

THE CONTRIBUTION OF GAS EXPANSION TO PEAK WIDTH IN GAS CHROMATOGRAPHY

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Gas chromatographic columns typically operate with atmospheric exit pressure and an inlet pressure in the range of 10 to 30 p.s.i.g. The upstream pressure is required to overcome the frictional losses for gas transport through the packed bed. If one were to ride along with a tagged sample of carrier gas, it would be observed that the velocity of the gas increases as the exit of the bed is approached. It is the purpose of this discussion to evaluate the effects this gas expansion has upon the operating behavior of the chromatographic column.

KEULEMANS¹ recognized that the residence time of the carrier gas is decreased by gas expansion but did not incorporate this observation into his so-called rate model for chromatograph operation. The rate model appeals to chemical engineers because this model has enjoyed considerable success in application to other fixed-bed processes. The current chromatographic literature apparently favors the "HETP" model; undoubtedly this preference stems from the ease with which physical intuition may be used to model transport processes. This paper attempts to show that the rate model can include the contribution of gas expansion without appeal to "physical reasonableness".

The development of the rate model proceeds through combination of material, rate and equilibrium equations. The resulting partial differential equation is reduced to an ordinary differential equation by use of the Laplace transform, and the solution to the problem is found from the moments of transformed equation. Dimensional variables are indicated by lower case letters*, dimensionless variables are denoted by upper case letters, and dimensionless groups are symbolized by upper case script letters. Reference conditions for dimensionless variables are taken at the inlet to the column. Inlet conditions are indicated by a subscript "o" and outlet values by the subscript "l".

The rate of gas flow through a packed bed has received considerable attention, and for a differential segment of a column the velocity is proportional to the pressure gradient

$$u = k \left(\frac{dp}{dx} \right)^N \quad (1)$$

The parameter k of eqn. (1) is a function of viscosity, void fraction and the units chosen for the equation. ERGUN² has shown that the parameter N is a function of the particle Reynolds number and therefore is constant in an isothermal chromato-

* Lower case "s" is used exclusively for the Laplace transform parameter.

graphic column. The Reynolds number for a chromatograph is usually less than 10 and consequently the parameter N is unity; the flow in the packed column is "laminar". Eqn. (1) may be combined with the ideal gas law and integrated; the dimensionless density, velocity and residence time which stems from this integration are given as follows:

$$P = \frac{\rho}{\rho_0} = (1 - \mathcal{A}X)^{1/2} \quad (2a)$$

$$U = \frac{u}{u_0} = (1 - \mathcal{A}X)^{-1/2} \quad (2b)$$

$$T_e = \frac{\tau}{\tau_0} = \frac{2}{3} \left(\frac{1 - P^3}{1 - P^2} \right) \quad (2c)$$

where ρ , ρ_0 are the fluid densities at any point and at the inlet of the bed;

\mathcal{A} is a dimensionless group evaluated experimentally through eqn. (2a) or which also may be found from the ERGUN² relation;

$X = x/l$ is the dimensionless length parameter in the column;

$\tau_0 = l/u_0$ is the transit time through the bed based upon initial conditions in the column;

τ is the actual transit time to a point in the column.

Eqns. (2a) to (2c) have been developed before¹; the task of this discussion is to incorporate these parameters into the differential equations which describe column operation.

Although there is some experimental evidence to the contrary for packed beds, the usual form of the axial diffusive transport equation for packed beds ignores the contribution of pressure diffusion and thus the mole flux of a binary mixture is given as

$$n_a = -\rho d_{\text{eff}} \frac{dY'}{dx} + Y'(n_a + n_s) \quad (3)$$

in which n_a is the mole flux of component a , n_s is the mole flux of carrier gas, ρ is the molal density, d_{eff} is the effective bed diffusivity, Y' is the mole fraction of a , and the sum of $n_a + n_s$ is constant in an isothermal packed column. It is further assumed that axial diffusive processes are binary; this assumption is valid very shortly after the pulse has entered the column. Thus the material balance equation for a differential segment of a packed bed is the familiar relation

$$F_{g\rho} \frac{\partial Y'}{\partial t} + F_s \frac{\partial q}{\partial t} = F_g \frac{d}{dx} \left(\rho d_{\text{eff}} \frac{\partial Y'}{\partial x} \right) - \rho u F_g \frac{dY'}{dx} \quad (4a)$$

