Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Chromatographic Kinetics and the Phenomenon of Tailing

George H. Weiss[a]
[a] PHYSICAL SCIENCES LABORATORY DIVISION OF COMPUTER RESEARCH & TECHNOLOGY, NATIONAL INSTITUTES OF HEALTH, BETHESDA, MARYLAND

To cite this Article Weiss, George H.(1982) 'Chromatographic Kinetics and the Phenomenon of Tailing', Separation Science and Technology, 17: 15, 1609 — 1622

To link to this Article: DOI: 10.1080/01496398208055645

URL: http://dx.doi.org/10.1080/01496398208055645

SEPARATION SCIENCE AND TECHNOLOGY, 17(15), pp. 1609–1622, 1982-83

Chromatographic Kinetics and the Phenomenon of Tailing

GEORGE H. WEISS

PHYSICAL SCIENCES LABORATORY
DIVISION OF COMPUTER RESEARCH & TECHNOLOGY
NATIONAL INSTITUTES OF HEALTH
BETHESDA, MARYLAND 20205

Abstract

This paper contains a reformulation of the kinetic equations that describe transport in a chromatographic column, to allow the possibility of describing adsorption at different types of sites. It is shown that in place of the partial differential equation

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x} \tag{*}$$

that is the usual starting point for any analysis, one obtains a partial integro-differential equation. While only a formal solution to this equation is possible, the central limit theorem of probability guarantees that in a wide variety of cases the solution for an isolated peak will approach the Gaussian form, so that (*) is applicable. Next the conditions necessary to insure the appearance of tailing or permanent asymmetry in an isolated peak are considered. Two models that lead to tailing are considered. In the first there is a single adsorption phase, but the residence time distribution has an infinite variance. The second consists of a random distribution of first-order rate constants.

INTRODUCTION

Giddings and Eyring appear to have been the first to develop a stochastic or microscopic model for the kinetics of chromatrography (*1*), in contrast to a macroscopic model phrased in terms of a partial differential equation. They were interested in the elution profile for a column in which a molecule could be in one of two states: mobile or stationary with first-order kinetics describing the interchange between states. They showed that after a sufficient number of interchanges between the two states takes place, the elution profile becomes essentially a Gaussian when the initial loading is a pulse. They also considered a generalization in which two types of adsorption sites are allowed. This generalization is of interest as it has been proposed as a mechanism for producing tailing (*2*), i.e., when the two adsorption site types have very different desorption rates. It should be pointed out, however, that asymmetry produced in this way is necessarily transient in consequence of the central limit theorem of probability. Van Holde also discussed a two-state model in which there is no strictly adsorbed state but in which the speed in the two states is different (*3*). From the beginning of these investigations, the generalization to a system with a single mobile state and *n* types of adsorption states has suggested itself. Symbolically the system can be represented as

$$M \begin{matrix} \nearrow\!\!\!\swarrow S_1 \\ \rightleftharpoons S_2 \\ \searrow\!\!\!\nwarrow S_n \end{matrix} \qquad (1)$$

This system with $n = 2$ was originally analyzed by Giddings and Eyring (*1*) as well as by Beynon et al. (*4*) and McQuarrie (*5*). The monograph by Giddings contains a formal analysis of systems which may be more complicated than the scheme of Eq. (1) (*6*). However, that analysis makes use of a quasi-equilibrium assumption and does not give a full kinetic treatment.

In this paper I will make use of some recent developments in solid-state physics to develop transport equations for chromatographic systems starting from models on a microscopic level (*7–11*). A quantitative, if crude, measure of tailing will be introduced and evaluated for a variety of linear models, of which the scheme of Eq. (1) is typical. I will show that at sufficiently long times the asymmetry in a peak resulting from Eq. (1) must tend to zero. This is otherwise obvious since the central limit theorem of probability guarantees that an isolated peak will approach the Gaussian form at sufficiently long times (*12*). It should be noted, parenthetically, that this does not rule out transient tailing and is not, therefore, inconsistent with the suggestion of Keller and Giddings (*2*). It does say that in an infinitely long column all peaks based on the model of Eq. (1) will tend to the Gaussian. Two linear models will be described in the present paper that lead to peak asymmetry that increases with time. The first of these is that of a system with a single stationary or adsorption state in which the desorption kinetics reflect more complicated processes than can be described by a first-order reaction. The second is one in which the transitions between the mobile and adsorbed phases is assumed to be first order, but the rate constants for each transition are assumed to be randomly distributed. These models are only suggested as possibilities, and there may be many other possible linear models that will exhibit tailing. The possibility of tailing due to nonlinear isotherms (cf., for example, Ref. *13*) will not be explored in this article. As a by-product of this investigation, I will derive a more general transport equation than has so far appeared in the literature of chromatographic processes.

