s = suffix denoting shape of channel
t = time, hr.
U = average liquid velocity in bed, ft./sec.
$U_s(r,l)$ = average liquid velocity in channel, ft./sec.
y = distance variable down pore, ft.
z = distance variable down channel, ft.

Greek Letters

α = volume of pore of depth λ, cu. ft.
β = fraction volume of pores participating in dispersion, dimensionless
$\beta(\lambda)$ = relative volume of pore of depth λ to associated void channel, dimensionless
$\overline{\beta^2}$ = mean square depth of pores, $\frac{1}{1+\beta^2}\int_0^\infty \beta(\lambda)\lambda^2 d\lambda$
$\gamma(y,t)$ = tracer concentration in pore, mass/vol. liquid
δ = Dirac delta function
η_v = liquid holdup in channels, dimensionless
θ = mean residence time in bed, hr.
λ = depth of pore, ft.
μ = viscosity, lb./ft.-hr.
μ_1 = first moment of concentration-time distribution, time
μ_2 = second moment of concentration-time distribution, time^2
ξ_s = shape factor (13)
ϕ = fraction of pores filled with liquid, dimensionless
$\Omega(p) = \int_0^\infty \beta(\lambda)\frac{\tanh\omega}{\omega}d\lambda$
$\omega = \lambda\sqrt{p/D}$

Shape Factor

$S_B = \frac{I_1 I_2}{\epsilon_v} - 1$
$S_v = \Sigma\, k_s\, d_s$
$S_p = \frac{s}{3}\beta^{-2}$
$I_1 = \Sigma_s\, \xi_s \int_0^\infty dl \int_0^\infty \epsilon_s \frac{l^2}{r^2}dr$
$I_2 = \Sigma_s \frac{1}{\xi_s}\int_0^\infty dl \int_0^\infty \epsilon_s \frac{r^2}{l^2}dr$
$d_s = \int_0^\infty r^2 dr \int_0^\infty \epsilon_s dl$, mean square radius for channels of shape s
ϵ_v = fraction voids in channels, dimensionless
ϵ_s = voidage due to species of channels, dimensionless

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Perturbation Velocities in Gas-Liquid Partition Chromatographic Columns

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The characteristic velocities in binary and particular ternary cases allow straightforward calculation of equilibrium partition coefficients for components present in both flowing and fixed phases. It is shown in the case of a general *N*-component flowing phase that *N*-1 characteristic velocities arise. In theory *N*-1 equilibrium partition coefficients can be obtained from measurements of these velocities. It is also shown that radioactive tagging of one component provides a distinct characteristic velocity, which can be used either to obtain the N^{th} equilibrium coefficient or to eliminate a parameter which is especially subject to experimental error.

The analytically determined characteristic velocities are compared with pulse velocities obtained from numerical solution of the original balance equations. The agreement over a range of solute concentrations is excellent.

Gas-liquid partition chromatography (GLPC) has been shown experimentally to be a valid and convenient tool for measuring equilibrium information for gas-liquid systems. The normal experimental procedure involves the determination of the residence time in a packed column of a small sample of gaseous material. The latter is soluble in a nonvolatile liquid which is fixed on the porous solid packing. The sample is swept through the bed by an elution gas which is normally relatively insoluble in the fixed liquid phase.

Stalkup and Kobayashi (3) have extended the experimental investigations to cover the case of an elution gas which is appreciably soluble in the fixed liquid phase. They have also reviewed the literature on both the experimental and theoretical aspects of GLPC.

It is the purpose of this paper to extend the theoretical analysis of the motion of multicomponent gas mixtures through beds packed with porous material supporting a fixed liquid phase. In particular equations applicable to the systems studied by Stalkup and Kobayashi are derived.

BALANCE AND EQUILIBRIUM EQUATIONS

Under the experimental conditions normally encountered in GLPC the following assumptions are more or less valid: constant temperature and pressure, both fixed and flowing phases are effectively one-dimensional, and total molar concentration is constant.

