shown earlier. Any concentration variation of a solute then advances at the particle velocity of the solute, unaffected by the presence and behavior of other solutes.

While the $h_i$ mathematics contains the equations of linear chromatography as a limiting case, the capacity-factor concept of linear chromatography becomes useless in the nonlinear case. This is because the $k'$ values, equal to $(\rho/\epsilon)q_i/c_i$ by their definition and needed for the calculation of retention times or volumes, depend on the local concentrations and cannot even be calculated until after the problem at hand has been solved.

### 8. Langmuir sample cases

To demonstrate the application of the $h$-transformation and the ease with which analytical solutions can be obtained with it in many instances, this section takes the reader step by step through the calculation of three sample cases: a five-component

frontal analysis, a three-component separation by displacement development, and a two-component overload elution. The examples illustrate different aspect of working with the transformation – patterns originating from a single source, multiple interferences of shocks from different sources, and interferences involving diffuse waves – and are essentially independent of one another. Any one, or all, may be skipped without loss of continuity.

### 8.1. Frontal analysis

The effluent composition history of a five-component frontal analysis will be calculated for conditions as shown in Table 2. This is a straightforward application of the $h$-transformation, not involving any wave interferences. As a specific example, a case with five solutes was chosen, but the procedure is equally applicable to any larger or smaller number of solutes. General equations for $n$ solutes are given at the end of this section, and for Riemann problems other than frontal analysis in the next section.

### 8.1.1. Plateau compositions

With five components, there will be five waves and four intermediate plateaus (see Section 5). As shown in pattern (III.4) in Section 6, the plateau compositions in terms of $h_i$ are given entirely by the roots of the entering and initial fluid compositions, $h_i'$ and $h_i^\circ$, respectively. All solutes are absent from the column initially, so the five $h_i^\circ$ equal the reciprocals of the five $a_i$ coefficients. The plateau compositions in terms of roots thus are:

| entering fluid: | $h_1'$, | $h_2'$, | $h_3'$, | $h_4'$, | $h_5'$ | |
|---|---|---|---|---|---|---|
| plateau 2: | $1/a_1$, | $h_2'$, | $h_3'$, | $h_4'$, | $h_5'$ | |
| plateau 3: | $1/a_1$, | $1/a_2$, | $h_3'$, | $h_4'$, | $h_5'$ | (III.23) |
| plateau 4: | $1/a_1$, | $1/a_2$, | $1/a_3$, | $h_4'$, | $h_5'$ | |
| plateau 5: | $1/a_1$, | $1/a_2$, | $1/a_3$, | $1/a_4$, | $h_5'$ | |
| initial fluid: | $1/a_1$, | $1/a_2$, | $1/a_3$, | $1/a_4$, | $1/a_5$ | |

For the entering concentrations in Table 2, Eqs. (III.5) yields the following root values:

$$h_1' = 0.06374, \quad h_2' = 0.12018, \quad h_3' = 0.20132, \quad h_4'$$
$$= 0.38061, \quad h_5' = 0.62749 \quad \text{(III.24)}$$

(all in g cm$^{-3}$). With these values and the $a_i$ values

Table 2
Conditions of sample case of five-component frontal analysis

| Column | Length | $L = 10$ cm | |
|---|---|---|---|
| | Diameter | $D = 1$ cm | |
| | Volume | $V = (\pi/4)LD^2 = 7.854$ cm$^3$ | |
| | Void fraction | $\epsilon = 0.38$ | |
| Sorbent | Bulk density | $\rho = 1.1$ g/cm$^3$ column | |
| | Langmuir coefficients | $a_1 = 20$ cm$^3$ g$^{-1}$ | $b_1 = 2$ mmol$^{-1}$ cm$^3$ |
| | | $a_2 = 12$ | $b_2 = 1$ |
| | | $a_3 = 7$ | $b_3 = 0.5$ |
| | | $a_4 = 4$ | $b_4 = 0.2$ |
| | | $a_5 = 2$ | $b_5 = 0.1$ |
| Entering fluid | Concentrations | $c_1 = 1.0$ mmol cm$^{-3}$ | |
| | | $c_2 = 1.2$ | |
| | | $c_3 = 0.8$ | |
| | | $c_4 = 1.3$ | |
| | | $c_5 = 0.9$ | |
| Operating conditions | Volumetric flow-rate | $\dot{V} = 1$ cm$^3$ min$^{-1}$ | |
| | Linear velocity | $v^\circ = \dot{V}/[\epsilon(\pi/4)D^2] = 3.351$ cm min$^{-1}$ | |

in Table 2, Eqs. (III.6) with the root sets (III.23) gives the following solute concentrations:

| | $c_1$ | $c_2$ | $c_3$ | $c_4$ | $c_5$ | |
|---|---|---|---|---|---|---|
| plateau 2: | 0 | 2.042 | 0.939 | 1.396 | 0.928 | mmol cm$^{-3}$ |
| plateau 3: | 0 | 0 | 2.465 | 1.792 | 1.018 | |
| plateau 4: | 0 | 0 | 0 | 3.944 | 1.218 | |
| plateau 5: | 0 | 0 | 0 | 0 | 2.550 | |

### 8.1.2. Wave velocities

As was shown in Section 5, all waves in frontal analysis with Langmuir sorption equilibrium are shocks. With the $h_i^\circ$ equal to the $1/a_i$ and the resulting cancellations, Eqs. (III.18) gives the following expressions for the adjusted shock velocities:

wave 1: $(u_\Delta)_1 = v^\circ(\epsilon/\rho)a_2a_3a_4a_5h_1'h_2'h_3'h_4'h_5'$

wave 2: $(u_\Delta)_2 = v^\circ(\epsilon/\rho)a_3a_4a_5h_2'h_3'h_4'h_5'$

wave 3: $(u_\Delta)_3 = v^\circ(\epsilon/\rho)a_4a_5h_3'h_4'h_5'$

wave 4: $(u_\Delta)_4 = v^\circ(\epsilon/\rho)a_5h_4'h_5'$

wave 5: $(u_\Delta)_5 = v^\circ(\epsilon/\rho)h_5'$                 (III.25)

### 8.1.3. Emergence times

The times at which the various plateau compositions begin to emerge from the column can be

calculated from the velocities above. Plateau 5, first to emerge, begins to do so when wave 5, the fastest, exits the column; plateau 4, when wave 4 exits; and so on; and the entering fluid, when wave 1 exits. The adjusted emergence times are obtained by division of the column length, $L$, by the adjusted wave velocities.

Usually, the volumetric flow-rate $\dot{V}$ instead of the linear velocity $v^\circ$ is given. The latter is the volumetric rate divided by the cross-sectional void area, so that $v^\circ\epsilon = (\dot{V}/V)L$. With this substitution and the velocities in Eqs. (III.25), the adjusted emergence times turn out to be:

plateau 5: $(\tau)_5 = (V/\dot{V})(\rho/h_5') = 13{:}46$ min

plateau 4: $(\tau)_4 = (V/\dot{V})(\rho/a_5h_4'h_5') = 18{:}52$ min

plateau 3: $(\tau)_3 = (V/\dot{V})(\rho/a_4a_5h_3'h_4'h_5') = 22{:}28$ min

plateau 2: $(\tau)_2 = (V/\dot{V})(\rho/a_3a_4a_5h_2'h_3'h_4'h_5')$
$= 26{:}42$ min

entering fluid: $(\tau)_1 = (V/\dot{V})(\rho/a_2a_3a_4a_5h_1'h_2'h_3'h_4'h_5')$
$= 34{:}54$ min

All real emergence times $(t)_i$ are longer by the time span $L/v^\circ = \epsilon V/\dot{V}$ it takes to displace one column

void (see Eqs. (III.16)). With the data in Table 2 that time span is 2:59 min.

This completes the calculation. The resulting effluent history is plotted in Fig. 7.

### 8.1.4. General equations for frontal analysis

For $n$-component frontal analysis in general the root sets of the plateaus are:

plateau $k$:

$$h_i = 1/a_i \quad \text{for } i < k$$

$$h_i = h_i' \quad \text{for } i \geq k \tag{III.26}$$

$$k = 1,...,n + 1$$

(indices: 1 = entering fluid; $n + 1$ = initial fluid). The concentrations in the plateaus are given by Eqs. (III.6) with these root values, and the adjusted emergence times are

$$(\tau)_k = (V/\dot{V})\rho \left[ \prod_{i=k+1}^{n} a_i \prod_{i=k}^{n} h_i \right]^{-1} \tag{III.27}$$

Thus, all quantities of interest are easily calculated from the roots $h_i'$ of the entering fluid, the $a_i$ coefficients, and the operating data (sorbent bulk density, column volume, and flow-rate).

### 8.2. General equations for Riemann problems

The equations for frontal analysis are readily generalized for any Riemann problem (uniform initial and constant entry conditions, but without restrictions as to the presence or absence of solutes anywhere). This requires the replacement of the $1/a_i$



Fig. 7. Frontal analysis: effluent history under conditions in Table 2.

in Eqs. (III.26) by the roots of the initial fluid, $h_i^\circ$. The concentrations in the plateaus then are again given by Eqs. (III.6). In Eqs. (III.27) for the adjusted emergence times, no or not all $h_i^\circ$ cancel against $a_i$. Also, some or all waves may be nonsharpening. Thus, for shocks:

$$(\tau_\Delta)_k = (V/\dot{V})\rho \left[ h_k^\circ \prod_{i=1}^{n} a_i \prod_{i=1}^{k_1} h_i^\circ \prod_{i=k}^{n} h_i' \right]^{-1}$$

for all waves with $h_k' > h_k^\circ$ \hfill (III.28)

For compositions within nonsharpening waves, to which Eqs. (III.17) instead of Eqs. (III.19) applies, the adjusted time at which the value of the varying root in the effluent has reached $h_k$ is given by

$$\tau_{h_k} = (V/\dot{V})\rho \left[ h_k^2 \prod_{i=1}^{n} a_i \prod_{i=1}^{k_1} h_i^\circ \prod_{i=k+1}^{n} h_i' \right]^{-1}$$

for all waves with $h_k' < h_k^\circ$ \hfill (III.29)

### 8.3. Displacement development[8]

The column length and time of operation required for complete resolution of a three-component mixture by fully effective displacement development and the concentrations in the emerging bands will be determined. The conditions are given in Table 3. Apart from being of interest for displacement development, the example demonstrates how, more generally, multiple wave interferences can be handled.

