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Coupled Transport Processes in Semipermeable Media. Analytical Solutions of the Linearized Governing Equations

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March 1990

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Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

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LBL–24725

Coupled Transport Processes in Semipermeable Media. Analytical Solutions of the Linearized Governing Equations

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March 1990

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Engineering and Geosciences Division, of the U. S. Department of Energy under Contract No. DE–AC03–76SF00098.

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ABSTRACT — The thermodynamics of irreversible processes leads to nonlinear governing equations for direct and coupled mass transport processes. Analytical solutions of linearized versions of these equations can be used to verify numerical solutions of the nonlinear equations under conditions such that nonlinear terms are relatively small. This report presents derivations of the analytical solutions for one-dimensional and axisymmetric geometries.

GOVERNING EQUATIONS

Carnahan and Jacobsen (1990) have derived the governing equations for a saturated, porous or fractured system in which fluxes of heat, mass and electrical charge are driven by gradients of temperature, hydraulic potential, chemical potential and electrical potential. The derivations were based on the thermodynamics of irreversible processes.

Under the assumptions that gravitational and electrical forces are negligible, that no chemical reactions occur in the system, that the fluid phase is an ideal solution of a single solute, and that partial specific volumes and entropies of solute and solvent are constant, the balance equations are

$$\Gamma_1 \frac{\partial T}{\partial t} = -\nabla \cdot J_q - J_v \cdot \nabla P - \frac{\beta_f T}{\kappa_f} \nabla \cdot J_v - \frac{RT}{C_s M_s} J_s^o \cdot \nabla C_s, \tag{1}$$

$$\Lambda_1 \frac{\partial P}{\partial t} = -\nabla \cdot J_q - J_v \cdot \nabla P - \frac{c_{p,f}\, \rho_f}{\beta_f} \nabla \cdot J_v - \frac{RT}{C_s M_s} J_s^o \cdot \nabla C_s, \tag{2}$$

$$\epsilon_f \frac{\partial C_s}{\partial t} = -\nabla \cdot J_s, \tag{3}$$

where T is the temperature, P is the pressure, C_s is the concentration of the solute, J_q is the heat flux, J_v is the volume flux, J_s is the solute flux in the laboratory reference frame, J_s^o is the diffusional solute flux relative to motion of solvent, and Γ_1 and Λ_1 are shorthand notation for

$$\Gamma_1 = \epsilon_f\, \rho_f\, c_{v,f} + \epsilon_n\, \rho_n\, c_{v,n}, \tag{4a}$$

$$\Lambda_1 = \epsilon_f\, \rho_f\, c_{v,f} \frac{\kappa_f}{\beta_f} + \epsilon_n\, \rho_n\, c_{v,n} \frac{\kappa_n}{\beta_n}. \tag{4c}$$

All other symbols are defined in the Notation.

The fluxes to be used in (1)–(3) are given by the phenomenological equations

$$J_q = -L_{qq} \frac{\nabla T}{T} - L_{qv} \nabla P - L_{qs} \frac{RT}{C_s M_s} \nabla C_s, \tag{5}$$

$$J_v = -L_{vq} \frac{\nabla T}{T} - L_{vv} \nabla P - L_{vs} \frac{RT}{C_s M_s} \nabla C_s, \tag{6}$$

$$J_s^o = -L_{sq} \frac{\nabla T}{T} - L_{sv} \nabla P - L_{ss} \frac{RT}{C_s M_s} \nabla C_s, \tag{7}$$

with the reciprocal relations

$$L_{qs} = L_{sq}, \quad L_{qv} = L_{vq}, \quad L_{vs} = L_{sv}. \tag{8}$$

The two solute fluxes, J_s and J_s°, are related by

$$J_s = C_s\, J_v + \left(1 - C_s\, \overline{V}_s\right) J_s^\circ, \tag{9}$$

and therefore the solute flux in the laboratory frame of reference is given by

$$\begin{aligned} J_s = &- \left[C_s\, L_{vq} + \left(1 - C_s\, \overline{V}_s\right) L_{sq}\right] \frac{\nabla T}{T} \\ &- \left[C_s\, L_{vv} + \left(1 - C_s\, \overline{V}_s\right) L_{sv}\right] \nabla P \\ &- \left[C_s\, L_{vs} + \left(1 - C_s\, \overline{V}_s\right) L_{ss}\right] \frac{RT}{C_s M_s} \nabla C_s. \end{aligned} \tag{10}$$

When (5)–(7) and (10) are substituted into (1)–(3), a system of nonlinear governing equations is obtained. These equations were solved numerically by Jacobsen and Carnahan (1990). Under conditions such that the nonlinear terms are small relative to linear terms in the governing equations, the numerical results were verified by comparison with analytical solutions derived from linear versions of the governing equations. The analytical solutions were useful also in estimating contributions of nonlinear terms to magnitudes of the primary variables (T, P, C_s) and the fluxes.

Derivations of Analytical Solutions

The phenomenological equations (5), (6) and (7) may be made linear by assuming constancy of the phenomenological coefficients and by replacing factors of temperature and solute concentration by average values, denoted below by T_m and $C_{s,m}$, respectively. The linear phenomenological equations are

$$J_q = -L_{qq} \frac{\nabla T}{T_m} - L_{qv} \nabla P - L_{qs} \frac{RT_m}{C_{s,m} M_s} \nabla C_s, \tag{11}$$

$$J_v = -L_{vq} \frac{\nabla T}{T_m} - L_{vv} \nabla P - L_{vs} \frac{RT_m}{C_{s,m} M_s} \nabla C_s, \tag{12}$$

$$\begin{aligned} J_s = &- \left[C_{s,m}\, L_{vq} + \left(1 - C_{s,m}\, \overline{V}_s\right) L_{sq}\right] \frac{\nabla T}{T_m} \\ &- \left[C_{s,m}\, L_{vv} + \left(1 - C_{s,m}\, \overline{V}_s\right) L_{sv}\right] \nabla P \\ &- \left[C_{s,m}\, L_{vs} + \left(1 - C_{s,m}\, \overline{V}_s\right) L_{ss}\right] \frac{RT_m}{C_{s,m} M_s} \nabla C_s, \end{aligned} \tag{13}$$

The governing equations (1), (2) and (3) can be made linear by neglecting products of derivatives:

$$\Gamma_1 \frac{\partial T}{\partial t} = -\nabla \cdot J_q - \frac{\beta_f\, T_m}{\kappa_f} \nabla \cdot J_v, \tag{14}$$

$$\Lambda_1 \frac{\partial P}{\partial t} = -\nabla \cdot J_q - \frac{c_{p,f}\,\rho_f}{\beta_f} \nabla \cdot J_v, \tag{15}$$

$$\epsilon_f \frac{\partial C_s}{\partial t} = -\nabla \cdot J_s, \tag{16}$$

When the expressions for the fluxes from the phenomenological equations are substituted into the governing equations above, the only space derivative terms are second derivatives:

$$\frac{\partial T}{\partial t} = D_{TT}\,\nabla^2 T + D_{TP}\,\nabla^2 P + D_{TS}\,\nabla^2 C_s, \tag{17}$$

$$\frac{\partial P}{\partial t} = D_{PT}\,\nabla^2 T + D_{PP}\,\nabla^2 P + D_{PS}\,\nabla^2 C_s, \tag{18}$$

$$\frac{\partial C_s}{\partial t} = D_{ST}\,\nabla^2 T + D_{SP}\,\nabla^2 P + D_{SS}\,\nabla^2 C_s. \tag{19}$$

