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EFFECT OF NON-EQUILIBRIUM IN GAS CHROMATOGRAPHY

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SUMMARY

The effect of the finite rate of mass transport of solute between the moving and stationary phases in gas chromatography is investigated theoretically by means of a time-constant approach. Tailing and shift of the peak maximum toward larger times are found; the shift is not consistent with treatment of the effect as a simple contribution to the effective diffusion constant.

INTRODUCTION

The various theories of the line shapes obtained in gas chromatographic (GC) work have been critically reviewed by Giddings[1], who lists numerous references. The major factors affecting peak shape are summarized in the Van Deemter equation[2], and include eddy diffusion (caused by the irregular paths the gas takes through the column packing), molecular diffusion in the vapor phase, and resistance to mass transfer between the stationary liquid phase and the moving vapor phase. Common practice has been to lump these three effects together as a theoretical plate height or an effective diffusion constant, thereby obtaining gaussian peaks. A number of more detailed analyses led to such complicated mathematical expressions that numerical evaluation was not attempted[3,4]; one notable exception to this is the probabilistic approach of Giddings and coworkers[1,5], which under normal experimental conditions yields a relatively simple asymptotic formula.

The principal difficulty with the analysis of line shapes by means of the differential equation for diffusion in a moving gas stream is that of taking into account non-equilibrium effects in the mass transport of solute between the stationary liquid phase and the moving vapor phase. Inclusion of these leads to a pair of coupled partial differential equations which can be solved formally, but the solutions are not easy to evaluate numerically, being double integrals with Bessel functions in the integrand[3]. Nevertheless, the approach through the differential equations for diffusion has much to recommend it, in that the variations in gas flow-rate, molecular diffusion constant, and distribution coefficient (if we have a non-linear isotherm) with distance along the column are easily included in the equations.

Vink has carried out line shape calculations by means of a mesh technique for solving the partial differential equations[6,7]. Olson has studied the contribution of

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carrier gas expansion in the column to peak width[8]. Kocirik[9] and Yamazaki[10] have used moment methods in the analysis of non-equilibrium chromatographic line shapes, and Houghton[11] has developed a perturbation method for simultaneously handling diffusion and non-equilibrium effects in mass transport between the mobile and stationary phases. Certainly the most general and thorough analysis of the entire line shape problem is the stochastic approach developed by Giddings and coworkers[1,5].

We present here a method of taking mass transport into account approximately by means of a time constant. This yields a single linear differential equation, the solution of which is not difficult. Plots of peaks are given for a number of values of the effective diffusion constant and of the mass transport time constant.

ANALYSIS

Here we derive and solve a differential equation determining line shapes in GC. Let

K = distribution coefficient of solute between the solvent and the vapor phase
x = distance from the inlet of the column
$v(x)$ = carrier gas velocity at the point x
$C(x,t)$ = gas phase solute concentration at the point x and time t
$C_l(x,t)$ = liquid phase solute concentration at the point x and time t
$D(x)$ = effective gaseous diffusion constant
$B\mathrm{d}x$ = volume of liquid phase between x and $x+\mathrm{d}x$
$A\mathrm{d}x$ = volume of gaseous phase between x and $x+\mathrm{d}x$.

We consider the material balance for the volume element included in dx during a time interval dt. To permit non-equilibrium between the moving (vapor) and stationary (liquid) phases, we set

$$C_l(x,t) = KC(x,t-\tau) \tag{1}$$

where τ is a time constant measuring the lag in response of the solute concentration in the liquid to the concentration in the vapor.

The solute coming in from the left equals to

$$v(x)\cdot A\cdot C(x,t)\mathrm{d}t - AD(x)\frac{\partial C(x,t)\mathrm{d}t}{\partial x}$$

(bulk flow) (gaseous diffusion)

The solute coming in from the right equals to

$$-v(x+\mathrm{d}x)\cdot A\cdot C(x+\mathrm{d}x,t)\mathrm{d}t + AD(x+\mathrm{d}x)\frac{\partial C(x+\mathrm{d}x,t)\mathrm{d}t}{\partial x}$$

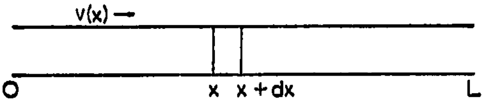


Fig. 1. Column geometry.

