CHROM. 5020

NONADDITIVITY OF THE GAS AND LIQUID PHASE MASS-TRANSFER RESISTANCES IN GAS CHROMATOGRAPHY

S. WIČAR AND J. NOVÁK
Institute of Instrumental Analytical Chemistry, Czechoslovak Academy of Sciences, Brno (Czechoslovakia)

(Received August 31st, 1970)

SUMMARY

The results of a number of papers dealing with the isolation of the 'C' terms of the VAN DEEMTER equation and with the interpretation of the respective results led, in many cases, to discrepancies that could not be explained satisfactorily in virtue of the classical VAN DEEMTER or GOLAY's equations. Abandoning the principle of the independence of the processes controlling the interphase mass transfer in a chromatographic column led to a modified HETP equation, the qualitative predictions of which are in very good agreement with the experimental results.

INTRODUCTION

The very useful concept of the additivity of the partial resistances to the mass transfer between two phases, representing one of the basic presuppositions in WHITMAN's film theory[1], was applied to gas–liquid chromatography (GLC) as early as in the pioneer papers by LAPIDUS AND AMUNDSON[2] and by VAN DEEMTER *et al.*[3,4]. The analytical substantiation of the above concept was later[5] seen in the results of GOLAY's solution of the equation of the solute mass balance in a capillary column[6].

From the viewpoint of the stochastic theories on the growth of the variance of the chromatographic zone (*c.f. e.g.* GIDDINGS[7]), the presupposition of the above additivity is equivalent to an assumption on the independence between the processes taking place in the mass transfer within both phases in the chromatographic column.

The existence of a number of papers dealing with the isolation of the 'C' terms in the Van Deemter equation has been a practical consequence of the conviction about the applicability of the above additivity principle. To this effect, changes have been utilized of the HETP brought about by changes in the retentive capacity[8], by changes in the column length at a constant column inlet or column outlet pressure[9], by changes of the pressure within the column of a given length, or by varying the kind of carrier gas[10–15]. As long as the authors of the individual papers limited themselves to finding such pairs of the C_G and C_L values that complied with the measured HETP and flow velocity values, their efforts were always successful. However, the attempts at a further qualitative or even quantitative interpretation of the values obtained often led to paradox results. For instance, PERRETT AND PURNELL[16] found a very significant dependence of the gas-phase mass-transfer term (C_G) on the loading of the support by the stationary phase (within a range of 0.5–20 wt. % the value of the C_G term arose about 80 %). Further, in the paper by GIDDINGS *et al.*[9] devoted, besides other objectives, to the correlation of the data measured on columns of different lengths in terms of the equation $\hat{H} = (B'/P_2u_2 + C'_GP_2u_2)f_1 + C_Lu_2f_2$, one can notice a significant decrease of the C_L coefficient with decreasing column length (mean column pressure). Similar difficulties were encountered also by HAZELDEAN AND SCOTT[15] in testing the GOLAY[6] and KHAN[17] equations by working with nylon capillaries at various absolute pressures. SAHA AND GIDDINGS[18] found a correlation between the diameter of the column packing particles and the C_L coefficient. Finally, NOVÁK *et al.*[19] ascertained an expressive growth of the C_L coefficient upon raising the absolute column pressure, while the C_G' coefficient ($C_G = C_G'P$) was decreasing at the same time.

THEORETICAL

The simplest analytical model for describing the mass transfer between the phases in the chromatographic column is indubitably an idealized capillary column with the walls coated by a homogeneous film of the stationary phase. In such a column, one may define two continuous concentration fields of the solute in both phases. When neglecting the longitudinal diffusion and, further, assuming the axial symmetry of the concentration fields and laminar flow, it is then possible to write for the solute mass balance in the phases

$$\frac{\partial c}{\partial t} = D_G\left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r}\right) - 2u_0\left(1 - \frac{r^2}{a^2}\right)\frac{\partial c}{\partial z} \qquad (1)$$

and

$$\frac{\partial c'}{\partial t} = D_L\left(\frac{\partial^2 c'}{\partial r^2} + \frac{1}{r}\frac{\partial c'}{\partial r}\right) \qquad (2)$$