FUNDAMENTAL EQUATIONS

In what follows I will consider the development of a concentration profile in the absence of boundaries. The observable concentration at x at time t will be denoted by $\rho(x, t)$. If there are n types of adsorbed states, as in Eq. (1), then $\rho(x, t)$ is the sum of concentrations in the mobile and adsorbed phases. Let $c(x, t)$ be the concentration at x of mobile molecules, and let $c_i(x, t)$ be the corresponding concentration in adsorbed phase i. By conservation of mass, one can write

$$\rho(x, t) = c(x, t) + \sum_i c_i(x, t) \tag{2}$$

For simplicity I consider only the case of a column with spatially uniform properties. Let the matrix be characterized by a diffusion constant D, and assume that in the absence of a diffusive mechanism, molecules move through the column at speed v. The transport equation resulting from these assumptions is

$$\frac{\partial \rho}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} \tag{3}$$

To complete this set of equations we must describe kinetics of the transition between the mobile and adsorbed phases. If k_i denotes the first-order rate constants for the transition $M \rightarrow S_i$ and k_i' denotes the rate constants for the reverse reaction, then we have

$$\partial c_i/\partial t = k_i c - k_i' c_i, \qquad i = 1, 2, \ldots, n \tag{4}$$

More complicated schemes for modeling these transitions will be discussed later. Equations (2)–(4) constitute one formulation of the generalized transport equations. It is not yet the most convenient starting point since the observable concentration is $\rho(x, t)$, and it is therefore desireable to have a single equation for this quantity and no other. We will carry out the relevant transformation in a later paragraph, after discussing a more general description of transitions between the mobile and adsorbed phases.

Let us suppose that the transition $S_i \rightarrow M$ consists of several intermediate steps, or more generally that one a molecule is in S_i the desorption time is a random variable. Let the probability density for this random time be denoted by $\psi_i(t)$. When first-order kinetics apply, $\psi_i(t)$ necessarily has the form

$$\psi_i(t) = k_i' \exp(-k_i' t) \tag{5}$$

Other more detailed pictures of the transition that involve intermediates lead to more complicated forms for $\psi_i(t)$. However, let us simply retain $\psi_i(t)$ in general form without immediately specifying its properties. For simplicity I will retain the assumption that the adsorption event $M \rightarrow S_i$ can be described by first-order kinetics, although it is not difficult to generalize this assumption. When a general form for $\psi_i(t)$ is retained, Eq. (4) is to be replaced by

$$\frac{\partial c_i}{\partial t} = k_i c(x, t) - k_i \int_0^t c(x, \tau) \psi_i(t - \tau)\, d\tau \tag{6}$$

To see this we note that the rate of change of the concentration in S_i at time t is due either to influx from the mobile phase or due to molecules that entered S_i at time τ and remained for a time $t - \tau$ before desorbing. It can be verified that in the special case when Eq. (5) is substituted into Eq. (6), one finds Eq. (4). Equations (2) and (3) remain valid whatever the form of $\psi_i(t)$.

