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COMPUTATIONAL ASPECTS OF TWO COMPONENT CHROMATOGRAPHY

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Computational aspects of two component chromatography*)

by

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ABSTRACT

This paper deals with the theory of multicomponent chromatography, initiated by Rhee, Aris and Amundsen. Explicit formulas are presented for the case of two components.

KEY WORDS & PHRASES: *Multicomponent chromatography, quasilinear hyperbolic systems*

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*) This report will be submitted for publication elsewhere.

1. INTRODUCTION

In analytical chemistry chromatography is a well-known method for separation of a mixture into its components. The separation is accomplished by the distribution of components of the mixture over two phases in close contact with each other. There exist many variations in the method of separation. Usually attempts to construct a theoretical model are restricted to the case of gas-liquid column chromatography, where a carrier fluid flows through a long thin cylinder ("column"), partially packed with a solid adsorbing material. The desired separation can be achieved when the mixture to be fed into the column contains only components with distinct adsorption affinity toward the solid stationary phase.

Since there is a large number of parameters in the process involved, we have the possibility to optimize the separation.

Important parameters are temperature, pressure, flow-velocity and packing of the column. The following assumptions have to be made to reach a reasonably simple model:

1. Temperature and flow-velocity are constant in time and place.
2. Longitudinal and radial diffusion are neglected.
3. At any place and time there is adsorption equilibrium and exchange of matter in adsorption is instantaneous.

An elegant use of wave theory was made by RHEE, ARIS & AMUNDSON [5]. Their method is reviewed in sections 2.1 and 2.3. Combining a one-dimensional transport equation with a certain expression for the adsorption, they were able to derive a new coordinate system, similar to Jacobi's ellipsoidal coordinates (HILBERT & COURANT [1]). With this system a convenient description of the separation process can be given. The dynamics of a single component in a chromatographic column under the assumptions as above were described by SMIT, SMIT & DE JAGER [6],[7]. In this report results are given for two component systems.

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2. THE MODEL EQUATIONS

2.1. The Riemann problem

Consider a chromatographic column with constant cross section. Apart from the carrier gas there are two chemical components, A_1, A_2. The concentration in mobile and solid phases is denoted by c_i resp. n_i $i = 1,2$; each in moles per unit volume of their own phase. The void fraction of the column is a constant ε $(0<\varepsilon<1)$. The total concentration f_i of component A_i satisfies

$$(2.1) \qquad f_i = \varepsilon c_i + (1-\varepsilon) n_i .$$

Since the adsorption process is quite complex we cannot describe its dynamics in exact equations and, therefore we make simplifying assumptions. The concentrations n_i are generally considered to be nonlinear functions of mobile phase concentrations;

$$(2.2) \qquad n_i = H_i(c_1, c_2) \qquad i = 1,2.$$

These relations are assumed to hold for all positions at any time and are called adsorption isotherms. We will discuss this in more detail in section 2.2.

Because of the constant cross section the above process can be described in one space variable. The incompressible mobile phase is supposed to have a constant velocity u. Consequently, the flux q_i of component A_i satisfies $q_i = u\varepsilon c_i$. The mass conservationlaw for component A_i over a segment (z_1, z_2) of the column implies

$$(2.3) \qquad \frac{d}{dt} \int_{z_1}^{z_2} f_i(z,t)\,dz + q_i(z_2,t) - q_i(z_1,t) = 0.$$

If f_i and q_i are continuously differentiable this yields in the limit $z_2 \to z_1$

$$\frac{\partial f_i}{\partial t} + \frac{\partial q_i}{\partial z} = 0.$$

Let Z be the characteristic length of the column. Substitution of the expression for the flux q_i and introduction of new dimensionless independent variables $x = z/Z$ and $\tau = u\varepsilon t/Z$ leads to the transportequation

$$\frac{\partial c_i}{\partial x} + \frac{\partial f_i}{\partial \tau} = 0 \qquad i = 1,2.$$

Under the assumption that the 2*2 matrix $F = (\frac{\partial f_i}{\partial c_j})$ has two distinct real eigenvalues for all values of the arguments (c_1,c_2), the set of equations (2.4) is called a quasilinear hyperbolic system. In chemical terms this assumption corresponds to two solute components flowing with different velocities through the column, which means separation into pure components after a sufficiently large time interval. In order to have a well posed problem we also need suitable initial- and boundary conditions,

$$(2.5) \qquad \begin{array}{llll} c_i = c_i^{in} & \text{at } \tau = 0 & (\text{"initial"}) & \\ & & & i = 1,2. \\ c_i = c_i^{e} & \text{at } x = 0 & (\text{"entry"}) & \end{array}$$

The problem (2.4) with (2.5) can be solved with the theory of Riemann invariants. When there are more than two components, the existence of so-called generalized Riemann invariants is not guaranteed for these quasilinear hyperbolic systems. However, with certain restrictions on the initial- and boundary data a solution exists. Problems that can be solved in this way are also known as Riemann problems, see LAX [4]. In this paper we restrict ourselves to the cases of one and two components.

2.2. Adsorption isotherms

In section 2.1 a functional relation (2.2) was assumed between each n_i and c_1,c_2. This relation is usually called the adsorption isotherm. A frequently used, nonlinear expression is the Langmuir isotherm [3]. By assuming adsorption equilibrium at any place and time we have for each component separately that rate of adsorption equals rate of desorption. The adsorption rate of A_i is proportional to the product of concentration c_i and free adsorbing area of the stationary phase, where the total adsorbing area is scaled to 1. The rate of desorption is proportional to the fraction of area occupied by A_i.
For two components we have accordingly

$$\begin{aligned} k_1c_1(1-n_1-n_2) &= k_3n_1, \\ k_2c_2(1-n_1-n_2) &= k_4n_2. \end{aligned} \tag{2.6}$$