The initial conditions may be formulated by the equations

$$c(0,r,z) = c'(0,r,z) = 0 \qquad (3)$$

The boundary condition determining the concentration signal at the column inlet in a case of elution analysis can be expressed by

$$c(t,r,0) = c_0\,\delta(t) \qquad (4)$$

The boundary condition (eqn. 4) has to be further supplemented by four equations, describing the radial concentration distribution at the outsets. One of these equations follows from the above postulated symmetry of the concentration field in the mobile phase,

$$\frac{\partial c}{\partial r}(t,0,z) = 0 \qquad (5)$$

the second one from the impermeability of the capillary wall for the solute

$$\frac{\partial c'}{\partial r}(t,a_1,z) = 0 \qquad (6)$$

and the remaining two boundary conditions describe the properties of both concentration fields at the phase interface. Let us suppose instantaneous equilibration at the interface, then

$$c'(t,a,z) = kc(t,a,z) \tag{7}$$

Further, let us suppose that there may occur no solute accumulation at the interface, then

$$\frac{D_G v_L}{D_L v_G} \frac{\partial c}{\partial r} (t,a,z) = \frac{\partial c'}{\partial r} (t,a,z) \tag{8}$$

The radial concentration distribution complying with conditions 5–8 is shown schematically in Fig. 1.

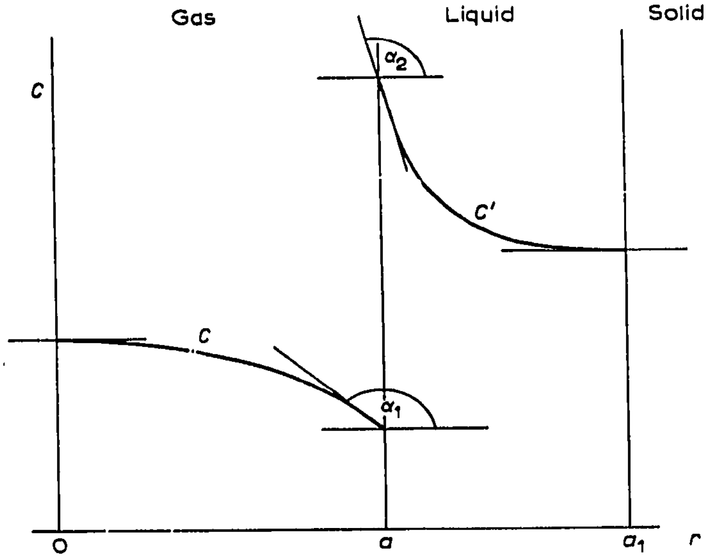

Fig. 1. Scheme of the radial concentration distribution in an idealized capillary column. $\text{tg}\alpha_2/\text{tg}\alpha_1 = D_G v_L/D_L v_G$.

The system of eqns. 1–8 may be simplified, at least formally, by introducing the following substitutions:

$$C = c/c_0 \qquad C' = c'/c_0 \tag{9, 10}$$

$$T = tu_0/l \qquad L = z/l \qquad R = r/a \qquad Q = r/d_f \tag{11–14}$$

$$\beta = D_G l/u_0 a^2 \qquad \gamma = D_L l/u_0 d_f^2 \qquad \delta = D_G/D_L \tag{15–17}$$

$$\xi = a/d_f \doteq 2v_G/v_L \tag{18}$$

This results in a system of dimensionless equations

$$\frac{\partial C}{\partial T} = \beta \left(\frac{\partial^2 C}{\partial R^2} + \frac{1}{R}\frac{\partial C}{\partial R}\right) - 2(1 - R^2)\frac{\partial C}{\partial L} \tag{1a}$$

$$\frac{\partial C'}{\partial T} = \gamma \left(\frac{\partial^2 C'}{\partial Q^2} + \frac{1}{Q}\frac{\partial C'}{\partial Q}\right) \tag{2a}$$

$$C(0,R,L) = C'(0,Q,L) = 0 \tag{3a}$$

$$C(T,R,0) = \delta(T) \tag{4a}$$

$$\frac{\partial C}{\partial R}(T,0,L) = 0 \tag{5a}$$

$$\frac{\partial C'}{\partial Q}(T,\xi + 1,L) = 0 \tag{6a}$$

$$C'(T,\xi,L) = kC(T,1,L) \tag{7a}$$

$$\frac{\delta\xi}{2}\frac{\partial C}{\partial R}(T,1,L) = \frac{\partial C'}{\partial Q}(T,\xi,L) \tag{8a}$$

$$T \geqq 0, \qquad 0 \leqq R \leqq 1, \qquad \xi \leqq Q \leqq \xi + 1, \qquad 0 \leqq L \leqq 1$$

