On the Theory of Multicomponent Chromatography

Hyun-Ku Rhee, R. Aris and N. R. Amundson

Phil. Trans. R. Soc. Lond. A 1970 **267**, 419-455
doi: 10.1098/rsta.1970.0050

ON THE THEORY OF MULTICOMPONENT CHROMATOGRAPHY

By HYUN-KU RHEE, R. ARIS and N. R. AMUNDSON
University of Minnesota

(*Communicated by K. G. Denbigh, F.R.S.—Received* 15 *December* 1969)

CONTENTS

A theoretical study of multicomponent chromatography is here presented in which the system is considered to be one-dimensional, isothermal, locally at equilibrium and to have negligible diffusion effects. The discussion starts with constant initial and entry conditions and goes on to stepwise constant data with an arbitrary number of discontinuities. The Langmuir adsorption isotherm is perfectly fitted to the exposition of the mathematical theory of quasilinear equations for it leads to explicit forms for the Riemann invariants and characteristic parameters. This paper develops the theory of simple waves and of shock waves on an independent basis and illustrates this theory by the construction of solutions and the analysis of the interaction of waves. It is shown incidentally that the entropy change across a shock is consistent with the second law of thermodynamics. The separation of solutes is discussed and brief consideration is given to the problems associated with non-uniform geometry and non-isothermal adsorption.

Vol. 267. A. 1182. (Price £1; U.S. $2.60) 28 [Published 30 October 1970

INTRODUCTORY REMARKS AND NOTATION

The chromatographic process has come into a considerable prominence during the last half century as an analytical device, and more recently important industrial operations have used the technique or one of its variants. All such processes have in common the feature that a fluid phase containing one or more adsorbable components flows through a fixed bed containing an adsorbent.

The theoretical study of multicomponent chromatography has been the subject of many papers. The first mathematical description was presented by Wilson (1940) who, however, overlooked the dependence of the concentration of one component upon the others. Several observations, qualitatively correct, were made by De Vault (1943). Later, Walter (1945) considered the formation of chromatograms, assuming a chemical equilibrium between adsorbed materials and dissolved ones, and obtained explicit solutions. Glueckauf (1946, 1949) introduced Langmuir isotherms to analyse two and three solute problems rigorously, though his treatment did not bring out the connexion with the classical theory of quasilinear equations. An independent study was carried out by Sillen (1950) who presented analogous results by using the so-called 'ψ-condition' that holds for constant initial and entry conditions. Bayle & Klinkenberg (1954) presented the mathematical formulation of multicomponent systems as well as a critical review of the previous theory. These authors also claimed that the experimental results were not in conflict with the relation between the coexisting concentrations.

Recently, a theoretical analysis of multicomponent ion exchange in fixed beds was presented by Klein, Tondeur & Vermeulen (1967). Tondeur & Klein (1967) also extended the approach originated by Walter (1945) to multicomponent systems. Although these authors were successful to some extent with mass-action-type isotherms, several parts seem somewhat intuitive and empirical. Moreover, their discussion is confined to some special cases and thus may not be coordinated adequately to the general approach. Helfferich (1967, 1968)† considered similar problems and achieved a further advance by employing the so-called h-transformation.

In this paper we wish to develop a systematic and rigorous theory of multicomponent chromatography with an ideal column. The term 'ideal', as used in this problem, connotes the following conditions:

1. The system is one-dimensional in the direction of flow with uniform cross-sectional area.
2. The volumetric flow rate and the void fraction of the bed are constant.
3. Effects of diffusion are negligible compared with the convective transport, and there is no channelling.
4. Local equilibrium is established between two phases everywhere at any time.
5. The process is isothermal and isochoric.

Such a theory, since only convective transport is important, is based on the mathematical theory of quasilinear systems of partial differential equations of first order. The mathematical model has also attracted the interest of many mathematicians who have elucidated the general features of such conservation equations. Construction of solutions has been discussed through finite difference schemes (Lax 1957; Oleinik 1957; Glimm 1965). A numerical scheme was first developed by Courant, Isaacson & Rees (1952) and has been refined by various authors (cf. Jeffrey & Taniuti 1964). By assuming the existence of generalized Riemann invariants, Lax (1957) was able to generalize the simple wave theory and also able to develop a general theory of discontinuities. This, however, is subject to a severe restriction because, for a system of more than

† The present work had been completed when we learned of Helfferich's discussions, but little overlap is observed.

two equations, a Riemann invariant of a type strictly analogous to the one for a system of two equations cannot exist in general (Jeffery & Taniuti 1964; Glimm 1965).

The present approach is restricted to Riemann's problem in which the boundary data are constant, for this is a sufficient condition for the existence of Riemann invariants. The first section is concerned with the derivation of the fundamental differential equation that can be used with a general isotherm, while in the second section the isotherms of Langmuir type are introduced. These have been proved to be an adequate description of many multicomponent systems and lead to explicit formulae.

The three sections following establish the basic theory. First the generalized Riemann invariants and characteristic parameters are generated by following an independent scheme and this is followed by the theory of simple waves and of shock waves; this development is also shown to be compatible with the one established by Lax (1957). In § 6 we examine the entropy change across a shock to be assured that the second law of thermodynamics is satisfied.

The next section discusses in detail the construction of the solution in terms of simple waves and shock waves. It gives physical meaning to some observations made for special cases, and includes some numerical examples.

Although it originated from the class of Riemann's problem, the theory finds its natural application to the class of stepwise constant initial and entry value problems which are necessarily involved with interactions between waves. In § 8 interactions are classified and in § 9 analyses are performed for every case of potential interest. Applications are illustrated by a typical example, the so-called chromatographic cycle, which shows how different solute species are separated from one another.

Finally, we search for possible extensions of the present approach and briefly discuss radial and non-isothermal chromatography.

Notation

The following are the principal symbols used in this paper. Some of the ephemeral symbols are not listed. Dimensions are given in terms of mass (M), length (L), time (t), temperature (T), and amount of solute species (mol).

A_i	ith solute species
$A(z)$	cross-sectional area (L^2)
C_f	heat capacity per unit volume of fluid phase ($\mathrm{ML^{-1}\,t^{-2}\,T^{-1}}$)
C_s	heat capacity per unit volume of solid phase ($\mathrm{ML^{-1}\,t^{-2}\,T^{-1}}$)
$C^{(k)}$	characteristic of the kth kind
c_i	molar concentration of species A_i in fluid phase ($\mathrm{mol\,L^{-3}}$)
D	$1+\sum_{i=1}^{M} K_i c_i$, dimensionless
d	depth of cylindrical bed (L)
f_i	total molar concentration of species A_i in both phases ($\mathrm{mol\ L^{-3}}$)
G	Gibbs free energy per unit volume ($\mathrm{M\,L^{-1}\,t^{-2}}$)
H	enthalpy per unit volume ($\mathrm{M\,L^{-1}\,t^{-2}}$)
H_i	molar enthalpy of species A_i in solid phase ($\mathrm{M\,L^2\,t^{-2}\,mol^{-1}}$)
h_i	molar enthalpy of species A_i in fluid phase ($\mathrm{M\,L^2\,t^{-2}\,mol^{-1}}$)
$J_i^{(k)}$	(k)-Riemann invariant, dimensionless
K_i	Langmuir isotherm parameter ($\mathrm{L^3\,mol^{-1}}$)

$\mathscr{M}_i^{(k)}$	molar flux of species A_i through a (k)-shock (mol L^{-3})
N	limiting concentration of adsorbed solute (mol L^{-3})
n_i	molar concentration of adsorbed A_i (mol L^{-3})
Q	volumetric flow rate ($\mathrm{L}^3\,\mathrm{t}^{-1}$)
r	radial distance (L)
r_0	radius of central channel (L)
S	entropy per unit volume ($\mathrm{M\,L^{-1}\,t^{-2}\,T^{-1}}$)
$S^{(k)}$	(k)-shock line
T	temperature (T)
t	time (t)
u	interstitial velocity of fluid phase ($\mathrm{L\,t^{-1}}$)
x	dimensionless position variable
Z	characteristic length of the system (L)
z	distance in flow direction (L)
$\Gamma^{(k)}$	path of the kth kind in $\Phi(M)$ or $\Omega(M)$
γ_{ij}	relative adsorptivity, dimensionless
ΔH_i	heat of adsorption per mole of A_i ($\mathrm{ML^2\,t^{-2}\,mol^{-1}}$)
ϵ	fractional void space of fixed bed, dimensionless
η	dimensionless time variable along the τ-axis
Θ	fractional coverage of adsorption sites, dimensionless
$\Lambda_{(k)}$	$NK_i(D-\phi_i/J_i^{(k)})$, dimensionless
μ_i	chemical potential of species A_i ($\mathrm{M\,L^2\,t^{-2}\,mol^{-1}}$)
ξ	dimensionless position variable along the x-axis
π_m	subspace, $\Phi(M-1)$; $\phi_m \equiv 0$
σ	characteristic direction in the physical plane, dimensionless
σ^{s}	direction of shock propagation, dimensionless
τ	dimensionless time variable
$\Phi(M)$	M-dimensional concentration space
ϕ_i	$K_i c_i$, dimensionless concentration of species A_i in fluid phase
$\Omega(M)$	M-dimensional ω-space
ω	characteristic parameter, dimensionless

Brackets

$[a]$	jump of the quantity a across a discontinuity
$\{a_i\}$	collection of M elements of a_i associated with the subscript

Superscripts

e	entry condition
i	initial condition
(k)	kth kind
l	left-hand side of shock
o	fixed
r	right-hand side of shock
s	shock
*	higher value

Subscripts

i, j, k, l, m	solute species in multicomponent systems
(k)	kth kind
M	number of solute species appearing in the system or equivalently the most adsorbable species
$\circ$	fixed
0	initial point
$1, 2, 3$	solute species A_1, A_2, A_3
$*$	lower value

1. Fundamental differential equation

Consider an ideal chromatographic column of void fraction ϵ through which a fluid mixture containing M different solutes $\{A_i\}$ flows with linear velocity u. Let c_i represent the concentration of the solute A_i in the fluid phase and n_i its concentration in the solid phase, both being expressed in moles per unit volume of their own phase. Then the material balance for each solute component A_i in a section between planes distant z and $z+\Delta z$ from the entrance to the bed over a time period t to $t+\Delta t$ yields, in the limit, the following quasilinear system of M partial differential equations of first order:

$$\frac{\partial c_i}{\partial x}+\frac{\partial f_i}{\partial \tau} = 0, \tag{1.1}$$

$$f_i = \epsilon c_i+(1-\epsilon)\, n_i, \tag{1.2}$$

$$n_i = n_i(c_1, c_2, \ldots, c_M) \tag{1.3}$$

for $i = 1, 2, \ldots, M$. Here x and τ are the dimensionless independent variables defined as

$$x = z/Z, \text{ a dimensionless distance,} \tag{1.4}$$

$$\tau = \epsilon ut/Z, \text{ a dimensionless time,} \tag{1.5}$$

respectively, and Z is the characteristic length of the column. In equation (1.3) the functions n_i, representing the equilibrium relationship between the adsorbed phase and the fluid phase, may be regarded in general as continuous functions of $\{c_i\}$ with as many derivatives as may be required.

According to the conventional mathematical theory, the system (1.1) is totally hyperbolic if the matrix of coefficients $f_{i,j}$ has M real, distinct eigenvalues where

$$f_{i,j} \equiv \partial f_i/\partial c_j \quad (i,j = 1, 2, \ldots, M). \tag{1.6}$$

The formal solution of the equations first requires the determination of the M eigenvalues $\lambda_{(k)}$ (characteristic directions in the (τ, x)-plane) and the right eigenvectors $\boldsymbol{r}_{(k)}$ of the matrix. These are all functions of $\{c_i\}$ and lead to the generalized Riemann invariants $J^{(k)}$ by the solution of the equation

$$(\boldsymbol{\nabla}_c J^{(k)})\,.\,\boldsymbol{r}_{(k)} = 0 \quad (k = 1, 2, \ldots, M), \tag{1.7}$$

where $\boldsymbol{\nabla}_c$ denotes the gradient in the concentration space. It can be shown that there exist precisely $M-1$ independent Riemann invariants $J^{(k)}$ which, together with the eigenvalues $\lambda_{(k)}$, play the key role in the construction of solutions. In practice, however, the method is by no means promising except for some special cases for which the eigenvalues can be obtained explicitly.

We shall therefore confine our discussion to a class of special, yet standard, initial and entry value problems and follow an independent approach. Suppose the initial and entry data are specified by two different constant states of concentrations with a jump discontinuity at the origin:

$$\left.\begin{cases}\text{at} & \tau = 0, \quad c_i = c_i^{\mathrm{i}} \quad \text{(a constant)} \\ \text{at} & x = 0, \quad c_i = c_i^{\mathrm{e}} \quad \text{(a constant)}\end{cases}\right\} \tag{1.8}$$

for $i = 1, 2, \ldots, M$ and

$$c_i^{\mathrm{i}} \neq c_i^{\mathrm{e}} \tag{1.9}$$

for some i. The superscripts i and e denote the initial and entry data, respectively. A problem of this class is called a Riemann's problem.

It has been proved that, if it is unique, the solution of a Riemann's problem is a function of x/τ only (Sillen 1950; Lax 1957). Let us suppose that the solution has been obtained for the Riemann's problem represented by equations (1.1), (1.8) and (1.9). If this is denoted by

$$c_i = c_i(x/\tau) \quad (i = 1, 2, \ldots, M), \tag{1.10}$$

and I_i is the inverse function of c_i, so that

$$x/\tau = I_i(c_i) = I_j(c_j) \quad (i, j = 1, 2, \ldots, M),$$

there must be a system of relations:

$$c_j = c_j(I_i(c_i)) = g_{ji}(c_i) \quad (i, j = 1, 2, \ldots, M). \tag{1.11}$$

It then follows that there exists a one-parameter representation of the solution and that its image in the M-dimensional concentration space lies on a single curve. We shall call such a curve a Γ.

If along the curve Γ we introduce the directional derivative

$$\frac{\mathscr{D}f_i}{\mathscr{D}c_i} = \sum_{j=1}^{M} \frac{\partial f_i}{\partial c_j}\frac{\mathrm{d}g_{ji}}{\mathrm{d}c_i}, \tag{1.12}$$

then the system (1.1) becomes

$$\frac{\partial c_i}{\partial x} + \frac{\mathscr{D}f_i}{\mathscr{D}c_i}\frac{\partial c_i}{\partial \tau} = 0 \quad (i = 1, 2, \ldots, M)$$

which can be rearranged in the form

$$\sigma \equiv \left(\frac{\mathrm{d}\tau}{\mathrm{d}x}\right)_{\omega} = \frac{\mathscr{D}f_i}{\mathscr{D}c_i}, \tag{1.13}$$

where ω is a parameter running along the curve Γ. Since σ must be the same for every i, it follows that

$$\frac{\mathscr{D}f_1}{\mathscr{D}c_1} = \frac{\mathscr{D}f_2}{\mathscr{D}c_2} = \ldots = \frac{\mathscr{D}f_M}{\mathscr{D}c_M}. \tag{1.14}$$

Equation (1.14) is the fundamental differential equation of the Riemann's problem, the solution of which generates the one-parameter family (1.11); i.e. the curve Γ in the M-dimensional concentration space. It was given by Glueckauf (1946, 1949) for two solutes and by Bayle & Klinkenberg (1954) for many solutes.

Furthermore, equation (1.13) can be rearranged by employing the parameter ω in the form

$$f_{i,1}\frac{\mathrm{d}c_1}{\mathrm{d}\omega} + \ldots + (f_{i,i} - \sigma)\frac{\mathrm{d}c_i}{\mathrm{d}\omega} + \ldots + f_{i,M}\frac{\mathrm{d}c_M}{\mathrm{d}\omega} = 0 \quad (i = 1, 2, \ldots, M),$$

or briefly in matrix form

$$(\boldsymbol{\nabla}_c \boldsymbol{f} - \sigma \boldsymbol{I})\,\mathrm{d}\boldsymbol{c}/\mathrm{d}\omega = 0, \tag{1.15}$$

where $\boldsymbol{f}$ or $\boldsymbol{c}$ represents the vector-valued function of M elements $\{f_i\}$ or $\{c_i\}$, respectively. The condition that there exists a non-trivial solution for $\mathrm{d}\boldsymbol{c}/\mathrm{d}\omega$ entails

$$|\boldsymbol{\nabla}_c \boldsymbol{f} - \sigma \boldsymbol{I}| = 0. \tag{1.16}$$

Consequently, σ defined as in equation (1.13) is the same as the characteristic direction in the physical plane of τ and x.

2. Langmuir adsorption isotherm

The equilibrium relation n_i which is usually called the adsorption isotherm is, in general, a complicated nonlinear function of $\{c_i\}$ in which mutual influences among different solutes are taken into account. Since the ideal localized monolayer model was introduced by Langmuir (1916), the Langmuir relation has been extensively employed not only for single solute systems but also for multiple solutes (see, for example, Wilson 1940, and particularly Glueckauf 1946, 1949). A rigorous discussion was given by De Boer (1953) and experimental evidence of its validity has been presented (see, for example, Shen & Smith 1968*b*).

