An irreversible thermodynamic description of membrane-confined electrophoresis (MCE) applied to a solution of the time- and electrical-potential-space-dependent continuity equation for MCE

Introduction

Irreversible thermodynamics [Onsager, 1931a; Onsager, 1931b; de Groot and Mazur, 1962; Katchalsky and Curran, 1965], also known as nonequilibrium thermodynamics, is a theoretical framework that has been used to describe a variety of transport processes. The theory is generally applicable to coupled flows in multi-component systems, and is applied here to membrane-confined electrophoresis (MCE). (The cgs system is used to express most parameters in MCE, and is the default system used here, though the mks system is used for some parameters.)

Along with presenting the relevant theoretical context, this work presents a method of simulation that is built on that which Claverie, Dreux and Cohen [1975] described in their solution to the Lamm equation, but differs in several respects. To correctly implement their concentration dependence, the transport coefficients are defined as spatially-independent parameters. To correctly evaluate the concentration-dependent transport coefficients at the time to be evaluated, the concentrations are calculated iteratively. By such an evaluation of the concentration-dependent transport coefficients at both the time already evaluated and the time being evaluated, the accuracy of each new set of concentrations is maximised. Computational artefacts are reduced by first calculating all concentrations in one order, then recalculating all concentrations in the opposite order, and averaging the results. The time-and-distance-dependent continuity equation for the rectangular coordinate system of MCE yields results of integration that are simpler than those obtained from the Lamm equation, which is the time-and-radial-position-dependent continuity equation that pertains to analytical ultracentrifugation [Moody, 2011]. Additionally, a simple coupled-flow equation has been implemented.

The application of irreversible thermodynamics (Sections A, I and G) provides a proper description of molar flows in the system. Mass flows are calculated from the molar flows (Section I), and these mass flows are used in the applicable continuity equation (Section A). An integral, finite-element approach then yields a numerical solution to the continuity equation (Sections B and C). The solution presented here is referred to as a "second approximate solution," to distinguish it from the type of approximate solution previously obtained by similar finite-element approaches. The aim of all of these solutions is to calculate solute concentrations throughout the system sequentially from one point in time to the next.

The second approximate solution can be used non-iteratively, but is then expected to gradually accumulate errors that, depending on the system, may become significant after many time increments. An iterative application of the second approximate solution (Section J) yields a general solution to the continuity equation. The time taken to calculate a set of results with the iterative approach will be proportional to the average number of iterations per time increment. Concentrations and concentration-dependent transport coefficients change very little from one time point to the next, however, so convergence, as judged by a marked decrease in change with further iterations, is likely to take just a few iterations per time point, provided that the acceptance criterion is not set too stringently. When analysing a system with highly concentration-dependent transport coefficients and high solute concentrations that change rapidly, the iterative process should be most advantageous.

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Section A: An application of irreversible thermodynamics to membrane-confined electrophoresis (MCE)

The application of irreversible thermodynamics [Onsager, 1931a; Onsager, 1931b; de Groot and Mazur, 1962; Katchalsky and Curran, 1965] to MCE yields the flow equation. Given the flow equation, the coupled flow diffusion and electrophoretic mobility coefficients can be defined. The flow equation requires a description of the conjugate molar forces in the system. For MCE, those forces are primarily due to electrical and chemical potential gradients, and secondarily involve gravitational potential gradients that are only significant for solutes that, relative to electrophoretic velocities, exhibit rapid transport at 1 g.

The sum of the electrical, chemical and gravitational potential gradients equals ∇U_k

The molar flow of solute component k in the system frame of reference is

$$\vec{J}_k = \overrightarrow{J_k^S} + \frac{c_k}{M_k}\vec{v}_0 = \sum_{q=1}^{n} L_{k,q}\vec{X}_q + \frac{c_k}{M_k}\vec{v}_0,$$

(A1)

where $\overrightarrow{J_k^S}$ is the molar flow of component k in the solvent frame of reference, $\vec{v}_o$ is the velocity of the solvent flow through the system, M_k is the molar mass of solute component k, c_k is the mass concentration of solute component k, $\vec{X}_q$ is the conjugate molar force (Equations A2, A14 and I16) of solute component q, $L_{k,q}$ is the coupled-flow-phenomenological coefficient linking the molar flow of solute component k to the conjugate molar force of solute component q, and n is the total number of solute components. (Each solute component is indexed by an integer that is greater than or equal to 1, and less than or equal to n. With the exception of its velocity through the system, the solvent component is treated implicitly, and by implication, is assigned an index of 0.) The molar flow of component k in the system frame of reference bears a somewhat complicated relationship to the mass flow, $\vec{I}_k$, of component k in the system frame of reference. (See **Section I: Calculating valence, molar mass, chemical potential and partial specific volume for a multi-species component.**) The molar flow of component k in the solvent frame of reference is discussed further in Section G (**The dissipation function and the Curie-Prigogine principle**). The molar mass of a component is discussed below, and described in detail in Section I. In Equation N55 of Section N (**A simple coupled-flow equation for MCE**), $\frac{c_k}{M_k}\vec{v}_0$ is expressed in terms of conjugate molar forces and coupled-flow-phenomenological coefficients.

In an MCE system at a fixed point on the surface of the Earth, the gradient of the total molar potential of solute component q is equal to

$$\nabla U_q = -\vec{X}_q = \nabla\mu_q + z_q F \nabla\Psi + M_q \nabla g_E h\,,$$

(A2)

where U_q is the total molar potential of solute component q, μ_q is the chemical potential of solute component q, z_q is the valence of solute component q, F is the cgs Faraday, Ψ is the cgs electrical potential, M_q is the molar mass of solute component q, g_E (the standard acceleration due to gravity) is the magnitude of the gravitational field at the Earth's surface, and h is the height above the Earth's surface. The component parameter μ_q is equal to $(\mu_q)_N$, which is the number average of the chemical potentials of all species of component q, but in general, $\nabla(\mu_q)_N$ does not equal $(\nabla\mu_q)_N$, which is the number average of the chemical potential gradients of all species of component q. In general, z_q is equal to $(z_q)_g$, which is the ξ-dependent valence of component q, and M_q is equal to $(M_q)_g$, which is the ξ-dependent molar mass of component q. (For the definitions of μ_q, z_q and M_q in the general case, see **Section I: Calculating valence, molar mass, chemical potential and partial specific volume for a multi-species component**. In the limit as all concentration and pressure gradients approach zero, the component parameters, $\nabla\mu_q$, z_q and M_q become the number averages of the corresponding species parameters of component q. Furthermore, based on an expectation of charge neutrality, z_q of any component should be zero. Conditions in which z_q can be nonzero are proposed following Equation I17, and examined more deeply in **Section M: Effects of ionic strength on (apparent) reduced valence and zeta potential**.) The molar gravitational potential of component q due to the Earth's gravitational acceleration is $M_q g_E h$. As h decreases in the direction of g_E, the gravitational force is described by $-M_q\nabla g_E h = -M_q g_E(\partial[h - h_0]/\partial h)_t = -M_q g_E$, where the reference height, h_0, is typically considered to be zero. It will be shown that $-M_q\nabla g_E h$ is negligible in most cases in MCE.

Each chemical potential is a function of time, t, and spatial position. The electrical potential will also be shown to depend on space and time. Each molar gravitational potential, $M_q g_E h$, varies spatially with h, but as $(\partial h/\partial t)_{space} = 0$, $M_q g_E h$ can only vary temporally if M_q varies temporally. Thus, the time dependence of each molar gravitational potential is proportional to the time dependence of M_q. For a single-species component, $(\partial M_q/\partial t)_{space} = 0$ and $(\partial z_q/\partial t)_{space} = 0$. For a multi-species component in a system that has not yet reached steady state, if $\nabla\mu_q \neq 0$, μ_q is almost certain to vary with time, in which case, where $(\partial\mu_q/\partial t)_{space} \neq 0$, $(\partial M_q/\partial t)_{space} \neq 0$ and $(\partial z_q/\partial t)_{space} \neq 0$. (See **Steady state** at the end of this section. Also see **Section I: Calculating valence, molar mass, chemical potential and partial specific volume for a multi-species component.**) Furthermore, even for a system composed of single-species components, for each of which, $(\partial z_q/\partial t)_{space} = 0$, if a gradient in the chemical potential of any component varies with time, then in all likelihood, where $(\partial\mu_q/\partial t)_{space} \neq 0$ for at least one component, $(\partial\Psi/\partial t)_{space} \neq 0$. (See **Section H: Factors affecting the electrical field in MCE.**) Thus, once an electrical current starts to flow, the electrical potential in an MCE system will probably become time dependent, and remain so until the system reaches steady state.