The analytical solution of the parabolic system 1a–8a has not yet been found. However, it may easily be proved by applying the theory of physical similarity (*cf.* WIČAR[20]) to the capillary columns obeying the system 1a–8a that the number of the theoretical plates of the idealized capillary column is a function of all the variable parameters occurring in the system 1a–8a except the functions C and C' themselves and the variables T, R, Q, and L. Hence, there holds

$$N = N(\beta,\gamma,\delta,k,\xi) \tag{19}$$

The individual criterions and simplexes occurring in the above symbolic equation have different roles; the values of β and γ characterize the maximum attainable mass-transfer rates, under given conditions, in the individual phases. For the gaseous phase and for the criterion β, the above statement may be documented for instance by the results of TAYLOR[21] and ARIS[22]. On the other hand, the quantities δ, k, and ξ, occurring in the boundary conditions, signify obviously certain limitations for the above maximum values.

From this viewpoint, the condition 8a is particularly important; if no solute accumulation is to occur at the phase interface, the rates of the mass fluxes in both phases must be mutually coordinated. Therefore, any limitation in the possibilities of the mass transfer in the stationary phase (a decrease of the γ value caused, for instance, by increasing the d_f) will inevitably also induce a decrease in the mass-transfer rate in the mobile phase, regardless the fact that the β value itself remains unchanged. Similarly, a decrease of the β value brings about a decrease in the mass transfer in the stationary phase with the γ value remaining unchanged.

When introducing the presupposition of quasi-ideality (long-time approximation) of the chromatographic process into our consideration, which presupposition is common in the theory of gas chromatography, one may look for a direct relation between the values of β, γ, and the variance of the concentration band caused by a finite rate of the interphase mass transfer.

The classical GOLAY theory which leads, in its consequences, to the mutual independence of the mass-transfer processes taking place in both phases expresses the final variance by the sum of the partial variances:

$$H = F_1(k)l/\beta + F_2(k)l/\gamma = \sigma_G{}^2/l + \sigma_L{}^2/l \tag{20}$$

Hence, one may easily derive for the individual variances:

$$\sigma_G{}^2 = \frac{F_1(k)a^2l}{D_G}u_0, \qquad \sigma_L{}^2 = \frac{F_2(k)d_f{}^2l}{D_L}u_0 \tag{21}$$

Now, let us assume, in compliance with eqn. 8a, that the processes effective in the mass transfer in both phases are interdependent; employing the elementary theory of probability, one may easily find a combination law for the resultant variance*:

$$H = \sigma^2/l = \sigma_G^2/l + \sigma_L^2/l + 2\rho_{GL}\sqrt{\sigma_G\sigma_L/l} =$$

$$= F_1(k)\frac{a^2}{D_G}u_o + F_2(k)\frac{d_f^2}{D_L}u_o + 2\rho_{GL}u_o\sqrt{F_1(k)F_2(k)\frac{a^2d_f^2}{D_GD_L}} \qquad (22)$$

In accordance with eqn. 19, the correlation coefficient ρ_{GL} may be regarded as an undefined function of exclusively the quantities k, δ, and ξ, *i.e.*,

$$\rho_{GL} = \rho_{GL}(k,\delta,\xi) \qquad (23)$$

Without the knowledge of the solution of the system of eqns. 1a–8a, the actual shape of the function ρ_{GL} expressed by eqn. 23 may be obtained only experimentally. Eqn. 22 may be written, referring to the conventional formal notation, to read:

$$H = (C_G + C_L + 2\rho_{GL}\sqrt{C_GC_L})u_o \qquad (24)$$

or, after introducing the mean pressure and the mean flow velocity to respect, at least approximately, the mobile phase compressibility,

$$\hat{H} = (C_L + C_G'\bar{P} + 2\rho_{GL}(\bar{P})\sqrt{C_LC_G'\bar{P}})\bar{u} \qquad (25)$$

DISCUSSION AND CONCLUSIONS

First, let us go into the two fundamental phenomenological theories of gas–liquid chromatography, VAN DEEMTER's theory and the GOLAY theory of the capillary column, and investigate the effect of that critical step in them which leads to the principle of the additivity of the partial resistances.

