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Non-Diffusive Models for Pressure-Swing Adsorption

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This paper examines the industrial process popularly known as 'pressure-swing adsorption' from both analytical and numerical points of view. After a derivation of the equations of motion and a description of the important stages involved in the process it is shown that for the case of a binary mixture the problem may be treated analytically in constant-pressure stages, and simplified in variable-pressure stages. This leads naturally to discussion of the N-species case where the governing hyperbolic differential equations have some unusual features which must be accommodated in numerical strategies. Some numerical calculations are also reported, in which the analytical work plays a major part

1. Introduction

PRESSURE-SWING adsorption (PSA) is a process used in many branches of the chemical engineering industry to separate mixed gases. A stream of the gas mixture is passed through one (or more) columns packed with a bed of granular material having different affinities for the various gas components. A typical production process involves cyclic changes in pressure and is controlled by a sequence of adjustments to valves at the two ends of the column(s). Some stages are constant-pressure 'flow' stages, others are 'pressurization' or 'depressurization' stages in which the gas either enters or leaves the column(s) at one end only.

The number of operating arrangements is great, since enriched gas collected from one stage may be used as feed at a later stage in the same or an interlinked column. However, in all operating arrangements the physical and chemical processes within a column are similar, so it is important to understand the structure of the governing equations and to suggest versatile computational procedures. For a specific operational scheme such procedures could then be used to calculate the response to different pressurization and depressurization sequences, the eventual periodic response and the manner by which this is approached. Important parameters such as the product purity and the specific energy consumption could also be predicted.

The increasing usage of PSA processes as efficient and cost-effective methods for gas separation has given rise to a large literature on the subject, many existing studies being of an experimental nature and concerning themselves with optimum operating arrangements. An example of this is the recent study by Kapoor & Yang (1988) who considered the optimization of a specific PSA cycle via an interior penalty function, using a simplified equilibrium model. The study by Sundaram & Wankat (1988) was concerned with rapid cycling so that the effects of pressure drop along the column were minimized. Analysis was again performed on a binary (two-component) mixture and some shocks were detected. Recent quantitative studies include that of Hassan, Raghavan & Ruthven (1987), who investigated a particular cycle for the production of nitrogen, and were able to make some estimates of optimum yield rates. Hassan, Ruthven & Raghavan (1986) had earlier considered a mathematical model of a binary mixture for a 2-bed, four-step PSA cycle. Under certain simplifying assumptions the partial differential equations were reduced to a set of ordinary differential and nonlinear algebraic equations which were solved by orthogonal collocation. Qualitative agreement with experimental results was indicated.

A comprehensive survey of applications of PSA processes, together with a survey of analytical and numerical treatments of mathematical models and some comparisons with experiment, has recently been completed by Kirkby & Kenney (1988). This shows that in most treatments diffusive effects have been neglected and that instantaneous equilibrium has also been assumed. For the production of oxygen from air, Flores Fernandez & Kenney (1983) have shown these assumptions to be reasonable. For general N-component gas mixtures these assumptions yield a hyperbolic system of partial differential equations, which normally are nonlinear. Previously published analyses (for example (Flores Fernandez & Kenney, 1983; Mitchell & Shendalman, 1972; Chan, Hill & Wong, 1981)) have all treated binary mixtures, usually with simplifying assumptions concerning the amount of each species adsorbed when the partial pressures are specified. Another common assumption has been that the flow is isothermal, though as noted below the inclusion of non-isothermal effects does not prove to be a major complication. An example of a study which included temperature effects was that performed by Chiang, Hwong, Lee and Chen (1988), who considered a binary mixture. It is also worth noting that studies have been made which include diffusive effects. Two recent examples of such PSA treatments are given by Shin & Knaebel (1987) who considered diffusion with spherical adsorbent particles, using linear adsorption isotherms, and Doong and Yang (1987), who considered N-component zeolite sorbents, simplifying the Fickian diffusion equations for the two types of pore by assuming parabolic concentration profiles for the crystals and pellets. Both studies showed qualitative agreement with experiment.

On the present theory, all binary mixtures can be treated analytically in the constant-pressure stages and can be reduced (via a transformation of the 'hodograph' type) to the solution of a pair of linear, first-order hyperbolic equations in the pressurization and depressurization stages. These treatments demonstrate features which will be present in N-component processes and which a general numerical strategy must accommodate. In particular, one of the characteristic speeds is always infinite, so that a time-marching scheme must be chosen carefully (neglect of inertial effects means that flow speeds at all column cross-sections are interrelated at each instant). Also, nonlinearity means that abrupt jumps or 'concentration shocks' are liable to form and then propagate along the column.

After derivation of the governing equations for an N-component mixture and analysis of the above features, the paper divides into two parts. The first, consisting of sections 4 and 5, gives details of the analytic procedure for the binary mixture. The second, consisting of sections 6.1 and 6.2, discusses a numerical approach in which the analytical work plays a major part.

2. The mathematical model

In a one-dimensional treatment of an adsorbent-packed column $0<z<L$ having cross-sectional area A, void fraction ε, total gas density ρ and mean flow speed u, the mass flow rate is $m = \varepsilon A\rho u$. If y_i denotes the volume fraction of the species S_i in the gas mixture, then $c_i = \rho y_i$ and $p_i = R\theta c_i$ are the concentration and the partial pressure of S_i, while the total pressure is $p = \rho R\theta$, where θ is the temperature, R is the gas constant and

$$p = \sum_{i=1}^{N} p_i, \qquad \sum_{i=1}^{N} y_i = 1. \tag{2.1}$$

Inertial and flow-resistance effects are neglected, so that $p = p(t)$ is uniform along the column at each instant. Changes in the temperature θ also are neglected, though it is worth noting that little of the analysis is changed by the addition of the temperature equation, and we choose to make this assumption only for reasons of clarity. With this simplification we find that

$$\rho = \rho(t) = \sum_{i=1}^{N} c_i, \qquad p(t) = R\theta\rho(t). \tag{2.2}$$

At a given cross-section z the adsorbed mass of S_i is taken to be in instantaneous chemical equilibrium with the partial pressures $\{p_j\}$ at (z, t). When the adsorbed mass of S_i per unit volume of adsorbent is written as $\varepsilon(1-\varepsilon)^{-1}c_iK_i(p_j, \theta)$, the total mass of the species S_i per unit length of the column becomes

$$\varepsilon A(1+K_i)c_i \equiv \varepsilon A Q_i(\boldsymbol{c}, \theta).$$

The mass balance equation for each species S_i is

$$\frac{\partial}{\partial t}(\varepsilon A Q_i) + \frac{\partial}{\partial z}(\varepsilon A\rho y_i u) = 0,$$

which takes the form

$$\frac{\partial}{\partial t}Q_i(\boldsymbol{c}) + \frac{\partial}{\partial z}(uc_i) = 0 \qquad (\text{where } \boldsymbol{c} = (c_j)) \tag{2.3}$$

since dependence on θ is suppressed in this isothermal model. Summing equations (2.3) and using (2.2) gives the continuity equation

$$\sum_{i=1}^{N} \frac{\partial Q_i}{\partial t} + \rho(t)\frac{\partial u}{\partial z} = 0, \tag{2.4}$$

which relates the divergence of the flow velocity u to the rates of increase of the total concentrations Q_i at each cross-section. Equation (2.4) may be used to eliminate all derivatives of u from the system (2.3), so yielding

$$\sum_{j=1}^{N}\left(Q_{ij} - \frac{c_i}{\rho}\sum_{m=1}^{N} Q_{mj}\right)\frac{\partial c_j}{\partial t} + u\frac{\partial c_i}{\partial z} = 0, \qquad i = 1, 2, \ldots, N, \tag{2.5}$$

where Q_{ij} denotes the partial derivatives

$$Q_{ij} \equiv \frac{\partial Q_i}{\partial c_j} = Q_{ij}(\mathbf{c}).$$

In equations (2.3), (2.4) and (2.5) the equilibrium capacities $K_i(\mathbf{p}, \theta)$, and consequently the functions $Q_i(\mathbf{c}, \theta)$, are described by 'adsorption isotherms' which characterize the adsorbent material and the various species present in the gas mixture. Many workers (see (Kirkby and Kenney, 1988)) assume linear independent isotherms $k_i = \text{const}$, while others use either Freundlich isotherms (see, for example, (Atkins, 1978)), in which

$$\sum_{i=1}^{N} c_i K_i \propto p^{\gamma} \qquad (\gamma < 1)$$

with the K_i in fixed ratios $K_i = k_i K$ ($k_i = \text{const}$), or Langmuir isotherms (Richter *et al.*, 1982) for which

$$K_i = \frac{\alpha k_i}{1 + \sum_{j=1}^{N} k_j p_j} = \frac{\beta \mu_i}{1 + \sum_{j=1}^{N} \mu_j c_j}, \tag{2.6}$$

where α, k_i and $\mu_i = R\theta k_i$, $\beta = \alpha/R\theta$ are constants. This latter case yields expressions for the coefficients in (2.5) as

$$Q_{ij} = (1 + K_i)\delta_{ij} - \mu_i c_i \frac{\beta \mu_j}{(1 + \sum_{j=1}^{N} \mu_j c_j)^2}. \tag{2.7}$$

In all cases, the quantities Q_{ij} depend only on $\mathbf{c}$, so that equations (2.4) and (2.5) reveal many of the important features of the system governing isothermal PSA cycles, as follows.

1. Since all terms in (2.4) and (2.5) involve first derivatives, the system of $N + 1$ equations for c_i ($i = 1, 2, \ldots, N$) and u defines no natural scale of time.
2. The system is invariant under transformations of the type

$$t \to \tau(t), \qquad u(z, t) \to \frac{u(z, t)}{\tau'(t)} \equiv v(z, t).$$

Time behaves purely as a label for successive states of the system. At each instant, the states are always taken to be in chemical equilibrium, with mass transport

$$\varepsilon A \int c_i u \,\mathrm{d}t = \varepsilon A \int c_i v \,\mathrm{d}\tau$$

of the ith species determined solely by continuity requirements. The time scale during each process stage is determined by the history of mass flux at one of the open ends, $z = 0$, or $z = L$.

3. Equilibrium considerations show that the system of partial differential equations is hyperbolic. However, one of the characteristic speeds is infinite, since summation of the equations (2.5) gives

$$\sum_{i=1}^{N} \frac{\partial c_i}{\partial z} = 0,$$

consistently with (2.2). In the (z, t)-plane, each line $t = \text{const}$ is characteristic.