The mks/cgs electrical field in the MCE system is

$$\vec{E} = -\varpi \nabla \Psi \,,$$

(A3)

where ϖ is the applicable electrical-potential conversion factor. (See Notes following **List of selected parameters, their indices, and their cgs or mks dimensions.**)

The MCE system is open, but bounded by semi-permeable membranes at two opposite ends. The total electrical current, i, is carried by small ions that are able to flow through the semi-permeable membranes, and thus, from one end of the system to the other. Furthermore, the geometry of the MCE instrument is such that, between the membranes, the current density, $\vec{j}$, should be invariant with position, so that $\nabla \cdot \vec{j} = 0$ everywhere at all times. Due to conservation of current, and because there are no sources or sinks of current within the system, $\nabla i = 0$ everywhere at all times. (See **Section H: Factors affecting the electrical field in MCE.**)

By definition, free-flowing components freely permeate the membranes, partially-confined components flow more slowly through the membranes than they do through the system between the membranes, and membrane-confined components never permeate the membranes. Conceivably, some components could flow more swiftly through the membranes than they do through the system between the membranes, but as the solution conditions outside the system are kept constant by continuous and rapid buffer replenishment, once dialysis has reached steady state across the membranes, such components would appear to behave just like free-flowing components that permeate the membranes and the system between with equal ease.

In MCE, the sample occupies a system with rectangular geometry, through which the current is oriented parallel to g_E, which usually ensures that all flows of solute components within the system are even, laminar and vertically directed. Thus, each ∇U_q is significant in the vertical direction only. Consequently, vector notation can be neglected, and a single spatial variable can be used to describe all spatial dependencies of interest in the system. Density gradients that increase with height are unstable in the Earth's gravitational field. To avoid such instabilities, the system must be set up to ensure that the solution density increases as height decreases, on the basis of which, the spatial variable chosen, ξ, is defined as the magnitude of a downward and vertically directed spatial vector, $\vec{\xi}$. Thus, ξ describes the inverted vertical position in the MCE system. Henceforth, therefore, with a few exceptions, E, v_k, J_k, I_k and ξ are used in place of $\vec{E}$, $\vec{v}_k$, $\vec{J}_k$, $\vec{I}_k$ and $\vec{\xi}$, respectively, where $\vec{v}_k$ is the velocity of component k in the system frame of reference. The upper membrane is defined as the upper boundary of the system, the position of which is denoted as ξ_m. The lower membrane is defined as the lower boundary of the system, the position of which is denoted as ξ_b.

On the basis of the relationship described by Equation A3, ξ can be considered the natural independent variable of choice in MCE, as the derivative of the electrical potential with respect to ξ is proportional to the electrical field: $(\partial\Psi/\partial\xi)_t = -E/\varpi$. (See **Section H: Factors affecting the electrical field in MCE.**) Hence, ξ is the parameter associated with the electrical-potential-space in the title of this work. As ξ and h are oppositely directed, where the dimensionality of ξ and h is the same, $d\xi/dh = -1$.

Chemical potential

The chemical potential of component k is given by

$$\mu_k = (\mu_k)_0 + RT ln\gamma_k c_k \ ,$$

(A4)

where R is the ideal gas constant, T is the absolute temperature, γ_k is the activity coefficient of solute component k, and the constant $(\mu_k)_0$ is the standard-state chemical potential of solute component k. Given that μ_k is a function of the temperature of the system, the pressure of the system and the concentrations of all solute components in the system,

$$\nabla\mu_k = \left(\frac{\partial\mu_k}{\partial\xi}\right)_t = \left(\frac{\partial\mu_k}{\partial T}\right)_{t,P,c}\left(\frac{\partial T}{\partial\xi}\right)_t + \left(\frac{\partial\mu_k}{\partial P}\right)_{t,T,c}\left(\frac{\partial P}{\partial\xi}\right)_t + \sum_{w=1}^{n}\left(\frac{\partial\mu_k}{\partial c_w}\right)_{t,T,P,c_{a\neq w}}\left(\frac{\partial c_w}{\partial\xi}\right)_t ,$$

(A5)

where P is the pressure of the system, and c_w is the mass concentration of solute component w.

Temperature control ensures that

$$\left(\frac{\partial T}{\partial \xi}\right)_t = 0\,.$$

(A6)

A standard thermodynamic relation, when applied to a multi-species component in the presence of concentration and pressure gradients, yields

$$\left(\frac{\partial \mu_k}{\partial P}\right)_{t,T,c} = M_k \bar{v}_k\,,$$

(A7)

where $\bar{v}_k = (\bar{v}_k)_{Pg}$ (defined in Section I) is the ξ-dependent partial specific volume of the system with respect to solute component k, and $M_k = (M_k)_g$ (also defined in Section I) is the same molar mass parameter that applies to Equation A2.

Applying a convenient form of Bernoulli's equation to the MCE system yields

$$P = P_m + g_E \int_{\xi_m}^{\xi} \rho d\xi + \rho \frac{v_0^2}{2}\,,$$

(A8)

where ρ is the cgs solution density, P_m is the pressure at ξ_m, and v_0 is the velocity of the solvent (component 0) in the system frame of reference.

As the density of the solvent, ρ_0, tends to be constant with, or only weakly dependent on, ξ, $(\partial\rho_0/\partial\xi)_t$ is almost certain to be negligible. As ρ is likely to be dominated by ρ_0, $(\partial\rho/\partial\xi)_t$ is likely to be negligible. Furthermore, except where $(\partial\rho_0/\partial t)_\xi \neq 0$, $(\partial v_0/\partial\xi)_t = 0$ throughout the system by virtue of geometry. Finally, $(\partial g_E/\partial\xi)_t = 0$ throughout the system by virtue of scale. Thus, the sought after derivative of the preceding expression for P can be approximated as

$$\left(\frac{\partial P}{\partial \xi}\right)_t = \rho g_E + \left(\frac{\partial \rho}{\partial \xi}\right)_t \frac{v_0^2}{2} \cong \rho g_E ,$$

(A9)

so that

$$\left(\frac{\partial \mu_k}{\partial P}\right)_{t,T,c} \left(\frac{\partial P}{\partial \xi}\right)_t \cong M_k \bar{v}_k \rho g_E .$$

(A10)

For $M_k\bar{v}_k\rho \leq 10^7$ g/mol (approximately),

$$\left(\frac{\partial \mu_k}{\partial P}\right)_{t,T,c} \left(\frac{\partial P}{\partial \xi}\right)_t \leq 10^{10} \ \frac{g \cdot cm}{mol \cdot s^2} .$$

(A11)

While the upper value of this range may seem significant, it is still less than 0.2% of $M_k\bar{v}_k\rho\omega_{min}^2r_{min}$, which is the radially directed molar gravitational force at the lowest possible radial position (approximately 5.7 cm), r_{min}, and the lowest practical angular velocity (2π[3,000 RPM]/[60 s/min]), ω_{min}, in the Beckman-Coulter XL-A/I analytical ultracentrifuge.

For the remaining part of $\nabla\mu_k$,

$$\sum_{w=1}^{n} \left(\frac{\partial \mu_k}{\partial c_w}\right)_{t,T,P,c_{k\neq w}} \left(\frac{\partial c_w}{\partial \xi}\right)_t = RT\left(\frac{\partial lnc_k}{\partial \xi}\right)_t \left[1 + c_k \sum_{w=1}^{n} \left(\frac{\partial c_w}{\partial c_k}\right)_t \left(\frac{\partial ln\gamma_k}{\partial c_w}\right)_{t,T,P,c_{a\neq w}}\right].$$

(A12)

The term in square brackets describes the deviation of μ_k from van ‘t Hoff behaviour.

The sum of the above descriptions of the various parts of $\nabla\mu_k$ yields the gradient of the chemical potential of component k in the system. Thus,

$$\nabla\mu_k = \left(\frac{\partial \mu_k}{\partial \xi}\right)_t = M_k \bar{v}_k \rho g_E + RT\left(\frac{\partial lnc_k}{\partial \xi}\right)_t \left[1 + c_k \sum_{w=1}^{n} \left(\frac{\partial c_w}{\partial c_k}\right)_t \left(\frac{\partial ln\gamma_k}{\partial c_w}\right)_{t,T,P,c_{a\neq w}}\right],$$

(A13)

where the gravitational force term, $M_k\bar{v}_k\rho g_E$, is usually negligible ($M_k\bar{v}_k\rho g_E < 0.002\cdot M_k\bar{v}_k\rho\omega_{min}^2 r_{min}$). For cases where $M_k\bar{v}_k\rho g_E$, may not be negligible, its contribution to the total mass flow can be estimated by evaluating the system at zero electrical current.