The D_{IJ} are functions of the material properties, phenomenological coefficients and the average values of temperature and solute concentration and are defined by

$$D_{TT} = \frac{1}{\Gamma_1}\left(\frac{L_{qq}}{T_m} + \frac{\beta_f}{\kappa_f} L_{vq}\right), \tag{20a}$$

$$D_{TP} = \frac{1}{\Gamma_1}\left(L_{qv} + \frac{\beta_f T_m}{\kappa_f} L_{vv}\right), \tag{20b}$$

$$D_{TS} = \frac{1}{\Gamma_1}\left(L_{qs} + \frac{\beta_f T_m}{\kappa_f} L_{vs}\right)\frac{RT_m}{C_{s,m} M_s}, \tag{20c}$$

$$D_{PT} = \frac{1}{\Lambda_1 T_m}\left[L_{qq} + \left(\frac{c_{p,f}\,\rho_f}{\beta_f}\right) L_{qv}\right], \tag{20d}$$

$$D_{PP} = \frac{1}{\Lambda_1}\left[L_{qv} + \left(\frac{c_{p,f}\,\rho_f}{\beta_f}\right) L_{vv}\right], \tag{20e}$$

$$D_{PS} = \frac{1}{\Lambda_1}\left[L_{qs} + \left(\frac{c_{p,f}\,\rho_f}{\beta_f}\right) L_{vs}\right]\frac{RT_m}{C_{s,m} M_s}, \tag{20f}$$

$$D_{ST} = \frac{1}{\epsilon_f T_m}\left[C_{s,m}\,L_{vq} + \left(1 - C_{s,m}\,\overline{V}_s\right) L_{sq}\right], \tag{20g}$$

$$D_{SP} = \frac{1}{\epsilon_f}\left[C_{s,m}\,L_{vv} + \left(1 - C_{s,m}\,\overline{V}_s\right) L_{sv}\right], \tag{20h}$$

$$D_{SS} = \frac{1}{\epsilon_f}\left[C_{s,m}\,L_{vs} + \left(1 - C_{s,m}\,\overline{V}_s\right) L_{ss}\right]\frac{RT_m}{C_{s,m} M_s}, \tag{20i}$$

where Γ_1 and Λ_1 are defined by (4). To complete the mathematical formulation of the problem the initial and boundary conditions must be specified. Initially all variables are assigned constant values.

The boundary conditions for T, P and C_s at the inner boundary are derived from the constant heat, solute and solvent fluxes imposed there. In a one-dimensional coordinate system, the flux boundary is located at $x = 0$, and in radial coordinates, the flux boundary is located at $r = a$. At the outer boundary, located at infinity, T, P and C_s are held constant and equal to their initial values.

The analytical solution for the system of equations above is obtained using the Laplace transform method (Carslaw and Jaeger, 1959). The transformed system of equations is given by

$$s\overline{T} - T_i = D_{TT}\,\nabla^2\overline{T} + D_{TP}\,\nabla^2\overline{P} + D_{TS}\,\nabla^2\overline{C}_s, \tag{21}$$

$$s\overline{P} - P_i = D_{PT}\,\nabla^2\overline{T} + D_{PP}\,\nabla^2\overline{P} + D_{PS}\,\nabla^2\overline{C}_s, \tag{22}$$

$$s\overline{C}_s - C_{s,i} = D_{ST}\,\nabla^2\overline{T} + D_{SP}\,\nabla^2\overline{P} + D_{SS}\,\nabla^2\overline{C}_s, \tag{23}$$

where T_i, P_i and $C_{s,i}$ are the initial values of temperature, pressure and solute concentration.

Solutions for the Fully Coupled Case in a One-Dimensional Geometry

In a one-dimensional coordinate system, $\nabla^2 = \partial^2/\partial x^2$. Using this definition in (21), (22) and (23), the transformed equations in one-dimension are

$$s\overline{T} - T_i = D_{TT}\,\frac{\partial^2\overline{T}}{\partial x^2} + D_{TP}\,\frac{\partial^2\overline{P}}{\partial x^2} + D_{TS}\,\frac{\partial^2\overline{C}_s}{\partial x^2}, \tag{24}$$

$$s\overline{P} - P_i = D_{PT}\,\frac{\partial^2\overline{T}}{\partial x^2} + D_{PP}\,\frac{\partial^2\overline{P}}{\partial x^2} + D_{PS}\,\frac{\partial^2\overline{C}_s}{\partial x^2}, \tag{25}$$

$$s\overline{C}_s - C_{s,i} = D_{ST}\,\frac{\partial^2\overline{T}}{\partial x^2} + D_{SP}\,\frac{\partial^2\overline{P}}{\partial x^2} + D_{SS}\,\frac{\partial^2\overline{C}_s}{\partial x^2}. \tag{26}$$

Noting that $\exp(-\lambda x)$ and $\exp(\lambda x)$ are solutions of

$$\frac{\partial^2 f}{\partial x^2} = \lambda^2 f, \tag{27}$$

for f, a function of x, and λ, a positive constant, it is reasonable to assume that solutions of the transformed equations above will involve exponential functions. Only exponential functions with negative arguments can satisfy the outer boundary condition, so the solutions for $\overline{T}$, $\overline{P}$ and $\overline{C}_s$ will be assumed to be of the following form:

$$\overline{T} = \frac{T_i}{s} + A\exp(-\lambda\,x), \tag{28}$$

$$\overline{P} = \frac{P_i}{s} + B\exp(-\lambda\,x), \tag{29}$$

$$\overline{C}_s = \frac{C_{s,i}}{s} + E\exp(-\lambda\,x). \tag{30}$$

where, as above, λ is a positive constant to be determined and A, B and E are to be determined from the inner boundary conditions. Substituting the expressions for $\overline{T}$, $\overline{P}$ and $\overline{C}_s$ above into the governing

equations (24), (25) and (26) yields the following matrix equation

$$\lambda^2 \begin{pmatrix} D_{TT} & D_{TP} & D_{TS} \\ D_{PT} & D_{PP} & D_{PS} \\ D_{ST} & D_{SP} & D_{SS} \end{pmatrix} \begin{pmatrix} A \\ B \\ E \end{pmatrix} = s \begin{pmatrix} A \\ B \\ E \end{pmatrix}, \tag{31}$$

which will have a nonzero solution if and only if λ is chosen such that

$$\det(\lambda^2 \mathbf{D} - s\,\mathbf{I}) = 0 \tag{32}$$

(Boyce and DiPrima, 1969). $\mathbf{D}$ is the matrix of coefficients in (31), and $\mathbf{I}$ is the identity matrix. The equation defined by (32) is a cubic in λ^2/s:

$$d_1 \left(\frac{\lambda^2}{s}\right)^3 - d_2 \left(\frac{\lambda^2}{s}\right)^2 + d_3 \left(\frac{\lambda^2}{s}\right) - 1 = 0, \tag{33}$$

where

$$d_1 = D_{TT}D_{PP}D_{SS} + D_{TP}D_{PS}D_{ST} + D_{TS}D_{PT}D_{SP}$$

$$- D_{TT}\left(D_{PS}D_{SP}\right) - D_{PP}\left(D_{TS}D_{ST}\right) - D_{SS}\left(D_{TP}D_{PT}\right), \tag{34a}$$

$$d_2 = D_{TP}D_{PT} + D_{TS}D_{ST} + D_{PS}D_{SP}$$

$$- D_{TT}D_{PP} - D_{TT}D_{SS} - D_{PP}D_{SS}, \tag{34b}$$

$$d_3 = D_{TT} + D_{PP} + D_{SS}. \tag{34c}$$

For a cubic of the form

$$y^3 + p\,y^2 + q\,y + r = 0, \tag{35}$$

Burington (1949) gives the following expression for the roots,

$$y_i = 2\sqrt{-\alpha}\cos\left[\frac{\theta}{3} + \frac{2\pi}{3}(i-1)\right] - \frac{p}{3}, \quad i = 1, 2, 3. \tag{36}$$

The intermediate variables, α and θ, are defined by

$$\alpha = \frac{1}{9}\left(3q - p^2\right), \tag{37}$$

$$\cos\theta = \begin{cases} -\sqrt{\eta^2/\alpha^3}, & \text{if } \eta > 0, \\ +\sqrt{\eta^2/\alpha^3}, & \text{if } \eta \le 0, \end{cases} \tag{38}$$

where

$$\eta = \frac{1}{54}\left(2p^3 - 9pq + 27r\right). \tag{39}$$

The expression in (36) assumes that all of the roots are real. The sign of $\alpha^3 + \eta^2$ indicates whether the roots of the cubic are real or imaginary. If $\alpha^3 + \eta^2 > 0$, then two of the roots are imaginary; if

$\alpha^3 + \eta^2 \leq 0$, then all of the roots are real. It is difficult to check this condition *a priori* for α and η defined in terms of the d_i,

$$\alpha = \frac{1}{3d_1}\left(d_3 - \frac{d_2^2}{3d_1}\right), \tag{40}$$

$$\eta = \frac{1}{2d_1}\left(\frac{d_2 d_3}{3d_1} - \frac{2d_2^3}{27d_1^2} - 1\right). \tag{41}$$

In this derivation, it has been assumed that $\alpha^3 + \eta^2 \leq 0$. When the analytical solution is calculated for given values of the material properties, phenomenological coefficients and other input parameters, this condition is checked by calculating $\alpha + (\eta/\alpha)^2$. This alternate, but equivalent, form is used because, in practice, the magnitudes of α and η are quite large.