The continuity equation for component k in the flowing phase under these conditions is

$$\frac{\partial c_k}{\partial t} = -\frac{\partial}{\partial x}[c_k (V_k)_x] + R_k \qquad k = 1, 2, \ldots\ldots, N \quad (1)$$

Total continuity is assured by

$$\frac{\partial}{\partial x}(W_x) = \sum_{k=1}^{N}\frac{R_k}{c} \quad (2)$$

where $c\,W_x = \sum_k c_k (V_k)_x$

If the motion of component k relative to the center of moles can be expressed as

$$c_k[(V_k)_x - W_x] = -c\mathcal{D}\frac{\partial y_k}{\partial x} \quad (3)$$

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Equation (1) becomes, since c is constant and $c_k = y_k c$

$$\frac{\partial y_k}{\partial t} - \frac{R_k}{c} + y_k \sum_{j=1}^{N} \frac{R_j}{c} = - W_x \frac{\partial y_k}{\partial x} + \frac{\partial}{\partial x}\left(\mathcal{D} \frac{\partial y_k}{\partial x} \right) \quad (4)$$

The source R_k may be approximated by

$$R_k = M_k\,(\overline{c}_k - c_k) = - \frac{1-\epsilon}{\epsilon} \frac{\partial w_k}{\partial t} \quad (5)$$

This implies a homogeneous stationary phase at any point in the bed, which is in turn implied by the assumption of unidimensionality. Finally the equilibrium relationship between the $\overline{y}_k$ and w_k is assumed to be of the form

$$\overline{y}_k = K_k\, x_k = \frac{K_k\, w_k}{\sum_j w_j + w_{N+1}} \quad (6)$$

where w_{N+1} is the concentration of the nonvolatile liquid in the stationary phase.

POINT-EQUILIBRIUM EQUATIONS

Equations (4) to (6) form the basis for numerical calculations to be discussed in the final section of this paper. For the present it is assumed that diffusion may be neglected and that equilibrium obtains between flowing and stationary phases at any point in the bed. Equation (6) may then be written as

$$w_k = w_{N+1} \frac{x_k}{1 - \sum_j x_j} = w_{N+1} \frac{y_k/K_k}{1 - \sum_j y_j/K_j} \quad (7)$$

With the definition

$$\beta = \frac{(1-\epsilon)\, w_{N+1}}{\epsilon\, c}$$

a constant for a given experiment Equation (4) can be reduced to

$$\frac{\partial y_k}{\partial t} + \beta \left\{ \frac{\partial}{\partial t}\left[\frac{y_k/K_k}{1 - \sum_j y_j/K_j} \right] - y_k \frac{\partial}{\partial t} \left[\frac{\sum_j y_j/K_j}{1 - \sum_j y_j/K_j} \right] \right\} + W_x \frac{\partial y_k}{\partial x} = 0 \quad (8)$$

If the K_j are assumed concentration independent, differentiation of the terms in brackets leads to

$$\left\{ 1 + \frac{\beta}{K_k} \left[\frac{1 - \sum_j' y_j/K_j - y_k}{(1 - \sum_j y_j/K_j)^2} \right] \right\} \frac{\partial y_k}{\partial t} + W_x \frac{\partial y_k}{\partial x} + \frac{y_k}{K_k} \left[\frac{1 - K_k}{(1 - \sum_j y_j/K_j)^2} \right] \sum_j{}' \frac{1}{K_j} \frac{\partial y_j}{\partial t} = 0 \quad (9)$$

The Equations (9) (of which $N-1$ are independent) can be augmented by

$$d\,y_k = \frac{\partial y_k}{\partial t} dt + \frac{\partial y_k}{\partial x} dx = 0 \qquad k = 1, \ldots, N-1 \quad (10)$$

and the resulting homogeneous set of $2N$-2 equations analyzed for its characteristics. The latter will be just the N-1 propagation velocities of an infinitesimal disturbance of the system at steady state.

INFINITE DILUTION EQUATIONS

If component N is assumed to be a noncondensable carrier gas (K_N very large), and if the $N-1$ condensable components are assumed to be present only in the infinitesimal disturbance, Equation (9) becomes

$$\alpha_{kk} \frac{\partial y_k}{\partial t} + W_x \frac{\partial y_k}{\partial x} = 0 \quad (11)$$

where $\alpha_{kk} = 1 + \beta/K_k$, since $y_k \doteq 0$. The set of governing equations may be written in the form

$$\begin{pmatrix} \alpha_{11} & & 0 & W_x & & 0 \\ & \alpha_{22} & & & W_x & \\ 0 & & \ddots & 0 & & \ddots \\ & & \alpha_{N-1,N-1} & & & W_x \\ dt & & & dx & & \\ & \ddots & 0 & & \ddots & 0 \\ 0 & & dt & 0 & & dx \end{pmatrix} \begin{pmatrix} \dfrac{\partial y_1}{\partial t} \\ \dfrac{\partial y_2}{\partial t} \\ \vdots \\ \dfrac{\partial y_{N-1}}{\partial t} \\ \dfrac{\partial y_1}{\partial x} \\ \vdots \\ \dfrac{\partial y_{N-1}}{\partial x} \end{pmatrix} = \vec{0} \quad (12)$$

At a point moving with a characteristic disturbance velocity the solution for the vector of partials is nontrivial, which means that the determinant of the matrix in (12) must be zero. This condition is satisfied if

$$\frac{\alpha_{kk}}{dt} = \frac{W_x}{dx} \quad (13)$$

or

$$\frac{dx}{dt} = (W_c)_k = \frac{W_x}{\alpha_{kk}} \quad (14)$$

Equation (14) follows immediately from (11) in this simple case where the $\alpha_{kj} = 0$, $k \neq j$. In finite dilution cases analysis of matrices similar to those in Equation (12), but containing nonzero α_{kj}, is necessary.