Applying the above descriptions of the various parts of ∇U_k, the gradient of the total molar potential of solute component k in an MCE system can be written as

$$\nabla U_k = -\vec{X}_k = -M_k(1-\bar{v}_k\rho)g_E - z_k F\frac{E}{\varpi} + RT\left(\frac{\partial lnc_k}{\partial\xi}\right)_t\left[1 + c_k\sum_{w=1}^{n}\left(\frac{\partial c_w}{\partial c_k}\right)_t\left(\frac{\partial ln\gamma_k}{\partial c_w}\right)_{t,T,P,c_{a\neq w}}\right],$$

(A14a)

and, assuming $|M_k(1 - \bar{v}_k\rho)|g_E < 0.002|M_k(1 - \bar{v}_k\rho)|\omega_{min}^2 r_{min}$, ∇U_k can be approximated as

$$\nabla U_k = -\vec{X}_k = -z_k F\frac{E}{\varpi} + RT\left(\frac{\partial lnc_k}{\partial\xi}\right)_t\left[1 + c_k\sum_{w=1}^{n}\left(\frac{\partial c_w}{\partial c_k}\right)_t\left(\frac{\partial ln\gamma_k}{\partial c_w}\right)_{t,T,P,c_{a\neq w}}\right],$$

(A14b)

where $\vec{X}_k$ is the conjugate molar force (Equations A2 and I16) of solute component k. In general, the system in the MCE instrument would have be maintained at a temperature well below 273.15 K, or $|M_k(1 - \bar{v}_k\rho)|$ would have to exceed approximately 10^7 g/mol, before $M_k(1 - \bar{v}_k\rho)g_E$ would make a clearly detectable contribution to the gradient. (See Equation A23b.)

Using Equation A14b to describe the conjugate molar force of solute component q, the molar flow of solute component k in the system frame of reference, given in Equation A1, can be re-written as

$$J_k = \sum_{q=1}^{n} L_{k,q}\left\{z_q\frac{F}{\varpi}E + M_q(1-\bar{v}_q\rho)g_E - RT\left(\frac{\partial lnc_q}{\partial\xi}\right)_t\left[1 + c_q\sum_{w=1}^{n}\left(\frac{\partial c_w}{\partial c_q}\right)_t\left(\frac{\partial ln\gamma_q}{\partial c_w}\right)_{t,T,P,c_{a\neq w}}\right]\right\} + \frac{v_0 c_k}{M_k},$$

(A15a)

when the effects due to gravity are included, or

$$J_k = \sum_{q=1}^{n} L_{k,q} \left\{ z_q \frac{F}{\varpi} E - RT \left(\frac{\partial lnc_q}{\partial \xi} \right)_t \left[1 + c_q \sum_{w=1}^{n} \left(\frac{\partial c_w}{\partial c_q} \right)_t \left(\frac{\partial ln\gamma_q}{\partial c_w} \right)_{t,T,P,c_{a \neq w}} \right] \right\} + \frac{v_0 c_k}{M_k},$$

(A15b)

when the effects due to gravity are excluded.

For the effect of component q on component k, the coupled-flow-electrophoretic mobility coefficient is defined as

$$\boldsymbol{u}_{k,q} = \frac{M_q}{c_q} L_{k,q} z_q \frac{F}{\varpi},$$

(A16)

and the coupled-flow-diffusion coefficient is defined as

$$\boldsymbol{D}_{k,q} = \frac{M_q}{c_q} L_{k,q} RT \left[1 + c_q \sum_{w=1}^{n} \left(\frac{\partial c_w}{\partial c_q} \right)_t \left(\frac{\partial ln\gamma_q}{\partial c_w} \right)_{t,T,P,c_{a \neq w}} \right],$$

(A17)

so that

$$J_k = \sum_{q=1}^{n} \frac{c_q}{M_q} \left[\boldsymbol{u}_{k,q} E - \boldsymbol{D}_{k,q} \left(\frac{\partial lnc_q}{\partial \xi} \right)_t \right] + \frac{v_0 c_k}{M_k}.$$

(A18)

Like $L_{k,q}$, $\boldsymbol{u}_{k,q}$ and $\boldsymbol{D}_{k,q}$ link the molar flow of solute component k to the conjugate molar force of solute component q. Unlike $L_{k,q}$, $\boldsymbol{u}_{k,q} \neq \boldsymbol{u}_{q,k}$, and $\boldsymbol{D}_{k,q} \neq \boldsymbol{D}_{q,k}$.

An application of irreversible thermodynamics to the continuity equation for MCE

Equation A18 describes the molar flow of one solute component in a multi-component system in the MCE instrument, and derives from the application of irreversible thermodynamics to MCE [Godfrey, 1989; Laue et al., 1989; Moody and Shepard, 2004]. The result is similar to that obtained from the application of irreversible thermodynamics to analytical ultracentrifugation (AUC) [Williams et al., 1958; Fujita, 1962; Fujita, 1975].

Each coupled-flow-electrophoretic mobility (Equation A16) and coupled-flow-diffusion (Equation A17) coefficient is described in terms of its corresponding phenomenological coefficient, $L_{k,q}$. In the absence of magnetic fields or Coriolis forces, the reciprocal relations give $L_{k,q} = L_{q,k}$, but for q not equal to k, there is no equation that describes $L_{k,q}$ in terms of independently determinable parameters. (In the presence of magnetic fields or Coriolis forces, resort must be made of the more general form of the reciprocal relations mentioned in **Section G: The dissipation function and the Curie-Prigogine principle.**) For $L_{k,k}$,

$$\lim_{c_{q\neq k}\to 0} L_{k,k} = \frac{c_k}{N_A M_k f_k},$$

(A19)

where N_A is Avogadro's number and f_k is the frictional coefficient of solute component k, but this equation only applies in the limit as all solute concentrations other than that of solute component k approach zero. Nevertheless, if there are no solute components other than k, and if f_k, c_k and M_k are known, $L_{k,k}$ is the one phenomenological coefficient that can be calculated.

For a system of n components, there are n $L_{k,q=k}$ values and $(n^2 - n)/2$ $L_{k,q\neq k} = L_{q\neq k,k}$ values (assuming the absence of magnetic fields or Coriolis forces). Given n linearly independent equations in the form of Equation A1, in which the n values of $L_{k,q=k}$, the n values of $\vec{X}_q$, and the n values of $\vec{J}_k$ are known, the remaining unknowns, which are the $(n^2 - n)/2$ $L_{k,q\neq k} = L_{q\neq k,k}$ values, could be calculated for any part of the system in which n did not exceed 3, as for $n > 3$, $(n^2 - n)/2 > n$.

Of all the parameters needed to calculate $L_{k,k}$, f_k is the most challenging to determine. In the absence of solute components other than k, f_k can be calculated from the Stokes equation,

$$f_k = 6\pi\eta R_k^*,$$

(A20)

if R_k^*, the Stokes radius of an equivalent sphere of solute component k, and η, the solution viscosity, are known. The applicability of the Stokes equation, however, is questionable except as c_k approaches zero, at which point, η becomes identical to the solvent viscosity. Given the restricted applicability of Equation A19, the prospects for calculating $\mathbf{D}_{k,q}$ or $\mathbf{u}_{k,q}$

would hardly be less promising if $L_{k,k}$ could not be calculated under any conditions. (Nevertheless, for a practical approach to using such coefficients, see **Section N: A simple coupled-flow equation for MCE**.) The main utility of Equation A19 is to show that hydrodynamic parameters appear in the denominator of the one phenomenological coefficient that can be calculated. Thus, if expressions for other phenomenological coefficients were found, it would not be surprising if they too included hydrodynamic parameters in their denominators. (It should thus come as no surprise that no hydrodynamic parameters are found in Equation N10, from which the phenomenological coefficients of its sources cancel.)

In general, for n > 2 at least, $L_{k,q}$, $\mathbf{D}_{k,q}$ and $\mathbf{u}_{k,q}$ cannot be calculated from other experimentally determinable parameters, and cannot be determined directly by any practical or routine approach. (For an attempt to calculate $L_{k,q}$ values from results obtained from special cases of systems in which n ≤ 3, see the discussion following Equation N44.) Informative parameters derived from $L_{k,q}$, $\mathbf{D}_{k,q}$ and $\mathbf{u}_{k,q}$ can be determined experimentally, however. These experimentally determinable parameters are the apparent diffusion coefficient, the apparent electrophoretic mobility coefficient, and the apparent reduced valence coefficient. (In reference to these coefficients, the word “apparent” is dropped henceforth, except parenthetically in the three definitive descriptions that immediately follow.)