Introducing $K_1 = k_1/k_3$, $K_2 = k_2/k_4$ and solving (2.6) for n_1,n_2 we find the Langmuir isotherm:

$$n_i = \frac{K_ic_i}{1+K_1c_1+K_2c_2}, \qquad i = 1,2, \tag{2.7}$$

or equivalent,

$$K_ic_i = \frac{n_i}{1-(n_1+n_2)}. \tag{2.7a}$$

Each mobile phase concentration is multiplied in (2.7) by a temperature dependent thermodynamic parameter K_i, which is a measure of adsorption affinity towards the stationary phase. Since the process is kept isotherm we may take the parameters as constants, with $K_1 < K_2$. In the derivation of (2.7) c_i can be replaced everywhere by c_i^α, with $0 < \alpha \leq 1$. This leads to a Freundlich-type isotherm;

$$n_i = \frac{K_ic_i^\alpha}{1+K_1c_1^\alpha+K_2c_2^\alpha}. \tag{2.8}$$

A variation of the Langmuir isotherm is the anti-Langmuir form, where competition in adsorption is replaced by some kind of cooperation

$$n_i = \frac{K_ic_i}{1-(K_1c_1+K_2c_2)}, \tag{2.9}$$

or equivalent,

$$K_ic_i = \frac{n_i}{1+n_1+n_2}. \tag{2.9a}$$

2.3. Constant states, simple waves and shock waves

In this section we give a description of the coordinate system as proposed in [5]. In this reference it is shown that by assuming a Langmuir type adsorption isotherm an alternative coordinate system can be derived, similar to the classical ellipsoidal coordinates in COURANT & HILBERT [1]. We need the following definitions (JEFFREY [2]):

DEFINITION 1. A constant state is a region in the x,τ-plane where the solution $c(x,\tau)$ is constant.

DEFINITION 2. A region in the x,τ-plane where the solution is in one-parameter form is called a simple wave, e.g. $\{c_1(x,\tau), c_2(c_1(x,\tau))\}$.

It is well known for continuous solutions that the region adjacent to a constant state must be a simple wave. Using the dependence of the solution on a single component in the simple wave regions, it is possible to rewrite $\partial f_i/\partial\tau$ as

$$\frac{\partial f_i}{\partial\tau} = \sum_{j=1}^{2} \frac{\partial f_i}{\partial c_j}\frac{\partial c_j}{\partial\tau} = \left(\sum_{j=1}^{2} \frac{\partial f_i}{\partial c_j}\frac{dc_j}{dc_i}\right) \equiv \frac{df_i}{dc_i}\cdot\frac{\partial c_i}{\partial\tau}\ .$$

Equation (2.4) now reads

$$(2.10)\qquad \frac{\partial c_i}{\partial x} + \frac{df_i}{dc_i}\cdot\frac{\partial c_i}{\partial\tau} = 0, \qquad i = 1,2.$$

In a characteristic direction $\rho = \frac{d\tau}{dx}$ of this quasi linear hyperbolic system the total differentials df_i/dc_i are equal:

$$(2.11)\qquad \rho = \frac{d\tau}{dx} = \frac{df_i}{dc_i} = \sum_{j=1}^{2} \frac{\partial f_i}{\partial c_j}\cdot\frac{dc_j}{dc_i} = \left(\sum_{j=1}^{2} \frac{\partial f_i}{\partial c_j}\frac{dc_j}{dD}\right)\frac{dD}{dc_i}\ .$$

Using matrix $F(= \partial f_i/\partial c_j)$ and assuming that $dc_i/dD \neq 0$ we find

$$(2.12)\qquad (F-\rho I)\frac{dc}{dD} = 0.$$

Consequently for non-trivial solutions ρ is an eigenvalue and $\frac{dc}{dD}$ is an eigenvector of F. The eigenvalues of F are labeled $\sigma_1,\sigma_2 (\sigma_1 \neq \sigma_2$ due to the hyperbolic character of the system). The two bundles of characteristics are indicated by C^1, C^2. With each σ_k a quantity ω_k is associated in the following way:

$$(2.13)\qquad \sigma_k = \varepsilon + (1-\varepsilon)\frac{\omega_k}{D}\ , \qquad k = 1,2.$$

The set $\{\omega_1, \omega_2\}$ forms the alternative coordinate system. Their values are separated by the thermodynamic constants and can be calculated from these constants and concentration values. (See also references [1] and [5]):

$$(2.14) \qquad 0 < \omega_1 < K_1 < \omega_2 < K_2.$$

Hence the σ_k satisfy the inequality

$$(2.15) \qquad \varepsilon < \sigma_1 < \sigma_2.$$

Since the σ_k are (scaled) reciprocal velocities of waves propagating in the column and ε is the (scaled) reciprocal carrier velocity

$$\left(\frac{dz}{dt} = u = u\varepsilon\,\frac{dx}{d\tau}\,,\ \text{so}\ \frac{dx}{d\tau} = \frac{1}{\varepsilon}\right),$$

it is clear that both waves are travelling at a lower speed than the carrier.

Since it is not always possible to have diverging bundles of characteristics, we also have to discuss discontinuous solutions. A necessary condition for characteristics not to intersect is that

$$(2.16) \qquad \frac{\partial \sigma_k}{\partial x} = \frac{d\sigma_k}{dD} \cdot \frac{\partial D}{\partial x} < 0.$$

As $d\sigma_k/dD = -2(1-\varepsilon)\omega_k/D^2$ is negative, this condition is equivalent with the condition that D increases with x. In case of D decreasing with x the characteristics will intersect and there can be no continuous solution.
With the mass conservation law (2.3) the well known jump relations can be found. Furthermore, the discontinuous solutions appear to meet all stability requirements for shocks as proposed by LAX [4] so they will be referred to as shock waves.
The occurrence of shockwaves can be inferred from the actual values of ω-variables.

For two components A_1, A_2 with given entry- and initial concentrations (2.5) the values of n_i are calculated according to the isotherm (2.7). The corresponding ω-values satisfy the relation

$$(2.17) \qquad \frac{K_1 n_1}{K_1 - \omega} + \frac{K_2 n_2}{K_2 - \omega} = 1.$$

Solving this equation for ω amounts to solving a polynomial equation in ω of degree two. For the entry state there are two roots ω_1^e, ω_2^e and in the initial state $\omega_1^{in}, \omega_2^{in}$. The relation (2.17) implies the following important identity

$$(2.18) \qquad D = \frac{K_1 K_2}{\omega_1 \omega_2},$$

where ω_1, ω_2 are the two roots of equation (2.17). Considering ω_1 and ω_2 as variables it appears that in the x,τ-plane they can only change one at a time and only ω_k changes its value (from ω_k^e on the left to ω_k^{in} on the right) on the wave given by σ_k (abbreviated: (k)-wave). It follows from (2.18) that D varies inversely proportional to ω_k on the (k)-wave. In case of a (k)-simple wave D must increase with x (2.16), ω_k must decrease with x, so $\omega_k^e > \omega_k^{in}$ is the condition for existence of a (k)-simple wave. When $\omega_k^e < \omega_k^{in}$ there must be a (k)-shock wave and $\omega_k^e = \omega_k^{in}$ implies there is no (k)-wave in the solution.