4. The remaining (finite) characteristic speeds of the system (2.5) have the form

$$\frac{\mathrm{d}z}{\mathrm{d}t} = V^{(r)} = \frac{u}{\lambda^{(r)}(\boldsymbol{c})}, \qquad r = 1, 2, \ldots, N-1,$$

where $\lambda^{(r)}$ is one of the (non-zero) eigenvalues of the (singular) matrix $\boldsymbol{A}$ having elements

$$A_{ij} \equiv Q_{ij} - \frac{c_i}{\rho} \sum_{m=1}^{N} Q_{mj} = A_{ij}(\boldsymbol{c}). \tag{2.8}$$

Since, in matrix notation, equation (2.5) has the form

$$\boldsymbol{A}\frac{\partial \boldsymbol{c}}{\partial t} + u\frac{\partial \boldsymbol{c}}{\partial z} = \boldsymbol{0}, \tag{2.5a}$$

premultiplication by the left-eigenvector $\boldsymbol{l}^{(r)T}$ corresponding to $\lambda^{(r)}$ $(r = 1, \ldots, N-1)$ gives the characteristic differential equation

$$\boldsymbol{l}^{(r)T}\frac{\mathrm{d}\boldsymbol{c}}{\mathrm{d}t} = \sum_{j=1}^{N} l_j^{(r)}, \qquad \frac{\mathrm{d}c_j}{\mathrm{d}t} = 0 \quad \text{along}\, \frac{\mathrm{d}z}{\mathrm{d}t} = V^{(r)}, \tag{2.9}$$

where $l_j^{(r)}$ are the elements of $\boldsymbol{l}^{(r)T}$.

5. It may be noted that the only derivative of u occurring in the system (2.4), (2.5) is $\partial u/\partial z$. This suggests that along $t = \text{const}$ there exists a second characteristic equation relating derivatives of u to those of c_i. This equation is given by the compatibility condition

$$\det\left(\begin{array}{c|c} \boldsymbol{Q} & \partial(u\boldsymbol{c})/\partial z \\ \hline 1\ 1 \cdots 1 & -\rho'(t) \end{array}\right) = 0, \qquad \boldsymbol{Q} \equiv (Q_{ij})$$

between the N equations (2.3) and the equation

$$\sum_{j=1}^{N} \frac{\partial c_j}{\partial t} - \rho'(t) = 0$$

which follows from differentiation of (2.2). Expansion of the $(N+1)$th-order determinant by its last column then gives

$$\sum_{i=1}^{N} B_i \frac{\partial(uc_i)}{\partial z} - (\det \boldsymbol{Q})\rho'(t) = 0, \tag{2.10}$$

where the cofactors B_i are obtained by replacing each element in the ith row of $\det \boldsymbol{Q}$ by 1 according to

$$B_i = -\det \begin{pmatrix} Q_{11} & Q_{12} \cdots Q_{1N} \\ 1 & 1 \;\cdots\; 1 \\ & \cdots \\ Q_{N1} & Q_{N2} \cdots Q_{NN} \end{pmatrix}.$$

Equation (2.10) is equivalent to

$$\frac{\partial}{\partial z}\{K(z,t)u\} = \rho'(t)M(z,t), \tag{2.11}$$

where the integrating factor K and the term M are given by

$$K(z,t) = \exp \int_0^z \frac{\sum_{i=1}^N B_i(\partial c_i/\partial \bar{z})}{\sum_{i=1}^N B_i c_i}\, d\bar{z},$$

$$M(z,t) = K(z,t)(\det \boldsymbol{Q}) \Big/ \sum_{i=1}^{N} B_i c_i.$$

Consequently the variation of flow speed u with z at a general instant is related to the current distribution of concentrations $\{c_i\}$ and the instantaneous rate of pressure change $p'(t) = R\theta\rho'(t)$ by

$$K(z,t)u(z,t) = U^-(t) + \rho'(t)\int_0^z M(\zeta,t)\, d\zeta. \tag{2.12}$$

Equation (2.12) reveals the simplifications occurring in the two special cases.

(a) Flow (constant-pressure) stages. In these $p'(t) = 0$, so that $\rho'(t) = 0$ gives $u(z,t)K(z,t) = U^-(t) = u(0,t)$, an arbitrary function of t.

(b) Column closed at $z = 0$. Since $U^-(t) = 0$, equation (2.12) expresses u as a function of the concentration distributions multiplied by $\rho'(t)$, which is itself proportional to the instantaneous rate of pressure increase. A similar simplification arises for $U^+(t) \equiv u(L,t) = 0$.

Cases (a) and (b) describe most stages in an operating cycle, as illustrated by the typical example in the next section.

3. The stages in a typical operating cycle

An operating cycle consists of a number of stages. The number of patented arrangements is large (see, for example, (Kirkby and Kenney, 1988)), but the example illustrated by Fig. 1 is representative.

Here, in stage 1, the gas mixture flows at a constant (high) pressure p_1 from

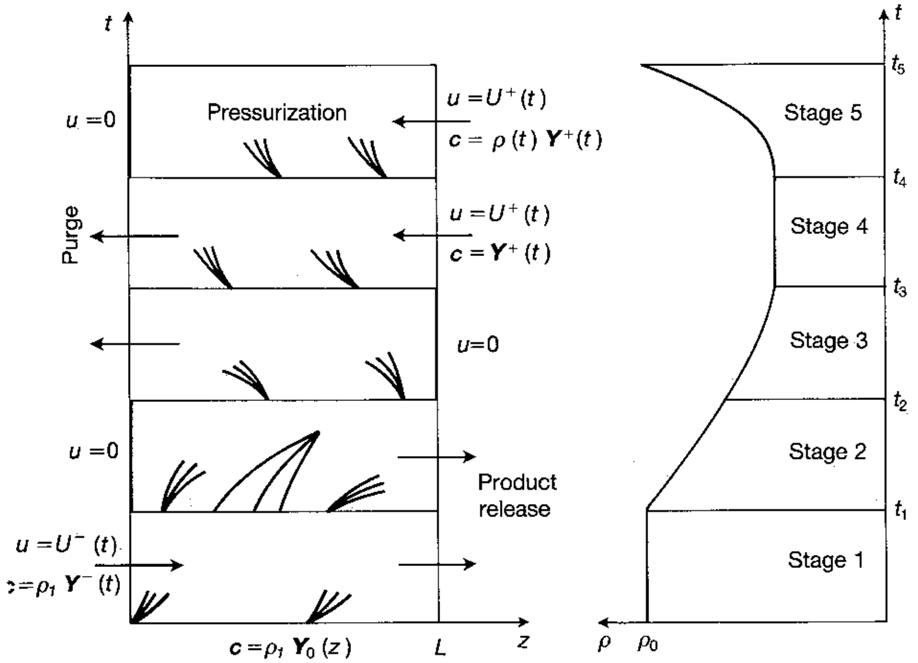

FIG 1 The stages in a typical operating cycle

$z = 0$ towards $z = I$. At time t_1 the inlet valve is closed, gas continues to flow through $z = L$ and the pressure falls monotonically during stage 2. At $t = t_2$ the valve at $z = L$ is closed, and the valve at $z = 0$ is opened, so that during stage 3 waste gas exhausts through $z = 0$. The pressure continues to fall until a reference (atmospheric) pressure is reached at $t = t_3$. During stage 4, a constant-pressure stage $t_3 < t < t_4$, the column is 'purged' by reintroducing at $z = L$ some of the 'waste' gas collected from $z = L$ during stage 2. At $t = t_4$, the valve at $z = 0$ is again closed and the column is repressurized by 'backfill' through $z = L$, partly by introducing some of the enriched product released during stage 2. At time $t = t_5$ the pressure returns to its initial value p_1. The cycle is then repeated.

It will be seen that 'fresh' gas mixture is introduced only during stage 1. Refined product is collected during stages 1 and (part of) 2, while the unwanted constituents are exhausted at $z = 0$ during stages 3 and 4.

Stages 1 and 4 are constant-pressure stages, so that equation (2.12) relates the local flow speed $u(z, t)$ to the respective inlet speeds $u(0, t) = U^-(t)$ and $-u(L, T) \equiv -U^+(t)$ by

$$\left.\begin{aligned} u(z, t) &= \frac{1}{K(z, t)} U^-(t), \quad \text{stage 1,} \\ u(z, t) &= \frac{K(L, t)}{K(z, t)} U^+(t), \quad \text{stage 4.} \end{aligned}\right\} \tag{3.1}$$

Since all the $N-1$ finite characteristic speeds are positive multiples of u, the corresponding characteristic curves have positive slopes during stages 1 and 2, but negative slopes during stages 3, 4 and 5. The only exception is at closed ends of the column, where the characteristic speeds are zero ($z=0$ during stages 2 and 5, $z=L$ during stage 3).

Consequently, the initial boundary-value problem appropriate to stage 1 is to specify the initial concentrations $c_i(z,0)=\rho_1 y_i(z,0)$ along $0<z<L$, together with the inlet concentrations $c_i(0,t)=\rho_1 Y_i^-(t)$ and inlet speed $U^-(t)$ during $0\leq t<t_1$. At each instant, equation (3.1) then relates $u(z,t)$ to $U^-(t)$ via the current concentration distributions $c_i(z,t)$. The evolution of $\boldsymbol{c}(z,t)$ is itself governed by the system (2.5).

Stage 4 is treated similarly, with 'initial' data $\boldsymbol{c}(z,t_3)$ determined as the final state of stage 3 and with inflow data $\boldsymbol{c}(L,t)=\boldsymbol{Y}^+(t)$, $u=U^+(t)$ specified on $z=L$.

For stage 2, 'initial' data $\boldsymbol{c}(z,t_1)$ are determined from stage 1. Since no gas flows across $z=0$, the $N-1$ characteristics coincide with $z=0$ during $t_1<t<t_2$. The concentrations $\boldsymbol{c}(0,t)=\boldsymbol{c}^-(t)$ cannot be specified independently since they evolve according to (2.5) which, on $z=0$, reduces to the set of *ordinary* differential equations

$$\sum_{j=1}^{N}\left(Q_{ij}-\frac{c_i^-}{\rho}\sum_{m=1}^{N}Q_{mj}\right)\frac{\mathrm{d}c_j^-}{\mathrm{d}t}=0, \qquad \rho=\sum_{j=1}^{N}c_j^-(t). \tag{3.2}$$

In this set of equations t is a redundant variable, so that solutions may be expressed in the form

$$c_j^-(t)=C_j\{\rho(t),\boldsymbol{Y}^-(t_1)\}=C_j\{\rho,\boldsymbol{Y}^-(t_1)\} \tag{3.3}$$

which relates the various species concentrations at $z=0$ to the changing density and to the final values $Y_i^-(t_1)$ of the inlet-volume fractions during stage 1. Also, as in case (b) of section 2, equation (2.12) simplifies during $t_1<t<t_2$ to give

$$u(z,t)=\frac{\rho'(t)}{K(z,t)}\int_0^z M(\zeta,t)\,\mathrm{d}\zeta. \tag{3.4}$$

Equation (3.4) shows that changes in density (or, equivalently, pressure) are the driving mechanism for flow and for the resulting changes in concentration distributions. Consequently, during stage 2 it is convenient to replace time by the evolution parameter $\tau=\rho_1-\rho(t)$ so that u is replaced by the pseudo-velocity

$$v\equiv\frac{u}{\tau'(t)}=\frac{-u}{\rho'(t)}=\frac{-1}{K(z,\tau)}\int_0^z M(\zeta,\tau)\,\mathrm{d}\zeta. \tag{3.5}$$

(As before, K and M are defined using spatial integrals at the current instant and so may be labelled by τ equally as well as by t.) The evolution of $\boldsymbol{c}$ is then determined from (2.5) with u replaced by v and t replaced by $\tau=\rho_1-\rho$, where $v(z,\tau)$ is determined at each instant from (3.5).