We shall assume the validity of the Langmuir relation for multicomponent systems and introduce the appropriate form for equation (1.3); i.e. for each components A_i we have

$$n_i = \frac{NK_i c_i}{1 + \sum_{j=1}^{M} K_j c_j} \quad (i = 1, 2, \ldots, M). \tag{2.1}$$

Here K_i is the reciprocal value of c_i when half the sites are occupied by molecules of A_i and the other half are vacant. The value of K_i may be determined experimentally and is strongly dependent upon the temperature T:

$$K_i = K_i^{\circ}\, T^{\frac{1}{2}}\, \mathrm{e}^{-\Delta H_i/RT}, \tag{2.2}$$

where ΔH_i is the heat of adsorption per mole of A_i. N, representing the saturation value of n_i, is defined as the maximum number of moles of solutes that can be adsorbed per unit volume of adsorbent. It is interesting to notice that N is a constant intrinsic to the adsorbent itself and K_i is a constant characteristic of the corresponding system of a single solute A_i.

De Vault (1943), on a completely independent basis, predicted various properties for adsorption isotherms represented by the first- and second-order derivatives. The Langmuir relation (2.1) satisfies all of those properties and thus represents what is termed a ‘favourable equilibrium’.

For convenience, we shall further assume that the solute components are arranged in such a way that

$$K_1 < K_2 < K_3 < \ldots < K_{M-1} < K_M. \tag{2.3}$$

This is equivalent to numbering the components in the order of the adsorptivity from the smallest to the largest since the relative adsorptivity may be defined as

$$\gamma_{i\mathrm{r}} \equiv \frac{n_i/c_i}{n_\mathrm{r}/c_\mathrm{r}} = \frac{K_i}{K_\mathrm{r}} \quad (i = 1, 2, \ldots, M), \tag{2.4}$$

where the subscript r denotes the reference species. For the Langmuir isotherm the relative adsorbtivities are independent of concentrations.

The Langmuir relation carries an underlying assumption that the solvent behaves as an inert component. If the solvent has a non-zero adsorptivity, but one which is smaller than any of the solutes, the Langmuir relation can be reduced to the form which excludes the solvent (equation (2.1)) by appropriately modifying the values of N and K_i (Rhee 1968). In particular, constant-separation-factor equilibrium relations introduced by Tondeur & Klein (1967) can be rewritten in the form of equation (2.1) excluding the least adsorbable component. An immediate consequence is that the least adsorbable component (i.e. the solvent almost invariably) is consistently passive in the process of exchange and thus may be treated with the corresponding modifications as if it were an inert component within the framework of the present study.

3. Riemann invariants and characteristic parameters

In the light of the form of the Langmuir isotherm, equation (2.1), we shall introduce the following dimensionless variables:

$$\phi_i = K_i c_i \quad (i = 1, 2, \ldots, M) \tag{3.1}$$

and

$$D = 1 + \sum_{i=1}^{M} \phi_i. \tag{3.2}$$

It then follows from equation (1.11) that ϕ_i as well as n_i may be regarded as a function of D alone; i.e.

$$\phi_i = \phi_i(D) \quad (i = 1, 2, \ldots, M), \tag{3.3}$$

and

$$n_i = N\phi_i(D)/D \quad (i = 1, 2, \ldots, M). \tag{3.4}$$

We further remark that the total coverage Θ of adsorption sites can be expressed in terms of the parameter D; i.e. from equation (3.4)

$$\Theta \equiv \sum_{i=1}^{M} n_i/N = 1 - 1/D. \tag{3.5}$$

Hence, the coverage Θ varies in the same direction as the parameter D.

Denoting differentiation with D as the independent variable along the Γ by $\mathrm{d}/\mathrm{d}D$, we can rewrite the fundamental differential equation (1.14) in the form

$$K_1 \frac{\mathrm{d}n_1/\mathrm{d}D}{\mathrm{d}\phi_1/\mathrm{d}D} = K_2 \frac{\mathrm{d}n_2/\mathrm{d}D}{\mathrm{d}\phi_2/\mathrm{d}D} = \ldots = K_M \frac{\mathrm{d}n_M/\mathrm{d}D}{\mathrm{d}\phi_M/\mathrm{d}D}. \tag{3.6}$$

Substituting equation (3.4), differentiating once more with respect to D and rearranging, we obtain

$$\frac{\dfrac{\mathrm{d}^2\phi_1}{\mathrm{d}D^2}}{\dfrac{1}{K_1\phi_1}\left(\dfrac{\mathrm{d}\phi_1}{\mathrm{d}D}\right)^2} = \frac{\dfrac{\mathrm{d}^2\phi_2}{\mathrm{d}D^2}}{\dfrac{1}{K_2\phi_2}\left(\dfrac{\mathrm{d}\phi_2}{\mathrm{d}D}\right)^2} = \ldots = \frac{\dfrac{\mathrm{d}^2\phi_M}{\mathrm{d}D^2}}{\dfrac{1}{K_M\phi_M}\left(\dfrac{\mathrm{d}\phi_M}{\mathrm{d}D}\right)^2} = \frac{\sum_{i=1}^{M}\dfrac{\mathrm{d}^2\phi_i}{\mathrm{d}D^2}}{\sum_{i=1}^{M}\dfrac{1}{K_i\phi_i}\left(\dfrac{\mathrm{d}\phi_i}{\mathrm{d}D}\right)^2}. \tag{3.7}$$

Since it follows from equation (3.2) that

$$\sum_{i=1}^{M}\frac{\mathrm{d}^2\phi_i}{\mathrm{d}D^2} = 0,$$

any solution to equation (3.7) must satisfy either

$$\sum_{i=1}^{M}\frac{1}{K_i\phi_i}\left(\frac{\mathrm{d}\phi_i}{\mathrm{d}D}\right)^2 = 0, \tag{3.8}$$

or

$$\frac{\mathrm{d}^2\phi_i}{\mathrm{d}D^2} = 0 \quad (i = 1, 2, \ldots, M). \tag{3.9}$$

Equation (3.8), however, cannot have any physical meaning since it would require at least one of the ϕ_i to be negative. Consequently, it is from equation (3.9) that the physically relevant solution may be determined. Direct integration of equation (3.9) gives

$$\phi_i - \phi_i^\circ = J_i(D - D^\circ) \quad (i = 1, 2, \ldots, M), \tag{3.10}$$

in which the superscript ∘ denotes the fixed state of concentrations and J_i is the integration constant to be determined. Adding the M equations in the system (3.10) together, we find that

$$\sum_{i=1}^{M} J_i = 1. \tag{3.11}$$

The system (3.10), being a one-parameter form of the solution, represents a straight line passing through the fixed point $\{\phi_i^\circ\}$ in the M-dimensional concentration space, $\Phi(M)$. This straight line is the Γ and has a direction given by the invariant set $\{J_i\}$.

We now substitute equation (3.10) back into the original differential equation (3.6) to obtain, after rearrangement, the equation

$$K_1(N-n_1/J_1) = K_2(N-n_2/J_2) = \dots = K_M(N-n_M/J_M) \equiv \omega, \tag{3.12}$$

whence

$$J_i = \frac{K_i n_i}{NK_i-\omega} \quad (i = 1, 2, \dots, M).$$

Here ω is a new parameter† which can be determined, for a given state of concentrations, by solving the following equation

$$\sum_{i=1}^{M} \frac{K_i n_i}{NK_i-\omega} = 1. \tag{3.13}$$

Equation (3.13) is an Mth order algebraic equation for ω and it can be shown that there exist M real, distinct, positive roots which can be arranged as

$$0 \leqslant \omega_{(1)} \leqslant NK_1 \leqslant \omega_{(2)} \leqslant NK_2 \leqslant \omega_{(3)} \dots \omega_{(M-1)} \leqslant NK_{M-1} \geqslant \omega_{(M)} \leqslant NK_M. \tag{3.14}$$

Consequently, there exist M different sets of J_i, to each of which there corresponds a different Γ. We shall denote the kth one as $\Gamma^{(k)}$ and the corresponding invariant set as $\{J_i^{(k)}\}$, where

$$J_i^{(k)} = \frac{K_i n_i}{NK_i-\omega_{(k)}} \quad (i = 1, 2, \dots, M). \tag{3.15}$$

It should be pointed out that J_i so defined corresponds to the generalized Riemann invariant (Lax 1957), $\{J_i^{(k)}\}$ being the (k)-Riemann invariants.

From equations (3.14) and (3.15), one can show that

$$0 < J_M^{(1)} < J_M^{(2)} < \dots < J_M^{(M-1)} < J_M^{(M)}, \tag{3.16}$$

and it is also observed that the sign of each Riemann invariant $J_i^{(k)}$ is fixed as shown in table 1.

Table 1. Sign of Riemann invariants, $J_i^{(k)}$

$J_i^{(k)}$	J_1	J_2	J_3	J_4	…	J_{M-2}	J_{M-1}	J_M
$J^{(1)}$	+	+	+	+	…	+	+	+
$J^{(2)}$	−	+	+	+	…	+	+	+
$J^{(3)}$	−	−	+	+	…	+	+	+
$J^{(4)}$	−	−	−	+	…	+	+	+
⋮	⋮	⋮	⋮	⋮		⋮	⋮	⋮
$J^{(M-2)}$	−	−	−	−	…	+	+	+
$J^{(M-1)}$	−	−	−	−	…	−	+	+
$J^{(M)}$	−	−	−	−	…	−	−	+

Rearranging equation (3.12), we obtain

$$\Lambda_{(k)} \equiv \omega_{(k)} D = NK_i(D-\phi_i/J_i^{(k)}), \tag{3.17}$$

and it can be shown from equation (3.10) that $\Lambda_{(k)}$, being independent of the choice of i, remains invariant along a $\Gamma^{(k)}$. Furthermore, it follows from equation (3.16) that

$$0 < \Lambda_{(1)} < \Lambda_{(2)} < \dots < \Lambda_{(M-1)} < \Lambda_{(M)}. \tag{3.18}$$

We further observe that equation (3.13) is a one-to-one, continuous mapping of the

---

† It will turn out later that ω is the characteristic parameter (cf. equation (3.20)).

concentration space $\Phi(M)$ onto the ω-space $\Omega(M)$. It can be shown that the inverse mapping is also continuous and given by

$$\phi_i = \left(\frac{NK_i}{\omega_{(i)}} - 1\right) \prod_{\substack{j=1 \\ j \neq i}}^{M} \frac{\dfrac{NK_i}{\omega_{(j)}} - 1}{\dfrac{K_i}{K_j} - 1} \quad (i = 1, 2, \ldots, M). \tag{3.19}$$

Hence, the two spaces $\Phi(M)$ and $\Omega(M)$ are homeomorphic with the homeomorphism given by equations (3.13) and (3.19). In order to obtain the image of a $\Gamma^{(k)}$ in $\Omega(M)$, we take the equation

$$\sum_{i=1}^{M} \frac{K_i n_i}{NK_i - \omega_{(m)}} = 1 \quad (m \neq k)$$

which, upon using equations (3.11) and (3.15) and rearranging, we can reduce to

$$(\omega_{(k)} - \omega_{(m)}) \sum_{i=1}^{M} \frac{J_i^{(k)}}{NK_i - \omega_{(m)}} = 0. \tag{3.20}$$

Equation (3.20) implies that $\omega_{(m)}$, if $m \neq k$, remains unchanged along a $\Gamma^{(k)}$ because $\omega_{(k)} \neq \omega_{(m)}$ and $\{J_i^{(k)}\}$ is invariant along a $\Gamma^{(k)}$. Since then only $\omega_{(k)}$ varies along a $\Gamma^{(k)}$, its image in $\Omega(M)$ lies on a straight line parallel to the $\omega_{(k)}$-axis. Here we remark that the homeomorphism corresponds to the h-transformation of Helfferich (1968). Incidentally, the ω-coordinate system is very similar to the characteristic coordinate system associated with a system of two equations (Courant & Friedrichs 1948; Rhee 1968) and, in this sense, $\omega_{(k)}$ will be called the generalized characteristic parameter.

In the space $\Omega(M)$, the physically relevant portion is finite and bounded as follows:

$$\left.\begin{aligned} NK_{k-1} \leqslant \omega_{(k)} \leqslant NK_k \quad (2 \leqslant k \leqslant M), \\ 0 \leqslant \omega_{(1)} \leqslant NK_1. \end{aligned}\right\} \tag{3.21}$$

Consider next the $(M-1)$-dimensional subspace $\pi_m : \phi_m \equiv 0$. It follows from equation (3.13) that one of $\{\omega_{(k)}\}$ must be equal to NK_m and hence, from equation (3.21), that $\omega_{(m)} = NK_m$ or $\omega_{(m+1)} = NK_m$. Therefore, the image of the subspace π_m in $\Omega(M)$ consists of two planes $\omega_{(m)} = NK_m$ and $\omega_{(m+1)} = NK_m$. The only exception is the subspace π_M whose image is a single plane $\omega_{(M)} = NK_M$. The origin of $\Phi(M)$ represents the pure state $\{0\}$ for which equation (3.13) generates the M roots $\{NK_k\}$. The image of the pure state in $\Omega(M)$ is then given by the point $\omega_{(k)} = NK_k$, $k = 1, 2, \ldots, M$. (Figure 3, whose main bearing is in a later connexion, illustrates this incidentally by showing the region of $\Omega(3)$ that corresponds to the positive octant of $\Phi(3)$ and by indicating the point in $\Omega(3)$ corresponding to the origin of $\Phi(3)$.)

We summarize this in tables 2 and 3.

TABLE 2. CORRESPONDENCE BETWEEN $\Phi(M)$ AND $\Omega(M)$

space	$\Phi(M)$	$\Omega(M)$
state	$\{\phi_i\}$	$\{\omega_{(k)}\}$
Γ	straight and slanted	straight and parallel to axis
pure state	$\{0\}$	$\{NK_k\}$
subspace, $\pi_m : \phi_m = 0$	plane $\phi_m = 0$	two planes, $\omega_{(m)} = NK_m$ and $\omega_{(m+1)} = NK_m$

Table 3. Pertinent parameters along a $\Gamma^{(k)}$

parameter	$m = k$	$m \neq k$
$\omega_{(m)}$	variable	invariant
$\Lambda_{(m)}$	invariant	variable
$\{J_i^{(m)}\}$	invariant	variable

4. Characteristics and simple waves

In § 1 we observed that equation (1.13) defines the characteristic direction and it is now obvious that there exist M different directions. We shall denote the kth characteristic as $C^{(k)}$, where its direction is given by

$$\sigma_{(k)} \equiv (\mathrm{d}\tau/\mathrm{d}x)_{\omega_{(k)}} = \epsilon + (1-\epsilon)\,\omega_{(k)}/D \tag{4.1}$$

$$= \epsilon + (1-\epsilon)\,\Lambda_{(k)}/D^2. \tag{4.2}$$

Applying equation (3.14) or (3.18), we find that

$$\epsilon < \sigma_{(1)} < \sigma_{(2)} < \dots < \sigma_{(M-1)} < \sigma_{(M)}. \tag{4.3}$$

Note that ϵ corresponds to the reciprocal of the fluid velocity while $\sigma_{(k)}$ represents the reciprocal of the propagation speed of a disturbance. (The term 'disturbance' will be used to represent a discontinuity in some derivatives.)

It is well known that a region of constant state in the physical plane is bounded by C-characteristics, necessarily straight lines because $\sigma_{(k)}$ remains constant for every k (Lax 1957). Since a constant state has a point image in $\Phi(M)$, it follows from § 1 that the solution adjacent to a constant state must have its image along a Γ emanating from the point image and thus one set of Riemann invariants is constant. This leads us to

Theorem 4.1. If $\mathscr{B}$ is part of the boundary of a constant state and is a $C^{(k)}$, then all (k)-Riemann invariants on the other side of $\mathscr{B}$ are constant.

Proof. Suppose the (l)-Riemann invariants remain the same across $\mathscr{B}$ where $l \neq k$. Since then $\Lambda_{(l)}$ is constant and $\omega_{(l)}$ is held constant along a $C^{(l)}$ (cf. equation (4.1)), it follows from equation (3.17) that D remains constant along a $C^{(l)}$ and so every ϕ_i is also constant. In figure 1 consider a point P on $\mathscr{B}$ and draw the $C^{(l)}$ passing the point P. Since $\sigma_{(l)} \neq \sigma_{(k)}$ and the $C^{(l)}$, carrying constant values of $\{\phi_i\}$, remains straight across $\mathscr{B}$, we encounter a contradiction that $\mathscr{B}$ is not the boundary.

Consequently, we must have $l = k$ and this establishes the theorem.

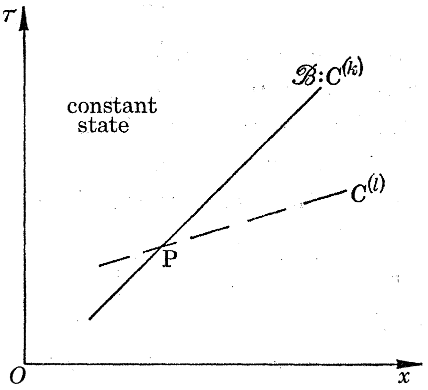


Figure 1. Solution adjacent to a constant state.