For two components we have the following picture in the x,τ-plane (see also figures in section 4). Going from the initial (τ=0) to the entry state (x=0):

1. The initial constant state cs(0) with D-value $D_0, \omega_1 = \omega_1^{in}, \omega_2 = \omega_2^{in}$, $D_0 = K_1 K_2 / \omega_1^{in} \omega_2^{in}$.
2. The (1)-wave, shock- or simple wave, where ω_1 changes to the entry value.
3. The intermediate constant state cs(1) $\omega_1 = \omega_1^e, \omega_2 = \omega_2^{in}, D_1 = K_1 K_2 / \omega_1^e \omega_2^{in}$.
4. The (2)-wave, shock- or simple wave, where ω_2 changes to the entry value.
5. The entry constant state cs(2) $\omega_1 = \omega_1^e, \omega_2 = \omega_2^e, D_2 = K_1 K_2 / \omega_1^e \omega_2^e$.

The lower and upper σ_k-limit of a (k)-simple wave can be calculated with (2.13)

$$(2.19) \qquad \begin{aligned} \sigma^{min} &= \varepsilon + (1-\varepsilon)\omega_k^{in}/D_{k-1}, \\ \sigma^{max} &= \varepsilon + (1-\varepsilon)\omega_k^e/D_k. \end{aligned}$$

The reciprocal velocity of a (k)-shock wave is calculated from the jump conditions and the entropy condition (see [5] and WHITHAM [8]).

$$(2.20) \qquad \sigma_k^s = \varepsilon + (1-\varepsilon)\omega_k^{in}/D_k .$$

In the following sections we will analyse some possible wave structures and interactions in the cases of one and two components.

3. ONE COMPONENT CHROMATOGRAPHY

3.1. Shock wave solution

The case of one component adsorbing in a clean column is rather simple, there is just one shock wave with reciprocal velocity

$$(3.1) \qquad \sigma^s = \varepsilon + (1-\varepsilon)\omega^e,$$

where the ω^e-value is calculated from the entry concentration. The dependence on variables is given in table I.

$$\boxed{\begin{aligned} \frac{\partial\sigma^s}{\partial K} &= \frac{(1-\varepsilon)}{(1+Kc)^2} \\ \frac{\partial\sigma^s}{\partial c} &= -(1-\varepsilon)\left(\frac{K}{1+Kc}\right)^2 \end{aligned}}$$

table I Derivatives of reciprocal velocity with respect to thermodynamic parameter and entry concentration.

As seen from the formulas of table I, changes are larger in magnitude for small ε and low concentration c. An increase in parameter K corresponds to more adsorption and slowing down of the wave front. An increase in c results in an acceleration of the wave.

3.2. Simple wave solution

A single simple wave is associated with the removal of one adsorbed component from a column. It is characterized by its two bounding characteristics;

$$(3.2) \qquad \sigma^{\min} = \varepsilon + (1-\varepsilon)\,\frac{(\omega^{in})^2}{K}\,, \qquad \sigma^{\max} = \varepsilon + (1-\varepsilon)K,$$

where the ω-value is calculated from the initial concentration. The dependence upon K and c is displayed in table II:

$\sigma^{\max}$	$1 - \varepsilon$	0
$\sigma^{\min}$	$(1-\varepsilon)(1-n)^2(1-2n)$	$-2(1-\varepsilon)K^2(1-n)^3$
$\sigma^{\max} - \sigma^{\min}$	$(1-\varepsilon)(1-(1-n)^2(1-2n))$	$2(1-\varepsilon)K^2(1-n)^3$

table II Derivatives with respect to thermodynamic parameter (first column) and concentration (second column).

Since the derivatives of the difference are positive, the simple wave spreads out for K and/or c increasing. However, the derivative of $\sigma^{\min}$ with respect to K is not definite in sign, for $n < \frac{1}{2}$ it is positive, for $n > \frac{1}{2}$ negative.

4. TWO COMPONENT CHROMATOGRAPHY

4.1. An initially clean column

Next we consider the adsorption of two components A_1, A_2 flowing into a clean column. In the model this results in two shock waves S^1 and S^2. In constant state (2) both components enter the column, at S^2 component A_2 is completely adsorbed so constant state (1) contains only component A_1 and in constant state (0) the initial empty state of the column is still preserved. The values of ω_1^e, ω_2^e are calculated from entry concentrations.

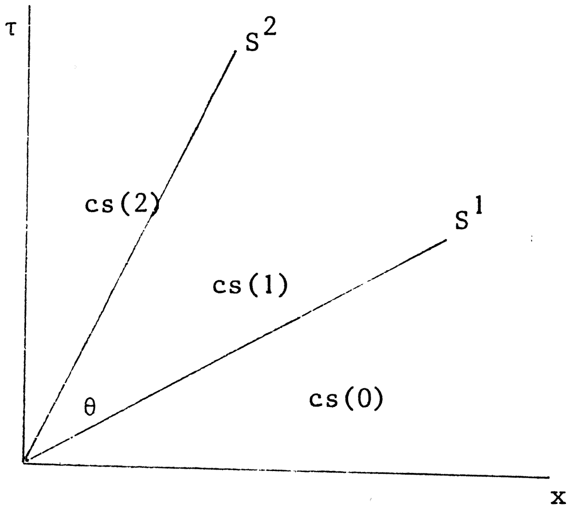


figure 1 Adsorption over two shock waves

The reciprocal shock velocities are

(4.1)
$$\sigma_1^s = \varepsilon + (1-\varepsilon)\,\frac{\omega_1^e}{D_0} = \varepsilon + (1-\varepsilon)\omega_1^e,$$
$$\sigma_2^s = \varepsilon + (1-\varepsilon)\,\frac{\omega_2^e}{D_1} = \varepsilon + (1-\varepsilon)\,\frac{\omega_1^e\omega_2^e}{K_1}\,.$$

The difference between the two shock waves directions is equal to

(4.2)
$$\boxed{\begin{aligned}
&\Delta = \sigma_2^s - \sigma_1^s = (1-\varepsilon)\,\frac{\omega_1^e}{K_1}\,(\omega_2^e - K_1)\,.\\
&\frac{\partial\Delta}{\partial K_1} = -\,(1-\varepsilon)\left(-\frac{K_2 c_1}{(1+K_1c_1+K_2c_2)^2} + \frac{\partial\omega_1^e}{\partial K_1}\right)\\
&\frac{\partial\Delta}{\partial K_2} = \frac{(1-\varepsilon)}{K_1}\left(\frac{\partial\omega_1^e}{\partial K_2}\,(\omega_2^e - K_1) + \omega_1^e\,\frac{\partial\omega_2^e}{\partial K_2}\right)\\
&\frac{\partial\Delta}{\partial c_1} = -\,(1-\varepsilon)\left(-\frac{\omega_1^e\omega_2^e}{(1+K_1c_1+K_2c_2)^2} + \frac{\partial\omega_1^e}{\partial c_1}\right)\\
&\frac{\partial\Delta}{\partial c_2} = \frac{(1-\varepsilon)}{K_1}\left(\frac{\partial\omega_1^e}{\partial c_2}\,(\omega_2^e - K_1) + \omega_1^e\,\frac{\partial\omega_2^e}{\partial c_2}\right)
\end{aligned}}$$

table III Derivatives of Δ with respect to thermodynamic parameters and entry concentrations

