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A GENERAL SOLUTION OF SOLUTE DIFFUSION WITH REVERSIBLE REACTION

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Abstract—A general method of analysis is presented for the solution of the problem of diffusion of a solute in a finite medium in which a first-order reversible reaction takes place. In this problem, a solute from a well-stirred solution of finite volume diffuses into a material of finite volume. Inside the material volume, the diffusing solute is immobilized into a non-diffusing product at a rate proportional to the concentration of the 'solute free-to-diffuse'. A reversible reaction also takes place. General analytical solutions are presented for the concentrations of the 'solute free-to-diffuse' and the 'immobilized solute' in the three-dimensional material volume as a function of time and space. To illustrate the application, the general solution for the one-dimensional, time dependent case is used to obtain the solution of a specific diffusion problem inside a slab, cylinder and sphere.

NOMENCLATURE

a, radius of a cylinder or sphere; or half thickness of a slab;
A, surface area for material;
$C(r, t)$, concentration of solute free-to-move in the medium;
C_0, initial concentration of solute in the solution;
D, diffusion coefficient in equation (30a);
$f_1(\mathbf{x})$, initial concentration of solute free-to-move in the medium;
$f_2(\mathbf{x})$, initial concentration of immobilized solute in the medium;
$J_m(x)$, Bessel function;
$k(\mathbf{x})$, coefficient in equation (1d);
$K_\delta = \frac{\delta a^2}{D}$, coefficient in equation (33b);
$K_\eta = \frac{\eta a^2}{D}$, coefficient in equation (33b);
$K_v = \frac{Aa}{V}$, coefficient in equation (33d);
m, exponent which is taken as $\frac{1}{2}$, 0 and $-\frac{1}{2}$ for slab, cylinder and sphere respectively;
N_i, normalization integral defined by equation (12b);
p, the Laplace transform variable;
$P(\mathbf{x}, t)$, the source term in equation (1a);
r, the space variable;
$S(r, t)$, concentration of solute immobilized in the medium;
t, time variable;
$T_1(\mathbf{x}, t)$, concentration of solute free-to-move in the medium;
$T_2(\mathbf{x}, t)$, concentration of solute immobilized in the medium;
$u_1(x, t)$, particular solution of equation (27a);
$\mathbf{x}$, general space coordinate;
x, one-dimensional space coordinate;
V, volume of the solution;
$w(\mathbf{x}, t)$, coefficient in equation (1a);

Greek letters

α_1, α_2, coefficients in equation (1b);
$\alpha, \beta(\mathbf{x})$, coefficients in the boundary condition operator (1b);
$\psi_1(x), \psi_2(x)$, eigenfunctions defined by equations (5a) and (5b);
$\phi(t)$, concentration of solute in the solution;
ϕ_0, initial concentration of solute in the solution;
μ_i, eigenvalues;
γ, coefficient in equation (1d);
$\xi = \frac{r}{a}$, dimensionless space variable;
δ, η, coefficients in equation (30b);
$\tau = \frac{Dt}{a^2}$, dimensionless time variable;

Scalar product (f_1, f_2) of two functions is defined as

$$(f_1, f_2) \equiv \int_V w(\mathbf{x}) f_1(\mathbf{x}) f_2(\mathbf{x}) \mathrm{d}v.$$

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INTRODUCTION

THE PROBLEM of solute diffusion from a well-stirred limited volume of solution into a material region of finite volume is of interest in numerous engineering applications. A limited number of studies available in the literature on this subject are concerned only with the analysis of very specific situations [1–3]. Here we consider a general problem in which a solute from a finite volume of well-stirred solution diffuses into a finite material volume. The concentration of the solute in the solution depends only on time and is determined by a mass balance at the boundaries of the material region; that is, the amount of solute leaving the solution should be equal to that entering the material region through its boundary surfaces. Then, as the solute diffuses through the region, a first-order reversible reaction takes place. That is, the solute is immobilized at rate proportional to the concentration of the 'solute free-to-diffuse' to form a non-diffusing product with a reversible process. Let $T_1(\mathbf{x},t)$ be the concentration to the 'solute free-to-diffuse' at the location $\mathbf{x}$ and $T_2(\mathbf{x},t)$ be the concentration of the non-diffusing (i.e. immobilized) solid at the location $\mathbf{x}$ in the material volume V. The mathematical formulation of this mass diffusion problem is given by

$$w(\mathbf{x})\left[\frac{\partial T_1(\mathbf{x},t)}{\partial t}+\frac{\partial T_2(\mathbf{x},t)}{\partial t}\right]+LT_1(\mathbf{x},t)=P(\mathbf{x},t), \quad \mathbf{x}\in V, \quad t>0 \qquad (1a)$$

$$\frac{\partial T_2(\mathbf{x},t)}{\partial t}=\sigma_1 T_1(\mathbf{x},t)-\sigma_2 T_2(\mathbf{x},t), \quad \mathbf{x}\in V, \quad t>0 \qquad (1b)$$