As noted before, solutions involving exponential functions with positive arguments cannot satisfy the boundary conditions at infinity. Therefore, the λ_i are defined by

$$\lambda_i = \mu_i \sqrt{s}, \quad i = 1, 2, 3, \tag{42}$$

where

$$\mu_i = \left\{\frac{d_2}{3d_1} + 2\sqrt{-\alpha}\cos\left[\frac{\theta}{3} + \frac{2\pi}{3}(i-1)\right]\right\}^{\frac{1}{2}}, \quad i = 1, 2, 3. \tag{43}$$

The solutions to the transformed equations can be written as

$$\overline{T} = \frac{T_i}{s} + \sum_{i=1}^{3} A_i \exp\left(-\mu_i \sqrt{s}\, x\right), \tag{44}$$

$$\overline{P} = \frac{P_i}{s} + \sum_{i=1}^{3} B_i \exp\left(-\mu_i \sqrt{s}\, x\right), \tag{45}$$

$$\overline{C}_s = \frac{C_{s,i}}{s} + \sum_{i=1}^{3} E_i \exp\left(-\mu_i \sqrt{s}\, x\right), \tag{46}$$

assuming that $\mu_i \geq 0$ for $i = 1, 2, 3$.

Equation (31) holds for all values of i, so it can be used to express the B_i and E_i coefficients in terms of the A_i:

$$B_i = b_i A_i, \tag{47}$$

where

$$b_i = \frac{\mu_i^2 (D_{TT} D_{PS} - D_{TS} D_{PT}) - D_{PS}}{\mu_i^2 (D_{TS} D_{PP} - D_{TP} D_{PS}) - D_{TS}}, \tag{48}$$

and

$$E_i = e_i A_i, \tag{49}$$

for

$$e_i = \frac{\mu_i^2 \left(D_{TT} D_{SP} - D_{TP} D_{ST}\right) - D_{SP}}{\mu_i^2 \left(D_{TP} D_{SS} - D_{TS} D_{SP}\right) - D_{TP}}. \tag{50}$$

The A_i can then be determined from the inner boundary conditions,

$$J_{q,inc} = -\frac{L_{qq}}{T_m} \frac{\partial T}{\partial x}\bigg|_{x=0} - L_{qv} \frac{\partial P}{\partial x}\bigg|_{x=0} - L_{qs} \frac{RT_m}{C_{s,m} M_s} \frac{\partial C_s}{\partial x}\bigg|_{x=0}, \tag{51}$$

$$J_{v,inc} = -\frac{L_{vq}}{T_m} \frac{\partial T}{\partial x}\bigg|_{x=0} - L_{vv} \frac{\partial P}{\partial x}\bigg|_{x=0} - L_{vs} \frac{RT_m}{C_{s,m} M_s} \frac{\partial C_s}{\partial x}\bigg|_{x=0}, \tag{52}$$

$$J^{\circ}_{s,inc} = -\frac{L_{sq}}{T_m} \frac{\partial T}{\partial x}\bigg|_{x=0} - L_{sv} \frac{\partial P}{\partial x}\bigg|_{x=0} - L_{ss} \frac{RT_m}{C_{s,m} M_s} \frac{\partial C_s}{\partial x}\bigg|_{x=0}, \tag{53}$$

and

$$J_{s,inc} = C_{s,m}\, J_{v,inc} + \left(1 - C_{s,m}\, \overline{V}_s\right) J^{\circ}_{s,inc}. \tag{54}$$

Transforming the boundary conditions and solving (54) for $J^{\circ}_{s,inc}$ yield

$$\frac{J_{q,inc}}{s} = -\frac{L_{qq}}{T_m} \frac{\partial \overline{T}}{\partial x}\bigg|_{x=0} - L_{qv} \frac{\partial \overline{P}}{\partial x}\bigg|_{x=0} - L_{qs} \frac{RT_m}{C_{s,m} M_s} \frac{\partial \overline{C}_s}{\partial x}\bigg|_{x=0}, \tag{55}$$

$$\frac{J_{v,inc}}{s} = -\frac{L_{vq}}{T_m} \frac{\partial \overline{T}}{\partial x}\bigg|_{x=0} - L_{vv} \frac{\partial \overline{P}}{\partial x}\bigg|_{x=0} - L_{vs} \frac{RT_m}{C_{s,m} M_s} \frac{\partial \overline{C}_s}{\partial x}\bigg|_{x=0}, \tag{56}$$

$$\frac{J_{s,inc} - C_{s,m}\, J_{v,inc}}{s(1 - C_{s,m}\, \overline{V}_s)} = -\frac{L_{sq}}{T_m} \frac{\partial \overline{T}}{\partial x}\bigg|_{x=0} - L_{sv} \frac{\partial \overline{P}}{\partial x}\bigg|_{x=0} - L_{ss} \frac{RT_m}{C_{s,m} M_s} \frac{\partial \overline{C}_s}{\partial x}\bigg|_{x=0}. \tag{57}$$

Substituting the expressions for $\overline{T}$, $\overline{P}$ and $\overline{C}_s$ from (44), (45) and (46) into the transformed boundary conditions above and multiplying through by $1/\sqrt{s}$ yield

$$\frac{J_{q,inc}}{s\sqrt{s}} = \sum_{i=1}^{3} l_{qi}\, \mu_i\, A_i, \tag{58}$$

$$\frac{J_{v,inc}}{s\sqrt{s}} = \sum_{i=1}^{3} l_{vi}\, \mu_i\, A_i, \tag{59}$$

$$\frac{J_{s,inc} - C_{s,m}\, J_{v,inc}}{s\sqrt{s}(1 - C_{s,m}\, \overline{V}_s)} = \sum_{i=1}^{3} l_{si}\, \mu_i\, A_i, \tag{60}$$

where

$$l_{qi} = \frac{L_{qq}}{T_m} + L_{qv} b_i + L_{qs} \frac{RT_m}{C_{s,m} M_s} e_i, \tag{61}$$

$$l_{vi} = \frac{L_{vq}}{T_m} + L_{vv} b_i + L_{vs} \frac{RT_m}{C_{s,m} M_s} e_i, \tag{62}$$

$$l_{si} = \frac{L_{sq}}{T_m} + L_{sv} b_i + L_{ss} \frac{RT_m}{C_{s,m} M_s} e_i. \tag{63}$$