Before putting eqn. (4a) into dimensionless form, it is necessary to note that d_{eff} depends upon molecular diffusivity, eddy axial diffusivity (caused primarily by differences in gas transit times around particles) and the packing density of column. The effective diffusivity-density product is defined by the relation

$$\rho d_{\text{eff}} = \frac{\rho \bar{d}_m}{T} + \rho d_e \quad (4b)$$

The tortuosity factor, T , accounts for the longer path lengths which molecules make while diffusing around the bed packing by molecular processes. The tortuosity contribution is included in the usual correlations of the eddy diffusivity, d_e . The ρd_m product is constant for molecular diffusion in the pressure range of 0.1 to 10 atm and thus the ρd_m term does not change throughout the bed. Somewhat in contrast to the usual analysis given in textbooks upon chromatography, CAIRNS AND PRAUSNITZ³ have shown that the eddy axial diffusivity of both gases and liquids is best correlated as a function of the interstitial velocity alone. There is a transition region between the "laminar" and "turbulent" packed-bed flow regimes in which the axial diffusivity is nearly independent of velocity. However gas velocities are seldom high enough to be in the transition region in chromatograph operation. Thus in this analysis it is assumed that the density-axial eddy diffusivity product, ρd_e , is also independent of position within the column. Thus upon substitution of eqns. (2a-c) into eqn. (4a) the dimensionless form of the material balance equation is obtained as:

$$\frac{P}{T_{el}} \frac{\partial Y}{\partial T} + \frac{\mathcal{H}}{T_{el}} \frac{\partial Q}{\partial T} + \frac{\partial Y}{\partial X} = \mathcal{B} \frac{\partial^2 Y}{\partial X^2} \quad (5)$$

The dimensionless parameters in eqn. (5) have the following significance:

$T = t/(\tau_0 T_{el})$ dimensionless time;

$T_{el} = T_e$ evaluated at the end of the column and is incorporated to render the transit time through a bed of inert packing as unity;

$\mathcal{H} = F_s q_\infty / F_g \rho_0 Y_0'$ the distribution parameter;

$\mathcal{B} = d_{eff0} / u_0 l$ the inverse length Peclet (Bodenstein) number;

$Y = Y' / Y_0'$ relative mole fraction in the gas phase;

$Q = q / q_\infty$ dimensionless concentration in the solid phase;

Y_0' = reference mole fraction absorbable component in gas phase;

q = average solute concentration in the solid phase;

q_∞ = the solid concentration in equilibrium with $Y_0' \rho_0$;

H = Henry's law constant defined from $Y_0' \rho_0 = H q_\infty$.

The mass transfer rate between the gas and the solid can be represented adequately (this point will be extended below) by the two-film model as:

$$\frac{\partial q}{\partial t} = k_y a \rho (Y' - Y'_i) = k_s a (q_i - q) \quad (6)$$

where k_y is the gas film mass transfer coefficient;

k_s is the "solid film" mass transfer coefficient;

a is the area to volume ratio for the solid phase;

subscript i denotes interfacial conditions.

A typical form of the correlation for the gas-film mass transfer coefficient⁴ has the following form:

$$\frac{k_y Y_{blm}}{u F_g} = 1.15 \left(\frac{d_p u F_g}{\nu} \right)^{-1/2} \left(\frac{\nu}{d_m} \right)^{-2/3} \quad (7)$$

in which Y_{blm} , the log-mean inert (carrier) gas correction is essentially unity for chromatograph operation. Since the Reynolds number and Schmidt group are in-

dependent of pressure for dilute solute conditions, the gas-film mass transfer coefficient is given as

$$k_y = k_{y0}U \quad (8)$$

and k_{y0} is independent of gas pressure.

Thus in dimensionless form eqn. (6) becomes

$$\frac{\partial Q}{\partial T} = \mathcal{F}(Y - Y_i) = \mathcal{S}(Q_i - Q) \quad (9)$$

where $\mathcal{F} = (k_{y0}al/u_0) HT_{el}$ = number of gas-film transfer units based upon entrance conditions;

$\mathcal{S} = (k_s al/u_0) T_{el}$ = number of solid-film transfer units based upon entrance conditions.