subject to the boundary conditions

$$BT_1(\mathbf{x},t)=\phi(t), \quad \mathbf{x}\in S, \quad t>0 \qquad (1c)$$

$$\frac{d\phi(t)}{dt}+\gamma\int_S k(\mathbf{x})\frac{\partial T_1(\mathbf{x},t)}{\partial n}\,ds=0, \quad \mathbf{x}\in S, \quad t>0 \qquad (1d)$$

and the initial conditions

$$T_k(\mathbf{x},0)=f_k(\mathbf{x}), \quad k=1,2, \quad \mathbf{x}\in V \qquad (1e)$$

$$\phi(0)=\phi_0 \qquad (1f)$$

where the operators B and L are defined as

$$L\equiv-\nabla\cdot[k(\mathbf{x})\nabla] \qquad (1g)$$

$$B\equiv\alpha+\beta(\mathbf{x})k(\mathbf{x})\frac{\partial}{\partial n} \qquad (1h)$$

$\partial/\partial n$ is the normal derivative at the boundary surface S in the *outward* direction, α is a constant, $\beta(\mathbf{x})$ and $k(\mathbf{x})$ are coefficients.

In this mass diffusion problem we are concerned with the determination of the distribution of concentrations of the 'solute free-to-diffuse', $T_1(\mathbf{x},t)$, and the 'immobilized component', $T_2(\mathbf{x},t)$, in the material region V. The solution of this problem is given in the following section.

ANALYSIS

This problem can be solved by the combined application of the Laplace transform and the finite integral transform as now described.

The Laplace transform of the system (1) with respect to the time variable t yields

$$pw(\mathbf{x})[\hat{T}_1(\mathbf{x},p)+\hat{T}_2(\mathbf{x},p)]-w(\mathbf{x})[f_1(\mathbf{x})+f_2(\mathbf{x})]+L\hat{T}_1(\mathbf{x},p)=\hat{P}(\mathbf{x},p), \quad \mathbf{x}\in V \qquad (2a)$$

$$p\hat{T}_2(\mathbf{x},p)-f_2(\mathbf{x})=\sigma_1\hat{T}_1(\mathbf{x},p)-\sigma_2\hat{T}_2(\mathbf{x},p), \quad \mathbf{x}\in V \qquad (2b)$$

$$B\hat{T}_1(\mathbf{x},p)=\hat{\phi}(p), \quad \mathbf{x}\in S \qquad (2c)$$

$$\hat{\phi}(p)=\frac{1}{p}\left[\phi_0-\gamma\int_S k(\mathbf{x})\frac{\partial\hat{T}_1(\mathbf{x},p)}{\partial n}\,ds\right], \quad \mathbf{x}\in S \qquad (2d)$$

where p is the Laplace transform variable and the superscript ($\hat{}$) denotes the Laplace transform of the function with respect to t.

Equation (2a) is integrated over the region V, the volume integral involving the L operator is changed to the surface integral; we find

$$\int_S k(\mathbf{x})\frac{\partial\hat{T}_1(\mathbf{x},p)}{\partial n}\,ds=p(1,\hat{T}_1+\hat{T}_2)-(1,f_1+f_2)-\int_V\hat{P}(\mathbf{x},p)dv \qquad (3a)$$

where the *scalar product* of two functions $f_1(\mathbf{x})$ and $f_2(\mathbf{x})$ is defined as

$$(f_1,f_2)\equiv\int_V w(\mathbf{x})f_1(\mathbf{x})f_2(\mathbf{x})dv. \qquad (3b)$$

This result is introduced into equation (2d) and the resulting expression for $\hat{\phi}(p)$ is substituted into equation (2c); we obtain

$$B\hat{T}_1(\mathbf{x},p)+\gamma(1,\hat{T}_1+\hat{T}_2)=g(p) \qquad (4a)$$

where

$$g(p)=\frac{1}{p}\left[\phi_0+\gamma(1,f_1+f_2)+\gamma\int_V\hat{P}(\mathbf{x},p)dv\right]. \qquad (4b)$$

Now, the problem is reduced to the solution of equations (2a) and (2b) subject to the boundary condition (4). The problem defined by equation (2a), (2b) and (4) can be solved by the application of the finite integral transform technique. The development of the integral transform pair and the use of this transform pair for the solution of the problem are described below.

Development of the integral transform pair

To develop the integral transform pair appropriate for the solution of the above problem we consider the following eigenvalue problem

$$\mu^2 w(\mathbf{x})[\psi_1(\mathbf{x}) + \psi_2(\mathbf{x})] = L\psi_1(\mathbf{x}), \qquad \mathbf{x}\in V \quad (5a)$$

$$\mu^2\psi_2(\mathbf{x}) = \sigma_2\psi_2(\mathbf{x}) - \sigma_1\psi_1(\mathbf{x}), \qquad \mathbf{x}\in V \quad (5b)$$

$$B\psi_1(\mathbf{x}) + \gamma(1,\psi_1 + \psi_2) = 0, \qquad \mathbf{x}\in S \quad (5c)$$

where the linear operators L and B are defined by equations (1g) and (1h) respectively.