Equations (58), (59) and (60) can be solved for the A_i. The result is

$$A_i = \frac{1}{s\sqrt{s}} G_i = \frac{1}{s\sqrt{s}} \frac{g_i}{\Delta \mu_i}, \quad i = 1, 2, 3, \tag{64}$$

where

$$g_1 = (l_{v2} l_{s3} - l_{v3} l_{s2}) J_{q,inc} + (l_{q3} l_{s2} - l_{q2} l_{s3}) J_{v,inc}$$
$$+ (l_{q2} l_{v3} - l_{q3} l_{v2}) \left(\frac{J_{s,inc} - C_{s,m} J_{v,inc}}{1 - C_{s,m} \overline{V}_s} \right), \tag{65a}$$

$$g_2 = (l_{v3} l_{s1} - l_{v1} l_{s3}) J_{q,inc} + (l_{q1} l_{s3} - l_{q3} l_{s1}) J_{v,inc}$$
$$+ (l_{q3} l_{v1} - l_{q1} l_{v3}) \left(\frac{J_{s,inc} - C_{s,m} J_{v,inc}}{1 - C_{s,m} \overline{V}_s} \right), \tag{65b}$$

$$g_3 = (l_{v1} l_{s2} - l_{v2} l_{s1}) J_{q,inc} + (l_{q2} l_{s1} - l_{q1} l_{s2}) J_{v,inc}$$
$$+ (l_{q1} l_{v2} - l_{q2} l_{v1}) \left(\frac{J_{s,inc} - C_{s,m} J_{v,inc}}{1 - C_{s,m} \overline{V}_s} \right), \tag{65c}$$

and

$$\Delta = l_{q1} (l_{v2} l_{s3} - l_{v3} l_{s2}) + l_{q2} (l_{v3} l_{s1} - l_{v1} l_{s3}) + l_{q3} (l_{v1} l_{s2} - l_{v2} l_{s1}). \tag{66}$$

The final forms for the solutions in the transform space are

$$\overline{T} = \frac{T_i}{s} + \frac{1}{s\sqrt{s}} \sum_{i=1}^{3} G_i \exp\left(-\mu_i \sqrt{s}\, x\right), \tag{67}$$

$$\overline{P} = \frac{P_i}{s} + \frac{1}{s\sqrt{s}} \sum_{i=1}^{3} b_i G_i \exp\left(-\mu_i \sqrt{s}\, x\right), \tag{68}$$

$$\overline{C}_s = \frac{C_{s,i}}{s} + \frac{1}{s\sqrt{s}} \sum_{i=1}^{3} e_i G_i \exp\left(-\mu_i \sqrt{s}\, x\right), \tag{69}$$

where the G_i are defined implicitly in (64), the μ_i are defined by (43), the b_i by (48) and the e_i by (50). All of these variables are free of the transform variable s. The solutions above can be inverted

using the two inversion formulas:

$$\mathcal{L}^{-1}\left\{\frac{k}{s}\right\} = k, \tag{70}$$

$$\mathcal{L}^{-1}\left\{\frac{k}{s\sqrt{s}}\exp\left(-\nu\sqrt{s}\,\right)\right\} = k\left[2\sqrt{\frac{t}{\pi}}\exp\left(-\frac{\nu^2}{4t}\right) - \operatorname{erfc}\left(\frac{\nu}{2\sqrt{t}}\right)\right], \tag{71}$$

where k is a constant independent of s, and erfc is the complementary error function. In the second inversion formula, $\nu = \mu_i\, x$, and letting

$$\xi_i = \frac{\mu_i\, x}{2\sqrt{t}}, \tag{72}$$

the inverted solutions for the fully coupled case can be written

$$T = T_i + \sum_{i=1}^{3} G_i\left[2\sqrt{\frac{t}{\pi}}\exp\left(-\xi_i^2\right) - \mu_i\, x\operatorname{erfc}(\xi_i)\right], \tag{73}$$

$$P = P_i + \sum_{i=1}^{3} b_i G_i\left[2\sqrt{\frac{t}{\pi}}\exp\left(-\xi_i^2\right) - \mu_i\, x\operatorname{erfc}(\xi_i)\right], \tag{74}$$

$$C_s = C_{s,i} + \sum_{i=1}^{3} e_i G_i\left[2\sqrt{\frac{t}{\pi}}\exp\left(-\xi_i^2\right) - \mu_i\, x\operatorname{erfc}(\xi_i)\right], \tag{75}$$

where $G_i = g_i/(\Delta\mu_i)$ and g_i is defined by (65), Δ by (66) and μ_i by (43). The procedure for calculating T, P and C_s from the equations above is given in the third section.

In the uncoupled case and when thermal osmosis and thermal filtration are included, D_{TS} and D_{PS} are zero. In these two cases, the definition of the b_i in (48) is indeterminant. There are two approaches to obtaining the solutions in these cases: the b_i may be redefined by

$$b_i = \frac{1 - \mu_i^2\, D_{TT}}{\mu_i^2\, D_{TP}}, \tag{76}$$

or the solution may be rederived starting with a simplified version of the system of governing equations. The second approach is presented in the fourth section.

Solutions for the Fully Coupled Case in a Radial Geometry

In this case, the system of transformed equations is given by (21), (22) and (23) with $\nabla^2 = \partial^2/\partial r^2 + (1/r)\,\partial/\partial r$. The modified Bessel functions of order zero, I_0 and K_0, are solutions of the differential equation,

$$\frac{\partial^2 \mathcal{F}}{\partial r^2} + \frac{1}{r}\frac{\partial \mathcal{F}}{\partial r} = \lambda^2\,\mathcal{F}, \tag{77}$$

for λ a constant. It is therefore reasonable to assume that solutions of the transformed equations can be written in terms of I_0 and K_0. For large arguments, however, I_0 increases exponentially, so

solutions involving I_0 cannot satisfy the outer boundary conditions, which are that the solutions tend to their initial values as r increases. Therefore, I_0 is discarded as a possibility, and solutions of the following form are assumed:

$$\overline{T} = \frac{T_i}{s} + A\,K_0\left(\lambda r\right), \tag{78}$$

$$\overline{P} = \frac{P_i}{s} + B\,K_0\left(\lambda r\right), \tag{79}$$

$$\overline{C}_s = \frac{C_{s,i}}{s} + E\,K_0\left(\lambda r\right). \tag{80}$$

Substituting these expressions into (21), (22) and (23) leads to the same matrix equation (30) as that derived when a one-dimensional coordinate system was used, and consequently many of the intermediate steps are the same for the one-dimensional and radial coordinate systems. Using the results from the previous section, the solutions in the transform space can be written

$$\overline{T} = \frac{T_i}{s} + \sum_{i=1}^{3} A_i\,K_0\left(\mu_i\sqrt{s}\,r\right), \tag{81}$$

$$\overline{P} = \frac{P_i}{s} + \sum_{i=1}^{3} b_i\,A_i\,K_0\left(\mu_i\sqrt{s}\,r\right), \tag{82}$$

$$\overline{C}_s = \frac{C_{s,i}}{s} + \sum_{i=1}^{3} e_i\,A_i\,K_0\left(\mu_i\sqrt{s}\,r\right). \tag{83}$$

where the b_i are given by (48) or (76) depending on the coupling, the e_i are given by (50) and the μ_i are given by (43). As with the one-dimensional solution, the A_i can be determined using the transformed inner boundary conditions and (53):

$$\frac{J_{q,inc}}{s} = -\frac{L_{qq}}{T_m}\frac{\partial\overline{T}}{\partial r}\bigg|_{r=a} - L_{qv}\frac{\partial\overline{P}}{\partial r}\bigg|_{r=a} - L_{qs}\frac{RT_m}{C_{s,m}M_s}\frac{\partial\overline{C}_s}{\partial r}\bigg|_{r=a}, \tag{84}$$

$$\frac{J_{v,inc}}{s} = -\frac{L_{vq}}{T_m}\frac{\partial\overline{T}}{\partial r}\bigg|_{r=a} - L_{vv}\frac{\partial\overline{P}}{\partial r}\bigg|_{r=a} - L_{vs}\frac{RT_m}{C_{s,m}M_s}\frac{\partial\overline{C}_s}{\partial r}\bigg|_{r=a}, \tag{85}$$

$$\frac{J_{s,inc} - C_{s,m}\,J_{v,inc}}{s\left(1 - C_{s,m}\,\overline{V}_s\right)} = -\frac{L_{sq}}{T_m}\frac{\partial\overline{T}}{\partial r}\bigg|_{r=a} - L_{sv}\frac{\partial\overline{P}}{\partial r}\bigg|_{r=a} - L_{ss}\frac{RT_m}{C_{s,m}M_s}\frac{\partial\overline{C}_s}{\partial r}\bigg|_{r=a}. \tag{86}$$