Since $\rho(x, t)$ is the measureable concentration, it is convenient to have a single equation in terms of this function. To derive this equation, we introduce Laplace transforms with respect to t:

$$\begin{aligned} \rho^*(x, s) &= \int_0^\infty \rho(x, t) \exp(-st)\, dt \\ c_i^*(x, s) &= \int_0^\infty c_i(x, t) \exp(-st)\, dt \\ \psi_i^*(s) &= \int_0^\infty \psi_i(t) \exp(-st)\, dt \end{aligned} \tag{7}$$

The Laplace transform of Eq. (6) is

$$c_i^*(x, s) = \frac{k_i}{s}(1 - \psi_i^*(s))c^*(x, s) \tag{8}$$

so that the $c_i^*(x, s)$ can all be expressed in terms of $c^*(x, s)$. The transform $c^*(x, s)$ can be expressed in terms of $\rho^*(x, s)$ by taking the transform of Eq. (2) and making use of Eq. (8). In this way we find that

$$c^*(x, s) = Q^*(s)\rho^*(x, s) \tag{9}$$

where

$$Q^*(s) = \left[1 + \frac{1}{s}\sum_{i=1}^{n} k_i(1 - \psi_i^*(s))\right]^{-1} \tag{10}$$

The inverse transform of this function will be denoted by $Q(t)$. Equation (9) is then equivalent to

$$c(x, t) = \int_0^t \rho(x, \tau)Q(t - \tau)\, d\tau \tag{11}$$

by the convolution property of the Laplace transform. Hence the general form of the transport equation based on our microscopic model is

$$\frac{\partial \rho}{\partial t} = \int_0^t Q(t - \tau)\left[D\frac{\partial^2 \rho(x, \tau)}{\partial x^2} - v\frac{\partial \rho}{\partial x}(x, \tau)\right] d\tau \tag{12}$$

Both the Giddings-Eyring and van Holde models assume that diffusion in the mobile phases is negligible, and set $D = 0$. In the former of these models there is only a single mobile phase, and the resulting form of $Q^*(s)$ is

$$Q^*(s) = \left(1 + \frac{k}{s + k'}\right)^{-1} \tag{13}$$

The inverse transform, $Q(t)$, is

$$Q(t) = \delta(t) - k\exp(-(k + k')t) \tag{14}$$

where $\delta(t)$ is the Dirac delta function. Consequently, Eq. (12) is, in detail,

$$\frac{\partial \rho}{\partial t} + v\frac{\partial \rho}{\partial x} = vk\int_0^t e^{-(k+k')(t-\tau)}\frac{\partial \rho(x, \tau)}{\partial x}\, dx \tag{15}$$

By differentiation with respect to t, this can also be transformed into the partial differential equation

$$\frac{\partial^2 \rho}{\partial t^2} + v\frac{\partial^2 \rho}{\partial x \partial t} + (k + k')\frac{\partial \rho}{\partial t} + k'v\frac{\partial \rho}{\partial x} = 0 \qquad (16)$$

which is certainly a more complicated kinetic equation than one is accustomed to seeing in the context of chromatography. Nonetheless, probabilistic limit laws allow us to conclude that the Gaussian peak is reached as a limit of the solution (*12*). It should also be noted that when diffusion is negligible, one can solve the elution problem rather simply, since in this case the amount of molecules remaining in the column is

$$R(t) = \int_0^L \rho(x, t)\, dx \qquad (17)$$

where L is the length of the column.

EVALUATION OF MOMENTS

So far I have presented a formal theory. In general the theory, depending as it does on the function $Q(t)$ which is hard to evaluate in detail, cannot be solved in complete generality. Nevertheless, useful information can be obtained from relatively simple properties of $Q(t)$ that are readily calculable. In particular, this information resides in the moments of the observed concentration. Although $\rho(x, t)$ is not itself a probability density, the equivalent function

$$\rho(x, t) / \int_0^\infty \rho(x, 0)\, dx$$

can be so identified, since it is nonnegative, and normalized to 1, as can be verified by integrating Eq. (12) over all x. An analysis of the moments will enable us to study the spreading of an isolated peak as well as providing a measure of the asymmetry of the peak as a function of time. For simplicity I will consider only the case of pulse loading so that $\rho(x, 0) = \rho_0\delta(x)$, and also assume that $D = 0$ so that diffusive transfer in the mobile phase is negligible. A more general theory can be developed but the essential qualitative features are to be found in the simpler theory.