The (apparent) diffusion coefficient of solute component k is

$$D_k = \frac{M_k}{c_k\left(\frac{\partial lnc_k}{\partial \xi}\right)_t}\sum_{q=1}^{n}\frac{c_q}{M_q}\left(\frac{\partial lnc_q}{\partial \xi}\right)_t \boldsymbol{D}_{k,q} = \frac{M_k}{\left(\frac{\partial c_k}{\partial \xi}\right)_t}\sum_{q=1}^{n}\frac{1}{M_q}\left(\frac{\partial c_q}{\partial \xi}\right)_t \boldsymbol{D}_{k,q}$$

$$= \frac{M_k}{\left(\frac{\partial c_k}{\partial \xi}\right)_t} RT\sum_{q=1}^{n} L_{k,q}\left(\frac{\partial lnc_q}{\partial \xi}\right)_t\left[1 + c_q\sum_{w=1}^{n}\left(\frac{\partial c_w}{\partial c_q}\right)_t\left(\frac{\partial ln\gamma_q}{\partial c_w}\right)_{t,T,P,c_{a\neq w}}\right],$$

(A21)

and the (apparent) electrophoretic mobility coefficient of solute component k is

$$u_k = \frac{M_k}{c_k}\sum_{q=1}^{n}\frac{1}{M_q}c_q\boldsymbol{u}_{k,q} + \frac{v_0}{E} = \frac{M_k}{c_k}\frac{F}{\varpi}\sum_{q=1}^{n} L_{k,q}z_q + \frac{v_0}{E}$$

(A22)

where, for a multi-species component, $M_k = (M_k)_J$ is the molar-flow-average molar mass of component k. (See **Section I: Calculating valence, molar mass, chemical potential and partial specific volume for a multi-species component.**) Resort to $(M_k)_J$ is necessary for the definition of the mass flow of component k in terms of the molar flow of component k. As mass is conserved but molarity is not, the mass flow of component k is preferable to the molar flow of component k when casting the continuity equation, the solution to which provides the sought-after description of transport in the system.

Excluding the effects due to gravity, the (apparent) reduced valence coefficient of solute component *k* is defined as

$$\sigma_k = \frac{Eu_k}{D_k} = \frac{\left(\frac{\partial lnc_k}{\partial\xi}\right)_t\left(E\sum_{q=1}^{n}\frac{1}{M_q}c_q\boldsymbol{u}_{k,q} + v_0\frac{c_k}{M_k}\right)}{\sum_{q=1}^{n}\frac{1}{M_q}\left(\frac{\partial c_q}{\partial\xi}\right)_t\boldsymbol{D}_{k,q}} = \frac{\left(\frac{\partial lnc_k}{\partial\xi}\right)_t\left(\sum_{q=1}^{n}\frac{1}{M_q}c_q\boldsymbol{\sigma}_{k,q}\boldsymbol{D}_{k,q} + v_0\frac{c_k}{M_k}\right)}{\sum_{q=1}^{n}\frac{1}{M_q}\left(\frac{\partial c_q}{\partial\xi}\right)_t\boldsymbol{D}_{k,q}}$$

$$= \frac{\left(\frac{\partial lnc_k}{\partial\xi}\right)_t\left(E\frac{F}{\varpi}\sum_{q=1}^{n} L_{k,q}z_q + v_0\frac{c_k}{M_k}\right)}{RT\sum_{q=1}^{n}L_{k,q}\left(\frac{\partial lnc_q}{\partial\xi}\right)_t\left[1 + c_q\sum_{w=1}^{n}\left(\frac{\partial c_w}{\partial c_q}\right)_t\left(\frac{\partial ln\gamma_q}{\partial c_w}\right)_{t,T,P,c_{a\neq w}}\right]},$$

(A23a)

while including the effects due to gravity yields

$$\sigma_k = \frac{\left(\frac{\partial lnc_k}{\partial\xi}\right)_t\left[E\frac{F}{\varpi}\sum_{q=1}^{n} L_{k,q}z_q + g_E\sum_{q=1}^{n} L_{k,q}M_q\left(1-\bar{v}_q\rho\right) + v_0\frac{c_k}{M_k}\right]}{RT\sum_{q=1}^{n}L_{k,q}\left(\frac{\partial lnc_q}{\partial\xi}\right)_t\left[1 + c_q\sum_{w=1}^{n}\left(\frac{\partial c_w}{\partial c_q}\right)_t\left(\frac{\partial ln\gamma_q}{\partial c_w}\right)_{t,T,P,c_{a\neq w}}\right]},$$

(A23b)

where, for the effect of component *q* on component *k*, $\boldsymbol{\sigma}_{k,q}$ is the coupled-flow analogue of σ_k. As shown in Section N, $\boldsymbol{\sigma}_{k,q} = E\boldsymbol{u}_{k,q}/\boldsymbol{D}_{k,q}$ (Equation N10). Like $\boldsymbol{u}_{k,q}$ and $\boldsymbol{D}_{k,q}$, $\boldsymbol{\sigma}_{k,q}$ links the molar flow of solute component *k* to the conjugate molar force of solute component *q*. Also like $\boldsymbol{u}_{k,q}$ and $\boldsymbol{D}_{k,q}$, $\boldsymbol{\sigma}_{k,q} \neq \boldsymbol{\sigma}_{q,k}$. While σ_k cannot be completely defined without specifying *E*, on which it explicitly depends, this might be viewed as a virtue, as unlike u_k, σ_k preserves information regarding the field dependence of transport, including some effects that might be expected in cases of field-dependent solvent velocity. (At a minimum, for u_k to be field-independent, v_0 would have to be proportional to E over the range of experimentally practical fields.)

Because σ_k is proportional to the ratio of u_k and D_k, and because both u_k and D_k, are proportional to the highly fraught parameter, $(M_k)_J$ (see Equations I13 to I15), the two $(M_k)_J$ terms cancel in σ_k. As shown in Section I, however, M_j and other parameters pertaining to multi-species components are no less inconvenient. Such issues are rendered moot, however, by working, as in Section C (**A solution to the t- and ξ-dependent continuity equation for MCE in terms of species**), with species rather than components.

Along with D_k, either u_k or σ_k are the transport coefficients needed to describe MCE results or simulate transport in MCE. In principle, for each solute component, all three of these parameters can be determined experimentally, though in practice, for complicated systems, it can be difficult to obtain more than an average or approximate value of some parameters by analysis of experimental data.

The coupled flow coefficients, $\mathbf{D}_{k,q}$ and $\mathbf{u}_{k,q}$, are distinct from $D_{k,j}$ and $u_{k,j}$, respectively, which, respectively, are the t-dependent, ξ-independent scalar coefficients derived from D_k and u_k in Section B (**Steps taken to solve the t- and ξ-dependent continuity equation for MCE**), and are also distinct from $D_{k,e}$ and $u_{k,e}$, respectively, which, respectively, are the diffusion and electrophoretic mobility coefficients of species e of component k in Section C. To highlight their distinction from similarly denoted parameters, $\mathbf{D}_{k,q}$ and $\mathbf{u}_{k,q}$ are shown in bold typeface.

The relationship between J_k and I_k is given by $I_k = M_k J_k$, the derivation of which is shown in Section I (**Calculating valence, molar mass, chemical potential and partial specific volume for a multi-species component**). Thus, in terms of D_k and u_k, or D_k and σ_k, the mass flow of solute component k can be written as

$$J_k M_k = I_k = c_k \left[u_k E - D_k \left(\frac{\partial ln c_k}{\partial \xi} \right)_t \right]$$

or

$$J_k M_k = I_k = c_k D_k \left[\sigma_k - \left(\frac{\partial ln c_k}{\partial \xi} \right)_t \right].$$

(A24)

The total mass flow is

$$I = \sum_{k=1}^{n} I_k .$$

(A25)

As a function of t and ξ, the continuity equation for MCE can be written as

$$\left(\frac{\partial c}{\partial t} \right)_\xi = - \left(\frac{\partial I}{\partial \xi} \right)_t$$

or

$$\sum_{k=1}^{n} \left(\frac{\partial c_k}{\partial t} \right)_\xi = - \sum_{k=1}^{n} \left(\frac{\partial I_k}{\partial \xi} \right)_t ,$$

(A26)

where

$$c = \sum_{k=1}^{n} c_k$$

(A27)

is the total solute concentration.

Applying the finite-element approach of Claverie [Claverie et al., 1975; Cox and Dale, 1981], a numerical solution to the t- and ξ-dependent form of the continuity equation for MCE can be obtained. (See **Section B: Steps taken to solve the t- and ξ-dependent continuity equation for MCE.**)

Averages

Equations A24 and A25 can be combined to yield

$$I = \sum_{k=1}^{n} \left[c_k D_k \sigma_k - D_k \left(\frac{\partial c_k}{\partial \xi} \right)_t \right]$$

or

$$I = \sum_{k=1}^{n} \left[c_k u_k E - D_k \left(\frac{\partial c_k}{\partial \xi} \right)_t \right],$$

(A28)

which is the equation of total mass flow.