The assumption of linear gas-solid equilibrium yields a dimensionless equation connecting the interfacial compositions

$$PY_i = Q_i \quad (10)$$

Y_i and Q_i can be eliminated from eqn. (9) to obtain a simplified rate expression

$$\frac{\partial Q}{\partial T} = \mathcal{R}(PY - Q) \quad (11)$$

where $\mathcal{R} = \mathcal{F}\mathcal{S}/(\mathcal{F} + \mathcal{S}P)$, a dimensionless overall rate parameter which is a function of position in the bed.

Denoting a Laplace transformed variable by an overbar and assuming that pulse samples are fed to the column, eqns. (11) and (5) are combined through Laplace transformation to yield

$$\frac{sP\bar{Y}}{T_{el}} \left(1 + \frac{\mathcal{H}\mathcal{R}}{s + \mathcal{R}} \right) + \frac{d\bar{Y}}{dX} = \mathcal{R} \frac{d^2\bar{Y}}{dX^2} \quad (12)$$

where s is the Laplace transform parameter.

The simplest and perhaps most useful boundary conditions for eqn. (12) are that the column is fed with a Dirac pulse and can be considered to be a finite section of a column of infinite length. Accordingly,

$$\bar{Y}(0) = 1 \quad (13a)$$

and

$$\lim_{X \rightarrow \infty} \bar{Y} = 0 \quad (13b)$$

A useful approximate solution to eqns. (12) and (13) is obtained by computing the moments of $Y(X)$. The n^{th} moment of the output response is defined as

$$n^{\text{th}} \text{ moment about } \mathcal{M} = \int_0^{\infty} (T - \mathcal{M})^n Y(X, T) dt \quad (14)$$

When \mathcal{M} is zero the moments are said to be about the origin, and when \mathcal{M} is the first moment about the origin (the mean), the higher moments are "about the mean".

In chromatography the zeroth moment, the area under the peak, is proportional to the quantity of trace component fed into the column. The first moment about the origin is a linear function of the absorptivity of the partitioning fluid for the trace component. The second moment about the mean or variance is used to characterize the spread of the peak; the magnitudes of the variance measure the extent of overlapping of two adjacent trace components. The variance is the highest moment that is commonly used to describe the spreading of the peaks, for it is found that the chromatographic response for most systems is very nearly Gaussian. Thus if one treats eqn. (12) by a method whereby the first two moments of the response function may be recovered, then a useful description of the system response is established.

Upon change of the independent variable from X to P eqn. (12) becomes

$$\frac{1}{\bar{Y}} \frac{d\bar{Y}}{dP} = \frac{2P^2}{T_{el}\mathcal{A}} s \left(1 + \frac{\mathcal{H}\mathcal{R}}{s + \mathcal{R}} \right) - \frac{\mathcal{B}\mathcal{A}}{2P\bar{Y}} \left\{ \frac{d^2\bar{Y}}{dP^2} - \frac{1}{P} \frac{d\bar{Y}}{dP} \right\} \quad (15)$$

Eqn. (15) may be solved by Picard's method, and the moments of the response function \bar{Y} are found from the operation

$$\lim_{s \rightarrow 0} \left(-\frac{d}{ds} \right)^n \bar{Y}(X) = \int_0^\infty T^n Y(T, X) dT \quad (16)$$

Although the algebra is messy, the moment solution is straightforward and yields the following results:

$$\text{Zeroth moment} = 1 = \mathcal{M}_0 \quad (17a)$$

$$\begin{aligned} \text{First moment (mean)} = \mathcal{M}_1 = & (1 + \mathcal{H}) \left\{ 1 - \left(\frac{\mathcal{B}}{T_{el}} \right) \left[(1 - P) + \right. \right. \\ & \xi \left(\frac{1}{P} - 1 \right) + \xi^2 \left(\frac{1}{P^3} - 1 \right) + 3\xi^3 \left(\frac{1}{P^5} - 1 \right) + 15\xi^4 \left(\frac{1}{P^7} - 1 \right) + \\ & \left. \left. 105\xi^5 \left(\frac{1}{P^9} - 1 \right) + 945\xi^6 \left(\frac{1}{P^{11}} - 1 \right) \dots \right] \right\} \quad (17b) \end{aligned}$$

