

CHROM. 6246

COMPARISON OF EQUATIONS DESCRIBING MASS TRANSFER IN
PACKED BEDS

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(Received May 23rd, 1972)

SUMMARY

The first six moments are given for four equations commonly used to describe mass transfer in packed beds. In each case the first ordinary moment is found to be independent of the mechanism of mass transfer. The skewness and kurtosis vary as $N^{-1/2}$ and N^{-1} , respectively, where N is the number of theoretical plates. For a sufficiently large number of theoretical plates all models converge to a Gaussian curve.

INTRODUCTION AND DEFINITIONS

Many important processes, such as gas adsorption, liquid extraction, gas chromatography (GC), and catalytic processing, are based in part on dynamic partitioning between a moving and a stationary phase. The problem of obtaining an adequate mathematical description of these processes has been attacked again and again from a number of viewpoints, but the main contributions have been from two fields: chemical engineering and GC. In this paper we use a standard mathematical method of analysis by moments to compare the most common equations for mass transfer in packed beds.

The number of different equations proposed for describing dynamic adsorption is a result of the mathematical difficulty of the problem. Most theories of dynamic adsorption consider only one or two mechanisms of mass transfer, although a number of mechanisms could be important. Further these theories usually include additional simplifying assumptions such as a linear partition isotherm, constant diffusion coefficients for diffusion in both the mobile and stationary phases, a dilute concentration of adsorbate in the mobile phase, and a constant temperature across the adsorption bed. In spite of these and other simplifications, the final expressions are usually quite complex and their use requires the help of tables and/or computers. The complexity of these expressions prevents them from giving a clear insight into their physical nature.

Analysis by moments is a very powerful mathematical tool and can be used as a means of comparing the previously derived equations for breakthrough curves. From an experimental viewpoint only the first five or six moments need be calculated; the higher moments are difficult to determine from experimental data.

For this reason the first six moments characterize a breakthrough curve as accurately as is needed for a comparison between theory and experiment, and to support this view we will give here the first six statistical moments calculated from some of the well known theories of GC.

The moments given here are the temporal moments, *i.e.*, calculated using powers of the time coordinate. If these moments are taken about $t = 0$, this defines the ordinary temporal moments.

$$\bar{M}_i = \int_0^{\infty} t^i c(t) dt \quad (1)$$

The central temporal moments are calculated about the first ordinary moment, *viz.*,

$$M_i = \int_0^{\infty} (t - \bar{M}_1)^i c(t) dt \quad (2)$$

A well known method of calculating ordinary moments uses the i^{th} derivative of the Laplace transform of $c(t)$. If

$$\tilde{c}(s) = \mathcal{L}c(t) \quad (3)$$

the i^{th} ordinary moment is

$$\bar{M}_i = (-1)^i \lim_{s \rightarrow 0} \frac{d^i}{ds^i} \tilde{c}(s) \quad (4)$$

By expanding eqn. 2, the i^{th} central moment is found to be

$$M_i = \bar{M}_i - i\bar{M}_{i-1}\bar{M}_1 + \frac{i(i-1)}{2!} \bar{M}_{i-2}\bar{M}_1^2 \dots \quad (5)$$

These calculations can be speeded up by taking

$$\tilde{c}(s) = e^{-as+bs^2-cs^3+ds^4-es^5+fs^6} \quad (6)$$

From eqns. 4 and 5 it follows that

$$\bar{M}_1 = a \quad (7a-f)$$

$$M_2 = 2b$$

$$M_3 = 6c$$

$$M_4 = 12b^2 + 24d$$

$$M_5 = 120(bc + e)$$

$$M_6 = 120(b^3 + 6bd + 3c^2 + 6f)$$

Using these moments we define the number of theoretical plates, N , the skewness, γ_1 , and the kurtosis, γ_2 , as follows:

$$N = \frac{\bar{M}_1^2}{M_2} \quad (8)$$

$$\gamma_1 = \frac{M_3}{M_2^{\frac{3}{2}}} \quad (9)$$

$$\gamma_2 = \frac{M_4}{M_2^2} - 3 \quad (10)$$

ANALYSIS OF EQUATIONS

The theoretical chamber model

The first widely used theory¹ of peak spreading in chromatography assumed that the column could be visualized as a series of equivolume chambers, and that in each chamber a rapid mixing of sorbate took place. These assumptions lead directly to an equation for the breakthrough curve, for if there is perfect mixing of a unit pulse input in the first chamber, the output from that chamber must be proportional to the quantity of sorbate remaining in the chamber, *i.e.*,