We may now introduce the following definition of a simple wave.

Definition (Lax 1957). A continuous solution in a region of the physical plane for which all (k)-Riemann invariants are constant is called a (k)-simple wave.

According to this definition, theorem 1 may be rephrased as follows:

Corollary. The solution adjacent to a constant state bounded by a $C^{(k)}$ is a (k)-simple wave and has its image along the $\Gamma^{(k)}$ issuing from the point image of the constant state.

In a (k)-simple wave region, there exists a one-parameter family of solutions

$$\phi_i - \phi_i^\circ = J_i^{(k)}(D - D^\circ) \quad (i = 1, 2, \ldots, M). \tag{4.4}$$

Also $\sigma_{(k)}$ is a monotone function of D because $\Lambda_{(k)}$ is constant. Furthermore, every $C^{(k)}$ is straight, since the condition that $\omega_{(k)}$ is held constant entails the fact that D and so also the ϕ_i remain constant along it. These arguments may be expressed in the form of

Theorem 4.2. A (k)-simple wave region is covered by a family of straight $C^{(k)}$.

In a (k)-simple wave, it is required that

$$\frac{\partial\sigma_{(k)}}{\partial x} = \frac{\mathrm{d}\sigma_{(k)}}{\mathrm{d}D}\frac{\partial D}{\partial x} < 0 \tag{4.5}$$

for otherwise the characteristic $C^{(k)}$ would overlap. On the other hand, from equations (4.2) and (4.4), we have

$$\frac{\mathrm{d}\sigma_{(k)}}{\mathrm{d}D} < 0, \tag{4.6}$$

$$\frac{\mathrm{d}\phi_i}{\mathrm{d}D} = J_i^{(k)}\begin{cases} < 0 & (i < k), \\ > 0 & (i \geqslant k). \end{cases} \tag{4.7}$$

In addition, we observe that

$$\omega_{(k)}D = \Lambda_{(k)} = \text{constant}. \tag{4.8}$$

Consequently, we have

Theorem 4.3. In a (k)-simple wave, D and ϕ_i for $i \geqslant k$ increase in the x-direction while $\omega_{(k)}$ and ϕ_i for $i < k$ decrease in the x-direction.

Corollary. In a (k)-simple wave, the coverage Θ increases in the x-direction.

5. SHOCK WAVES

If it happens that

$$\frac{\partial\sigma_{(k)}}{\partial x} > 0 \quad \text{or} \quad \frac{\partial D}{\partial x} < 0, \tag{5.1}$$

then the characteristics would overlap and the solution could not be determined uniquely. This can be resolved by allowing the discontinuities in the solution itself.

At a discontinuity equation (1.1) is no longer valid and must be replaced by conservation equations expressing the fact that the discontinuity propagates with such a speed that there is no accumulation of material or energy at the discontinuity. Therefore, we have

$$\sigma^{\mathrm{s}} \equiv \left(\frac{\mathrm{d}\tau}{\mathrm{d}x}\right)^{\mathrm{s}} = \frac{[f_i]}{[c_i]} \tag{5.2}$$

for any i, where σ^{s} is the reciprocal of the propagation speed of the discontinuity and the symbol [ ] denotes the jump of the quantity enclosed across the discontinuity. Equation (5.2) is the generalized Rankine–Hugoniot relation.

Since adsorption equilibrium is established, σ^s is the same for all i and therefore the following compatibility condition must be satisfied:

$$\frac{[f_1]}{[c_1]} = \frac{[f_2]}{[c_2]} = \dots = \frac{[f_M]}{[c_M]}. \tag{5.3}$$

Equations (5.2) and (5.3) together form a system of M algebraic equations. Hence, given the state on one side, the state on the other side can be determined if one of the concentrations or the value of σ^s is known.

These conditions, however, are not sufficient to determine the physically relevant solution since an ambiguity still exists concerning the direction of jumps. More generally, it is well known that the solution of the system (1.1), defined in the sense of weak solutions (Lax 1954), is not uniquely determined by the data, equation (1.8), until we introduce an additional condition that regulates the direction of any jump discontinuities. Such a condition, which is usually called the 'entropy' condition, is obtained not from the conservation law for a discontinuity but from arguments based on the conservation law for a continuous field.

For the present problem the 'entropy' condition can be deduced directly from equation (5.1) which originated from equation (1.1):

THEOREM 5.1 ('Entropy' condition). Across a discontinuity† the parameter D and so the coverage Θ decrease from the left-hand side to the right.

In the limit as a discontinuity becomes very weak, the compatibility condition (5.3) is reduced to the fundamental differential equation (1.14). This implies that the image of a discontinuity is tangent to a Γ at each end and thus there may exist M different kinds. Recalling the fact that Γ's are straight, we assert that the image of a discontinuity lies on a Γ and so equation (5.3) is an integral of equation (1.14). Along a $\Gamma^{(k)}$, for instance, we have

$$\left.\begin{aligned} &K_i[c_i]/J_i^{(k)} = K_j[c_j]/J_j^{(k)} \quad (i \neq j), \\ \text{and} \qquad &\mathscr{D}f_i = \frac{\mathscr{D}c_i}{\mathscr{D}c_j} Df_j = \frac{K_j J_i^{(k)}}{K_i J_j^{(k)}} \mathscr{D}f_j \quad (i \neq j). \end{aligned}\right\} \tag{5.4}$$

Integrating the latter relation along the $\Gamma^{(k)}$, we obtain

$$K_i[f_i]/J_i^{(k)} = K_j[f_j]/J_j^{(k)} \quad (i \neq j)$$

and comparing with the former, we find that equation (5.3) is satisfied. This is true for any k and hence there exist M different solutions of equation (5.3). It can be further shown that there are only M and no more solutions (Rhee 1968). Consequently there follows

THEOREM 5.2. A discontinuity necessarily has its image along a Γ and there are M different kinds.

Consider a discontinuity with image on a $\Gamma^{(k)}$. Since then the (k)-Riemann invariants remain constant across it, the states on both sides can be connected by a one-parameter family

$$[\phi_i] = J_i^{(k)}[D] \quad (i = 1, 2, \dots, M) \tag{5.5}$$

and the propagation direction is given by

$$\sigma^s_{(k)} \equiv \left(\frac{d\tau}{dx}\right)^s_{(k)} = \epsilon + (1-\epsilon)\,\Lambda_{(k)}/D^l D^r, \tag{5.6}$$

---

† The characteristic field $\sigma_{(k)}$ being non-degenerate, every discontinuity may be identified with a shock. This becomes obvious in the later part.

where a superscript l or r denotes the left- or right-hand side of the discontinuity, respectively, and

$$\begin{aligned}\Lambda_{(k)} \equiv \omega^{\mathrm{l}}_{(k)} D^{\mathrm{l}} &= NK_i(D^{\mathrm{l}} - \phi^{\mathrm{l}}_i / J^{(k)}_i) \\ = \omega^{\mathrm{r}}_{(k)} D^{\mathrm{r}} &= NK_i(D^{\mathrm{r}} - \phi^{\mathrm{r}}_i / J^{(k)}_i).\end{aligned} \tag{5.7}$$

Suppose that two discontinuities of different kinds are adjacent to each other: this is shown in figure 2 as a diagram of D and x for a fixed τ. Applying equations (5.6) and (5.7) to each discontinuity, one can show that

$$\sigma^{\mathrm{s}}_{(k+1)} - \sigma^{\mathrm{s}}_{(k)} = (1-\epsilon)\,\frac{NK_k}{D^{\circ}}\left\{\frac{\phi^{\mathrm{r}}_k}{D^{\mathrm{r}} J^{(k)}_k} - \frac{\phi^{\mathrm{l}}_k}{D^{\mathrm{l}} J^{(k+1)}_k}\right\} > 0,$$

because $J^{(k)}_k > 0$ and $J^{(k+1)}_k < 0$. This is true for any k and thus

$$\epsilon < \sigma^{\mathrm{s}}_{(1)} < \sigma^{\mathrm{s}}_{(2)} < \ldots < \sigma^{\mathrm{s}}_{(M-1)} < \sigma^{\mathrm{s}}_{(M)}. \tag{5.8}$$

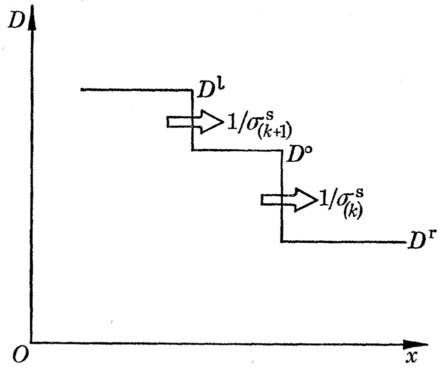


FIGURE 2. Two discontinuities of different kinds.

Since $D^{\mathrm{l}} > D^{\mathrm{r}}$ from the 'entropy' condition, it follows that

$$\sigma^{\mathrm{l}}_{(k)} < \sigma^{\mathrm{s}}_{(k)} < \sigma^{\mathrm{r}}_{(k)}. \tag{5.9}$$

For completeness, we also compare $\sigma^{\mathrm{s}}_{(k)}$ with $\sigma^{\mathrm{l}}_{(k+1)}$ as well as $\sigma^{\mathrm{r}}_{(k-1)}$ to obtain, by applying equations (5.6) and (5.7), the inequality

$$\sigma^{\mathrm{l}}_{(k+1)} > \sigma^{\mathrm{s}}_{(k)} > \sigma^{\mathrm{r}}_{(k+1)}. \tag{5.10}$$

According to Lax (1957), equations (5.9) and (5.10) are precisely the inequalities characterizing shocks and thus we have

THEOREM 5.3. Every discontinuity appearing in this study is a shock.

A shock, if its image lies on a $\Gamma^{(k)}$, is called a (k)-shock and its propagation path a (k)-shock line $S^{(k)}$. The concentration field along an $S^{(k)}$ is called a (k)-shock wave.

6. ENTROPY CHANGE ACROSS A SHOCK

In this section we shall prove that the 'entropy' condition given by theorem 5.1 does not violate the second law of thermodynamics.

Consider a finite interval of the column, $a^{\mathrm{l}}(\tau) < x < a^{\mathrm{r}}(\tau)$, that contains a (k)-shock at the time τ. Denoting the shock position by $x = x^{\mathrm{s}}(\tau)$, we remark that

$$\frac{\mathrm{d}x^{\mathrm{s}}}{\mathrm{d}\tau} = \frac{1}{\sigma^{\mathrm{s}}_{(k)}}, \tag{6.1}$$

$$\frac{\mathrm{d}a^{\mathrm{l}}}{\mathrm{d}\tau} = \frac{\mathrm{d}a^{\mathrm{r}}}{\mathrm{d}\tau} = \frac{1}{\epsilon} \tag{6.2}$$

for the fluid phase and
$$\frac{\mathrm{d}a^{\mathrm{l}}}{\mathrm{d}\tau} = \frac{\mathrm{d}a^{\mathrm{r}}}{\mathrm{d}\tau} = 0 \tag{6.3}$$
for the solid phase since it is stationary.

The equation of continuity for the species A_i is then given by
$$\frac{\mathrm{d}}{\mathrm{d}\tau}\int_{a^{\mathrm{l}}}^{a^{\mathrm{r}}} f_i(x,\tau)\,\mathrm{d}x = 0 \quad (i = 1, 2, \ldots, M). \tag{6.4}$$

The integrand being discontinuous, equation (6.4) can be rewritten by applying Reynold's transport theorem as follows:
$$\int_a^{a^{\mathrm{r}}} \frac{\partial f_i}{\partial\tau}\,\mathrm{d}x + \left\{f_i(a^{\mathrm{r}},\tau)\,\frac{\mathrm{d}a^{\mathrm{r}}}{\mathrm{d}\tau} - f_i(a^{\mathrm{l}},\tau)\,\frac{\mathrm{d}a^{\mathrm{l}}}{\mathrm{d}\tau}\right\} - \{f_i(x^{\mathrm{s}}+0,\tau) - f_i(x^{\mathrm{s}}-0,\tau)\}\,\frac{\mathrm{d}x^{\mathrm{s}}}{\mathrm{d}\tau} = 0.$$

We then introduce equations (1.2), (6.1), (6.2) and (6.3) and take the limit as $a^{\mathrm{r}} - a^{\mathrm{l}} \to 0$ to obtain
$$\frac{(1-\epsilon)}{\sigma^{\mathrm{s}}_{(k)}}\left\{\frac{\Lambda_{(k)}}{D^{\mathrm{l}}D^{\mathrm{r}}}\,(c^{\mathrm{r}}_i - c^{\mathrm{l}}_i) - (n^{\mathrm{r}}_i - n^{\mathrm{l}}_i)\right\} = 0$$
or
$$\mathscr{M}^{(k)}_i \equiv \frac{(1-\epsilon)}{\sigma^{\mathrm{s}}_{(k)}}\left\{\frac{\Lambda_{(k)}}{D^{\mathrm{l}}D^{\mathrm{r}}}\,c_i - n_i\right\} = \text{constant} \quad (i = 1, 2, \ldots, M), \tag{6.5}$$
where $\mathscr{M}^{(k)}_i$ represents the molar flux of A_i through a (k)-shock. Equation (6.5) is consistent with the previous result; cf. equations (5.5) and (5.7).

Now applying equation (5.7), one can show that
$$\mathscr{M}^{(k)}_i = -\frac{(1-\epsilon)}{\sigma^{\mathrm{s}}_{(k)}}\,\frac{n^{\mathrm{l}}_i n^{\mathrm{r}}_i}{NJ^{(k)}_i}\begin{cases} > 0 & (i < k), \\ < 0 & (i \geqslant k). \end{cases} \tag{6.6}$$

This equation, when combined with the 'entropy' condition, implies that at a (k)-shock the molar flux of A_i is in the direction of increasing coverage Θ if $i \geqslant k$.

Since the process is isothermal, the entropy change across a (k)-shock can be expressed in the form
$$T[S]^{\mathrm{l}}_{\mathrm{r}} = [H]^{\mathrm{l}}_{\mathrm{r}} - [G]^{\mathrm{l}}_{\mathrm{r}}, \tag{6.7}$$
in which $[S]^{\mathrm{l}}_{\mathrm{r}}$ denotes the difference $S^{\mathrm{l}} - S^{\mathrm{r}}$ and
$$H = \sum_{i=1}^{M}\{\epsilon c_i h_i + (1-\epsilon)\,n_i H_i\}, \tag{6.8}$$
$$G = \sum_{i=1}^{M}\mu_i f_i, \tag{6.9}$$
where h_i or H_i is the molar enthalpy of A_i in the fluid or solid phase, respectively, and μ_i is the chemical potential of A_i.

