

A LUMPED-FILM MODEL FOR GAS-LIQUID PARTITION CHROMATOGRAPHY

PART II. EXPERIMENTAL EVALUATION OF ANALYTICAL SOLUTIONS

JAMES E. FUNK* AND GERALD HOUGHTON

*Chemical Engineering Department, Division of Engineering Research,
University of Pittsburgh, Pa. (U.S.A.)*

(Received December 21st, 1960)

In Part I (*cf.* FUNK AND HOUGHTON¹) the differential equations governing non-ideal gas-liquid partition chromatography (G.L.C.) have been derived and simplified by introducing the concept of a lumped liquid film in which the lumping point is the midpoint of the liquid film. The resulting equations were solved by finite difference methods using an IBM-704 digital computer so that the program could be used to simulate the behavior of a typical column under various operating conditions. However, if certain simplifying assumptions are made, it is possible to obtain certain analytical solutions to the differential equations of G.L.C. that are particularly useful for determining the effect of operating variables on the elution time, but are too complex to use to evaluate changes in shape of the elution curve (*cf.* FUNK AND HOUGHTON²).

If the assumptions of no pressure drop ($\partial P/\partial z = 0$) and linear solubility ($K_2 = 0$) are made in equations (1), (10), (12) and (14) of Part I¹, the following partial differential equations result:

$$\frac{\partial X}{\partial t} = E \frac{\partial^2 X}{\partial z^2} - u \frac{\partial X}{\partial z} - \frac{k_G R T A}{\varepsilon} (X - X_i) \quad (1)$$

$$c_i = K_1 P X_i \quad (2)$$

$$\frac{\partial c_m}{\partial t} = \frac{D_L}{A y^2} (c_i - c_m) = \frac{k_G P}{A y} (X - X_i) \quad (3)$$

These equations still allow for the presence of a finite diffusion rate and longitudinal dispersion. c_m is the concentration at the midpoint in the liquid film (*i.e.*, $c_m(z, h/2, t)$). It will be shown later that the lumping point can be chosen anywhere in the liquid film, so that $A y = m h$ where m is an empirical factor measuring the average fractional penetration of the solute into the liquid film.

* Westinghouse Electric Corporation, Bettis Atomic Power Division, Pittsburgh, Pa.

ANALYTICAL SOLUTIONS FOR THE LUMPED-FILM MODEL

Two analytical solutions have been obtained (*cf.* FUNK AND HOUGHTON²) to eqns. (1), (2) and (3) by treating G.L.C. as a boundary value problem with time varying boundary conditions as shown in Fig. 1. A pulse of solute of mole fraction X_0 and duration

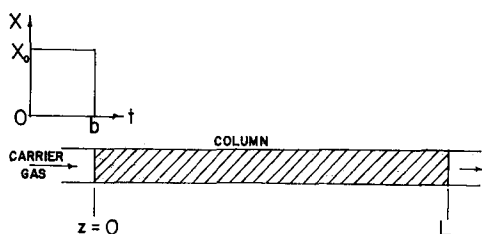


Fig. 1. The boundary value problem of G.L.C.

b is introduced into the carrier gas stream at the column inlet. The initial conditions are therefore all zero, so that:

$$\begin{aligned} X(z, 0) = X_i(z, 0) &= 0 \\ c_m(z, 0) = c_i(z, 0) &= 0 \end{aligned} \quad (4)$$

and the time-varying boundary conditions are:

$$X(0, t) = \begin{cases} 0, & t < 0 \\ X_0, & 0 < t < b \\ 0, & t > b \end{cases} \quad (5)$$

If $E = 0$ in eqn. (1), the boundary value problem of Fig. 1 reduces to the initial value problem discussed in Part I with b equal to $L_1/u \varepsilon$ (*cf.* FUNK AND HOUGHTON¹, Fig. 2).

Subject to the boundary conditions of Fig. 1, two analytical solutions may be obtained to eqns. (1), (2) and (3) with and without longitudinal dispersion.