Displacement development has been discussed in detail in Parts I and II (see Sections I.13 and II.9). A mixture containing the solutes to be separated is charged for a finite time to a column initially free of sorbates and is then displaced with a solute having a higher affinity for the sorbent than do the components of the mixture (see Fig. 8). The start of injection of the mixture generates a set of response waves as in frontal analysis. All these waves accordingly are shocks. The switch to injection of the developer generates a second set of waves. If displacement is fully effective, these waves also are shocks. The shocks of the two sets interfere, causing the solutes of the mixture to sort themselves out into
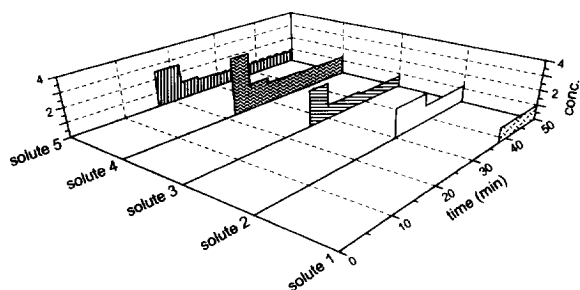
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[8]See also work by Rhee and Amundson [31] and Frenz and Horvath [32].

Table 3
Conditions of sample case of three-component displacement development

| Column | Diameter | $D = 5$ cm | | |
|---|---|---|---|---|
| | Void fraction | $\epsilon = 0.38$ | | |
| Sorbent | Bulk density | $\rho = 1.0$ g/cm$^3$ column | | |
| | Langmuir coefficients | $a_1 = 8$ cm$^3$ g$^{-1}$ | $b_1 = 1.6$ mmol$^{-1}$ cm$^3$ | |
| | | $a_2 = 5$ | $b_2 = 1$ | |
| | | $a_3 = 2.5$ | $b_3 = 0.5$ | |
| | | $a_4 = 1.5$ | $b_4 = 0.3$ | |
| Mixture | Concentrations | $c_1 = 0.8$ | $c_2 = 1.0$ | $c_3 = 1.2$ mmol cm$^{-3}$ |
| | Amount | $V^{(m)} = 600$ cm$^3$ | | |
| | Injection time | $\Delta t = V^{(m)}/\dot{V} = 40$ min | | |
| Displacer | Concentration | $c_1 = 5.0$ mmol cm$^{-3}$ | | |
| Operating conditions | Volumetric flow-rate | $\dot{V} = 15$ cm$^3$ min$^{-1}$ | | |
| | Linear velocity | $v° = \dot{V}/[\epsilon(\pi/4)D^2] = 2.010$ cm min$^{-1}$ | | |

individual bands that eventually travel all at the same velocity, close-up, separated only by shocks. While the final pattern is easy to determine, the resolution distances and times can only be found by a calculation of the transient behavior.

A good way to start working on a problem with multiple interferences of waves is to lay out the topology of the wave pattern in distance and time, to have a clear picture of which waves interfere with which others. It may not be known at the outset which waves are self-sharpening and which are nonsharpening, and which solutes are present in or absent from which plateaus between the waves, but the topology of the pattern often is nevertheless unambiguous. If there are several possibilities, the



Fig. 8. Displacement development: operating procedure (for three-component separation, schematic).

correct choice becomes apparent once an early portion of the pattern has been calculated.

A topology diagram is compiled step by step, starting with the waves originating at the column inlet, establishing their interferences, then identifying the new waves arising from them, establishing the interferences of those waves, and so on. For the case at hand, Fig. 9 shows such a construction step by step. Waves will be called for short "$h_1$ wave," "$h_2$ wave," etc., indicating which root varies across. In the topology diagram the index of the respective varying root is shown in a circle.

*Step 1*

The distance and time axes are laid out, for convenience not at right angles to avoid crowding in the area of large distance and long time. On the time axis, the times of start of injection of mixture and displacer are marked as points A and B, respectively. The start of injection of the mixture (solutes 2, 3, and 4) at time $t = 0$ (point A) produces three shocks with varying roots $h_2$, $h_3$, and $h_4$ (slowest to fastest wave). The switch to injection of the displacer (solute 1) at time $t = \Delta t$ (point B), involving all four solutes, produces four waves with varying $h_1$, $h_2$, $h_3$, and $h_4$ (slowest to fastest), whose sharpening behavior remains to be ascertained. Although their actual trajectories in the distance–time plane are straight, the waves are shown as curves in a way that leaves enough room for entries identifying the plateau zones between the waves and stating their compositions.

The first interference is that of the fastest wave of the second set with the slowest of the first, that is, of
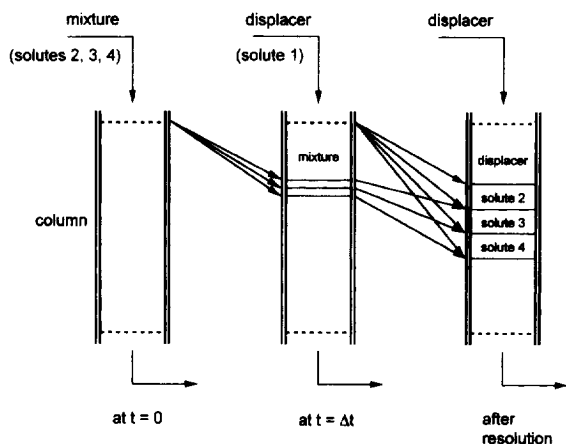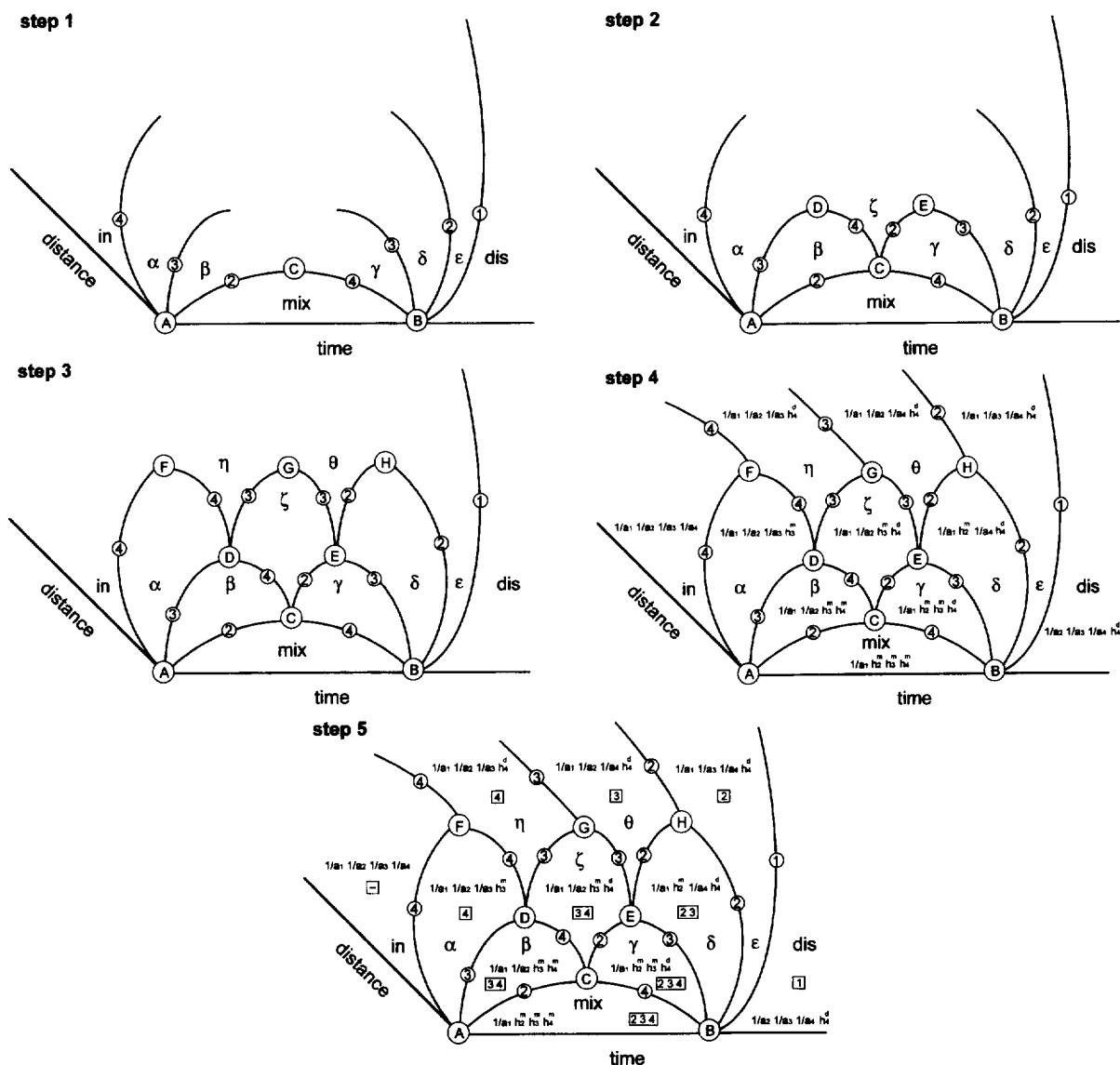
Fig. 9. Displacement development: step-by-step construction of wave topology in three-component separation. A, B,... = locations of wave interferences; α, β,... = designations of plateaus; numbers in circles = indices of varying roots; numbers in square boxes = solutes present in plateaus; root sets shown in plateaus.

the $h_4$ wave of the former with the $h_2$ wave of the latter. This point is marked C.

For identification, the various plateaus separated by the waves are named and their names are entered in the diagram: Downstream of the $h_4$ wave originating from A the column is still in its initial composition, "in". Between the $h_2$ wave from A and the $h_4$ wave from B, the composition is that of the

injected mixture, "mix". Upstream of the $h_1$ wave from B is the displacer, "dis". The other plateaus between the waves are given Greek letters α to ε, left to right.

