f	refers to free part of drop
h	refers to heavy fluid
i	refers to bulk interface
l	refers to light fluid
t	refers to top draining film

LITERATURE CITED

Chappelear, D. C., "Models of a liquid drop approaching an interface," *J. Colloid Sci.*, **16**, 186 (1961).

Elton, G. A. H., and R. G. Picknett, "The coalescence of aqueous droplets with an oil-water interface," in *Proc. of Second Intern. Congr. on Surface Activity*, **1**, 288 (1957).

Hartland, S., "The pressure distribution in axisymmetric draining films," *J. Colloid Interface Sci.*, **35**, 227 (1971).

———., and J. R. Robinson "The dynamic equilibrium of a rigid sphere at a deformable liquid-liquid interface," *ibid.*, 372.

Hartland, S., and S. M. Wood, "Effect of Applied Force on Drainage of the Film Between a Liquid Drop And Horizontal Surface," *AIChE J.*, **19**, 810 (1973).

Huh, C., and L. E. Scriven, "Shapes of axisymmetric fluid interfaces of unbounded extent," *J. Colloid Interface Sci.*, **30**, 323 (1969).

Princen, H. M., "The shape of a fluid drop at a liquid-liquid interface," *J. Colloid Sci.*, **18**, 178 (1963).

Wood, S. M., and S. Hartland, "The shape of a drop trapped between two horizontal surfaces," *AIChE J.*, **18**, 1041 (1972).

Manuscript received March 27, 1973; revision received and accepted April 12, 1973.

Some New Results for Chromatographic Kinetics Studies

G. A. MILLER and J. E. BAILEY

Department of Chemical Engineering
University of Houston, Houston, Texas 77004

Chromatographic phenomena have recently enjoyed wide application in experimental techniques aimed at transport properties and reaction kinetic data. Motivated by theoretical studies of Kubin, (1965), Padberg and Smith (1968), Schneider and Smith (1968), and Suzuki and Smith (1968a, 1968b) have developed chromatographic techniques for studies in catalysis and heat transfer (Sagara et al., 1970). The basic working tools for these methods are relationships among the system properties and moments of the response of a packed bed to a pulse tracer input.

In all previous work these moments have been developed in detail for a variety of specific models of heat and mass transfer resistance and chemical reaction. In addition, an explicit form, usually a square wave, has universally been assumed for the input pulse. The intention of this note is to present new derivations of moment-system property relationships which hold for input pulses of arbitrary shapes and for general transport and kinetic models.

By representing interchange of tracer between the carrier gas and the stationary phase with a transfer function, the analysis of tracer motion in the carrier gas can be completed without regard to the details of the interchange process. The results thus obtained are therefore applicable to any type of interchange situation. To complete the analysis for any specific case, then, one need only compute constants derived from the model of local exchange alone. This affords a considerable reduction in the required algebraic labor. In a conceptual sense, therefore, this work bears analogies to the moment-source theory due to Horn (1971).

Irreversible chemical reaction for both the cases of no mass transfer resistance and with mass transfer resistance within the immobile phase pellets will be employed as an example to illustrate the local exchange calculation. This problem, first broached by Stevens and Squires (1972), has not yet been treated in the literature.

GENERAL DERIVATION OF MOMENT RELATIONSHIPS

The conservation equation for tracer flowing in a packed tube may be written

$$-\frac{D_z}{\alpha}\frac{\partial^2 c}{\partial z^2} + v\frac{\partial c}{\partial z} + \gamma\frac{\partial c}{\partial t} + \Delta c = 0 \qquad (1)$$

with boundary and initial conditions

$$c(z, 0) = 0 \qquad (2)$$

$$c(0, t) = c_0(t) \qquad (3)$$

$$\lim_{z \to \infty} c(z, t) \text{ is finite} \qquad (4)$$

The term Δc in Equation (1) represents interchange between the flowing and stationary phases and is best discussed in terms of the Laplace transformed equations which are