I. *Analytical solution for constant pressure, linear solubility and longitudinal dispersion*
($E \neq 0$)

The analytical solution for this case can be obtained by using a method similar to that outlined by LAPIDUS AND AMUNDSON³. However, the result summarized below distinguishes between rate processes taking place in both the gas and liquid phases and introduces physically measurable quantities that are characteristic of each process:

$$\begin{aligned} X(L, t) = \int_0^t \left(X(0, t - \tau) \left\{ e^{\left(\frac{uL}{2E} - \gamma_1\tau\right)} \left[\frac{L}{2\sqrt{\pi E \tau^3}} e^{\left(\frac{-L^2}{4E\tau} - \gamma_2\tau\right)} - \right. \right. \right. \\ \left. \left. - \frac{L\sqrt{\gamma_2 P}}{2\sqrt{\pi E}} \int_0^\tau \frac{1}{\lambda\sqrt{\tau - \lambda}} e^{\left(\frac{-L^2}{4E} - \gamma_2\lambda\right)} J_1\left(\sqrt{\gamma_2 P \lambda (\tau - \lambda)}\right) d\lambda \right] \right\} \right) d\tau \end{aligned} \quad (6)$$

where:

$$\gamma_1 = \frac{D_L}{\Delta y^2} \left[\frac{k_G}{\frac{D_L K_1}{\Delta y} + k_G} \right] \quad (7)$$

$$\gamma_2 = K_1 \gamma_1 \quad (8)$$

$$\gamma_3 = -\gamma_1 + \frac{RTA\Delta y}{\epsilon} \gamma_2 + \frac{u^2}{4E} \quad (9)$$

In eqn. (6) J_1 is a Bessel function of the first order and $X_0(0, t - \tau)$ is the boundary condition at the entrance to the column given by eqn. (5). The complexity of eqn. (6) makes it difficult to obtain a clear relationship between the retention time or the shape of the elution curve and the physical properties of the system. In this respect the numerical solution of Part I is simpler to use and in addition accounts for the effects of nonlinear solubility and pressure drop. Furthermore, by the use of the computer program in Part I, it has been demonstrated that although the longitudinal dispersion coefficient affects the shape of the elution curve, it does not affect the retention time. Therefore, by neglecting the effects of longitudinal dispersion, it is possible to obtain a simple relationship between the elution time and the physical variables in G.L.C., so that this case will be considered next.

2. *Analytical solution for constant pressure, linear solubility and no longitudinal dispersion ($E = 0$)*

The differential equations describing G.L.C. with no longitudinal dispersion are eqns. (1), (2) and (3) with $E = 0$. Although the final result for this case has already been quoted by FUNK AND HOUGHTON², the details have not previously been given.

Equations (1), (2) and (3) can be combined and written as follows:

$$\frac{\partial X}{\partial t} = -u \frac{\partial X}{\partial z} - \gamma_4 X + \gamma_5 c_m \quad (10)$$

$$\frac{\partial c_m}{\partial t} = \gamma_6 X - \gamma_1 c_m \quad (11)$$

where:

$$\gamma_4 = \frac{RTA\Delta y}{\epsilon} \gamma_2 = \frac{K_1 RTA\Delta y}{\epsilon} \gamma_1 \quad (12)$$

$$\gamma_5 = \gamma_4 / K_1 P \quad (13)$$

$$\gamma_6 = \gamma_2 P \quad (14)$$

Taking the Laplace transforms of eqns. (10) and (11) and combining the results by noting that $\gamma_1 \gamma_4 = \gamma_5 \gamma_6$, we obtain:

$$\frac{x(L, s)}{x(0, s)} = \exp \left[-\frac{L}{u} s \left(\frac{s + \gamma_1 + \gamma_4}{s + \gamma_1} \right) \right] \quad (15)$$

The ratio $x(L,s)/x(0,s)$ will be referred to as the column transfer function. If a pulse of duration b and height X_0 is used for the input, $x(0,s)$ (cf. Fig. 1 and eqns. (4) and (5)), then the inverse transform can be obtained by convolution utilizing the two theorems below:

$$\mathcal{L}^{-1} \left[\frac{d}{d\gamma^4} g(s) \right] = \frac{d}{d\gamma^4} G(t) \quad (16)$$

$$\frac{d}{dt} \left[t^p I_p(\alpha t) \right] = \alpha t^p I_{p-1}(\alpha t) \quad (17)$$

