

CHROM. 8749

MOMENT ANALYSIS FOR REACTION CHROMATOGRAPHY

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(Received July 10th, 1975)

SUMMARY

The theoretical treatment of the elution profile in reaction chromatography by the moment analysis technique is presented. The mass balance equations describing linear chromatography (equilibrium and non-equilibrium) involving multiple phases and multiple components are solved by means of the Laplace transform followed by the projective resolution method. From the solutions, the zero and the first normal moments of the elution curves for both reactants and products are calculated.

INTRODUCTION

The use of a chromatographic column as a chemical reactor has been widely applied in both analytical and kinetic investigations. Earlier work in this field has been reviewed by Saha and Mathur¹, Choudlay and Daraisway², Van Swaary³ and Berezkin⁴. The theoretical aspects of reaction chromatography have also been considered by many workers; Kočířik⁵ used the moment analysis technique to elucidate the elution profile of reaction chromatography, and obtained the zero to fourth statistical moments of the elution curve due to a reactant. Nakagaki and Nishino⁶ and Kallen and Heilbronner⁷ used plate theory in discussing the change of the positions and shapes of chromatograms due to both reactants and products with regard to variations in column characteristics. All of these workers, however, based their work on the idea that the reaction $A \rightarrow B$ takes place on a single stationary phase, and A and B are distributed between the mobile and stationary phases. However, in practice, there can be many more species of products that are formed from a reactant molecule, either reversibly or irreversibly and either simultaneously or successively. Also, there must be more than two phases that can contribute to the reaction and the distribution of these species; for instance, the mobile-stationary interphase, stationary liquid-solid support interphase and solid support phase. In this paper, we have attempted to obtain the moment equations for reaction chromatography involving multiple phases and multiple components.

EQUILIBRIUM SYSTEM

We first consider that reactants introduced into a column undergo chemical

conversions to yield several types of products and all of the species present are distributed between the gas and stationary phases to establish instantaneous equilibrium. In this instance, the following simultaneous partial differential equations can be established:

$$\left. \begin{aligned} (1+k_1) \partial C_1 / \partial t + u \partial C_1 / \partial z &= D \partial^2 C_1 / \partial z^2 - \sum_{j=1}^n k_{1j} C_j \\ (1+k_2) \partial C_2 / \partial t + u \partial C_2 / \partial z &= D \partial^2 C_2 / \partial z^2 - \sum_{j=1}^n k_{2j} C_j \\ \vdots & \\ (1+k_n) \partial C_n / \partial t + u \partial C_n / \partial z &= D \partial^2 C_n / \partial z^2 - \sum_{j=1}^n k_{nj} C_j \end{aligned} \right\} \quad (1)$$

where C_1, C_2, \dots, C_n are the concentrations of 1, 2, \dots , n species in mobile phase, respectively, k_1, k_2, \dots, k_n denote their distribution ratios, D is effective diffusion coefficient which is considered here to be constant for all species, and k_{ij} ($i, j = 1, 2, \dots, n$) is the rate constant of first order chemical reaction, u is carrier linear velocity, t is time and z is column length coordinate. If there is no solute in the column at $t = 0$, and the input distribution of the i th species is expressed in the form, $f_i(t)$, the initial and boundary conditions can be given as

$$C_i(0, z) = 0, C_i(t, 0) = f_i(t), C_i(t, \infty) = 0, (i = 1, 2, \dots, n) \quad (2)$$

The application of matrix representation simplifies eqns. 1 and 2 to

$$\left. \begin{aligned} K_D \partial C / \partial t + u \partial C / \partial z &= D \partial^2 C / \partial z^2 - K_R C \\ C(0, z) = 0, C(t, 0) &= F(t), C(t, \infty) = 0 \end{aligned} \right\} \quad (3)$$

where

$$K_R = \begin{bmatrix} k_{11} & k_{12} & \dots & k_{1n} \\ k_{21} & k_{22} & \dots & k_{2n} \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ k_{n1} & k_{n2} & \dots & k_{nn} \end{bmatrix}$$