The Laplace transform of Eq. (12) is, when $D = 0$,

$$s\rho^*(x, s) + vQ^*(s)\frac{\partial \rho^*}{\partial x} = \rho_0\delta(x) \qquad (18)$$

which is easily solved. The solution is

$$\frac{\rho^*(x, s)}{\rho_0} = \begin{cases} \dfrac{1}{vQ^*(s)} \exp\left(-\dfrac{sx}{vQ^*(s)}\right), & x \geq 0 \\ 0, \quad x < 0 \end{cases} \tag{19}$$

from which the normalization property is readily inferred. Another quantity that can be found from Eq. (19) is the Laplace transform of the amount of retained molecules at time t. Equation (19) implies the result

$$R^*(s) = \frac{\rho_0}{s}\left[1 - \exp\left(-\frac{sx}{vQ^*(s)}\right)\right] \tag{20}$$

Both Eqs. (19) and (20) can be inverted exactly to yield $\rho(x, t)$ and $R(t)$ for the Giddings-Eyring model, but such an inversion is not generally possible in any more complicated cases. It is therefore reasonable to seek measures of useful information about the peak that do not depend on an exact inversion. Such a measure is provided by the spatial moments $r_n(t)$ defined by

$$r_n(t) = \int_0^\infty x^n \rho(x, t)\, dx/\rho_0 \tag{21}$$

The Laplace transform of these moments can be calculated from Eq. (19), and is found to be

$$r_n^*(s) = \frac{n!}{s^{n+1}}(vQ^*(s))^n \tag{22}$$

exactly.

Since the inversion of $Q^*(s)$ is not readily accomplished, it would be impossible to give a complete transient analysis of the $r_n(t)$ without resort to numerical inversion of the Laplace transforms (*14*). Nonetheless Eq. (22) can yield useful information on the behavior of the $r_n(t)$ at sufficiently long times. To see what is involved, consider the Giddings-Eyring model for which results can be calculated exactly. The mean peak position and the variance of the peak can be written in terms of $g(t) = 1 - \exp(-(k + k')t)$ as

$$r_1(t) = \frac{vk'}{k + k'}t + \frac{vk}{(k + k')^2}g(t)$$

$$\sigma^2(t) = r_2(t) - r_1^2(t) = \frac{4kk'}{(k + k')^3}\left(t - \frac{g(t)}{k + k'}\right) - \frac{2kk't}{(k + k')^3}g(t)$$

$$+\frac{2k^2}{(k+k')^4}(g(t)-(k+k')te^{-(k+k')t})-\frac{k^2}{(k+k')^4}g^2(t) \quad (23)$$

In the limit $(k+k')t \gg 1$, most terms in these expressions can be neglected and we find the simpler long-time results:

$$r_1(t) \sim \frac{vk't}{(k+k')}, \qquad \sigma^2(t) \sim \frac{2v^2kk't}{(k+k')^3} \quad (24)$$

The limit just stated, $(k+k')t \gg 1$, can be given a physical interpretation. It says that the time must be large enough to insure that the number of interchanges between mobile and adsorbed phases is much greater than unity. When this condition holds, the methods of renewal theory can be used to show that in the stated limit peak shape will be very close to Gaussian (*15*).

In the case of multisite adsorption with a finite number of site types, it would be extremely difficult to write down the analogue of Eq. (23) valid for all time, but it is possible rather directly to calculate the analogue of Eq. (24), the long time limit. It is somewhat more difficult to specify the time at which the Gaussian peak becomes a useful approximation, but we can approach this problem by calculating a function that measures the skewness of the distribution. This measure of asymmetry is used in statistics (*16*), and will be denoted by $\gamma(t)$. In our present notation it can be written

$$\gamma(t) = (r_3(t) - 3r_1(t)r_2(t) + 2r_1^3(t))/\sigma^3(t) \quad (25)$$

This quantity is exactly equal to zero for any symmetric peak and in particular for a Gaussian. The fundamental idea in what follows is to calculate the long time behavior of $r_i(t)$ from the small $|s|$ behavior of the $r_i^*(s)$ (*17*). In this way I will show that at sufficiently long times, $\gamma(t)$ goes like $(T/t)^{1/2}$, where T is a constant with the dimensions of time that can be calculated in terms of the rate constants.