Second moment about the mean (variance):

$$\begin{aligned} \mathcal{M}_2 = & \frac{2\mathcal{H}}{\mathcal{F}} \left(\frac{\mathcal{M}_1}{1 + \mathcal{H}} \right) + \frac{\mathcal{H}}{\mathcal{F}} \left[\left(\frac{1 + P^2}{T_{el}} \right) - \left(\frac{\mathcal{B}}{T_{el}} \right) 2(1 - P^2) \right] + \\ & + (1 + \mathcal{H})^2 \left(\frac{\mathcal{B}}{T_{el}} \right) \left[\left(\frac{1 + P^2}{T_{el}} \right) + \left(\frac{\mathcal{B}}{T_{el}} \right) \left\{ -8\mathcal{A} + 2\xi \ln P + 6\xi^2 \left(1 - \frac{1}{P^2} \right) + \right. \right. \\ & \left. \left. + \frac{47}{2} \xi^3 \left(1 - \frac{1}{P^4} \right) + 152\xi^4 \left(1 - \frac{1}{P^6} \right) + \dots \right\} \right] \quad (17c) \end{aligned}$$

$$\xi = \frac{\mathcal{B}\mathcal{A}}{2} = \frac{\mathcal{B}}{T_{el}} \frac{(1 - P^3)}{3}, \text{ a perturbation parameter.}$$

Eqn. (17b) indicates that the form of the mean is altered only in a minor way when gas expansion is considered. The time scaling parameter for the mean $(1/u_0)T_{el}$ is selected to preserve the form of the mean; the time scaling parameter is the transit time through the external voidage of the column. The effect of gas expansion decreases the holding time in the bed through coupling with the axial dispersion parameter. One may note that all of the terms inside the square brackets of eqn. (17b) are positive. Since the parameter \mathcal{B} is small (see the example problem which follows) in chromatographic operation, the contribution of gas expansion is small.

The variance for column operation without expansion is given as follows:

$$\mathcal{M}_2 = 2\mathcal{H}\left(\frac{1}{\mathcal{S}} + \frac{1}{\mathcal{F}}\right) + 2(1 + \mathcal{H})^2\mathcal{B} \quad (18)$$

Examination of eqn. (17c) indicates that when P approaches unity eqn. (17c) approaches eqn. (18). One notes that gas expansion may make a significant contribution to the width of the sample peak. One also notes that \mathcal{B}/T_{el} is the inverse length Peclet number based upon the actual transit time in the column.

To gain a more complete appreciation for the significance of eqns. (17b) and (17c), it may be useful to attempt an *a priori* estimation of the peak behavior of a representative gas chromatograph column. This computation is divided into two parts: first a calculation of the parameters in the model and then an approximation of the output peak shape.

An outline of the parameters in the model is as follows:

1. Estimate the inlet velocity with the ERGUN relation.
2. Find the capacity parameter \mathcal{H} from the "popcorn" model for the chromatographic support.
3. Use the CARBERRY relation to find \mathcal{F} .
4. Evaluate \mathcal{S} with the "solid-diffusion" model.
5. Estimate the Peclet group parameter with CAIRN's data and the molecular diffusivity.

The sample problem is based upon the physical parameters shown in Table I.

TABLE I

PHYSICAL PARAMETERS FOR A SAMPLE CALCULATION

Carrier gas: helium	$\mu = 1.85 \times 10^{-4}$ poise
Sample: <i>n</i> -butane	
Column length: 2 m	
Column temperature: 300° K	
Column support: porous 80-120 mesh "chromosorb", 1.5×10^{-2} cm diameter	
External voids in the column: $F_{\theta} = 0.42$	
Gas volume fraction in support: $F_{\theta l} = 0.60$	
Liquid volume fraction in support: $F_{ll} = 0.10$	
Henry's Law constant: $h = 200$ torr/(gmol/l)	
B.E.T. pore radius ($2v_p/a_p$) = 50 Å	

The exit pressure of the column is assumed to be atmospheric, and the set of pressure drops across the column which are used in this calculation as the independent variable are listed in Table II.