The most useful averages that can be applied to the total mass flow equation are the overall gradient-average diffusion coefficient, D_G, and the overall weight-average electrophoretic mobility coefficient, u_w. The diffusion coefficients and concentration gradients of all solute components are used to calculate D_G, while the electrophoretic mobility coefficients and concentrations of all solute components are used to calculate u_w. Respectively, these averages can be calculated as

$$D_G = \frac{\sum_{k=1}^{n} D_k \left(\frac{\partial c_k}{\partial \xi} \right)_t}{\sum_{k=1}^{n} \left(\frac{\partial c_k}{\partial \xi} \right)_t} = \frac{\sum_{k=1}^{n} D_k \left(\frac{\partial c_k}{\partial \mathrm{r}} \right)_t}{\sum_{k=1}^{n} \left(\frac{\partial c_k}{\partial \mathrm{r}} \right)_t}$$

(A29)

and, in terms of its product with E,

$$E u_w = E \frac{\sum_{k=1}^{n} u_k c_k}{\sum_{k=1}^{n} c_k} = \frac{\sum_{k=1}^{n} \sigma_k D_k c_k}{\sum_{k=1}^{n} c_k} = (\sigma D)_w ,$$

(A30)

where $(\sigma D)_w$ is the weight average of the product, $\sigma_k D_k$, for all solute components. Applied to the flow equation, D_G and u_w yield

$$I = \left[c u_w E - D_G \left(\frac{\partial c}{\partial \xi} \right)_t \right].$$

(A31)

In general, at any time up to and including steady state,

$$E \frac{u_w}{D_G} = \left[\frac{E \sum_{k=1}^{n} u_k c_k}{\sum_{k=1}^{n} c_k} \right] \left[\frac{\sum_{k=1}^{n} \left(\frac{\partial c_k}{\partial \xi} \right)_t}{\sum_{k=1}^{n} D_k \left(\frac{\partial c_k}{\partial \xi} \right)_t} \right] = \left(\frac{\partial lnc}{\partial \xi} \right)_t \left[\frac{E \sum_{k=1}^{n} u_k c_k}{\sum_{k=1}^{n} D_k \left(\frac{\partial c_k}{\partial \xi} \right)_t} \right]$$

$$= \left(\frac{\partial lnc}{\partial \xi} \right)_t \left[\frac{\sum_{k=1}^{n} \sigma_k D_k c_k}{\sum_{k=1}^{n} D_k \left(\frac{\partial c_k}{\partial \xi} \right)_t} \right].$$

(A32)

Though general, this equation cannot be applied to the case of all $(\partial c_k/\partial \xi)_t = 0$, except by taking the limit as all $(\partial c_k/\partial \xi)_t$ become vanishingly small after having first been perturbed from zero. Such a limiting case pertains in the approach to steady state at zero field, provided that a field has been applied long enough to perturb $(\partial c_k/\partial \xi)_t$ from zero. Steady state is dealt with next.

Steady state

Throughout an MCE system (hence, at all ξ) at steady state, $(\partial c/\partial t)_\xi = 0$, $I = I_\infty$ is constant, and all derivatives of I_∞ equal zero, where I_∞ is the total mass flow of all solute components at steady state. Furthermore, at steady state, all system properties become t-independent, so that all partial differentials with respect to all spatial dimensions, including ξ, become ordinary differentials. Additionally, it is assumed here that all partial differentials with respect to the spatial dimensions other than ξ are zero. For the steady state condition, then, Equations A24 and A25 yield

$$\sum_{k=1}^{n} \left[c_k D_k \sigma_k - D_k \frac{dc_k}{d\xi} \right] = \sum_{k=1}^{n} I_{k,\infty} = I_\infty ,$$

or, applying the definition of σ_k in Equation A23a,

$$\sum_{k=1}^{n}\left[c_k u_k E - D_k \frac{dc_k}{d\xi}\right] = \sum_{k=1}^{n} I_{k,\infty} = I_\infty \ ,$$

(A33)

where the expression in square brackets is equal to $I_{k,\infty}$, which is the mass flow of solute component k at steady state. Due to conservation of mass, at steady state, throughout the system, $dI_\infty/d\xi = 0$ and each $dI_{k,\infty}/d\xi = 0$. (Conservation of mass ensures that $(\partial c_k/\partial t)_\xi = -(\partial I_k/\partial \xi)_t$. Thus, when $(\partial c_k/\partial t)_\xi = 0$, as it does at steady state, $(\partial I_k/\partial \xi)_t = 0$.) Furthermore, for membrane-confined components, $(I_\infty)_{mc} = 0$ and each $(I_{k,\infty})_{mc} = 0$, where $(I_\infty)_{mc}$ is the total mass flow of all membrane-confined solute components at steady state, and $(I_{k,\infty})_{mc}$ is the mass flow of membrane-confined solute component k at steady state. Nevertheless, as a consequence of their concentration dependence, each D_k, σ_k, u_k and E can, and most likely will, be ξ-dependent at steady state, except for the zero-field case where each $dc_k/d\xi = 0$ at all ξ.

Although the mass flow of each solute component is ξ-independent at steady state, the mass flows of individual species of a solute component may be ξ-dependent at steady state. In general, throughout the system, the mass flows of the species of a solute component sum to a ξ-independent constant at steady state, and if all those species are membrane-confined, that constant is equal to zero. (The dependence of species concentrations on the concentration of the component comprising those species, versus the independence of the concentration of one component from the concentrations of other components, accounts for the difference in expectations for the mass flow of a species versus the mass flow of a component at steady state.)

In the limit as steady state, or infinite time, is approached, I approaches I_∞ in general, and zero for membrane-confined components. Applying this limit to a re-arrangement of Equation A31 results in

$$\lim_{t\to\infty} E\frac{u_w}{D_G} = \lim_{t\to\infty}\left[\left(\frac{\partial lnc}{\partial \xi}\right)_t + \frac{I}{cD_G}\right] = \frac{dlnc}{d\xi} + \frac{I_\infty}{cD_G} \, .$$

(A34)

Applying the steady-state condition, in which each $I_k = I_{k,\infty}$ generally, to Equation A28 (expressed in terms of σ_k and D_k) shows that, for each solute component, k,

$$\lim_{t\to\infty}\left[c_k D_k \sigma_k - D_k\left(\frac{\partial c_k}{\partial\xi}\right)_t\right] = I_{k,\infty}\ .$$

(A35)

Dividing this equation by D_k yields

$$\lim_{t\to\infty}\left[c_k\sigma_k - \left(\frac{\partial c_k}{\partial\xi}\right)_t\right] = \frac{I_{k,\infty}}{D_k}\,.$$

(A36)

Taking the sum over all k results in

$$\lim_{t\to\infty}\sum_{k=1}^{n}\left[c_k\sigma_k - \left(\frac{\partial c_k}{\partial\xi}\right)_t\right] = \lim_{t\to\infty}\left[\sum_{k=1}^{n} c_k\sigma_k - \sum_{k=1}^{n}\left(\frac{\partial c_k}{\partial\xi}\right)_t\right] = \lim_{t\to\infty}\left[c\frac{\sum_{k=1}^{n} c_k\sigma_k}{\sum_{k=1}^{n} c_k} - \sum_{k=1}^{n}\left(\frac{\partial c_k}{\partial\xi}\right)_t\right]$$
$$= \lim_{t\to\infty}\left[c\sigma_w - \left(\frac{\partial c}{\partial\xi}\right)_t\right] = \sum_{k=1}^{n}\frac{I_{k,\infty}}{D_k}\,.$$

(A37)

When Equations A34 and A37 are applied solely to all membrane-confined components at steady state, I_∞ is replaced with $(I_\infty)_{mc} = 0$ in the former equation, and each $I_{k,\infty}$ is replaced with $(I_{k,\infty})_{mc} = 0$ in the latter equation. Division of Equation A37 by c, and inclusion of the membrane-confined components only, yields

$$\lim_{t\to\infty}\left[\sigma_w - \left(\frac{\partial lnc}{\partial\xi}\right)_t\right] = \frac{1}{c}\sum_{k=1}^{n}\frac{\left(I_{k,\infty}\right)_{mc}}{D_k} = 0.$$

(A38)

Thus,

$$\lim_{t\to\infty}\sigma_w = \lim_{t\to\infty}\left(\frac{\partial lnc}{\partial\xi}\right)_t + \frac{1}{c}\sum_{k=1}^{n}\frac{\left(I_{k,\infty}\right)_{mc}}{D_k} = \frac{dlnc}{d\xi} + \frac{1}{c}\sum_{k=1}^{n}\frac{\left(I_{k,\infty}\right)_{mc}}{D_k} = \frac{dlnc}{d\xi}\,.$$

(A39)

Combining the results of Equations A34 and A39 shows that

$$\lim_{t\to\infty} E\frac{u_w}{D_G} = \lim_{t\to\infty}\sigma_w\ .$$

(A40)