*Step 2*

At point C, the interference of an $h_4$ wave and an $h_2$ wave produces two new waves: an $h_4$ and an $h_2$ wave, the former faster than the latter. These two

give rise to two new interferences: of the $h_4$ wave from C with the $h_2$ wave from A, and of the $h_2$ wave from C with the $h_4$ wave from B. (Note that waves with higher index of the varying root are faster, see Eqs. (III.12) and Eqs. (III.13).) The trajectories of the two new waves are added, the plateau between the new waves is named $\zeta$, and the respective points of the new interferences are marked D and E.

*Step 3*

Interference of the $h_4$ wave from C with the $h_3$ wave from A, at D, produces two new waves: an $h_4$ and an $h_3$ wave. Similarly, interference of the $h_2$ wave from C with the $h_3$ wave from B, at E, produces a new $h_2$ and a new $h_3$ wave. Their trajectories are entered as curves, and the plateaus between them are named $\eta$ and $\theta$.

The next possible interferences are those of the two $h_4$ waves from A and D, of the two $h_3$ waves from D and E, and of the two $h_2$ waves from E and B, each involving two waves with the same varying root. A plateau between two coherent waves with same varying root (same affinity cut) shrinks if either or both waves are shocks (see Section 4). In the case at hand they all do because all waves originating from point A are frontal analysis waves and therefore are shocks. [Note a variation of a root, increasing or decreasing in the direction of flow, retains its sharpening behavior when its trajectory crosses that of a variation of another root; see criterion (III.22).] The three points of merger of waves are marked F, G, and H, and the trajectories of the resulting three new waves are drawn in. The wave pattern is now complete.

*Step 4*

The compositions of the plateaus of the initial fluid, mixture, and displacer in terms of roots are now established as follows. Without calculation, values can be assigned to all roots of the initial fluid (no solutes) and the first root of the mixture (solute 1 absent) because roots must equal reciprocal $a_i$ coefficients of absent solutes and condition (III.10) allows no root other than $h_1$ to assume the value $1/a_1$:

initial fluid:    $h_1 = 1/a_1,$      $h_2 = 1/a_2,$
                  $h_3 = 1/a_3,$      $h_4 = 1/a_4$
                                                   (III.30)
mixture:    $h_1 = 1/a_1,$      $h_2 = h_2^{(m)},$
            $h_3 = h_3^{(m)},$      $h_4 = h_4^{(m)}$

where the still unknown other three roots of the mixture are written $h_i^{(m)}$.

For the displacer, three root values must equal the reciprocals of the $a_i$ values of the absent solutes 2, 3, and 4. However, since condition (III.10) allows any $1/a_i$ other than $1/a_1$ to be either $h_i$ or $h_{i-1}$, the root indices cannot be assigned until the value of the fourth root has been calculated. Here, Eqs. (III.9) with $c_1$, $a_1$, and $b_1$ from Table 3 gives a value larger than $1/a_4$ (see Eq. (III.32) farther below), which must therefore be assigned to $h_4$. Accordingly, with this value written as $h_4^{(d)}$,

displacer:    $h_1 = 1/a_2,$      $h_2 = 1/a_3,$

$$h_3 = 1/a_4, \quad h_4 = h_4^{(d)} \qquad (III.31)$$

The root sets for the initial fluid, mixture and displacer are now entered into the respective zones of the diagram.

*Step 5*

The compositions of the other plateaus in terms of the roots of the initial, mixture, and displacer compositions as given by Eqs. (III.30) and (III.31) can now be established by an examination of which root varies across which wave, in the same fashion as pattern (III.4) in Section 6 was deduced. For example, going from the displacer to the mixture, $h_2$ must vary from $1/a_3$ to $h_2^{(m)}$ and can do so only across the $h_2$ wave between plateaus $\epsilon$ and $\delta$; accordingly, it must equal $1/a_3$ in plateau $\epsilon$, and $h_2^{(m)}$ in both plateaus $\delta$ and $\gamma$. The root sets of all plateaus are entered into the diagram.

Since a solute $k$ is absent if a root equals $1/a_k$, it can now be seen which solutes are present in which plateaus:

| | |
|---|---|
| initial fluid: | contains no solutes |
| mixture: | contains solutes 2, 3, and 4 |
| displacer: | contains solute 1 |
| plateau $\alpha$: | contains solute 4 |
| plateau $\beta$: | contains solutes 3 and 4 |
| plateau $\gamma$: | contains solutes 2, 3, and 4 |
| plateau $\delta$: | contains solutes 2 and 3 |
| plateau $\epsilon$: | contains solute 2 |
| plateau $\zeta$: | contains solutes 3 and 4 |
| plateau $\eta$: | contains solute 4 |
| plateau $\theta$: | contains solute 3 |

The solutes in the respective plateaus are entered into the diagram, shown in square boxes.

The construction of the topology diagram is now complete. The detailed and lengthy description might make things seem complicated. However, having gone through this exercise once, the reader will find the procedure fast and easy to apply to any new situation.

Equations for the wave velocity can now be established as follows. Since condition (III.10) requires $1/a_i < h_i^{(m)} < 1/a_{i+1}$ and since $h_4^{(d)} > h_4^{(m)}$, it can now also be seen that all waves are shocks because in each case the value of the varying root decreases in the direction of flow [see criterion (III.22)]. The velocities are given by Eqs. (III.18), which requires the root sets of the plateaus on the upstream and downstream sides of the respective shock (note that only one root varies across each shock). The resulting equations are listed in the third column of Table 4. As the entries show, the velocities of the four final shocks, originating from points F, G, H, and B, are given by identical equations; this confirms that a final constant pattern traveling without further change is eventually attained.

The calculation of real concentrations and velocities requires, in addition to the $a_i$, numerical values

of $h_4^{(d)}$ and the $h_i^{(m)}$. With Eqs. (III.9) for the former and Eqs. (III.5) for the latter, the data in Table 3 yield:

mixture: $h_2^{(m)} = 0.25418$, $h_3^{(m)} = 0.50312$,

$h_4^{(m)} = 1.1094$ g cm$^{-3}$ (III.32)

displacer: $h_4 = 1.125$

The adjusted shock velocities calculated with these values and the $a_i$ from Table 3 are listed in the last column of Table 4. The concentrations in the various plateaus could easily be calculated with Eqs. (III.6) from the root sets in Fig. 9 with the root and $a_i$ values from Eq. (III.32) and Table 3. However, for a calculation of the resolution distances this is not necessary. The only concentrations of interest are those in the single-component bands emerging from the column after complete resolution (plateaus $\alpha$, $\eta$, $\theta$, and $\epsilon$). These turn out to be:

plateau $\alpha$: $c_4 = 2.21$ mmol cm$^{-3}$

plateau $\theta$: $c_3 = 3.63$ mmol cm$^{-3}$

plateau $\eta$: $c_4 = 2.29$

plateau $\epsilon$: $c_2 = 4.63$

[All but that of solute 4 in plateau $\alpha$ could instead

Table 4
Shock velocities in sample case of three-component displacement development

| Shock between | | Varying | Adjusted shock velocity[a] | |
|---|---|---|---|---|
| Plateau upstream | Plateau downstream | root | $u_\Delta$ | |
| $\alpha$ | Initial | $h_4$ | $v°(\epsilon/\rho)h_4^{(m)}$ | $= 0.8457$ cm min$^{-1}$ |
| $\beta$ | $\alpha$ | $h_3$ | $v°(\epsilon/\rho)a_4 h_3^{(m)} h_4^{(m)}$ | $= 0.6396$ |
| Mixture | $\beta$ | $h_2$ | $v°(\epsilon/\rho)a_3 a_4 h_2^{(m)} h_3^{(m)} h_4^{(m)}$ | $= 0.4064$ |
| $\gamma$ | Mixture | $h_4$ | $v°(\epsilon/\rho)a_2 a_3 a_4 h_2^{(m)} h_3^{(m)} h_4^{(m)} h_4^{(m)}$ | $= 2.2862$ |
| $\delta$ | $\gamma$ | $h_3$ | $v°(\epsilon/\rho)a_2 a_3 h_2^{(m)} h_3^{(m)} h_4^{(d)}$ | $= 1.3738$ |
| $\epsilon$ | $\delta$ | $h_2$ | $v°(\epsilon/\rho)a_2 h_2^{(m)} h_4^{(d)}$ | $= 1.0923$ |
| Displacer | $\epsilon$ | $h_1$ | $v°(\epsilon/\rho)h_4^{(d)}$ | $= 0.8594$ |
| $\zeta$ | $\beta$ | $h_4$ | $v°(\epsilon/\rho)a_3 a_4 h_3^{(m)} h_4^{(m)} h_4^{(d)}$ | $= 1.7989$ |
| $\gamma$ | $\zeta$ | $h_2$ | $v°(\epsilon/\rho)a_3 a_4 h_2^{(m)} h_3^{(m)} h_4^{(d)}$ | $= 0.4122$ |
| $\eta$ | $\alpha$ | $h_4$ | $v°(\epsilon/\rho)a_4 h_4^{(m)} h_4^{(d)}$ | $= 1.4302$ |
| $\zeta$ | $\eta$ | $h_3$ | $v°(\epsilon/\rho)a_4 h_3^{(m)} h_4^{(d)}$ | $= 0.6486$ |
| $\theta$ | $\zeta$ | $h_3$ | $v°(\epsilon/\rho)a_3 h_3^{(m)} h_4^{(d)}$ | $= 1.0810$ |
| $\delta$ | $\theta$ | $h_2$ | $v°(\epsilon/\rho)a_3 h_2^{(m)} h_4^{(d)}$ | $= 0.5461$ |
| $\eta$ | Initial | $h_4$ | $v°(\epsilon/\rho)h_4^{(d)}$ | $= 0.8594$ |
| $\theta$ | $\eta$ | $h_3$ | $v°(\epsilon/\rho)h_4^{(d)}$ | $= 0.8594$ |
| $\epsilon$ | $\theta$ | $h_2$ | $v°(\epsilon/\rho)h_4^{(d)}$ | $= 0.8594$ |

[a] In the calculation of resolution distances for given volume of mixture, the factor $v°\epsilon$ cancels and need not be carried. It is retained here for clarity.

have been obtained with a Tiselius construction (see Sections I.13 and II.7)].