$$K_D = \begin{bmatrix} k_1 & & & 0 \\ & k_2 & & \\ & & \cdot & \\ & & & \cdot \\ 0 & & & k_n \end{bmatrix}$$

$$C(t,z) = \begin{bmatrix} C_1(t,z) \\ C_2(t,z) \\ \vdots \\ C_n(t,z) \end{bmatrix}$$

and

$$F(t) = \begin{bmatrix} f_1(t) \\ f_2(t) \\ \vdots \\ f_n(t) \end{bmatrix}$$

The Laplace transform of eqn. 3 with respect to t leads to the following ordinary differential equation:

$$\left. \begin{aligned} D \frac{d^2 \bar{C}}{dz^2} - u \frac{d \bar{C}}{dz} - \bar{G} \bar{C} &= 0 \\ \bar{C}(s,0) = \bar{F}(s), \bar{C}(s,\infty) &= 0 \end{aligned} \right\} \quad (4)$$

where s is the Laplace variable with respect to t , $\bar{C}(s,z)$ and $\bar{F}(s)$ denote the Laplace transforms of $C(t,z)$ and $F(t)$, respectively, and $\bar{G} = K_R + s K_D$. The solution of eqn. 4 is given^{8,9} by

$$\bar{C}(s,z) = \exp \{ [u/2D - \sqrt{(u/2D)^2 + (\bar{G}/D)}] z \} \cdot \bar{F}(s) \quad (5)$$

in which the exponential part becomes an $(n \times n)$ matrix function that can be resolved as described below. If \bar{G} is given as a regular matrix ($|\bar{G}| \neq 0$), its eigenvalues λ_i ($i = 1, 2, \dots, n$), which are distinct from each other, are obtained by solving the equation

$$|\bar{G} - \lambda E_n| = 0 \quad (6)$$

where E_n is the n th order unit matrix and $||$ denotes a determinant.

Then, with the aid of projective expression (Sylvester's theorem⁹), the exponential term in eqn. 5 can be written as

$$\begin{aligned} \exp \{ [u/2D - \sqrt{(u/2D)^2 + (\bar{G}/D)}] z \} &= \\ &= \sum_{i=1}^n P_i \exp \{ [u/2D - \sqrt{(u/2D)^2 + (\lambda_i/D)}] z \} \end{aligned} \quad (7)$$

where P_i is the projective matrix for λ_i and is given by the following equation:

$$P_i = \frac{(\bar{G} - \lambda_1 E_n) (\bar{G} - \lambda_2 E_n) \cdots (\bar{G} - \lambda_{i-1} E_n) (\bar{G} - \lambda_{i+1} E_n) \cdots (\bar{G} - \lambda_n E_n)}{(\lambda_i - \lambda_1) (\lambda_i - \lambda_2) \cdots (\lambda_i - \lambda_{i-1}) (\lambda_i - \lambda_{i+1}) \cdots (\lambda_i - \lambda_n)} \quad (8)$$

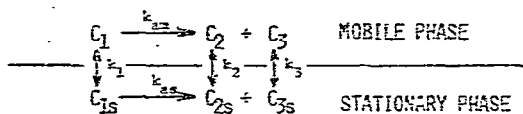


Fig. 1. Equilibrium partition model.

In order to obtain the explicit forms of the statistical moments from the solution of eqn. 4, we now consider the example illustrated in Fig. 1, where C_1 , C_2 and C_3 are the concentrations of a reactant and two products in the mobile phase, respectively. If the reactant is converted into products with rate constants k_{am} in the mobile phase and k_{as} in the stationary phase, the mass balance is described by the following equation:

$$\begin{aligned} (1 + k_1)\partial C_1/\partial t + u \partial C_1/\partial z &= D \partial^2 C_1/\partial z^2 - k_a C_1 \\ (1 + k_2)\partial C_2/\partial t + u \partial C_2/\partial z &= D \partial^2 C_2/\partial z^2 + k_a C_1 \\ (1 + k_3)\partial C_3/\partial t + u \partial C_3/\partial z &= D \partial^2 C_3/\partial z^2 + k_a C_1 \end{aligned} \quad (9)$$