For the analysis one can assume that when $|s|$ is small, $Q^*(s)$ can be expanded as

$$Q^*(s) \sim Q_0 + Q_1 s + Q_2 s^2 + \cdots \quad (26)$$

where the Q_i are constants to be calculated from Eq. (10). When there are n first-order reactions as in Eq. (1), the Q's can be expressed in terms of quantities

$$\Gamma_j = \sum_{i=1}^{n} k_i/(k_i')^{j+1} \tag{27}$$

where Γ_j has the dimensions of $(\text{time})^j$. The first four of the Q_i are:

$$\begin{aligned} Q_0 &= 1/(1+\Gamma_0) \\ Q_1 &= Q_0^2\Gamma_1 \\ Q_2 &= Q_0^3\Gamma_1^2 - Q_0^2\Gamma_2 \\ Q_3 &= Q_0^4\Gamma_1^3 - 2Q_0^3\Gamma_1\Gamma_2 + Q_0^2\Gamma_3 \end{aligned} \tag{28}$$

The next step in the analysis is to substitute Eq. (26) into the expression for $r_i^*(s)$ in Eq. (22) and collect terms like s^{-m}, $m = 1, 2, 3, \ldots$, which correspond to terms $t^{m-1}/(m-1)!$ in the long-time expansion of the $r_n(t)$. In this way we find

$$\begin{aligned} r_1(t) &\sim v(Q_0t + Q_1) \\ r_2(t) &\sim v^2(Q_0^2t^2 + 4Q_0Q_1t + 2[2Q_0Q_2 + Q_1^2]) \\ r_3(t) &\sim v^3(Q_0^3t^3 + 9Q_0^2Q_1t^2 + 18(Q_0Q_1^2 + Q_0^2Q_2)t \\ &\quad + 6(Q_1^3 + 3Q_0^2Q_3 + 6Q_0Q_1Q_2)) \end{aligned} \tag{29}$$

We find, by using these expressions, that the variance associated with the peak is

$$\sigma^2(t) \sim 2Q_0Q_1v^2t \tag{30}$$

and the long-time form for the skewness defined in Eq. (25) is

$$\gamma(t) \sim \frac{3}{\sqrt{2}} \frac{(Q_1^2 + Q_0Q_2)}{Q_0^{1/2}Q_1^{3/2}t^{1/2}} \tag{31}$$

which tends to zero as t increases indefinitely. Thus the shape of the peak approaches symmetry so that for the present model tailing is a transient phenomena. A mathematical argument based on the central limit theorem suffices to show that the resulting peak must in fact be Gaussian.

KINETIC REQUIREMENTS FOR TAILING

It has been shown that a distribution of a finite number of rate constants necessarily leads to the absence of tailing in the long-time limit, although the argument does not rule out transient asymmetry. Is there any model that leads to tailing that does not vanish as time increases? I will construct two models that have that property. Probably there are others.

The motivation for the first model starts from the observation that it is no more than assumption that the kinetics of transitions between mobile and adsorbed phases can be described as being first order. Actual transitions may be much more complicated due to steric factors and to intermediate steps in the transition. Let us therefore consider a simple model with a single type of adsorbing site. Let us further retain the assumption that the transition M→S follows first-order kinetics. The reverse transition S→M will be assumed to reflect in its kinetics the different factors mentioned above. Because of these factors we will make the assumption that once adsorbed, a molecule can remain adsorbed for a long period. This property will be translated into an assumption about the long-time behavior of $\psi(t)$. When kinetics are first order $\psi(t) = k' \exp(-k't)$, and

$$\psi^*(s) = \left(1 + \frac{s}{k'}\right)^{-1} = \sum_{n=0}^{\infty} (-1)^n \frac{s^n}{(k')^n} \tag{32}$$

i.e., $\psi^*(s)$ has a Taylor series around $s = 0$ which is equivalent to saying that all moments of residence in the adsorbed phase are finite. In the present model we will assume that $\psi^*(s)$ can be expanded around $s = 0$ as

$$\psi^*(s) = 1 - \mu s + a s^{\alpha} + \cdots \tag{33}$$

in which $1 < \alpha < 2$, and μ and a are constants. The constant μ is just the average residence time for a single sojourn in the adsorbed phase. Equation (33) implies that the second moment, or variance of this residence time, is infinite although the average is finite. An example of a residence density with these properties is

$$\psi(t) = \left(\frac{\mu^3}{2\pi t^5}\right)^{1/2} \exp\left(-\frac{\mu}{2t}\right) \tag{34}$$

The corresponding transform is

$$\begin{aligned}\psi^*(s) &= (1 + \sqrt{2\mu s}) \exp(-\sqrt{2\mu s}) \\ &\sim 1 - \mu s + \frac{(2\mu s)^{3/2}}{3} \cdots \end{aligned} \tag{35}$$

which is of the form shown in Eq. (33), with $\alpha = 3/2$.