TABLE II
 SAMPLE CALCULATION

Δp (p.s.i.)	P_i	\mathcal{A}	T_{el}	μ_0 (cm/sec)	\mathcal{N}_{Re}	\mathcal{M}_1	\mathcal{F} $\times 10^{-4}$	\mathcal{S} $\times 10^{-2}$	\mathcal{B} $\times 10^4$	Second moment			\mathcal{M}_2 total
										\mathcal{S} $\times 10^2$	\mathcal{F} $\times 10^5$	\mathcal{B} $\times 10^2$	
4	0.785	0.383	0.903	2.2	0.036	14.8	2.96	23.4	3.09	1.18	0.834	1.79	0.159
8	0.647	0.582	0.834	3.9	0.079	14.8	1.84	12.0	2.18	2.30	1.28	1.70	0.108
12	0.550	0.698	0.796	5.3	0.118	14.8	1.46	8.43	1.88	3.28	1.55	1.64	0.106
16	0.478	0.772	0.778	6.4	0.18	14.8	1.17	6.85	1.74	4.28	1.86	1.58	0.110
20	0.423	0.822	0.748	7.3	0.23	14.8	0.983	5.73	1.66	4.82	2.21	1.576	0.114

$$H = 0.10; \mathcal{K} = 12.8.$$

The ERGUN correlation is given by eqn. (19)

$$\left(\frac{\Delta p}{\rho} \cdot \frac{2gc}{u_m^2}\right) \left(\frac{d_p}{l}\right) \mathcal{N}_{Re} \frac{F_g^3}{F_s^2} = 300 + 3.5 \frac{\mathcal{N}_{Re}}{F_s} \quad (19)$$

One finds that the second right-hand term does not contribute significantly to the arithmetic mean velocity, u_m ; this fact means that the gas flow is laminar.

The "popcorn" model for the chromatographic support gains the appellation from descriptions of the photomicrographs of these materials. The loaded support is viewed as resembling caramel popcorn; the liquid partitioning fluid is distributed rather uniformly upon the rough surfaces of the diatomaceous earth. The absorbable components of the sample reach the partitioning liquid by the following steps: convection with the carrier gas, diffusion through the "gas film" around the support particle, diffusion through the void spaces of the solid support, and finally absorption into the partitioning liquid. A material balance upon an absorbable component in the interior of the support yields the following equation for the definition of the dimensionless Henry's law constant, H :

$$H = \frac{h}{F_{gl}h + R'T'F_{ll}} \quad (20)$$

where h = dimensional Henry's law constant, torr/(gmol/l);

$R'T'$ = gas constant \times absolute temperature with units of h ;

F_{gl} = volume fraction gas in the interior of the support;

F_{ll} = volume fraction absorber liquid in the support.

The parameter F_{gl} may be calculated from the "pore volume" of the support and the parameter F_{ll} may be calculated from the weight loading of the support. The parameter \mathcal{K} is then found as

$$\mathcal{K} = \frac{F_s}{F_g H} \quad (21)$$

The CARBERRY model (eqn. 7) may be combined with the definition of the parameter \mathcal{F} to yield

$$\mathcal{F} \equiv \frac{k_y}{u_0} \frac{6l}{d_p} = T_{el} H \quad (22a)$$

$$= (6.27 \times 10^3) \mathcal{N}_{Re}^{-1/2} T_{el} \quad (22b)$$

The solid-diffusion transport parameter is defined after eqn. (9) as

$$\mathcal{S} = \frac{k_{sa} l}{u_0} T_{el} \quad (23a)$$

It may be shown that the mass-transfer parameter is adequately represented as

$$k_{sa} = \frac{60 d_t}{d_p^2} \quad (23b)$$

where d_t is the effective internal diffusivity in the particle. The internal diffusivity has been shown by MASON⁵ to be given by the relation

$$d_t (\text{cm}^2/\text{sec}) = 0.842 \times 10^{-4} \left(\frac{2v_p}{a_p} \right) \left(\frac{T}{M} \right)^{1/2} \frac{F_{gt}}{T} \quad (24)$$

where in eqn. (24)

M = molecular weight of the diffusing component;

T = absolute temperature, °K;

v_p = B.E.T. pore volume, cm³/g support;

a_p = B.E.T. surface area, m²/g support;

T = tortuosity in the support.

Equation (24) is based upon the dusty-gas model for Knudsen diffusion within the support. WEISS⁶ has shown that the tortuosity is best correlated as

$$T = \frac{\sqrt{3}}{F_{gt}} \quad (25)$$

The parameters in Table I are inserted into eqns. (23a), (24) and (25) to yield the values given in Table II.