We note that h_i and H_j remain the same across a shock and thus we have
$$[H]^{\mathrm{l}}_{\mathrm{r}} = \lim_{a^{\mathrm{r}}-a^{\mathrm{l}}\to 0}\frac{\mathrm{d}}{\mathrm{d}\tau}\int_{a^{\mathrm{r}}}^{a^{\mathrm{l}}} H\,\mathrm{d}x$$
$$= \frac{(1-\epsilon)}{\sigma^{\mathrm{s}}_{(k)}}\sum_{i=1}^{M}\left\{\frac{\Lambda_{(k)}}{D^{\mathrm{l}}D^{\mathrm{r}}}\,[c_i]^{\mathrm{l}}_{\mathrm{r}}\,h_i - [n_i]^{\mathrm{l}}_{\mathrm{r}}\,H_i\right\}$$
which, upon applying equations (5.5) and (6.5), may be reduced to
$$[H]^{\mathrm{l}}_{\mathrm{r}} = \frac{(1-\epsilon)}{\sigma^{\mathrm{s}}_{(k)}}\,\frac{\Lambda_{(k)}}{D^{\mathrm{l}}D^{\mathrm{r}}}\,[D]^{\mathrm{l}}_{\mathrm{r}}\sum_{i=1}^{M}(-\Delta H_i)\,\frac{J^{(k)}_i}{K_i}, \tag{6.10}$$

where
$$-\Delta H_i \equiv h_i - H_i > 0. \tag{6.11}$$

Since $J_i^{(k)} < 0$ for $i < k$ while $J_i^{(k)} > 0$ for $i \geqslant k$ and it follows from equations (2.2) and (2.3) that $(-\Delta H_i) > (-\Delta H_j)$ for $i > j$, there exists a lower bound of the summation:

$$\sum_{i=1}^{M} (-\Delta H_i) \frac{J_i^{(k)}}{K_i} > (-\Delta H_{k-1}) \sum_{i=1}^{M} \frac{J_i^{(k)}}{K_i}.$$

Furthermore, each term $J_i^{(k)}/K_i$ is invariant along the $\Gamma^{(k)}$ (the image of shock) which intersects at one end the subspace $\omega_{(k)} = NK_k$ in the space $\Omega(M)$. At the point of intersection $\{\phi_i^\circ : \phi_k \equiv 0\}$, we have

$$J_i^{(k)} = \frac{K_i n_i^\circ}{N(K_i - K_k)} \quad (i \neq k),$$
$$J_k^{(k)} = 1 - \sum_{i \neq k} J_i^{(k)}$$

and thus
$$\sum_{i=1}^{M} \frac{J_i^{(k)}}{K_i} = \frac{1}{K_k} + \sum_{i \neq k} \frac{n_i^\circ}{N(K_i - K_k)} \left(1 - \frac{K_i}{K_k}\right)$$
$$= \frac{1}{K_k}\left(1 - \sum_{i \neq k} \frac{n_i^\circ}{N}\right) = \frac{1}{K_k D^\circ} > 0. \tag{6.12}$$

Hence
$$[H]_{\mathrm{r}}^{\mathrm{l}} > 0. \tag{6.13}$$

On the other hand, the chemical potential μ_i jumps from one side of the (k)-shock to the other, whereas it assumes the same value on both phases because of the equilibrium. Therefore, we have

$$[G]_{\mathrm{r}}^{\mathrm{l}} = \lim_{a^{\mathrm{r}} - a^{\mathrm{l}} \to 0} \frac{\mathrm{d}}{\mathrm{d}\tau} \int_{a^{\mathrm{r}}}^{a^{\mathrm{l}}} G\,\mathrm{d}x$$
$$= \frac{(1-\epsilon)}{\sigma_{(k)}^{\mathrm{s}}} \sum_{i=1}^{M} \left\{ \frac{\Lambda_{(k)}}{D^{\mathrm{l}} D^{\mathrm{r}}} [\mu_i c_i]_{\mathrm{r}}^{\mathrm{l}} - [\mu_i n_i]_{\mathrm{r}}^{\mathrm{l}} \right\}$$
$$= \sum_{i=1}^{M} \mathscr{M}_i^{(k)} [\mu_i]_{\mathrm{r}}^{\mathrm{l}}. \tag{6.14}$$

To obtain the last form equation (6.5) has been used. Recalling the one-parameter family (5.5) and equation (6.6), we observe that every term in the summation becomes negative and thus

$$[G]_{\mathrm{r}}^{\mathrm{l}} < 0. \tag{6.15}$$

Consequently, we obtain
$$[S]_{\mathrm{r}}^{\mathrm{l}} > 0. \tag{6.16}$$

This implies that entropy increases in the direction of increasing total coverage Θ, and thus the 'entropy' condition is consistent with the second law of thermodynamics.

7. CONSTRUCTION OF SOLUTION

We will be concerned here with how to combine the results obtained in the previous sections to construct the solution of a Riemann's problem. It is clear that the initial discontinuity has its range of influence centred at the origin in the physical plane and this region is our main interest because outside we simply have two constant states corresponding to the initial and entry data, respectively. It is, therefore, convenient to construct the wave solution in the physical plane, from which the concentration profile can be established without difficulty.

Given the initial and entry data $\{\phi_m^{\mathrm{i}}\}$ and $\{\phi_m^{\mathrm{e}}\}$, we begin with the homeomorphism (3.13) to determine the sets $\{\omega_{(k)}^{\mathrm{i}}\}$ and $\{\omega_{(k)}^{\mathrm{e}}\}$, which are the images of data in the space $\Omega(M)$.

(*a*) *Existence and uniqueness*

In $\Omega(M)$ the images of the initial and entry data would lie on two different points, I and E respectively, and thus the image of a solution is given by a continuous path that connects I and E by a set of Γ's. A $\Gamma^{(k)}$ being straight and parallel to the $\omega_{(k)}$-axis, such a path always exists and hence a solution.

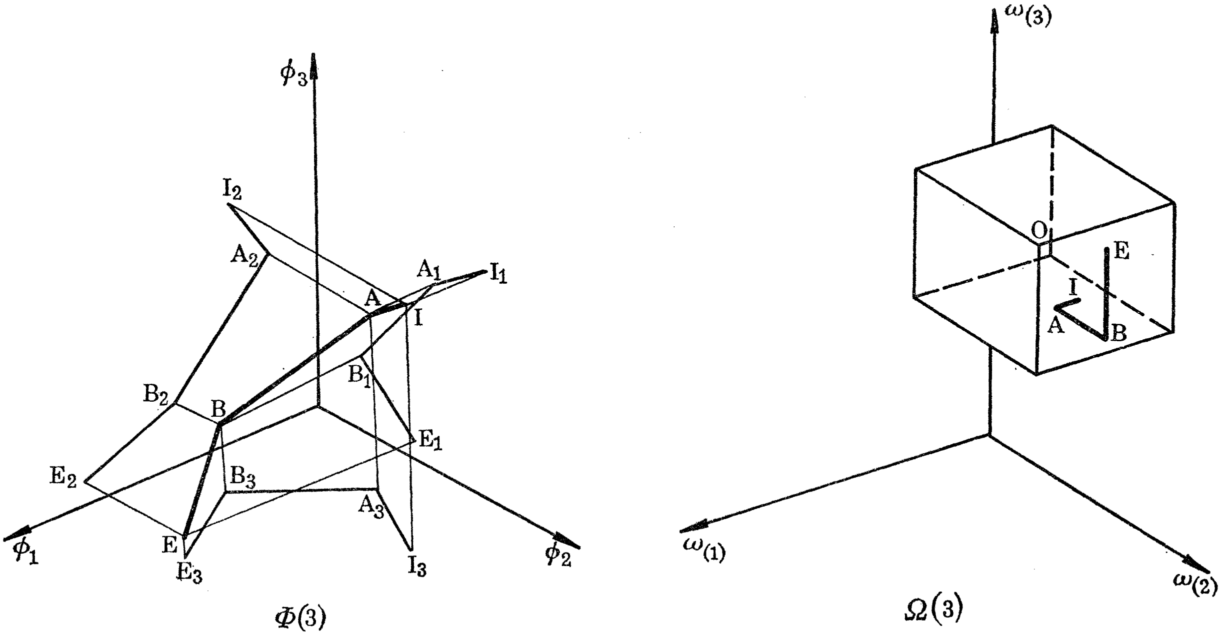


FIGURE 3. Schematic portraits of a solution in the spaces $\Phi(3)$ and Ω (3).

Before making any general observations the situation for $M = 3$, as illustrated in figure 3, may serve to show the matter more clearly. The points I and E represent the initial and entry conditions and if we pass from I, the state when $\tau = 0$, to E, the state when $x = 0$, we shall be moving counterclockwise in the (x, τ)-plane. Now the inequalities on the $\sigma_{(k)}$ and $\sigma^{s}_{(k)}$ show that we must use a sequence of $\Gamma^{(k)}$'s in the order $k = 1, 2, 3$ in passing from I to E. In $\Omega(3)$ there is clearly a unique path IABE consisting of segments of lines parallel to the axes of $\omega_{(1)}, \omega_{(2)}, \omega_{(3)}$ in that order, and this path has an image in $\Phi(3)$. If the coverage increases in going from I to A then it must be a (1)-shock since from theorem 5.1 D decreases from left to right of the shock (i.e. it increases as we move counterclockwise over the physical plane). On the other hand, if the coverage decreases then by theorem 4.2 we have a (1)-simple wave. Thus for each segment of the path we have a simple test of whether it represents a continuous or discontinuous transition between states.

In the general situation, the path may consist of many segments of Γ's of various kinds. To a $\Gamma^{(k)}$ there corresponds either a (k)-simple wave centred at the origin, which is represented by a family of straight $C^{(k)}$, or a (k)-shock wave, which is given by a straight (k)-shock line $S^{(k)}$, depending upon the parameter D. It then follows from the inequalities (4.3), (5.8), (5.9), and (5.10) that the path must be composed of at most M segments each of which is part of a Γ of a distinct kind and which are arranged in the order of ascending (k) as one passes from I to E. Clearly such a path always exists and is unique. This establishes the existence of a unique solution.

The general situation is shown in figure 4, where it is seen that there is a succession of waves which are either shocks (i.e. degenerate waves such as $S^{(1)}$ and $S^{(k)}$) or centred simple waves (as $C^{(2)}$, $C^{(k-1)}$, $C^{(M)}$), separating regions of constant state. These states may be denoted by a bracketed index, so that $\phi_m^{(k)}$ is the dimensionless concentration of the mth species between the (k)- and $(k+1)$-wave regions. Thus ϕ_m^{i}, the initial concentration, corresponds to $\phi_m^{(0)}$ and ϕ_m^{e}, the entry concentration to $\phi_m^{(M)}$. The angle between the boundaries of the initial and entry states is the range of influence of the discontinuity at the origin.

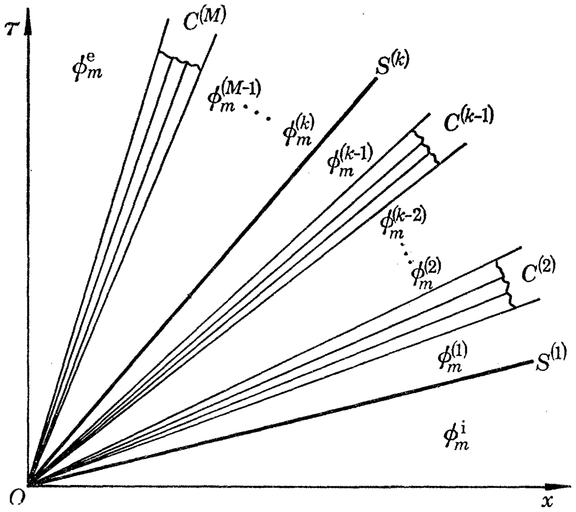


FIGURE 4. Schematic portrait of a solution in the physical plane, showing regions of constant state separated either by shock waves S or by centred simple waves C. ——, Characteristic; ——, shock line.

(b) *Constant states*

Since $\omega_{(k)}$ varies only across a (k)-wave, be it a shock wave or a simple wave, the kth constant state must correspond to the vortex

$$(\omega_{(1)}^{\mathrm{e}}, \omega_{(2)}^{\mathrm{e}}, \ldots, \omega_{(k)}^{\mathrm{e}}, \omega_{(k+1)}^{\mathrm{i}}, \ldots, \omega_{(M)}^{\mathrm{i}}) \tag{7.1}$$

of the path between I and E in $\Omega(M)$. The inverse mapping given by equation (3.19) may then be used to determine the concentrations $\phi_m^{(k)}$ in the kth constant state.

Another approach is motivated by the recurrence formulae

$$\Lambda_{(k)} = \omega_{(k)}^{\mathrm{i}}\, D^{(k-1)} = \omega_{(k)}^{\mathrm{e}} D^{(k)} \quad (k = 1, 2, \ldots, M) \tag{7.2}$$

and

$$\phi_m^{(k-1)} - J_m^{(k)}\, D^{(k-1)} = \phi_m^{(k)} - J_m^{(k)}\, D^{(k)}$$

for

$$\frac{\phi_m^{(k-1)}}{1 - NK_m/\omega_{(k)}^{\mathrm{i}}} = \frac{\phi_m^{(k)}}{1 - NK_m/\omega_{(k)}^{\mathrm{e}}} \quad (k = 1, 2, \ldots, M). \tag{7.3}$$

From these we obtain

$$D^{(k)} = D^{\mathrm{i}} \prod_{j=1}^{k} \frac{\omega_{(j)}^{\mathrm{i}}}{\omega_{(j)}^{\mathrm{e}}} = D^{\mathrm{e}} \prod_{j=k+1}^{M} \frac{\omega_{(j)}^{\mathrm{e}}}{\omega_{(j)}^{\mathrm{i}}} \tag{7.4}$$

and

$$\phi_m^{(k)} = \phi_m^{\mathrm{i}} \prod_{j=1}^{k} \frac{1 - NK_m/\omega_{(j)}^{\mathrm{e}}}{1 - NK_m/\omega_{(j)}^{\mathrm{i}}} = \phi_m^{\mathrm{e}} \prod_{j=k+1}^{M} \frac{1 - NK_m/\omega_{(j)}^{\mathrm{i}}}{1 - NK_m/\omega_{(j)}^{\mathrm{e}}} \quad (m = 1, 2, \ldots, M) \tag{7.5}$$

for $k = 1, 2, \ldots, M$.

(c) *Wave solutions*

Once every constant state is determined, it is straightforward to construct the wave solutions. For the (k)-wave, where $1 \leqslant k \leqslant M$, we proceed as follows:

(i) If $\omega_{(k)}^{\mathrm{e}} > \omega_{(k)}^{\mathrm{i}}$, we apply equation (4.2)

$$\sigma_{(k)} = \epsilon + (1-\epsilon)\, \Lambda_{(k)}/D^2 \quad \text{for} \quad D^{(k)} \leqslant D \leqslant D^{(k-1)} \tag{7.6}$$

with $\Lambda_{(k)} = \omega^{\mathrm{e}}_{(k)} D^{(k)}$ and draw as many straight $C^{(k)}$'s as desired from the origin to generate the centered (k)-simple wave. The constant values of $\{\phi_i\}$ along each $C^{(k)}$ are determined from equation (4.4):

$$\phi_m = \phi^{(k)}_m - J^{(k)}_m (D - D^{(k)}) \quad (m = 1, 2, \dots, M) \tag{7.7}$$

for $D^{(k)} < D < D^{(k-1)}$ with $J^{(k)}_m = K_m n^{(k)}_m / (NK_m - \omega^{\mathrm{e}}_{(k)})$.

(i) If $\omega^{\mathrm{e}}_{(k)} < \omega^{\mathrm{i}}_{(k)}$, we apply equation (5.6) in the form of

$$\sigma^{\mathrm{s}}_{(k)} = \epsilon + (1 - \epsilon)\, \omega^{\mathrm{i}}_{(k)} / D^{(k)} \tag{7.8}$$

and draw a straight $S^{(k)}$ from the origin to give the (k)-shock wave.

(ii) If $\omega^{\mathrm{e}}_{(k)} = \omega^{\mathrm{i}}_{(k)}$, then by equation (7.2) we must have

$$D^{(k)} = D^{(k-1)} \tag{7.9}$$

and this implies that the (k)-wave does not appear in the solution. For such a degenerate case, the image in $\Omega(M)$ will not contain a segment of $\Gamma^{(k)}$.

(*d*) *Special cases*

If one or more of the solute species are absent from the initial bed or from the entry mixture, it is to be expected that some interesting features may appear. These are certainly of potential interest in the practice of chromatography and thus worth examining in detail.

In § 3 we learned that the subspace $\pi_m : \phi_m = 0$ consists of two planes $\omega_{(m)} = NK_m$ and $\omega_{(m+1)} = NK_m$ in the space $\Omega(M)$; the case $m = M$ is exceptional and π_M is the plane $\omega_{(M)} = NK_M$ in $\Omega(M)$. This implies that π_m has connexions with the outside, $\Omega(M) - \pi_m$, only through $\Gamma^{(m)}$ or $\Gamma^{(m+1)}$. Furthermore, it is observed that $\omega_{(m)}$ increases along a $\Gamma^{(m)}$ toward π_m while $\omega_{(m+1)}$ decreases along a $\Gamma^{(m+1)}$ towards π_m. When associated with theorems 4.3 and 5.1, these arguments lead us to

THEOREM 7.1.

(i) A particular species A_m can be exhausted through an (m)-shock wave or an $(m+1)$-simple wave.

(ii) A particular species A_m can emerge through an (m)-simple wave or an $(m+1)$-shock wave.

(iii) The species A_M can be exhausted through an (M)-shock wave and emerge through an (M)-simple wave.

The last statement is obvious from the fact that π_M consists of a single plane $\omega_{(M)} = NK_M$ in $\Omega_{(M)}$. It is not difficult to deduce from the theorem the following corollary:

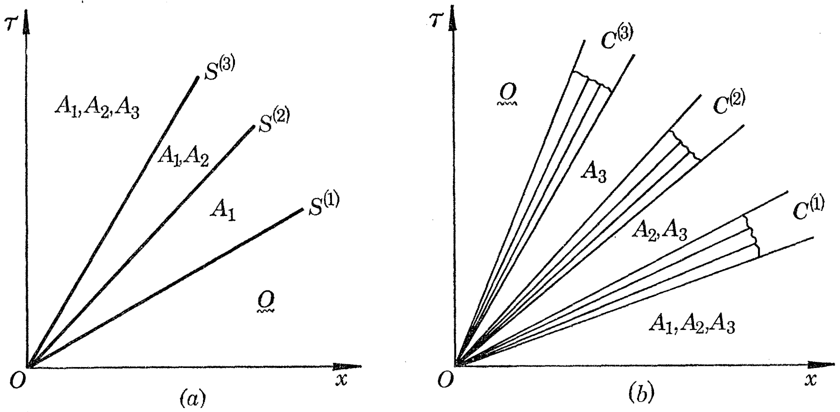
Corollary

(i) A particular species A_m, once it is exhausted, cannot appear again in the front.

(ii) At a particular position in the column, only one solute can vanish or emerge at one time.