When Eq. (33) holds, $Q^*(s)$ can be expanded as

$$Q^*(s) = Q_0 + Q_1 s^{\alpha-1} + \cdots \tag{36}$$

where

$$Q_0 = (1 + k\mu)^{-1}, \qquad Q_1 = kaQ_0^2 \tag{37}$$

The combination of Eqs. (22) and (36) implies that at sufficiently large times, the moments of the peak take the form

$$\begin{aligned} r_1(t) &\sim v\left(Q_0 t + \frac{Q_1 t^{2-\alpha}}{\Gamma(3-\alpha)} + \cdots\right) \\ r_2(t) &\sim v^2\left(Q_0^2 t^2 + \frac{4Q_0 Q_1 t^{3-\alpha}}{\Gamma(4-\alpha)} + \cdots\right) \\ r_3(t) &\sim v^3\left(Q_0^3 t^3 + \frac{18Q_0^2 Q_1 t^{4-\alpha}}{\Gamma(5-\alpha)} + \cdots\right) \end{aligned} \tag{38}$$

Thus at sufficiently long times [more precisely, when $(Q_0/Q_1)t^{\alpha-1} \gg 1$], the average peak position will appear to increase linearly with time. However, the variance of the peak can be expressed in this approximation as

$$\sigma^2(t) \sim \frac{2(\alpha-1)}{\Gamma(4-\alpha)} Q_0 Q_1 t^{3-\alpha} \tag{39}$$

When $\alpha = 2$, this reduces to the classical first-power dependence of the variance. Whenever the parameter α is less than 2 as is presently assumed, the variance grows at a faster rate than t. The expressions in Eq. (38) can also be used to calculate the skewness parameter defined in Eq. (25). In the present case the asymptotic result is

$$\gamma(t) \sim \frac{3}{2^{3/2}}\left(\frac{Q_0}{2Q_1}\,\frac{\Gamma(4-\alpha)}{(\alpha-1)}\right)^{1/2} \frac{(\alpha-2)}{(4-\alpha)} t^{(\alpha-1)/2} \tag{40}$$

to lowest order in t. Several features of this formula are of interest. First, the peak is skewed to the left because of the restriction that $\alpha < 2$. Second, as time increases the skewness increases, and finally, as $\alpha \to 1$, the skewness also increases. These qualitative properties are related to the infinite variance of the residence times that is a consequence of the assumption of Eq. (33).

The results just described are derived for a single site model in which the residence times in the adsorbed phase have a finite mean but an infinite variance, and in which the Laplace transform of the residence time density has the property shown in Eq. (33). Similar results are obtainable from a model in which there are a multiplicity of sites with first-order kinetics (Eq. 1), but in which the rate constants are assumed to be randomly distributed. To derive the relevant relations, one starts by assuming a joint density for the forward and backward rate constants, $p(k, k')$. That is to say, $p(k, k')\, dk\, dk'$ is the probability that a forward (first-order) rate constant is between k and $k + dk$, and a backward rate constant is between k' and $k' + dk'$. The continuous analogue of Eq. (9) with the assumption of random rate constants is

$$c^*_{k,k'}(x, s) = \frac{kp(k, k')}{s + k'} c^*(x, s) \tag{41}$$

which implies that the function $Q^*(s)$ appearing in Eq. (10) is

$$Q^*(s) = \left(1 + \int_0^\infty \int_0^\infty \frac{kp(k, k')}{s + k'} dk\, dk'\right)^{-1} \tag{42}$$

