

A LUMPED-FILM MODEL FOR GAS-LIQUID PARTITION
CHROMATOGRAPHY

PART I. NUMERICAL METHODS OF SOLUTION

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Two theoretical approaches have been taken to gas-liquid partition chromatography (G.L.C.)—the first may be termed the plate theory and the second the rate theory. The major results of both theories have been summarized by KEULEMANS¹. The plate theory or H.E.T.P. method has been used successfully to analyze experimental data by MARTIN AND SYNGE², MAYER AND TOMPKINS³, GLUECKAUF⁴ and VAN DEEMTER, ZUIDERWEG AND KLINKENBERG⁵. The main drawback of the plate theory is that the H.E.T.P. is a semi-empirical quantity that is calculated from the elution curve and although it serves as a concept by which the experimental data may be analyzed and explained, it is not a quantity fundamental enough to be derived solely from the physical properties of the system. On the other hand, the rate theory begins by formulating the partial differential equations governing G.L.C. such that the physical properties of the system occur as coefficients. Because the resulting equations are too complex to solve analytically it is usual to make three simplifying assumptions.:

1. The equilibrium concentrations in the gas and liquid phases are directly proportional (linear chromatography).
2. Equilibrium between liquid and vapor phases is established immediately (instantaneous equilibrium).
3. Axial diffusion may be neglected.

Chromatography subject to the above assumptions is commonly called ideal chromatography, and theories of ideal chromatography have been developed by BOYD, ADAMSON AND MYERS⁶, LAPIDUS AND AMUNDSON⁷, KLINKENBERG⁸, and THOMAS⁹. GIDDINGS AND EYRING¹⁰, however, have treated the diffusional processes involved by the random walk method, thus obtaining an interesting molecular theory of chromatography. The main drawback to the rate theory, apart from the above assumptions, is that, in order to simplify the differential equations for solution, it is necessary to introduce an arbitrary rate constant, usually a mass transfer coefficient or a reaction velocity constant, whose value is obtained by fitting the analytical

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solution to the elution curve. However, VAN DEEMTER *et al.*⁵ have discussed a method of estimating the rate constant from the physical properties of the system, subject to the assumptions of ideal chromatography.

The object of the present work is to remove some or all of the restrictions involved in the assumption of ideal chromatography and to devise a method, based on the rate theory, to predict the shape and position of the elution curve from the physical properties of the system alone without the use of an arbitrary rate constant. This has been accomplished (*cf.* FUNK AND HOUGHTON¹¹) by using a lumped-film model for the liquid phase. All three restrictions involved in the assumption of ideal chromatography are removed by programming the differential equations on an IBM-704 digital computer using finite difference methods. The computer solution can also be used to account for the effects of nonlinear solubility and column pressure drop. Analytical solutions will also be reported in Part II for the cases where the restrictions of instantaneous equilibrium and/or no longitudinal dispersion are removed.

THE PARTIAL DIFFERENTIAL EQUATIONS OF NON-IDEAL CHROMATOGRAPHY

There are three phases present in G.L.C.—a flowing vapor phase and a stationary involatile liquid phase coated on to an impermeable solid phase. A binary system is assumed with a solute and carrier gas in the vapor phase and solute and solvent in the liquid phase. The one-dimensional continuity equation for the vapor phase is:

$$\frac{\partial X}{\partial t} = E \frac{\partial^2 X}{\partial z^2} - \left(u - \frac{2E}{P} \frac{\partial P}{\partial z} \right) \frac{\partial X}{\partial z} - \frac{k_G R T A}{\epsilon} (X - X_t) + \frac{E X}{P} \frac{\partial^2 P}{\partial z^2} \quad (1)$$

If the gas flow in the packed bed is laminar and unidirectional, then Darcy's law may be applied as follows:

$$u = \frac{K P}{\eta} \frac{dP}{dz} \quad (2)$$

Also for compressible flow:

$$u P = u_i P_i \quad (3)$$

Solution of eqns. (2) and (3) yields (*cf.* KEULEMANS¹):

$$P = \sqrt{P_i^2 - \frac{z}{L} (P_i^2 - P_o^2)} \quad (4)$$

whence:

$$\frac{\partial P}{\partial z} = - \frac{1}{P} \frac{(P_i^2 - P_o^2)}{2L} \quad (5)$$

$$\frac{\partial^2 P}{\partial z^2} = \frac{1}{P^3} \left(\frac{P_i^2 - P_o^2}{2L} \right)^2 \quad (6)$$

For the liquid phase it is assumed that the diffusion coefficient, D_L , is independent of

concentration and that diffusion in the thin uniform film of partitioning liquid is unidirectional, so that:

$$\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial y^2} \quad (7)$$

If it is assumed that there is a gas film resistance of the Whitman type at the interface between the liquid and vapor phases, the concentration changes are depicted in Fig. 1 as a function of time as the solute passes into the liquid phase and is eluted out again. The boundary conditions to be applied to eqn. (7) may be obtained by referring to Fig. 1. and are as follow:

$$\left(\frac{\partial c}{\partial y}\right)_{y=h} = 0 \quad (8)$$

$$D_L \left(\frac{\partial c}{\partial y}\right)_{y=0} = k_G P (X - X_t) \quad (9)$$

where k_G is the Whitman gas film coefficient.