Stage 3 is similar to stage 2, but with reversed flow and with $U^+=0$. Again using $\tau\equiv\rho_1-\rho(t)$ as the timelike parameter during $t_2<t<t_3$ reduces equation

(2.12) to the relationship

$$v = \frac{-u}{\rho'(t)} = \frac{1}{K(z,\tau)} \int_L^z M(\zeta,\tau)\,d\zeta \tag{3.6}$$

between the pseudo-velocity v and the density reduction τ. Characteristics travel in the direction of decreasing z except at $z = L$, where the system (2.5) reduces to an ordinary differential system with solution analogous to (3.3) in the form

$$c_j(L,t) = c_j^+(t) = C_j\{\rho_1 - \tau, \mathbf{Y}^+(t_2)\}.$$

During the pressurization stage 5, the natural timelike parameter is $\tau = \rho(t) - \rho_4 + \tau_4$, for $\tau_4 \leqslant \tau \leqslant \tau_5 = \tau_4 + \rho_0 - \rho_4$. The 'initial' data at $\tau = \tau_4$ are given by the final distribution of $\mathbf{c}$ in stage 4. The boundary conditions are more complicated. Through each point $\tau_4 \leqslant \tau < \tau_5$ of $z = L$ exactly $N - 1$ finite-speed characteristics enter the solution region so that it is appropriate to specify $c_j(L,\tau) = \rho(t)Y_j^+(t)$ (only $N-1$ independent quantities, since $\sum c_i = \rho$). The inlet flow speed cannot however be independently specified. It is determined by the closed end condition $U^- = 0$, which from (2.12) yields

$$v = \frac{u}{\tau'} = \frac{u}{\rho'(t)} = \frac{1}{K(z,\tau)} \int_0^z M(\zeta,\tau)\,d\zeta. \tag{3.7}$$

Even though boundary conditions are imposed at both $z = 0$ and $z = L$ during stage 5, a numerical procedure suitable for stage 3 does not require much modification. In each case, a modified form ($t \to \tau$, $u \to v$) of the system (2.5) is used to govern the evolution of $\mathbf{c}(z,\tau)$, while the corresponding distribution of pseudo-velocity v is determined as a solution to the ordinary differential equation (2.11) in the form (3.7) rather than (3.6).

During stages 1 and 2 the finite characteristic speeds are positive, while in stages 3 to 5 they are negative. The domains of dependence for the system (2.5) have the forms indicated in Fig. 1, suggesting the use of upwind differences in z. Also, from physical considerations it is expected that all finite characteristic speeds satisfy $|dz/dt| < |u|$, $|dz/d\tau| < |v|$.

It may be noted also that, just as ρ is a natural means for defining a timelike variable in stages 2, 3 and 5, mass inflow is the appropriate choice in the constant-pressure stages 1 and 4. Thus, in stage 1, the choice

$$\tau = \int_0^t U^-(T)\,dT$$

gives

$$v(0,\tau) = 1, \qquad \text{mass inflow} = \rho_1 A\tau,$$

while during stage 4, the choice

$$\tau = \tau_3 - \int_{t_3}^t U^+(T)\,dT$$

gives

$$v(L,\tau) = -1, \qquad \text{mass inflow} = \rho_4 A(\tau - \tau_3).$$

4. The binary mixture

The general situation, with three or more constituents in the gas mixture, is too complicated to allow a predominantly analytic treatment. Effective analysis must be largely numerical. However, to reveal the phenomena which should be expected (and which a numerical procedure must be capable of handling) it is useful to treat the binary mixture analytically.

For $N=2$, the singular 2×2 matrix $\boldsymbol{A}$ of (2.8) has the characteristic equation

$$\lambda^2 - \lambda(A_{11} + A_{22}) = 0,$$

so that the unique finite characteristic speed of (2.5) is

$$\frac{\mathrm{d}z}{\mathrm{d}t} = \frac{u}{A_{11} + A_{22}},$$

where

$$A_{11} + A_{22} = \frac{c_1(Q_{22} - Q_{21}) + c_2(Q_{11} - Q_{12})}{c_1 + c_2}.$$

The corresponding left eigenvector of $\boldsymbol{A}$ is

$$\boldsymbol{l}^T = (A_{21}, A_{22}) = (-A_{11}, -A_{12}) = (-A_{11}, A_{22}),$$

so that the differential equation holding along each characteristic is

$$\frac{\mathrm{d}c_1}{\mathrm{d}c_2} = \frac{A_{22}}{A_{11}} = \frac{c_1 Q_{22} - c_2 Q_{12}}{c_2 Q_{11} - c_1 Q_{21}}$$

or, equivalently,

$$\frac{\mathrm{d}Q_1}{\mathrm{d}Q_2} = \frac{c_1}{c_2}, \qquad Q_i = Q_i(\boldsymbol{c}). \tag{4.1}$$

Integration of (4.1) provides a relationship between c_1 and $c_1 + c_2 = \rho(t)$ which depends also on the value c taken by c_1 at points of that characteristic having a reference density ρ_0. Thus the concentrations c_1 and c_2 may be expressed in the forms

$$c_1 = P\{\rho(t), c\}, \qquad c_2 = \rho(t) - P\{\rho(t), c\}, \tag{4.2}$$

where

$$\frac{\partial P}{\partial \rho} = \left\{1 + \frac{\mathrm{d}c_2}{\mathrm{d}c_1}\bigg|_c\right\}^{-1} = \frac{A_{22}}{A_{11} + A_{22}}, \qquad P(\rho_0, c) \equiv c.$$

4.1 *Constant Pressure*

Equation (4.2) shows that, in each constant-pressure stage, both c_1 and $\rho - c_1$ are constant along each c-characteristic. Equation (4.2) simplifies to

$$c_1 = C(c).$$

Moreover, the right-hand side of equation (2.11) vanishes so that uK depends only on t. Also it is allowable to choose the integrating factor K of the form

$$K = K(c_1) = K\{C(c)\},$$

where

$$\frac{K'(c_1)}{K} = \frac{(Q_{21} - Q_{22}) - (Q_{12} - Q_{11})}{(Q_{21} - Q_{22})c_1 + (Q_{12} - Q_{11})(\rho - c_1)}.$$

The characteristics $c = \text{const}$ are then determined from

$$\left.\frac{\mathrm{d}z}{\mathrm{d}t}\right|_c = \frac{u_0(t)}{(A_{11} + A_{22})K(c_1)}, \qquad u = \frac{u_0(t)}{K(c_1)}.$$

When an appropriate timelike variable $\tau(t)$ is introduced, defined by $\tau'(t) = u_0(t)$, it is seen that for a binary mixture *the concentration distributions in any constant-pressure stage evolve as in a simple wave* described by

$$(A_{11} + A_{22})K(c_1)\frac{\partial c_1}{\partial \tau} + \frac{\partial c_1}{\partial z} = 0. \tag{4.3}$$

If the characteristics are labelled by the parameter ξ such that $z = \xi$ at $t = t_0$ (a reference time when $\tau = \tau_0$) then the solution may be written as†

$$\left.\begin{aligned} &c_1 = \hat{C}(\xi), \qquad c_2 = \rho - \hat{C}(\xi), \qquad u = u_0(t)/K\{\hat{C}(\xi)\}, \\ &(A_{11} + A_{22})K\{\hat{C}(\xi)\}(z - \xi) = \int_{t_0}^{t} u_0(\hat{t})\,\mathrm{d}\hat{t} \equiv \tau - \tau_0. \end{aligned}\right\} \tag{4.4}$$

As in simple waves, the dependence of $\partial z/\partial \tau = -\xi_\tau/\xi_z$ on the disturbance $c_1 = \hat{C}(\xi)$ causes the characteristics either to spread out or to converge, so tending to form an abrupt jump in c_1 (a 'shock'). Spreading occurs in portions of the signal where ξ_z decreases with t, while convergence occurs in portions where ξ_z increases with t. Since differentiation of (4.4) gives

$$\xi_z = \frac{1}{1 + (\tau - \tau_0)S'(\xi)},$$

where $S(\xi) = [(A_{11} + A_{22})K\{\hat{C}(\xi)\}]^{-1}$ is the 'pseudo-speed' of each ξ characteristic, it is seen that 'spreading' portions of a disturbance are those in which $S'(\xi)$ has the same sign as $u_0(t)$. 'Steepening' portions are those in which $S'(\xi)$ and $u_0(t)$ have opposite signs. A 'shock' forms when ξ_z first becomes infinite, which is at the earliest time t for which

$$(\tau - \tau_0)S'(\xi) = S'(\xi)\int_{t_0}^{t} u_0(\hat{t})\,\mathrm{d}\hat{t} = -1. \tag{4.5}$$

For flow towards $z = L$ this can happen only on characteristics for which S *decreases* with z, while for flow towards $z = 0$ it can occur only on characteristics for which S *increases* with z. Equation (4.5) generalizes the familiar shock-

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† Substantially this representation was obtained by Professor Eric Varley at an early stage of the Oxford Study Group with Industry, 1985.

formation criterion for simple waves and shows that shocks form on characteristics $\xi=\xi^*$, where $S'(\xi)\,\mathrm{sgn}\,u_0$ has a local maximum. The instant of shock formation is given by

$$\tau-\tau_0=\int_{t_0}^{t} u_0(\hat{t})\,\mathrm{d}\hat{t}=\frac{-1}{S'(\xi^*)}.$$

Subsequent growth of shocks is treated in section 5.

4.2 *Varying Pressure*

In pressurization stage 5 or in depressurization stages, 2,3 the concentrations along each ξ characteristic depend on $\rho=\rho(t)$, as well as on the concentration $c_1=c(\xi)$ associated with the reference density. Expressions (4.2), together with the fact that $\boldsymbol{A}$, $\boldsymbol{B}$, $\boldsymbol{Q}$, etc. are defined in terms of c_1 and c_2, suggests that a change to characteristic coordinates (ξ, t) be made.