Equation A40 only applies to the membrane-confined components at steady state. Solving Equation A40 for D_G shows that, at steady state, $D_G = Eu_w/\sigma_w$ for the membrane-confined components. Furthermore, Equation A30 shows that, in general, $Eu_w = (\sigma D)_w$. Thus, for membrane-confined components at steady state, $D_G = (\sigma D)_w/\sigma_w$. Neither of these expressions for D_G is especially well defined for the case of steady state at zero field, however. Nevertheless, information about that system state can be gained from Equation A40 via Equation A39. As both $d\ln c/d\xi = 0$ and $I_\infty = 0$ at zero field at steady state, Equation A39 shows that, at zero field at steady state, $\sigma_w = 0$. Applying this result to Equation A40 shows that $Eu_w/D_G = 0$ at zero field at steady state. For all of this to hold, for the membrane-confined components, as the field approaches zero and the system approaches steady state at zero field, Eu_w must approach zero faster than D_G. Expressed as limits applied to $D_G = (\sigma D)_w/\sigma_w$,

$$\lim_{E\to 0}\left(\lim_{t\to\infty} D_G\right) = \lim_{E\to 0}\left[\lim_{t\to\infty}\frac{(\sigma D)_w}{\sigma_w}\right] = \frac{\sigma_w D_w}{\sigma_w} = D_w$$

(A41)

is obtained for membrane-confined components at steady state at zero field. (As the system approaches steady state at zero field, each σ_k approaches zero, as does σ_w, so that $(\sigma D)_w$ can be equated to $\sigma_w D_w$ as E approaches zero and t approaches infinity.)

Plateau regions

Plateau regions are defined as parts of the system where all $(\partial c_k/\partial\xi)_t = 0$. In the limit as all $(\partial c_k/\partial\xi)_t$ approach 0, Equation A28 simplifies to

$$\lim_{\left(\frac{\partial c_k}{\partial \xi}\right)_t \to 0} I = \sum_{k=1}^{n} c_k D_k \sigma_k = c(\sigma D)_w$$

or

$$\lim_{\left(\frac{\partial c_k}{\partial \xi}\right)_t \to 0} I = \sum_{k=1}^{n} c_k u_k E = cEu_w\ .$$

(A42)

Thus, $I = c(\sigma D)_w = cEu_w$ in plateau regions.

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Section B: Steps taken to solve the t- and ξ-dependent continuity equation for MCE

The following finite-element method for solving the t- and ξ-dependent continuity equation requires a resort to discrete spatial elements and a finite time increment. The method further requires the flow of each solute component to be zero at the system boundaries, ξ_m and ξ_b. Thus, except for the implicitly treated and presumably membrane-permeant solvent component, the finite-element solution shown is applied to membrane-confined solute components only. However, it is always possible to contrive a virtually infinite system that includes the membrane-bound system, and extends well beyond both membranes. For the virtually infinite system, at some appropriately distant points far from the membranes, the zero-flow boundary conditions can be imposed on membrane-permeant components, so that the same finite-element method can be used to solve the continuity equation for both membrane-confined and membrane-permeant components, albeit with different systems, which have different boundary positions, applied to the different types of components. (For simplicity, except for its much longer length, the virtually infinite system can be treated as having the same geometry as the membrane-bound system.) For each partially-confined component, both the membrane-bound and the virtually infinite system can be applied, with the proportion of time increments for which the virtually infinite system is applied set equal to the proportion of the partially-confined component that exhibits membrane-permeant behaviour. For both the membrane-bound and the virtually infinite systems, as usual, the solute components are treated explicitly, while the solvent component is treated implicitly.

The solution begins with an integration that takes advantage of the boundary conditions to eliminate the partial derivatives with respect to ξ. To that end, the continuity equation (Equation A26) is first multiplied by H, which is an arbitrary function of ξ, and then integrated over the entire range of ξ. (Ultimately, H will be replaced by a set of N functions of ξ indexed by i, where 1 ≤ i ≤ N.) Thus,

$$\sum_{k=1}^{n}\int_{\xi_m}^{\xi_b}\left(\frac{\partial c_k}{\partial t}\right)_{\xi} Hd\xi = -\sum_{k=1}^{n}\int_{\xi_m}^{\xi_b}\left(\frac{\partial I_k}{\partial \xi}\right)_{t} Hd\xi.$$

(B1)

Integrating the right hand side of this equation by parts results in

$$-\sum_{k=1}^{n}\int_{\xi_m}^{\xi_b}\left(\frac{\partial I_k}{\partial \xi}\right)_{t} Hd\xi = -\left[\sum_{k=1}^{n}[H(\xi_b)I_k(\xi_b) - H(\xi_m)I_k(\xi_m)] - \sum_{k=1}^{n}\int_{\xi_m}^{\xi_b}\left(\frac{\partial H}{\partial \xi}\right)_{t} I_k d\xi\right],$$

(B2)

where $I_k(\xi)$ is I_k at ξ and H(ξ) is H at ξ. As the boundary conditions in MCE are $I_k(\xi_m) = 0$ and $I_k(\xi_b) = 0$, where ξ_m is the location of the upper boundary and ξ_b is the location of the lower boundary, the preceding equation reduces to

$$-\sum_{k=1}^{n}\int_{\xi_m}^{\xi_b}\left(\frac{\partial I_k}{\partial \xi}\right)_{t} Hd\xi = \sum_{k=1}^{n}\int_{\xi_m}^{\xi_b}\left(\frac{\partial H}{\partial \xi}\right)_{t} I_k d\xi\ .$$

(B3)

Furthermore, as H is independent of t, $(\partial H/\partial \xi)_t = dH/d\xi$. Thus,

$$\sum_{k=1}^{n}\int_{\xi_m}^{\xi_b}\left(\frac{\partial H}{\partial \xi}\right)_{t} I_k d\xi = \sum_{k=1}^{n}\int_{\xi_m}^{\xi_b}\frac{dH}{d\xi} I_k d\xi,$$

(B4)

and Equation B1 becomes

$$\sum_{k=1}^{n}\int_{\xi_m}^{\xi_b}\left(\frac{\partial c_k}{\partial t}\right)_{\xi} H d\xi = \sum_{k=1}^{n}\int_{\xi_m}^{\xi_b}\frac{dH}{d\xi} I_k d\xi.$$

(B5)

Next, c_k is approximated as the sum of N products, each of which consists of a ξ-dependent function, P_h, multiplied by a corresponding ξ-independent coefficient, $c_{k,h}$, which nevertheless remains a function of t. With both P_h and $c_{k,h}$ indexed by h, where $1 \leq h \leq N$,

$$c = \sum_{k=1}^{n} c_k = \sum_{k=1}^{n}\sum_{h=1}^{N} c_{k,h} P_h.$$

(B6)

Each element, h, corresponds to a point, ξ_h. By convention, $\xi_1 = \xi_m$ and $\xi_N = \xi_b$. Despite the association of h with spatial parameters such as ξ_h, $c_{k,h}$ is independent of ξ, so that $(\partial c_{k,h}/\partial\xi)_t = dc_{k,h}/d\xi = 0$ at all ξ. (Each $c_{k,h}$ is ξ-independent, and at all ξ is equal to the value of c_k at ξ_h.) Figures B1 through B6 show, for the case of equal spacing between adjacent ξ_h, the consequences of using the hat function (also known as the triangular function) for each P_h, along with the corresponding set of ξ-independent solute component concentration coefficients, $c_{k,h}$.

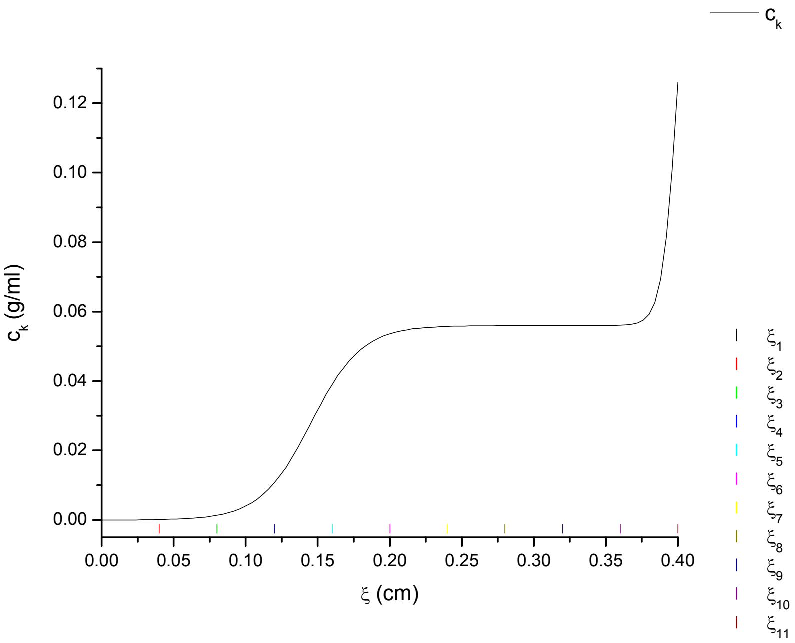

Figure B1. An example of c_k versus ξ at a single time, t. Specific points, ξ_h, are shown, where $1 \leq h \leq N$, and the points are equally spaced. A value of N = 11 was chosen for this example.