The final equation that couples the vapor phase and liquid phase equations is the equilibrium solubility isotherm:

$$c_t = K_1 P X_t + K_2 P^2 X_t^2 \quad (10)$$

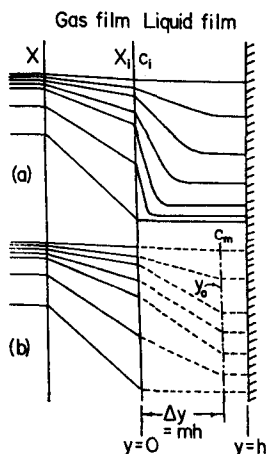


Fig. 1. Concentration distributions in the liquid film as a function of time; (a) variable depth of penetration, (b) assuming constant depth of penetration.

Equation (10) has a nonlinear term that allows for non-ideality in the liquid phase.

The general assumptions used in the derivation of the above equations are enumerated below:

(1) Uniform one-dimensional flow through a uniformly-packed bed.

(2) Longitudinal dispersion in the gas phase can be adequately represented by an eddy diffusivity, E , which is independent of position and concentration.

(3) The presence of a Whitman-type¹² gas film resistance, k_G , at the gas-liquid interface.

(4) The diffusion coefficient in the liquid phase, D_L , is independent of concentration.

(5) Pressure drops through the bed are governed by Darcy's law.

(6) Ideal gases and gas mixtures.

In order to conveniently solve the above equations, it is necessary to formulate a model that will eliminate the independent variable, y . This has been accomplished by representing the liquid film as a lumped system using finite difference techniques.

THE LUMPED-FILM MODEL FOR THE LIQUID PHASE

The function $c(z, y, t)$ can be expanded about some point y_0 in the liquid film by means of Taylor's series so that the second derivative becomes:

$$\begin{aligned} \frac{\partial^2 c(z, y, t)}{\partial y^2} &= \frac{1}{\Delta y^2} \left[c(z, y_0 - \Delta y, t) - c(z, y_0, t) \right] - \\ &\quad - \frac{1}{\Delta y^2} \left[c(z, y_0, t) - c(z, y_0 + \Delta y, t) \right] \end{aligned} \quad (11)$$

If Δy is always required to be the distance from the surface of the liquid film to the lumping point, y_0 , then eqn. (9) may be approximated by:

$$D_L \left[\frac{c_t - c(z, y_0, t)}{\Delta y} \right] = k_G P(X - X_t) \quad (12)$$

If Δy is also the distance from the lumping point to the surface of the solid, eqn. (8) leads to the approximation:

$$\frac{c(z, y_0, t) - c(z, y_0 + \Delta y, t)}{\Delta y} = 0 \quad (13)$$

The only way for Δy to satisfy both of the above requirements is for m in Fig. 1 to be $1/2$. In this case, eqns. (7), (11), (12) and (13) may be combined to give a single-section lumped-film model represented by the following differential-difference equation:

$$\frac{\partial c_m}{\partial t} = \frac{D_L}{\Delta y^2} (c_t - c_m) \quad (14)$$

where:

$$c_m = c(z, h/2, t)$$

and:

$$\Delta y^2 = h/2 \quad (15)$$

It is evident that a single-section approximation will only apply when the liquid film is thin, so that the depth of penetration is of the order of one-half the film thickness.

This argument leads to the possibility of m having an average value other than $1/2$, and this case will be treated in Part II as the penetration model.

ELIMINATION OF INTERFACIAL CONCENTRATIONS FROM THE EQUATIONS

For the case of a nonlinear solubility isotherm, substitution of eqn. (12) into eqn. (10) eliminates c_i and leads to the following quadratic in X_i :

$$K_3 X_i^2 + K_4 X_i - (k_G P X + D_L c_m / \Delta y) = 0 \quad (16)$$

where:

$$K_3 = \frac{D_L K_2 P^2}{\Delta y} \quad (17)$$

$$K_4 = \frac{D_L K_1 P}{\Delta y} + k_G P \quad (18)$$

Solving for X_i we obtain:

$$X_i = -K_5/2 \pm \sqrt{K_5^2/4 + (k_G P X + D_L c_m / \Delta y) / K_3} \quad (19)$$

where:

$$K_5 = K_4 / K_3 \quad (20)$$

Equation (19) may now be used to eliminate X_i from eqn. (1) for the case of nonlinear solubility.