The inlet inverse Peclet group, \mathcal{B} , is found from eqn. (5) as

$$\mathcal{B} = \frac{\rho d_m}{\rho_0 u_0 l T_{el}} + \frac{\rho d_e}{\rho_0 u_0 l} \quad (26)$$

The eddy diffusivity is found from the CAIRNS AND PRAUSNITZ³ correlation to be in the "laminar" range in which

$$\frac{d_e}{u_0 d_p} = 2.64 \left(\frac{F_g}{F_s} \right) \quad (27)$$

The first right-hand term of eqn. (26) is roughly inversely proportional to the inlet velocity and the second term is independent of inlet velocity. The calculated values for the inverse Peclet group are listed in Table II.

The terms which appear in eqn. (17c) thus have been estimated from existing correlations; the evaluation of the second moment, \mathcal{M}_2 , is listed in the last four columns of Table II. It may be seen that the fluid-film mass transfer resistance does not contribute to this moment; the axial dispersion processes are the most important sources of peak-width.

The small contributions of gas expansion and mass transfer to the moments indicate that an adequate approximation for the response of the system may be found from the solution to the equation

$$\mathcal{G} \frac{\partial^2 Y}{\partial X^2} - \frac{\partial Y}{\partial X} - (\mathcal{K} + 1) \frac{\partial Y}{\partial T} = 0 \quad (28)$$

with the boundary conditions of eqns. (13a) and (13b). In terms of the first and second moments the solution to eqn. (28) is found to be

$$Y = \left(\frac{\mathcal{M}_1/T}{(\pi \mathcal{G})^{1/2}} \right) \cdot \exp \left(-\frac{(\mathcal{M}_1 - T)^2}{\mathcal{G}} \right) \quad (29)$$

where

$$\mathcal{G} = \frac{2\mathcal{M}_2 T}{\mathcal{M}_1}$$

The approximate solution is obtained by using the values for \mathcal{M}_1 and \mathcal{M}_2 of eqns. (17b) and (17c) in eqn. (29). The calculated response for $\Delta p = 12$ p.s.i. is shown in Fig. 1. It may be seen that a slight "tail" is found in the peak.

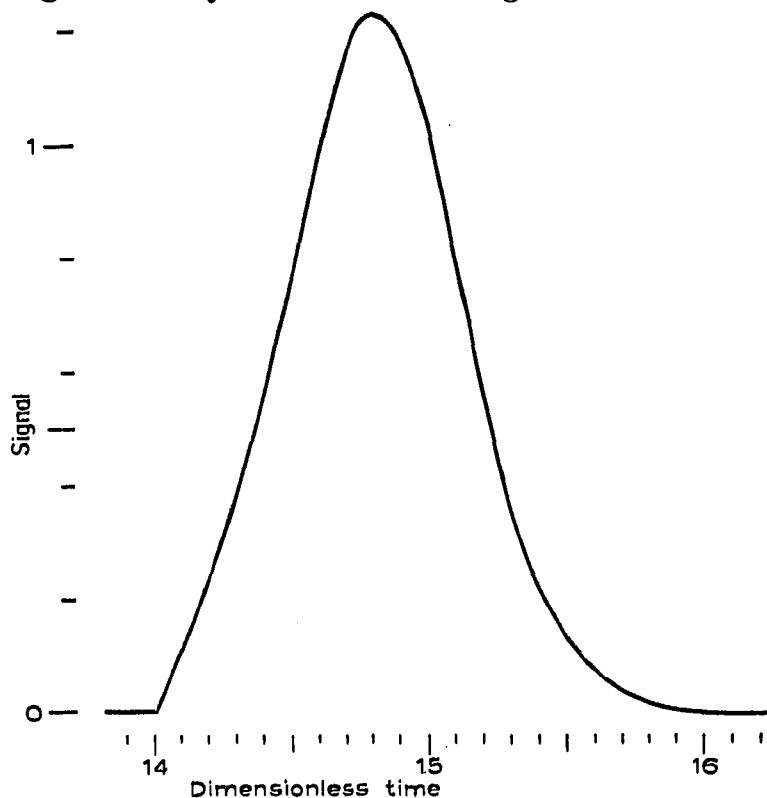


Fig. 1. Calculated signal vs. dimensionless time.