where $k_a = k_{am} + k_{as} k_1$. The matrix \bar{G} becomes

$$\bar{G} = \begin{bmatrix} k_a + s(1 + k_1) & 0 & 0 \\ -k_a & s(1 + k_2) & 0 \\ -k_a & 0 & s(1 + k_3) \end{bmatrix} \quad (10)$$

and from eqn. 6 the eigenvalues of \bar{G} are obtained as

$$\left. \begin{aligned} \lambda_1 &= k_a + s(1 + k_1) \\ \lambda_2 &= s(1 + k_2) \\ \lambda_3 &= s(1 + k_3) \end{aligned} \right\} \quad (11)$$

From eqn. 8, the projective matrices P_1 , P_2 and P_3 for λ_1 , λ_2 and λ_3 are written as

$$P_1 = \begin{bmatrix} 1 & 0 & 0 \\ -k_a/(\lambda_1 - \lambda_2) & 0 & 0 \\ -k_a/(\lambda_1 - \lambda_3) & 0 & 0 \end{bmatrix}; P_2 = \begin{bmatrix} 0 & 0 & 0 \\ -k_a/(\lambda_2 - \lambda_1) & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix}; P_3 = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ -k_a/(\lambda_3 - \lambda_1) & 0 & 1 \end{bmatrix} \quad (12)$$

Substitution of eqns. 11 and 12 into eqn. 7 leads to

$$\begin{aligned} &e^{\{[(u/2D) - \sqrt{(u/2D)^2 + (\bar{G}/D)z}]\}z} = \\ &= \left\{ \begin{array}{ccc} e^{\{[(u/2D) - \sqrt{a_1}]z\}} & 0 & 0 \\ k_a \{e^{\{[(u/2D) - \sqrt{a_1}]z\}} - e^{\{[(u/2D) - \sqrt{a_2}]z\}}\}/\lambda_2 - \lambda_1 & e^{\{[(u/2D) - \sqrt{a_2}]z\}} & 0 \\ k_a \{e^{\{[(u/2D) - \sqrt{a_1}]z\}} - e^{\{[(u/2D) - \sqrt{a_3}]z\}}\}/\lambda_3 - \lambda_1 & 0 & e^{\{[(u/2D) - \sqrt{a_3}]z\}} \end{array} \right\} \end{aligned} \quad (13)$$

where $a_1 = (u/2D)^2 + \lambda_1/D$, $a_2 = (u/2D)^2 + \lambda_2/D$ and $a_3 = (u/2D)^2 + \lambda_3/D$.

As the input distribution of the reactant, $f_1(t)$, can be regarded as the Dirac δ -function for the pulse-like introduction, then

$$\tilde{F}(s) = \begin{bmatrix} m \\ 0 \\ 0 \end{bmatrix} \quad (14)$$

where m represents the amount of the reactant in a unit of δ -function. By combining eqns. 13 and 14 with eqn. 5, we obtain

$$\left. \begin{aligned} \tilde{C}_1(s, z) &= m e^{[(u/2D) - \sqrt{A_1}]z} \\ \tilde{C}_2(s, z) &= mk_a e^{uz/2D} [e^{-z\sqrt{A_1}} - e^{-z\sqrt{A_2}}] / \lambda_2 - \lambda_1 \\ \tilde{C}_3(s, z) &= mk_a e^{uz/2D} [e^{-z\sqrt{A_1}} - e^{-z\sqrt{A_3}}] / \lambda_3 - \lambda_1 \end{aligned} \right\} \quad (15)$$