The case of a linear solubility isotherm may be obtained by letting $K_3 \rightarrow 0$ in eqn. (19) and using the positive sign in front of the square root, so that:

$$X_i = K_6 X + K_7 c_m \quad (21)$$

where:

$$K_6 = k_G P / K_4 \quad (22)$$

$$K_7 = D_L / \Delta y K_4 \quad (23)$$

Equation (21) may be used to eliminate X_i from eqn. (1) for the case of linear solubility.

INITIAL AND BOUNDARY CONDITIONS

Fig. 2 shows the conditions for an initial value problem that is closely allied to the experimental conditions actually found in G.L.C. The slug of solute of mole fraction X_0 is trapped between two gates that can be opened simultaneously at $t = 0^+$ to introduce the solute into the carrier gas stream. It is assumed that the flow is established instantaneously and that there are no end effects in the column. The initial

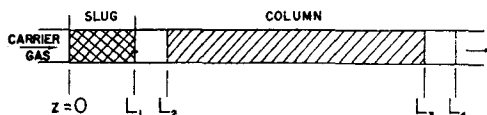


Fig. 2. The initial value problem of G.L.C.

conditions for this case are then:

$$X(z,0) = \begin{cases} X_0, & 0 < z < L_1 \\ 0, & z > L_1 \end{cases} \quad (24)$$

$$c_i(z,0) = c_m(z,0) = 0, \quad L_2 < z < L_3$$

and the boundary conditions are:

$$\text{Gas velocity} = \begin{cases} u, & L_2 < z < L_3 \\ u\epsilon, & z < L_2 \text{ and } z > L_3 \end{cases} \quad (25)$$

$$\text{Gas film coefficient} = \begin{cases} h_G, & L_2 < z < L_3 \\ 0, & z < L_2 \text{ and } z > L_3 \end{cases}$$

The solution to the problem is the mole fraction of solute in the gas phase passing the detector as a function of time, $X(L_4, t)$, and can be obtained by solving the differential equations in finite difference form. The numerical solution obtained completely removes the restrictions of ideal chromatography and can therefore be used to account for the effects of nonlinear solubility, finite diffusion rates, axial diffusion and column pressure drop.

FINITE DIFFERENCE EQUATIONS

In order to obtain the difference equations in a form explicit in the variables X and c_m , the finite difference approximations are made forward in time and backward in space as follows:

$$\frac{\partial^2 X}{\partial z^2} = \frac{X(i+1, j) - 2X(i, j) + X(i-1, j)}{\Delta z^2} \quad (26)$$

$$\frac{\partial X}{\partial z} = \frac{X(i, j) - X(i-1, j)}{\Delta z} \quad (27)$$

$$\frac{\partial X}{\partial t} = \frac{X(i, j+1) - X(i, j)}{\Delta t} \quad (28)$$

$$\frac{\partial c_m}{\partial t} = \frac{c_m(i, j+1) - c_m(i, j)}{\Delta t} \quad (29)$$

The finite difference equations are obtained by substituting eqns. (26), (27), (28) and (29) into eqns. (1) and (14) and using eqns. (19) or (21) to eliminate X_t . The results for nonlinear and linear isotherms are summarized below:

1. Nonlinear solubility isotherm

$$X(i, j+1) = \beta_1(P)X(i, j) + \beta_2(P)X(i-1, j) + \beta_3(P)X(i+1, j) + \frac{h_G(i)RTA\Delta t}{\epsilon} \left[-K_5(i)/2 + \sqrt{K_5^2(i)/4 + (h_G(i)P(i)X(i, j) + D_L c_m(i, j)/\Delta y)/K_3(i)} \right] \quad (30)$$

$$c_m(i, j + 1) = c_m(i, j) + \left[\frac{k_G(i)P(i)\Delta t}{\Delta y} \right] X(i, j) - \quad (31)$$

$$- \frac{k_G(i)P(i)\Delta t}{\Delta y} \left[-K_5(i)/2 + \sqrt{K_5^2(i)/4 + (k_G(i)P(i)X(i, j) + D_{LC}m(i, j)/\Delta y)/K_3(i)} \right]$$

where:

$$\beta_1(P) = 1 - \frac{2E\Delta t}{\Delta z^2} - \frac{u(i)\Delta t}{\Delta z} + \frac{2E\Delta t}{\Delta z P(i)} \frac{dP(i)}{dz} - \frac{k_G(i)RTA\Delta t}{\epsilon} + \frac{E}{P(i)} \frac{d^2P(i)}{dz^2} \quad (32)$$

$$\beta_2(P) = \frac{u(i)\Delta t}{\Delta z} - \frac{2E\Delta t}{\Delta z P(i)} \frac{dP(i)}{dz} + \frac{E\Delta t}{\Delta z^2} \quad (33)$$