Equations (14) for $k = 1,2,\ldots,N-1$ describe the standard analytical chromatographic procedure, wherein a small sample is injected into a carrier gas stream. Separation is a consequence of the different values of $(W_c)_k$ for the various components of the sample.

BINARY GAS EQUATIONS

The restriction that the K_j be independent of concentration is easily removed for a binary flowing phase. Equation (8) may be differentiated and rearranged to give

$$\left\langle 1 + \beta K_1 K_2 \left\{ \frac{(K_1-1)y_1\left[1 - y_2 \dfrac{d \ln K_2}{d\,y_2}\right] + (K_2-1)y_2\left[1 - y_1 \dfrac{d \ln K_1}{d\,y_1}\right]}{[(K_1-1)(K_2-1) + (K_1-1)y_1 + (K_2-1)y_2]^2} \right\} \right\rangle \frac{\partial y_1}{\partial t} + W_x \frac{\partial y_1}{\partial x} = 0 \quad (15)$$

where $y_1 + y_2 = 1$.

The single characteristic velocity is then

$$W_c = \frac{W_x}{\left\langle 1 + \beta K_1 K_2 \left\{ \dfrac{(K_1-1)y_1\left[1 - y_2 \dfrac{d \ln K_1}{d\,y_2}\right] + (K_2-1)y_2\left[1 - y_1 \dfrac{d \ln K_2}{d\,y_1}\right]}{[(K_1-1)(K_2-1) + (K_1-1)y_1 + (K_2-1)y_2]^2} \right\} \right\rangle} \quad (16)$$

Under the conditions that $\left| y_j \dfrac{d \ln K_j}{d\,y_j} \right| << 1$ this is essentially Equation (7) of the paper by Stalkup and Kobayashi (3).

TABLE 1

$L = 30$ cm. $\beta = 10.7$ $K_1 = 1.45$ $K_2 = 50.0$ $W_x = 3.44$ cm./sec.
(corresponds to propane-methane at 50 lb./sq. in. abs., 40°F.)

y_1	$(W_c)_1$, cm./sec. Equation (15)	$(W_c)_1$, cm./sec. numerical solution* of Equation (4)	$(W_c)_1$†, cm./sec. infinite dilution, Equation (20)	$(W_c)_1$†, cm./sec. infinite dilution, numerical solution*
0	0.406	0.408	0.406	0.409
0.1	0.392	0.394	0.356	0.359
0.3	0.372	0.373	0.329	0.334
0.5	0.356	0.356	0.278	0.280
0.7	0.364	0.367	0.224	0.227
0.9	0.526	0.543	0.169	0.170
1.0	3.44	—	0.139	—

† Corresponds to a radioactively tagged tracer of component 1.

* Numerical solution with $\mathfrak{D}/W_xL = 0.02$, $ML/W_x = 10^4$.

It might be noted that Equation (15) is applicable to the determination of the concentration dependence of one of the K's, provided that both the conjugate K is known and that the term $(d \ln K_j)/(dy_j)$ for the unknown K is reasonably well behaved. If for example K_1 is desired and K_2 given, the experiments would begin at vanishingly small y_1, where (16) is

$$W_c = \frac{W_x}{1 + \dfrac{\beta K_2}{K_1(K_2 - 1)}} \qquad (17)$$

which may be solved for the unknown K_1. The knowledge of K_1 for increasing y_1 could be obtained starting from this initial point, $(d \ln K_1)/(dy_1)$ being generated in the process.

It is also noted that Equations (16) and (17) are insensitive to K_2 if $K_2 >> 1$. Stalkup and Kobayashi were able to determine the concentration dependence of propane in methane-propane mixtures by means of the method outlined above; the K value for methane is quite large in their experiments and thus does not have to be known accurately.