The inverse transforms of the above equations become

$$\left. \begin{aligned} C_1(t, z) &= \frac{mz\sqrt{A_1}}{2t\sqrt{\pi t}} \exp\left(\frac{uz}{2D} - \frac{B_1 t}{A_1} - \frac{A_1 z^2}{4t}\right) \\ C_2(t, z) &= \frac{mzk_a}{2\sqrt{\pi}(k_2 - k_1)} \cdot e^{uz/2D} \int_0^t \frac{1}{\tau\sqrt{\tau}} \exp[k_a(t-\tau)/(k_2 - k_1)] \cdot \\ &\quad \left[\sqrt{A_1} \exp\left(-\frac{B_1 \tau}{A_1} - \frac{A_1 z^2}{4\tau}\right) - \sqrt{A_2} \exp\left(-\frac{B_2 \tau}{A_2} - \frac{A_2 z^2}{4\tau}\right) \right] d\tau \\ C_3(t, z) &= \frac{mzk_a}{2\sqrt{\pi}(k_3 - k_1)} \cdot e^{uz/2D} \int_0^t \frac{1}{\tau\sqrt{\tau}} \exp[k_a(t-\tau)/(k_3 - k_1)] \cdot \\ &\quad \left[\sqrt{A_1} \exp\left(-\frac{B_1 \tau}{A_1} - \frac{A_1 z^2}{4\tau}\right) - \sqrt{A_3} \exp\left(-\frac{B_3 \tau}{A_3} - \frac{A_3 z^2}{4\tau}\right) \right] d\tau \end{aligned} \right\} \quad (16)$$

where

$$\begin{aligned} A_1 &= (1 + k_1)/D; B_1 = (u/2D)^2 + k_a/D \\ A_2 &= (1 + k_2)/D; B_2 = (u/2D)^2 \\ A_3 &= (1 + k_3)/D; B_3 = (u/2D)^2 \end{aligned}$$

By solving these equations, it is possible to discuss the effects of kinetic constants on the reaction chromatogram.

The zero moments (peak area) for the elution curves due to the reactant and the products are obtained from eqn. 15 as

$$\left. \begin{aligned} M_{01} &= \tilde{C}_1(0, z) = m \exp\left\{[(u/2D) - \sqrt{(u/2D)^2 + (k_a/D)}]z\right\} \\ M_{02} &= \tilde{C}_2(0, z) = m(1 - \exp\{[(u/2D) - \sqrt{(u/2D)^2 + (k_a/D)}]z\}) \\ M_{03} &= \tilde{C}_3(0, z) = m(1 - \exp\{[(u/2D) - \sqrt{(u/2D)^2 + (k_a/D)}]z\}) \end{aligned} \right\} \quad (17)$$

and the first normal moments (retention time) as

$$\left. \begin{aligned}
 t_{R1} &= \lim_{s \rightarrow 0} (-\partial/\partial s) \ln C_1(s, z) = (1+k_1)z/2D\sqrt{r} \\
 t_{R2} &= \lim_{s \rightarrow 0} (-\partial/\partial s) \ln C_2(s, z) = (k_1-k_2)/k_a \\
 &\quad + \frac{(1+k_1)z e^{-z\sqrt{r}}/2D\sqrt{r} - (1+k_2)ze^{-uz/2D}/u}{e^{-z\sqrt{r}} - e^{-uz/2D}} \\
 t_{R3} &= \lim_{s \rightarrow 0} (-\partial/\partial s) \ln C_3(s, z) = (k_1-k_3)/k_a \\
 &\quad + \frac{(1+k_1)z e^{-z\sqrt{r}}/2D\sqrt{r} - (1+k_3)ze^{-uz/2D}/u}{e^{-z\sqrt{r}} - e^{-uz/2D}}
 \end{aligned} \right\} \quad (18)$$

where $r = (u/2D)^2 + (k_a/D)$.