$$\beta_3(P) = \frac{E\Delta t}{\Delta z^2} \quad (34)$$

2. Linear solubility isotherm

$$X(i, j + 1) = \beta_2(P)X(i - 1, j) + \beta_3(P)X(i + 1, j) + \beta_4(P)X(i, j) + \beta_5(P)c_m(i, j) \quad (35)$$

$$c_m(i, j + 1) = \beta_6(P)c_m(i, j) + \beta_7(P)X(i, j) \quad (36)$$

where:

$$\beta_4(P) = 1 - \frac{2E\Delta t}{\Delta z^2} - \frac{u(i)\Delta t}{\Delta z} + \frac{2E\Delta t}{\Delta z P(i)} \frac{dP(i)}{dz} + \frac{E}{P(i)} \frac{d^2P}{dz^2} - \quad (37)$$

$$- K_6(i)AD_LK_1RT\Delta t/\Delta y\epsilon$$

$$\beta_5(P) = K_7(i)k_G(i)ART\Delta t/\epsilon \quad (38)$$

$$\beta_6(P) = 1 - K_6(i)D_L\Delta t/\Delta y^2 \quad (39)$$

$$\beta_7(P) = K_6(i)P(i)D_LK_1\Delta t/\Delta y^2 \quad (40)$$

The coefficients $\beta(P)$ are functions of pressure and therefore eqns. (3), (4), (5) and (6) must be utilized to evaluate the pressure dependence.

The above equations may be solved by dividing the chromatographic column into axial increments, Δz , such that $z = i\Delta z$, and using time increments Δt such that $t = j\Delta t$. The numerical solution is then obtained by a marching process, starting with the initial conditions and using two time-distance grids, one for X and the other for c_m . The equations have been programmed in Fortran language for an IBM-704 digital computer.

STABILITY AND CONVERGENCE OF THE NUMERICAL SOLUTION

In the numerical solution of partial differential equations by finite differences, the concepts of stability and convergence are very important. The term convergence is used to denote how close the solution of the difference equations approaches the exact solution of the differential equations in the limit as the size of the increments (Δz and Δt) is reduced to zero. The relationship between Δz and Δt is determined, however, by the stability criterion. If the error is defined as the departure of the numer-

ical solution from the exact solution, then stability deals with the growth and amplification of this error.

The cause of instability in the numerical solution of partial differential equations has been discussed by a number of writers¹³⁻¹⁵, some of whom attribute instability to round-off errors, while others claim that it is inherent in the difference equations. RICHTMYER¹⁵ has shown that in the numerical solution of the simple parabolic heat equation, instability may not be concerned with round-off errors, but rather is the property of the particular system of difference equations. The same view is taken in the present work, even though the same formal results can be achieved by considering the problem as one of propagation of round-off error, as discussed by HOUGHTON¹⁶.

A differential equation is said to be unstable if it yields an unbounded output for a bounded input. This behavior is an inherent characteristic of the equation. To extend this concept to difference equations, it is only necessary to state that a stable solution will result if the coefficients of the difference equations are fixed so that the output is bounded for any bounded input. The fact that the bounded input may be round-off error (among other forms of disturbance) provides a connection with the round-off method of determining instability. For the case of constant pressure ($dP/dz = 0$ and $d^2P/dz^2 = 0$) with a linear solubility isotherm, eqns. (35) and (36) become:

$$X(i, j + 1) = \alpha_2 X(i - 1, j) + \alpha_3 X(i + 1, j) + \alpha_4 X(i, j) + \alpha_5 c_m(i, j) \quad (41)$$

$$c_m(i, j + 1) = \alpha_6 c_m(i, j) + \alpha_7 X(i, j) \quad (42)$$

where:

$$\alpha_2 = \frac{u\Delta t}{\Delta z} + \frac{E\Delta t}{\Delta z^2} \quad (43)$$

$$\alpha_3 = \frac{E\Delta t}{\Delta z^2} \quad (44)$$

$$\alpha_4 = 1 - \frac{2E\Delta t}{\Delta z^2} - \frac{u\Delta t}{\Delta z} - K_6 A D_L K_1 R T \Delta t / \Delta y \epsilon \quad (45)$$

$$\alpha_5 = K_7 k_G A R T \Delta t / \epsilon \quad (46)$$

$$\alpha_6 = 1 - K_6 D_L \Delta t / \Delta y^2 \quad (47)$$

$$\alpha_7 = K_6 P D_L K_1 \Delta t / \Delta y^2 \quad (48)$$

If $\delta_X(i, j)$ is assumed to be any bounded disturbance along the j^{th} row of the X grid and $\delta_c(i, j)$ is any bounded disturbance along the j^{th} row of the c_m grid, a sufficient condition for the output of the difference equations to be bounded is:

$$|\delta_X(i, j + 1)| \leq |\delta_X(i, j)| \quad (49)$$

$$|\delta_c(i, j + 1)| \leq |\delta_c(i, j)| \quad (50)$$

Using the triangle inequality, it is easily shown that eqns. (49) and (50) are satisfied for eqns. (41) and (42) if:

$$|\alpha_2| + |\alpha_3| + |\alpha_4| + |\alpha_5| \leq 1 \quad (51)$$

$$|\alpha_6| + |\alpha_7| \leq 1 \quad (52)$$

Substituting the values of α from eqns. (43) to (48) into eqns. (51) and (52), the stability criteria become:

$$\Delta t \leq \frac{1}{\frac{2E}{\Delta z^2} + \frac{u}{\Delta z} + \frac{k_G RT A D_L K_1}{\epsilon \Delta y \left(\frac{D_L K_1}{\Delta y} + k_G \right)}} \quad (53)$$

$$\Delta t \leq \frac{\Delta y^2 \left(\frac{D_L K_1}{\Delta y} + k_G \right)}{D_L k_G} \quad (54)$$

It should be noted that eqn. (53) reduces to the criterion for the simple parabolic diffusion equation (*i.e.*, $\Delta t \leq \Delta z^2/2E$) if there is no flow ($u = 0$) and no mass transfer ($k_G = 0$).

The convergence of the numerical solution to the analytical solution as Δz is reduced is shown in Fig. 3. The analytical solution chosen was that for linear solubility

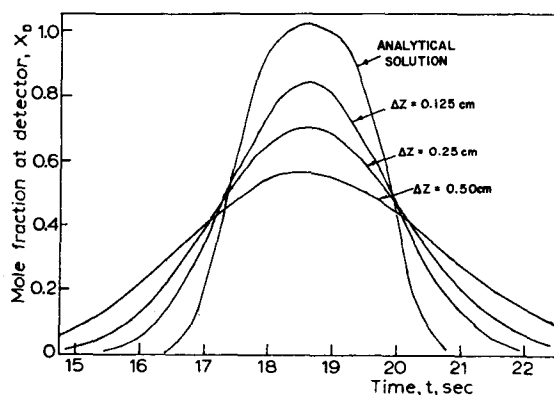


Fig. 3. Convergence of the numerical solution holding Δt constant and changing Δz .

with no pressure drop and no longitudinal diffusion (*cf.* FUNK AND HOUGHTON¹¹, equation (10)).

The effect of reducing Δt is illustrated by taking the case of longitudinal dispersion in a tube with no packing governed by the equation

$$\frac{\partial X}{\partial t} + u \frac{\partial X}{\partial z} = E \frac{\partial^2 X}{\partial z^2} \quad (55)$$

Subject to the initial and boundary conditions of Fig. 2, the analytical solution is easily shown to be (*cf.* BOURNIA, COULL AND HOUGHTON¹⁷):

$$X = \frac{1}{2} \operatorname{erf} \left(\frac{L_4 - ut}{2 \sqrt{Et}} \right) + \frac{1}{2} \operatorname{erf} \left(\frac{L_1 - L_4 + ut}{2 \sqrt{Et}} \right) \quad (56)$$

The numerical solution of eqn. (55) can be obtained from the computer program merely by setting $k_G = 0$ and $dP/dz = 0$ in the coefficients of the difference equations (35) and (36). The effect of lowering Δt shown by Fig. 4 is to reduce the accuracy, which is the converse of what is expected. This phenomenon has been noted by REIHING AND CURLEE¹⁸, who have suggested that there is some optimum Δt for the

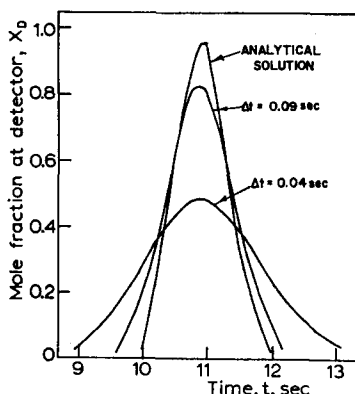


Fig. 4. Convergence of the numerical solution holding Δz constant and changing Δt .

best accuracy. REIHING AND CURLEE point out that the difference equation for pure transport (*i.e.*, eqn. (55) in difference form with $E = 0$) is most accurate when Δt is the maximum allowable value, since the relation $u = \Delta z/\Delta t$ must also be satisfied. However, the difference equation for pure diffusion (*i.e.*, eqn. (55) in difference form with $u = 0$) becomes more accurate as Δt tends to zero within the stability criterion. In the present case the optimum Δt has been generally found to be the maximum Δt allowable for stability, an observation that also agrees with the findings of REIHING AND CURLEE. Hence in all cases the stability and the accuracy have been optimized by making Δt only slightly less than that demanded by eqns. (53) and (54). By thus maximizing Δt , it has been found that the numerical solutions are accurate enough to provide a reliable semi-quantitative picture of the effect of various parameters on the performance of gas-liquid chromatographic columns.