CONCLUSIONS

It has been shown that the effect of gas expansion upon the operation of a gas chromatograph may be estimated with the rate model for column operation. However, it has been found that the contribution of gas expansion is likely to be small for typical conditions of column operation. Thus one may use the incompressible fluid form of the rate model for chromatographic separations merely by using the average velocity in the bed.

NOMENCLATURE

Dimensional variables

- a = external area of support/volume of support, cm^{-1}
 a_p = B.E.T. surface area, m^2/g support
 d_e = eddy diffusivity, cm^2/sec
 d_{eff} = effective diffusivity, cm^2/sec
 d_i = internal diffusivity, cm^2/sec
 d_m = molecular diffusivity, cm^2/sec
 d_p = particle diameter, cm
 g_c = gravitational force constant
 h = Henry's law constant $\text{torr}/(\text{gmol}/\text{l})$
 k_y = gas-film mass transfer coefficient, cm/sec
 k_s = solid-film mass transfer coefficient, cm/sec
 l = length of bed, cm
 n_a = mol flux of adsorbable component, $\text{gmol}/\text{cm}^2 \cdot \text{sec}$
 n_s = mol flux of inerts, $\text{gmol}/\text{cm}^2 \cdot \text{sec}$
 p = pressure, dynes/cm^2
 q = concentration in solid phase, gmol/l
 q_∞ = concentration in solid phase in equilibrium with $\rho_0 Y_0'$
 s = Laplace transform variable
 t = time, sec
 u = interstitial velocity, cm/sec
 u_0 = initial interstitial velocity, cm/sec
 v_0 = inlet superficial velocity, cm/sec
 x = axial distance, cm
 μ = viscosity, poise
 ν = kinematic viscosity, cm^2/sec
 ρ = gas density, gmol/cm^3
 ρ_0 = gas density at inlet
 τ = carrier gas transit time through column, sec
 τ_0 = l/u_0 , carrier gas transit time through the column based upon initial conditions, sec

Dimensionless variables

- F_g = external gas volume per volume of bed
 F_s = $(1 - F_g)$, volume fraction apparent solid phase
 F_{gt} = volume fraction gas in the solid phase

- F_{li} = volume fraction partitioning liquid in the solid phase
 H = Henry's Law parameter defined in eqn. (20)
 P = ρ/ρ_0 , dimensionless pressure
 Q = q/q_∞ , dimensionless solid phase concentration
 T = $t/(\tau_0 T_{el})$, dimensionless time
 T_e = τ/τ_0 , residence time contraction ratio
 T_{el} = T_e evaluated at the end of the bed
 U = u/u_0 , dimensionless velocity
 X = x/l , dimensionless length
 Y = Y/Y_0 , dimensionless mole fraction
 Y' = mole fraction of absorbable component
 Y_0' = reference mole fraction absorbable component
 Γ = tortuosity

Dimensionless groups

- \mathcal{A} = $\Gamma - (\rho_i/\rho_0)^2$, gas expansion group
 \mathcal{B} = $d_{eff}/u_0 l$, inverse length Peclet group
 \mathcal{F} = $(k_{y0} a l H T_{el})/u_0$, fluid-film transport group
 \mathcal{H} = $F_s q_\infty / F_g \rho_0 Y_0'$, equilibrium parameter
 \mathcal{M}_1 = first moment about origin
 \mathcal{M}_2 = variance
 \mathcal{N}_{Re} = $d_p u_0 / \nu_0$, Reynolds number
 \mathcal{R} = $\mathcal{F}\mathcal{S}/(\mathcal{F} + \mathcal{S}P)$, number of transfer units
 \mathcal{S} = $(k_s a l T_{el})/u_0$, solid-film transport group
 ξ = $\mathcal{B}\mathcal{A}/2$, perturbation group

APPENDIX: SOLUTION TO EQUATION (15)

Eqn. (15) is rewritten as

$$\frac{d \ln \bar{Y}}{dP} = G - \frac{\xi}{PY} \left[\frac{d^2 \bar{Y}}{dP^2} - \frac{1}{P} \frac{d\bar{Y}}{dP} \right] \quad (\text{A.1})$$

where

$$G = \frac{2P^2}{\mathcal{A}T_{el}} sZ;$$

$$Z = 1 + \frac{\mathcal{H}\mathcal{R}}{s + \mathcal{R}};$$

and $\xi = \mathcal{B}\mathcal{A}/2$ and is a perturbation expansion parameter.