The inverse transform is then:

$$\frac{X(L,t)}{X_0} = \begin{cases} 0, & 0 < t < L/u \\ \int_{t-b}^t e^{-\gamma_1 \left(\tau - \frac{L}{u} \right) - \frac{L}{u} \gamma_4} \sqrt{\frac{\gamma_1 \gamma_4 L/u}{\tau - \frac{L}{u}}} I_1 \left[2 \sqrt{\gamma_1 \gamma_4 \frac{L}{u} \left(\tau - \frac{L}{u} \right)} \right] d\tau, & t > L/u \end{cases} \quad (18)$$

If it is first assumed that the duration of the pulse is short ($b \ll L/u$), secondly that the modified Bessel function, I_1 , can be approximated by its asymptotic expansion and thirdly that $\lim_{b \rightarrow 0} \int_{t-b}^t f(\tau) d\tau = b f(\tau)$, then the retention time can be obtained by determining the time at which the resulting function maximizes (cf. FUNK AND HOUGHTON²). The result of applying this procedure is as follows:

$$t_R = \frac{L}{u} \left(1 + \frac{K_1 R T A \Delta y F}{\epsilon} \right) \quad (19)$$

where:

$$F = \frac{1}{2} - \frac{3u}{4\gamma_4 L} + \frac{1}{2} \sqrt{1 - \frac{3u}{\gamma_4 L}} \quad (20)$$

It is the factor F in the above equation that allows for the effect of a finite mass transfer rate on the retention time. Under the normal operating conditions of G.L.C. the liquid film is thin and the column is long, so that F is very close to unity. Further, since the apparent retention time, t'_R , is t_R minus the transport time without chromatography, L/u , we obtain:

$$t'_R = \frac{L K_1 R T A \Delta y}{u \epsilon} \quad (21)$$

If the lumping point is taken as the midpoint of the liquid film, then $\Delta y = h/2$ and the volume of stationary liquid per unit volume of column, V , is equal to Ah , so that:

$$t'_R = \frac{1}{2} \frac{L K_1 R T V}{u \epsilon} \quad (22)$$

However, it is possible to choose the lumping point anywhere in the liquid film, so that this case will now be considered separately as the penetration model.

PENETRATION MODEL

Referring to Part I (Fig. 1 and eqns. (11) to (15)), it may easily be seen that the lumping points varies with time as the solute passes into the liquid film and then out again. It is clear that the lumping point for a single section approximation is defined in such a way that the concentration gradient on one side is large and on the other side, small. Since the position of this lumping point varies only with time, it is possible to define a time-average penetration depth, mh , such that $\Delta y = mh$. If the lumping point is arbitrarily taken as the midpoint of the liquid film $m = 1/2$, which accounts for the factor of $1/2$ in eqn. (22), but assuming an average fractional penetration depth of m , eqn. (22) becomes:

$$t'_R = m \frac{LK_1RTV}{u\epsilon} \quad (23)$$

where m may vary between zero and unity.

Eqn. (23) can be put in a more usable form by combining Raoult's law with the Clausius-Clapeyron equation for the vapor pressure, p^0 , to obtain K_1 as a function of temperature. The useful forms of eqn. (23) may be summarized as follows:

$$t'_R = m \frac{L\rho_MRTV}{p^0u\epsilon} = m \frac{L\rho_MRTV}{Bu\epsilon} \exp(\Delta H/RT) \quad (24)$$

B is the pre-exponential constant in the Clausius-Clapeyron equation and ρ_M is the molal density of the stationary liquid phase.