EFFECT OF COLUMN OPERATING CONDITIONS ON THE ELUTION CURVE

The IBM-704 computer program of the equations of chromatography has been used to simulate the behavior of a typical chromatography column under various operating conditions. The system chosen was the elution of a pure isobutylene slug with

an argon carrier gas using dinonyl phthalate as the stationary phase. The parameter study was made by choosing a standard set of operating conditions and then changing each of the variables one at a time, holding all other conditions constant. The standard conditions chosen were as follow:

$$\begin{array}{ll}
 T = 298^{\circ}\text{K} & L_1 = 5 \text{ cm} \\
 P = 1 \text{ atm.} & L_2 - L_1 = 1 \text{ cm} \\
 A = 131.2 \text{ cm}^2/\text{cm}^3 & L_3 - L_2 = 50 \text{ cm} \\
 u = 5 \text{ cm/sec} & L_4 - L_3 = 1 \text{ cm} \\
 \varepsilon = 0.40 & X_0 = 1.00 \\
 h = 1.4 \cdot 10^{-4} \text{ cm} & K_1 = 0.00114 \\
 D_L = 6.7 \cdot 10^{-7} \text{ cm}^2/\text{sec} & K_2 = 0
 \end{array}$$

Transport time without chromatography = 12.3 sec

The values of D_L and K_1 at various temperatures were taken from the data of HOUGHTON, KESTEN, FUNK AND COULL¹⁹.

1. Effect of gas film coefficient, k_G

Fig. 5 shows that the peak mole fraction passes through a minimum as k_G varies in the range 0 to 10^{-3} g-mole/sec. cm². atm., while the peak time increases from the transport

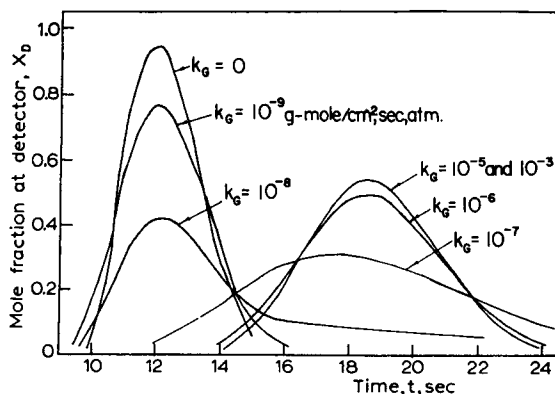


Fig. 5. Effect of gas film coefficient.

time with no chromatography (12.3 sec) to a maximum value of 18.5 sec when k_G is greater than 10^{-5} . The possible effect of a high gas film resistance on the shape and peak time of the elution curve has not generally been appreciated.

2. Effect of longitudinal dispersion

As E is increased in the range 0.0674 to 6.74 cm²/sec, Fig. 6 shows that the peak becomes broader, but the peak time does not change significantly. It is noted that the longitudinal dispersion coefficient E must be at least a factor of ten greater than the molecular diffusivity ($D_G = 0.0674$ cm²/sec) before the effect becomes appreciable.

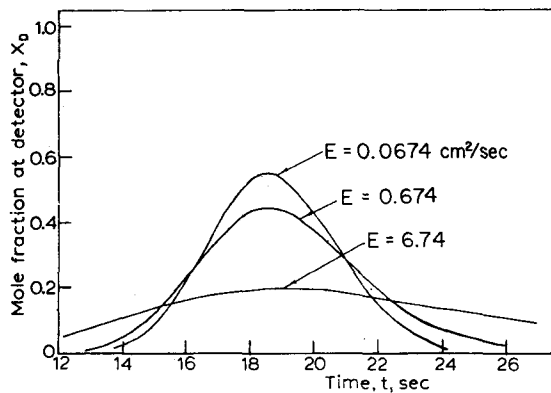


Fig. 6. Effect of longitudinal dispersion.