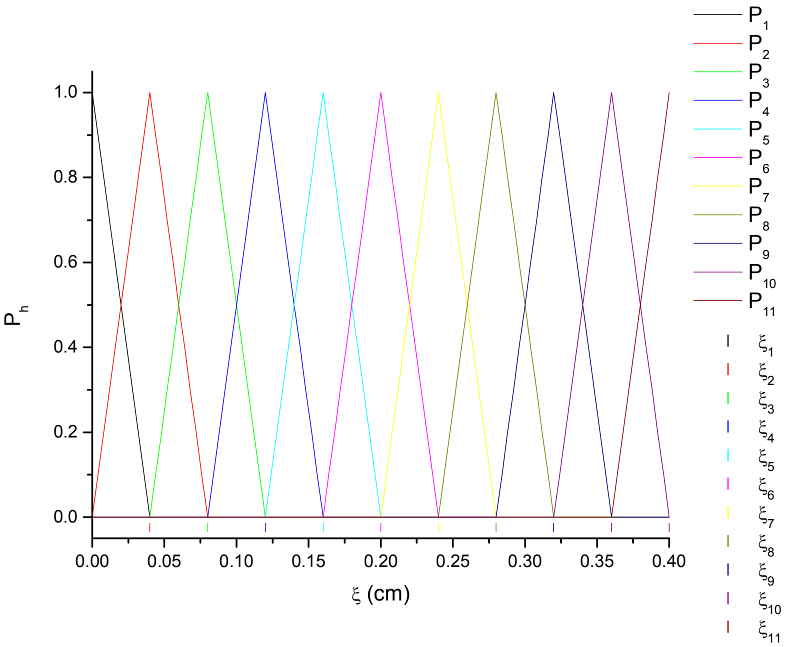

Figure B2. An example, corresponding to that shown in Figure B1, of P_h versus ξ. Each P_h function is independent of t. The same ξ_h values shown in Figure B1 are those applied here to the P_h functions. (See Equations B58 to B63 for a more general description of the P_h functions in the form of hat functions.)

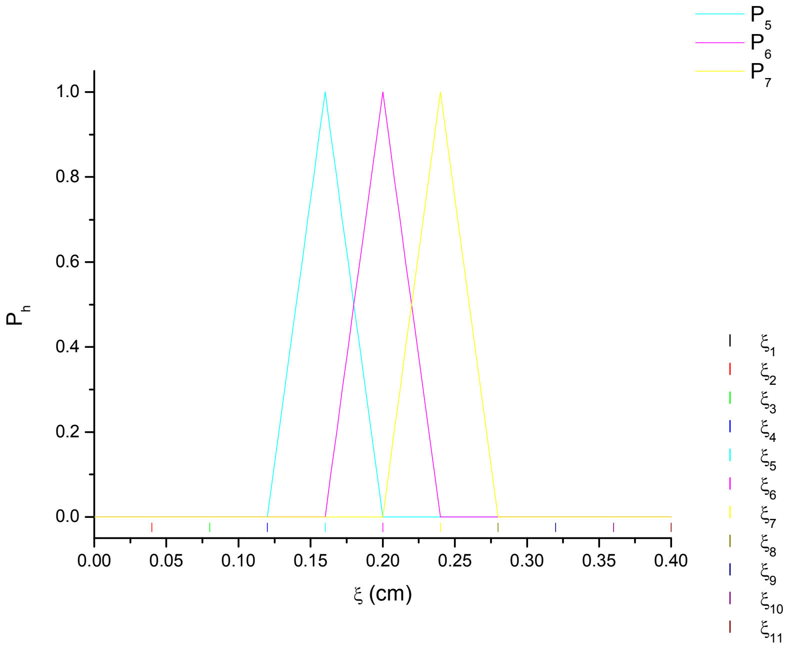

Figure B3. A detail of Figure B2, showing just three of the P_h functions versus ξ. The system boundaries are $\xi_1 = \xi_m = 0$ cm and $\xi_N = \xi_{11} = \xi_b = 0.4$ cm. In this example, where the points are equally spaced, each $\Delta\xi_h$ is the same, and is described by Equation B38. (Equations B53 to B57 describe each $\Delta\xi_h$ in general.) Calculation of ξ_h is given by Equation B36 in general, and by Equation B37 for the case of each $\Delta\xi_h$ being equal. Equations B58 to B63 describe each P_h function and its derivative.

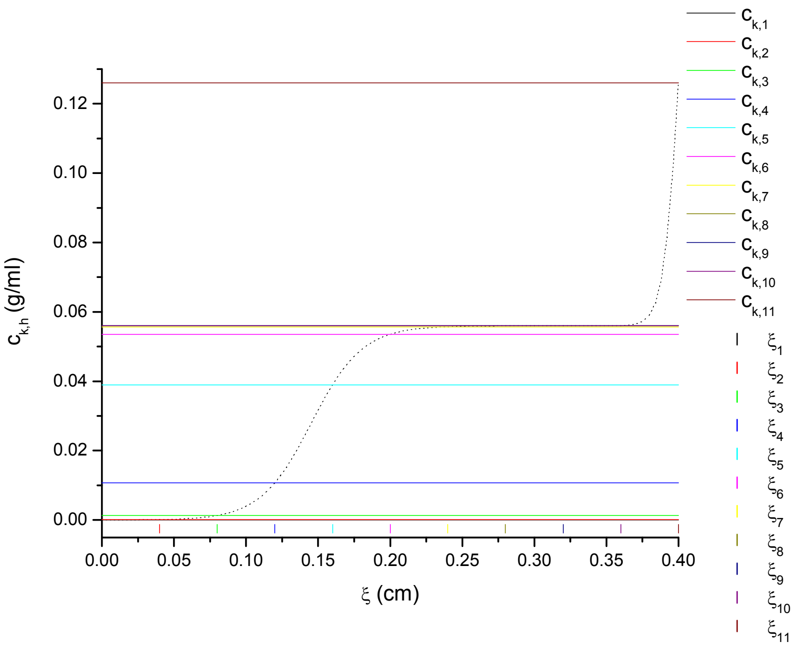

Figure B4. The ξ-independent concentrations, $c_{k,h}$, that describe c_k at time t. (Compare this figure with Figure B1, which shows c_k as a function of ξ at time t.) Though each $c_{k,h}$ is ξ-independent, this figure shows that the value of each $c_{k,h}$ at all ξ is equal to the value of c_k at ξ_h. (As c_k depends on both ξ and t, each $c_{k,h}$ remains t-dependent, however.)

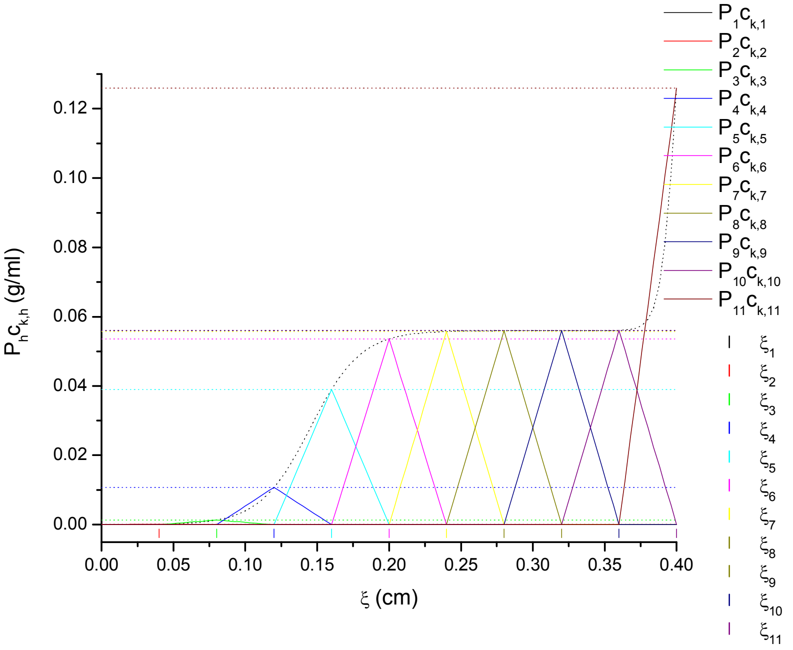

Figure B5. $P_h c_{k,h}$ versus ξ, where each $P_h c_{k,h}$ is obtained by multiplying each P_h shown in Figure B2 by the corresponding $c_{k,h}$ shown in Figure B4.