Differentiation with respect to P shall be denoted by a prime ('') and the iterative solutions for \bar{Y} are indicated as \bar{Y}_j . The solutions are obtained by the definite integration of eqn. (A.1):

$$\ln (\bar{Y}_1/1) = \int_1^P G dP^* \quad (\text{star} = \text{dummy variable}) \quad (\text{A.2})$$

$$\bar{Y}_1 = \exp \int_1^P G dP^* \quad (\text{A.3a})$$

and

$$\bar{Y}'_1 = G \bar{Y}_1 \quad (\text{A.3b})$$

$$\bar{Y}''_1 = (G^2 + G') \bar{Y}_1 \quad (\text{A.3c})$$

Thus

$$\frac{d \ln \bar{Y}_2}{dP} = G - \xi \left[\left(\frac{G}{P} \right)^2 + \frac{1}{P} \left(\frac{G}{P} \right)' \right] \quad (\text{A.4})$$

$$\bar{Y}_2 = \exp \int_1^P (G - \xi H) dP^* \quad (\text{A.5})$$

where

$$H = G \left(\frac{G}{P} \right) + \left(\frac{G}{P} \right)'$$

Thus by iteration

$$\bar{Y}_4 = \exp \int_1^P (G - \xi H + \xi^2 I + \xi^3 J + \xi^4 K \dots) dP^* \quad (\text{A.6})$$

where

$$I = \frac{2GH}{P} + \left(\frac{H}{P} \right)'$$

$$J = \frac{2GI + H^2}{P} + \left(\frac{I}{P} \right)'$$

$$K = \frac{2GJ + 2HI}{P} + \left(\frac{J}{P} \right)'$$

Eqn. (A.6) is of the form of a moment generating function. The zeroth moment of Y , related to the area of the chromatographic peak, is unity because the limits of G , H , I , J ... as s approaches zero are zero. The first moment of Y is obtained as

$$\mathcal{M}_1 = \lim_{s \rightarrow 0} \left(\frac{d}{ds} \right) \int_P^1 (G - \xi H + \xi^2 I - \xi^3 J \dots) dP^* \quad (\text{A.7})$$

Denoting differentiation and the limiting process with respect to the Laplace transform variable with an overdot ($\dot{}$), eqn. (A.7) is then written as

$$\mathcal{M}_1 = \int_P^1 (\dot{G} - \xi \dot{H} + \xi^2 \dot{I} - \xi^3 \dot{J} \dots) dP^* \quad (\text{A.8})$$

In like manner the second moment about the mean is found as

$$\mathcal{M}_2 = \int_1^P (\ddot{G} - \xi \ddot{H} + \xi^2 \dot{I} - \xi^3 \dot{J} \dots) dP^* \quad (\text{A.9})$$

One then applies the chain rule to obtain eqn. (17). The coefficients in eqns. (A.8) and (A.9) are listed in Table AI.

TABLE AI
COEFFICIENTS OF TERMS

Term	$\frac{2(I + \mathcal{H})}{\mathcal{A}T_{el}}$	$\frac{2(I + \mathcal{H})}{\mathcal{A}T_{el}}$	$\frac{4\mathcal{H}}{\mathcal{A}T_{el}}$	$\frac{4\mathcal{H}}{\mathcal{A}T_{el}}$
Function	Eqn. (A.8)	Eqn. (A.9)	Eqn. (A.9)	Eqn. (A.9)
G	P^2	—	$-P^2$	$-P^3$
H	1	$2P^3$	-1	$-P$
I	$-P^{-2}$	$8P$	P^{-2}	—
J	$+3P^{-4}$	$-2P^{-1}$	$-3P^{-4}$	—
K	$-15P^{-6}$	$12P^{-3}$	$+15P^{-6}$	—
L	$+105P^{-8}$	$-94P^{-5}$	$-105P^{-8}$	—
M	$-945P^{-10}$	$912P^{-7}$	$+945P^{-10}$	—

SUMMARY

The effect of gas expansion upon peak width is estimated for the "rate model" formulation of the transport processes in a chromatograph. The retention parameter is reduced by gas expansion, and the peak variance is increased. The rate model is useful for *a priori* estimates of column performance.

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