Consider now the conventional adsorption process (formation of a chromatogram) for which the initial bed is clean. The entry mixture contains M solute species and each species must vanish somewhere in the column. It follows directly from theorem 7.1 that A_m must be exhausted through the (m)-shock wave for $1 \leqslant m \leqslant M$. In other words, each species disappears successively in the order of decreasing adsorptivity along the column. This fact was proved for an arbitrary adsorption isotherm by De Vault (1943). The physical plane portrait is shown for $M = 3$ in figure 5(*a*).

For the conventional desorption process (development of a chromatogram) we have the pure solvent flowing into the column, whereas the initial bed is a uniform chromatogram of M solute species. Therefore each species must emerge somewhere in the column. According to theorem 7.1, A_m must emerge through the (m)-simple wave for $1 \leqslant m \leqslant M$ and thus the physical plane portrait would be as shown in figure 5 (*b*).



(*a*) (*b*)

FIGURE 5. (*a*) The saturation of a column $(M = 3)$. (*b*) The elution of a column $(M = 3)$.

Another interesting example is produced by the alternating data; i.e.

$$\left.\begin{array}{lll} \phi^{\mathrm{i}}_m = 0 & \text{if} & m \text{ is even} \\ \text{and} \quad \phi^{\mathrm{e}}_m = 0 & \text{if} & m \text{ is odd;} \end{array}\right\} \tag{7.10}$$

or vice versa. It is clear that, along the column, exhaustion of species A_m alternates with emergence of species A_{m-1}. According to theorem 7.1, however, A_{m-1} may emerge through the (m)-shock wave or be exhausted through the (m)-simple wave while in these two kinds of waves A_m is respectively exhausted or emerges. A number of different cases can occur depending upon the data specified; these are suggested in the basic profile-patterns for $M = 3$ by Klein, Tondeur & Vermeulen (1967). In any case, once the sets $\{\omega^{\mathrm{e}}_{(k)}\}$ and $\{\omega^{\mathrm{i}}_{(k)}\}$ are determined, construction of a solution is fairly straightforward. Moreover, half of $\{\omega_{(k)}\}$ are given by NK_i where $\phi_i = 0$ (cf. example 4 in the next subsection).

(*e*) *Numerical examples*

The following examples will serve as good illustrations of application. Since each case was considered previously, we shall present the solutions in the form of graphs with little further discussion. All have in common the following parameter values:

$$\epsilon = 0.4,$$
$$N = 1.0 \text{ mole/litre of adsorbent.}$$

Further information is given in the table that precedes each graph. The concentrations are given in moles per litre of fluid phase and the units of K_m are, of course, the reciprocal of concentration.

Example 1 $(M = 3)$:

m	1	2	3
K_m	5.0	7.5	10.0
c^{i}_m	0.032	0.114	0.075
c^{e}_m	0.150	0.060	0.020
$\omega^{\mathrm{i}}_{(m)}$	2.797	5.409	8.974
$\omega^{\mathrm{e}}_{(m)}$	2.445	6.667	9.586

Figure 6 shows the sequence of waves, a shock $S^{(1)}$ followed by two centred simple waves, $C^{(2)}$ and $C^{(3)}$. Values of ϕ_3 are shown on certain rays and the other values may be obtained from figure 7 which shows the profiles of ϕ_1, ϕ_2, and ϕ_3 when $\tau = 4$.

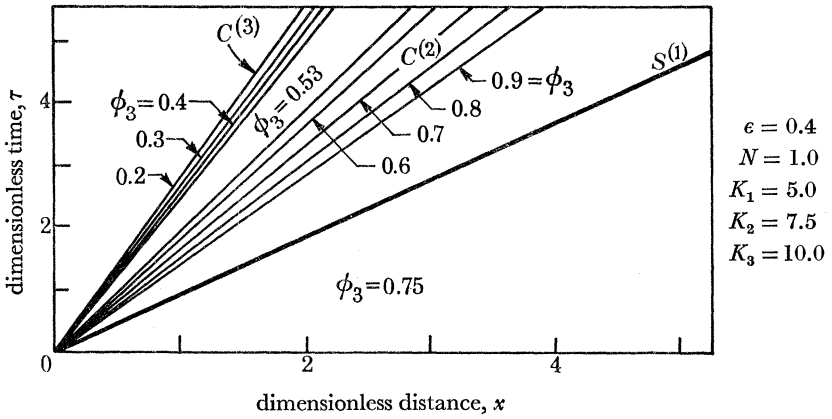


FIGURE 6. Physical plane portrait of the solution to example 1.

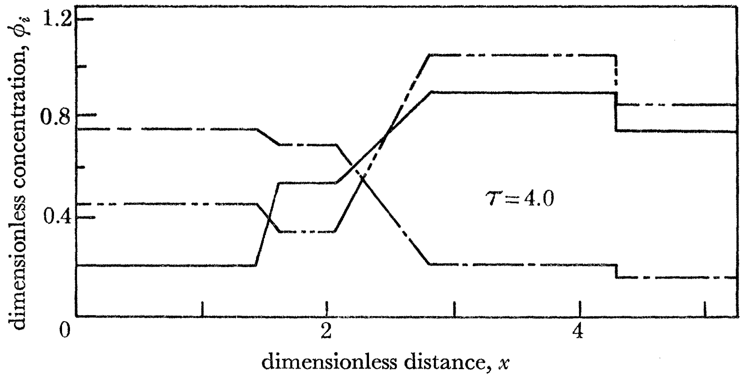


FIGURE 7. Concentration profiles at $\tau = 4.0$: example 1. — - —, Solute A_1; — - - —, solute A_2; ——, solute A_3.

Example 2 ($M = 3$):

m	1	2	3
K_m	5.0	10.0	15.0
c_m^{i}	0	0	0
c_m^{e}	0.05	0.05	0.05
$\omega_{(m)}^{\mathrm{i}}$	5.0	10.0	15.0
$\omega_{(m)}^{\mathrm{e}}$	3.387	7.050	12.563

This is the conventional saturation of a clean bed of adsorbent and three shocks divide the physical plane in the manner of figure 5(*a*). They can be seen in the lower part of figure 16 where $\tau \leqslant 3$ and the concentration profiles are shown in the first section of figure 17.

Example 3 ($M = 3$):

m	1	2	3
K_m	5.0	10.0	15.0
c_m^{i}	0.05	0.05	0.05
c_m^{e}	0	0	0
$\omega_{(m)}^{\mathrm{i}}$	3.387	7.050	12.563
$\omega_{(m)}^{\mathrm{e}}$	5.0	10.0	15.0

This is just the reverse of the previous example, representing the elution of the previously saturated column, and the physical plane is as shown in figure 5 (*b*). These two examples will be combined later in discussing the development of the chromatogram, and this particular wave is identical with the part of figure 16 which lies to the left of $S^{(3)}$.

Example 4 ($M = 4$):

m	1	2	3	4
K_m	5.0	10.0	12.5	20.0
c_m^{i}	0.04	0	0.02	0
c_m^{e}	0	0.06	0	0.04
$\omega_{(m)}^{\mathrm{i}}$	4.075	10.0	10.575	20.0
$\omega_{(m)}^{\mathrm{e}}$	5.0	5.40	12.5	15.434

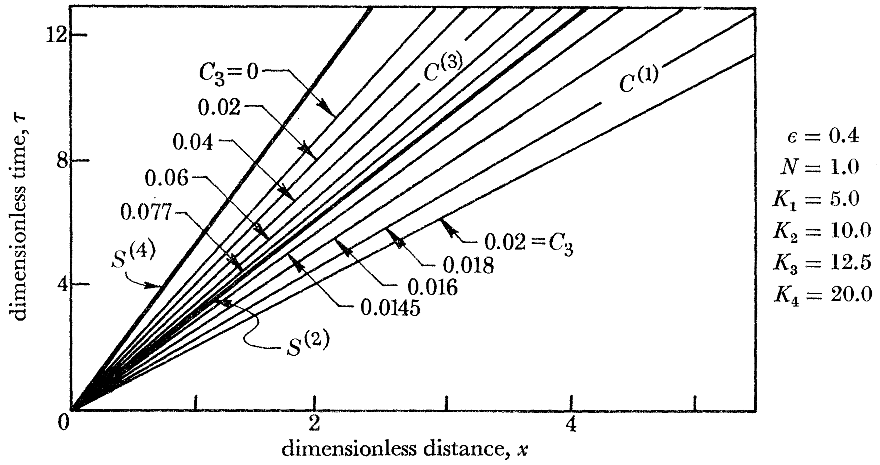


FIGURE 8. Physical plane portrait of the solution to example 4.

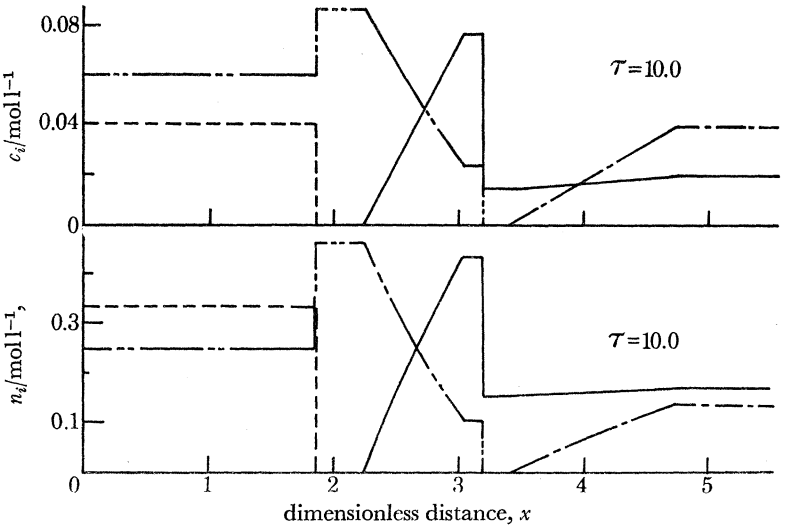


FIGURE 9. Concentration profiles at $\tau = 10.0$: example 4. ———, Solute A_1; ——·——, solute A_2; ——, solute A_3; ------, solute A_4.

In this case a bed saturated by two solutes is being eluted by a stream carrying two more strongly adsorbed solutes. A system of two simple waves and two shocks is obtained as shown in figure 8. Figure 9 shows the distribution of solutes both in the fluid and solid phases.

8. Stepwise data and patterns of interaction

The fundamental differential equation (1.14) is unchanged if one changes the origin of the coordinate system arbitrarily. Furthermore, the Riemann invariants and the characteristic parameters are determined in terms of concentrations only. It then follows that, given a jump discontinuity along the τ- or x-axis, the image of solution in $\Phi(M)$ or $\Omega(M)$ is independent of the position in the physical plane. Consequently, the simple wave theory as well as the shock wave theory can be equally well applied with the same homeomorphism (3.13) to any point in the physical plane if a discontinuity is introduced at the point.

The present theory therefore finds its natural extension to a class of problems associated with stepwise initial and/or entry data. The solution as a whole can be established by constructing the centred wave solutions separately from each point of discontinuity. This is the characteristic of hyperbolic systems. After a finite period of time, however, any two wave solutions centred at two different, but adjacent, points of discontinuity will meet each other so that an overlapped region appears in which the solution is influenced by two different sets of data at the same time. Such a phenomenon is called an interaction between waves. Comparing the physical plane portraits of simple waves and shock waves, one may classify all the probable situations as given in the following theorem. Each item is so obvious from the inequalities (4.3), (5.8), (5.9), and (5.10) that any further discussion seems superfluous.

Theorem 8.1: Patterns of intersection.

(i) Pattern I: two shock waves of the same kind necessarily interact with each other.

(ii) Pattern II: a simple wave and a shock wave of the same kind necessarily interact with each other.

(iii) Pattern III: a (k)-wave (either simple or shock) necessarily interacts with an (m)-wave, travelling behind it if $m < k$, or travelling ahead of it if $m > k$.

Corollary

(i) Two simple waves of the same kind do not interact with each other.

(ii) A (k)-wave does not interact with an (m)-wave, travelling behind it if $m > k$, or travelling ahead of it if $m < k$.

When two waves meet with each other, one may consider that a new Riemann's problem is generated. Furthermore, upon reflecting the image in $\Omega(M)$ we can establish the basic principles of interaction as follows:

(i) No penetration is allowed between waves of the same kind; i.e. a (k)-shock is simply superposed upon another (k)-shock and a (k)-simple wave is continuously absorbed by a (k)-shock.

(ii) When a (k)-wave interacts with an (m)-wave where $m \neq k$, it is clear that the image of the interaction region in $\Omega(M)$ lies completely on a plane on which only $\omega_{(k)}$ and $\omega_{(m)}$ are variable. In fact, the image is a rectangle, two adjacent sides of which are the images of waves before the interaction, while the other two represent the images after interaction (cf. figures 12 to 14). Hence, a (k)-simple or shock wave transmits across another wave of different kind to generate the transmitted (k)-simple or shock wave, respectively, on the other side. These arguments lead us to

Theorem 8.2: Basic principles of interaction.

(i) Superposition (pattern I).

Two shock waves of the same kind are instantly superposed when interacting.

(ii) Absorption (pattern II).
A simple wave is continuously absorbed by a shock wave of the same kind while interacting.
(iii) Transmission (pattern III).
Two waves of different kinds transmit across each other while interacting.

The absorption will result in a continuous decay of the shock since the simple wave is expansive and thus the process of interaction may go on indefinitely. The process of transmission, on the other hand, necessarily terminates after a finite period of time.

During the process of interaction, not only the corresponding shock line but also the characteristics involved will be curved or refracted instantly because the state of concentrations varies. This fact may be regarded as the accelerated motion of a shock or a disturbance. When a (k)-simple wave transmits across an (m)-wave where $m \neq k$, the parameter $\omega_{(k)}$ remains invariant along each $C^{(k)}$ and thus it follows from equation (4.1) that

$$\left(\frac{\partial \sigma_{(k)}}{\partial D}\right)_{\omega_{(k)}} = -(1-\epsilon)\,\omega_{(k)}/D^2 < 0. \tag{8.1}$$

Theorem 8.3. A disturbance is accelerated (or decelerated) if D increases (or decreases) as it propagates.

When a (k)-shock wave interacts with an (m)-wave, it is clear that $\Lambda_{(k)}$ remains constant if $m = k$ while both $\omega^{\mathrm{l}}_{(k)}$ and $\omega^{\mathrm{r}}_{(k)}$ remain invariant if $m \neq k$. From equations (5.6) and (5.7), we have

$$\left(\frac{\partial \sigma^{\mathrm{s}}_{(k)}}{\partial D^{\mathrm{l}}}\right)_{\Lambda_{(k)}} < 0, \quad \left(\frac{\partial \sigma^{\mathrm{s}}_{(k)}}{\partial D^{\mathrm{r}}}\right)_{\Lambda_{(k)}} < 0; \tag{8.2}$$

$$\left(\frac{\partial \sigma^{\mathrm{s}}_{(k)}}{\partial D^{\mathrm{l}}}\right)_{\omega^{\mathrm{r}}_{(k)}} < 0, \quad \left(\frac{\partial \sigma^{\mathrm{s}}_{(k)}}{\partial D^{\mathrm{r}}}\right)_{\omega^{\mathrm{l}}_{(k)}} < 0. \tag{8.3}$$

Consequently, we obtain

Theorem 8.4. A shock is accelerated (or decelerated) if D^{l} and/or D^{r} increases (or decreases) as it propagates.

9. INTERACTION ANALYSIS

For a stepwise data problem, the wave propagation inevitably leads to interactions between waves issuing from different points of discontinuity. In order to obtain the complete solution, it is necessary to analyse each interaction that may be involved. In this section we shall be concerned with separate analysis of each pattern, applications of which will be illustrated in the next section.

(a) *Superposition and absorption*

First, we shall consider the superposition of two shocks as shown in figure 10. When two shocks of the same kind meet each other, the two are instantly superposed so that the intermediate state P disappears and the new shock, being of the same kind, propagates with a constant speed given by the reciprocal of

$$\sigma^{\mathrm{s}}_{(k)} = \epsilon + (1-\epsilon)\,\Lambda_{(k)}/D^{\mathrm{l}}D^{\mathrm{r}}. \tag{9.1}$$

As an example of absorption we shall consider a (k)-simple wave overtaking a (k)-shock wave. For a more general discussion we assume that the simple wave is not centred but based on distributed data given along the τ-axis as shown in figure 11. Since the (k)-Riemann invariants remain constant everywhere, there exists a one-parameter representation of the whole solution. D^{r} remaining constant, we may identify D^{l} with D along the shock line which, in turn, corresponds to the entry data along the τ-axis. We also assume that the entry condition is prescribed by an

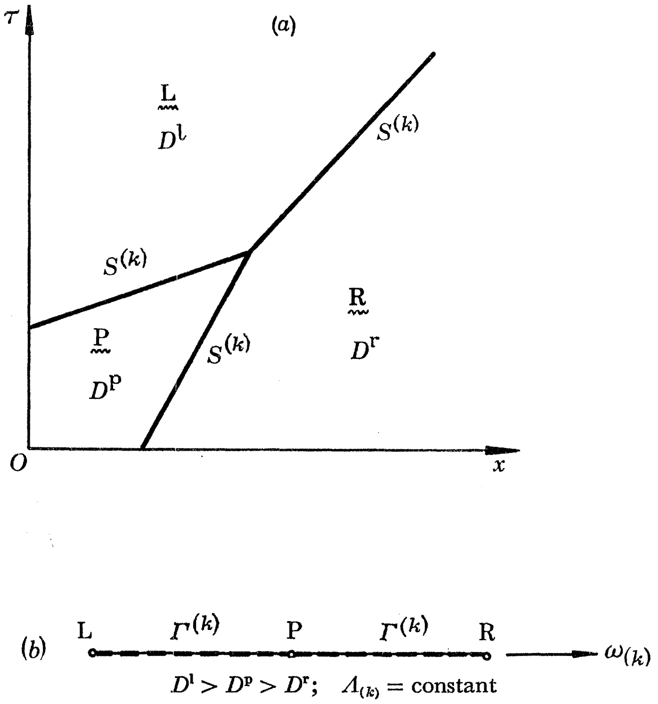


FIGURE 10. Superposition of two (k)-shocks (pattern I). (a) Physical plane portrait. (b) Image in $\Omega(M)$: – – –, image of a shock.