Definition of

$$z=Z(\xi,t),\qquad Z_t=u/\lambda,\qquad Z_\xi=l(\xi,t)$$

leads to replacement of the derivatives according to

$$\frac{\partial}{\partial z}\rightarrow\frac{1}{l}\frac{\partial}{\partial\xi},\qquad \frac{\partial}{\partial t}\rightarrow\frac{\partial}{\partial t}-\frac{u}{\lambda l}\frac{\partial}{\partial\xi}.$$

Here $l(\xi,t)$, which measures the spacing of the ξ characteristics, is related to the characteristic speed through the compatibility condition

$$\frac{\partial l}{\partial t}=\frac{\partial}{\partial\xi}\left(\frac{u}{\lambda}\right). \tag{4.6}$$

Transformation of equation (2.11) in this binary case ($N=2$) leads to

$$\frac{\partial}{\partial\xi}\{\hat{K}(\rho,c)u\}=\hat{M}(\rho,c)l(\xi,t)\rho'(t), \tag{4.7}$$

where $\hat{K}(\rho,c)$ and $\hat{M}(\rho,c)$ are defined by

$$\frac{\hat{K}_c}{\hat{K}}=\sum_{i=1}^{2}B_i\frac{\partial c_i}{\partial c}\Big/\sum_{i=1}^{2}B_ic_i=\frac{(B_1-B_2)P_c(\rho,c)}{(B_1-B_2)P+\rho B_2},$$

$$\frac{\hat{M}}{\hat{K}}=\frac{\det\boldsymbol{Q}}{(B_1-B_2)P+\rho B_2},\qquad B_1=Q_{21}-Q_{22},\quad B_2=Q_{12}-Q_{11}.$$

Equations (4.6) and (4.7) form a linear system for u and l. They may be simplified to the form

$$\frac{\partial l}{\partial\rho}=\frac{\partial w}{\partial\xi},\qquad \frac{\partial}{\partial\xi}\{\lambda\hat{K}(\rho,c)w\}=\hat{M}(\rho,c)l,\qquad c=c(\xi) \tag{4.8}$$

by using ρ as the timelike variable and writing

$$u=\lambda\rho'(t)w(\xi,\rho),\qquad \lambda=A_{11}+A_{22}=\lambda(\rho,c).$$

The fact that w (but not c) may readily be eliminated from the system (4.8) illustrates the subsidiary rôle taken by u in the original system (2.3) and (2.4). However, it is preferable not to perform this elimination but to rearrange (4.8) in characteristic form as

$$\frac{\partial l}{\partial \rho}=\frac{1}{\lambda}\left(\frac{\hat{M}}{\hat{K}}\right)l-\left(\frac{\hat{K}_c}{\hat{K}}+\frac{\lambda_c}{\lambda}\right)c'(\xi)w, \tag{4.9}$$

$$\frac{\partial w}{\partial \xi}=\frac{1}{\lambda}\left(\frac{\hat{M}}{\hat{K}}\right)l-\left(\frac{\hat{K}_c}{\hat{K}}+\frac{\lambda_c}{\lambda}\right)c'(\xi)w. \tag{4.10}$$

Equation (4.9) may be regarded as an evolution equation along each ξ characteristic, governing the spreading of that characteristic from its neighbours. Equation (4.10) (like (4.7)) governs the distribution of speed at each instant (or equivalently for each value of ρ). It may be noted that the coefficients in (4.9) and (4.10) involve exactly the combinations $\hat{K}_c/\hat{K}$ and $\hat{M}/\hat{K}$ arising in the definitions of $\hat{K}$ and $\hat{M}$, and so are readily written in terms of ρ and $c(\xi)$.

Initial and boundary conditions appropriate for (4.9) and (4.10) are determined by reference to equivalent problems in the (z, t)-plane for each of the stages 2, 3 and 5 (see Fig. 2).

Stages 2 and 3 are of similar type. Also, since each ξ characteristic within $0<z<L$ in stage 3 has emerged from stage 2 the single function $c=d_1(\xi)$ relates c to ξ in both stages. The resulting boundary-value problems for (4.9) and (4.10) are shown in Fig. 3 for stages 2 and 3. Note that, in each case, ρ *decreases* with time.

Initial conditions for stage 2 are found by inverting $\xi=\xi_1(z)$ as $z=z_1(\xi)$, so giving

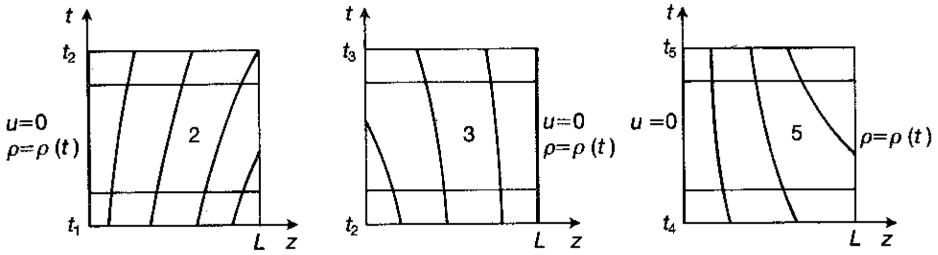
$$l(\xi, \rho_1)=l_1(\xi)=z_1'(\xi).$$

From the solution $l(\xi, \rho)$ to (4.9) and (4.10), $z=Z(\xi, t)=\hat{Z}(\xi, \rho)$ is found by integrating

$$\hat{Z}_\xi=l \quad \text{with} \quad \hat{Z}(z_0, \rho)=0.$$

This yields the outflow conditions by relating ξ to ρ through the solution $\xi=\chi_2(\rho)$ of

$$\hat{Z}(\xi, \rho)=L.$$



$\xi=\xi_1(z)$ $c=d_1(\xi)$ $\xi=\xi_2(z)$ $c=d_1(\xi)$ $\xi=\xi_4(z)$ $c=d_4(\xi)$

FIG. 2. Initial and boundary conditions for stages 2, 3 and 5

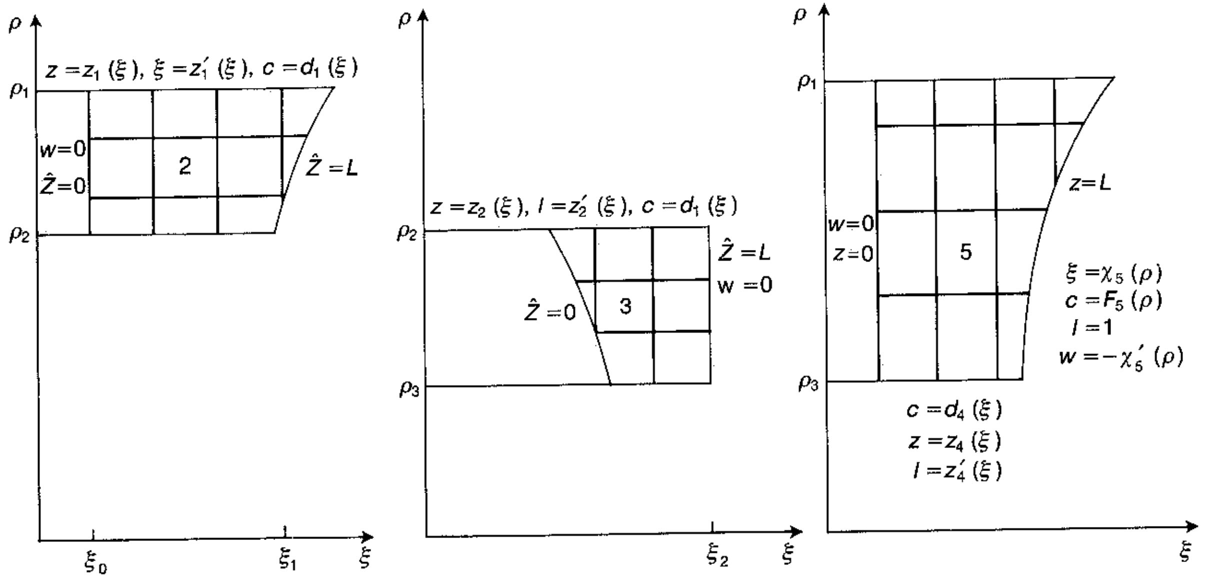


FIG. 3. Boundary-value problems for equations (4.9), (4.10) and (4.11) (stages 2, 3 and 5). Notice that integration along the characteristics $\rho = \text{const}$ proceeds in the direction counter to the gas flow

Also it yields the final state of stage 2 (and initial state for stage 3) in the form

$$z = \hat{Z}(\xi, \rho_2) = z_2(\xi).$$

Stage 3 is integrated similarly in $\xi_0 < \xi \leq \xi_2$ using the initial conditions $w(\xi_2, \rho) = 0$, $\hat{Z}(\xi_2, \rho) = L$, so giving the final state $z = \hat{Z}(\xi, \rho_3) = z_3(\xi)$ and the output conditions $\xi = \chi_3(\rho)$ through the relation $\hat{Z}(\chi_3(\rho), \rho) = 0$.

The pressurization stage, stage 5, is somewhat different, since some ξ characteristics *enter* the flow region through the *open* end $z = L$ where the concentration $c = F_5(\rho)$ is specified. To determine the relation $\xi = \chi_5(\rho)$ which holds along $\hat{Z} = L$ (see Fig. 3) the equation

$$\hat{Z}_\xi(\xi, \rho) = l, \qquad \hat{Z}(\xi_5, \rho) = 0$$

is integrated to give

$$\int_{\xi_5}^{\chi_5(\rho)} l(\xi, \rho)\, \mathrm{d}\xi = \hat{Z}(\chi_5(\rho), \rho) = L.$$

Since there is no loss of generality in taking $l = 1$ along $\hat{Z} = L$, differentiation gives

$$0 = l(\chi_5(\rho), \rho)\chi_5'(\rho) + \int_{\xi_5}^{\chi_5(\rho)} l_\rho\, \mathrm{d}\xi = \chi_5'(\rho) + \int_{\xi_5}^{\chi_5(\rho)} w_\xi\, \mathrm{d}\xi.$$

Consequently the ‘free boundary problem’ defining the path $\xi = \chi_5(\rho)$ in the (ξ, ρ)-plane is

$$\mathrm{d}\chi_5/\mathrm{d}\rho = -w(\chi_5, \rho) \tag{4.11}$$

together with the subsidiary conditions

$$l(\chi_5(\rho), \rho) = 1, \qquad c = F_5(\rho). \tag{4.12}$$

5. Abrupt jumps

The characteristics of the nonlinear system (2.4), (2.5) may coalesce and then overlap in the (z, t)-plane, so causing the solution to become multivalued. To prevent this, a discontinuity in u and $\mathbf{c}$, analogous to a gas-dynamic shock, must be introduced. This jump models a region of abrupt change in u and $\mathbf{c}$, where the equilibrium assumption and the neglect of inertia effects are not valid.