All data needed for the calculation of the resolution distances are now at hand. Inspection of the topology diagram in Fig. 9 with attention to which solutes are present where shows that the farthest distance solutes 2 and 3 travel together is to point H, where plateau $\delta$ ends. Accordingly, $z_H$ is the distance needed for resolution of these two solutes. Similarly, the farthest distance solutes 3 and 4 travel together is to point G, the end of plateau $\zeta$, making $z_G$ the resolution distance of those two solutions. Only calculation of both can show which of the two distances is the longer one. Also of interest might be $z_F$, the distance needed to consolidate solute 4 into one band (plateau $\eta$) at its higher concentration. Closed-form algebraic equations for all interference and resolution distances and times in terms of the roots and $a_i$ coefficients can be derived, but are lengthy for mixtures of more than two components. Unless problems of exactly the same nature – same number of components, same sharpening behavior of all waves – recur repeatedly, a step-by-step approach is more practical. That method, employed here, consists of calculating time and distance coordinates of interference points from those of previous points in the pattern and the velocities of the interfering waves and repeating the procedure for points farther out [33]. With reference to Fig. 10, the $\tau$ and $z$ coordinates of a point * at which waves from points $x$ and $y$ and with adjusted velocities $u_x$ and $u_y$ interfere is given by the "triangle formula"
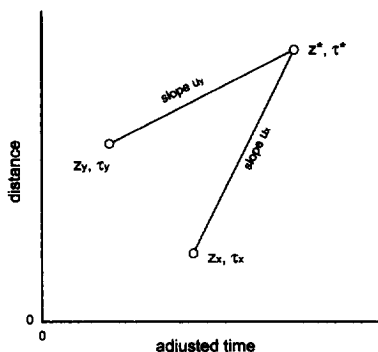


Fig. 10. Basis of triangle formula (III.33): trajectories of two shocks with different origins $z_x$, $\tau_x$ and $z_y$, $\tau_y$, interfering at $z^*$, $\tau^*$.

$$\tau^* = \frac{z_x - z_y + \tau_y u_y - \tau_x u_x}{u_y - u_x},$$

$$z^* = z_x + (\tau^* - \tau_x)u_x$$

or (III.33)

$$z^* = z_y + (\tau^* - \tau_y)u_y$$

For example, for point C, at which waves from A and B interfere, the input is

$$z_x = z_A = 0,$$
$$\tau_x = \tau_A = 0,$$
$$u_x = (u_\Delta)_{mix \to \beta} = 0.4064 \text{ cm min}^{-1},$$
$$z_y = z_B = 0,$$
$$\tau_y = \tau_B = \Delta t = 40 \text{ min}$$
$$u_y = (u_\Delta)_{\gamma \to mix} = 2.2862 \text{ cm min}^{-1}$$

Using Eqs. (III.33) and the velocities from Table 4 one obtains

$$\tau_C = \frac{(u_\Delta)_{\gamma \to mix}\Delta t}{(u_\Delta)_{\gamma \to mix} - (u_\Delta)_{mix \to \beta}} = 48.64 \text{ min},$$

$$z_C = \tau_C(u_\Delta)_{mix \to \beta} = 19.77 \text{ cm}$$

With the $\tau$ and $z$ coordinates of point C established, those of point D are calculated from those of points A and C; those of E from those of C and B; and so on. With the triangle Eqs. (III.33) programmed, this can be done in little time even with only a pocket calculator. In the case at hand, the distances of interest turn out to be:

| resolution 2/3 | resolution 3/4 | consolidation of 4 |
| --- | --- | --- |
| $z_H = 27.9$ cm, | $z_G = 56.1$ cm, | $z_F = 67.2$ cm |

Lastly, the time of operation required is the time it takes for the last wave of the pattern to emerge. That is the wave with which the displacer displaces plateau $\epsilon$, originating at point B ($z = 0$, $\tau = \Delta t$). The respective adjusted wave velocity from Table 4 gives

$$t_{end} = \tau_{end} + L/v^\circ = L(1/(u_\Delta)_{disp \to \epsilon} + 1/v^\circ)$$

$$= \frac{(\pi/4)LD^2}{\dot{V}}\left(\frac{\rho}{h_4^{(d)}} + \epsilon\right) \qquad (III.34)$$

With the data in Table 3 and for a column of 60 cm length, the real time is found to be 99:40 min.

This completes the calculation. The quantitative distance–adjusted time diagram is shown in Fig. 11.

Beyond giving results for a specific case, the calculation sheds light on the function of the displacer. How the displacer acts depends on the value of its only root, $h^{(d)}$. In the calculated example, that root was larger than the largest of the mixture, making displacement completely effective with all waves being shocks. If $1/a_4 < h^{(d)} < h_4^{(m)}$, the $h_4$ wave from B via C and D to F is nonsharpening and its merger with the $h_4$ shock from A extends over some distance and time, eventually resulting in a single shock; also, the concentration of solute 4 then is higher in plateau α than in the final band η (behavior as in Fig. 21 of Part II). If $1/a_3 < h^{(d)} < 1/a_4$, solute 4 is absent from plateaus γ, ζ, and η, and a pulse of solute 4 "runs away" from the displacement pattern, losing its flat top when the nonsharpening $h_4$ wave from B merges with the $h_4$ shock from A at point F (behavior as in Fig. 24 of Part II). Similarly, if $1/a_2 < h^{(d)} < 1/a_3$, solute 4 behaves in the same way but, in addition, solute 3 is absent from plateaus δ and θ and forms another run-away pulse that loses its flat top at point G. Lastly, if $1/a_1 < h^{(d)} < 1/a_2$, solute 2 in addition is absent from plateau ε, and all three solutes now travel as pulses while the displacer remains entirely ineffective. These considerations show that the quality of a displacer can be judged by its root according to Eqs. (III.9), a large value being desirable. Too high an affinity of the displacer for

the sorbent (high value of its $a_i$ coefficient) is seen not to be desirable: It will make the displacer slow, perhaps slower than the solutes of the mixture and so letting them run away. The $a_i$ coefficient of the displacer must be larger than those of the components of the mixture for displacement development to be possible at all, and should be reasonably larger than $a_2$ to ensure good sharpness of the shock layer with which solute 2 is displaced, but an affinity exceeding these requirements is detrimental.

## 8.4. Elution from an overloaded column[9]

The column response in elution of a two-component mixture from a column under conditions of concentration and volume overload will be calculated. Simple algebraic equations in terms of the roots of the mixture cover the entire behavior, with the sole exception of the shock front of the pulse of the solute of lower affinity after that pulse has lost its flat top. The conditions are listed in Table 5. General equations for emergence times of waves are given at the end of the section. This example illustrates the application of the transformation in a situation in which interference involves a diffuse wave.

Elution of a binary mixture under overload conditions has been discussed in detail in Part II (see Section II.9). A fairly concentrated mixture is charged for a finite time to a column initially free of solutes, and is then developed with pure solvent (or carrier gas). The start of injection of the mixture and the switch to solvent each generate a set of coherent response waves. With only two solutes as considered here, each of these sets consists of two waves, one each with varying $h_1$ and $h_2$. Until injection is switched, conditions are as in frontal analysis, so both response waves of the first set are shocks. The switch from mixture to solvent entails the opposite composition variation, so both its response waves are nonsharpening. If the column is long enough, the faster wave of the second set will catch up and interfere with the slower wave of the first. Still farther downstream, the two fast waves will merge, and so will the two slow ones.
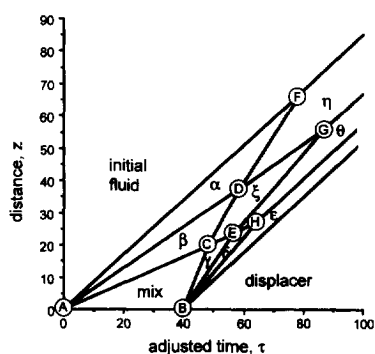


Fig. 11. Displacement development: distance-adjusted time diagram for three-component separation under conditions in Table 3.

[9]See also work by Rhee et al. [5,6] and Golshan-Shirazi and Guiochon [34].

Table 5
Conditions of sample case of two-component elution under conditions of concentration and volume overload

| Column | Diameter | $D = 1$ cm | |
|---|---|---|---|
| | Void fraction | $\epsilon = 0.38$ | |
| Sorbent | Bulk density | $\rho = 1.1$ g/cm$^3$ column | |
| | Langmuir coefficients | $a_1 = 4$ cm$^3$ g$^{-1}$ | $b_1 = 0.50$ mmol$^{-1}$ cm$^3$ |
| | | $a_2 = 2$ | $b_1 = 0.25$ |
| Mixture | Concentrations | $c_1 = 0.50$ | $c_2 = 0.48$ mmol cm$^{-3}$ |
| | Amount | $V^{(m)} = 2$ cm$^3$ | |
| | Injection time | $\Delta t = V^{(m)}/\dot{V} = 2$ min | |
| Operating conditions | Volumetric flow-rate | $\dot{V} = 1$ cm$^3$ min$^{-1}$ | |
| | Linear velocity | $v^\circ = \dot{V}/[\epsilon(\pi/4)D^2] = 3.3506$ cm min$^{-1}$ | |

As in the previous example, a good way to start is to lay out the topology of the wave pattern in distance and time (see Fig. 12). Both sets of waves are generated at the column inlet ($z = 0$), the first at point A ($t = 0$) with beginning injection of the mixture, the second at point B ($t = \Delta t$) with the switch to injection of solvent as eluent. In Fig. 12 the spreading nonsharpening waves are shaded and the indices of the varying roots of the four waves are shown in circles. The first interference occurs when the leading edge of the faster wave of the second set (a nonsharpening $h_2$ wave) catches up with the slower wave of the first (an $h_1$ shock). The distance–time point where this happens is marked C'. Since one of the two waves is diffuse, interference extends over a finite distance and time span, in this case along a distance–time curve from C' to C", where interference is complete. Later, the two $h_2$ waves from A and C'–C" merge at D, and so do the two $h_1$
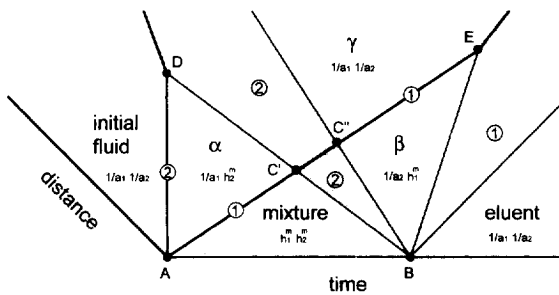


Fig. 12. Overload elution: topology of wave pattern of two-component case. Diffuse waves shown shaded; α, β,... = plateaus; numbers in circles = indices of varying roots; sets of roots shown in plateaus.

waves from B and C" at E. The mergers do occur because in each case one wave is a shock, so that the plateau between them shrinks (see Section 4).