We now consider the expansion of the function $\hat{T}_k(\mathbf{x},p)$, $k = 1,2$, in terms of the eigenfunctions of the above eigenvalue problem in the form

$$\hat{T}_k(\mathbf{x},p) = \sum_{i=1}^{\infty} A_i(p)\psi_{ki}(\mathbf{x}), \qquad k = 1,2, \quad \mathbf{x}\in V \quad (6)$$

where the summation is taken over all discrete eigenvalues. To determine the coefficients $A_i(p)$, the orthogonality condition for these eigenfunctions is needed. It can be shown that the following relations hold among the eigenfunctions $\psi_{1k} \equiv \psi_1(\lambda_k,\mathbf{x})$, $\psi_{2k} \equiv \psi_2(\lambda_k,\mathbf{x})$ with $k = i$ or j:

$$(\mu_i^2-\mu_j^2)(\psi_{1i},\psi_{1j}) = \int_S k(\mathbf{x})\begin{vmatrix}\psi_{1i}(\mathbf{x}) & \dfrac{\partial\psi_{1i}(\mathbf{x})}{\partial n}\\ \psi_{1j}(\mathbf{x}) & \dfrac{\partial\psi_{1j}(\mathbf{x})}{\partial n}\end{vmatrix}\mathrm{d}s + \sigma_2\int_V w(\mathbf{x})\begin{vmatrix}\psi_{1i}(\mathbf{x}) & \psi_{2i}(\mathbf{x})\\ \psi_{1j}(\mathbf{x}) & \psi_{2j}(\mathbf{x})\end{vmatrix}\mathrm{d}v \quad (7)$$

and

$$(\mu_i^2-\mu_j^2)(\psi_{2i},\psi_{2j}) = -\sigma_1\int_V w(\mathbf{x})\begin{vmatrix}\psi_{1i}(\mathbf{x}) & \psi_{2i}(\mathbf{x})\\ \psi_{1j}(\mathbf{x}) & \psi_{2j}(\mathbf{x})\end{vmatrix}\mathrm{d}v. \quad (8)$$

Equation (7) is multiplied by σ_1, equation (8) by σ_2 and the results are added

$$(\mu_i^2-\mu_j^2)\sum_{k=1}^{2}\sigma_k(\psi_{ki},\psi_{kj}) = \sigma_1\int_S k(\mathbf{x})\begin{vmatrix}\psi_{1i}(\mathbf{x}) & \dfrac{\partial\psi_{1i}(\mathbf{x})}{\partial n}\\ \psi_{1j}(\mathbf{x}) & \dfrac{\partial\psi_{1j}(\mathbf{x})}{\partial n}\end{vmatrix}\mathrm{d}s. \quad (9)$$

The functions $\psi_{1i}(\mathbf{x})$ and $\psi_{1j}(\mathbf{x})$, obtained from the boundary condition (5c), are introduced into the RHS of equation (9). After some manipulation we find

$$(\mu_i^2-\mu_j^2)\sum_{k=1}^{2}\sigma_k(\psi_{ki},\psi_{kj}) = \frac{\sigma_1}{\alpha}\begin{vmatrix}-\gamma(1,\psi_{1i}+\psi_{2i}) & \displaystyle\int_S k\frac{\partial\psi_{1i}}{\partial n}\mathrm{d}s\\ -\gamma(1,\psi_{1j}+\psi_{2j}) & \displaystyle\int_S k\frac{\partial\psi_{1j}}{\partial n}\mathrm{d}s\end{vmatrix}. \quad (10)$$

Now, the integration of equation (5a) over V gives

$$\int_S k(\mathbf{x})\frac{\partial\psi_1}{\partial n}\mathrm{d}s = -\mu^2(1,\psi_1+\psi_2). \quad (11)$$

Introducing this expression on the RHS of equation (10) and after some manipulation we obtain the following orthogonality relation

$$\alpha\sum_{k=1}^{2}\sigma_k(\psi_{ki},\psi_{kj}) + \gamma\sigma_1(1,\psi_{1i}+\psi_{2i}) \times(1,\psi_{1j}+\psi_{2j}) = \delta_{ij}N_i \quad (12a)$$

where δ_{ij} is the kroneker delta and

$$N_i \equiv \alpha\sum_{k=1}^{2}\sigma_k(\psi_{ki},\psi_{ki}) + \gamma\sigma_1(1,\psi_{1i}+\psi_{2i})^2. \quad (12b)$$

This orthogonality relation is now used to determine the coefficients $A_i(p)$ in the expansion (6). That is, both sides of equation (6) are multiplied by

$$w(\mathbf{x})[\alpha\sigma_k\psi_{kj}(\mathbf{x}) + \gamma\sigma_1(1,\psi_{1j}+\psi_{2j})]$$

and the result is added for $k = 1$ and 2, integrated over the region V and the orthogonality condition is utilized; one immediately obtains the expression for $A_i(p)$. When this expression is introduced into the expansion (6) we obtain

$$\hat{T}_k(\mathbf{x},p) = \sum_{i=1}^{\infty}\frac{1}{N_i}\psi_{ki}(\mathbf{x})\left[\alpha\sum_{k=1}^{2}\sigma_k(\psi_{ki},\hat{T}_k) + \gamma\sigma_1(1,\psi_{1i}+\psi_{2i})(1,\hat{T}_1+\hat{T}_2)\right]. \quad (13a)$$