$$-\frac{D_z}{\alpha}\frac{d^2\tilde{c}}{dz^2} + v\frac{d\tilde{c}}{dz} + \gamma s\tilde{c} + \Delta\tilde{c} = 0 \tag{5}$$

$$\tilde{c}\,(0, s) = \tilde{c}_0(s) \tag{6}$$

$$\lim_{z\to\infty} \tilde{c}\,(z, s) \text{ is finite} \tag{7}$$

As will be illustrated later with an example, the transformed exchange rate $\Delta\tilde{c}$ may be expressed as

$$\Delta\tilde{c} = H(s)\,\tilde{c} \tag{8}$$

for all linear models of transport to the stationary phase and reaction or adsorption within the stationary phase. Naturally the form of the transfer function $H(s)$ will depend on the physical situation under consideration. It is, however, most efficient to complete derivation of the moments without reference to a particular case.

Solving Equation (5) subject to conditions (6) through (8) yields

$$\tilde{c}\,(z, s) = \tilde{c}_0(s)e^{\frac{\lambda(s)z}{v}} \tag{9}$$

where

$$\lambda(s) = \frac{1 - \sqrt{1 + 4A[\gamma s + H(s)]}}{2A} \tag{10}$$

and

$$A = \frac{D_z}{\alpha v^2} \tag{11}$$

The moments of the tracer response, defined as

$$m_n(z) = \int_0^\infty t^n\, c(z, t)\,dt \tag{12}$$

may now be computed from Equation (9) using the well-known formula

$$m_n(z) = (-1)^n \lim_{s\to 0} \frac{d^n\tilde{c}\,(z, s)}{ds^n}. \tag{13}$$

The results for the first three moments are

$$m_0(z) = m_0(0)e^{\lambda_0 z/v} \tag{14}$$

$$m_1(z) = \left[\, m_1(0) - m_0(0)\lambda_0'\frac{z}{v}\right] e^{\lambda_0 z/v} \tag{15}$$

$$m_2(z) = \left\{ m_2(0) - 2m_1(0)\frac{z}{v}\lambda_0' + m_0(0) \cdot \left[\lambda_0''\frac{z}{v} + \left(\lambda_0'\frac{z}{v}\right)^2\right]\right\} e^{\frac{\lambda_0 z}{v}} \tag{16}$$

where

$$\lambda_0 = \frac{1 - \sqrt{1 + 4AH_0}}{A} \tag{17}$$

$$\lambda_0' = \frac{-(\lambda + H_0')}{\sqrt{1 + 4AH_0}} \tag{18}$$

and

$$\lambda_0'' = \frac{-H_0''}{\sqrt{1 + 4AH_0}} + \frac{2A(\gamma + H_0')^2}{(1 + 4AH_0)^{3/2}} \tag{19}$$

In all of the above expressions a prime on λ or H indicates differentiation with respect to s while a subscript zero on these quantities denotes evaluation at $s = 0$.

Much simpler expressions are obtained for the absolute moments, defined as

$$\mu_n'(z) = \frac{m_n(z)}{m_0(z)} \tag{20}$$

as well as the second central moment

$$\mu_2(z) = \mu_2'(z) - \mu_1'^2(z) \tag{21}$$

These equations combined with the m_n moments given above reveal that

$$\mu_1'(z) - \mu_1'(0) = -\lambda_0'\frac{z}{v} \tag{22}$$

$$\mu_2(z) - \mu_2(0) = \lambda_0''\frac{z}{v} \tag{23}$$

All of the equations just presented are valid for an arbitrary input function and for arbitrary interchange models. They can be used to relate experimentally determined moments to the system parameters which appear in A, H_0, H_0', and H_0''. In the following section the case of an irreversible chemical reaction will be considered.