$$c_i(t) = \frac{p}{t_b} e^{-(pt/t_b)} \tag{11}$$

where

p is the number of theoretical chambers

t_b is the flowthrough time for the entire column, calculated as

$$t_b = \frac{([1 - \varepsilon]k + \varepsilon)x}{V} \tag{12}$$

where

ε is the fractional interparticle volume

V is the superficial carrier gas velocity

x is the length of the column

k is the partition coefficient for the sorbate between equal volumes of mobile and stationary phase, dimensionless.

The Laplace transform of the output from the first chamber is

$$\tilde{c}_i(s) = (1 + st_b/p)^{-1} \tag{13}$$

and from p chambers in series

$$\tilde{c}(s) = \prod_{i=1}^{i=p} c_i(s) \tag{14}$$

$$= (1 + st_b/p)^{-p} \tag{15}$$

This last equation can be inverted to give

$$c(t) = \frac{p^p t^{p-1}}{\Gamma(p)(t_b)^p} e^{-(pt/t_b)} \tag{16}$$

However, inversions are not always simple to obtain or once obtained, the most useful way to characterize the effects of mass transfer in the column.

Let us look at what can be determined from the Laplace transform, eqn. 15, without going through the inversion procedure. Eqn. 15 can be rewritten as

$$\tilde{c}(s) = e^{-\left\{ p \ln \left\{ \frac{st_b}{p} + 1 \right\} \right\}}$$

or

$$\tilde{c}(s) = e^{-\left\{ t_b - \frac{s^2 t_b^2}{2p} + \frac{s^3 t_b^3}{3p^2} - \frac{s^4 t_b^4}{4p^3} + \frac{s^5 t_b^5}{5p^4} - \frac{s^6 t_b^6}{6p^5} \dots \right\}} \tag{17}$$

from which, by eqn. 7

$$\begin{aligned} \bar{M}_1 &= t_b & M_4 &= 3t_b^4(1/p^2 + 2/p^3) \\ M_2 &= t_b^2/p & M_5 &= 4t_b^5(5/p^3 + 6/p^4) \\ M_3 &= 2t_b^3/p^2 & M_6 &= 120t_b^6 \left\{ \frac{1}{8p^3} + \frac{13}{12p^4} + \frac{1}{p^5} \right\} \end{aligned} \quad (18a-f)$$

These moments give detailed information about the nature of the breakthrough curve. For example, the average holdup time, given by \bar{M}_1 , is independent of the number of theoretical chambers. Furthermore, the number of theoretical plates, calculated from the first and second moments of eqn. 7 is precisely equal to the number of theoretical chambers.

The skewness of the curve, and the kurtosis are, in order,

$$\gamma_1 = 2/\sqrt{p} \quad (19)$$

$$\gamma_2 = 6/p \quad (20)$$

Both the skewness and kurtosis are useful parameters to characterize breakthrough curves, but from the equations for the moments it is seen that with $p \gg 10$, $M_4 \approx 3M_2^2$. These last results tell us that for large p the breakthrough curve so closely approximates a Gaussian curve that experimental measurements of the difference are difficult to obtain.

Film limited mass transfer

The first widely used theory² in chemical engineering to describe mass transfer in packed beds relied on the concept that mass transfer between the moving and the stationary phase is limited by diffusion through a thin film separating the phases. This can be regarded as a more complex theoretical chamber model in which the basic assumptions are now: (1) the stationary phase consists of an infinite number of chambers; (2) in each chamber there is a rapid mixing of sorbate and (3) the rate of mass transfer between a chamber and the moving phase is proportional to the difference in equilibrium between these phases.