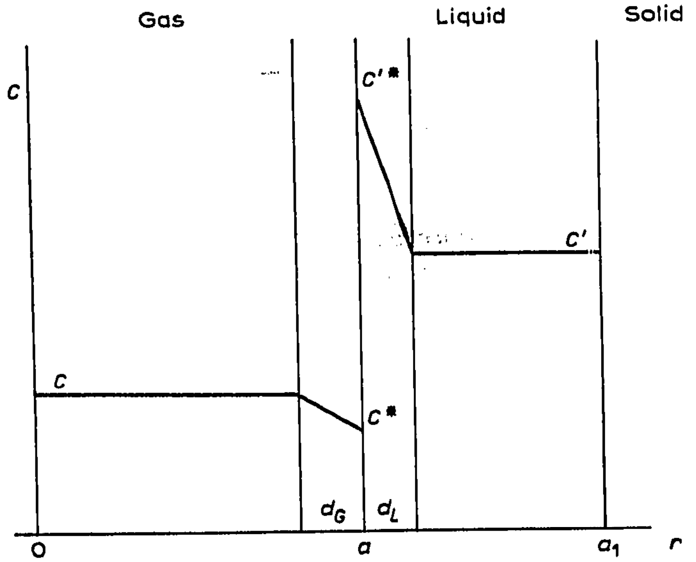

Fig. 2. Radial concentration distribution according to the film theory. d_G,d_L = effective thicknesses of the gas and liquid diffusion films, respectively.

---

* A similar procedure has been used by JONES[23] for combining the variances produced in the stationary and mobile part of the gaseous phase.

The VAN DEEMTER theory assumes the radial concentration distribution in accordance with the film theory (Fig. 2). The concentrations c^* and $c^{*\prime}$ at the phase interface are colligated with each other by the relation $c^{*\prime} = kc^*$; there holds for both partial mass-transfer coefficients

$$1/K_{OG} = 1/K_G + 1/kK_L \tag{26}$$

Hence, the presupposition of the additivity of the partial resistances to mass transfer in both phases has been introduced in the very description of the model of the mass transfer at the interface.

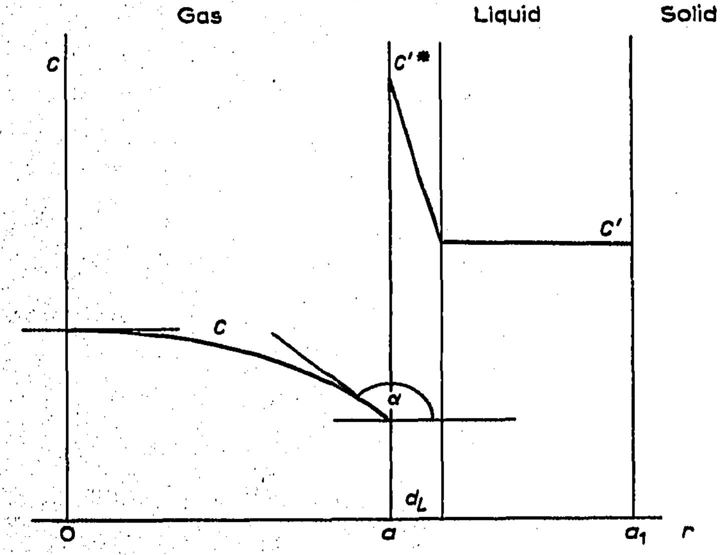

Fig. 3. Radial concentration distribution according to GOLAY's theory. d_L = effective thickness of the liquid diffusion film, $\operatorname{tg}\alpha = (K_L a/2D_G)\,(c' - c'^*)$.