LOCAL EXCHANGE CALCULATIONS FOR AN IRREVERSIBLE CHEMICAL REACTION

Suppose that the irreversible reaction

$$A \rightarrow B$$

occurs at the surface of the stationary phase and the rate of reaction per unit volume of stationary phase is kc, where c is the concentration of A. It is instructive to consider first the simplest mass transport situation where there is no resistance to mass transfer, that is, the A concentration is c at all points of the stationary phase surface at a particular axial position. Then the capacity term γ and the interchange term Δc are given by

$$\gamma = 1 + \frac{(1 - \alpha)}{\alpha}\beta \tag{24}$$

and

$$\Delta c = \frac{1 - \alpha}{\alpha}kc \tag{25}$$

respectively. For this simple case the transfer function $H(s)$ is the constant

$$\frac{\Delta\tilde{c}}{\tilde{c}} = H(s) = \left(\frac{1 - \alpha}{\alpha}\right)k \tag{26}$$

so that

$$H_0 = \frac{1 - \alpha}{\alpha}k \tag{27}$$

and

$$H_0' = H_0'' = 0 \tag{28}$$

Next a more realistic mass transfer situation will be considered which incorporates diffusion and reaction within the spherical pellets. In this instance the transfer term is

$$\Delta c = \frac{3}{R}D\frac{(1 - \alpha)}{\alpha}\left.\frac{\partial c_i}{\partial r}\right|_{r=R} \tag{29}$$

where c_i is the reactant concentration within the pellets. Here $\gamma = 1$. The necessary transfer function representing interchange between the flowing and stationary phases may be derived by solving the unsteady mass balance for reactant within the pellets:

$$\frac{D}{\beta}\left[\frac{\partial^2 c_i}{\partial r^2} + \frac{2}{r}\frac{\partial c_i}{\partial r}\right] - \frac{\partial c_i}{\partial t} - \frac{k\,c_i}{\beta} = 0 \tag{30}$$

subject to the conditions

$$\frac{\partial c_i}{\partial r} = 0 \quad \text{at} \quad r = 0 \tag{31}$$

$$c_i = c \quad \text{at} \quad r = R \tag{32}$$

and

$$c_i = 0 \quad \text{at} \quad t = 0 \tag{33}$$

The Laplace transform of the solution to this problem is

$$\tilde{c}_i = \tilde{c}\,\frac{R \sinh\,(r\sqrt{K(s)})}{r \sinh\,(R\sqrt{K(s)})} \tag{34}$$

where

$$K(s) = \frac{\beta}{D}\left[\,s + \frac{k}{\beta}\,\right] \tag{35}$$

Utilizing Equation (34) in Equation (29) reveals that for this problem

$$H(s) = \frac{3}{R^2}\,D\left(\frac{1-\alpha}{\alpha}\right)$$

$$[\mathrm{R}\sqrt{\mathrm{K(s)}}\ \coth\,(\mathrm{R}\sqrt{\mathrm{K(s)}}\,) - 1] \tag{36}$$

so that

$$H_0 = \frac{3}{R^2}\,D\left(\frac{1-\alpha}{\alpha}\right)[h_0 \coth h_0 - 1] \tag{37}$$

$$H_0' = \frac{3\beta}{2}\left(\frac{1-\alpha}{\alpha}\right)\frac{\frac{1}{2}\sinh(2h_0) - h_0}{h_0 \sinh^2 h_0} \tag{38}$$

and

$$H_0'' = \frac{R^2}{2Dk \sinh^2\,(h_0)}\,H_0 - \frac{\beta}{2k}\,H_0' \tag{39}$$

The parameter h_0 in the above expressions is the familiar Thiele modulus:

$$h_0 = R\sqrt{\frac{k}{D}} \tag{40}$$

Evaluation of the constants H_0, H_0', and H_0'' completes the determination of moments for this relatively complex model. To determine the moments, one need only substitute these expressions into the general formulae presented in the previous section.