COMPARISON OF THE LUMPED-FILM MODEL AND THE EQUILIBRIUM MODEL

LAPIDUS AND AMUNDSON³ have obtained an analytical solution for the case where equilibrium between the liquid and vapor phases is established instantaneously at any point in the column. Their result can be obtained by making D_L and k_G infinite and setting $\Delta y = h$ in eqn. (15). The Laplace transform for this model can be obtained by letting $\gamma_1 \rightarrow \infty$ in eqn. (15) and using L'Hospital's rule on the exponent of the exponential. The column transfer function then becomes:

$$\frac{x(L,s)}{x(0,s)} = \exp \left[-\frac{L}{u} s \left(1 + \frac{K_1RTAh}{\epsilon} \right) \right] \quad (25)$$

Inspection of transform (25) shows that the equilibrium model simply leads to a pure time delay of $LK_1RTAh/u\epsilon$ beyond the normal transport time of L/u , so that remembering that $V = Ah$, we obtain:

$$t'_R = \frac{LK_1RTV}{u\epsilon} \quad (26)$$

Furthermore, it is clear from eqn. (25) that the equilibrium model leads to no change in either the size or the shape of the pulse. However, the transform (15), obtained by using the lumped-film model, leads to eqn. (18) which shows that a finite rate of chromatography, introduced by the coefficients D_L and k_G , not only produces a delay beyond the transport time, but also produces a change in the shape of the elution curve. The effect of k_G on the elution curve and retention time has already been illustrated in Part I by the use of the computer program.

Comparison of eqns. (22), (23) and (26) shows that the average fractional depth of penetration, m , for the simple lumped-film model is $1/2$, while that for the equilibrium model is 1.0 . Experiments, that will now be discussed, have shown that in actual practice, m has values in the range $0.6 - 0.9$, depending largely upon the film thickness and the slug length, and that at constant film thickness the assumption of a constant value for m in eqn. (24) is remarkably good.

EXPERIMENTAL

In order to evaluate the application of eqns. (23) and (24) to elution times actually observed in G.L.C., an apparatus was constructed that conformed as closely as possible to the boundary conditions of Fig. 1. The solute used was isobutylene (Matheson CP) in a carrier stream of helium. The stationary phase was dinonyl phthalate (National Research Corporation, specially refined Narcoil-40) uniformly coated on to 30-60 mesh firebrick (Burrell Corporation Kromat-FB).

The slug of pure isobutylene ($X_0 = 1$) was confined in a slug chamber between two stopcocks lubricated with glycerine. Two slug chambers were available, one holding 3.0 cm^3 and the other 6.7 cm^3 of gas. They could be filled through capillary side arms connected to the isobutylene supply. Arrangements were made to divert the helium stream to the top of the chromatographic column while the slug chamber was being filled. To introduce the slug into the helium stream, it was only necessary to open the two stopcocks and divert the carrier gas from the top of the column back through the slug chamber. The slug entered the packed bed almost as soon as it issued from the slug chamber. The chromatographic column itself and the slug chambers were constructed from 7 mm i.d. Pyrex glass tubing and the column was packed to a length of about 100 cm. The detector was a thermal conductivity gauge constructed from the tungsten filament of a Westinghouse No. 1819 miniature light bulb and was placed directly in the gas stream only 3.5 cm from the end of the packed section. Another similar filament was placed 100 cm downstream in the same tube to compensate for flow variations. The two filaments formed two arms of a chopper-stabilized Wheatstone bridge, the unbalance voltage being recorded on a Leeds and Northrup Azar recorder with a time constant of 1 sec and a chart speed of 3 in. per minute. Since the detectors were bare filaments placed directly in the gas stream, their time constants were very low, so that no errors in the elution time could be attributed to measurement lags. The slug chamber, the chromatographic column and the detectors were all surrounded by a water jacket provided with water circulating from a thermo-

stated bath. In this way the column temperature could be maintained at any temperature in the range 20–80° to within $\pm 0.05^\circ$. Carrier gas flow rates in the range 7–70 cm³/min could be accurately measured within $\pm 0.5\%$ by means of a soap bubble flow meter. The pressure drop across the column was less than 7.5 cm Hg for all the flow rates used. The volumetric flow rates, Q , for use in the equations were calculated at the average column pressure.