For the special case of $\hat{T}_k(\mathbf{x},p) = 1/\alpha\sigma_k$ we obtain from this expansion the following identity

$$\sum_{i=1}^{\infty}\frac{1}{N_i}\psi_{ki}(\mathbf{x})(1,\psi_{1i}+\psi_{2i}) = \left[\alpha\sigma_k + \frac{\sigma_k}{\sigma_2}\gamma(1,\sigma_1+\sigma_2)\right]^{-1}. \quad (13b)$$

The expansion (13a) can be split up into two parts to define the desired integral transform pair as

Inversion formula:

$$\hat{T}_k(\mathbf{x},p) = \sum_{i=1}^{\infty}\frac{1}{N_i}\psi_{ki}(\mathbf{x})\hat{T}_i(p), \qquad k = 1,2. \quad (14)$$

Finite integral transform:

$$\hat{T}_i(p) = \alpha\sum_{k=1}^{2}\sigma_k(\psi_{ki},\hat{T}_k) + \gamma\sigma_1(1,\psi_{1i}+\psi_{2i})(1,\hat{T}_1+\hat{T}_2) \quad (15)$$

where N_i is defined by equation (12b).

Method of solution

The above finite integral transform pair is applied to solve the problem defined by equations (2a) and (2b) subject to the boundary condition (4) as now described.

Equations (2a), (2b), (5a) and (5b) are multiplied by $\sigma_1\psi_{1i}(\mathbf{x})$, $\sigma_2 w(\mathbf{x})\psi_{2i}(\mathbf{x})$, $\sigma_1\hat{T}_1(\mathbf{x},p)$ and $\sigma_2 w(\mathbf{x})\hat{T}_2(\mathbf{x},p)$, respectively, integrated over the region V, the results are added, the volume integral involving the L operator is changed into the surface integral and after some manipulations we obtain

$$(p+\mu_i^2)\sum_{k=1}^{2}\sigma_k(\psi_{ki},\hat{T}_k) = \sum_{k=1}^{2}\sigma_k(\psi_{ki},f_k) + \sigma_1\int_S k(\mathbf{x})\begin{vmatrix}\psi_{1i}(\mathbf{x}) & \dfrac{\partial\psi_{1i}(\mathbf{x})}{\partial n}\\ \hat{T}_1(\mathbf{x},p) & \dfrac{\partial\hat{T}_1(\mathbf{x},p)}{\partial n}\end{vmatrix}\mathrm{d}s + \int_V \psi_{1i}(\mathbf{x})\hat{P}(\mathbf{x},p)\mathrm{d}v \quad (16a)$$

To evaluate the integrand of the surface integral in this expression, $\psi_{1i}(\mathbf{x})$ and $\hat{T}_1(\mathbf{x},p)$ are determined from equations (5c) and (4a) respectively and introduced into the integrand; the equation (16a) takes the form

$$(p+\mu_i^2)\sum_{k=1}^{2}\sigma_k(\psi_{ki},\hat{T}_k) = \sum_{k=1}^{2}\sigma_k(\psi_{ki},f_k) + \sigma_1\left\{\frac{1}{\alpha}\begin{vmatrix}-\gamma(1,\psi_{1i}+\psi_{2i}) & \displaystyle\int_S k(\mathbf{x})\frac{\partial\psi_{1i}}{\partial n}\mathrm{d}s\\ g(p)-\gamma(1,T_1+T_2) & \displaystyle\int_S k(\mathbf{x})\frac{\partial\hat{T}_1}{\partial n}\mathrm{d}s\end{vmatrix}\right. + \int_V \psi_{1i}(\mathbf{x})\hat{P}(\mathbf{x},p)\mathrm{d}v \quad (16b)$$

By integrating equations (5a) and (2a) over the region V and changing the volume integral to the surface integral we respectively obtain

$$\int_S k(\mathbf{x})\frac{\partial\psi_1(\mathbf{x})}{\partial n}\mathrm{d}s = -\mu^2(1,\psi_1+\psi_2) \quad (17a)$$

$$\int_S k(\mathbf{x})\frac{\partial\hat{T}_1(\mathbf{x},p)}{\partial n}\mathrm{d}s = p(1,\hat{T}_1+\hat{T}_2) - (1,f_1+f_2) - \left(\frac{1}{w},P\right). \quad (17b)$$

These results are introduced into equation (16b), the definition of the integral transform (15) is utilized and after some manipulations we obtain

$$\bar{\hat{T}}_i(p) = \frac{1}{p+\mu_i^2}\tilde{f}_i + \frac{\alpha\sigma_1}{p+\mu_i^2}\int_V \psi_{1i}(\mathbf{x})\hat{P}(\mathbf{x},p)\mathrm{d}v + \sigma_1(1,\psi_{1i}+\psi_{2i})\left\{\left(\frac{1}{p}-\frac{1}{p+\mu_i^2}\right)\times[\phi_0+\gamma\cdot(1,f_1+f_2)] + \frac{\gamma}{p}\int_V \hat{P}(\mathbf{x},p)\mathrm{d}v\right\} \quad (18a)$$

where

$$\tilde{f}_i = \alpha\sum_{k=1}^{2}\sigma_k(\psi_{ki},f_k) + \gamma\sigma_1(1,\psi_{1i}+\psi_{2i})(1,f_1+f_2). \quad (18b)$$