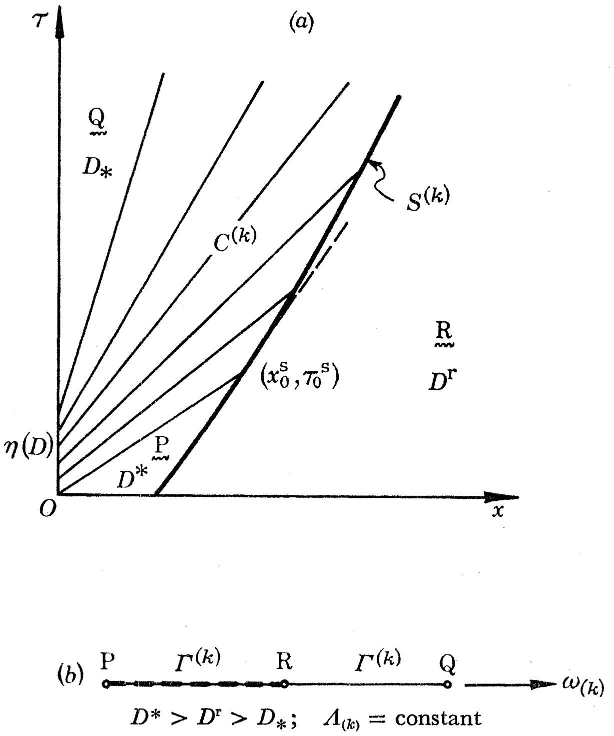


FIGURE 11. Absorption of a (k)-simple wave by a (k)-shock wave (pattern II). (a) Physical plane portrait. (b) Image in $\Omega(M)$: ——, image of a simple wave; – – – image of a shock.

invertible function so that the intercept η may be obtained in terms of D. Along the shock line, therefore, we have two equations

$$\begin{cases} \tau^{\mathrm{s}} - \eta(D) = \sigma_{(k)} x^{\mathrm{s}}, & (9.2) \\ \dfrac{\mathrm{d}\tau^{\mathrm{s}}}{\mathrm{d}x^{\mathrm{s}}} = \dfrac{\mathrm{d}\tau^{\mathrm{s}}}{\mathrm{d}D} \bigg/ \dfrac{\mathrm{d}x^{\mathrm{s}}}{\mathrm{d}D} = \sigma^{\mathrm{s}}_{(k)}, & (9.3) \end{cases}$$

which may be combined to yield

$$(\sigma^{\mathrm{s}}_{(k)}) - \sigma_{(k)}) \frac{\mathrm{d}x^{\mathrm{s}}}{\mathrm{d}D} - \frac{\mathrm{d}\sigma_{(k)}}{\mathrm{d}D} x^{\mathrm{s}} = \frac{\mathrm{d}\eta}{\mathrm{d}D}. \tag{9.4}$$

This is an ordinary differential equation which, if solved subject to the pertinent initial conditions

$$x^{\mathrm{s}} = x^{\mathrm{s}}_0 \quad \text{at} \quad D = D^*, \tag{9.5}$$

will generate x^{s} as a function of D. τ^{s} is then determined from equation (9.2). The set of x^{s} and τ^{s} so obtained is the parametric representation of the curved shock line.

Substituting equations (4.2) and (5.6) with $D^{\mathrm{l}} \equiv D$ into equation (9.4) and rearranging, we obtain

$$(D - D^{\mathrm{r}}) \frac{\mathrm{d}x^{\mathrm{s}}}{\mathrm{d}D} + \frac{2D^{\mathrm{r}}}{D} x^{\mathrm{s}} = \frac{D^{\mathrm{r}}}{(1-\epsilon) A_{(k)}} D^2 \frac{\mathrm{d}\eta}{\mathrm{d}D}.$$

This can be reduced to the form

$$\frac{\mathrm{d}}{\mathrm{d}D} \left\{ \left(\frac{D - D^{\mathrm{r}}}{D} \right)^2 x^{\mathrm{s}} \right\} = \frac{D^{\mathrm{r}}}{(1-\epsilon) A_{(k)}} (D - D^{\mathrm{r}}) \frac{\mathrm{d}\eta}{\mathrm{d}D} \tag{9.6}$$

since $D \neq D^{\mathrm{r}}$. Now integrating from $D = D^*$, we determine the solution as follows:

$$x^{\mathrm{s}}(D; A_{(k)}, D^{\mathrm{r}}) = x^{\mathrm{s}}_0 \left(\frac{1 - D^{\mathrm{r}}/D^*}{1 - D^{\mathrm{r}}/D} \right)^2 + \frac{D^{\mathrm{r}}}{(1-\epsilon) A_{(k)}} \left(\frac{D}{D - D^{\mathrm{r}}} \right)^2 \int_{D^*}^{D} (D - D^{\mathrm{r}}) \frac{\mathrm{d}\eta}{\mathrm{d}D} \mathrm{d}D$$

or, by applying integration by parts,

$$x^{\mathrm{s}}(D; A_{(k)}, D^{\mathrm{r}}) = x^{\mathrm{s}}_0 \left(\frac{1 - D^{\mathrm{r}}/D^*}{1 - D^{\mathrm{r}}/D} \right)^2 + \frac{D^{\mathrm{r}}}{(1-\epsilon) A_{(k)}} \left(\frac{D}{D - D^{\mathrm{r}}} \right)^2 \left\{ (D - D^{\mathrm{r}})\, \eta(D) - \int_{D^*}^{D} \eta(D)\, \mathrm{d}D \right\}. \tag{9.7}$$

Incidentally, we observe from equation (9.7) that $x^{\mathrm{s}} \to \infty$ as $D \to D^{\mathrm{r}}$ and thus the interaction will go on indefinitely unless $D_* > D^{\mathrm{r}}$. This implies that a shock can never disappear.

If the simple wave is centred, we may put $\eta \equiv 0$ without loss of generality to obtain

$$x^{\mathrm{s}}(D; A_{(k)}, D^{\mathrm{r}}) = x^{\mathrm{s}}_0 \left(\frac{1 - D^{\mathrm{r}}/D^*}{1 - D^{\mathrm{r}}/D} \right)^2. \tag{9.8}$$

Otherwise, we shall take the point $(x^{\mathrm{s}}_0, \tau^{\mathrm{s}}_0)$ as the new origin of the coordinate system to have $x^{\mathrm{s}}_0 \equiv 0$ and thus

$$x^{\mathrm{s}}(D; A_{(k)}, D^{\mathrm{r}}) = \frac{D^{\mathrm{r}} D^2}{(1-\epsilon) A_{(k)} (D - D^{\mathrm{r}})} \left\{ \eta(D) - \frac{1}{D - D^{\mathrm{r}}} \int_{D^*}^{D} \eta(D)\, \mathrm{d}D \right\}. \tag{9.9}$$

If convenient, we may consider that the simple wave is based on data distributed along the x-axis. We then replace equation (9.2) with the equation

$$\tau^{\mathrm{s}} = \sigma_{(k)} (x^{\mathrm{s}} - \xi(D)), \tag{9.10}$$

where $\xi(D)$ is the inverse of the data function, and apply the same procedure (Rhee 1968).

In the case when a (k)-shock wave is overtaking a (k)-simple wave, everything remains unchanged from the above except for the interchange of roles between D^{r} and D^{l} and between D^* and D_*. With these adjustments it is then possible to apply the same expressions, equations (9.8) and (9.9).

(*b*) *Transmission*

Here the two waves involved in the interaction are of different kinds and thus neither Riemann invariants remain constant throughout the whole region. Of course, the state of concentrations changes simultaneously on both sides of each wave. Despite such complexity, a rather complete analysis can be performed by using the Riemann invariants and the characteristic parameters judiciously. In the following we shall assume that a (k)-wave interacts with an (m)-wave where $m > k$.

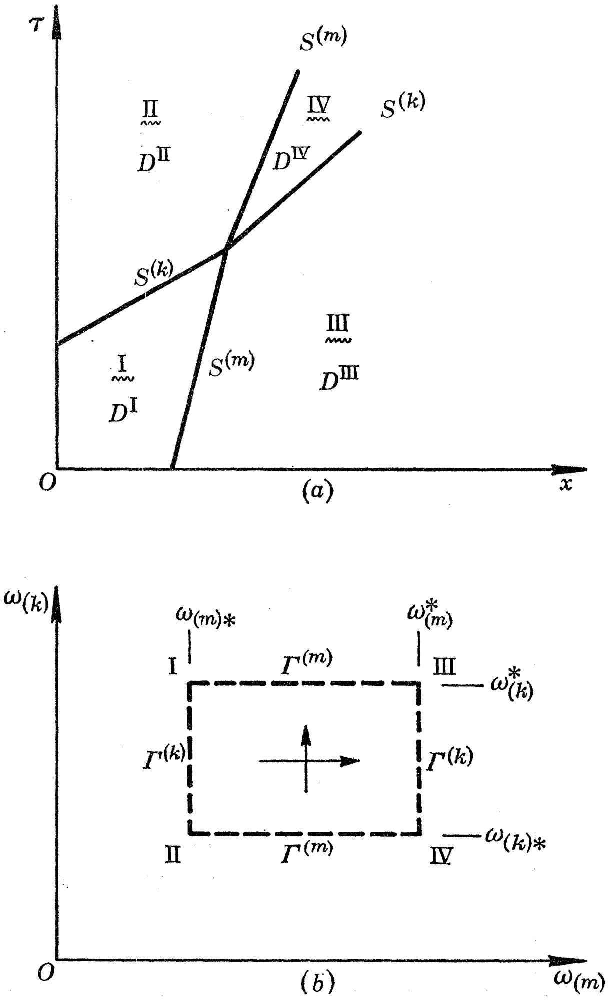


FIGURE 12. Transmission between two shock waves (pattern III). (*a*) Physical plane portrait. (*b*) Image in $\Omega(M)$: – – –, image of a shock.

(i) *Two shock waves*

The interaction is an instantaneous process as shown in figure 12. After the interaction, a new state IV appears between the two transmitted waves. Two shocks after transmitting across each other propagate with constant speeds whose reciprocals are

$$\sigma^{\mathrm{S}}_{(k)} = \epsilon + (1-\epsilon)\,\omega_{(k)*}/D^{\mathrm{III}} \tag{9.11}$$

and

$$\sigma^{\mathrm{S}}_{(m)} = \epsilon + (1-\epsilon)\,\omega^*_m/D^{\mathrm{II}}, \tag{9.12}$$

respectively.

(ii) *A simple wave and a shock wave*

Again we shall assume that the simple wave is based on data distributed along the τ-axis so that the intercepts of the $C^{(k)}$ characteristics are defined by a function $\eta(D)$. As shown in figure 13, the image of the interaction region occupies the rectangle I II IV III and the image of the (m)-shock recedes from I III ($\Gamma^{(m)}$) to II IV ($\Gamma^{(m)}$) as the interaction goes on. At one moment during the interaction, for instance, distribution of solutes along the bed will be given by the path

(II—ⓐ → ⓑ → III).

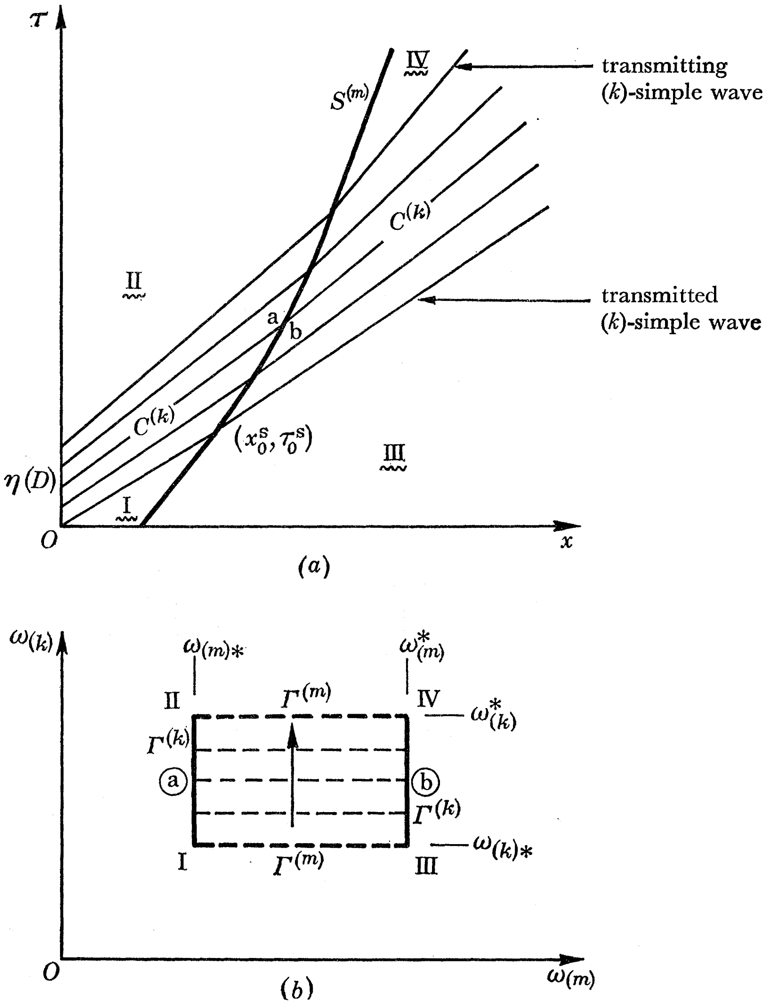


FIGURE 13. Transmission between a simple wave and a shock wave (pattern III). (*a*) Physical plane portrait. (*b*) Image in $\Omega(M)$: ——, image of a simple wave; – – –, image of a shock.