The limiting behavior of Equation (16) is interesting. In the algebraically simpler case that $K_2 >> K_1$, $K_2 >> 1$, and $(d \ln K_1)/(dy_1) << 1$, (16) becomes

$$W_c = \frac{W_x}{1 + \beta\left[\dfrac{K_1(1 - y_1)}{(K_1 - y_1)^2}\right]} \qquad (18)$$

It can be seen that (a) as $y_1 \rightarrow 0$, $W_c \rightarrow \dfrac{W_x}{1 + \beta/K_1}$, as is predicted for the infinite dilution case; (b) for $K_1 > 1$, $y_1 \rightarrow 1$, $W_c \rightarrow W_x$, as would be expected for a single-component gas phase; (c) for $K_1 < 1$, $y_1 \rightarrow K_1$, W_c becomes infinite, which is of course expected when condensation occurs.

USE OF A RADIOACTIVE TRACER AS THE PERTURBATION

If the system is perturbed by a small tagged sample of one of the components present in the elution gas mixture, the characteristic velocity for the radioactive molecules is in general different from that of the chemically identical but untagged molecules. This can be shown more easily for the case of a ternary gas phase, in which one component has a very large K value (for example the carrier gas). The other two components are chemically identical, one being tagged and at vanishingly small concentration. The set (9) reduces to the two equations

$$\left[1 + \beta\frac{(1 - y_1)K}{(K - y_1)^2}\right]\frac{\partial y_1}{\partial t} + \beta\frac{y_1(1 - K)}{(K - y_1)^2}\frac{\partial y_2}{\partial t} + W_x\frac{\partial y_1}{\partial x} = 0 \qquad (19)$$

$$\left[1 + \frac{\beta}{K - y_1}\right]\frac{\partial y_2}{\partial t} + W_x\frac{\partial y_2}{\partial x} = 0 \qquad (20)$$

where subscript 1 refers to the untagged material, subscript 2 to the tagged material, and K is their common equilibrium constant. The corresponding characteristic velocities are

$$(W_c)_1 = \frac{W_x}{1 + \beta\dfrac{(1 - y_1)K}{(K - y_1)^2}} \qquad (21)$$

$$(W_c)_2 = \frac{W_x}{1 + \dfrac{\beta}{K - y_1}} \qquad (22)$$

Two data points taken by Koonce (*1*) confirm this result for the system methane-propane-*n*-decane at room temperature and moderate pressure (50 to 100 lb./sq.in. abs.).

It might be noted here that the various velocities $[W_x, (W_c)_i]$ can usually be determined to good accuracy, while β is subject to errors from several sources. The two pieces of information available from (21) and (22) allow the elimination of β and explicit solution for K:

$$K = \frac{\alpha y_1}{\alpha - 1 + y_1} \quad \text{where } \alpha = \frac{\dfrac{W_x}{(W_c)_1} - 1}{\dfrac{W_x}{(W_c)_2} - 1} \qquad (23)$$

NUMERICAL CALCULATIONS

Equations (4) to (6) for a binary gas phase have been solved numerically on the Rice University computer to find the range of the dimensionless parameters $\mathfrak{D}/W_xL$ and M_kL/W_x for which the assumptions of point equilibrium and negligible diffusion effect are valid. At the same time the effect of non-infinitesimal perturbation was investigated by scaling the mathematical disturbance to correspond to the sample size used by Stalkup and Kobayashi in their experimental work.

As might be expected the residence time for a disturbance in the steady state is not appreciably effected by dispersion or mass transfer rate in the physically realistic range of $\mathfrak{D}/W_xL$ and M_kL/W_x. It was found for the binary gas that the computed characteristic velocity agreed quite closely with that predicted by Equation (15), with K_1 and K_2 assumed constant. This agreement is shown in Table 1. The results were essentially independent of the size of the disturbance in the ranges of sample volume and column length corresponding to the physical experiments.

NOTATION

c_k = concentration of component k in the flowing phase
$\overline{c_k}$ = concentration of component k in equilibrium with w_k
c = total molar concentration in the gas phase
$\mathfrak{D}$ = effective dispersion coefficient
ϵ = fraction of bed volume occupied by flowing phase
K_k = equilibrium distribution parameter for component k
L = column length
M_k = mass transfer parameter for component k
R_k = source strength of component k in the flowing phase
t = time variable
$(V_k)_x$ = velocity of component k in the flowing phase
W_c = characteristic velocity of a perturbation
W_x = molar average velocity of the flowing phase
w_k = concentration of component k in the stationary phase
x = distance variable
x_k = mole fraction of component k in the stationary phase
y_k = mole fraction of component k in the flowing phase
$\overline{y_k}$ = mole fraction of component k in equilibrium with x_k

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