The GOLAY model is substantially more involved; the radial concentration distribution presupposed in this model is shown schematically in Fig. 3. A hybrid model is apparently at stake here — the rate of the mass transfer in the mobile phase obeys the equation of diffusion while the rate of the mass transfer in the liquid phase is described, similarly as in VAN DEEMTER's model, by means of the partial mass-transfer coefficient K_L. At the phase interface, two boundary conditions apply. One of them colligates the concentrations in the mobile and in the stationary phases at the interface by the relation $c'^* = kc^*$, the other one describes the mass fluxes at the interface by the Fourier relation

$$2\,\frac{D_G}{a}\,\frac{\partial c}{\partial r}\,(t,a,z) = K_L[c' - kc(t,a,z)] \tag{27}$$

which is analogous to the condition described by eqn. 8. Hence, the exact solution of the GOLAY model would have to lead to an interdependence between both partial processes in the mass transfer. The resultant independence of C_G and C_L is a consequence of the simplification of the model during the solution. The decisive step is undoubtedly the substitution of eqn. 21 into eqn. 17a (in GOLAY's notation) which implies the concentration field in the mobile phase to be independent of the rate of the mass transfer in the stationary phase.

The concept of the mutual dependence of the mass transfer in both phases may easily be applied also to packed columns. Let us turn back to eqn. 22, supplemented now by the terms accounting for the variances due to longitudinal and eddy diffusion,

$$\hat{H} = A + B'/\bar{P}\bar{u} + C_G'\bar{P}\bar{u} + C_L\bar{u} + 2\rho_{GL}(\bar{P})\sqrt{C_LC_G'\bar{P}}\,\bar{u} \qquad (28)$$

and compare it with the classical VAN DEEMTER equation

$$\hat{H} = A + B'/\bar{P}\bar{u} + C_G'\bar{P}\bar{u} + C_L\bar{u} \qquad (29)$$

Both equations may be divided by the average velocity of the mobile phase, $\bar{u}$:

$$\hat{H}/\bar{u} = A/\bar{u} + B'/\bar{P}\bar{u}^2 + C_G'\bar{P} + C_L + 2\rho_{GL}(\bar{P})\sqrt{C_LC_G'\bar{P}} \qquad (28a)$$

$$\hat{H}/\bar{u} = A/\bar{u} + B'/\bar{P}\bar{u}^2 + C_G'\bar{P} + C_L \qquad (29a)$$

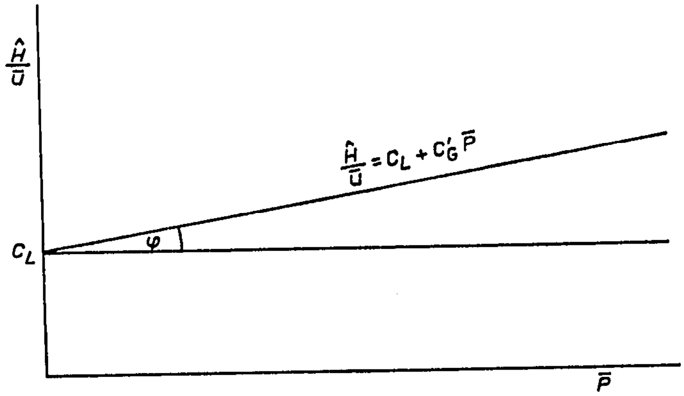

Fig. 4. Scheme of the isolation of the C_L and C_G' coefficients according to the classical concepts (eqn. 29a).

In a region of higher flow velocities of the mobile phase, where the plate height is dominated by the rate of the interphase solute-transfer, the two first members of the right-hand sides in eqns. 28a and 29a may be neglected to a good approximation. In compliance with the classical eqn. 29, one could easily isolate the C_L and C_G' coefficient by plotting the ratio $\hat{H}/\bar{u}$ against the mean column pressure $\bar{P}$ (*cf.* Fig. 4). On the other hand, eqn. 28a, when neglecting the dependence of ρ_{GL} on $\bar{P}$ (for instance by introducing the mean value, $\overline{\rho_{GL}}$, within the given interval of the mean pressure $\bar{P}$), renders the curves resulting from the composition of the straight lines $\hat{H}/\bar{u} = C_G'\bar{P} + C_L$ and the parabolas $\hat{H}/\bar{u} = 2\overline{\rho_{GL}}\sqrt{C_LC_G'\bar{P}}$ (Fig. 5).