### 8.4.1. Plateau compositions

In terms of roots, the compositions of all plateaus can be written down immediately. Writing $h_i^{(m)}$ for the roots of the mixture composition:

mixture:
$$h_1 = h_1^{(m)}, \qquad h_2 = h_2^{(m)} \qquad \text{(III.35)}$$

The roots of the initial fluid and of the eluent, both free of solutes, are

initial fluid and eluent:
$$h_1{}^\circ = 1/a_1, \qquad h_2{}^\circ = 1/a_2 \qquad \text{(III.36)}$$

Across the slower wave of the first set, $h_2$ remains at $h_2^{(m)}$, its value in the mixture, while $h_1$ varies and must do so all the way from $h_1^{(m)}$ to $1/a_1$ because is cannot vary across the faster wave. Thus, the roots of plateau α between the waves of the first set are

plateau α: $\qquad h_1 = 1/a_1, \qquad h_2 = h_2^{(m)} \qquad$ (III.37)

Because one root equals $1/a_1$, solute 1 is absent. Similarly, across the slower wave of the second set, $h_2$ remains $1/a_2$, only $h_1$ varies and does so all the way from $1/a_1$ to $h_1^{(m)}$, its value in the mixture, making the root set of plateau β between these waves

plateau β: $\qquad h_1 = h_1^{(m)}, \qquad h_2 = 1/a_2 \qquad$ (III.38)

Because one root equals $1/a_2$, solute 2 is absent. In

the new plateau $\gamma$ that develops after wave interference is complete, $h_1$ must be the same as in plateau $\alpha$, and $h_2$ the same as in plateau $\beta$. Thus:

plateau $\gamma$:     $h_1 = 1/a_1$,     $h_2 = 1/a_2$     (III.39)

showing that both solutes are absent. Plateaus $\alpha$ and $\beta$ are seen to be flat tops of pulses of pure solutes 2 and 1, respectively, both with shock fronts and nonsharpening tails. The pulses lose their flat tops at the distance–time points marked D and E, respectively, where the leading edges of the nonsharpening waves catch up with the shocks.

For the composition of the injected mixture given in Table 5, Eqs. (III.7) yields

$$h_1^{(m)} = 0.298842, \quad \text{g cm}^{-3}$$
$$h_2^{(m)} = 0.569908$$
$$(III.40)$$

With these values, Eqs. (III.9) gives:

plateau $\alpha$:     $c_2 = (a_2 h_2^{(m)} - 1)/b_2 = 0.559$ mmol cm$^{-3}$
plateau $\beta$:     $c_1 = (a_1 h_1^{(m)} - 1)/b_1 = 0.391$ mmol cm$^{-3}$

These are the concentrations of the flat tops.

### 8.4.2. Wave velocities

Explicit equations for the various adjusted wave velocities in terms of the $a_i$ coefficients and the roots of the mixture composition are obtained from Eqs. (III.19) and Eqs. (III.20) with use of the respective root sets in Eqs. (III.35) to (III.39). For the two shocks from point A:

$$(u_\Delta)_{\text{mix}\to\alpha} = v^\circ(\epsilon/\rho)a_2 h_1^{(m)} h_2^{(m)},$$
$$(u_\Delta)_{\alpha\to\text{init}} = v^\circ(\epsilon/\rho)h_2^{(m)}$$
$$(III.41)$$

and for the compositions within the two nonsharpening waves from point B:

$$(u_c)_{\text{el}\to\beta} = v^\circ(\epsilon/\rho)a_1 h_1^2,$$
$$(u_c)_{\beta\to\text{mix}} = v^\circ(\epsilon/\rho)a_1 a_2 h_1^{(m)} h_2^2$$
$$(III.42)$$

(Subscripts mix→$\alpha$ etc. state the plateaus upstream and downstream of the respective wave, with the arrow pointing from the former to the latter.)

Also of interest are the adjusted velocities of the slowest and fastest compositions of the nonsharpen-

ing waves, that is, the compositions in which the varying root still or already has the same value as in the adjacent plateau. With the roots of the plateaus as seen in Fig. 12:

$$(u_c)'_{\text{el}\to\beta} = v^\circ(\epsilon/\rho)(1/a_1)$$
$$(u_c)''_{\text{el}\to\beta} = v^\circ(\epsilon/\rho)a_1(h_1^{(m)})^2$$
$$(u_c)'_{\beta\to\text{mix}} = v^\circ(\epsilon/\rho)(a_1/a_2)h_1^{(m)}$$
$$(u_c)''_{\beta\to\text{mix}} = v^\circ(\epsilon/\rho)a_1 a_2 h_1^{(m)}(h_2^{(m)})^2$$
$$(III.43)$$

where primes and double primes refer to the slowest and fastest compositions (trailing edge and leading edge of the wave), respectively.

In the same way the adjusted velocities of the $h_1$ shock and the nonsharpening $h_2$ wave after their interference can be obtained:

$$(u_\Delta)_{\beta\to\gamma} = v^\circ(\epsilon/\rho)h_1^{(m)}$$
$$(u_c)_{\gamma\to\alpha} = v^\circ(\epsilon/\rho)a_2 h_2^2$$
$$(u_c)'_{\gamma\to\alpha} = v^\circ(\epsilon/\rho)(1/a_2)$$
$$(u_c)''_{\gamma\to\alpha} = v^\circ(\epsilon/\rho)a_2(h_2^{(m)})^2$$
$$(III.44)$$

### 8.4.3. Times and distances of interference

The adjusted-time and distance coordinates of point C', where interference begins, are established with the triangle formula Eqs. (III.33) from those of A and B and the velocities $(u_\Delta)_{\text{mix}\to\alpha}$ and $(u_c)''_{\beta\to\text{mix}}$ in Eqs. (III.41) and Eqs. (III.43). The coordinates of C" can be found by integration along the shock trajectory from C' to C" [10]. The coordinates of D and E, where the flat tops of the pulses of solutes 2 and 1 end, can then again be calculated with the triangle formula from those of A, C', B, and C" and the velocities $(u_\Delta)_{\alpha\to\text{in}}$, $(u_c)''_{\gamma\to\alpha}$, $(u_\Delta)_{\beta\to\gamma}$, and $(u_c)''_{\text{el}\to\beta}$

---

[10] An explicit analytical solution for interference of a shock with a diffuse nonsharpening wave can be obtained if the latter is 'self-centered', that is, if the trajectories of its compositions all originate from one and the same distance–time point or can be linearly extrapolated to such a point. This makes it possible to give an analytical solution for attenuation of the pulse of solute 1 after disappearance of its flat top at E [35]. However, the nonsharpening $h_2$ wave is no longer self-centered after interference along C'–C" and, therefore, the trajectory of the shock front of the pulse of solute 2 from D on out must be found by numerical integration.

from Eqs. (III.41), Eqs. (III.43) and Eqs. (III.44). The coordinates are

$$\tau_{C'} = \frac{h_2^{(m)}\Delta t}{h_2^{(m)} - 1/a_1} = 3{:}34 \text{ min},$$

$$z_{C'} = (u_\Delta)_{\text{mix}\to\alpha}\tau_{C'} = 1.41 \text{ cm},$$

$$\tau_{C''} = \left(1 + \frac{1/a_1(h_2^{(m)} - 1/a_1)}{(1/a_2 - 1/a_1)^2}\right)\Delta t = 4{:}34 \text{ min},$$

$$z_{C''} = u'_{c\beta\to\text{mix}}(\tau_{C''} - \Delta t) = 1.77 \text{ cm},$$

$$\tau_D = \frac{h_2^{(m)}(h_2^{(m)} - h_1^{(m)})\Delta t}{(h_2^{(m)} - 1/a_1)(h_2^{(m)} - 1/a_2)^2} = 13{:}49 \text{ min},$$

$$z_D = (u_\Delta)_{\alpha\to\epsilon} = 9.11 \text{ cm},$$

$$\tau_E = \left(1 + \frac{1/a_1(h_2^{(m)} - 1/a_1)}{(1/a_2 - 1/a_1)(h_1^{(m)} - 1/a_1)}\right)\Delta t$$
$$= 15{:}06 \text{ min},$$

$$z_E = (u_c)''_{\text{el}\to\beta}(\tau_E - \Delta t) = 5.42 \text{ cm} \qquad \text{(III.45)}$$

Note that $z_{C'}$ is the column length required for complete resolution of solutes 1 and 2. The quantitative distance-adjusted time diagram is shown in Fig. 13.

### 8.4.4. General equations for emergence times and construction of effluent histories
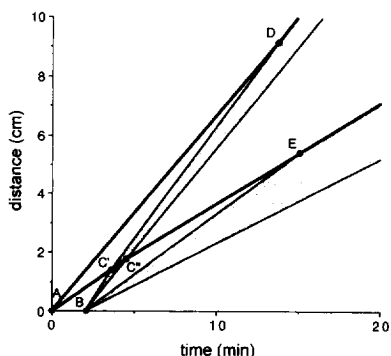
General equations for the adjusted emergence



Fig. 13. Overload elution: distance-adjusted time diagram for two-component case under conditions in Table 5.

times of the shocks and compositions within the nonsharpening waves are listed in Table 6. They can be used for compilation of effluent concentration histories of columns of given lengths, $L$. A good way to proceed is first to establish in which sequence the waves and plateaus emerge from the column. This is done by comparing the column length to the interference distances $z_{C'}$, $z_{C''}$, $z_D$, and $z_E$. The adjusted emergence times of the waves are then calculated with the equations in Table 6. Finally, the root sets of any plateaus or pulse apexes are transformed into concentrations with Eqs. (III.8). In this way, the entire pattern can be calculated with simple algebraic equations. The only exception is the shock front of the pulse of solute 1 after disappearance of its flat top at point D; here, numerical integration is required.