Substituting the expressions for $\overline{T}$, $\overline{P}$ amd $\overline{C}_s$ from (81), (82) and (83) into the equations above and multiplying through by $1/\sqrt{s}$ result in three equations for the A_i,

$$\frac{J_{q,inc}}{s\sqrt{s}} = \sum_{i=1}^{3} l_{qi}\,\mu_i\,A_i\,K_1\left(\mu_i\sqrt{s}\,a\right), \tag{87}$$

$$\frac{J_{v,inc}}{s\sqrt{s}} = \sum_{i=1}^{3} l_{vi}\,\mu_i\,A_i\,K_1\left(\mu_i\sqrt{s}\,a\right), \tag{88}$$

$$\frac{J_{s,inc} - C_{s,m}\,J_{v,inc}}{s\sqrt{s}\,(1 - C_{s,m}\,\overline{V}_s)} = \sum_{i=1}^{3} l_{si}\,\mu_i\,A_i\,K_1\left(\mu_i\sqrt{s}\,a\right), \tag{89}$$

where the l_{qi}, l_{vi} and l_{si} are defined by (61), (62) and (63). Solving these yields the same results as in the one-dimensional case: the A_i are defined by equations (64) through (66).

The final expressions for the solutions in the transform space for the fully coupled case are

$$\overline{T} = \frac{T_i}{s} + \frac{1}{s\sqrt{s}}\sum_{i=1}^{3} G_i\,\frac{K_0\left(\mu_i\sqrt{s}\,r\right)}{K_1\left(\mu_i\sqrt{s}\,a\right)}, \tag{90}$$

$$\overline{P} = \frac{P_i}{s} + \frac{1}{s\sqrt{s}}\sum_{i=1}^{3} b_i\,G_i\,\frac{K_0\left(\mu_i\sqrt{s}\,r\right)}{K_1\left(\mu_i\sqrt{s}\,a\right)}, \tag{91}$$

$$\overline{C}_s = \frac{C_{s,i}}{s} + \frac{1}{s\sqrt{s}}\sum_{i=1}^{3} e_i\,G_i\,\frac{K_0\left(\mu_i\sqrt{s}\,r\right)}{K_1\left(\mu_i\sqrt{s}\,a\right)}, \tag{92}$$

where the b_i, e_i, G_i and μ_i are defined by equations (48), (50), (63) and (43), respectively, and all are free of the transform variable s. These solutions can be inverted using the inversion formula (70) and

$$\mathcal{L}^{-1}\left\{\frac{1}{s\sqrt{s}}\,\frac{K_0\left(\mu_i\sqrt{s}\,r\right)}{K_1\left(\mu_i\sqrt{s}\,a\right)}\right\} =$$

$$\frac{2\,a\,\mu_i}{\pi}\int_0^{\infty}\left[1 - \exp\left(-\frac{t\,u^2}{a^2\,\mu_i{}^2}\right)\right]\frac{Y_0(ru/a)\,J_1(u) - J_0(ru/a)\,Y_1(u)}{J_1^2(u) + Y_1^2(u)}\,\frac{du}{u^2} \tag{93}$$

(Carslaw and Jaeger, 1959). Because of the difficulty in calculating the integral in (93), it is computationally more efficient to numerically invert the solutions in the transform space using an algorithm by Stehfest (1970). A procedure for calculating $\overline{T}$, $\overline{P}$ and $\overline{C}_s$ from equations (90) through (92) is outlined below.

Computational Procedure for the Fully Coupled Case

The analytical solutions for the one-dimensional and radial coordinate systems for the uncoupled and all of the coupled cases, including the fully coupled case, can be computed as follows:

1. calculate the D_{IJ} from (20),
2. calculate the d_j, for $j = 1, 2, 3, 4$, from (34),
3. calculate α and η from (40) and (41),
4. calculate θ from (38),
5. calculate the μ_i from (43),

6. calculate the b_i from (76) in the uncoupled case and when thermal osmosis and thermal filtration are included or from (48) in all other cases,
7. calculate the e_i from (50),
8. calculate the l_{qi}, l_{vi} and l_{si} from (61), (62) and (63),
9. calculate $J_{v,inc}$ from the incoming solvent and solute fluxes, $J_{0,inc}$ and $J_{s,inc}$, using $J_{v,inc} = J_{0,inc}\overline{V}_0 + J_{s,inc}\overline{V}_s$,
10. calculate the g_i from (65) and Δ from (66),
11. calculate the G_i from $G_i = g_i/(\Delta\mu_i)$,
12. in the one-dimensional case, calculate T, P and C_s from (73), (74) and (75) using $\xi_i = \mu_i x/2\sqrt{t}$ and in the radial case, calculate $\overline{T}$, $\overline{P}$ and $\overline{C}_s$ from (90), (91) and (92) and numerically invert them to obtain T, P and C_s.

In steps 5 through 12 above, $i = 1, 2, 3$.

Solutions for the Uncoupled and Thermal Osmosis Cases in One Dimension

In the thermal osmosis case, that is, when thermal osmosis and thermal filtration are included, all of the phenomenological coefficients corresponding to the indirect processes are zero except for the coefficients of thermal filtration and thermal osmosis, L_{qv} and L_{vq}. In the uncoupled case, both of these coefficients are zero as well. In both cases, D_{TS} and D_{PS} defined by (20), are zero, which simplifies the system of transformed equations:

$$s\overline{T} - T_i = D_{TT}\,\nabla^2\overline{T} + D_{TP}\,\nabla^2\overline{P}, \tag{94}$$

$$s\overline{P} - P_i = D_{PT}\,\nabla^2\overline{T} + D_{PP}\,\nabla^2\overline{P}, \tag{95}$$

$$s\overline{C}_s - C_{s,i} = D_{ST}\,\nabla^2\overline{T} + D_{SP}\,\nabla^2\overline{P} + D_{SS}\,\nabla^2\overline{C}_s. \tag{96}$$

In the system above, solutions for $\overline{T}$ and $\overline{P}$ may be obtained independently of that for $\overline{C}_s$, and once they have, $\overline{C}_s$ may be determined from (96).

Assuming solutions for $\overline{T}$ and $\overline{P}$ of the same form as those in (28) and (29) yields the following matrix equation:

$$\lambda^2 \begin{pmatrix} D_{TT} & D_{TP} \\ D_{PT} & D_{PP} \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} = s \begin{pmatrix} A \\ B \end{pmatrix}, \tag{97}$$

Equation (97) will have a nonzero solution only if the determinant of the coefficient matrix for the corresponding homogeneous matrix equation is zero:

$$(D_{PP}D_{TT} - D_{PT}D_{TP})\,\lambda^4 - (D_{PP} + D_{TT})\,s\,\lambda^2 + s^2 = 0. \tag{98}$$

The roots of (98) are

$$\lambda^2 = s\frac{(D_{PP} + D_{TT}) \pm \sqrt{(D_{TT} - D_{PP})^2 + 4D_{PT}D_{TP}}}{2\,(D_{TT}D_{PP} - D_{PT}D_{TP})}, \tag{99}$$

and therefore,

$$\lambda = \pm\sqrt{s\frac{(D_{PP}+D_{TT}) \pm \sqrt{(D_{TT}-D_{PP})^2+4D_{PT}D_{TP}}}{2\,(D_{TT}D_{PP}-D_{PT}D_{TP})}}. \tag{100}$$

It is necessary to determine which combination of signs in (100) yields positive values of λ because only positive values, and hence negative arguments in the exponential functions in (28) and (29), will give solutions that satisfy the boundary conditions at infinity. D_{TT}, D_{PP}, D_{TP} and D_{PT} are all positive, because the material properties and phenomenological coefficients in the definitions are all positive. Substituting the expressions for D_{TT}, D_{PP}, D_{TP} and D_{PT} from (20) yields the following expression for the denominator in (100):

$$D_{TT}D_{PP} - D_{PT}D_{TP} = \frac{1}{\Gamma_1 \Lambda_1}\left(\frac{c_{p,f}\,\rho_f}{T_m\,\beta_f} - \frac{\beta_f}{\kappa_f}\right)(L_{qq}L_{vv} - L_{qv}L_{vq}). \tag{101}$$