As a check on the results for the example, the limiting behavior for h_0 approaching zero has been determined. In this limit, the model with intraparticle resistance should give the same relationships as the no resistance model. Since (1)

$$h_0 \coth h_0 - 1 = \frac{h_0^2}{3} - \frac{h_0^4}{45} + \ldots, \tag{41}$$

it follows that

$$\lim_{h_0\to 0} H_0 \Big|_{\substack{\text{intraparticle}\\ \text{resistance}\\ \text{model}}} = \left(\frac{1-\alpha}{\alpha}\right) a = H_0 \Big|_{\substack{\text{no}\\ \text{resistance}\\ \text{model}}} \tag{42}$$

It can likewise be shown that

$$\lim_{h_0\to 0} H_0'' \Big|_{\substack{\text{intraparticle}\\ \text{resistance}\\ \text{model}}} = 0 \tag{43}$$

and

$$\lim_{h_0\to 0}\,[\gamma + H_0'] \Big|_{\substack{\text{intraparticle}\\ \text{resistance}\\ \text{model}}} = 1 + \lim_{h_0\to 0} H_0' \Big|_{\substack{\text{intraparticle}\\ \text{resistance}\\ \text{model}}}$$

$$= 1 + \beta\left(\frac{1-\alpha}{\alpha}\right) = [\gamma + H_0']_{\substack{\text{no resistance}\\ \text{model}}} \tag{44}$$

It is interesting that in the final comparison, the limiting value of H_0' has the effect of modifying the capacity term so that it is the same as the capacity term for the model devoid of mass transfer resistance. Thus, in the limiting case of zero Thiele modulus, the moments for the resistance model reduce correctly to those for the simpler situation.

NOTATION

A = defined in Equation (11)
c = tracer concentration in the flowing phase
$\tilde{c}$ = Laplace transform of c
c_i = tracer concentration within the pores of the stationary phase
c_0 = concentration of tracer in the feed
D_z = axial dispersion coefficient
D = effective diffusivity
k = reaction rate constant
H = local exchange transfer function
h_0 = Thiele modulus
m_n = nth moment of tracer response
r = radial coordinate within an immobile phase pellet
R = radius of immobile phase pellet
s = Laplace transform parameter
t = time
v = axial flow velocity
z = axial position

Greek Letters

α = interstitial void fraction
β = intraparticle void fraction
γ = capacity ratio = $\dfrac{\text{fluid volume at bulk fluid concentration}}{\text{interstitial volume}}$
λ = function defined in Equation (10)
μ_n = nth absolute moment
μ_n' = nth central moment

LITERATURE CITED

Abramowitz, M., and I. A. Stegun, *Handbook of Mathematical Functions*, p. 85, Dover, New York (1968).

Horn, F. J. M., "Calculation of Dispersion Coefficients by Means of Moments," *AIChE J.*, **17**, 613 (1971).

Kubin, M., "Beitrag zur Theorie der Chromatographie, I, II," *Coll. Czech. Chem. Comm.*, **30**, 1104, 2900 (1965).

Padberg, G., and J. M. Smith, "Chemisorption Rates by Chromatography," *J. Catalysis*, **12**, 172 (1968).

Sagara, M., P. Schneider, and J. M. Smith, "The Determination of Heat-Transfer Parameters for Flow in Packed Beds using Pulse Testing and Chromatography Theory," *Chem. Eng. J.*, **1**, 47 (1970).

Schneider, P., and J. M. Smith, "Adsorption Rate Constants from Chromatography," *AIChE J.*, **14**, 763 (1968).

Stevens, W. R., and R. G. Squires, "Isomerization of Cyclopropane in a Pulsed Microreactor," in *Chemical Reaction Engineering. Proc. of the Fifth European/Second Intern. Symp. on Chem. Reaction Eng.*, pp. 32-35. Elsevier, Amsterdam (1972).

Suzuki, M., and J. M. Smith, "Chemisorption Studies by Chromatography: Hydrogen on Copper-Zinc Oxide," *J. Catalysis*, **21**, 336 (1971a).

————., "Hydrogen Exchange Rates on Nickel by Chromatography," *ibid.*, **23**, 321 (1971b).

Manuscript received February 8, 1973; revision received March 26 and accepted April 5, 1973.