Therefore, the net flow of solute into the volume element is given by

$$\left\{A\frac{\partial}{\partial x}\left[D(x)\frac{\partial C(x,t)}{\partial x}\right]-A\frac{\partial}{\partial x}\left[v(x)C(x,t)\right]\right\}\mathrm{d}x\mathrm{d}t \tag{2}$$

Now the net accumulation of solute in the volume element in the time interval $\mathrm{d}t$ is given by

$$\begin{aligned}&A\mathrm{d}x\cdot C(x+\mathrm{d}x/2,t+\mathrm{d}t)+B\mathrm{d}x\cdot C_l(x+\mathrm{d}x/2,t+\mathrm{d}t)\\&\qquad-A\mathrm{d}x\cdot C(x+\mathrm{d}x/2,t)-B\mathrm{d}x\cdot C_l(x+\mathrm{d}x/2,t)\end{aligned} \tag{3}$$

On using eqn. 1 to replace C_l in expression 3, we obtain

$$A\frac{\partial C(x,t)}{\partial t}+BK\frac{\partial C(x,t-\tau)}{\partial t} \tag{4}$$

Conservation of solute molecules then yields

$$\frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}-vC\right)=\frac{\partial C}{\partial t}+\frac{BK}{A}\frac{\partial C(x,t-\tau)}{\partial t} \tag{5}$$

This equation is fairly general; it permits us to take into account the effect of pressure drop in the column in increasing $v(x)$ and $D(x)$ with increasing x, and the effect of failure of solute to reach local equilibrium between the vapor and liquid phases.

Normal practice is to set $\tau=0$, assume that D and v are independent of x, that the column extends to infinity in both directions, and that the initial distribution of solute is given by $C(x,0)=C_0\delta(x)$, where $\delta(x)$ is the Dirac δ-function. The solution to eqn. 5 under these conditions is readily obtainable by Fourier transform methods, and is shown in many texts to be

$$C(x,t)=\frac{C_0}{2\pi}\left(\frac{\pi v}{ADt}\right)^{\frac{1}{2}}\exp\left[\frac{-(x-v't/V)^2}{4ADt/V}\right] \tag{6}$$

where $V=A+BK$, and $v'=vA$.

We proceed as just described, except that we do not set $\tau=0$. We expand $\partial C(x,t-\tau)/\partial t$ in a Taylor's series and drop terms above those linear in τ to obtain

$$D\frac{\partial^2 C}{\partial x^2}-\frac{v\partial C}{\partial x}=\left(1+\frac{BK}{A}\right)\frac{\partial C}{\partial t}-\frac{BK\tau}{A}\frac{\partial^2 C}{\partial t^2} \tag{7}$$

The substitutions (L = length of column)

$$x=Lx_1$$

$$t=\frac{L(A+BK)}{vA}t_1$$

$$D_1=D/Lv$$

$$\tau_1=vKAB\tau/(A+BK)^2$$

convert eqn. 7 into

$$D_1\frac{\partial^2 C}{\partial {x_1}^2}-\frac{\partial C}{\partial x_1}=-\tau_1\frac{\partial^2 C}{\partial {t_1}^2}+\frac{\partial C}{\partial t_1} \tag{8}$$

We note that in the absence of resistance to mass transport between phases, the position of the peak maximum with respect to x_1 should be at $x_1 = 1$ (with $x = L$) when $t_1 = 1$ (with $t = L(A + BK)/vA$).

We use the method of separation of variables, assuming $C(X_1,t_1) = X(x_1)T(t_1)$ to obtain

$$D_1 X'' - X' + \lambda X = 0 \tag{9}$$

and

$$\tau_1 T'' - T' - \lambda T = 0 \tag{10}$$

where λ is the separation constant. We wish to fit initial conditions, $C(x,0)$, by means of Fourier transform techniques, so we assume $X(x_1) = \exp(ikx_1)$; this, with eqn. 9, yields

$$\lambda = D_1 k^2 + ik \tag{11}$$

and the solution to eqn. 10 is then

$$T_k(t_1) = A(k) \exp\left[\frac{t_1}{2\tau_1} - \frac{(1 + 4\tau_1\lambda)^{\frac{1}{2}} t_1}{2\tau_1}\right] \tag{12}$$

We obtain as the general solution to eqn. 8

$$C(x_1,t) = \int_{-\infty}^{\infty} A(k) \exp(ikx_1) T_k(t_1) \mathrm{d}k \tag{13}$$

Taking $C(x_1,0) = C_0 \delta(x_1)$ yields

$$A(k) = \frac{C_0}{2\pi} \int_{-\infty}^{\infty} \delta(x_1) \exp(-ikx_1) \mathrm{d}x_1 = \frac{C_0}{2\pi}$$

and

$$C(x_1,t_1) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(ikx_1) \exp\left[\frac{t_1}{2\tau_1} - \frac{(1 + 4\tau_1 D_1 k^2 + i4\tau_1 k)^{\frac{1}{2}} t_1}{2\tau_1}\right] \mathrm{d}k \tag{14}$$

Writing the square root in eqn. 14 in standard form, $a + ib$, yields

$$a(k) = \tfrac{1}{2}\{(1 + 4\tau_1 D_1 k^2) + [(1 + 4\tau_1 D_1 k^2)^2 + 16\tau_1{}^2 k^2]^{\frac{1}{2}}\}$$
$$b(k) = 2\tau_1 k / a(k) \tag{15}$$