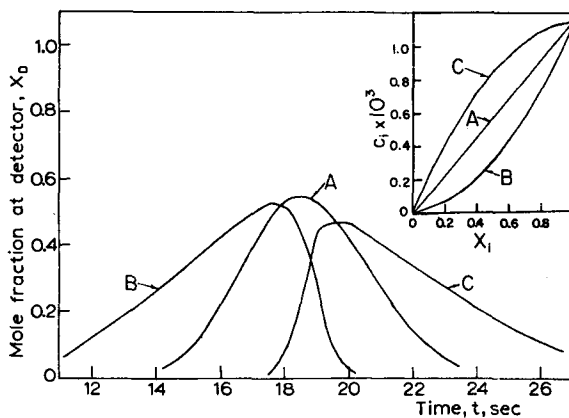


Fig. 7. Effect of a nonlinear solubility isotherm.

| | $K_1 \cdot 10^3$ | $K_2 \cdot 10^3$ |
|---|------------------|------------------|
| A | 1.14 | 0 |
| B | 0.14 | + 1.0 |
| C | 2.22 | - 1.08 |

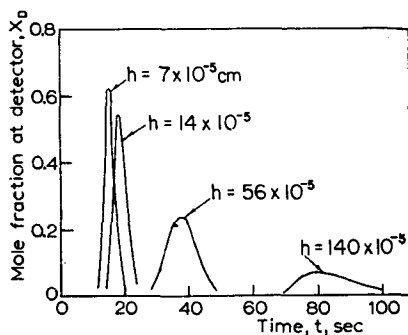


Fig. 8. Effect of liquid film thickness.

3. *Effect of a nonlinear solubility isotherm*

Fig. 7 shows that departures from ideality in the liquid phase result in considerable skewness and tailing in the elution curve with consequent displacement of the peak. The direction of the tailing is related to the type of nonlinearity as predicted by KEULEMANS¹.

4. *Effect of liquid film thickness*

As the liquid film thickness is increased, Fig. 8 shows that the curves become broader and more skewed, while the peak time is directly proportional to the film thickness. In comparing these curves it has been assumed that the depth of penetration into the liquid phase increases as the liquid film thickness increases. Although this would no doubt be true for very thin films, it would certainly not apply to very thick films which would essentially behave as semi-infinite media.

5. *Effect of temperature*

Fig. 9 shows that as temperature increases, the peak time decreases and the curves become sharper. As is found in practice, good separation must represent a compromise between peak time and band width.

6. *Effect of slug length*

The areas under the curves of Fig. 10 increase in proportion to the increase in slug length. The peak time increases because it takes longer for the centerline of a larger slug to move to the detector. The curves of Fig. 10 closely resemble those obtained by PORTER *et al.*²⁰ by applying the H.E.T.P. approach to the elution of slugs of varying size.

7. *Effect of total pressure*

As indicated by Fig. 11, a tenfold change in total pressure has no significant effect on either the peak time or peak mole fraction—a fact that has been verified experimentally for systems that are relatively ideal.

8. *Effect of initial slug concentration*

The curves of Fig. 12 are linear multiples of each other; that is, the curve for $X_0 = 1$ is merely four times the curves for $X_0 = 0.25$, indicating that slug concentration has no effect on the elution curve if X/X_0 is the variable.

9. *Effect of carrier gas velocity*

Fig. 13 shows that the peak time is inversely proportional to the velocity, as predicted by the analytical result of FUNK AND HOUGHTON¹¹. Further, Fig. 13 shows that as the peak time increases, the area under the curve apparently increases, a fact easily explained by the following mass balance at the detector:

$$\text{Area} = \int_0^{\infty} X_D dt = \frac{X_0 L_1 P_t}{\epsilon u P_0} \quad (57)$$

Equation (57) shows that the area increases as the carrier velocity, u , decreases.

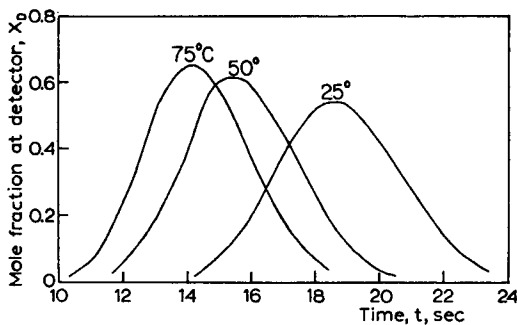


Fig. 9. Effect of temperature.

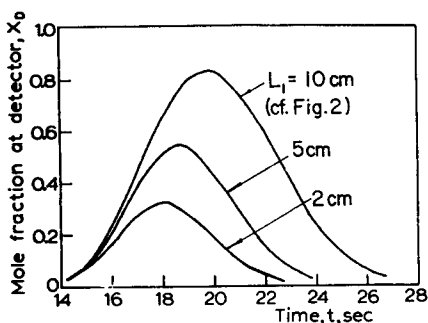


Fig. 10. Effect of slug length.

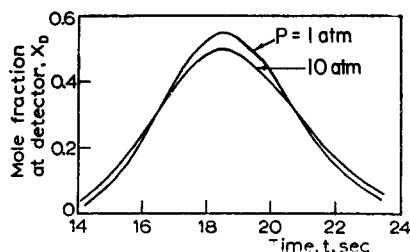


Fig. 11. Effect of total pressure.