On the right-hand side of (101), the first two factors are positive because each individual term in them is positive. The third factor is positive because the phenomenological coefficients are constrained by $(L_{qq}L_{vv} - L_{qv}L_{vq}) > 0$ (Katchalsky and Curran, 1967). Therefore, the denominator in (100) is positive. The second term in the numerator of (100) is positive and can be rewritten as

$$(D_{PP}-D_{TT})^2 + 4\,D_{PT}D_{TP} = (D_{PP}+D_{TT})^2 - 4\,(D_{PP}D_{TT} - D_{PT}D_{TP}). \tag{102}$$

By (101), the second term in parentheses on the right-hand side of (102) is positive, so

$$D_{PP}+D_{TT} > \sqrt{(D_{PP}+D_{TT})^2 - 4\,(D_{PP}D_{TT} - D_{PT}D_{TP})}, \tag{103}$$

and therefore, the numerator of (100) is always positive. Letting

$$\lambda_i = \mu_i\sqrt{s},\ \ i = 1,2, \tag{104}$$

λ_1 and λ_2 are real and positive for μ_1 and μ_2 defined by

$$\mu_1 = \sqrt{\frac{(D_{PP}+D_{TT}) - \sqrt{(D_{TT}-D_{PP})^2+4\,D_{PT}D_{TP}}}{2\,(D_{TT}D_{PP}-D_{PT}D_{TP})}}, \tag{105a}$$

$$\mu_2 = \sqrt{\frac{(D_{PP}+D_{TT}) + \sqrt{(D_{TT}-D_{PP})^2+4\,D_{PT}D_{TP}}}{2\,(D_{TT}D_{PP}-D_{PT}D_{TP})}}. \tag{105b}$$

The solutions for the transformed variables $\overline{T}$ and $\overline{P}$ can now be written as

$$\overline{T} = \frac{T_i}{s} + \sum_{i=1}^{2} A_i\,\exp\left(-\mu_i\sqrt{s}\,x\right), \tag{106}$$

$$\overline{P} = \frac{P_i}{s} + \sum_{i=1}^{2} B_i\,\exp\left(-\mu_i\sqrt{s}\,x\right), \tag{107}$$

where the μ_i are defined by (105).

Using (97), the B_i can be expressed in terms of the A_i by $B_i = b_i A_i$, where the b_i are given by (76). The transformed inner boundary conditions can be used to determine the A_i. In the uncoupled case, they are

$$\frac{J_{q,inc}}{s} = -\frac{L_{qq}}{T_m} \frac{\partial \overline{T}}{\partial x}\bigg|_{x=0}, \tag{108}$$

$$\frac{J_{v,inc}}{s} = -L_{vv} \frac{\partial \overline{P}}{\partial x}\bigg|_{x=0}, \tag{109}$$

and in the thermal osmosis case, they are

$$\frac{J_{q,inc}}{s} = -\frac{L_{qq}}{T_m} \frac{\partial \overline{T}}{\partial x}\bigg|_{x=0} - L_{qv} \frac{\partial \overline{P}}{\partial x}\bigg|_{x=0}, \tag{110}$$

$$\frac{J_{v,inc}}{s} = -\frac{L_{vq}}{T_m} \frac{\partial \overline{T}}{\partial x}\bigg|_{x=0} - L_{vv} \frac{\partial \overline{P}}{\partial x}\bigg|_{x=0}. \tag{111}$$

Substituting the solutions for $\overline{T}$ and $\overline{P}$ from (106) and (107) into the transformed boundary conditions above yields the following equations for the A_i:

$$\frac{J_{q,inc}}{s\sqrt{s}} = \sum_{i=1}^{2} l_{qi}\, \mu_i\, A_i, \tag{112}$$

$$\frac{J_{v,inc}}{s\sqrt{s}} = \sum_{i=1}^{2} l_{vi}\, \mu_i\, A_i, \tag{113}$$

where in the uncoupled case, the l_{qi} and l_{vi} are defined by

$$l_{qi} = \frac{L_{qq}}{T_m}, \tag{114}$$

$$l_{vi} = b_i\, L_{vv}, \tag{115}$$

and in the thermal osmosis case, they are defined by

$$l_{qi} = \frac{L_{qq}}{T_m} + b_i\, L_{qv}, \tag{116}$$

$$l_{vi} = \frac{L_{vq}}{T_m} + b_i\, L_{vv}. \tag{117}$$

Solving (112) and (113) for the A_1 and A_2 and substituting these results into (106) and (107) give the final forms for the solutions in the transform space:

$$\overline{T} = \frac{T_i}{s} + \frac{1}{\Delta s\sqrt{s}} \sum_{i=1}^{2} \frac{g_i}{\mu_i} \exp\left(-\mu_i \sqrt{s}\, x\right), \tag{118}$$

$$\overline{P} = \frac{P_i}{s} + \frac{1}{\Delta s \sqrt{s}} \sum_{i=1}^{2} \frac{b_i\, g_i}{\mu_i} \exp\left(-\mu_i \sqrt{s}\, x\right), \tag{119}$$

where

$$g_1 = l_{v2}\, J_{q,inc} - l_{q2}\, J_{v,inc}, \tag{120a}$$

$$g_2 = l_{q1}\, J_{v,inc} - l_{v1}\, J_{q,inc}, \tag{120b}$$

and

$$\Delta = l_{q1} l_{v2} - l_{q2} l_{v1}. \tag{121}$$

In (118) and (119) the b_i are defined by (76), the μ_i by (105), and the l_{qi} and l_{vi} are defined by (114) and (115) in the uncoupled case and by (116) and (117) when thermal osmosis and thermal filtration are included.

Using the inversion formulas (70) and (71), the inverted solutions for the uncoupled and thermal osmosis cases are

$$T = T_i + \sum_{i=1}^{2} G_i \left[2\sqrt{\frac{t}{\pi}} \exp\left(-\xi_i^2\right) - \mu_i\, x\, \mathrm{erfc}(\xi_i) \right], \tag{122}$$

$$P = P_i + \sum_{i=1}^{2} b_i\, G_i \left[2\sqrt{\frac{t}{\pi}} \exp\left(-\xi_i^2\right) - \mu_i\, x\, \mathrm{erfc}(\xi_i) \right], \tag{123}$$

where the b_i are defined by (76) and the μ_i by (105) and as in the first section, $G_i = g_i/(\Delta\, \mu_i)$ and $\xi_i = \mu_i\, x/(2\sqrt{t})$, where Δ is defined by (121) and the g_i by (120).

The solution for C_s remains to be determined. Substituting the expressions for $\overline{T}$ and $\overline{P}$ from (118) and (119) into (96), the governing equation for $\overline{C}_s$, yields

$$D_{SS}\, \nabla^2 \overline{C}_s - s\, \overline{C}_s = -\frac{1}{\sqrt{s}} \sum_{i=1}^{2} \left(D_{ST} + b_i\, D_{SP}\right) G_i\, \mu_i^2 \exp\left(-\mu_i \sqrt{s}\, x\right) - C_{s,i}, \tag{124}$$

which may be solved using the method of undetermined coefficients (Boyce and DiPrima, 1969). The first step is to find the general solution to the homogeneous equation, and the second is to look for a particular solution to the nonhomogeneous equation. Combining the results from the two steps gives the final solution.