We are interested in the time dependence of the concentration at $x = L$ (with $x_1 = 1$); with this substitution and the use of De Moivre's theorem we obtain

$$C(1,t_1) = \frac{C_0}{2\pi} \int_{-\infty}^{\infty} \exp[(1 - a)t_1/2\tau_1] \cdot \{\cos(k - kt_1/a) + i \sin(k - kt_1/a)\} \mathrm{d}k$$

Since $a(k)$ is an even function of k, the exponential is an even function of k, the cosine is even, and the sine is odd. The integral thus reduces to

$$C(1,t_1) = \frac{C_0}{\pi} \int_{0}^{\infty} \exp[t_1(1 - a)/2\tau_1] \cos(k - kt_1/a) \mathrm{d}k \tag{16}$$

We did not find this integral tractable to further analysis, so evaluated it numerically on an XDS Sigma 7 computer for a variety of values of τ_1 and D_1. Approximately 0.6 min of computer time was required to generate each curve.

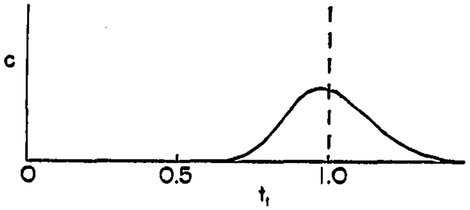
Written in terms of our dimensionless parameters and variables, eqn. 6 becomes

$$C(x_1,t_1) = \frac{C_0}{(4\pi D_1 t_1)^{\frac{1}{2}}} \exp[-(x_1-t_1)^2/4D_1t_1] \tag{17}$$

We shall be interested in comparing the results of eqn. 17 with the results of eqn. 16. At the detector end of the column x_1 equals to unity, and we can readily demonstrate that $C(1,t_1)$ takes on its maximum value at

$$t_1(\text{max.}) = (1+D_1{}^2)^{\frac{1}{2}} - D_1 \tag{18}$$

i.e., at values of t_1 which are less than unity. We further note that $C(1,t_1)$ is not a gaussian function of t_1; in fact, it is seen in Fig. 2 to be skewed somewhat and to show tailing toward larger values of t_1. (It is often tacitly assumed that because $C(x_1t)$ is a gaussian function of x, it is also a gaussian in t, the abscissa of recorder plots. This is not the case.)



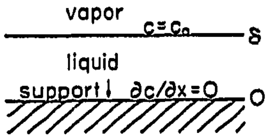


Fig. 2. Line shape from linear equilibrium theory. $D_1 = 0.01$; $\tau = 0$.

Fig. 3. Model for calculating the time constant τ.

A rough estimate of τ, the time constant associated with mass transport between phases, is readily obtained as follows. We consider the standard problem of diffusion into a layer of liquid phase of thickness δ, backed by an impervious support, and placed in contact with a reservoir of solute at fixed concentration C_0 at $t=0$ (see Fig. 3). $\partial C/\partial x$ $(0,t)=0$, and $C(\delta,t)=C_0$ are the boundary conditions, and the simple one-dimensional diffusion equation is

$$D_l \frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t} \tag{19}$$

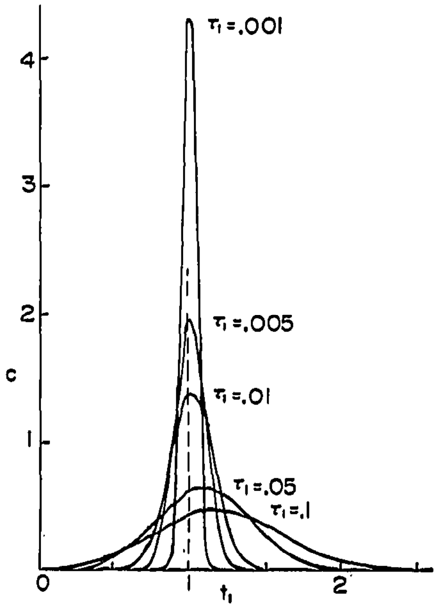
where D_l is the diffusion constant of the solute in the liquid phase. Solution of eqn. 19 by separation of variables and use of the boundary conditions gives

$$C = C_0 + \sum_{n=0}^{\infty} A_n \cos \frac{(2n+1)\pi x}{2\delta} \exp\left(-D_l\left[\frac{(2n+1)\pi}{2\delta}\right]^2 t\right) \tag{20}$$

as the form of the solution, from which we see that the longest time constant is

$$\tau_{\text{max.}} = \left(\frac{2\delta}{\pi}\right)^2 \Big/ D_l \tag{21}$$

which we take as our approximation to τ. τ is proportional to the square of the solvent loading on the column.