To make a measurement, the elution time of an isobutylene slug was first measured in the wet column; the transport time without chromatography was then measured under the same conditions using a nitrogen slug. However, by separate experiments conducted on dry firebrick, it was found that there was approximately a 10% difference in the transport times between nitrogen and isobutylene, the latter taking longer to appear. Typical results for dry firebrick are shown in Fig. 2—it is

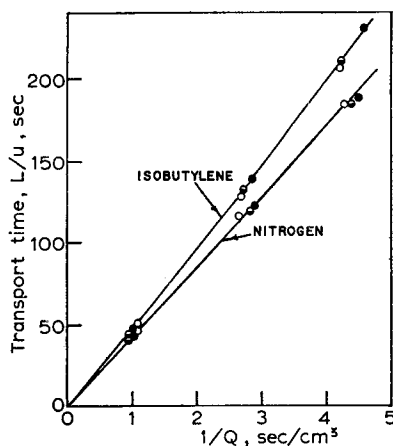


Fig. 2. Transport times through dry firebrick. $V_s = 6.7$ cm³. ● 31.0°; ● 45.0°; ○ 60.0°.

interesting to note that temperature has no detectable effect on the transport time of either isobutylene or nitrogen in the range 31–60°, indicating perhaps that adsorption is not the cause of the delay in the case of isobutylene. The reason for the delay is believed to be that isobutylene diffuses into and out of the pores in firebrick more slowly than nitrogen. By assuming that the pores in the wet firebrick were not filled with partitioning liquid, it was possible to make a correction for the difference in transport times of nitrogen and isobutylene, using the data from the dry column. The apparent retention time, t'_R , could then be computed by subtracting the corrected transport time, L/u , from the total elution time, t_R .

RESULTS AND DISCUSSION

Equations (23) and (24) may be applied to the experimental data by substituting $Q = ua\varepsilon$ and $V_p = LaV$, where a is the cross-sectional area of the column, Q is the

volumetric flow rate of carrier gas and V_p is the total volume of partitioning liquid present in the chromatographic column; the result is:

$$t'_R = \frac{mK_1RTV_p}{Q} = \frac{m\rho_MRTV_p}{p^0Q} = \frac{m\rho_MRTV_p}{BQ} \exp(\Delta H/RT) \quad (27)$$

According to eqn. (27), a plot of the apparent retention time t'_R versus $1/Q$ should be a straight line; Fig. 3 shows typical plots for various amounts of partitioning liquid at constant temperature. When the points of Fig. 3 were plotted on a larger scale, it was found that, although the lines were straight, they extrapolated backwards to give a small negative intercept on the t'_R axis when $1/Q = 0$. The cause of this effect

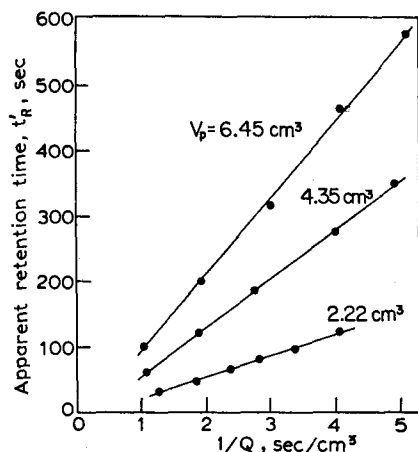


Fig. 3. Effect of amount of dinonyl phthalate on the elution of isobutylene at 31.0° . $V_s = 6.7$ cm³.

is not certain, but it could be due to unsteady state flow effects during the introduction of the slug, or perhaps to the non-uniform velocity distribution at the unpacked entrance to the column, or even to the effects of the finite rate of mass transfer on fluid flow in the region of the slug. It is interesting to point out that a finite mass transfer rate normal to a flowing fluid would be equivalent to increasing the effective viscosity of the carrier gas. However, the intercepts were small compared with the elution times in the present experiments.

Fig. 4 has plots of t'_R versus $1/Q$ for three different temperatures, showing that as the temperature is reduced, the elution time increases, as would be expected from eqn. (27). If the carrier velocity is constant, then according to eqn. (27) a plot of $\log(t'_R/T)$ versus $1/T$ should be a straight line of slope $\Delta H/R$, where ΔH is the latent heat of vaporization of isobutylene. Typical plots are shown in Fig. 5 for three different carrier gas velocities. The average of the slopes of the three lines gives $\Delta H = 5.30 \pm 0.05$ kcal/g-mole, compared with a value of 5.4 ± 0.2 kcal/g-mole calculated from the isobutylene vapor pressure data of COFFIN AND MAASS⁴.