The assumptions listed above lead rapidly to an equation for a breakthrough curve. If a mass transfer function, $g(t)$, is defined as the rate of transfer of sorbate to the stationary phase following exposure to a unit concentration of sorbate in a unit volume of mobile phase starting at time, $t = 0$, then

$$\int_0^t g(\tau) d\tau = \frac{(1-\epsilon)k}{\epsilon} (1 - e^{-\alpha t}) \quad (21)$$

where α is the time constant for mass transfer (sec^{-1}).

The differential equation describing mass transfer in the column is

$$\frac{V}{\epsilon} \frac{\partial c(t)}{\partial x} + \frac{\partial}{\partial t} \int_0^t c(\tau) g(t-\tau) d\tau + \frac{\partial c(t)}{\partial t} = 0 \quad (22)$$

The Laplace transforms of these last two equations are, respectively,

$$\tilde{g}(s) = \frac{(1-\epsilon)k\alpha}{s(\alpha+s)} \quad (23)$$

and

$$\frac{V}{\varepsilon} \frac{d\tilde{c}(s)}{dx} + s\tilde{c}(s) \cdot \tilde{g}(s) + s\tilde{c}(s) = 0 \tag{24}$$

By integration

$$\tilde{c}(s) = e^{-(sx/V)} \left\{ \frac{(1-\varepsilon)k\alpha}{\alpha + s} + \varepsilon \right\} \tag{25}$$

or

$$\tilde{c}(s) = e^{-(sx/V) - [(s(1-\varepsilon)kx)/V]} \left\{ 1 - \frac{s}{\alpha} + \left(\frac{s}{\alpha}\right)^2 - \left(\frac{s}{\alpha}\right)^3 + \left(\frac{s}{\alpha}\right)^4 \dots \right\} \tag{26}$$

So

$$\bar{M}_1 = \frac{[(1-\varepsilon)k + \varepsilon]x}{V} \tag{27a-f}$$

$$M_2 = \frac{2(1-\varepsilon)kx}{V\alpha}$$

$$M_3 = \frac{6(1-\varepsilon)kx}{V\alpha^2}$$

$$M_4 = \frac{12(1-\varepsilon)^2 k^2 x^2}{V^2 \alpha^2} + \frac{24(1-\varepsilon)kx}{V\alpha^3}$$

$$M_5 = 120 \left\{ \frac{(1-\varepsilon)^2 k^2 x^2}{V^2 \alpha^3} + \frac{(1-\varepsilon)kx}{V\alpha^4} \right\}$$

$$M_6 = 120 \left\{ \frac{(1-\varepsilon)^3 k^3 x^3}{V^3 \alpha^3} + \frac{9(1-\varepsilon)^2 k^2 x^2}{V^2 \alpha^4} + \frac{6(1-\varepsilon)kx}{V\alpha^5} \right\}$$

From these moments we can calculate the basic properties of the breakthrough curve. The number of theoretical plates, as defined by eqn. 8 is

$$N = \frac{[(1-\varepsilon)k + \varepsilon]^2 x\alpha}{2(1-\varepsilon)kV} \tag{28}$$

The skewness is

$$\gamma_1 = 3 \sqrt{\frac{V}{2(1-\varepsilon)kx\alpha}} \tag{29}$$

and the kurtosis

$$\gamma_2 = \frac{6V}{(1-\varepsilon)kx\alpha} \tag{30}$$

These last three equations give the basic properties of the breakthrough curve in a simple but exact form, and in each equation the effect of the physical parameters on mass transfer can be seen clearly. For example, the number of theoretical plates, the skewness, and the kurtosis vary as the superficial velocity

to the -1 , $1/2$ and 1 power, respectively. Instead of calculating moments from eqn. 25 we have the alternative of inversion. This particular equation for $c(t)$ is well known³, its use involves a modified Bessel function of order one, and it must be admitted that at least part of our incentive for the use of moment analysis is our difficulty to visualize directly the properties of the breakthrough curve from this function.

Intraparticle diffusion

The more recent theories of chromatography consider in detail the processes of diffusion that take place in the interparticle and intraparticle spaces. We will show here, how analysis by moments can reduce these seemingly complex equations to simple understandable forms.