NON-EQUILIBRIUM SYSTEM

If the solute present in a column may undergo distribution with finite speed, the mass balance equation involves the mass transfer terms, leading to

$$\left. \begin{aligned}
 \partial C_1/\partial t + u \partial C_1/\partial z &= D \partial^2 C_1/\partial z^2 - \sum_{j=1}^l k_{1j} C_j \\
 \partial C_2/\partial t + u \partial C_2/\partial z &= D \partial^2 C_2/\partial z^2 - \sum_{j=1}^l k_{2j} C_j \\
 &\quad \vdots \qquad \qquad \qquad \vdots \\
 \partial C_n/\partial t + u \partial C_n/\partial z &= D \partial^2 C_n/\partial z^2 - \sum_{j=1}^l k_{nj} C_j \\
 \partial C_{n+1}/\partial t &= - \sum_{j=1}^l k_{n+1,j} C_j \\
 &\quad \vdots \qquad \qquad \qquad \vdots \\
 \partial C_l/\partial t &= - \sum_{j=1}^l k_{lj} C_j
 \end{aligned} \right\} \quad (19)$$

where C_1, C_2, \dots, C_n denote the concentrations in the mobile phase and C_{n+1}, \dots, C_l those in the stationary phases.

Provided that there is no solute in the column at $t = 0$ and the i th species as a reactant is introduced into the mobile phase in the form of $f_i(t)$, the initial and boundary condition are reduced to

$$\left. \begin{aligned}
 C_i(0, z) = 0, C_i(t, 0) = f_i(t), C_i(t, \infty) = 0 &\quad \text{for } i = 1, 2, \dots, n \\
 C_i(0, z) = 0, C_i(t, 0) = 0 &\quad \text{for } i = n+1, \dots, l
 \end{aligned} \right\} \quad (20)$$

Transforming eqn. 19 into the Laplace domain, and using the matrix representation, we obtain

$$\begin{bmatrix} D \frac{d^2 \bar{C}_1}{dz^2} - u \frac{d \bar{C}_1}{dz} \\ D \frac{d^2 \bar{C}_2}{dz^2} - u \frac{d \bar{C}_2}{dz} \\ \vdots \\ D \frac{d^2 \bar{C}_n}{dz^2} - u \frac{d \bar{C}_n}{dz} \\ 0 \\ 0 \\ \vdots \\ 0 \end{bmatrix} = (K + s E_l) \begin{bmatrix} \bar{C}_1 \\ \bar{C}_2 \\ \vdots \\ \bar{C}_n \\ \bar{C}_{n+1} \\ \bar{C}_{n+2} \\ \vdots \\ \bar{C}_l \end{bmatrix} \quad (21)$$

where E_l is l th-order unit matrix and

$$K = \begin{bmatrix} k_{11} & k_{12} & \dots & k_{1l} \\ k_{21} & & \dots & k_{2l} \\ \vdots & & & \vdots \\ \vdots & & & \vdots \\ k_{l1} & & \dots & k_{ll} \end{bmatrix} \quad (22)$$

As elution of solutes is observable only for C_1, C_2, \dots, C_n in the chromatogram, the terms C_{n+1}, \dots, C_l are eliminated from eqn. 21 with the aid of Cramer's rule, to result in

$$\left. \begin{aligned} B (D \frac{d^2 \bar{C}}{dz^2} - u \frac{d \bar{C}}{dz}) - C = 0 \\ \bar{C}(s, 0) = \bar{F}(s), \bar{C}(s, \infty) = 0 \end{aligned} \right\} \quad (23)$$

where

$$B = \begin{bmatrix} |K + sE_l|_{11} & - |K + sE_l|_{21} & \dots & (-1)^{n+1} |K + sE_l|_{n1} \\ - |K + sE_l|_{12} & \dots & & \vdots \\ \vdots & & & \vdots \\ (-1)^n |K + sE_l|_{1n} & \dots & \dots & |K + sE_l|_{nn} \end{bmatrix} / |K + sE| \quad (24)$$

and

$$\bar{C}(s, z) = \begin{bmatrix} \bar{C}_1(s, z) \\ \bar{C}_2(s, z) \\ \vdots \\ \bar{C}_n(s, z) \end{bmatrix}$$

In eqn. 24, $|K + sE_i|_{ij}$ is the determinant of the sub-matrix obtained by eliminating the i th row and j th column from the matrix $K + sE_i$. The solution for eqn. 23 is calculated to give

$$\bar{C}(s, z) = \exp \left\{ \left[(u/2D) - \sqrt{(u/2D)^2 + (B^{-1}/D)} \right] z \right\} \bar{F}(s) \quad (25)$$

where B^{-1} is the inverse matrix of B .