To determine the fractional penetration depth, m , the data of Fig. 4 were replotted as t'_R/K_1RTV_p versus $1/Q$ so that according to eqn. (27) the slope should be m .

Fig. 4. Effect of temperature on the elution of isobutylene slugs using dinonyl phthalate on firebrick. $V_s = 3.0 \text{ cm}^3$; $V_p = 6.45 \text{ cm}^3$.

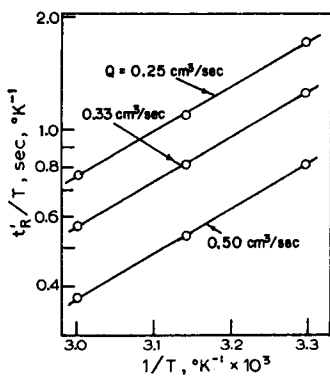
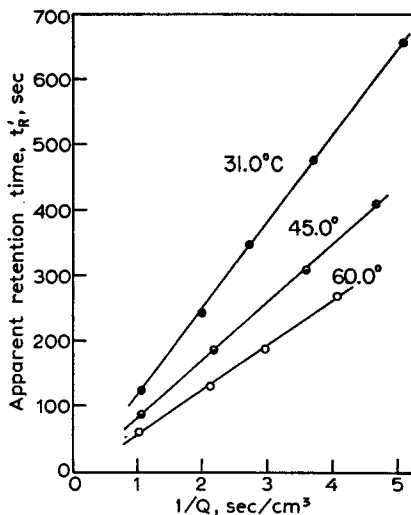
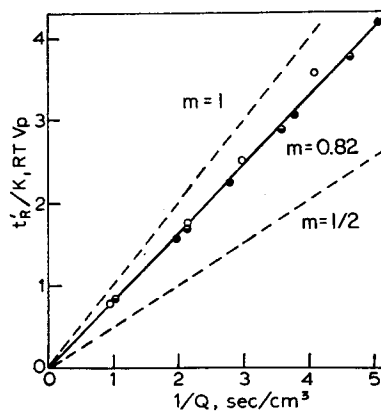


Fig. 5. Plot of $\log(t'_R/T)$ versus $1/T$ for the isobutylene-dinonyl phthalate system. $V_s = 3.0 \text{ cm}^3$; $V_p = 6.45 \text{ cm}^3$.

Fig. 6. Evaluation of the time-average penetration depth, m . $V_s = 3.0 \text{ cm}^3$; $V_p = 6.45 \text{ cm}^3$.
 ● 31.0°; ● 45.0°; ○ 60.0°.



Values of K_1 were taken from the data of HOUGHTON, KESTEN, FUNK AND COULL⁵. The best line through the data gives a value of $m = 0.82$ and correlates the data within $\pm 2\%$, with the exception of one point. The lines for $m = 1/2$ and $m = 1$ (equilibrium theory) are also shown in Fig. 6. It is evident that data on the same column at various temperatures and for a fixed slug length are very well correlated by a constant average depth of penetration.

Table I shows the effect of slug length, amount of partitioning liquid and temperature on the time-average fractional depth of penetration, m . The fact that m increases as the amount of partitioning liquid increases indicates that the effect of the impermeable solid support is significant at small film thicknesses. However, it is also clear that m is not a sensitive parameter, since its values are limited to the range 0.6–0.9 for the present experiments, and in fact an overall average value of 0.72 will correlate all the data in Figs. 2, 3 and 4 and Table I with an accuracy of better than $\pm 25\%$.