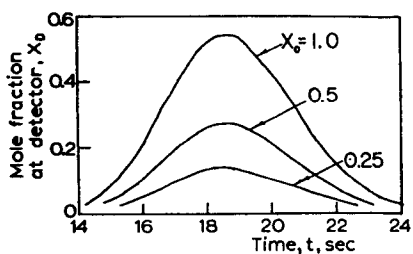


Fig. 12. Effect of initial slug concentration.

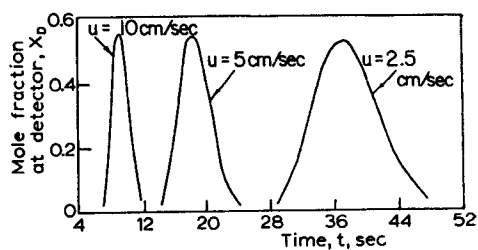


Fig. 13. Effect of carrier gas velocity.

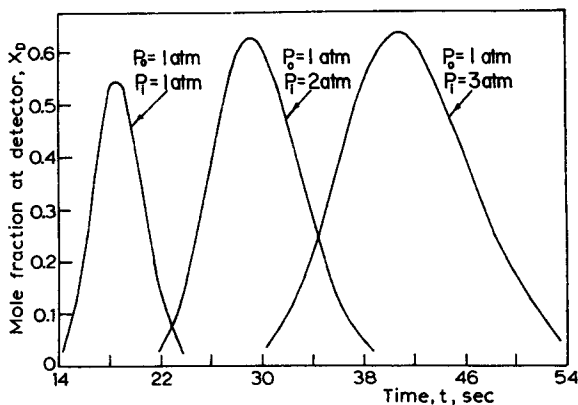


Fig. 14. Effect of column pressure drop.

10. *Effect of column pressure drop*

Fig. 14 shows that as the outlet pressure is held constant and the inlet pressure is increased, the peak time and the area under the elution curve increase. The area increases simply because a higher inlet pressure means more solute present in the slug. The peak time increases because the interstitial velocity decreases according to eqn. (3).

NOTATION

- A = mass transfer area per unit volume of empty column, cm^2/cm^3
 c = solute concentration in liquid phase, $\text{g-mole}/\text{cm}^3$
 c_i = interfacial solute concentration, $\text{g-mole}/\text{cm}^3$
 c_m = solute concentration at lumping point in liquid film, $\text{g-mole}/\text{cm}^3$
 D_L = molecular diffusivity in liquid phase, cm^2/sec
 E = longitudinal dispersion coefficient, cm^2/sec
 h = liquid film thickness, cm
 i = distance index in difference equations ($z = i\Delta z$)
 j = time index in difference equations ($t = j\Delta t$)
 k_G = gas film coefficient, $\text{g-mole}/\text{sec} \cdot \text{cm}^2 \cdot \text{atm}$.
 K = permeability of packed bed, dimensionless
 K_1, K_2 = constants in nonlinear isotherm
 $K_2, K_3, K_4, K_5, K_6, K_7$ = pressure-dependent parameters
 L = length, cm
 P = pressure, atm .
 P_i = column inlet pressure, atm .
 P_o = column outlet pressure, atm .
 R = Universal Gas Constant, $82.06 \text{ atm} \cdot \text{cm}^3/\text{g-mole} \cdot ^\circ\text{K}$
 t = time, sec
 T = absolute temperature, $^\circ\text{K}$
 u = axial velocity through voids, cm/sec
 u_i = axial velocity through voids at inlet, cm/sec
 X = mole fraction of solute in vapor phase
 X_D = mole fraction of solute passing the detector
 X_i = mole fraction of solute at gas-liquid interface
 X_0 = initial mole fraction of solute in slug
 y = distance into the liquid film, cm
 y_0 = a point in the liquid film, cm
 z = axial distance along column, cm
 $\alpha_1, \alpha_2, \alpha_3, \alpha_4, \alpha_5, \alpha_6, \alpha_7$ = pressure-dependent parameters
 $\beta_1, \beta_2, \beta_3, \beta_4, \beta_5, \beta_6, \beta_7$ = parameters dependent upon pressure and/or pressure gradient
 δ_c, δ_X = elements of a bounded set of numbers
 Δ = incremental change
 ϵ = void fraction
 η = viscosity, poise

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SUMMARY

The differential equations of non-ideal gas-liquid partition chromatography have been derived and simplified by introducing the concept of a lumped liquid film. The resulting equations have been solved numerically by finite difference methods using an IBM-704 digital computer. The stability and convergence of the computer solutions is discussed and the computer program is used to simulate the actual behavior of a typical column under various operating conditions. The system chosen for study was the elution of a slug of isobutylene with argon as the carrier gas and dinonyl phthalate as the stationary phase.

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