The properties of $Q^*(s)$ for $s \rightarrow 0$ will therefore depend on those of the double integral

$$U(s) = \int_0^\infty \int_0^\infty \frac{kp(k, k')}{s + k'} dk\, dk' \tag{43}$$

Let me begin by assuming that $U(0)$ is finite. It is just

$$U(0) = \int_0^\infty \int \frac{k}{k'} p(k, k')\, dk\, dk' = \left\langle \frac{k}{k'} \right\rangle \tag{44}$$

i.e., it is equal to the average equilibrium constant which will be assumed to be finite. It is convenient to define the integral

$$f(k') = \int_0^\infty kp(k, k')\, dk \tag{45}$$

so that

$$U(s) - U(0) = -s\int_0^\infty \frac{f(k')\,dk'}{k'(s+k')} = -\int_0^\infty \frac{f(us)}{u(u+1)}du \qquad (46)$$

in which the second form of the integral follows from the first by the change of variables $k' = su$. We observe that when $|s|$ is small, the behavior of the integral depends on the behavior of $f(k')$ near the origin in k', since $1/k'$ diverges there. One can rcover an expansion equivalent to that in Eq. (33) by assuming that near $k' = 0$, $f(k')$ behaves like $f(k') \sim A(k')^\beta$, where $0 < \beta < 1$ and A is a constant. Then it follows from an Abelian theorem for Laplace transforms *(17)* that

$$U(s) - U(0) \sim -As^\beta \int_0^\infty \frac{u^{\beta-1}\,\mathrm{d}u}{1+u} = -\frac{\pi A}{\sin(\pi\beta)}s^\beta \qquad (47)$$

for $s \sim 0$. Together with Eqs. (42) and (43), this result is exacly of the form of Eq. (36). We therefore see that the assumption of random rate constants together with a more specialized assumption on the density at long residence times ($k' \sim 0$) will produce tailing. No doubt one can find other forms of tailing behavior by varying the form of $f(k')$ or by assuming that residence in the mobile or stationary phases do not necessarily follow first-order kinetics. It is also clear that the equations that follow from a microscopic description of the chromatographic process are generally more complicated than the transport equation usually assumed to hold. However, the limit theorems of probability suffice to insure that the usually assumed transport equation is valid under a wide variety of circumstances. Finally, it is possible to generalize the equations developed here so as to include gradients and other inhomogeneities. However, no new points of interest are expected to emerge from this analysis.

REFERENCES

1. J. C. Giddings and H. Eyring, *J. Phys. Chem.*, *59*, 416 (1955).
2. R. A. Keller and J. C. Giddings, *J. Chromatogr.*, *3*, 205 (1960).
3. K. E. van Holde, *J. Chem. Phys.*, *37*, 1922 (1962).
4. J. H. Beynon, S. Clough, D. A. Crooks, and G. R. Lester, *Trans. Faraday Soc.*, *54*, 705 (1958).
5. D. A. McQuarrie, *J. Chem. Phys.*, *38*, 437 (1963).
6. J. C. Giddings, *Dynamics of Chromatography. I. Principles and Theory*, Dekker, New York, 1965.

7. F. W. Schimdlin, *Phys. Rev., B16,* 2362 (1977).
8. G. F. Leal Ferreira, *Ibid., B16*, 4719 (1977).
9. G. Pfister and H. Scher, *Adv. Phys., 27,* 747 (1978).
10. F. W. Schimdlin, *Philos. Mag., B41,* 535 (1980).
11. G. H. Weiss and R. J. Rubin, *Adv. Chem. Phys., 52*, 363 (1982).
12. G. H. Weiss, *Sep. Sci. Technol., 16*, 75 (1981).
13. J. B. Phillips, N. A. Wright, and M. F. Burke, *Ibid., 16*, 861 (1981).
14. B. Davies and B. Martin, *J. Comp. Phys., 33,* 1 (1979).
15. D. R. Cox, *Renewal Theory*, Wiley, New York, 1962.
16. M. G. Kendall and A. Stuart, *The Advanced Theory of Statistics*, Vol. 1, Griffin, London, 1958.
17. G. Doetsch, *Theorie und Anwendungen der Laplace-Transformation*, Dover Publications Reprint, New York, 1943.

Received by editor May 24, 1982