TABLE I
TIME AVERAGE PENETRATION DEPTH, m ,
FOR THE ISOBUTYLENE-DINONYL PHTHALATE SYSTEM ON FIREBRICK

Temperature °C	Slug volume V_s, cm^3	Wt. % dinonyl phthalate	Solubility $K_1 \times 10^4$ g-mole/ $\text{cm}^3 \cdot \text{atm}$.	Volume dinonyl phthalate V_p, cm^3	m
31.0	6.7	10.1	9.64	2.22	0.60
31.0	6.7	17.9	9.64	4.35	0.70
31.0	6.7	24.2	9.64	6.45	0.74
31.0	3.0	24.2	9.64	6.45	0.81
45.0	3.0	24.2	6.34	6.45	0.81
60.0	3.0	24.2	4.17	6.45	0.84

NOTATION

- a = cross-sectional area of chromatographic column, cm^2
 A = mass transfer area per unit volume of empty column, cm^2/cm^3
 b = duration of solute pulse, sec
 B = pre-exponential constant in Clausius-Clapeyron equation, atm
 c = solute concentration in liquid phase, g-mole/ cm^3
 c_i = interfacial solute concentration, g-mole/ cm^3
 c_m = solute concentration at lumping point in liquid film, g-mole/ cm^3
 D_L = molecular diffusivity in liquid phase, cm^2/sec
 E = longitudinal dispersion coefficient cm^2/sec
 F = dimensionless factor given by eqn. (20)
 h = liquid film thickness, cm
 ΔH = latent heat of vaporization of solute, cal/g-mole
 I_p = modified Bessel function of order p
 J_1 = Bessel function of order unity

k_G	= gas film coefficient, g-mole/sec.cm ² .atm
K_1, K_2	= constants in nonlinear solubility isotherm
L, L_1	= length, cm
\mathcal{L}	= Laplace transform
m	= time-average penetration depth, dimensionless
P	= column pressure, atm
p^0	= vapor pressure of solute gas, atm
Q	= volumetric gas flow rate, cm ³ /sec
R	= Universal Gas Constant, 82.06 atm. cm ³ /g-mole. °K
s	= Laplace parameter, complex variable
t	= time, sec
t_R	= retention time, sec
t'_R	= apparent retention time, sec
T	= absolute temperature, °K
u	= axial gas velocity through voids, cm/sec
V	= volume of partitioning liquid per unit volume of empty column, dimensionless
V_p	= total volume of partitioning liquid in chromatographic column, cm ³
V_s	= volume of slug, cm ³
X	= mole fraction of solute in vapor phase
X_i	= mole fraction of solute at gas-liquid interface
X_0	= initial mole fraction of solute in slug
Δy	= incremental distance in liquid film, cm
z	= axial distance along column, cm
$\gamma_1, \gamma_2, \gamma_3, \gamma_4, \gamma_5, \gamma_6$	= parameters defined in text
ε	= void fraction, dimensionless
λ	= variable of integration
ρ_M	= molal density of liquid phase, g-mole/cm ³
τ	= variable of integration

ACKNOWLEDGEMENT

One of us (J.E.F.) wishes to express his gratitude to the Westinghouse Corporation for a graduate fellowship.

SUMMARY

The differential equations governing gas-liquid partition chromatography have been simplified by using the assumptions of linear solubility and no pressure drop and introducing the concept of a lumped liquid film. Analytical solutions of the equations have been obtained for the cases with and without longitudinal dispersion. The solutions show that a finite rate of mass transfer into the liquid phase can affect both the shape of the elution curve and the retention time. A simple equation has been obtained relating the apparent retention time to the column variables and the depth of penetration into the liquid film. Experimental data on the elution of a pure iso-

butylene slug with helium using a stationary phase of dinonyl phthalate on firebrick has shown the average fractional depth of penetration to be in the range 0.6–0.9 under normal operating conditions. It was found that the penetration model correlates the retention time at various temperatures remarkably well, provided the slug size and the amount of stationary phase are held constant.

REFERENCES

- ¹ J. E. FUNK AND G. HOUGHTON, *J. Chromatog.*, 6 (1961) 193.
- ² J. E. FUNK AND G. HOUGHTON, *Nature*, 188 (1960) 389.
- ³ L. LAPIDUS AND N. R. AMUNDSON, *J. Phys. Chem.*, 56 (1952) 984.
- ⁴ C. C. COFFIN AND O. MAASS, *Trans. Roy. Soc. Can.*, 21 (1927) 33.
- ⁵ G. HOUGHTON, A. S. KESTEN, J. E. FUNK AND J. COULL, *J. Phys. Chem.*, 65 (1961) 649.

J. Chromatog., 6 (1961) 281–292