Equation (2.3) expresses conservation of the various species S_i. Consequently, across a discontinuity curve J, the jump conditions are

$$V[\![Q_i]\!] = [\![uc_i]\!], \qquad i = 1, 2, \ldots, N, \tag{5.1}$$

$$\sum_{i=1}^{N} [\![c_i]\!] = 0,$$

where $\mathrm{d}z/\mathrm{d}t = V$ is the speed of J and where $[\![f]\!] = f^+ - f^-$ denotes the jump in any quantity f across J. In a solution method for (2.4) and (2.5) it must be anticipated that jumps (5.1) may occur, with propagation speed which, in the weak discontinuity limit, reduces to any of the characteristic speeds $V^{(r)}$ of (2.9).

For a binary mixture with $c_2 = \rho(t) - c_1$, equations (5.1) reduce to

$$V = \frac{[\![uc_1]\!]}{[\![Q_1]\!]} = \rho \frac{[\![u]\!]}{[\![Q_1 + Q_2]\!]}. \tag{5.2}$$

Note that ρ, c_1^+ and c_1^- determine the ratio u^+/u^- of flowspeeds above and below the jump J as

$$\frac{u^+}{u^-} = \frac{\rho[\![Q_1]\!] - c_1^-[\![Q_1 + Q_2]\!]}{\rho[\![Q_1]\!] - c_1^+[\![Q_1 + Q_2]\!]} \tag{5.3}$$

independently of $\bar{u}$.

5.1 *Uniform-Pressure Stages*

When pressure remains constant equation (2.11) shows that, in regions where c_1 is continuous, Ku depends only on time. However Ku may be discontinuous across J. The expressions (4.4) describing the disturbance in a binary mixture should be amended as

$$u = \frac{u_0^\pm(t)}{K(c_1)}, \qquad c_1 = \hat{C}(\xi), \qquad z - \xi = S(\xi)\int_0^t u_0^\pm(\hat{t})\,\mathrm{d}\hat{t} = S(\xi)(\tau^\pm(t) - \tau_0). \tag{5.4}$$

This shows that two distinct relations between τ and t are required in the regions $\xi > \xi^+(t)$ and $\xi < \xi^-(t)$ above and below the jump. From (5.3) the functions $u_0^+(t)$, $u_0^-(t)$ defining $\tau^+(t)$ and $\tau^-(t)$ are found to be related by

$$\frac{u_0^+}{u_0^-} = \frac{K(c_1^+)}{K(c_1^-)} \frac{\rho[\![Q_1]\!] - c_1^-[\![Q_1 + Q_2]\!]}{\rho[\![Q_1]\!] - c_1^+[\![Q_1 + Q_2]\!]} = \hat{J}(c_1^+, c_1^-, \rho). \tag{5.5}$$

In stage 1, $c_1(\xi)$ and $u_0^-(t)$ are determined by initial conditions at $t = t_0$ and inflow conditions at $z = 0$, while in stage 4, $c_1(\xi)$ and $u_0^+(t)$ are determined by conditions at $t = t_3$ and inflow conditions at $z = L$.

Since $\mathrm{d}z/\mathrm{d}t = V$ along both $\xi = \xi^-(t)$ and $\xi = \xi^+(t)$, it is found that

$$\frac{\mathrm{d}\xi^-}{\mathrm{d}t} = \left\{\frac{V}{u_0^-} - S(\xi^-)\right\} \Big/ \left\{1 + S'(\xi)\int_0^t u_0^-(\hat{t})\,\mathrm{d}\hat{t}\right\}, \tag{5.6}$$

$$\frac{\mathrm{d}\xi^+}{\mathrm{d}t} = \left\{\frac{V}{u_0^+} - S(\xi^+)\right\} \Big/ \left\{1 + S'(\xi)\int_0^t u_0^+(\hat{t})\,\mathrm{d}\hat{t}\right\}.$$

Together with equations (5.2) and (5.5), these provide a coupled pair of ordinary differential equations for $\xi^+(t)$ and $\xi^-(t)$. Each solution defines related functions $\hat{J}$, $\tau^\pm$ of time, so allowing complete determination of the disturbance during a constant-pressure stage.

5.2 *Varying Pressure*

During the flow stages 2, 3 and 5 the formulation in section 4.2 using ρ and ξ as independent variables is appropriate. In this case, jump discontinuities must be inserted to prevent $l = Z_\xi$ becoming negative anywhere in the relevant solution region.

Since, throughout the solution, equations (4.2) hold, it follows that

$$c_1 = P(\rho, c), \qquad c_2 = \rho - P(\rho, c), \qquad c = c(\xi),$$

so that $Q_i = \hat{Q}_i(\rho, c)$. When the substitutions

$$u = \lambda\rho'(t)w(\xi, \rho), \qquad \lambda = \lambda(\rho, c)$$

are used, the conditions (5.2) across a jump J having

$$\frac{\mathrm{d}z}{\mathrm{d}\rho} = \frac{V}{\rho'(t)} = W, \qquad \xi = \xi^{\pm}(\rho), \qquad c = c^{\pm} = c\{\xi^{\pm}(\rho)\}$$

become

$$W = \rho\frac{[\![\lambda w]\!]}{[\![Q_1 + Q_2]\!]}, \qquad [\![\lambda wP]\!][\![Q_1 + Q_2]\!] = \rho[\![\lambda w]\!][\![Q_1]\!]. \tag{5.7}$$

Along the two paths $\xi = \xi^{\pm}(\rho)$ (see Fig. 4(b)) which define the characteristics meeting the jump J at ρ, use of the definitions $Z_\rho = w$, $Z_\xi = l$ leads to

$$W = w^+ + l^+\frac{\mathrm{d}\xi^+}{\mathrm{d}\rho} = w^- + l^-\frac{\mathrm{d}\xi^-}{\mathrm{d}\rho}. \tag{5.8}$$

Equations (5.7) and (5.8) are the conditions along the 'free boundaries' $\xi = \xi^{\pm}(\rho)$ which in general will occur within the solutions of (4.9) and (4.10). If ξ^+ and ξ^- have been evaluated at some value ρ, then $(5.7)_2$ rearranged analogously to (5.3) as

$$\frac{w^+}{w^-} = \left(\frac{\lambda^-}{\lambda^+}\right)\frac{\rho[\![Q_1]\!] - P^-[\![Q_1 + Q_2]\!]}{\rho[\![Q_1]\!] - P^+[\![Q_1 + Q_2]\!]}$$

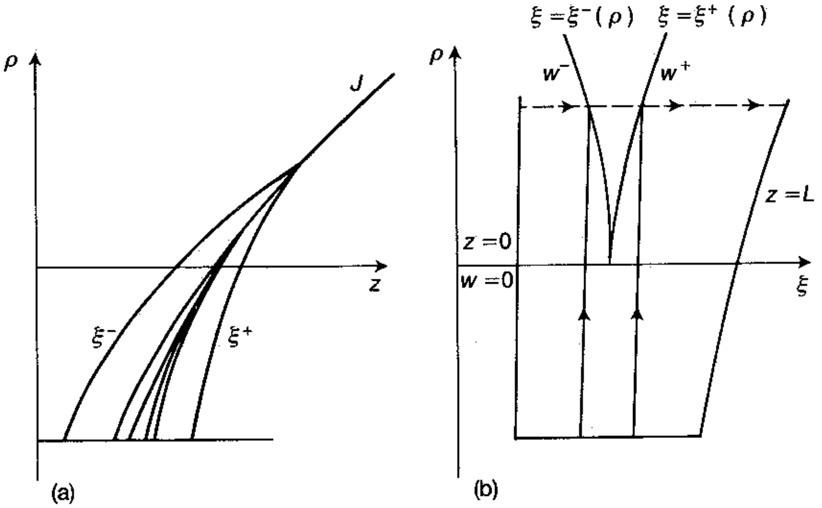


FIG. 4. Propagation of a jump J, as in stage 5 (a) Characteristics ξ^+, ξ^- in the (z, ρ)-plane; (b) paths $\xi = \xi^+(\rho)$, $\xi = \xi^-(\rho)$ in the (ξ, ρ)-plane

allows the boundary condition $w=0$ at a closed end to be used with equation (4.10), so giving $w(\xi, \rho)$ at all relevant values of ξ. Equation $(5.7)_1$ then determines W, so that (5.8) gives the pair of ordinary differential equations

$$d\xi^{\pm}/d\rho = \{W - w^{\pm}(\xi, \rho)\}/l^{\pm}(\xi, \rho). \tag{5.9}$$

These, together with equation (4.9), allow integration with respect to the timelike variable ρ.

6. Numerical aspects of the problem

6.1 *Numerical Solution of the Equations for Pressure-Swing Adsorption*

We have seen above how the equations for pressure-swing adsorption may be characterized as a hyperbolic system, and noted some special cases in which analytic solutions are available. In general however even for the 2-species case with no energy equation a numerical approach is required. For simplicity we concentrate on the 2-species case, though the method described below is applicable to any number of constituents. We include analysis of all five of the stages discussed in previous sections, and note that at each stage the numerical method must be modified to reflect the different characters of different parts of the process. Finally in section 6.2 some numerical results are given, both for a simple test problem in which the entire solution may be calculated, and a case where the Langmuir isotherms are used.