Since $\omega_{(m)}$ and $A_{(k)}$ remain constant on either side of the (m)-shock, we shall identify D^1 with D and write

$$\begin{cases} \tau^s - \eta(D) = \sigma^1_{(k)}\, x^s, & (9.13)\\ \dfrac{\mathrm{d}\tau^s}{\mathrm{d}x^s} = \dfrac{\mathrm{d}\tau^s}{\mathrm{d}D}\Big/\dfrac{\mathrm{d}x^s}{\mathrm{d}D} = \sigma^s_{(m)}, & (9.14)\end{cases}$$

along the shock line, where

$$\sigma^1_{(k)} = \epsilon + (1-\epsilon)\, A^1_{(k)}/D^2, \tag{9.15}$$

$$\sigma^s_{(m)} = \epsilon + (1-\epsilon)\, \omega^*_{(m)}/D. \tag{9.16}$$

Combination of equations (9.13) and (9.14) yields

$$(\sigma^{\mathrm{s}}_{(m)} - \sigma^{\mathrm{l}}_{(k)}) \frac{\mathrm{d}x^{\mathrm{s}}}{\mathrm{d}D} - \frac{\mathrm{d}\sigma^{\mathrm{l}}_{(k)}}{\mathrm{d}D} x^{\mathrm{s}} = \frac{\mathrm{d}\eta}{\mathrm{d}D}, \tag{9.17}$$

which is subject to the initial condition

$$x^{\mathrm{s}} = x^{\mathrm{s}}_0 \quad \text{at} \quad D = D^{\mathrm{I}}. \tag{9.18}$$

Substituting equations (9.15) and (9.16) into equation (9.17), we obtain

$$(D - \Lambda^{\mathrm{l}}_{(k)}/\omega^{*}_{(m)}) \frac{\mathrm{d}x^{\mathrm{s}}}{\mathrm{d}D} + \frac{2\Lambda^{\mathrm{l}}_{(k)}/\omega^{*}_{(m)}}{D} x^{\mathrm{s}} = \frac{D^2}{(1-\epsilon)\,\omega^{*}_{(m)}} \frac{\mathrm{d}\eta}{\mathrm{d}D},$$

and this can be rewritten in the form

$$\frac{\mathrm{d}}{\mathrm{d}D}\left\{\left(\frac{D - \Lambda^{\mathrm{l}}_{(k)}/\omega^{*}_{(m)}}{D}\right)^2 x^{\mathrm{s}}\right\} = \frac{D - \Lambda^{\mathrm{l}}_{(k)}/\omega^{*}_{(m)}}{(1-\epsilon)\,\omega^{*}_{(m)}} \frac{\mathrm{d}\eta}{\mathrm{d}D}. \tag{9.19}$$

The solution is then determined by direct integration:

$$\begin{aligned} x^{\mathrm{s}}(D; \Lambda^{\mathrm{l}}_{(k)}, \omega^{*}_{(m)}) = {} & x^{\mathrm{s}}_0 \left(\frac{D}{D^{\mathrm{I}}} \frac{D^{\mathrm{I}} - \Lambda^{\mathrm{l}}_{(k)}/\omega^{*}_{(m)}}{D - \Lambda^{\mathrm{l}}_{(k)}/\omega^{*}_{(m)}}\right)^2 \\ & + \frac{1}{(1-\epsilon)\,\omega^{*}_{(m)}} \left(\frac{D}{D - \Lambda^{\mathrm{l}}_{(k)}/\omega^{*}_{(m)}}\right)^2 \left\{(D - \Lambda^{\mathrm{l}}_{(k)}/\omega^{*}_{(m)})\,\eta(D) - \int_{D^{\mathrm{I}}}^{D} \eta(D)\,\mathrm{d}D\right\}. \end{aligned} \tag{9.20}$$

If the transmitting (k)-simple wave is centred, we can take $\eta \equiv 0$ to obtain

$$x^{\mathrm{s}}(D; \Lambda^{\mathrm{l}}_{(k)}, \omega^{*}_{(m)}) = x^{\mathrm{s}}_0 \left(\frac{D}{D^{\mathrm{I}}} \frac{D^{\mathrm{I}} - \Lambda^{\mathrm{l}}_{(k)}/\omega^{*}_{(m)}}{D - \Lambda^{\mathrm{l}}_{(k)}/\omega^{*}_{(m)}}\right)^2. \tag{9.21}$$

Otherwise, we shall take the point $(x^{\mathrm{s}}_0, \tau^{\mathrm{s}}_0)$ as the new origin of the coordinate system to have $x^{\mathrm{s}}_0 \equiv 0$ and hence

$$x^{\mathrm{s}}(D; \Lambda^{\mathrm{l}}_{(k)}, \omega^{*}_{(m)}) = \frac{D^2}{(1-\epsilon)\omega^{*}_{(m)}\,(D - \Lambda^{\mathrm{l}}_{(k)}/\omega^{*}_{(m)})} \left\{\eta(D) - \frac{1}{D - \Lambda^{\mathrm{l}}_{(k)}/\omega^{*}_{(m)}} \int_{D^{\mathrm{I}}}^{D} \eta(D)\,\mathrm{d}D\right\}. \tag{9.22}$$

The interaction terminates when $D = D^{\mathrm{II}}$. Along a $C^{(k)}$ both $\omega_{(k)}$ and $\Lambda_{(m)}$ remain constant across the (m)-shock. Therefore, the transmitted (k)-simple wave is established by drawing straight $C^{(k)}$'s of slope

$$\sigma^{\mathrm{r}}_{(k)} = \epsilon + (1-\epsilon)\left(\frac{\omega^{*}_{(m)}}{\omega_{(m)*}} \Lambda^{\mathrm{l}}_{(k)}\right) \Big/ D^2 \quad \text{for} \quad D^{\mathrm{I}} \geqslant D \geqslant D^{\mathrm{II}}, \tag{9.23}$$

and the state of concentrations is given by

$$\phi^{\mathrm{r}}_i = \phi^{\mathrm{l}}_i \frac{1 - NK_i/\omega^{*}_{(m)}}{1 - NK_i/\omega_{(m)*}} \quad (i = 1, 2, \ldots, M). \tag{9.24}$$

In the case when a (k)-shock wave is overtaking an (m)-simple wave, we shall identify D^{r} with D to obtain the parametric description of the shock line from equation (9.20) in the form

$$x^{\mathrm{s}}(D; \Lambda^{\mathrm{r}}_{(m)}, \omega^{*}_{(k)}). \tag{9.25}$$

(iii) *Two simple waves*

The physical plane portrait and its image in $\Omega(M)$ are shown in figure 14. There appears a non-simple wave region but it is clear that its image completely lies on a plane that is parallel to both the $\omega_{(k)}$-axis and the $\omega_{(m)}$-axis.

The solution in the non-simple wave region is determined by applying the mapping from the space $\Omega(M)$ onto the physical plane. The correspondence is illustrated with 25 mesh points. Along a $C^{(k)}$ both $\omega_{(k)}$ and $\Lambda_{(m)}$ remain constant whereas, along a $C^{(m)}$, both $\omega_{(m)}$ and $\Lambda_{(k)}$ remain invariant. Therefore, the curved portions I II and I III may be obtained by applying equation (9.20) with appropriate adjustments; i.e.

$$x^{\mathrm{s}}\,(D;\ \Lambda^{\mathrm{I}}_{(k)},\ \omega^{*}_{(m)}) \quad \text{for} \quad \mathrm{I\,II} \tag{9.26}$$

and

$$x^{\mathrm{s}}\,(D;\ \Lambda^{\mathrm{I}}_{(m)},\ \omega_{(k)*}) \quad \text{for} \quad \mathrm{I\,III.} \tag{9.27}$$

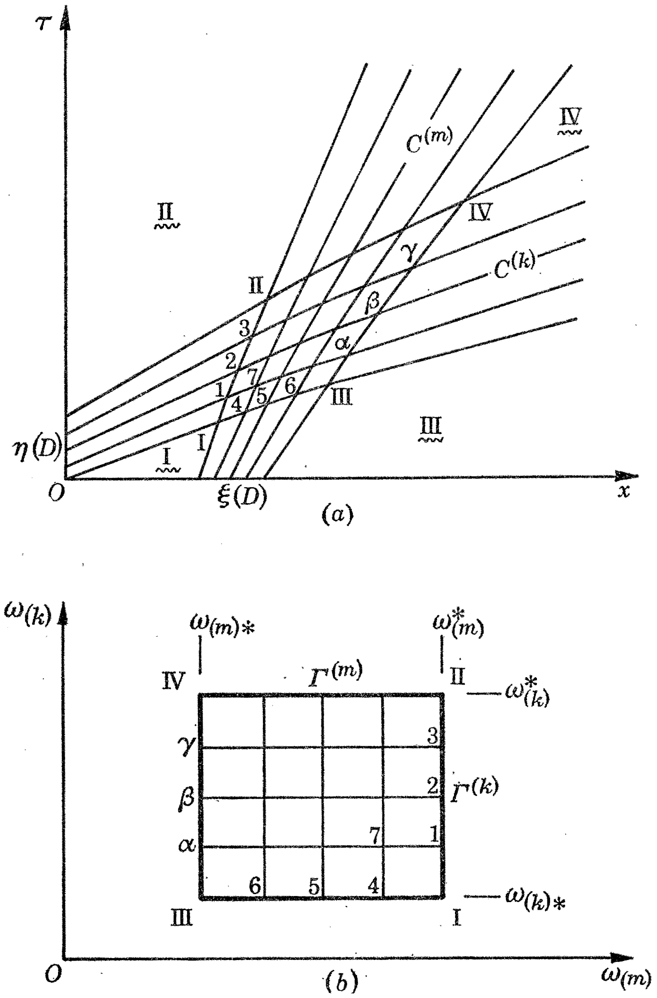


FIGURE 14. Transmission between two simple waves (pattern III). (*a*) Physical plane portrait. (*b*) Image in $\Omega(M)$: ——, Γ; ▬▬, image of a simple wave.

From the image in $\Omega(M)$, on the other hand, we can assign the values of $\omega_{(k)}$, $\omega_{(m)}$, $\Lambda_{(k)}$, and $\Lambda_{(m)}$ to each of the mesh points, which in turn provide the values of $\sigma_{(k)}$ and $\sigma_{(m)}$ at the same point:

$$\sigma_{(k)} = \epsilon + (1-\epsilon)\,\frac{\omega_{(k)}}{\Lambda_{(m)}}\,\omega_{(m)} \quad \text{for} \quad \omega_{(m)*} \leqslant \omega_{(m)} \leqslant \omega^{*}_{(m)}, \tag{9.28}$$

$$\sigma_{(m)} = \epsilon + (1-\epsilon)\,\frac{\omega_{(m)}}{\Lambda_{(k)}}\,\omega_{(k)} \quad \text{for} \quad \omega_{(k)*} \leqslant \omega_{(k)} \leqslant \omega^{*}_{(k)}. \tag{9.29}$$

The portion $\overline{17}$ of a $C^{(k)}$, for example, may be approximated by a straight line of slope

$$\sigma_{(k)} = \tfrac{1}{2}(\sigma^{1}_{(k)} + \sigma^{7}_{(k)}), \tag{9.30}$$

and the portion $\overline{47}$ of a $C^{(m)}$ can be drawn likewise to yield the mesh point 7 at the intersection. Iteration generates all the mesh points and thus the non-simple wave solution in the region I II IV III is established.

The transmitted (k)-simple wave is constructed by drawing straight $C^{(k)}$'s from the points III, α, β, γ, and IV with the corresponding slope, respectively. The same holds for the transmitted (m)-simple wave. As the number of mesh points is increased, an increasingly accurate solution can be attained.

10. CHROMATOGRAPHIC CYCLE

In § 7 (d) the conventional processes of saturation and elution were discussed. Complete solutions were also presented for $M = 3$ but the solution can be readily constructed for any M greater than three.

It has been observed that separation of different solutes may be accomplished by applying the above processes successively. Suppose a clean bed of adsorbent is first irrigated with a fluid mixture containing M different solutes $\{A_i\}$, laying down the sample to be developed into a chromatogram. After a finite period of time, τ_0, the inlet stream will be changed from the mixture to the pure solvent so that the chromatogram starts to be eluted. Since the entry condition may be regarded as stepwise data, there will naturally occur interactions between waves.

It is interesting to note that the image in $\Phi(M)$ or $\Omega(M)$ of the state along the bed at any instant is a closed curve, the so-called chromatographic cycle, which deforms as time increases. Deformation of the chromatographic cycle explains clearly how different solutes are separated.

We shall discuss the problem for $M = 3$ but the same procedure is certainly applicable for any M greater than three. The image in $\Phi(3)$ is presented to show how the chromatographic cycle deforms but, though this is a useful visualization, it is not necessary for the construction of a solution. This is important since picturing the image in $\Phi(M)$ or $\Omega(M)$ would be difficult for $M \geqslant 4$. By applying the result of the previous section, a complete analysis can be achieved, giving the solution as shown in figure 15. In the remainder of this section, we shall discuss in detail how the solution can be determined.

Until the moment $\tau = \tau_1$ when the first interaction starts, the solution may be obtained from § 7(d) and the distribution of solutes is represented by the chromatographic cycle

$$(\mathrm{O} \rightarrow \mathrm{E} \rightarrow \mathrm{F} \rightarrow \mathrm{P} \rightarrow \mathrm{Q} \rightarrow \mathrm{R} \rightarrow \mathrm{O}).$$

At $\tau = \tau_1$ the (1)-simple wave starts to overtake the (3)-shock wave (transmissive interaction) so that the state P disappears and the (3)-shock finds its image $(\overrightarrow{\mathrm{PQ}})$ receding toward $\overrightarrow{\mathrm{FG}}$. During this interaction the (3)-shock line and the transmitted (1)-simple wave are given by equations (9.21) and (9.23), respectively, with $k = 1$ and $m = 3$. Meanwhile, the chromatographic cycle becomes $(\mathrm{O} \rightarrow \mathrm{E} \rightarrow \mathrm{F} \rightarrow \textcircled{a} \rightarrow \textcircled{b} \rightarrow \mathrm{Q} \rightarrow \mathrm{R} \rightarrow \mathrm{O})$ for example. When the interaction is over at $\tau = \tau_\alpha$, the (3)-shock line separates the mixture containing A_2 and A_3 from the one containing A_1 and A_2 from the left to the right.

At $\tau = \tau_2$ (possibly $\tau_2 \leqslant \tau_\alpha$) the once-transmitted (1)-simple wave starts an interaction of pattern III with the (2)-shock wave. The (2)-shock line and the twice-transmitted (1)-simple wave are given by equations (9.22) and (9.23), respectively, with $k = 1$ and $m = 2$. The chromatographic cycle is now reduced to $(\mathrm{O} \rightarrow \mathrm{E} \rightarrow \mathrm{F} \rightarrow \mathrm{G} \rightarrow \textcircled{b} \rightarrow \textcircled{e} \rightarrow \mathrm{R} \rightarrow \mathrm{O})$. When the interaction is over at $\tau = \tau_\beta$, the (2)-shock line separates the mixture containing A_2 only from the one containing A_1 alone from the left to the right; i.e. chromatograms of pure A_1 and of pure A_2 are obtained.

The (2)-simple wave, on the other hand, also starts an interaction of pattern III with the (3)-shock wave at $\tau = \tau_3$. The (3)-shock line and the transmitted (2)-simple wave are given by equations (9.21) and (9.23), respectively, with $k = 2$ and $m = 3$. The chromatographic cycle now

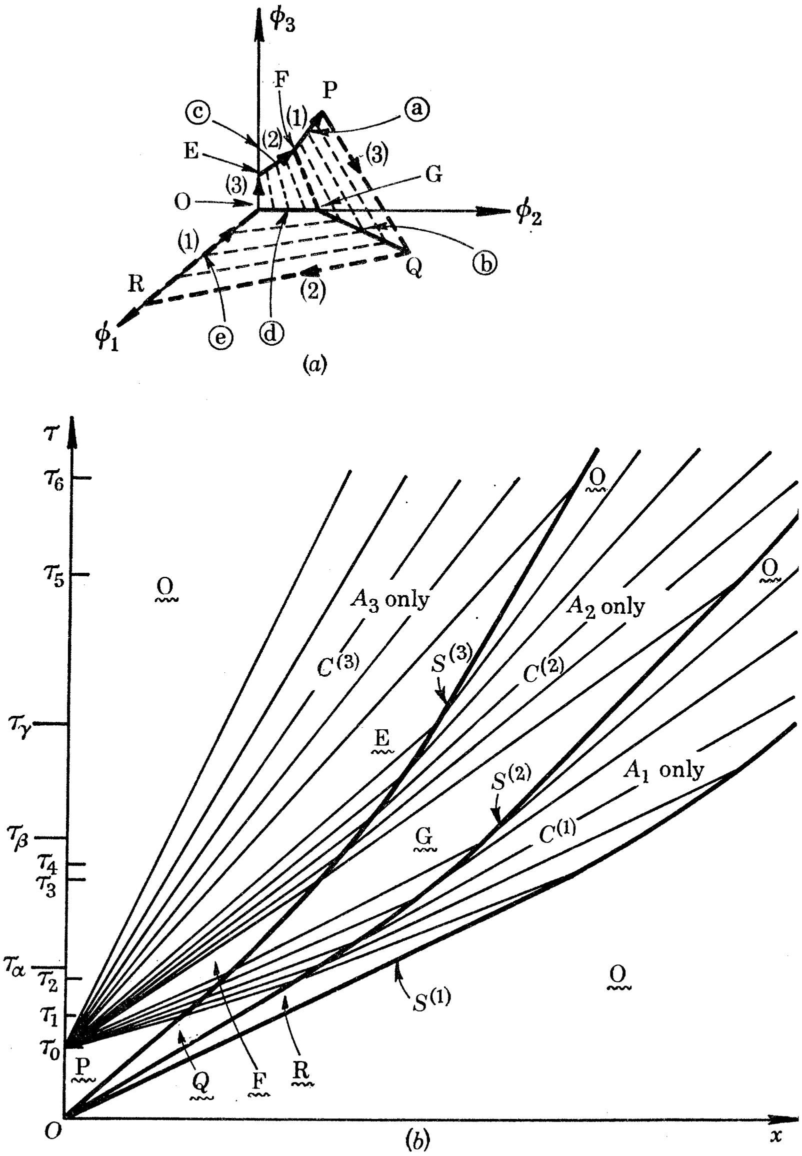


FIGURE 15. Separation of three solutes by successive operation of adsorption and desorption. (a) Concentration space, $\Phi(3)$; $\xrightarrow{(k)}$ image of (k)-simple wave; $\overset{(k)}{\dashrightarrow}$ image of (k)-shock. (b) Physical plane portrait.

becomes (O→E→ⓒ→ⓓ→G→O→R→O). When this interaction is over at $\tau = \tau_\gamma$, the (3)-shock line separates the mixture containing A_3 only from the one containing A_2 alone from the left to the right. Hence, the complete separation of three solutes, A_1, A_2 and A_3, is accomplished at $\tau = \tau_\gamma$.