From calculations it appears in table III that the derivatives with respect to K_1 and c_2 are negative definite and with respect to K_2 positive definite. The dependence upon c_1 is more complicated. In order to show the complexity of the influence of parameters figures 2 and 3 are added in the appendix. The former shows the tangent of the angle between S^1 and S^2 as a function of the logarithm of c_1, the latter as a function of K_2, while the other variables and parameters are constant.

4.2. Two components initially adsorbed

The case of two simple waves C^1 and C^2 corresponds with two adsorbed components A_1,A_2 going into the mobile phase

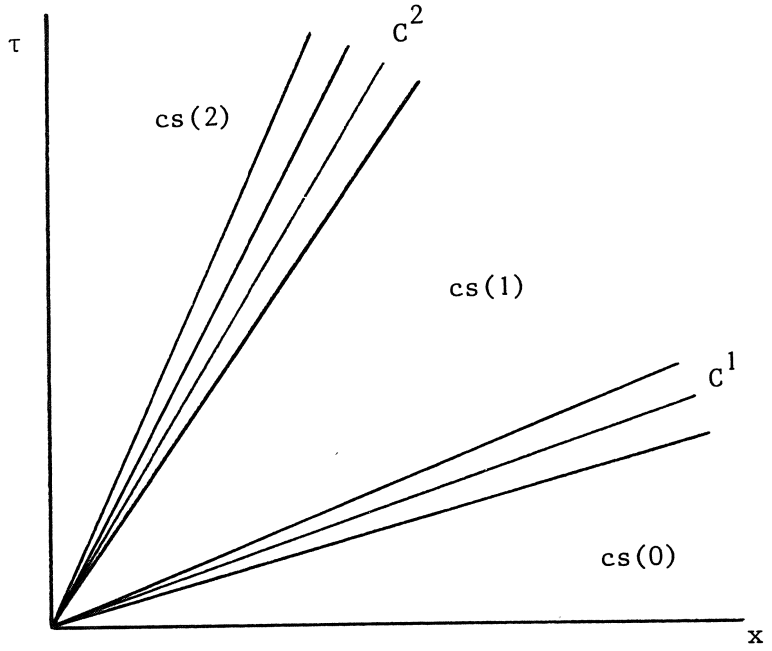


figure 4 Desorption over two simple waves

Again there are three constant states. The initial state of the column is in cs(0). After the first simple wave component A_1 is completely removed, so in cs(1) its concentration is zero. After the second simple wave A_2 disappears, consequently in cs(2) all concentrations are zero. The bounding characteristics of constant state (1) are denoted by σ_2^{min} and σ_1^{max}. The difference between these reciprocal characteristic speeds is

$$(4.3) \qquad \Delta = \sigma_2^{min} - \sigma_1^{max} = (1-\varepsilon)\,\frac{\omega_2^{in}}{K_2}\,(\omega_2^{in}-K_1),$$

where ω-values are calculated from initial concentrations. The dependence of Δ on concentrations and parameters is computed in table IV,

$$\frac{\partial\Delta}{\partial K_1} = \frac{1-\varepsilon}{K_2}\left((2\omega_2^{in}-K_1)\,\frac{\partial\omega_2^{in}}{\partial K_1} - \omega_2^{in}\right)$$

$$\frac{\partial\Delta}{\partial K_2} = \frac{1-\varepsilon}{K_2}\left(\left(\frac{\partial\omega_2^{in}}{\partial K_2} - \frac{\omega_2^{in}}{K_2}\right)\cdot(\omega_2^{in}-K_1) + \omega_2^{in}\,\frac{\partial\omega_2^{in}}{\partial K_2}\right)$$

$$\frac{\partial\Delta}{\partial c_1} = \frac{1-\varepsilon}{K_2}\left(\frac{\partial\omega_2^{in}}{\partial c_1}\,(\omega_2^{in}-K_1) + \omega_2^{in}\,\frac{\partial\omega_2^{in}}{\partial c_1}\right)$$

$$\frac{\partial\Delta}{\partial c_2} = \frac{1-\varepsilon}{K_2}\left(\frac{\partial\omega_2^{in}}{\partial c_2}\,(\omega_2^{in}-K_1) + \omega_2^{in}\,\frac{\partial\omega_2^{in}}{\partial c_2}\right)$$

table IV Derivatives of Δ with respect to thermodynamic parameters and initial concentrations.

The derivative with respect to c_1 is positive, the one with respect to c_2 is negative. The conclusion is that relatively low c_2-values tend to make Δ larger. The dependence on thermodynamic parameters is not easily expressed in the constants of the problem.

4.3. One component initially adsorbed, one component in solution

a) The case of permanent separation

Component A_2 enters the column, where A_1 has already been adsorbed. The adsorbed component dissolves in simple wave C^1, the new one adsorbs over shock wave S^2. For the two waves we have the following directions

$$\sigma_1^{min} = \varepsilon + (1-\ )\,\frac{(\omega_1^{in})^2}{K_1}, \qquad \sigma_1^{max} = \varepsilon + (1-\varepsilon)K_1,$$

$$(4.4)$$

$$\sigma_2^{s} = \varepsilon + (1-\varepsilon)\omega_2^{e}.$$

The minimal difference in σ between the two waves is equal to

$$(4.5)\qquad \Delta = \sigma_2^s - \sigma_1^{max} = (1-\varepsilon)(\omega_2^e - K_1).$$

This relation is differentiated with respect to all variables in table V. (c_1 is the concentration in the initial state, c_2 in the entry state in this case).

$$\boxed{\begin{aligned}
\frac{\partial\Delta}{\partial K_1} &= (1-\varepsilon)\left(\frac{\partial\omega_2^e}{\partial K_1} - 1\right) = -\,(1-\varepsilon)\\
\frac{\partial\Delta}{\partial K_2} &= (1-\varepsilon)\,\frac{\partial\omega_2^e}{\partial K_2} = (1-\varepsilon)(1-n_2)^2\\
\frac{\partial\Delta}{\partial c_1} &= (1-\varepsilon)\,\frac{\partial\omega_2^e}{\partial c_1} = 0\\
\frac{\partial\Delta}{\partial c_2} &= (1-\varepsilon)\,\frac{\partial\omega_2^e}{\partial c_2} = -\,(1-\varepsilon)\left(\frac{K_2}{1+K_2c_2}\right)^2
\end{aligned}}$$