The integral transform (18a) is substituted into the inversion formula (14), the identity (13b) is utilized and the inverse Laplace transform is taken. The solution of the problem defined by equations (1) becomes

$$T_k(\mathbf{x},t) = \sigma_1\left[\phi_0+\gamma(1,f_1+f_2) + \gamma\int_0^t\int_V P(\mathbf{x},t')\mathrm{d}v\,\mathrm{d}t'\right]\cdot\left[\alpha\sigma_k+\gamma(1,\sigma_1+\sigma_2)\frac{\sigma_k}{\sigma_2}\right]^{-1} + \sum_{i=1}^{\infty}\frac{1}{N_i}\mathrm{e}^{-\mu_i^2 t}\psi_{ki}(\mathbf{x})\left\{\alpha\sum_{k=1}^{2}\sigma_k(\psi_{ki},f_k) - \phi_0\sigma_1(1,\psi_{1i}+\psi_{2i}) + \alpha\sigma_1\int_0^t\int_V \psi_{1i}(\mathbf{x})P(\mathbf{x},t')\mathrm{e}^{\mu_i^2 t'}\mathrm{d}v\,\mathrm{d}t'\right\}. \quad (19)$$

THE ONE-DIMENSIONAL CASE

For the one-dimensional case the problem given by equations (1) becomes

$$w(x)\left[\frac{\partial T_1(x,t)}{\partial t}+\frac{\partial T_2(x,t)}{\partial t}\right] = \frac{\partial}{\partial x}\left[k(x)\frac{\partial T_1(x,t)}{\partial x}\right] + P(x,t), \quad \text{in } x_0\le x\le x_1, \quad t>0 \quad (20a)$$

$$\frac{\partial T_2(x,t)}{\partial t} = \sigma_1 T_1(x,t) - \sigma_2 T_2(x,t), \quad \text{in } x_0\le x\le x_1, \quad t>0 \quad (20b)$$

the boundary conditions take the form

$$\frac{\partial T_1(x_0,t)}{\partial x} = 0 \quad (20c)$$

$$\alpha T_1(x_1,t) + \beta k(x_1)\frac{\partial T_1(x_1,t)}{\partial x} = \phi(t) \quad (20d)$$

$$\frac{\mathrm{d}\phi(t)}{\mathrm{d}t} + \gamma k(x_1)\frac{\partial T_1(x_1,t)}{\partial x} = 0 \quad (20e)$$

and the initial conditions reduce to

$$T_k(x,0) = f_k(x), \quad k=1,2 \quad \text{in } x_0\le x\le x_1 \quad (20f)$$

$$\phi(0) = \phi_0. \quad (20g)$$

The solution of the problem (20) is obtainable from the one-dimensional form of the general solution given by equation (19); we find

$$T_k(x,t) = \left\{\phi_0+\gamma\int_{x_0}^{x_1} w(x')[f_1(x')+f_2(x')]\mathrm{d}x' + \gamma\int_0^t\int_{x_0}^{x_1} P(x',t')\mathrm{d}x'\,\mathrm{d}t'\right\}\cdot\left(\frac{\sigma_1\sigma_2}{\sigma_k}\right)\cdot\left\{\alpha\sigma_2+\gamma(\sigma_1+\sigma_2)\int_{x_0}^{x_1} w(x')\mathrm{d}x'\right\}^{-1}$$

$$+\sum_{i=1}^{\infty}\frac{1}{N_i}e^{-\mu_i^2 t}\psi_{ki}(x)\left\{\alpha\sum_{k=1}^{2}\sigma_k\int_{x_0}^{x_1}w(x')\right.$$
$$\times\psi_{ki}(x')f_k(x')dx' - \phi_0\sigma_1\int_{x_0}^{x_1}w(x')$$
$$\times[\psi_{1i}(x')+\psi_{2i}(x')]dx' + \alpha\sigma_1\int_0^t\int_{x_0}^{x_1}\psi_{1i}(x')$$
$$\left.\times P(x',t')e^{\mu_i^2 t'}dx'dt'\right\}, \qquad k=1,2 \quad (21)$$

where N_i is defined by equation (12b), that is

$$N_i=\alpha\sum_{k=1}^{2}\sigma_k\int_{x_0}^{x_1}w(x)\psi_{ki}^2(x)dx$$
$$+\gamma\sigma_1\left[\int_{x_0}^{x_1}w(x)[\psi_{1i}(x)+\psi_{2i}(x)]dx\right]^2. \quad (22)$$

The eigenfunctions $\psi_{ki}(x)$ and the eigenvalues μ_i needed for the solution (21) are determined as now described.