In the same manner as described in eqn. 7, the exponential part of eqn. 25 is defined by

$$\exp \left\{ \left[(u/2D) - \sqrt{(u/2D)^2 + (B^{-1}/D)} \right] z \right\} = \sum_{i=1}^n P_i \exp \left\{ \left[(u/2D) - \sqrt{(u/2D)^2 + (1/D\lambda_i)} \right] z \right\} \quad (26)$$

where λ_i is the i th eigenvalue of matrix B , which is obtained by solving the equation

$$|B - \lambda E_n| = 0 \quad (27)$$

and

$$P_i = \frac{(B - \lambda_1 E_n)(B - \lambda_2 E_n) \cdots (B - \lambda_{i-1} E_n)(B - \lambda_{i+1} E_n) \cdots (B - \lambda_n E_n)}{(\lambda_i - \lambda_1)(\lambda_i - \lambda_2) \cdots (\lambda_i - \lambda_{i-1})(\lambda_i - \lambda_{i+1}) \cdots (\lambda_i - \lambda_n)} \quad (28)$$

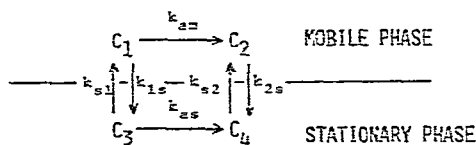


Fig. 2. Non-equilibrium partition model.

As an actual case of non-equilibrium chromatography, we now consider a model as shown in Fig. 2, where k_{1s} , k_{2s} , k_{s1} and k_{s2} are the rate constants of solute transfer between the phases. In this instance, the mass balance can be described by

$$\left. \begin{aligned} \partial C_1 / \partial t + u \partial C_1 / \partial z &= D \partial^2 C_1 / \partial z^2 - k_{1s} C_1 - k_{sm} C_1 + k_{s1} C_2 \\ \partial C_2 / \partial t + u \partial C_2 / \partial z &= D \partial^2 C_2 / \partial z^2 - k_{2s} C_2 + k_{sm} C_1 + k_{s2} C_4 \\ \partial C_3 / \partial t &= k_{1s} C_1 - k_{s1} C_3 - k_{as} C_3 \\ \partial C_4 / \partial t &= k_{2s} C_2 + k_{2s} C_2 - k_{s2} C_4 \end{aligned} \right\} \quad (29)$$

By Laplace transformation of eqn. 29 with respect to t and applying the result to eqn. 21, it is found that

$$K + sE = \begin{bmatrix} k_{1s} + k_{sm} + s & 0 & -k_{s1} & 0 \\ -k_{sm} & k_{2s} + s & 0 & -k_{s2} \\ -k_{1s} & 0 & k_{s1} + k_{as} + s & 0 \\ 0 & -k_{2s} & -k_{as} & k_{s2} + s \end{bmatrix} \quad (30)$$

From eqn. 24

$$B = \begin{bmatrix} |K + sE|_{11} & -|K + sE|_{21} \\ -|K + sE|_{12} & |K + sE|_{22} \end{bmatrix} / |K + sE| \quad (31)$$

where

$$\begin{cases} |K + sE| = s(k_{2s} + k_{s2} + s)[(k_{1s} + k_{am} + s)(k_{s1} + k_{as} + s) - k_{s1}k_{1s}] \\ |K + sE|_{11} = s(k_{s1} + k_{as} + s)(k_{2s} + k_{s2} + s) \\ |K + sE|_{21} = 0 \\ |K + sE|_{12} = -k_{am}(k_{s1} + k_{as} + s)(k_{s2} + s) - k_{1s}k_{as}k_{s2} \\ |K + sE|_{22} = (k_{1s} + k_{am} + s)(k_{s1} + k_{as} + s)(k_{s2} + s) - k_{1s}k_{s1}(k_{s2} + s) \end{cases}$$