For mass transfer controlled by diffusion into homogeneous spheres, the mass transfer function, $\tilde{g}(s)$, is equal to⁴

$$\tilde{g}(s) = \frac{12(1-\epsilon)kD}{\epsilon d_p^2 s} \left\{ \sqrt{\frac{sd_p^2}{4D}} \coth \left[\sqrt{\frac{sd_p^2}{4D}} \right] - 1 \right\} \quad (31)$$

where

d_p = sorbent particle diameter (cm)

D = intraparticle diffusion coefficient (cm²/sec).

Expanding the above function into an infinite series leads to

$$\bar{M}_1 = \frac{[(1-\epsilon)k + \epsilon]x}{V} \quad (32a-f)$$

$$M_2 = \frac{(1-\epsilon)kx}{V} \left\{ \frac{d_p^2}{30D} \right\}$$

$$M_3 = 15 \frac{(1-\epsilon)kx}{7V} \left\{ \frac{d_p^2}{30D} \right\}^2$$

$$M_4 = 3 \left\{ \frac{(1-\epsilon)kx}{V} \right\}^2 \left\{ \frac{d_p^2}{30D} \right\}^3 + \frac{45}{7} \frac{(1-\epsilon)kx}{V} \left\{ \frac{d_p^2}{30D} \right\}^4$$

$$M_5 = \frac{150}{7} \left\{ \frac{(1-\epsilon)kx}{V} \right\}^2 \left\{ \frac{d_p^2}{30D} \right\}^3 + 1875 \frac{(1-\epsilon)kx}{77V} \left\{ \frac{d_p^2}{30D} \right\}^4$$

$$M_6 = 15 \left\{ \frac{(1-\epsilon)kx}{V} \right\}^3 \left\{ \frac{d_p^2}{30D} \right\}^3 + \frac{6975}{49} \left\{ \frac{(1-\epsilon)kx}{V} \right\}^2 \left\{ \frac{d_p^2}{30D} \right\}^4 + \frac{777375(1-\epsilon)kx}{7007V} \left\{ \frac{d_p^2}{30D} \right\}^5$$

and from these moments

$$N = \frac{[(1-\epsilon)k + \epsilon]^2 x}{(1-\epsilon)kv} \left\{ \frac{30D}{d_p^2} \right\} \quad (33)$$

$$\gamma_1 = \frac{15}{7} \sqrt{\frac{V}{(1-\epsilon)kx}} \sqrt{\left\{ \frac{d_p^2}{30D} \right\}} \quad (34)$$

$$\gamma_2 = \frac{45}{7} \frac{V}{(1-\varepsilon)kx} \left\{ \frac{d_p^2}{30D} \right\} \quad (35)$$

and these factors, as in the previous example, give the effect of the physical parameters on the shape of the breakthrough curve.

If an equation for the breakthrough curve is needed, the simplest procedure is to use the moments given above with either an Edgeworth or Gramm-Charlier series. The alternate procedure of the inversion of the Laplace transform, $\tilde{c}(s)$, cannot be done in terms simpler than an infinite integral.

Interparticle diffusion

For mass transfer controlled by diffusion in the interparticle space, the differential equation is

$$D_\theta \frac{\partial^2 c(t)}{\partial x^2} - \frac{V}{\varepsilon} \frac{\partial c(t)}{\partial x} - \left\{ \left(\frac{1-\varepsilon}{\varepsilon} \right) k + 1 \right\} \frac{\partial c(t)}{\partial t} = 0 \quad (36)$$

where D_θ = interparticle diffusion coefficient (cm²/sec).

The Laplace transform of the above equation is

$$D_\theta \frac{d^2 \tilde{c}(s)}{dx^2} - \frac{V}{\varepsilon} \frac{d\tilde{c}(s)}{dx} - s \left\{ \left(\frac{1-\varepsilon}{\varepsilon} \right) k + 1 \right\} \tilde{c}(s) = 0 \quad (37)$$

from which on integration it follows that:

$$\tilde{c}(s) = e^{- \left\{ \left(\sqrt{\left[\frac{V}{\varepsilon D_\theta} \right]^2 + \frac{4s \left[(1-\varepsilon)k + \varepsilon \right]}{\varepsilon D_\theta}} - \left[\frac{V}{\varepsilon D_\theta} \right] \right) \frac{x}{2} \right\}} \quad (38)$$