Eigenfunctions and eigenvalues

The eigenvalue problem appropriate for the one-dimensional problem (20) is taken as the one-dimensional form of the above general eigenvalue problem (5). Then, equations (5a) and (5b) respectively reduce to

$$\frac{d}{dx}\left[k(x)\frac{d\psi_1(\mu,x)}{dx}\right]$$
$$+\mu^2 w(x)[\psi_1(\mu,x)+\psi_2(\mu,x)]=0,$$
$$\text{in}\quad x_0\le x\le x_1 \quad (23a)$$

$$\mu^2\psi_2(\mu,x)=\sigma_2\psi_2(\mu,x)-\sigma_1\psi_1(\mu,x)$$
$$\text{in}\quad x_0\le x\le x_1 \quad (23b)$$

and the boundary condition (5c) is taken as

$$\psi_1'(\mu,x_1)=0 \quad (23c)$$

$$\alpha\psi_1(\mu,x_1)+\beta k(x_1)\psi_1'(\mu,x_1)$$
$$+\gamma\int_{x_0}^{x_1}w(x)[\psi_1(\mu,x)+\psi_2(\mu,x)]dx=0. \quad (23d)$$

To replace the integral term in equation (23d) by a derivative, equation (23a) is integrated with respect to x from x_0 to x_1 and the boundary condition (23c) is utilized. We obtain

$$\int_{x_0}^{x_1}w(x)[\psi_1(\mu,x)+\psi_2(\mu,x)]dx$$
$$=-\frac{1}{\mu^2}k(x_1)\psi_1'(\mu,x_1). \quad (24)$$

Introducing equation (24) into equation (23d), the boundary condition at $x=x_1$ is transformed to

$$\alpha\psi_1(\mu,x_1)+\left(\beta-\frac{\gamma}{\mu^2}\right)k(x_1)\psi_1'(\mu,x_1)=0. \quad (25)$$

Now, equation (23b) is written as

$$\psi_2(\mu,x)=\frac{\sigma_1}{\sigma_2-\mu^2}\psi_1(\mu,x). \quad (26)$$

This expression is introduced into equation (23a) and the function $\psi_2(\mu,x)$ is eliminated. We obtain

$$\frac{d}{dx}\left[k(x)\frac{d\psi_1(\lambda,x)}{dx}\right]+\lambda^2 w(x)\psi_1(\lambda,x)=0 \quad (27a)$$

where

$$\lambda^2=\mu^2\left(1+\frac{\sigma_1}{\sigma_2-\mu^2}\right). \quad (27b)$$

The solution for $\psi_1(\lambda,x)$ may be written in the form

$$\psi_1(\lambda,x)=C_1u_1(\lambda,x) \quad (28)$$

where $u_1(\lambda,x)$ is a particular solution of equation (27a) which satisfies the boundary condition (23c) at $x=x_0$.

If the solution (28) should satisfy the boundary condition (25) we obtain the following eigencondition

$$\alpha u_1(\lambda,x_1)+\left(\beta-\frac{\gamma}{\mu^2}\right)k(x_1)u_1'(\lambda,x_1)=0 \quad (29)$$

and the eigenvalues μ_i are the roots of this equation.

Application to specific problems

To illustrate the application of the results of the foregoing general analysis to the solution of specific problems in plane, cylindrical and spherical geometrics we consider the following example.

Example. Consider a material region in the form of an infinite plate of thickness $2a$ (or a long cylinder or a sphere of diameter $2a$) is immersed into a well-stirred solution of finite volume. The concentration of the solute in the solution is always uniform and initially C_0, and the material volume is initially free from the solute. For times $t>0$, the diffusion of the solute into the material volume proceeds and a first order reversible reaction occurs inside the material volume. As a result a non-diffusing product is formed (i.e. solute is immobilized). Because of symmetry, we consider the material volume occupies the space $0\le r\le a$ and the solution is confined to the space $a\le r\le(a+l)$. We wish to determine the concentration of the 'solute free-to-diffuse' and the 'non-diffusing product' as a function of time and position in the material volume. The mass diffusion problem described here has been solved in [3] for slab, cylinder and sphere. We now demonstrate that these solutions are readily obtainable as special cases from the general results given in this paper.

Solution. Let $C(r,t)$ be the concentration of the 'solute free-to-diffuse' within the body and $S(r,t)$ be that of the immobilized solute, each being expressed as amount per unit volume of the body. The mathematical formulation of this mass diffusion process is given by

$$\frac{\partial C(r,t)}{\partial t}=D\frac{1}{r^{1-2m}}\frac{\partial}{\partial r}\left(r^{1-2m}\frac{\partial C}{\partial r}\right)-\frac{\partial S(r,t)}{\partial t};$$
$$\text{in}\quad 0\le r\le a,\quad t>0 \quad (30a)$$

$$\frac{\partial S(r,t)}{\partial t} = \delta C(r,t) - \eta S(r,t),$$

$$\text{in} \quad 0 \le r \le a, \quad t > 0 \qquad (30b)$$

where

$$m = \begin{cases} \frac{1}{2} \text{ for slab} \\ 0 \text{ for cylinder} \\ -\frac{1}{2} \text{ for sphere} \end{cases} \qquad (30c)$$