Compilation of the effluent history for a column of 7 cm length under the conditions listed in Table 5 may illustrate the procedure. A comparison with the interference distances shows the column to be shorter than $z_D$, but longer than $z_{C''}$ and $z_E$. Accordingly, the two pulses are resolved and the flat top of solute 1 has disappeared, but that of solute 2 has not. Thus, the sequence of emergence is: initial fluid/$h_2$ shock (front of pulse of solute 2)/plateau $\alpha$ (flat top of that pulse)/$h_2$ wave (diffuse rear of that pulse)/plateau $\gamma$ (no solutes)/$h_1$ shock (front of pulse of solute 1)/$h_1$ wave (diffuse rear of that pulse). The calculation of the adjusted emergence times and concentrations yields:

| | | |
|---|---|---|
| front of 1st pulse ($h_2$ shock    before merger) | 10:34 min | [Eq. (III.46)] |
| flat top of 1st pulse (plateau $\alpha$) | $c_2 = 0.559 \, M$ | [Eq. III.8 with $h_1 = 1/a_1$, $h_2 = h_2^{(m)}$] |
| rear of 1st pulse ($h_2$ wave after    interference) | front 11:00 min | [Eq. (III.53) with $h_2 = h_2^{(m)}$] |
| | rear 13:36 min | [Eq. (III.53) with $h_2 = 1/a_2$] |
| interval (plateau $\gamma$) | no solutes | |
| front of 2nd pulse ($h_1$ shock after    merger) | 19:44 min | [Eq. (III.50)] |
| apex of 2nd pulse | $c_1 = 0.336 \, M$ | [Eqs. (III.51) and (III.8)] |
| rear of 2nd pulse ($h_2$ wave) | rear 26:11 min | [Eq. (III.54) with $h_1 = 1/a_1$] |

(The emergence time of the front of the second pulse is also that of the apex.) In addition, a few intermediate concentrations within the two diffuse waves should be chosen and converted to roots with Eq. III.9 for calculation of their adjusted emergence times with Eqs. (III.53) and (III.54). All real emergence times are longer by $L/v° = 2{:}03$ min. The

Table 6
General equations for emergence times in two-component elution under overload conditions. $[F = v°(\epsilon/p)]$

| Wave | Range of validity | Value of constant root | Adjusted emergence time | |
|---|---|---|---|---|
| $h_2$ shock (front of pulse of solute 2; $h_2$ jump from $1/a_2$ to $h_2^{(m)}$ or apex value) | | | | |
| Before merger | $L \leq z_D$ | $h_1 = 1/a_1$ | $\tau_{\Delta h_2} = 1/(Fh_2^{(m)})$ | (III.46) |
| After merger | $L \geq z_D$ | $h_1 = 1/a_1$ | Requires numerical evaluation | |
| $h_1$ shock (front of pulse of solute 1; $h_1$ jump from $1/a_1$ to $h_2^{(m)}$ or apex value) | | | | |
| Before interference | $L \leq z_{C'}$ | $h_2 = h_2^{(m)}$ | $\tau_{\Delta h_1} = L/(Fa_2 h_1^{(m)} h_2^{(m)})$ | (III.47) |
| During interference | $z_{C'} \leq L \leq z_{C''}$ | $h_2^{(m)}$ varies from $h_2^{(m)}$ at $C'$ to $1/a_2$ at $C''$ | $\tau_{\Delta h_1} = \Delta t + a_1[(L/(Fa_2 h_1^{(m)}))^{1/2} - ((h_2^{(m)} - 1/a_1)\Delta t)^{1/2}]^2$ | (III.48) |
| After interference | $z_{C''} \leq L \leq z_E$ | $h_2 = 1/a_2$ | $\tau_{\Delta h_1} = L/(Fh_1^{(m)}) - [(h_2^{(m)} - 1/a_2)/(1/a_2 - 1/a_1)]\Delta t$ | (III.49) |
| After merger | $L \geq z_E$ | $h_2 = 1/a_2$ | $\tau_{\Delta h_1} = \Delta t + a_1 \left[ \left(\frac{L}{F}\right)^{1/2} - \left(\frac{(h_2^{(m)} - 1/a_1)(h_1^{(m)} - 1/a_1)}{1/a_2 - 1/a_1}\Delta t\right)^{1/2} \right]^2$ | (III.50) |
| | | | pulse apex: $h_1 = (L/Fa_1(\tau - \Delta t))^{1/2}$ (at $\tau = \tau_{\Delta h_1}$) | (III.51) |
| Nonsharpening $h_2$ wave (rear of pulse of solute 2; $h_2$ variation from $h_2^{(m)}$ or apex value to $1/a_2$) | | | | |
| Before interference | $L \leq z_{C'}$ | $h_1 = h_1^{(m)}$ | $\tau_{h_2} = \Delta t + L/[Fa_2 a_1 h_1^{(m)} h_2^2]$ for front end use $h_2 = h_2^{(m)}$; for rear end $h_2 = 1/a_2$ | (III.52) |
| During interference | $z_{C'} \leq L \leq z_{C''}$, $\tau_{h_2} \geq \tau_{\Delta h_1}$ $\tau_{h_2} \leq \tau_{\Delta h_1}$ | $h_1 = h_1^{(m)}$ $h_1 = 1/a_1$ | for $\tau \leq \tau_{\Delta h_1}$ use Eq. (III.53); for front end use $h_2 = h_2^{(m)}$ for $\tau \geq \tau_{\Delta h_1}$ use Eq. (III.52); for rear end use $h_2 = 1/a_2$ | |
| After interference | $z_{C''} \leq L \leq z_E$ | $h_1 = 1/a_1$ | $\tau_{h_2} = \frac{L}{Fa_2 h_2^2} + \left(1 - \frac{(h_2^{(m)} - 1/a_1)(h_1^{(m)} - 1/a_1)}{(h_2 - 1/a_1)^2}\right)\Delta t$ | (III.53) |
| After merger | $L \geq z_E$, $\tau_{h_2} \geq \tau_{\Delta h_1}$ | $h_1 = 1/a_1$ | for front end use $h_2 = h_2^{(m)}$, for rear end $h_2 = 1/a_2$ use Eq. (III.53); front end at $\tau_{\Delta h_2}$ (pulse apex); for rear end use $h_2 = 1/a_2$ | |
| Nonsharpening $h_1$ wave (rear of pulse of solute 1; $h_1$ variation from $h_1^{(m)}$ or apex value to $1/a_1$) | | | | |
| Before merger | $L \leq z_E$ | $h_2 = 1/a_2$ | $\tau_{h_1} = L/(Fa_1 h_1^2) + \Delta t$ for front end use $h_1 = h_1^{(m)}$, for rear end $h_1 = 1/a_1$ | (III.54) |
| After merger | $L \geq z_E$, $\tau_{h_1} \geq \tau_{\Delta h_1}$ | $h_2 = 1/a_2$ | use Eq. (III.54); front end at $\tau_{\Delta h_1}$ (pulse apex); for rear end use $h_1 = 1/a_1$ | |
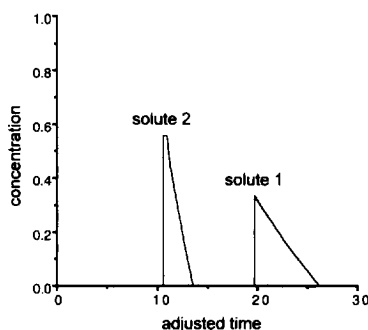
Fig. 14. Overload elution: effluent history of column of 7 cm length under conditions in Table 5.

complete effluent composition history is plotted in Fig. 14.

If the column length is such that interference remains incomplete (that is, if $z_{C'} < L < z_{C''}$), the emergence time of the $h_1$ shock is needed to determine which equation for the emergence times of roots of the nonsharpening wave must be used in which time range. The sequence of emergence from such a column is: initial fluid/$h_2$ shock/plateau $\alpha$/ early portion of $h_2$ wave/$h_1$ shock/late portion of $h_2$ wave/plateau $\beta$/$h_1$ wave/eluent. As Fig. 15 illustrates, the early portion of the $h_2$ wave, emerging ahead of the $h_1$ shock, has already interfered with it
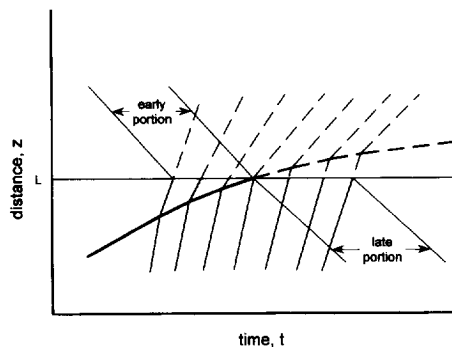


Fig. 15. Overload elution: distance–time representation of waves emerging from column while interfering (schematic). Not realized trajectories beyond column length ($L$) are shown as dashed lines.

in the column; the late portion, emerging behind the shock, has not[11].

## 9. Summary and assessment

Section 4 has presented an extensive set of rules and regularities for systems with Langmuir and Langmuir-like sorption equilibria as defined in Section 2. Perhaps the most general and useful of the rules is the existence of so-called affinity cuts of coherent waves, presenting an easily remembered picture of what kind of composition variations may and may not occur across coherent waves, and of the sequence of coherent waves in patterns arising from one original source. Section 5 then has demonstrated the application of the rules to a practical situation – multicomponent frontal analysis – and has shown that in such relatively simple cases all qualitative features of the response pattern can be predicted from the rules alone, without any calculations. The rules are based solely on the assumptions of ideal chromatography, coherent behavior, and Langmuir-like sorption equilibrium; the Langmuir equations themselves need not be valid. Moreover, the technique of deducing details of chromatographic behavior from an examination of particle velocities and wave velocities is general and can be applied equally well to systems with any other kinds of sorption equilibria.