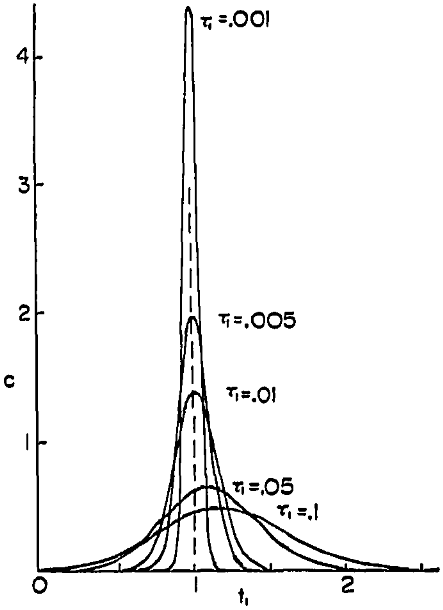
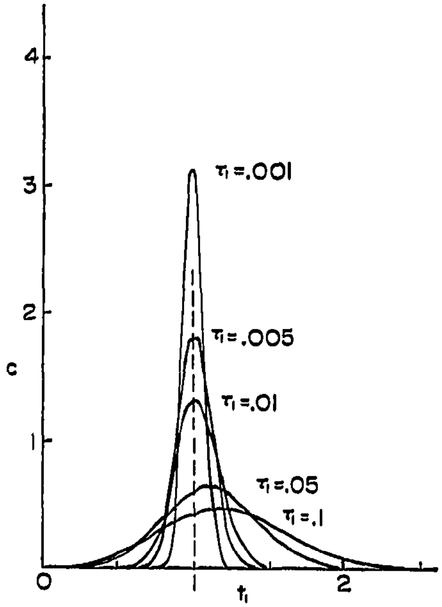


Fig. 4. Line shapes from linear nonequilibrium theory for various values of τ_1; $D_1 = 10^{-5}$.

Fig. 5. Line shapes for various values of τ_1; $D_1 = 5 \times 10^{-4}$.



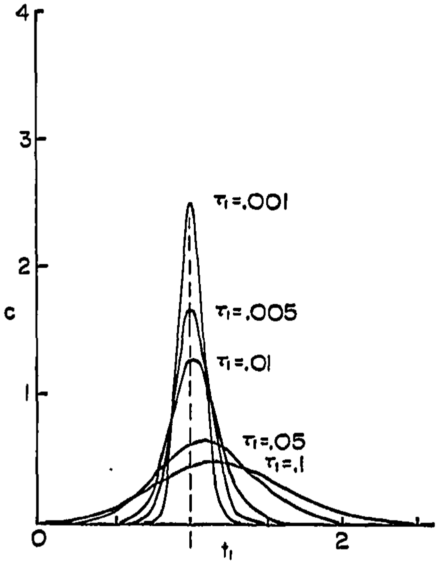


Fig. 6. Line shapes for various values of τ_1; $D_1 = 0.001$.

Fig. 7. Line shapes for various values of τ_1; $D_1 = 0.002$.

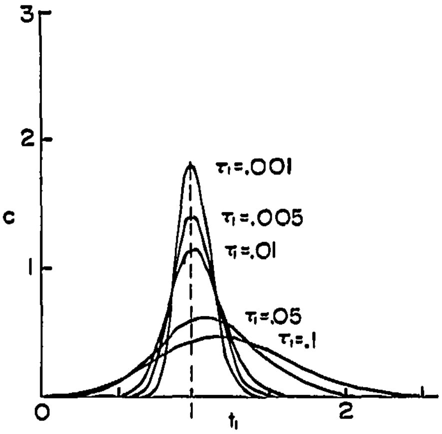


Fig. 8. Line shapes for various values of τ_1; D_1=0.005.

RESULTS

The results obtained by numerical integration of eqn. 16 are shown in Figs. 4 through 8. In each figure the dimensionless diffusion constant D_1 is fixed (10^{-5}, 5×10^{-4}, 10^{-3}, 2×10^{-3}, 5×10^{-3}) and the dimensionless time constant for mass transport is permitted to range through the values 10^{-3}, 5×10^{-3}, 10^{-2}, 5×10^{-2}, 10^{-1}.

We note that the asymmetry and tailing of the peaks observed earlier in Fig. 2 (for which our mass transport time constant was set equal to zero) are also observed when we permit τ to take on finite values. The position of the peak maximum is shifted toward *larger* values of t_1 with increasing τ, which is opposite to the effect noted in eqn. 18, that increasing the effective diffusion constant D_1 results in shifting the peak maximum toward lower values.

These results indicate that rate effects in the mass transport of solute between the stationary and the moving phase cannot be taken into account with complete accuracy by simply treating them as a contribution to a gaussian standard deviation.

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