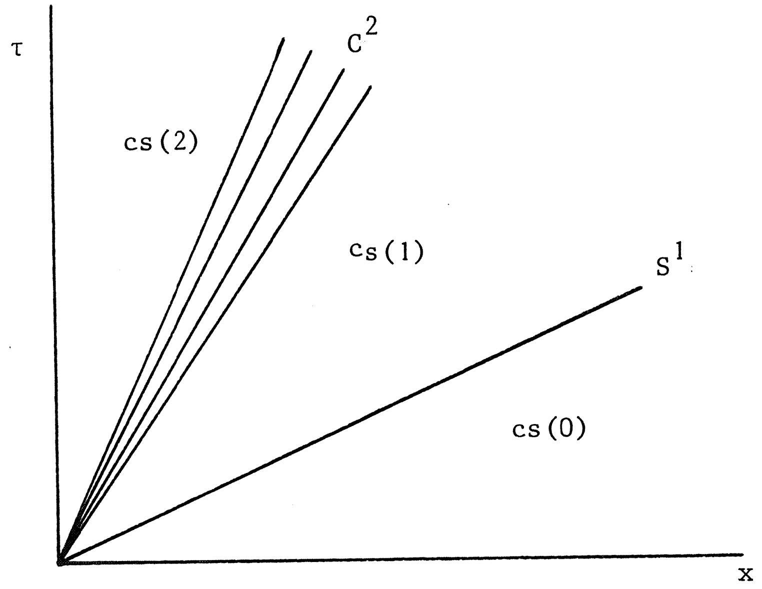
table V Derivatives of Δ with respect to thermodynamic parameter and concentrations.

We find that c_1 does not influence Δ, since σ_1^{max} is independent of c_1. The derivatives with respect to K_1 and c_2 are negative, with respect to K_2 positive. Again, low concentration values of the second component (the one with the largest adsorption affinity) tend to make Δ larger.

4.3. The case of a mixed constant state

b)

In the second case we have the same situation as in 4.3a, only the roles of A_1 and A_2 are interchanged.



figuur 5

The reciprocal wave velocities are

$$\sigma_1^s = \varepsilon + (1-\varepsilon)\,\frac{\omega_1^e\omega_2^{in}}{K_2}\,,$$

(4.6)

$$\sigma_2^{min} = \varepsilon + (1-\varepsilon)\,\frac{\omega_1^e(\omega_2^{in})^2}{K_1K_2}\,, \qquad \sigma_2^{max} = \varepsilon + (1-\varepsilon)\,\frac{\omega_1^e}{K_1}\,K_2.$$

In contrast to the first case the two components are now mixed in the constant state (1). The difference in σ between the shock wave and the nearest characteristic of the simple wave is equal to

$$(4.7)\qquad \Delta = (1-\varepsilon)\,\frac{\omega_1^e\omega_2^{in}}{K_1K_2}\,(\omega_2^{in}-K_1).$$

Differentiating Δ we find the following relations, where c_1 is the concentration of component A_1 in the entry state and c_2 the concentration of A_2 in the initial state, see table VI.

$$\frac{\partial\Delta}{\partial K_1} = -\ (1-\varepsilon)(1-n_1)(1-n_2)(1-n_1+n_1\,\frac{K_2}{K_1}\,(1-n_2))$$

$$\frac{\partial\Delta}{\partial K_2} = (1-\varepsilon)(1-n_1)(1-n_2)((1-n_2)(1-2n_2)\ +\frac{K_1}{K_2}\,n_2)$$

$$\frac{\partial\Delta}{\partial c_1} = -\ (1-\varepsilon)n_1(1-n_1)(1-n_2)(\frac{K_2}{K_1}\,(1-n_2)-1)$$

$$\frac{\partial\Delta}{\partial c_2} = (1-\varepsilon)n_2(1-n_1)(1-n_2)(2(1-n_2)-\frac{K_1}{K_2})$$

table VI Derivatives of Δ with respect to thermodynamic parameters and concentrations.

The derivatives with respect to K_1 and c_1 are negative, with respect to K_2 positive. The derivative with respect to c_2 is only negative when $n_2 > 1 - k_1/2K_2$.

In case $K_1 \approx K_2$ we find that the effect of changes in the variables is larger for ε small and low concentration values.

In the cases 4.1, 4.3a and 4.3b we find what might be expected for the thermodynamic constants, low values of K_1 and high values of K_2 make the gap between two waves larger. In case of two simple waves (4.2) there is no such simple relation for K-dependence. With regard to concentrations the situation is totally different for the two components. Except for 4.3b the dependence on c_2 is always the same, whereas the c_1-dependence changes in each case. Two simple waves and two shock waves is from a practical point of view the most interesting case (see figure 6). This will be treated in section 4.4.

4.4. The separation of two components

Taking piecewise constant boundary conditions on the τ-axis we assume a fluid containing two components A_1,A_2 enters a chromatographic column at $x = 0$ during the time interval $(0,\delta)$. There will be adsorption over two shock waves S^1 and S^2. After time δ clean fluid, entering the column at

$x = 0$ removes the adsorbed components in reverse order. This happens in two simple waves C^1 and C^2 issuing from the point $(0,\delta)$. In the physical plane we have the following interactions (see figure 6):

1. Shock S^2 meets simple wave C^1 at X_0.
2. This interaction ends at X_1.
3. Simple wave C^2 is adsorbed by shock S^2 in X_2.
   This interaction extends to infinity.
4. The same as (3) for simple wave C^1 and shock S^1 in X_3.

These are six constant states with D-values

$$\begin{aligned} &D_0 = D_4 = D_5 = 1 \text{ (only zero concentrations)}, \\ (4.8)\qquad &D_1 = \frac{K_1}{\omega_1^e}, \qquad D_2 = \frac{K_1K_2}{\omega_1^e\omega_2^e}, \qquad D_3 = \frac{K_2}{\omega_2^e} \quad . \end{aligned}$$

where ω-values are calculated from entry concentrations. For a detailed explanation of wave interactions we refer to [5] and [6].