The endeavour to express the C_G' and C_L values from the measured data by the classical relation 29 is equivalent to the seeking for the tangent or secant to the curves given by eqn. 28a. Therefore, the C_G' and C_L coefficients obtained from HETP *versus* flow velocity data in virtue of the conventional concepts represent some apparent values, $(C_G')_{\mathrm{app}}$ and $(C_L)_{\mathrm{app}}$. Hence, when calculating with the tangent and neglecting the first two members of the right-hand side of eqn. 28a, one obtains

$$(C_L)_{\mathrm{app}} = C_L + \overline{\rho_{GL}}\sqrt{C_LC_G'\bar{P}_0} \qquad (30)$$

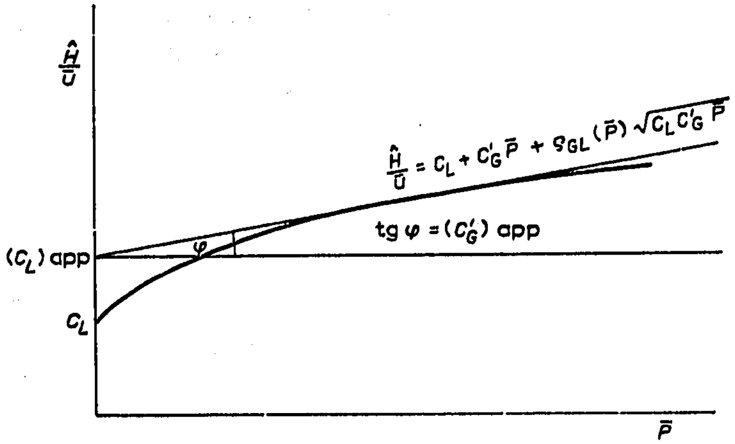

Fig. 5. Scheme of the isolation of the apparent C_L and C_G coefficients according to the concept of the interdependence between the gas and liquid mass-transfer terms.

where $\bar{P}_0$ stands for the mean pressure determining the position of the tangent on the curve given by eqn. 28a.

Hence, the obtained apparent value of C_L, $(C_L)_{\mathrm{app}}$, increases, on a given column, with increasing mean pressure $\bar{P}_0$ and with increasing C_G' (increasing gas phase diffusion coefficient), which is in conformity with the experimental experience. To illustrate the above account, Fig. 6 shows the plots of $\hat{H}/\bar{u}$ against $\bar{P}$ for octane with hydrogen, nitrogen, and argon as the carrier gases. The column was 190 cm long, packed with 10 wt. % of Apiezon L on Chezasorb (an equivalent of Chromosorb P) of the particle diameter 0.08–0.1 mm and kept at a temperature of 100°.

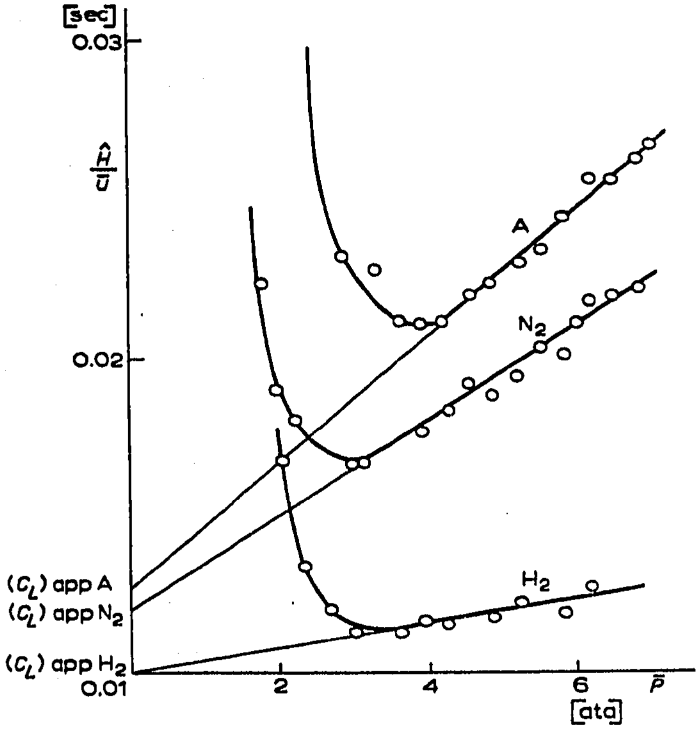

Fig. 6. Plot of $\hat{H}/\bar{u}$ *versus* $\bar{P}$ for octane chromatographed with A, N_2, and H_2 carrier gases, illustrating the dependence of the apparent C_L on the gas phase diffusion coefficient.