We assume that $N+1$ equispaced mesh points $z_0, z_1, \ldots, z_N$ are introduced along the column, with a corresponding time step dt, and that the stages take place over time intervals the commencements of which are labelled 0, t_1, t_2, t_3 and t_4 respectively. The whole cycle is assumed to be complete when $t=t_5$. At the start of stage 1, the quantities $\boldsymbol{c}(z, 0)$, $\boldsymbol{c}(0, t)$ and $u(0, t)$ are known, the density is constant, and the flow is from $z=0$ to $z=L$ along the column. To advance one time step we first solve the equation (see (2.5))

$$\left[Q_{11} - \frac{c_1}{\rho}(Q_{11}+Q_{21})\right]\frac{\partial c_1}{\partial t} + \left[Q_{12} - \frac{c_1}{\rho}(Q_{12}+Q_{22})\right]\frac{\partial c_2}{\partial t} + u(z, t)\frac{\partial c_1}{\partial z} = 0 \tag{6.1}$$

using a distribution $u(z, t)$ corresponding to the start of the time step. This will give a 'predicted' value of $\boldsymbol{c}(z, t)$ at the next time step. It should be noted that we only solve a single equation for $\boldsymbol{c}$ as we know values for the sum c_1+c_2. In the N-species case of course, we would solve $N-1$ of the equations

$$\sum_{j=1}^{N}\left(Q_{ij} - \frac{c_i}{\rho(t)}\sum_{m=1}^{N} Q_{mj}\right)\frac{\partial c_i}{\partial t} + \frac{u\,\partial\rho_i}{\partial t} = 0 \qquad (i=1, 2, \ldots, N). \tag{6.2}$$

We now update u by solving (see (2.10))

$$B_1\frac{\partial}{\partial z}(uc_1) + B_2\frac{\partial}{\partial z}(uc_2) = 0 \tag{6.3}$$

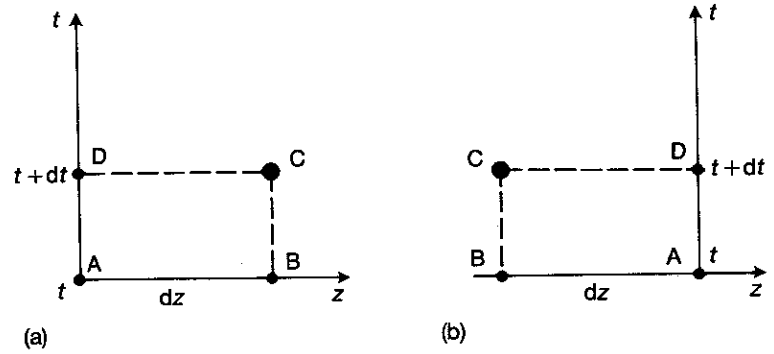


FIG. 5. Orientation of computational grid for stages 1, 2 and 3, 4 respectively

using the predicted values of c, to give the prediction of $u(z, t)$ at the end of the time step. This updated distribution for u may then be used to traverse the predictor–corrector cycle again if desired, but in practice this has not been found to be necessary unless very great accuracy is desired. Equation (6.3) is, of course in an especially simple form in stage 1 because the density is constant. To be more specific, writing (6.2) as

$$\alpha_1 \frac{\partial c_1}{\partial t} + \alpha_2 \frac{\partial c_2}{\partial t} + u \frac{\partial c_1}{\partial z} = 0 \tag{6.4}$$

we take into account the fact that the flow is from left to right along the column and use a simple 'box' scheme discretization (see Fig. 5(a)) to write (6.4) as

$$\alpha_1(c_{1_D} - c_{1_A} + c_{1_C} - c_{1_B}) + \alpha_2(c_{2_D} - c_{2_A} + c_{2_C} - c_{2_B}) + \lambda u_B(c_{1_C} - c_{1_D} + c_{1_B} - c_{1_A}) = 0, \tag{6.5}$$

where

$$\lambda = \delta t / \delta z.$$

Equation (6.5) may easily be rearranged to give an explicit formula for c_{1_C}, and discretizing (6.3) as

$$B_1((uc_1)_C - (uc_1)_D + (uc_1)_B - (uc_1)_A) + B_2((uc_2)_C - (uc_2)_D + (uc_2)_B - (uc_2)_A) = 0 \tag{6.6}$$

allows the derivation of an explicit formula for u_c in terms of the 'predicted' values of c. It may easily be shown that this method has $O(h^2)$ accuracy, and unconstrained stability. One of the reasons for this is that the CFL condition is always satisfied as a result of the analytical information known about the characteristics.

Equations (6.5) and (6.6) describe the general nature of the entire numerical method, but there are a number of alterations which must be made depending on which stage is under consideration. For stages in which the pressure, and therefore the density is not constant, so that the full version of equation (2.10) applies, (6.6) must be altered to read

$$B_1((uc_1)_C - (uc_1)_D + (uc_1)_B - (uc_1)_A) + B_2((uc_2)_C - (uc_2)_D + (uc_2)_B - (uc_2)_A) = 2\mathrm{d}z\rho'(t)\det \boldsymbol{Q}, \qquad (6.7)$$

where we assume that since the pressure is 'known', the density time derivative may be regarded as prescribed. In stages 3, 4 and 5, where flow is from right to left along the column, we naturally change the direction of differencing of equations (6.2) and (6.3). The net result of this is that Fig. 5(a) is changed to Fig. 5(b), and the formulae for c_{1_C} and u_C become

$$c_{1_C} = \frac{-\alpha_2\rho_c + \alpha_1[c_{1_A} + c_{1_B} - c_{1_D}] + \alpha_2[c_{2_A} + c_{2_B} - c_{2_D}] + \lambda u_B(c_{1_B} - c_{1_A} - c_{1_D})}{(\alpha_1 - \alpha_2 - \lambda u_B)},$$

$$u_C = \frac{B_1((uc_1)_D + (uc_1)_A - (uc_1)_B) + B_2((uc_2)_D + (uc_2)_A - (uc_2)_B) - 2\mathrm{d}z\rho'(t)\det \boldsymbol{Q}}{(B_1 - B_2)c_{1_C} + B_2\rho_C}. \qquad (6.8)$$

We must also consider how to deal with the stages in which, because of the infinite characteristic speed inherent in the problem, the boundary conditions arise naturally as the solutions of ordinary differential equations. Once again, in general we need only solve $N-1$ of these equations in the N-species case, and in the 2-species case a rearrangement of (3.2) gives

$$\frac{\mathrm{d}c_1}{\mathrm{d}t} = \frac{\rho'(t)[\rho^{-1}c_1(Q_{12} + Q_{22}) - Q_{12}]}{(Q_{11} - Q_{12}) + \rho^{-1}c_1(Q_{12} + Q_2 - Q_{21} - Q_{11})}, \qquad (6.9)$$

which may be solved by any standard method. The results presented below employed a simple 4th-order Runge–Kutta method to solve (6.9), which has proved accurate and easy to implement.

It remains to consider stage 5, where we have seen that the specification of the boundary conditions is slightly more complicated than in stages 1 to 4. Since in general we have u given at the left-hand end of the column and $\boldsymbol{c}$ at the right-hand end, we simply modify our differencing formulae as follows. To find the 'predicted' value of $\boldsymbol{c}$ the method used for right-to-left flow stages is used. An update of u may then be computed using a left-to-right difference as described for stage 1 but with a variable density, and the solution may be completed.

Before examining the numerical results produced by the scheme described above, some additional comments are relevant. We note first that the mathematical analysis of sections 1 to 5 has been indispensible in setting up the numerical method. The only reason why a simple box scheme is effective in this problem is that a complete knowledge of the characteristics has allowed us to identify the direction of wave propagation in each stage. For more general hyperbolic problems the one-sided difference methods used would capture only half the waves which may exist. It is also worth mentioning that it is possible to formulate another numerical scheme which makes even greater use of the analytical results. This relies on noting the fact that once a 'predicted' form of $\boldsymbol{c}$ has been calculated as described above, u may be calculated from equation (2.12) using the relevant definitions of $K(z, t)$ and $M(z, t)$ and the iteration loop continued without the need to use a finite-difference method for u. Although in principle it would be desirable to employ this exact solution for u, its extreme complexity and the appearance of the derivatives in $M(z, t)$ which would have to be estimated numerically make this scheme impractical. The exponentials involved would undoubtedly be a source of magnification of small errors, and it is unlikely that valuable results could be gained from this use of the exact solution. It is also worth pointing out that the box scheme described above, which has been chosen mainly for its simplicity, may be replaced by any alternative method without altering the basic structure of the method. Although for the simple cases described below the box method is perfectly satisfactory, if computation of cases where shock solutions existed was to be undertaken it is likely that a more sophisticated method would have to be used. The general form of the numerical scheme and its intimate dependence on the analysis would still remain, however.

6.2 *Numerical Results*

In order to test the proposed numerical method, two test cases were considered. For the first, a solution to all five stages of the problem was constructed. This case was of necessity simple and did not correspond to a realistic specification of the isotherms. It did however provide a worthwhile test of the efficiency and accuracy of the numerical method. We took $Q_1 = Q_2 = 1$, reducing the equations (2.3) to a set of standard conservation–convection type. Initial and boundary conditions were also chosen for simplicity. Specifically, we assumed that the five stages of the process took place in a column which extended from $z = 0$ to $z = 1$, and over the time intervals

$$[0\,, t_1),\quad [t_1\,, t_2),\quad [t_2\,, t_3),\quad [t_3\,, t_4),\quad [t_4\,, t_5)$$

so that stage I started at t_{I-1} and finished at t_I.

In stage 1, the conditions taken are

$$u(0, t) = 2t(t_1 - t), \qquad c_1(z, 0) = \tfrac{1}{2}\rho(1 - z),$$
$$c_1(0, t) = \tfrac{1}{2}\rho(1 + t_1 t^2 - \tfrac{2}{3}t^3), \qquad \rho = \rho_0 = \text{const},$$

so that the initial concentration is a simple linear profile, with associated exact solution

$$c_1 = \tfrac{1}{2}\rho(1 - z + t_1 t^2 - \tfrac{2}{3}t^3), \qquad u = 2t(t_1 - t).$$

In stage 2 the left-hand end is closed, so that $u = 0$ when $z = 0$. We also take

$$\rho(t) = (t_1 - t_2)^{-3}[(\rho_1 - \rho_0)(2t^3 - 3t^2(t_1 + t_2) + 6tt_1t_2)$$
$$+ \rho_1 t_1^2(t_1 - 3t_2) + \rho_0 t_2^2(3t_1 - t_2)],$$

so that $\rho'(t_1) = \rho'(t_2) = 0$, $\rho(t_1) = \rho_0$, $\rho(t_2) = \rho_1$.