The separation is completed after X_1. Component A_1 has been concentrated in the first wave, A_2 in the second. A new constant state with zero concentrations (= ideal separation) is created between the two waves. For a given time $t \geq \delta$ we investigate the location of A and B in figure 5. The shock S^2 is parametrized by ω_2, which runs from ω_2^e (at X_2) up to K_2 (at infinity). After laborious calculations we find

$$\begin{aligned} &X_A(\omega_2) = \frac{\delta K_1K_2}{(1-\varepsilon)\omega_1^e\omega_2^e} \cdot \frac{(K_2-\omega_1^e)(K_2-\omega_2^e)}{(K_2-\omega_2)^2(K_2-K_1)} \quad , \\ (4.9)\qquad & \\ &X_B(\omega_2) = \frac{1}{\varepsilon+(1-\varepsilon)K_1} \cdot \Bigl((\varepsilon+(1-\varepsilon) \frac{\omega_2^2}{K_2}\Bigr)X_A - \frac{\delta K_1^2}{\omega_1^e\omega_2^e} \cdot \frac{(K_2-\omega_2^e)(K_2-\omega_1^e)}{(K_2-K_1)^2}\Bigr). \end{aligned}$$

Consequently, the distance between A and B is

$$(4.10)\qquad (X_B-X_A)(\omega_2) = \frac{\delta K_1 n_2^e}{\varepsilon+(1-\varepsilon)K_1} * \left(\frac{K_1K_2}{K_2-K_1} + \left(\frac{\omega_2}{K_2-\omega_2}\right)^2 \cdot \left(K_2-K_1\left(\frac{K_2}{\omega_2}\right)^2\right)\right) .$$

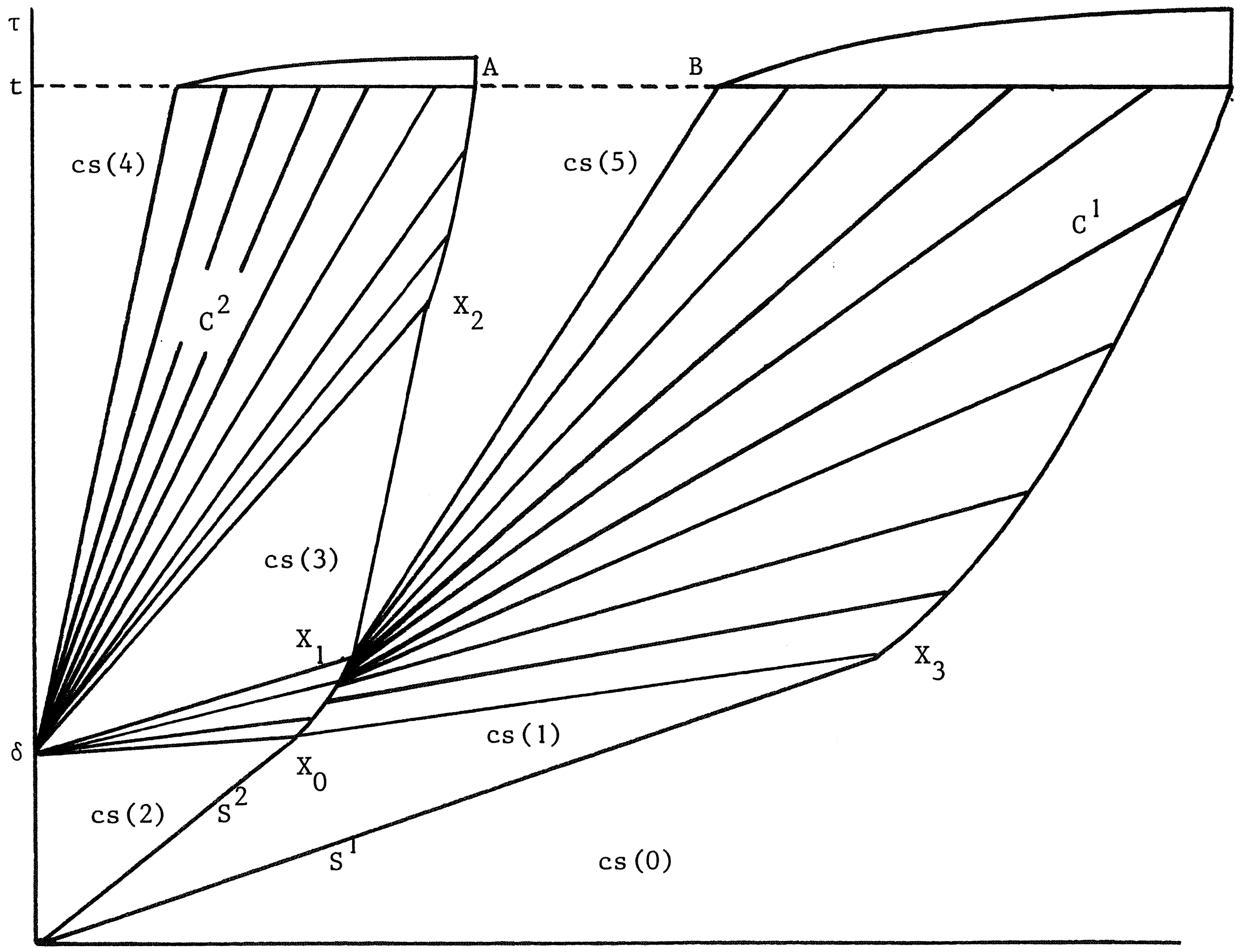


figure 6 The separation of two components, at line $\tau = t$ the concentrationprofiles are schematically indicated

The value of ω_2 in (4.10) is fixed by choosing a time t. Since the derivative of this last expression with respect to ω_2 is positive, it is clear that the distance between A and B increases in time. Another observation is the following; the parameter δ is a measure of the total amount of components brought into the column. A change in δ corresponds in the model merely to a scaling of all distances. We find as a result of this for increasing δ, a lower value of ω_2^e and consequently a smaller distance. This is in agreement with experimental trends. When K_1 is roughly equal to K_2, a situation where good separation is hard to obtain, (4.10) indicates that the distance between A and B will be large for low values of c_2.

5. CONCLUDING REMARKS

Apart from the restricting assumptions regarding diffusion, mentioned in section 1, one of the most disturbing elements is the adsorption isotherm. In reality the thermodynamic "constants" appear to fluctuate in dependence of changes in concentrations of all components. The other forms for isotherms mentioned in section 2.2 also cause some problems. The Freundlich-isotherm (2.8) is not differentiable in the origin. The anti-Langmuir isotherm (2.9) allows in principle the same procedure as in section 2.3, but there is a stability problem since the entropy condition is not consistent with this form of isotherm. Accordingly, the best choice seems to be the Langmuir form, where the K-values have to be estimated from numerical data. It is expected that for classes of related compounds reliable estimates of K-values can be obtained, with component interaction taken into account. Using these empirical values in the Langmuir form, the theory then yields information regarding the separation process. It will be interesting to compare theoretical results with real chromatograms. This can be done, for example by approximating the resulting concentration fluctuation functions with a series of orthogonal polynomials and comparing the coefficients of both series. For this purpose Chebyshev or Hermite polynomials can be used.