The slopes of the tangents to the curves, rendering the apparent values of C_G', $(C_G')_{\text{app}}$, are given by the relation

$$(C_G')_{\text{app}} = C_G' + \overline{\rho_{GL}}\sqrt{C_L C_G'/\bar{P}_o} \tag{31}$$

Thus, the measured value of $(C_G')_{\text{app}}$ rises with increasing values of C_L, in compliance with the papers by PURNELL AND PERRETT[16], and decreases with increasing P_o, as found by NOVÁK *et al.*[10].

LIST OF SYMBOLS

c = solute concentration in the mobile phase, expressed by the mass of solute in a unit volume of the empty column
c' = solute concentration in the stationary phase, expressed in the same units as quoted with c
D_G = diffusion coefficient of the solute in the mobile phase
D_L = diffusion coefficient of the solute in the stationary phase
u_o = mobile phase forward flow velocity averaged over the void cross-sectional area of the column
$\delta(t)$ = Dirac's delta function
a = distance of the gas–liquid interface from the capillary axis
a_1 = internal radius of the capillary tube
k = partition ratio
v_G = volume of the gaseous phase per unit volume of the empty column
v_L = volume of the liquid phase per unit volume of the empty column
d_f = (effective) thickness of the stationary liquid layer
$F_1(k) = (1 + 6k + 11k^2)/24(1 + k)^2$
$F_2(k) = k^3/6(1 + k)^2$
t,r,z = time, radius, and distance coordinates

REFERENCES

1 W. G. WHITMAN, *Chem. Metal. Eng.*, 29 (1923) 147.
2 L. LAPIDUS AND N. R. AMUNDSON, *J. Phys. Chem.*, 56 (1952) 984.
3 J. J. VAN DEEMTER, F. J. ZUIDERWEG AND A. KLINKENBERG, *Chem. Eng. Sci.*, 5 (1956) 271.
4 J. J. VAN DEEMTER, *2nd Informal Symp., GC Disc. Group, Cambridge, Sept. 1957.*
5 J. C. GIDDINGS, *Dynamics of Chromatography*, Part. I, M. Dekker, New York, 1965, p. 176.
6 M. J. E. GOLAY, in D. H. DESTY (Editor), *Gas Ghromatography 1958*, Butterworths, London, 1958, p. 36.
7 J. C. GIDDINGS, *J. Chem. Educ.*, 35 (1958) 588.
8 S. DAL NOGARE AND J. CHIU, *Anal. Chem.*, 34 (1962) 890.
9 J. C. GIDDINGS, S. L. SEAGER, L. R. STUCKI AND G. H. STEWART, *J. Clin. Anal. Chem.*, 32 (1960) 867.
10 R. H. PERRETT AND J. H. PURNELL, *Anal. Chem.*, 34 (1962) 1336.
11 R. H. PERRETT, *Anal. Chem.*, 37 (1965) 1346.
12 D. D. DE FORD, R. J. LOYD AND B. D. AYERS, *Anal. Chem.*, 35 (1963) 426.
13 J. C. GIDDINGS AND P. D. SCHETTLER, *Anal. Chem.*, 36 (1964) 1483.
14 J. C. STERNBERG AND R. E. POULSON, *Anal. Chem.*, 36 (1964) 58.
15 G. S. F. HAZELDEAN AND R. P. W. SCOTT, *J. Inst. Petrol.*, 48 (1962) 380.
16 R. H. PERRETT AND J. H. PURNELL, *Anal. Chem.*, 35 (1963) 430.
17 M. A. KHAN, in M. VAN SWAAY (Editor), *Gas Chromatography 1962*, Butterworths, London, 1962, p. 3.

18 W. C. Saha and J. C. Giddings, *Anal. Chem.*, 37 (1965) 830.
19 J. Novák, S. Wičar and P. Boček, *J. Chromatog.*, 53 (1970) 421.
20 S. Wičar, in E. Kovats (Editor), *5th Intern. Symp. on Separation Methods, Column Chromatography, Lausanne, 1969.*
21 G. Taylor, *Proc. Roy. Soc.* (*London*), A 219 (1953) 186.
22 A. Aris, *Proc. Roy. Soc.* (*London*), Z 235 (1956) 67.
23 W. Jones, *Anal. Chem.*, 33 (1961) 829.

J. Chromatog., 53 (1970) 429–438