The homogeneous equation is

$$D_{SS}\, \nabla^2 \overline{C}_s - s\, \overline{C}_s = 0, \tag{125}$$

which has as its general solution

$$\overline{C}_{s,H} = E_1 \exp\left(-x\sqrt{\frac{s}{D_{SS}}}\right) + E_2 \exp\left(x\sqrt{\frac{s}{D_{SS}}}\right), \tag{126}$$

where the E_i are constants. A particular solution to the nonhomogeneous equation is

$$\overline{C}_{s,N} = \frac{C_{s,i}}{s} + \sum_{i=1}^{2} F_i \exp\left(-\mu_i \sqrt{s}\, x\right), \tag{127}$$

where F_1 and F_2 are constants. Substituting this expression into (124) and solving for the F_i yield

$$F_i = \frac{f_i G_i}{s\sqrt{s}}, \tag{128}$$

where

$$f_i = \frac{\left(D_{ST} + b_i\, D_{SP}\right) \mu_i^2}{1 - D_{SS}\, \mu_i^2}. \tag{129}$$

The general solution to (124) is the sum of $\overline{C}_{s,H}$ and $\overline{C}_{s,N}$. The constant E_2 in $\overline{C}_{s,H}$ must, however, be zero in order for the boundary condition at infinity to be satisfied. The solution for $\overline{C}_s$ can now be written as

$$\overline{C}_s = \frac{C_{s,i}}{s} + E_1 \exp\left(-x\sqrt{\frac{s}{D_{SS}}}\right) + \sum_{i=1}^{2} F_i \exp\left(-\mu_i \sqrt{s}\, x\right), \tag{130}$$

where the F_i are given by (128) and E_1 is to be determined from the transformed inner boundary condition, which for both the uncoupled and thermal osmosis cases is

$$\frac{J_{s,inc} - C_{s,m}\, J_{v,inc}}{s\left(1 - C_{s,m}\, \overline{V}_s\right)} = -L_{ss}\, \frac{RT_m}{C_{s,m} M_s}\, \frac{\partial \overline{C}_s}{\partial x}\bigg|_{x=0}. \tag{131}$$

Substituting the expression for $\overline{C}_s$ from (130) in the equation above and solving for E_1 yield

$$E_1 = \frac{e_1}{s\sqrt{s}}, \tag{132}$$

where

$$e_1 = \frac{\sqrt{D_{SS}}\, C_{s,m}\, M_s}{L_{ss}\, R\, T_m} \left(\frac{J_{s,inc} - C_{s,m}\, J_{v,inc}}{1 - C_{s,m}\, \overline{V}_s}\right) - \sqrt{D_{SS}} \sum_{i=1}^{2} \mu_i\, f_i\, G_i. \tag{133}$$

The final form for $\overline{C}_s$ is

$$\overline{C}_s = \frac{C_{s,i}}{s} + \frac{e_1}{s\sqrt{s}} \exp\left(-x\sqrt{\frac{s}{D_{SS}}}\right) + \frac{1}{s\sqrt{s}} \sum_{i=1}^{2} f_i\, G_i \exp\left(-\mu_i \sqrt{s}\, x\right). \tag{134}$$

Using (70) and (71) to invert $\overline{C}_s$ gives

$$C_s = C_{s,i} + e_1 \left[2\sqrt{\frac{t}{\pi}} \exp\left(-\zeta^2\right) - x \operatorname{erfc}(\zeta) \right]$$

$$+ \sum_{i=1}^{2} f_i G_i \left[2\sqrt{\frac{t}{\pi}} \exp\left(-\xi_i^2\right) - \mu_i x \operatorname{erfc}(\xi_i) \right], \tag{135}$$

where

$$\zeta = \frac{x}{2\sqrt{t D_{SS}}}, \tag{136}$$

D_{SS} is defined by (10), e_1 by (133), the f_i by (129), $G_i = g_i/(\Delta\mu_i)$, the g_i by (120), Δ by (121), the μ_i by (105) and $\xi_i = \mu_i x/(2\sqrt{t})$.

Because of the complicated form of the solutions, it is exceedingly difficult to algebraically prove that the solutions for T, P and C_s in (73) through (75) reduce to those in (122), (123) and (135) in the uncoupled case and when thermal osmosis and thermal filtration are included. The equivalence of the solutions has been verified numerically by calculating the solutions for the uncoupled and thermal osmosis cases from the first section and comparing the results to those obtained by calculating the solutions derived in this section. The procedure used to calculate the latter is outlined in the last section.

Solutions for the Uncoupled and Thermal Osmosis Cases in a Radial Geometry

For the uncoupled and thermal osmosis cases, the simplified system of transformed equations is given by (94) to (96) with $\nabla^2 = \partial^2/\partial r^2 + (1/r)\,\partial/\partial r$. Assuming solutions of the form of (78) and (79) for $\overline{T}$ and $\overline{P}$ and following the procedure used in the previous section lead to the following expressions:

$$s\,\overline{T} - T_i = \sum_{i=1}^{2} A_i\, K_0\left(\mu_i \sqrt{s}\, r\right), \tag{137}$$

$$s\,\overline{P} - P_i = \sum_{i=1}^{2} b_i\, A_i\, K_0\left(\mu_i \sqrt{s}\, r\right), \tag{138}$$

where the b_i are given by (76), the μ_i by (105), and the A_i are to be determined from the inner boundary conditions. In the uncoupled case, the boundary conditions are

$$\frac{J_{q,inc}}{s} = -\frac{L_{qq}}{T_m} \left.\frac{\partial \overline{T}}{\partial r}\right|_{r=a}, \tag{139}$$

$$\frac{J_{v,inc}}{s} = -L_{vv} \left.\frac{\partial \overline{P}}{\partial r}\right|_{r=a}, \tag{140}$$

and in the thermal osmosis case, they are

$$\frac{J_{q,inc}}{s} = -\frac{L_{qq}}{T_m} \left.\frac{\partial \overline{T}}{\partial r}\right|_{r=a} - L_{qv} \left.\frac{\partial \overline{P}}{\partial r}\right|_{r=a}, \tag{141}$$

$$\frac{J_{v,inc}}{s} = -\frac{L_{vq}}{T_m}\frac{\partial \overline{T}}{\partial r}\bigg|_{r=a} - L_{vv}\frac{\partial \overline{P}}{\partial r}\bigg|_{r=a} . \tag{142}$$

Substituting the solutions for $\overline{T}$ and $\overline{P}$ from (137) and (138) into the equations above yields the following equations for the A_i:

$$\frac{J_{q,inc}}{s\sqrt{s}} = \sum_{i=1}^{2} l_{qi}\,\mu_i\,A_i\,K_1\left(\mu_i\sqrt{s}\,a\right), \tag{143}$$

$$\frac{J_{v,inc}}{s\sqrt{s}} = \sum_{i=1}^{2} l_{vi}\,\mu_i\,A_i\,K_1\left(\mu_i\sqrt{s}\,a\right), \tag{144}$$

where in the uncoupled case, the l_{qi} and l_{vi} are given by (114) and (115) and when thermal osmosis and thermal filtration are included by (116) and (117). Solving (143) and (144) for the A_i and substituting the results into (137) and (138) give the final expressions for $\overline{T}$ and $\overline{P}$:

$$\overline{T} = \frac{T_i}{s} + \frac{1}{s\sqrt{s}}\sum_{i=1}^{2} G_i\,\frac{K_0\left(\mu_i\sqrt{s}\,r\right)}{K_1\left(\mu_i\sqrt{s}\,a\right)}, \tag{145}$$

$$\overline{P} = \frac{P_i}{s} + \frac{1}{s\sqrt{s}}\sum_{i=1}^{2} b_i\,G_i\,\frac{K_0\left(\mu_i\sqrt{s}\,r\right)}{K_1\left(\mu_i\sqrt{s}\,a\right)}, \tag{146}$$

where the b_i are defined by (76), $G_i = g_i/(\Delta\mu_i)$, the g_i are defined by (120), Δ by (121) and the μ_i by (105).