The subsequent sections have laid out a mathematical transformation of the concentration variables with which the mathematics of Langmuir systems can be greatly simplified. Three sample cases have been calculated step by step to illustrate different facets of the practical application of the transforma-

[11]Details of the derivations have been given by Helfferich and Klein [35]. The equations in that source are for the mathematically equivalent case of ternary ion exchange, operate with normalizations, and are more general in that they cover injection of a square-wave pulse into any constant background that may also contain the solutes. The situation corresponding to overload elution and positive $b_i$ coefficients is Case 2. To recover the equations needed here, make the following substitutions: $h_i^{(m)}$ for $h_i^\circ$, $1/a_i$ for $h_i'$, $1/a_1 a_2$ for $\alpha$, and $z/[v^\circ(\epsilon/\rho)]$ for $z$. Also, the first Eq. A.93 contains an error: in the numerator of the factor in parentheses, $h_2^{(m)}$ should be replaced by $h_1^{(m)}$.

tion: wave patterns originating from a single starting variation, multiple interferences of shocks originating from several starting variations, and interference involving a diffuse wave. The examples have shown that, for many problems of practical interest, complete or nearly complete solutions can be obtained in the form of algebraic equations that can be evaluated by hand. Perhaps only a preparative-chromatography old-timer can appreciate the quantum leap of mathematical streamlining achieved. To mention but one example: The transformation allows resolution distances in effective displacement development of mixtures of a dozen or more components to be calculated in a short time on a pocket calculator equipped with a root finder. Although that separation technique had played a key role in the isolation of fission products and new elements as an outgrowth of the Manhattan Project of World War Two [36,37], it was developed empirically and the mathematics of its transients had taken until 1968 to progress to just three components [38]. The transformation was introduced into chromatography in the 1960s, and in retrospect one might regret that it has seen so little use through an age in which computers were not nearly as powerful and accessible as they are today, so that numerical computation of cases with more than only a few components was laborious and expensive. No doubt, the reason has been that publications describing the transformation have addressed the theoretician rather than the practitioner, and so have been more often quoted than read. Therefore, the effort has been made here to make the transformation more "user-friendly" and demonstrate the ease with which it can be handled even by someone who, like myself, is no friend of higher mathematics.

In competition with today's computer software for multicomponent non-linear chromatography, wave theory as presented here has the disadvantage of yielding results for the ideal case – without mass-transfer limitations, nonuniform volumetric flow-rate, flow irregularities, etc., for which corrections must be applied. The $h$-transformation is in addition restricted to Langmuir sorption equilibria. Therefore, usually, ideal wave theory cannot give answers accurate enough for design or optimization, and so cannot replace numerical computation. Rather, it

supplements it by providing a deeper understanding of chromatographic mechanisms and their physical causes, by teaching what kind of phenomena to expect under what conditions. This is true even for the $h$-transformation. The value of wave theory is greatest in the conceptual stage of development when creative new ideas are sought, countless options still are open, wide ranges of conditions are to be screened, and an approximate answer will do. Here, the computation of specific cases with elaborate software is inefficient compared with the insight wave theory can provide.

## 10. Glossary of symbols and terms

| | |
|---|---|
| $a_i$ | coefficient in Langmuir isotherm equation (Eqs. (III.1)) (cm$^3$ g$^{-1}$) |
| $b_i$ | coefficient in Langmuir isotherm equation (Eqs. (III.1)) (mmol$^{-1}$ cm$^3$) |
| $c$ | $\equiv \{c_1,...,c_n\}$, composition of moving phase (mmol cm$^{-3}$) |
| $c_i$ | concentration of solute $i$ in moving phase (per unit volume of moving phase) (mmol cm$^{-3}$) |
| $C_i$ | $\equiv \epsilon c_i + \rho q_i$, blind-man's concentration of solute $i$ (total amount per unit volume of column) (Appendix A) (mmol cm$^{-3}$) |
| $D$ | internal diameter of column (cm) |
| $h_i$ | $i$th root of Eq. (III.5) or (III.7), transformed composition variable (Section 5 and Section 6) (g cm$^{-3}$) |
| $k'$ | $= (\rho/\epsilon)q_i/c_i$, capacity factor in linear chromatography (Section 3) (dimensionless) |
| $L$ | column length (bed length in column) (cm) |
| $q_i$ | sorbent loading with solute $i$: amount of $i$ in sorbent (averaged over bead) per unit weight of sorbate-free sorbent (mmol g$^{-1}$) |
| $t$ | time (s) |
| $t_R$ | retention time in linear chromatography (Section 3) (s) |
| $t_0$ | deadtime in linear chromatography (Section 3) (s) |
| $u_j$ | adjusted particle velocity of solute $j$ (Section 6) (cm s$^{-1}$) |

$(u_c)_k$  adjusted coherent velocity of composition in wave with high key $k$ (varying root $h_k$) (Section 6) (cm s$^{-1}$)

$v^\circ$  linear velocity of moving-phase flow (cm s$^{-1}$)

$v_c$  $\equiv (\partial z / \partial t)_c$, linear coherent velocity (eigenvelocity) of composition $\{c_1,...,c_n\}$ in coherent wave (Section 3 and Section 4) (cm s$^{-1}$)

$(v_c)_k$  linear coherent velocity of composition in wave with high key $k$ (varying root $h_k$) (cm s$^{-1}$)

$v_{cj}$  $\equiv (\partial z / \partial t)_{cj}$, linear wave velocity of concentration $c_j$ (Eq. (I.4) in Section 3) (cm s$^{-1}$)

$v_\Delta$  linear wave velocity of coherent shock (Section 3) (cm s$^{-1}$)

$(v_\Delta)_k$  linear velocity of coherent shock with high key $k$ (varying root $h_k$) (cm s$^{-1}$)

$V$  column volume (cm$^3$)

$\dot{V}$  volumetric flow-rate (cm$^3$ s$^{-1}$)

$V^{(m)}$  volume of solute mixture to be separated (cm$^3$)

$z$  column position (linear distance from inlet end of bed) (cm)

$z_J$  distance coordinate of distance–time point J (cm)

$\Delta$  finite difference across shock (operator)

$\epsilon$  fractional volume of moving phase in column (dimensionless)

$\rho$  bulk density of sorbent: weight of sorbate-free sorbent per unit volume of column (g cm$^{-3}$)

$\tau$  $\equiv t - z/v^\circ$, adjusted time (Eqs. (III.16)) (s)

Table 7
Glossary of frequently used terms

| | |
|---|---|
| Adjusted time | time adjusted for displacement of fluid in interstitial void upstream of location (Eqs. (III.16)) |
| Adjusted velocity | distance traveled per unit of adjusted time (Section 7) |
| Affinity cut | of coherent wave: separates solutes into high- and low-affinity groups whose concentrations vary in opposite directions (Section 4) |
| Coherence | state in which coexisting concentrations advance jointly, at same velocity (state which waves in column strive to attain) (Section 3) |
| Coherence velocity | velocity of composition (common to all solutes) in coherent wave (Section 3) |
| Competitive equilibrium | equilibrium in which competition for sorption sites depresses uptake by sorbent (Section 2) |
| Composition | ensemble of concentrations of all solutes |
| Eigenvelocity | see coherent velocity |
| H function | left-hand side of Eqs. (III.6) |
| High key | see keys |
| History | concentration or composition as function of time at specified location |
| Keys | high key (higher affinity) and low key (lower affinity) of coherent wave: solutes whose concentrations vary in opposite directions and who are adjacent in affinity sequence (Section 4) |
| Langmuir system | system with Langmuir sorption isotherm, $q_j = a_j / [1 + \Sigma(b_i c_i)]$ (Section 2) |
| Langmuir-like system | system with sorption equilibrium without selectivity reversals and with competition for sorption capacity affecting distribution coefficients of all solutes in like manner (Section 2) |
| Low key | see keys |
| Nonsharpening wave | wave with natural tendency to spread (Section 3) |
| Particle velocity | average velocity of molecules of a solute in direction of flow (Section 3) |
| Plateau | zone of uniform composition extending over finite distance and time |
| Profile | concentration or composition as function of distance at given time |
| Riemann problem | system with uniform initial composition of column and constant composition of entering fluid |
| Root | root of $H$ function, transformed composition variable (Eqs. (III.6), (III.8)) |
| Selectivity | preference of sorbent for one solute over another |
| Selectivity reversal | preference of sorbent for one solute over another with variation of composition |
| Self-sharpening wave | wave with natural tendency to sharpen (Section 3) |
| Shock | wave that has remained (or has sharpened into) ideal discontinuity (Section 3) |
| Trajectory | curve traced by composition or shock in distance–time plane |
| Varying root | only root whose value varies across respective coherent wave (Section 7) |
| Wave | Variation of dependent variables (concentrations) with distance and time (Section 3) |
| Wave velocity | velocity of a concentration, composition, or shock in direction of flow (Section 3) |

$\tau_J$     adjusted time coordinate of distance–time point J (s)

$\tau_{h_k}$     adjusted emergence time of value of root $h_k$ (s)

$(\tau)_k$     adjusted breakthrough time of plateau $k$ in frontal analysis (s)

$\tau_{\Delta h_k}$     adjusted emergence time of coherent shock with varying root $h_k$ (s)

Solutes are numbered 1, 2,....,n in the sequence of decreasing affinity for the sorbent.

Primes refer to entering fluid or upstream side of a wave; double primes, to downstream side of a wave; superscripts ° to initial fluid; $^{(m)}$ to mixture to be separated; $^{(d)}$ to displacer in displacement development.

Distance–time points are lettered A, B,...; plateaus are lettered $\alpha$, $\beta$,...

Affinity cuts are denoted by a vertical line between high key and low key. A bar on the low-key side indicates that the low-affinity group has no members.

In distance–time diagrams, shock trajectories are shown as heavy lines; coherent nonsharpening waves are shown shaded and with trajectories of compositions as thin lines.

Definitions or explanations of frequently used technical terms are given in Table 7.

## Acknowledgments

## Appendix A

### Proof of rules for coherent waves [21]

Mathematical proofs of the rules deduced in Section 4 with logical arguments can be given as follows.

The mathematical conditions for Langmuir-like equilibrium are

$$\left(\frac{\partial (q_j/c_j)}{\partial c_k}\right)_{c_i(\text{all } i \neq k)} < 0 \qquad \text{for all } j \text{ and } k \qquad \text{(III.55)}$$

and

$$\frac{\mathrm{d}(q_j/c_j)/\mathrm{d}c}{\mathrm{d}(q_k/c_k)/\mathrm{d}c} > 0 \qquad \text{for all } j \text{ and } k \qquad \text{(III.56)}$$

where $\mathbf{c} \equiv \{c_1,...,c_n\}$ = composition. Condition (III.55) ensures competitive behavior, and (III.56) guarantees that all distribution coefficients increase or decrease jointly. Both conditions are obeyed by isotherms of the form $q_j = a_j c_j f(\mathbf{c})$, where $f(\mathbf{c})$ is a function of moving-phase composition. This includes the Langmuir equation (III.1) with positive $b_i$ coefficients.