This last equation can be inverted to give:

$$c(t) = \frac{x}{2} \sqrt{\frac{\left(\frac{(1-\varepsilon)k}{\varepsilon} + 1 \right) \left\{ x - \frac{Vt}{(1-\varepsilon)k + 1} \right\}^2}{\pi D_\theta t^3}} e^{- \frac{\left\{ x - \frac{Vt}{(1-\varepsilon)k + 1} \right\}^2}{4D_\theta t \left\{ \left(\frac{1-\varepsilon}{\varepsilon} \right) k + 1 \right\}}} \quad (39)$$

The square root factor in the exponent of eqn. 38 can be written as a binomial expansion; once this is done it is not difficult to find that:

$$\begin{aligned} \bar{M}_1 &= t_b & (40a-f) \\ M_2 &= t_b^2/N \\ M_3 &= 3t_b^3/N^2 \\ M_4 &= t_b^4(3/N^2 + 15/N^3) \\ M_5 &= t_b^5(30/N^3 + 105/N^4) \\ M_6 &= t_b^6(15/N^3 + 315/N^4 + 945/N^5) \end{aligned}$$

where N , to be consistent with eqn. 8, is

$$N = \frac{xV}{2D_\theta \varepsilon} \quad (41)$$

COMPARISON OF BREAKTHROUGH CURVES

Having calculated the moments from four well known chromatographic theories, let us look at their similarities and differences. For each theory the average holdup time, \bar{M}_1 , is independent of the mechanism of mass transfer and equal exactly to the flowthrough time, t_b . This independence permits us to calculate from a measured \bar{M}_1 value the partition coefficient, k , without having to correct for mass transfer effects.

Table I lists the skewness and kurtosis calculated from these breakthrough curves. One simplification has been made, namely $(1-\varepsilon)k \gg \varepsilon$, and this was needed only for the cases of film controlled and intraparticle diffusion controlled mass transfer. Note that in each model the skewness and kurtosis vary as $N^{-1/2}$ and N^{-1} power, respectively. Furthermore, the numerical coefficients for the skewness are not highly different from each other. The same is true, to a lesser degree, of the numerical coefficients for the kurtosis. Another point that we wish to make is that for $N \approx 100$ or greater, these curves become quite similar and differences between them, if perfect physical models of each could be constructed, would be difficult to measure experimentally. Finally, and this has been the main point of the paper, the effect of various physical parameters on the nature of a breakthrough curve can be rapidly determined through moment analysis.

TABLE I

VALUES FOR SKEWNESS (γ_1) AND KURTOSIS (γ_2) CALCULATED FROM BREAKTHROUGH CURVES BASED ON DIFFERENT MODELS

<i>Model</i>	γ_1	γ_2
Theoretical chamber	$2/\sqrt{N}$	$6/N$
Film controlled diffusion	$3/2\sqrt{N}$	$3/N$
Intraparticle diffusion	$15/(7\sqrt{N})$	$45/7N$
Interparticle diffusion	$3/\sqrt{N}$	$15/N$

LIST OF SYMBOLS

M_i	i th central moment (sec ^{i})
M_i	i th ordinary moment (sec ^{i})
t	Time following injection of sorbate into column (sec)
$c(t)$	Effluent outflow of sorbate at time t
s	Laplace coordinate (sec ⁻¹)
a, b, c, d, e, f	Coefficients for s
x	Length of column (cm)
N	Number of theoretical plates
γ_1	Skewness
γ_2	Kurtosis
t_b	Flowthrough time (sec)
ε	Fractional interparticle volume
V	Superficial carrier gas velocity (cm/sec)

k	Partition coefficient
p	Number of theoretical chambers
$g(t)$	Function for interphase mass transfer (sec^{-1})
α	Time constant for interphase mass transfer (sec^{-1})
τ	Integration parameter (sec)
D	Intraparticle diffusion coefficient (cm^2/sec)
d_p	Sorbent particle diameter (cm)
D_0	Interparticle diffusion coefficient (cm^2/sec)

ACKNOWLEDGEMENTS

The research described in this paper was performed with financial support from the U.S. Atomic Energy Commission (Contract AT (11-1)3019) and the U.S. Department of Health, Education, and Welfare (Center Grant ES00002).

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