The solution for $\overline{C}_s$ is obtained by substituting $\overline{P}$ from (138) into (96) and following the steps given in the fourth section. The general solution to the homogeneous equation (125) is

$$\overline{C}_{s,H} = E_1\,K_0\left(r\sqrt{s/D_{SS}}\right) + E_2\,I_0\left(r\sqrt{s/D_{SS}}\right), \tag{147}$$

where the E_i are constants. The nonhomogeneous equation is

$$D_{SS}\,\nabla^2\overline{C}_s - s\,\overline{C}_s = -\frac{1}{\Delta\sqrt{s}}\sum_{i=1}^{2}\left(D_{ST} + b_i\,D_{SP}\right)g_i\,\mu_i\,\frac{K_0\left(\mu_i\sqrt{s}\,r\right)}{K_1\left(\mu_i\sqrt{s}\,a\right)} - C_{s,i}, \tag{148}$$

a particular solution of which is

$$\overline{C}_{s,N} = \frac{C_{s,i}}{s} + \sum_{i=1}^{2} F_i\,\frac{K_0\left(\mu_i\sqrt{s}\,r\right)}{K_1\left(\mu_i\sqrt{s}\,a\right)}, \tag{149}$$

where the F_i are defined by (128). The general solution to (148) is the sum of $\overline{C}_{s,H}$ and $\overline{C}_{s,N}$. Because $I_0\left(\mu_i\sqrt{s}r\right)$ increases exponentially as r increases, the constant E_2 in $\overline{C}_{s,H}$ must be zero in order for

the boundary condition at infinity to be satisfied. Combining the expressions from (147) and (149), the solution for $\overline{C}_s$ can be written

$$\overline{C}_s = \frac{C_{s,i}}{s} + E_1 K_0\left(r\sqrt{s/D_{SS}}\right) + \sum_{i=1}^{2} F_i \frac{K_0\left(\mu_i \sqrt{s}\, r\right)}{K_1\left(\mu_i \sqrt{s}\, a\right)}, \tag{150}$$

where the only remaining unknown, E_1, can be determined using the inner boundary condition for $\overline{C}_s$. For both the uncoupled and thermal osmosis cases, the boundary condition is

$$\frac{J_{s,inc} - C_{s,m} J_{v,inc}}{s\left(1 - C_{s,m}\overline{V}_s\right)} = -L_{ss} \frac{RT_m}{C_{s,m} M_s} \left.\frac{\partial \overline{C}_s}{\partial r}\right|_{r=a}. \tag{151}$$

Substituting the expression for $\overline{C}_s$ from (150) in the equation above and solving for E_1 yield

$$E_1 = \frac{e_1}{s\sqrt{s}\, K_1\left(a\sqrt{s/D_{SS}}\right)}, \tag{152}$$

where e_1 is defined by (133). The final expression for $\overline{C}_s$ is

$$\overline{C}_s = \frac{C_{s,i}}{s} + \frac{e_1}{s\sqrt{s}} \frac{K_0\left(r\sqrt{s/D_{SS}}\right)}{K_1\left(a\sqrt{s/D_{SS}}\right)} + \frac{1}{s\sqrt{s}} \sum_{i=1}^{2} f_i\, G_i \frac{K_0\left(\mu_i \sqrt{s}\, r\right)}{K_1\left(\mu_i \sqrt{s}\, a\right)}. \tag{153}$$

where D_{SS} is defined by (10), e_1 by (133), the f_i by (129), $G_i = g_i/(\Delta\mu_i)$, the g_i by (120), Δ by (121), and the μ_i by (105). As noted in the second section, the solutions in (145), (146) and (153) may be analytically inverted using (70) and (93) or numerically inverted using the Stehfest (1970) algorithm. The procedure for calculating $\overline{T}$, $\overline{P}$ and $\overline{C}_s$ is outlined in the next section.

Computational Procedure for the Uncoupled and Thermal Osmosis Cases

For completeness, the procedure for calculating the analytical solutions for the uncoupled and thermal osmosis cases for the one-dimensional and radial geometries, derived in the fourth and fifth section, respectively, is outlined in this section. The computational procedure outlined in the third section could also be used.

1. calculate the D_{IJ} from (20),
2. calculate the μ_i from (105),
3. calculate the b_i from (76),
4. calculate the l_{qi} and l_{vi} for the uncoupled case from (114) and (115), and calculate the l_{qi} and l_{vi} when thermal osmosis and thermal filtration are included from (116) and (117),
5. calculate $J_{v,inc}$ from the incoming solvent and solute fluxes, $J_{0,inc}$ and $J_{s,inc}$, using $J_{v,inc} = J_{0,inc}\overline{V}_0 + J_{s,inc}\overline{V}_s$,
6. calculate the g_i from (120) and Δ from (121),
7. calculate the G_i from $G_i = g_i/(\Delta\,\mu_i)$,

8. calculate the f_i from (129),
9. calculate e_1 from (133),
10. in the one-dimensional case, calculate T, P and C_s from (122), (123) and (135) using $\xi_i = \mu_i\, x/2\sqrt{t}$ and $\zeta = x/2\sqrt{t\, D_{SS}}$, and in the radial case, calculate $\overline{T}$, $\overline{P}$ and $\overline{C}_s$ from (145), (146) and (153) and numerically invert them to obtain T, P and C_s.

In steps 5 through 10 above, $i = 1, 2$.

NOTATION

a	location of inner boundary in axisymmetric case	m
C_s	concentration of solute	kg/m^3
$\overline{C}_s$	Laplace transform of solute concentration	kg·s/m^3
$C_{s,i}$	initial value of solute concentration	kg/m^3
$C_{s,m}$	average concentration of solute	kg/m^3
C_0	concentration of solvent	kg/m^3
$c_{p,f}$	specific heat capacity of fluid phase at constant pressure	J/(K·kg)
$c_{p,n}$	specific heat capacity of solid phase at constant pressure	J/(K·kg)
$c_{v,f}$	specific heat capacity of fluid phase at constant volume	J/(K·kg)
$c_{v,n}$	specific heat capacity of solid phase at constant volume	J/(K·kg)
J_q	heat flux	W/m^2
$J_{q,inc}$	incoming heat flux at inner boundary	W/m^2
J_s	solute flux (laboratory frame of reference)	kg/m^2·s
$J_{s,inc}$	incoming solute flux (laboratory frame of reference) at inner boundary	kg/m^2·s
J_s^o	solute flux (defined relative to motion of solvent)	kg/m^2·s
$J_{s,inc}^o$	incoming solute flux (defined relative to motion of solvent) at inner boundary	kg/m^2·s
J_v	volume flux	m/s
$J_{v,inc}$	incoming volume flux at inner boundary	m/s
J_0	solvent flux (laboratory frame of reference)	kg/m^2·s
$J_{0,inc}$	incoming solvent flux (laboratory frame of reference) at inner boundary	kg/m^2·s
L_{qs}	coefficient of Dufour effect	kg/m·s
L_{sq}	coefficient of thermal diffusion	kg/m·s
L_{ss}	coefficient of mass diffusion (Fick's law)	kg^2/J·m·s
L_{sv}	coefficient of ultrafiltration	kg·m^2/J·s
L_{vq}	coefficient of thermal osmosis	m^2/s
L_{vs}	coefficient of chemical osmosis	kg·m^2/J·s
L_{vv}	coefficient of advection (Darcy's Law)	m^5/J·s
M_s	molecular weight of solute	kg/mole
P	pressure	Pa
$\overline{P}$	Laplace transform of pressure	Pa·s
P_i	initial value of pressure	Pa
r	radial distance	m
R	universal gas constant	J/K·mole
s	Laplace transform variable	s^{-1}
t	time	s

T	temperature	K
$\overline{T}$	Laplace transform of temperature	K·s
T_i	initial value of temperature	K
T_m	average temperature	K
$\overline{V}_s$	partial specific volume of solute	m^3/kg
x	distance	m
β_f	coefficient of thermal expansion of fluid phase	K^{-1}
β_n	coefficient of thermal expansion of solid phase	K^{-1}
ϵ_f	volume fraction of fluid phase	
ϵ_n	volume fraction of solid phase	
κ_f	coefficient of isothermal compressibility of fluid phase	m^2/N
κ_n	coefficient of isothermal compressibility of solid phase	m^2/N
ρ_f	density of fluid phase	kg/m^3
ρ_n	density of solid phase	kg/m^3

ACKNOWLEDGEMENT

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Engineering and Geosciences Division, of the U. S. Department of Energy under Contract No. DE–AC03–76SF00098.

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