On $t = t_1$, c_1 is given by the final concentration profile of c_1 from stage 1, and on the boundary $z = 0$ the relevant ordinary differential equations must be solved. The exact solution for this stage is

$$c_1 = \tfrac{1}{2}\rho(t)[1 + \tfrac{1}{3}t_1^3 - \rho(t)z/\rho_0], \qquad u = -\rho'(t)z/\rho(t).$$

In stage 3, the density is again decreased so that

$$\rho(t) = (t_2 - t_3)^{-3}[(\rho_2 - \rho_1)(2t^3 - 3t^2(t_2 + t_3) + 6tt_2t_3) + \rho_2 t_2^2(t_2 - 3t_3) + \rho_1 t_3^2(3t_2 - t_3)]$$

and $\rho'(t_2) = \rho'(t_3) = 0$, $\rho(t_2) = \rho_1$, $\rho(t_3) = \rho_2$. Again the solution on $t = t_2$ is that arising from stage 2, but this time ordinary differential equations are solved on the line $z = 1$. The exact solution now is

$$c_1 = \tfrac{1}{2}\rho(t)(1 + \tfrac{1}{3}t_1^3 - \rho_1/\rho_0) + \frac{\tfrac{1}{2}\rho^2(t)}{\rho_0}(1 - z), \qquad u = \frac{(1 - z)\rho'(t)}{\rho(t)}.$$

In stage 4 the density is constant and equal to ρ_2. We prescribe the velocity at $z = 1$ as

$$u(1, t) = \tfrac{1}{8}(t_3 - t)(t_4 - t)$$

and $c(1, t) = \frac{1}{2}(K_1 + K_2(U(t) - U(t_3)))$, where

$$K_1 = \rho_2(1 + \tfrac{1}{3}t_1^3 - \rho_1/\rho_0), \qquad K_2 = \rho_2^2/\rho_0,$$
$$U(t) = \tfrac{1}{8}[tt_3t_4 + \tfrac{1}{3}t^3 - \tfrac{1}{2}t^2(t_3 + t_4)],$$

and take $c(z, t_3)$ to be the concentration profile arising from stage 3. Here the exact solution is

$$c_1 = \tfrac{1}{2}(K_1 + K_2(1 - z + U(t) - U(t_3))), \qquad u = \tfrac{1}{8}(t_3 - t)(t_4 - t).$$

Finally, in stage 5, the left-hand end of the column is closed so that $u(0, t) = 0$. The solution at $t = t_4$ is the concentration profile resulting from stage 4, and the density is taken as

$$\rho(t) = \rho_0 + \frac{(t_5 - t)(\rho_2 - \rho_0)}{(t_5 - t_4)^2}[t + t_5 - 2t_4]$$

so that the repressurization is complete at $t = t_5$, when $\rho = \rho_0$ once again. Choosing to specify

$$c_1(1, t) = -\tfrac{1}{2}K_2\left(\frac{\rho(t)}{\rho_2}\right)^2 + \frac{1}{2}\frac{\rho(t)}{\rho_2}[K_1 + K_2(1 + U(t_4) - U(t_3))]$$

gives the analytic solution as

$$c_1 = -\tfrac{1}{2}zK_2\left(\frac{\rho(t)}{\rho_2}\right)^2 + \frac{1}{2}\frac{\rho(t)}{\rho_2}[K_1 + K_2(1 + U(t_4) - U(t_3))], \qquad u = \frac{\rho'(t)z}{\rho(t)}.$$

Figures 6 and 7 show respectively the predictions for concentration and velocity profiles along the column at typical times during each stage. The functional form of the density profile is also shown. Agreement is clearly very good, showing that the suggested method with the equations recast in their new form is both efficient and accurate.

Having shown via a simple test case that the proposed numerical method successfully combines a simple finite-difference method and theoretical analysis of the problem, we now turn to a more realistic and general case. We choose the

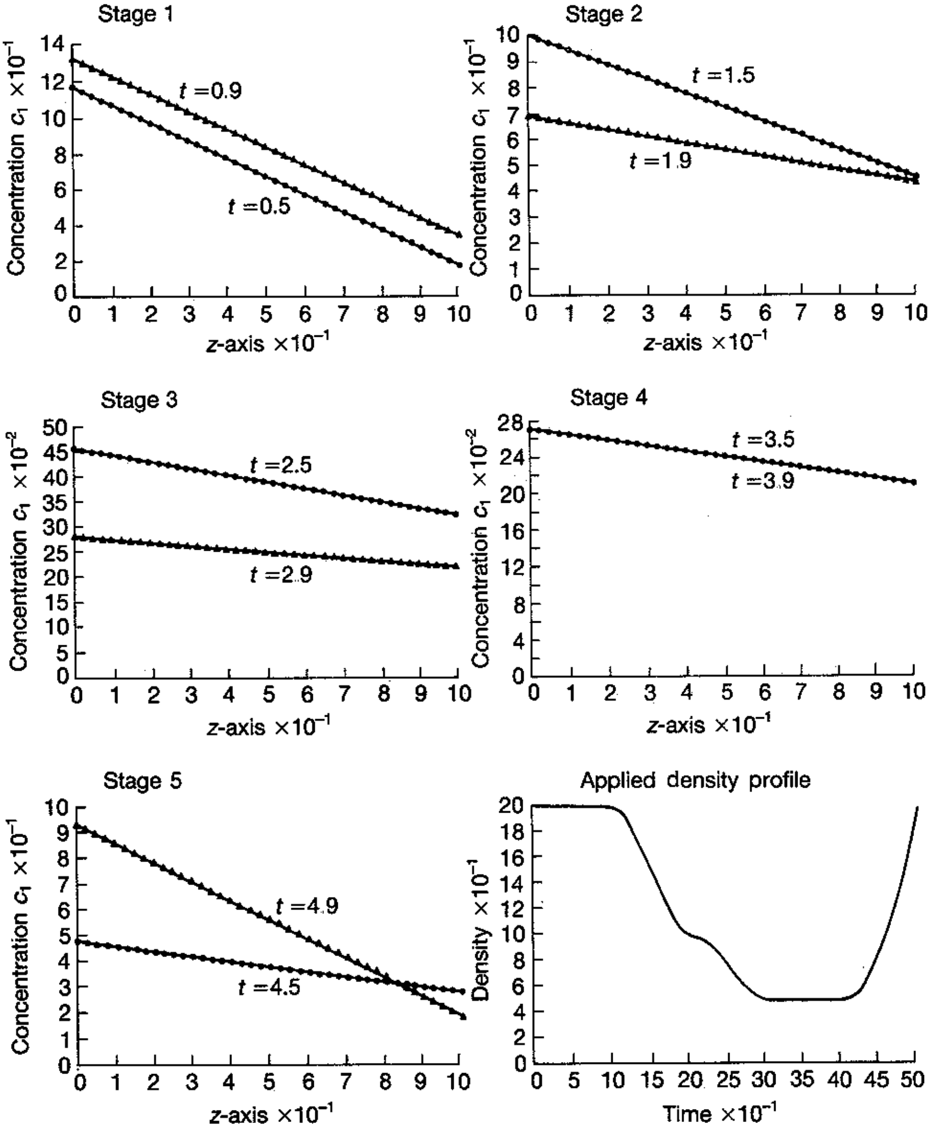


FIG. 6. Numerical (symbol) and exact (line) solutions for representative pressure-swing cycle

constants K_i to correspond to Langmuir isotherms (as in (Richter *et al.*, 1982)) so that

$$Q_{ij} = \left[1 + \frac{\beta\mu_i}{1 + \mu_1 c_1 + \mu_2 c_2}\right]\delta_{ij} - \mu_i c_i\left[\frac{\beta\mu_j}{(1 + \mu_1 c_1 + \mu_2 c_2)^2}\right].$$

Here β, μ_1 and μ_2 are constants and we assume that temperature changes are negligible. (As remarked earlier, the addition of an energy equation to all the foregoing analysis is straightforward, but for simplicity we do not consider such matters here.)

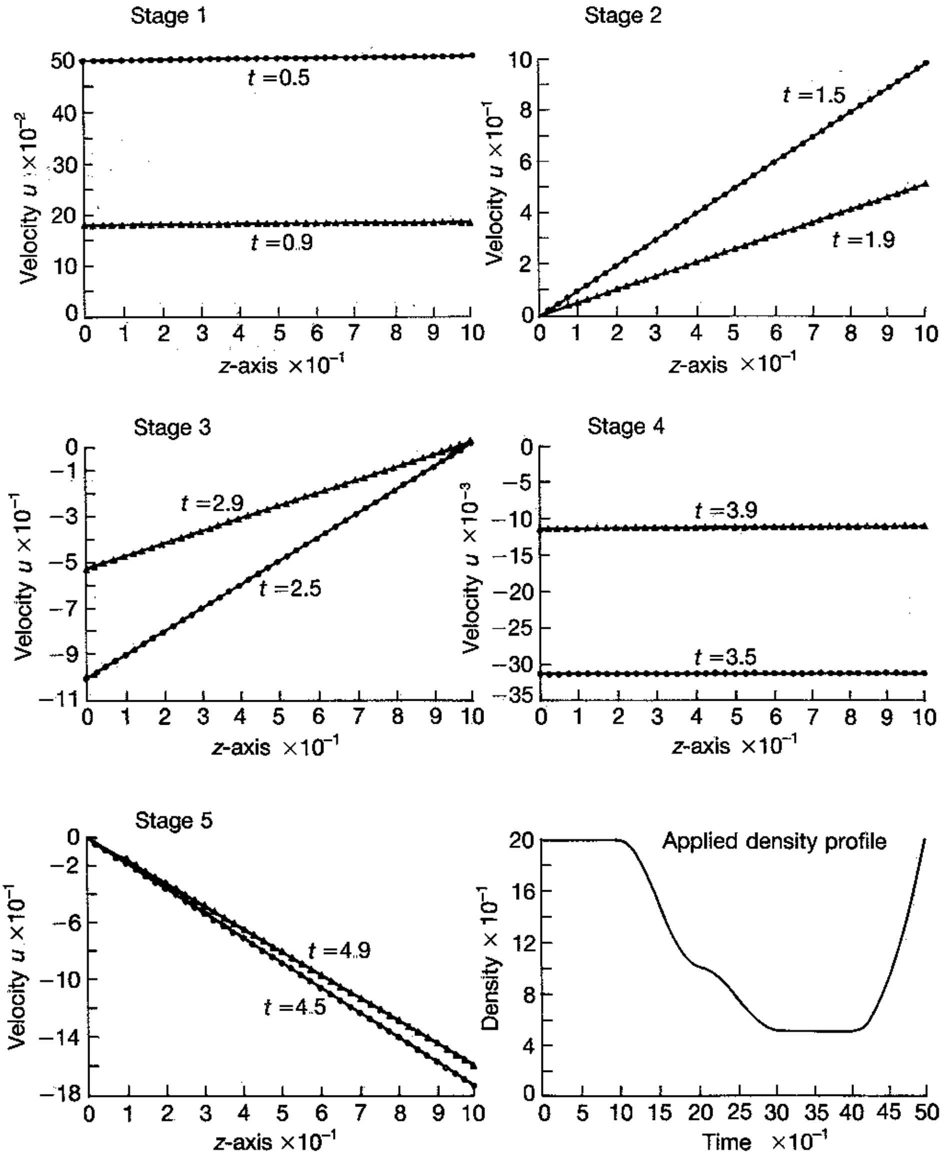


FIG. 7 Numerical (symbol) and exact (line) solutions for representative pressure-swing cycle

As remarked earlier for the constant-pressure stage 1 it is still possible to compute an analytic solution to the problem, though in later stages when the pressure varies we can no longer do this. Specifically, the stage-1 solution is

$$u = \frac{u(0, t)W(w)}{W(w_0(t))},$$

$$c_1 = \begin{cases} c_1(-b(c_1)[\tau - z/b(c_1)]) & (\tau < z/b_0), \\ c_0(\tau - z/b(c_1)) & (\tau > z/b_0), \end{cases}$$

where

$$W(w)=\begin{cases}\exp\left(\dfrac{2\gamma}{\Delta}\tan^{-1}\left(\dfrac{w-\gamma}{\Delta}\right)\right) & (2\gamma(1+\mu_1\rho)(1+\mu_2\rho)>\gamma^2),\\[2ex] \left(\dfrac{w-\gamma-D}{w-\gamma+D}\right)^{\gamma/D} & (2\gamma(1+\mu_1\rho)(1+\mu_2\rho)<\gamma^2),\end{cases}$$

$$w=1+\mu_2\rho+Bc_1, \qquad B=\mu_1-\mu_2, \qquad \gamma=\beta/2\rho,$$

$$2\gamma(1+\mu_1\rho)(1+\mu_2\rho)-\gamma^2=\begin{cases}\Delta^2 & \text{(if positive)},\\ -D^2 & \text{(if negative)},\end{cases}$$

$$b(c_1)=\begin{cases}\dfrac{w^2}{(w-\gamma)^2+\Delta^2}W(w),\\[2ex] \dfrac{w^2}{(w-\gamma)^2-D^2}W(w),\end{cases}$$

respectively,

$$\tau=\int_0^t\frac{u(0,s)}{W(w_0(s))}\,ds, \qquad b_0=b(c_1(0,0)).$$

The solution changes its form in the usual way depending on whether τ is greater or less than z/b_0 (that is, whether (z,τ) is to the left or the right of the last characteristic emanating from $(0,0)$) as shown in Fig. 8.