Meanwhile, the twice-transmitted (1)-simple wave may start an interaction of pattern II with the (1)-shock wave at $\tau = \tau_4$. As τ increases, the once-transmitted (2)-simple wave also starts an interaction of pattern II with the (2)-shock wave at $\tau = \tau_5$. The corresponding shock line is given by equation (9.9) with $k = 1$ or $k = 2$, respectively. The (3)-simple wave will also start to overtake the (3)-shock wave at $\tau = \tau_6$ and this interaction of pattern II is described by equation (9.8). Each interaction of pattern II in the above implies the disappearance of the constant state R, G, or E, respectively. Therefore the chromatographic cycle will be reduced to

$$(\mathrm{O} \rightarrow \mathrm{E}' \rightarrow \mathrm{O} \rightarrow \mathrm{G}' \rightarrow \mathrm{O} \rightarrow \mathrm{R}' \rightarrow \mathrm{O}),$$

where R′, for example, denotes an intermediate point on $\overline{\mathrm{OR}}$. Further operation of the chromatography will lead only to the lengthening of each chromatogram of a single solute which is not desirable although it results in a more distinct separation.

Finally, the physical plane portrait is completed as shown in figure 15 (*b*) from which the distribution of solutes can be read at any moment.

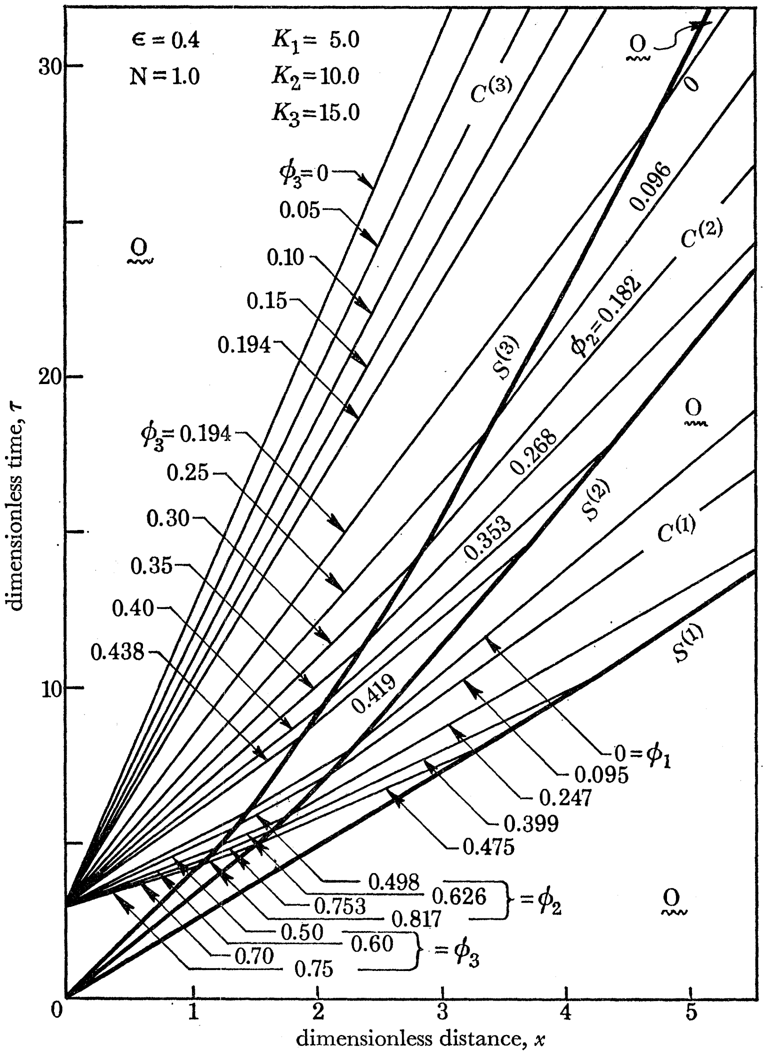


FIGURE 16. Physical plane portrait of solution to example 5.

A numerical example will be presented bearing the same items as in §7 (*e*):

Example 5 ($M = 3$):

m	1	2	3	remark
K_m	5.0	10.0	15.0	
c^{i}_m	0	0	0	
c^{e}_m	0.05	0.05	0.05	for $0 < \tau < 3.0$
	0	0	0	for $\tau > 3.0$
$\omega^{\mathrm{i}}_{(m)}$	5.0	10.0	15.0	
$\omega^{\mathrm{e}}_{(m)}$	3.387	7.050	12.563	for $0 < \tau < 3.0$
	5.0	10.0	15.0	for $\tau > 3.0$

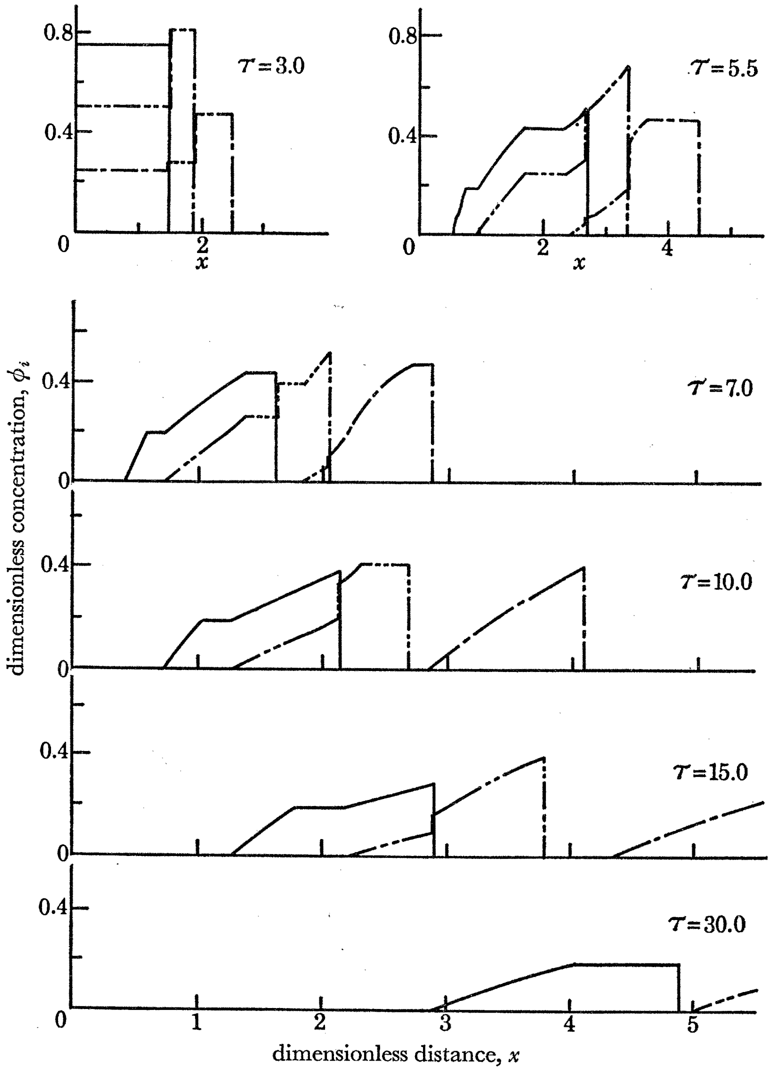


FIGURE 17. Concentration profiles at successive times: example 5.
– – – –, Solute A_1; –·–·–, solute A_2; ——, solute A_3.

This numerical example corresponds to the superposition and interaction of examples 2 and 3. Figure 16 shows the physical plane with the interaction of the simple waves and the shock waves. In figure 17 the distribution of solutes along the column is shown at various times. In the first part of the figure ($\tau = 3.0$) the sample has just been put on the column and the next two parts show the development of the chromatogram proceeding. By $\tau = 10$, A_1 has been separated from A_2 and A_3. The chromatographic mixture of these two continues to develop ($\tau = 15$) until they also have separated. It is clear from this calculation that a dimensionless column length of about 4.7 is needed to completely separate these three solutes. Since the sample was put on during a period of $\tau_0 = 3$ we have

$$\frac{\text{volume of sample}}{\text{volume of bed}} = \frac{\epsilon u A t_0}{zA} = \frac{\tau_0}{x} = \frac{3}{4.7}.$$

That this ratio is so remarkably large is the result of the particular values of K_i that were chosen, but it does show that with strong absorption and very different values of K_i the solutes can be separated remarkably easily.

11. EXTENSION OF THEORY

(a) *Radial chromatography*

The use of annular cylindrical beds, fed through a central channel and drained at the periphery, is of potential interest in cases where high throughput rates and wide but shallow beds are desired. Radial flow geometry is also characteristic of one operating method used in paper chromatography. The theoretical analysis of this process was first made by Lapidus & Amundson (1950) but was limited to the cases of linear isotherm and kinetic expressions.

It is noticed that the physical model deviates from the ideal column only by a geometrical factor, i.e. non-uniform cross-sectional area. For such a system there exists a scheme to extend the applicability of the present theory by a simple transformation of the space variable.

Consider a fixed bed of adsorbent with cross-sectional area $A(z)$ varying in the direction of flow. The system is otherwise an ideal column. The material balance for each component reads

$$\frac{\partial}{\partial z}\{\epsilon u(z)\, A(z)\, c_i\} + \frac{\partial}{\partial t}\{A(z) f_i\} = 0,$$

or

$$Q\frac{\partial c_i}{\partial z} + A(z)\frac{\partial f_i}{\partial t} = 0 \quad (i = 1, 2, \ldots, M), \tag{11.1}$$

where

$$Q \equiv \epsilon u(z)\, A(z) = \text{constant volumetric flow rate.} \tag{11.2}$$

We shall now define the dimensionless variables as

$$x = \int_{z_0}^{z} A(\zeta)\,\mathrm{d}\zeta \Big/ \int_0^Z A(\zeta)\,\mathrm{d}\zeta \tag{11.3}$$

and

$$\tau = Qt \Big/ \int_0^Z A(\zeta)\,\mathrm{d}\zeta. \tag{11.4}$$

Then the system (11.1) can be rewritten in the form

$$\frac{\partial c_i}{\partial x} + \frac{\partial f_i}{\partial \tau} = 0 \quad (i = 1, 2, \ldots, M), \tag{11.5}$$

which is identical to equation (1.1). It is also clear that the jump relation and the compatibility condition across a shock will be the same as equations (5.2) and (5.3). Consequently, all the formulae developed can be applied directly if the initial and entry data are compatible.

For an annular cylindrical bed with purely radial flow, the initial and entry conditions are

$$\left\{\begin{array}{lll}\text{at} & r = r_0, & c_i = c_i^{\mathrm{e}} \\ \text{at} & t = 0, & c_i = c_i^{\mathrm{i}}.\end{array}\right\} \tag{11.6}$$

Here the radial position r corresponds to z. If we choose the radius of the central channel r_0 as the characteristic radius, it follows from equations (11.3) and (11.4) that

$$x = (r/r_0)^2 - 1 \tag{11.7}$$

and

$$\tau = Qt/\pi r_0^2 d, \tag{11.8}$$

where d denotes the depth of the bed. Furthermore, equation (11.6) is reduced to

$$\left\{\begin{array}{lll}\text{at} & x = 0, & c_i = c_i^{\mathrm{e}},\\ \text{at} & \tau = 0, & c_i = c_i^{\mathrm{i}},\end{array}\right\} \tag{11.9}$$

that is, identical to equation (1.8).

For a spherical bed with spherical symmetry, one may put

$$x = (r/r_0)^3 - 1 \tag{11.10}$$

and

$$\tau = Qt/\tfrac{4}{3}\pi r_0^3 \tag{11.11}$$

to reduce the mathematical model to the form of equations (11.5) and (11.9).

In conclusion, chromatographic processes associated with a fixed bed of non-uniform cross-sectional area can be analysed equivalently by the present theory with the deformed transformation and normalization of the space variable given by equation (11.3).

(*b*) *Non-isothermal chromatography*

The temperature dependence of the adsorption isotherm has been observed experimentally (see, for example, Shen & Smith 1968*a*) and may be expressed for Langmuir isotherms by equation (2.2). It was also reported that such a dependence of the temperature produces effects that are of importance in analysing the performance of chromatography (Amundson, Aris & Swanson 1965). In this paragraph we shall discuss briefly how heat effects can be treated mathematically along with the present approach.

Consider a non-isothermal, adiabatic, and otherwise ideal column and assume that conduction in the direction of flow is negligible compared with convection and that thermal equilibrium is established between phases. Let C_{f} and C_{s} be the heat capacities per unit volume of the fluid and solid phases, respectively. Then the energy balance may be formulated to give the equation

$$Q\frac{\partial T}{\partial z} + A(z)\frac{\partial}{\partial t}\left\{\epsilon T + (1-\epsilon)\frac{C_{\mathrm{s}}}{C_{\mathrm{f}}}T\right\} - (1-\epsilon)\,A(z)\sum_{j=1}^{M}\frac{(-\Delta H_j)}{C_{\mathrm{f}}}\frac{\partial n_j}{\partial t} = 0 \tag{11.12}$$

for the temperature T, where C_{f}, C_{s} and $\{-\Delta H_i\}$ are assumed constant. If we put

$$c_{M+1} = T \tag{11.13}$$

and

$$n_{M+1} = \frac{C_{\mathrm{s}}}{C_{\mathrm{f}}}T - \sum_{j=1}^{M}\frac{(-\Delta H_j)}{C_{\mathrm{f}}}n_j, \tag{11.14}$$

then the function f_{M+1} defined by equation (1.2) has the property

$$f_{M+1,\,M+1} > 0, \tag{11.15}$$

which is consistent with f_i for $i = 1, 2, \ldots, M$. If we further introduce equations (11.3) and (11.4), equation (11.12) can be reduced to the form

$$\frac{\partial c_{M+1}}{\partial x} + \frac{\partial f_{M+1}}{\partial \tau} = 0. \tag{11.16}$$

With this simple form of energy balance we notice that the fundamental differential equation (1.14) remains the same except that the subscript i spans from one to $M+1$. Furthermore, the same is true for the compatibility condition (5.3). The present approach therefore finds a natural application to non-isothermal chromatography.

At the moment, however, no analytic scheme is promising because of the complicated temperature dependence given by equation (2.2). Another difficulty arises from the fact that the second order derivatives of $\{n_i\}$ with respect to the temperature are not consistent in sign. In other words, the system (1.1) plus equation (11.16) is not strictly nonlinear and thus the 'entropy' condition may not be so simple as given by theorem 5.1. Since the image of a discontinuity may not coincide with a Γ, one has to establish not only the solution to the fundamental differential equation but also the one to the compatibility condition.

Although it is not possible to have an analytical approach, numerical analysis should be straightforward for $M \leqslant 2$ within the framework of Reimann's problem. Further discussions will be presented along with numerical examples elsewhere.

REFERENCES

Amundson, N. R., Aris, R. & Swanson, R. 1965 *Proc. Roy. Soc. Lond.* A **286**, 129.
Bayle, G. G. & Klinkenberg, A. 1954 *Recl Trav. chim. Pays-Bas Belg.* **73**, 1037.
Courant, R. & Friedrichs, K. O. 1948 *Supersonic flow and shock waves.* New York: Interscience.
Courant, R., Isaacson, W. & Rees, M. 1952 *Communs pure appl. Math.* **5**, 243.
De Boer, J. H. 1953 *The dynamical character of adsorption.* Oxford: Clarendon Press.
De Vault, D. 1943 *J. Am. chem. Soc.* **65**, 532.
Glimm, J. 1965 *Communs pure appl. Math.* **18**, 697.
Glueckauf, E. 1946 *Proc. Roy. Soc. Lond.* A **186**, 35.
Glueckauf, E. 1949 *Discuss. Faraday Soc.* **7**, 12.
Helfferich, F. 1967 *Ind. Engng Chem. Fund.* **6**, 362.
Helfferich, F. 1968 *Adv. Chem. Ser.* no. **79**, 30.
Jeffrey, A. & Taniuti, T. 1964 *Nonlinear wave propagation.* New York: Academic Press.
Klein, G., Tondeur, D. & Vermeulen, T. 1967 *Ind. Engng Chem. Fund.* **6**, 339.
Langmuir, I. 1916 *J. Am. chem. Soc.* **38**, 2221.
Lapidus, L. & Amundson, N. R. 1950 *J. phys. Colloid Chem.* **54**, 821.
Lax, P. D. 1954 *Communs pure appl. Math.* **7**, 159.
Lax, P. D. 1957 *Communs pure appl. Math.* **10**, 537.
Oleinik, O. A. 1957 *Usp. mat. Nauk.* **12**, 3; translated in 1963 *Am. Math. Soc. Transl.* Ser. 2, no. **26**, 95.
Rhee, H. 1968 Ph.D. Thesis, University of Minnesota.
Shen, J. & Smith, J. M. 1968*a* *Ind. Engng Chem. Fund.* **7**, 100.
Shen, J. & Smith, J. M. 1968*b* *Ind. Engng Chem. Fund.* **7**, 106.
Sillen, L. G. 1950 *Ark. Kemi Miner. Geol.* **2**, 477.
Tondeur, D. & Klein, G. 1967 *Ind. Engng Chem. Fund.* **6**, 351.
Walter, J. E. 1945 *J. chem. Phys.* **13**, 229.
Wilson, J. N. 1940 *J. Am. chem. Soc.* **62**, 1583.