Granted the assumptions of ideal chromatography, the flux of solute $j$ (in mmol per unit cross-sectional area and unit time) in the direction of moving-phase flow can be expressed as

$$J_j = v_j C_j \qquad \text{(III.57)}$$

where $C_j \equiv \epsilon c_j + \rho q_j$ is the overall or "blind man's" concentration of $j$ (amount in both phases per unit volume of column), that is, the concentration an observer would find who can analyze for solutes but cannot distinguish between phases. [Eqs. (III.57) is an alternative to, and equivalent to, the normally used form $J_j = v° c_j$.] Conservation of matter (inflow minus outflow equals change in content) with Eqs. (III.57) requires

$$(\partial C_j/\partial t)_z = -\operatorname{div} J_j = -v_j(\partial C_j/\partial z)_t - C_j(\partial v_j/\partial z)_t$$

Using the chain rule for partial derivatives of three interdependent variables $q$, $r$, and $s$

$$(\partial q/\partial s)_r = -(\partial q/\partial r)_s(\partial r/\partial s)_q$$

to replace $(\partial C_j/\partial t)_z$ and then solving for $(\partial z/\partial t)_{C_j} \equiv v_{C_j}$ and writing $(\partial v_j/\partial C_j)_t$ for $(\partial v_j/\partial z)_t(\partial z/\partial C_j)_t$ one obtains[12]

$$v_{C_j} = v_j + C_j(\partial v_j/\partial C_j)_t$$

If the respective wave is coherent, the wave velocities of moving-phase, stationary-phase, and blind-man's concentrations of all solutes are equal, so that

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[12]This equation is analogous to the Landau–Lifshitz equation [39] relating particle and wave velocities in single-phase, compressible-fluid flow.

the coherent composition velocity $v_c$ common to all can be substituted for $v_{C_j}$:

$$v_c = v_j + C_j (\partial v_j / \partial C_j)_t \qquad (III.58)$$

All derivations to follow are in terms of blind-man's concentrations, $C_j$. However, coherence requires the derivatives $dq_i/dc_i$ of all solutes to be equal, and a decrease of all $q_i$ with increase of all $c_i$ is contrary to the criterion (III.55) for competitive sorption equilibrium. Accordingly, the moving-phase and stationary-phase concentrations of any solute and therefore also the blind-man's concentration of that solute increase or decrease jointly across a coherent wave. For this reason, the inequalities derived and rules formulated from them are equally valid in terms of moving-phase or stationary-phase concentrations.

For solutes slower and faster than the wave, Eqs. (III.58) gives

$$(\partial v_j / \partial C_j)_t > 0 \qquad \text{if } v_j < v_c$$
$$(\partial v_j / \partial C_j)_t < 0 \qquad \text{if } v_j > v_c \qquad (III.59)$$

That is, the particle velocity and concentration of a solute increase or decrease together if the solute is slower than the wave, and vary in opposite directions if the solute is faster than the wave. By definition of Langmuir-like sorption equilibria, the distribution coefficients of all solutes increase or decrease jointly across a wave, and Eq. I.5 shows that this is then true also for the particle velocities. It follows that the concentrations of solutes slower and faster than the wave must vary in opposite directions. With Eq. I.5, the solutes slower and faster than the wave can be identified as belonging to high-affinity and low-affinity groups, respectively, which do not overlap. This completes the proof of the affinity cut rule and elucidates its dependence on Langmuir-like sorption equilibrium.

A corollary of the second condition (III.59) is that the particle velocity and concentration of each solute vary in opposite directions if all solutes are faster than the wave. However, Eq. I.5 combined with the definition of Langmuir-like equilibrium requires all particle velocities to increase if all concentrations increase because all distribution coefficients then decrease. This makes it impossible for all solutes to be faster than the wave. On the other hand, the first condition (III.59) requires the particle velocity and

concentration of any solute slower than the wave to increase or decrease jointly, as is compatible with Eq. I.5 and Langmuir-like equilibrium even if all solutes are slower than the wave. This, combined with the equivalence of grouping by particle velocities or affinities, proves the rule that all solutes may belong to the high-affinity group, but not all to the low-affinity group.

For a solute whose particle velocity equals the wave velocity, Eqs. (III.58) gives

$$(\partial v_j / \partial C_j)_t = 0 \quad \text{or} \quad C_j \to 0 \qquad \text{if } v_j = v_c \qquad (III.60)$$

That is, if the particle velocity of a solute equals the wave velocity, the particle velocity may not vary with concentration, or the concentration must become infinitesimal (for an entirely absent solute, no particle velocity can be defined). If equilibrium is Langmuir-like, no velocity variation with concentration implies invariant strength of competition and must be shared by all solutes, but only one solute's particle velocity can equal the wave velocity. It follows that (a) no coherent composition variation is possible without variation in all particle velocities, and (b) the concentration of no more than one solute can become infinitesimal at any one point in or at a coherent wave. Furthermore, the fact that the particle velocity of such a solute at such a point must equal the wave velocity proves that the solute must be the high key or low key, because otherwise some members of its group would be faster than the wave and others slower, contrary to the definition of groups.

The behavior of ideal shocks, at which gradients $\partial v_j / \partial C_j$ cannot be defined, is not covered by Eqs. (III.58) and the conditions derived from it. Here, conservation of matter across the shock requires

$$(C_j' - C_j'') \, dz = (v_j' C_j' - v_j'' C_j'') \, dt$$

where $dz$ is the distance the shock advances in the time $dt$. With $dz/dt \equiv v_\Delta$ (velocity of the coherent shock) and after rearrangement:

$$\frac{v_\Delta - v_j''}{v_j' - v_j''} = \frac{C_j}{C_j' - C_j''} \qquad (III.61)$$

A consequences of this equation is:

$$C_j' = C_j'' \qquad \text{if} \quad v_j' = v_j'' \qquad (III.62)$$

All solutes are subject to this requirement. A coherent shock therefore cannot exist between plateaus with same particle velocities and thus same strength of competition.

Since all concentrations are positive, the right-hand side of Eqs. (III.61) is either larger than 1 or negative. Since all velocities are positive, the first alternative requires

$$v_\Delta > v_j' \text{ if } v_j' > v_j'' \quad \text{or} \quad v_\Delta < v_j' \text{ if } v_j' < v_j''$$

to make the left-hand side larger than 1. The second alternative requires

$$v_\Delta > v_j' \text{ if } v_j' < v_j'' \quad \text{or} \quad v_\Delta < v_j'' \text{ if } v_j' > v_j''$$

to make the left-hand side negative. All possibilities have in common:

$$v_\Delta < v_j', v_j'' \quad \text{or} \quad v_\Delta > v_j', v_j'' \quad \text{if } v_j' \neq v_j'' \qquad \text{(III.63)}$$

That is, no solute can be faster than the wave on one side, but slower than the wave on the other side. This makes the assignment of solutes to slower and faster groups and thus to high- and low-affinity groups unambiguous even at shocks.

Eqs. (III.61) can be rearranged:

$$\frac{C_j' - C_j''}{v_j' - v_j''} = \frac{C_j}{v_\Delta - v_j''} \qquad \text{(III.64)}$$

A consequence is

$$(C_j' - C_j'')/(v_j' - v_j'') > 0 \quad \text{if } v_j'' < v_\Delta$$
$$(C_j' - C_j'')/(v_j' - v_j'') < 0 \quad \text{if } v_j' > v_\Delta \qquad \text{(III.65)}$$

If sorption equilibrium is Langmuir-like, the shock side on which the particle velocity is lower is the same for all solutes, so that $(v_j' - v_j'')$ has the same sign for all solutes. Granted such behavior, conditions (III.65) show that the concentrations of solutes slower and faster than the shock vary in opposite directions. With the classification of slower and faster solutes into high- and low-affinity groups, respectively, this proves the affinity cut rule for coherent shocks.

Also, condition (III.65) shows that the solutes can all be slower than the shock, but cannot all be faster than it, because, as was shown before, the particle velocities necessarily increase if all concentrations increase. With Eq. I.5 this proves that at coherent shocks, too, all solutes may belong to the high-affinity group, but not all to the low-affinity group.

Another consequence of Eqs. (III.64) is

$$C_j' = 0 \qquad \text{if } v_j' = v_\Delta$$
$$C_j'' = 0 \qquad \text{if } v_j'' = v_\Delta \qquad \text{(III.66)}$$

That is, if a solute is present on only one side of the shock, its particle velocity equals the shock velocity. Since the particle velocities of all solutes at given composition differ, only one of them can equal the shock velocity, so that no more than one solute can be absent from the same side of the shock while being present on the other. Moreover, that solute must be a key, in order that the other members of its affinity group are either all slower or all faster than the shock, as required by the definition of groups.

This concludes the proof of the rules in Section 4, except for obvious consequences already pointed out in that section.

## Appendix B

### History of the *h*-transformation

The *h*-transformation is much more generally applicable than only to chromatography and has an interesting history. Apparently it was first formulated by J. P. M. Binet [40], a nineteenth-century French mathematician. Its use in problems involving elliptical equations of dynamics has been pioneered over a hundred years ago by the great C. G. J. Jacobi [41,42], in whose honor the roots are sometimes called "Jacobi elliptical coordinates". It has also been applied in multidimensional differential geometry [43]. Outside pure mathematics it is the basis of Dole's theory of multicomponent electrophoresis [44] and Underwood's widely used stripping-factor method for estimating the minimum reflux ratio in multicomponent distillation [45–48]. Other notable applications include the theories of multicomponent electro-diffusion by Pleijel [49], extended by Goldman [50] and Teorell [51] and perfected by Schlögl [27]. Apparently, the use of the transformation in chromatography was first suggested by Davidson [52] in 1949. It was later applied to multicomponent

gas chromatography without a carrier gas by Zhukhovitskii et al. [53], who assumed the sorbable species to have independent linear sorption isotherms, but to compete for space in the gas phase. Its use was developed in detail for multicomponent ion-exchange chromatography with constant separation factors [7,54] and adapted to Langmuir-type adsorption by Helfferich and Klein. For the latter problem, an essentially equivalent transformation was introduced later by Rhee et al. [5,6].[13] It seems that few, if any, of the quoted authors (myself included) were aware of the previous applications when rediscovering the transformation.

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