Figures 9 and 10 show respectively the concentration and velocity profiles for the case where $\beta=3.2$, $\mu_1=0.4$, $\mu_2=1.5$. The boundary conditions were the same as in the previous test case for stages 1 to 3, but had to be altered slightly in stages 4 and 5 to ensure the continuity of c_1. The comparison with the exact solution in stage 1 is clearly excellent and the effect of including the Langmuir isotherms can clearly be seen.

Computations were also carried out for 3- and 4-species cases with only minor changes being required in the computer coding.

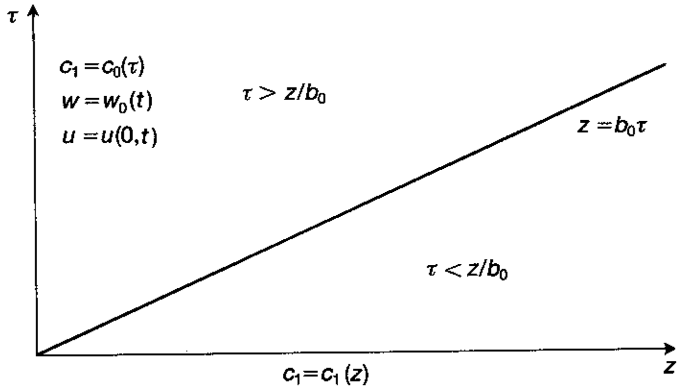


FIG. 8. Line where the solution to the stage-1 problem changes type in (z,τ)-space

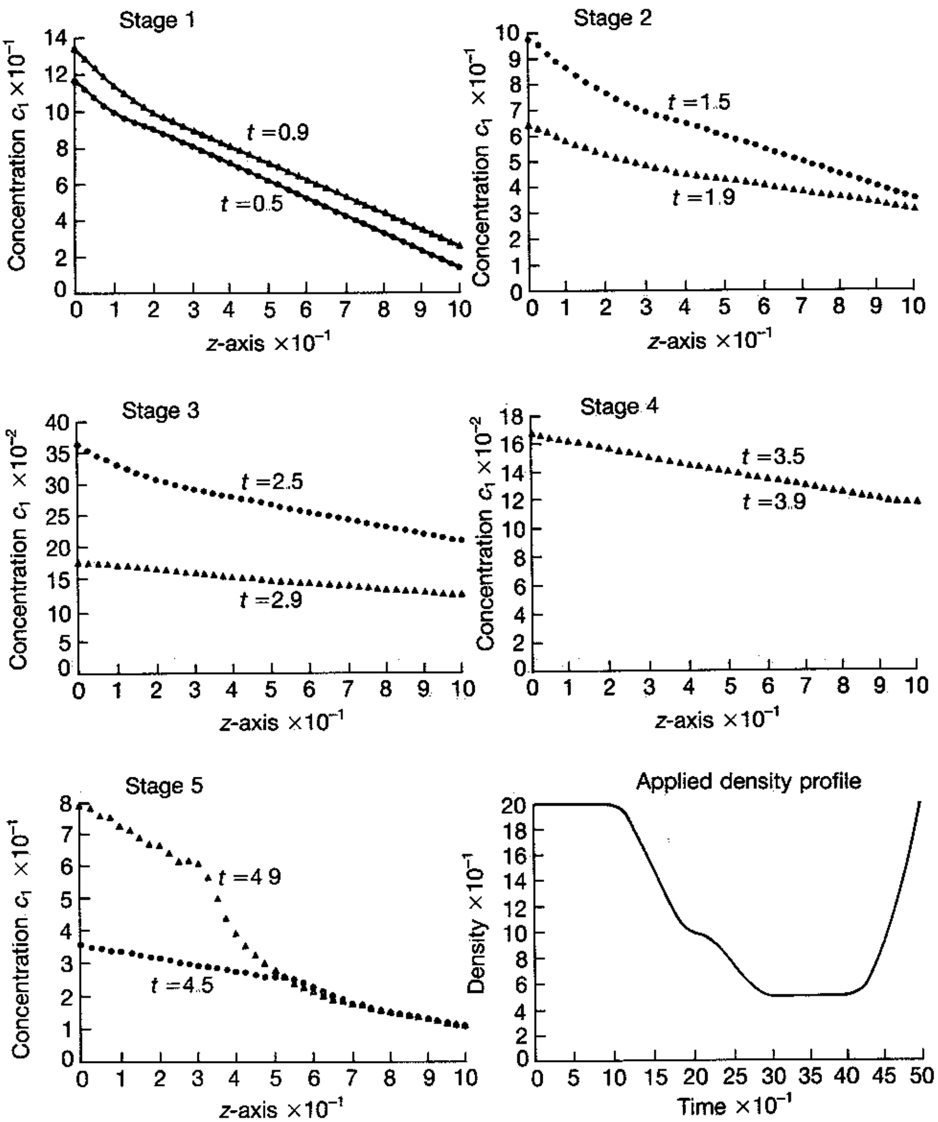


FIG. 9. Numerical (symbol) and exact (line) solutions for representative pressure-swing cycle in the case of Langmuir isotherms

7. Conclusions

A mathematical and numerical analysis of the industrial process of pressure-swing adsorption has been presented. The governing partial differential equations have been shown to be hyperbolic, but with an infinite characteristic speed. In order to allow a numerical solution of the equations to be carried out efficiently, they have been recast. The characteristics have been used to explain the more

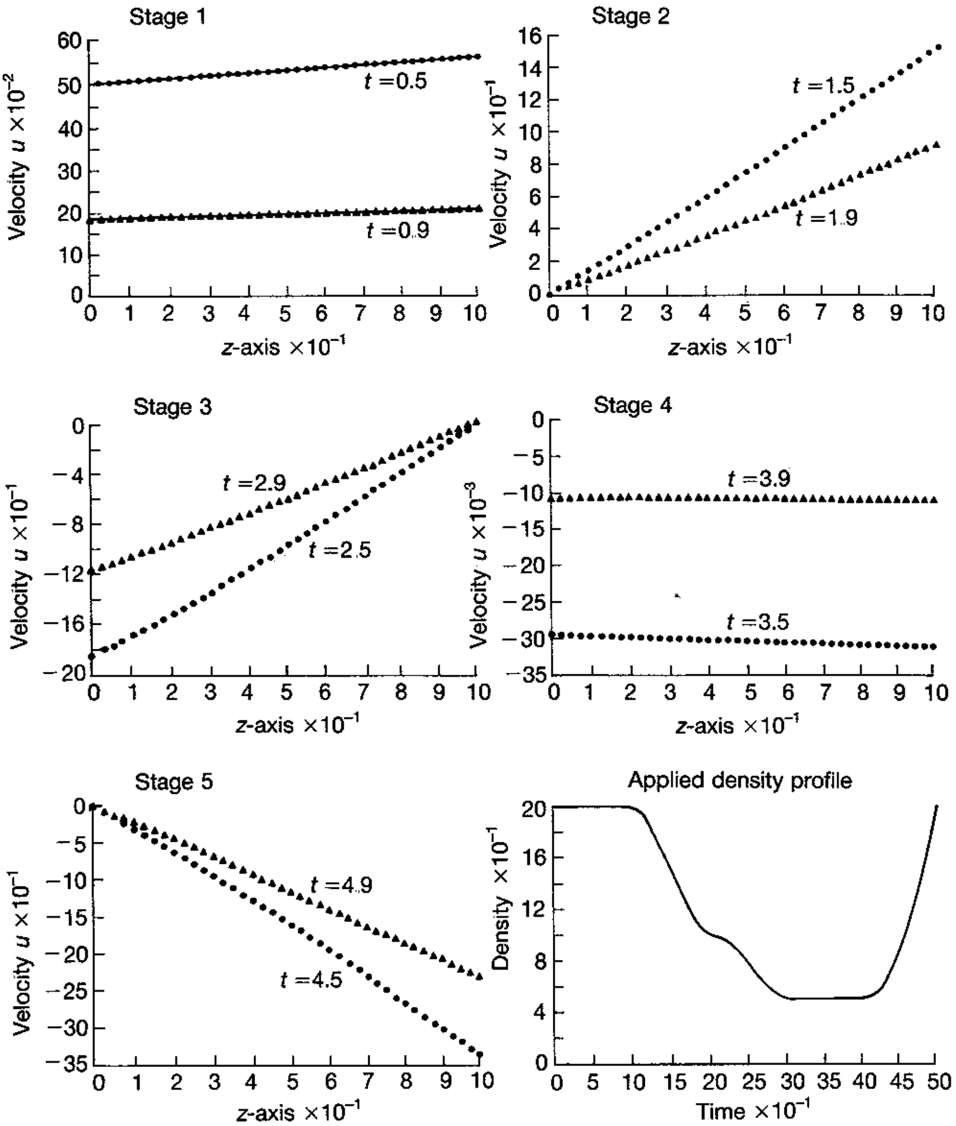


FIG 10. Numerical (symbol) and exact (line) solutions for representative pressure-swing cycle in the case of Langmuir isotherms

important details of the flow, and in some simplified cases it has been possible to construct analytic solutions to the governing equations. The mathematics of the problem has had a significant influence on the numerical scheme chosen, which has been shown to be accurate and efficient, and is easily applicable to the problem with more than two species. It could also be modified to take into account stages of the process which have not been considered here.

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