The boundary condition for this problem at $r = 0$ is written by the symmetry consideration as

$$\frac{\partial C(r,t)}{\partial r} = 0 \quad \text{at} \quad r = 0, \quad t > 0. \qquad (31a)$$

The boundary condition at $r = a$ is determined by the fact that the rate at which the solute leaves the solution of volume V should be equal to that at which the solute enters the material over the surface A (i.e. for a sphere $A = 4\pi a^2$). Then we write

$$V\frac{\partial C(r,t)}{\partial t} + AD\frac{\partial C(r,t)}{\partial r} = 0$$

$$\text{at} \quad r = a, \quad t > 0. \qquad (31b)$$

The initial conditions for the solute which is free-to-move and that immobilized in the material volume are taken as

$$C(r,t) = S(r,t) = 0 \quad \text{for} \quad t = 0, \quad 0 \le r \le a. \qquad (31c)$$

Finally, the initial concentration of the solute within the solution is C_0.

In order to bring this problem into a form readily comparable with the general problem considered previously, we define the following dimensionless variables

$$\xi = \frac{r}{a}, \quad \tau = \frac{Dt}{a^2}, \quad K_\delta = \frac{\delta a^2}{D},$$

$$K_\eta = \frac{\eta a^2}{D}, \quad K_v = \frac{Aa}{V}. \qquad (32)$$

Then the mass diffusion problem defined by equations (30) and (31) take the form

$$\xi^{1-2m}\left\{\frac{\partial C(\xi,\tau)}{\partial \tau} + \frac{\partial S(\xi,\tau)}{\partial \tau}\right\} = \frac{\partial}{\partial \xi}\left\{\xi^{1-2m}\frac{\partial C(\xi,\tau)}{\partial \xi}\right\},$$

$$\text{in} \quad 0 \le \xi \le 1, \quad \tau > 0 \qquad (33a)$$

$$\frac{\partial S(\xi,\tau)}{\partial \tau} = K_\delta C(\xi,\tau) - K_\eta S(\xi,\tau),$$

$$\text{in} \quad 0 \le \xi \le 1, \quad \tau > 0 \qquad (33b)$$

$$\frac{\partial C(0,\tau)}{\partial \xi} = 0, \qquad \text{for} \quad \tau > 0 \qquad (33c)$$

$$K_v\frac{\partial C(1,\tau)}{\partial \xi} + \frac{\partial C(1,\tau)}{\partial \tau} = 0, \quad \text{for} \quad \tau > 0 \qquad (33d)$$

$$C(\xi,0) = S(\xi,0) = 0, \qquad \text{in } 0 \le \xi \le 1 \qquad (33e)$$

and the concentration of the solute in the solution is initially C_0.

Clearly, the problem (33) is a special case of the general problem (20). By the comparison of these two problems we write

$$\left.\begin{aligned} &x = \xi, \quad t = \tau, \quad T_1 = C, \quad T_2 = S, \\ &w(x) = k(x) = \xi^{1-2m}, \quad P(x,t) = 0, \\ &x_0 = 0, \quad x_1 = 1, \quad \sigma_1 = K_\delta, \quad \sigma_2 = K_\eta, \\ &\alpha = 1, \quad \beta = 0, \quad \gamma = K_v, \quad \phi_0 = C_0, \\ &f_1(x) = f_2(x) = 0. \end{aligned}\right\} \qquad (34)$$

The solution of equation (27a) for $u(\lambda, x)$ for this particular case is

$$u(\lambda, x) = (\lambda\xi)^m J_m(\lambda\xi). \qquad (35)$$

Introducing this solution into equation (29), the eigencondition for the problem is determined as

$$J_m(\lambda) + \frac{K_v}{\mu^2}\lambda J_{1-m}(\lambda) = 0. \qquad (36)$$

Then, the eigenfunctions $\psi_k(\lambda, x)$, $(k = 1,2)$, are obtained by introducing the solution (35) into equations (26) and (28). We find

$$\psi_k(\lambda, x) = C_1\left(\frac{K_\delta}{K_\eta - \mu^2}\right)^{k-1}(\lambda\xi)^m J_{-m}(\lambda\xi),$$

$$(k = 1,2) \qquad (37a)$$

where

$$\lambda_i = \mu_i\sqrt{\left(1 + \frac{K_\delta}{K_\eta - \mu_i^2}\right)} \qquad (37b)$$

and the functions $x^m J_{-m}(x)$ and $x^m J_{1-m}(x)$ for $m = -\frac{1}{2}$, 0 and $\frac{1}{2}$ are listed in Table 1.