Experimental results are not yet available. In figure 7 a preliminary example of a theoretical chromatogram is given. This simulated chromatogram is obtained by summing a number of appropriately weighted Hermite functions and illustrates section 4.4.

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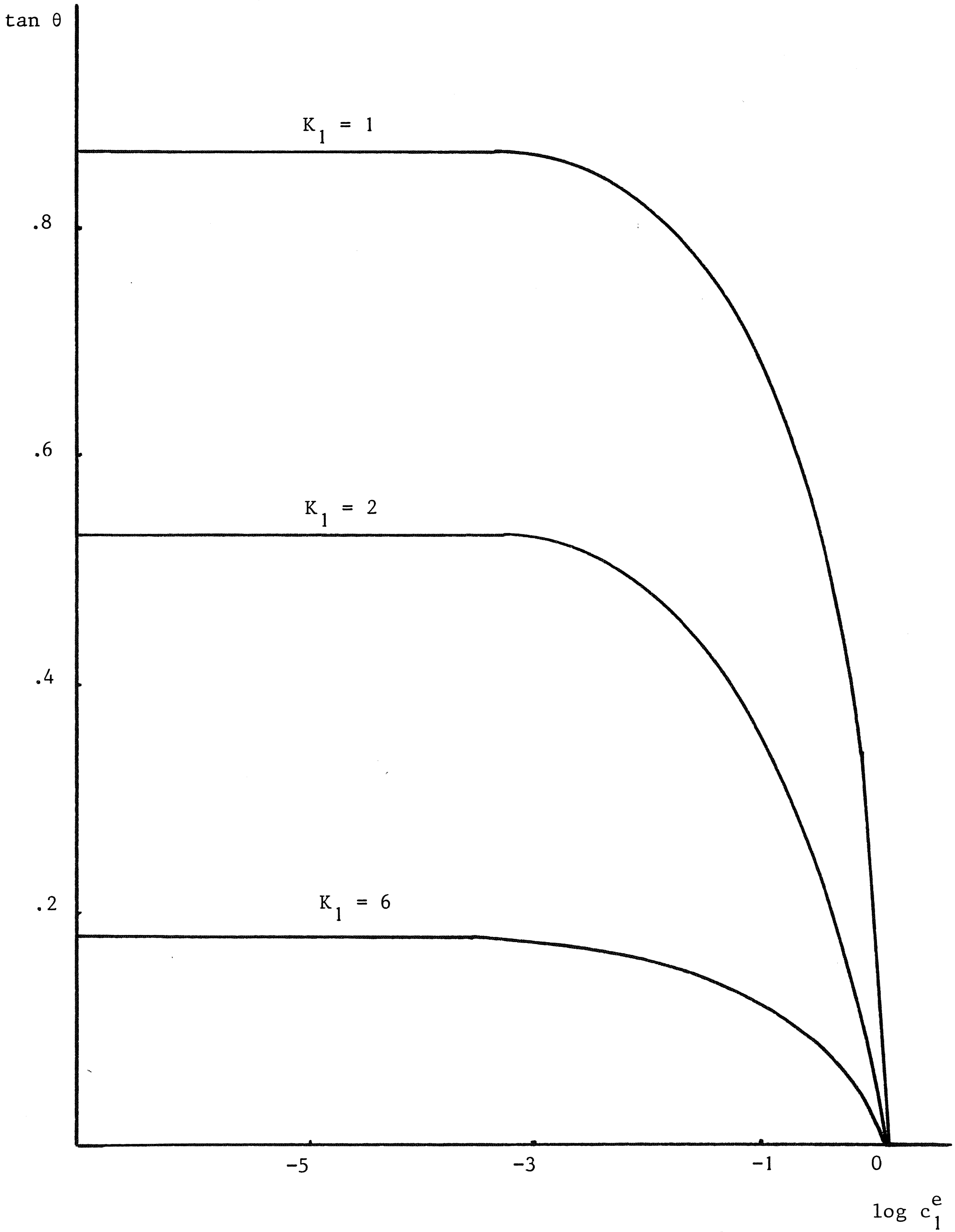

Figure 2 tan θ(θ in figure 1) as a function of log c_1^e, for fixed values of $\varepsilon = 0.4$, $K_2 = 25$ and the ratio $c_2^e/c_1^e = 2$. Three curves are drawn, each for a different value of K_1.