Therefore, the eigenvalues for B are obtained from eqn. 27 as

$$\left. \begin{aligned} \lambda_1 &= |K + sE|_{11} \\ \lambda_2 &= |K + sE|_{22} \end{aligned} \right\} \quad (32)$$

Combining eqns. 31 and 32 with eqn. 28, then substituting the resulting P_i into eqn. 26, we obtain

$$\begin{aligned} & e^{[(u/2D) - \sqrt{(u/2D)^2 + (B^{-1}/D)}]z} = \\ & = \begin{bmatrix} e^{[(u/2D) - \sqrt{a_{11}(s)}]z} & 0 \\ a_{12}(s) [e^{[(u/2D) - \sqrt{a_{11}(s)}]z} - e^{[(u/2D) - \sqrt{a_{22}(s)}]z}] & e^{[(u/2D) - \sqrt{a_{22}(s)}]z} \end{bmatrix} \quad (33) \end{aligned}$$

where

$$\begin{aligned} a_{11}(s) &= (u/2D)^2 + \frac{|K + sE|}{D |K + sE|_{11}} \\ a_{22}(s) &= (u/2D)^2 + \frac{|K + sE|}{D |K + sE|_{22}} \\ a_{12}(s) &= \frac{|K + sE|_{12}}{|K + sE|_{22} - |K + sE|_{11}} \end{aligned}$$

Provided that the input distribution is regarded as the Dirac δ -function, then

$$\tilde{F}(s) = \begin{bmatrix} m \\ 0 \end{bmatrix} \quad (34)$$

By using eqns. 33 and 34, the transformed solutions can be obtained from eqn. 25:

$$\left. \begin{aligned} \tilde{C}_1(s, z) &= m \exp\{[(u/2D) - \sqrt{a_{11}(s)}]z\} \\ \tilde{C}_2(s, z) &= m a_{12}(s) (\exp\{[(u/2D) - \sqrt{a_{11}(s)}]z\} - \exp\{[(u/2D) - \sqrt{a_{22}(s)}]z\}) \end{aligned} \right\} \quad (35)$$

From these equations, the zero and first normal moments for the reactant and the product are calculated, finally leading to

$$\left. \begin{aligned} M_{01} &= m \exp \{[(u/2D) - \sqrt{a_{11}(0)}]z\} \\ M_{02} &= m(1 - \exp \{[(u/2D) - \sqrt{a_{11}(0)}]z\}) \end{aligned} \right\} \quad (36)$$

and

$$\left. \begin{aligned} t_{R1} &= \frac{z a'_{11}(0)}{2\sqrt{a_{11}(0)}} \\ t_{R2} &= \frac{-z a'_{22}(0)/2\sqrt{a_{22}(0)} + z a'_{11}(0)/2\sqrt{a_{11}(0)} \cdot e^{uz/2D} + a'_{12}(0)}{1 - \exp \{[(u/2D) - \sqrt{a_{11}(0)}]z\}} \end{aligned} \right\} \quad (37)$$

respectively, where

$$a_{11}(0) = (u/2D)^2 + \left(k_{am} + \frac{k_{1s}k_{as}}{k_{s1} + k_{cs}}\right)/D$$

$$a_{22}(0) = (u/2D)^2$$

$$a'_{11}(0) = \left[1 + \frac{k_{s1}k_{1s}}{(k_{s1} + k_{as})^2}\right]/D$$

$$a'_{22}(0) = \frac{k_{2s} + k_{s2}}{D k_{s2}}$$

$$a'_{12}(0) = \frac{k_{1s}k_{s2} + k_{s1}k_{1s} - k_{s1}k_{2s} + k_{as}k_{2s} - k_{as}k_{2s} - k_{1s}k_{s1}k_{s2}}{k_{s2}(k_{1s}k_{as} + k_{am}k_{s1} + k_{am}k_{as})}$$

Finally, we emphasize that these results permit quantitative calculations of the retention behaviour and peak areas not only of reactants but also of products, the latter for the first time.

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