Then, for the special case (34) considered above, the solutions (21) simplify to

$$\frac{T_k(\xi,\tau)}{C_0} = \frac{(K_\delta/K_\eta)^{k-1}}{1 + \left(1 + \frac{K_\delta}{K_\eta}\right)\frac{K_v}{2(1-m)}} + \sum_{i=1}^{\infty}\frac{\left(\frac{K_\delta}{K_\eta - \mu_i^2}\right)^{k-1} e^{-\mu_i^2\tau}}{1 + \left\{1 + \frac{K_\delta K_\eta}{(K_\eta - \mu_i^2)^2}\right\}\left\{\frac{K_v}{2} - m\frac{\mu_i^2}{\lambda_i^2} + \frac{\mu_i^4}{2K_v\lambda_i^2}\right\}}$$

Table 1. Functions $x^m J_m(x)$ and $x^m J_{1-m}(x)$

m	$x^m J_{-m}(x)$	$x^m J_{1-m}(x)$
$\frac{1}{2}$	$\sqrt{\left(\frac{2}{\pi}\right)}\cos x$	$\sqrt{\left(\frac{2}{\pi}\right)}\sin x$
0	$J_0(x)$	$J_1(x)$
$-\frac{1}{2}$	$\sqrt{\left(\frac{2}{\pi}\right)}\frac{\sin x}{x}$	$\sqrt{\left(\frac{2}{\pi}\right)}\frac{\sin x - x\cos x}{x^2}$

$$\cdot \frac{(\lambda_i \xi)^m J_{-m}(\lambda_i \xi)}{\lambda_i^m J_{-m}(\lambda_i)}, \quad (k = 1, 2). \tag{38}$$

The concentration distribution for the free solute $T_1 = C$ and the immobilized solute $T_2 = S$ is obtainable from equation (38) by setting $k = 1$ or 2 for the cases of slab ($m = \frac{1}{2}$), cylinder ($m = 0$) and sphere ($m = -\frac{1}{2}$). It can readily be shown that the results obtained in the manner for $T_1 = C$ by setting $k = 1$, after some manipulation, are identical to those given by equations (14–73), (14–80) and (14–84) for slab, cylinder and sphere in [3].

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UNE SOLUTION GENERALE DE LA DIFFUSION D'UN SOLUTE AVEC UNE REACTION REVERSIBLE

Résumé—On présente une méthode générale d'analyse pour résoudre le problème de la diffusion d'un soluté dans un milieu fini dans lequel se produit une réaction réversible du premier ordre. Dans ce problème, un soluté dans une solution parfaitement brassée de volume fini diffuse dans un matériau de volume fini. Dans ce volume, le soluté est immobilisé dans un produit non diffusant, à une vitesse proportionnelle à la concentration du soluté libre. Une réaction réversible a lieu. Des solutions générales analytiques sont présentées pour les concentrations du soluté libre à la diffusion et du soluté immobilisé, dans le volume tridimensionnel, en fonction du temps et de l'espace. Pour illustration, la solution générale du cas monodimensionnel variable en fonction du temps est utilisé pour obtenir la solution d'un problème spécifique de diffusion dans une barre, un cylindre et une sphère.

EINE ALLGEMEINE LÖSUNG FÜR DIE DIFFUSION EINES GELÖSTEN STOFFES MIT REVERSIBLER REAKTION

Zusammenfassung — Es wird eine allgemeine Untersuchungsmethode für das Problem der Diffusion eines gelösten Stoffes in einem begrenzten Medium vorgelegt, in welchem eine reversible Reaktion erster Ordnung stattfindet. Bei diesem Problem diffundiert ein gelöster Stoff aus einer homogenen Lösung mit endlichem Volumen in einen Feststoffkörper endlichen Volumens. Innerhalb des Feststoffkörpers wird der diffundierende gelöste Stoff zu einem nicht diffundierenden Produkt umgewandelt und so gebunden, und zwar mit einer Geschwindigkeit, die der Konzentration des "frei diffundierenden gelösten Stoffes" proportional ist. Dabei spielt sich eine reversible Reaktion ab. Allgemeine analytische Lösungen werden für die Konzentration des "frei diffundierenden gelösten Stoffes" und des "fest gebundenen gelösten Stoffes" in einem dreidimensionalen Feststoffkörper als Funktion von Zeit und Ort angegeben. Um die Anwendung anschaulich zu zeigen, wird die allgemeine Lösung für den eindimensionalen, zeitabhängigen Fall dazu benutzt, die Lösung für ein spezifisches Diffusionsproblem in einer Platte, einem Zylinder und einer Kugel zu erhalten.

ОБЩЕЕ РЕШЕНИЕ ДЛЯ ПРОЦЕССА ДИФФУЗИИ РАСТВОРЕННОГО ВЕЩЕСТВА ПРИ ОБРАТИМОЙ РЕАКЦИИ

Аннотация — Предложен общий метод аналитического решения задачи о диффузии растворенного вещества в среде конечного объема при наличии обратимой реакции первого порядка. Растворенное вещество из хорошо перемешанного раствора конечного объема диффундирует в другой конечный объем, внутри которого диффузия замедляется пропорционально начальной концентрации. Одновременно происходит обратимая реакция. Представлены общие аналитические решения для концентраций растворенного вещества в трехмерном случае как функций координат и времени. В качестве иллюстрации общее решение для одномерного нестационарного случая использовано для получения решения частной задачи о диффузии внутри сплошного цилиндра и сферы.