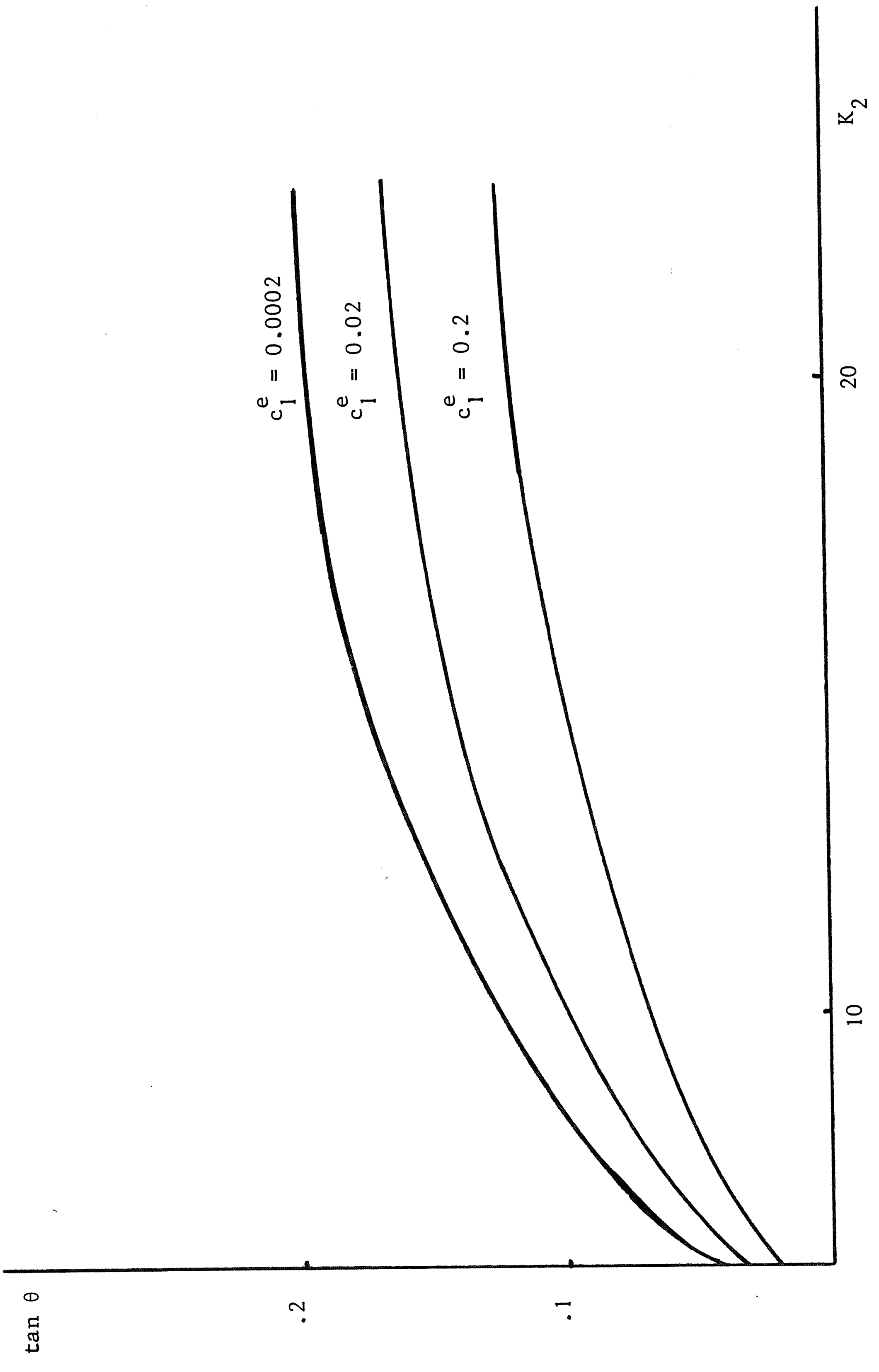

Figure 3 tan θ (θ in figure 1) as a function of K_2 for fixed values of $\varepsilon = 0.4$, $K_1 = 5$ and the ration $c_2^e/c_1^e = 2$. Three curves are drawn, each for a different value of c_1^e. The highest curve is almost invariant when the entry concentrations are further decreased.

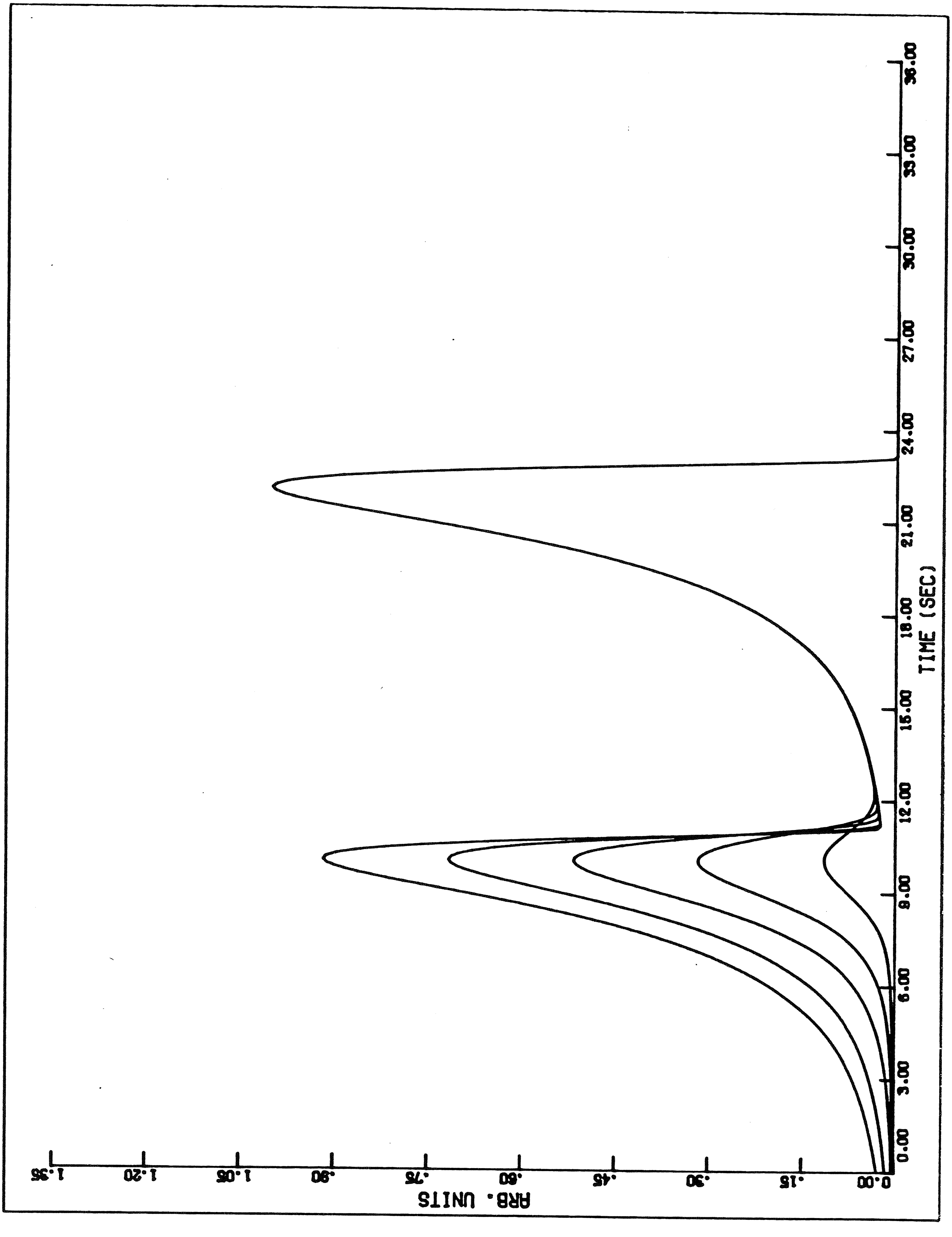
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Figure 7 The main feature of the five simulated two component chromatograms is the variation in the concentration of the second component. These diagrams are made by a computerprogram of the Department of Analytical Chemistry of the University of Amsterdam. The total concentration functions in time, with some arbitrary vertical measure are Hermite-series. In the present case realistic values for the coefficients in the series were chosen on the basis of the Langmuir isotherm.