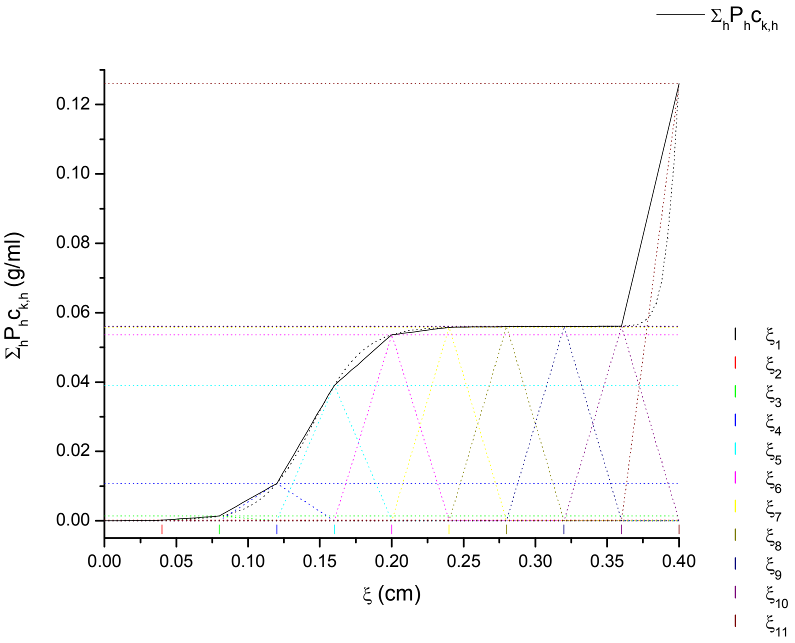

Figure B6. The sum, $\sum_{h=1}^{N} P_h c_{k,h}$, versus ξ. Each $P_h c_{k,h}$ used in the sum is shown individually in Figure B5.

For equally spaced points, $\xi_h = \xi_1 + [h - 1]\Delta\xi$, where Δξ is the spatial increment between any two adjacent points. Equations B54 to B57 describe Δξ for the general case, in which Δξ can be different for different pairs of adjacent spatial points. Equations B58 to B63 describe P_h and $dP_h/d\xi$ for P_h in the form of the hat function, and the case of potentially variable Δξ.

As $c_{k,h}$ is independent of ξ, $(\partial c_{k,h}/\partial t)_\xi = dc_{k,h}/dt$, so that

$$\sum_{k=1}^{n}\sum_{h=1}^{N}\frac{dc_{k,h}}{dt}\int_{\xi_m}^{\xi_b} P_h H d\xi = \sum_{k=1}^{n}\int_{\xi_m}^{\xi_b}\frac{dH}{d\xi} I_k d\xi.$$

(B7)

Expanding I_k (Equation A24) as

$$I_k = c_k D_k \left[\sigma_k - \left(\frac{\partial ln c_k}{\partial \xi} \right)_t \right] = \left[\sigma_k D_k c_k - D_k \left(\frac{\partial c_k}{\partial \xi} \right)_t \right],$$

and re-writing I_k in terms of the ξ-independent component concentration coefficients and corresponding ξ-dependent functions results in

$$I_k = \left[\sigma_k D_k \sum_{h=1}^{N} c_{k,h} P_h - D_k \sum_{h=1}^{N} c_{k,h} \frac{dP_h}{d\xi} \right].$$

(B8)

Substituting this for I_k in Equation B7 and rearranging slightly yields

$$\sum_{k=1}^{n} \sum_{h=1}^{N} \frac{dc_{k,h}}{dt} \int_{\xi_m}^{\xi_b} P_h H d\xi = \sum_{k=1}^{n} \int_{\xi_m}^{\xi_b} \frac{dH}{d\xi} \left[\sigma_k D_k \sum_{h=1}^{N} c_{k,h} P_h \right] d\xi - \sum_{k=1}^{n} \int_{\xi_m}^{\xi_b} \frac{dH}{d\xi} \left[D_k \sum_{h=1}^{N} c_{k,h} \frac{dP_h}{d\xi} \right] d\xi.$$

(B9)

The dependence of D_k (Equation A21) and σ_k (Equation A23) on the concentration, c_q, of each explicitly included solute component, q, renders D_k and σ_k ξ-dependent in all but special cases, such as t = 0, when all $(\partial c_q/\partial \xi)_t = 0$ at all ξ. (Where the solvent is compressible, it is remotely possible that, once |E| exceeds zero, $(\partial \rho_0/\partial \xi)_t \neq 0$, in which case, in all likelihood, $(\partial c_q/\partial \xi)_t$ will not equal zero at any position at any subsequent time.) A previously described [Cox and Dale, 1981], first approximate solution to a ξ- and t-dependent continuity equation for an MCE-like system was derived by treating D_k and the equivalent to Eu_k as ξ-independent. To obtain a second approximate solution to the continuity equation for MCE, D_k and σ_k are expressed in terms of ξ-independent coefficients that are separable from ξ-dependent functions. A first approximate solution that pertains to the case of $(\partial D_k/\partial \xi)_t = 0$ and $(\partial \sigma_k/\partial \xi)_t = 0$ at all ξ will then be derived from the second approximate solution later in this section (**The case of $(\partial \sigma_k/\partial \xi)_t = 0$ and $(\partial D_k/\partial \xi)_t = 0$ at all ξ**). In Section J (**Form of the general solution from Equation C32**), a general solution based on the second approximate solution will be presented.

First approximate solutions to the continuity equation for MCE have been, and in its initial application here, the second approximate solution will be, incorrectly applied to cases in which D_k, σ_k and Eu_k are ξ-dependent. Due to the typically weak ξ-dependence of D_k, σ_k and Eu_k, such first and second approximate solutions are likely to yield satisfactorily accurate results when applied to systems in which large and rapid concentration changes (as might arise from concentration gradients that are both high and steep) are absent. Sets of results obtained using the first approximate and second approximate solutions to the ξ- and t-dependent continuity equation for MCE are compared in **Section F (ξ-dependent functions to approximate $D_{k,e}$ and $\sigma_{k,e}$)**.

As it temporarily becomes more convenient to work with Eu_k and D_k instead of σ_k and D_k, Eu_k is approximated as the sum of N products, each of which consists of a ξ-dependent function, P_j, multiplied by a corresponding ξ-independent coefficient, $Eu_{k,j}$, which nevertheless remains a function of t. With both P_j and $Eu_{k,j}$ indexed by j, where $1 \le j \le N$,

$$Eu_k = \sum_{j=1}^{N} Eu_{k,j} P_j \; ,$$

(B10)

where each $Eu_{k,j}$ at all ξ is equal to Eu_k at ξ_j. The result expresses Eu_k as separable ξ-independent and ξ-dependent terms. Here, E and u_k, each of which is t- and ξ-dependent, are combined to implicitly form a single, t- and ξ-dependent parameter, $Eu_k = \upsilon_k$, where υ_k is the t- and ξ-dependent electrophoretic velocity of component k. (The total velocity is equal to that due to diffusion plus that due to electrophoresis, which includes the effect of solvent flow.) Thus, $Eu_{k,j} = \upsilon_{k,j}$, where υ_k is approximated as the sum of N products, each consisting of a ξ-dependent function, P_j, multiplied by a ξ-independent coefficient, $\upsilon_{k,j}$, which nevertheless remains a function of t.

To express D_k as separable ξ-independent and ξ-dependent terms, this transport coefficient is also approximated as the sum of N products, each of which consists of a ξ-dependent function, P_j, multiplied by a corresponding ξ-independent coefficient, $D_{k,j}$, which nevertheless remains a function of t. With both P_j and $D_{k,j}$ indexed by j, where $1 \le j \le N$,

$$D_k = \sum_{j=1}^{N} D_{k,j} P_j \,,$$

(B11)

where each $D_{k,j}$ at all ξ is equal to D_k at ξ_j.

Equations A23a, B10 and B11 are combined to express σ_k in terms of previously defined (Equations B10 and B11), separable ξ-independent and ξ-dependent terms. Thus,

$$\sigma_k = \frac{Eu_k}{D_k} = \frac{\sum_{j=1}^{N} Eu_{k,j} P_j}{\sum_{j=1}^{N} D_{k,j} P_j} \,.$$

(B12)

While the same approach has been used to express c_k, D_k and Eu_k in terms of ξ-independent coefficients of ξ-dependent functions, those ξ-independent coefficients and ξ-dependent functions are indexed by h in the case of c_k, but indexed by j in the case of D_k or Eu_k. At any given time, then, the ξ-dependent functions used in the description of c_k are expressed in terms of ξ_h, while the ξ-dependent functions used in the descriptions of D_k and Eu_k are expressed in terms of ξ_j. To use these parameters together in the same solution of the continuity equation, at each time point, the set of all ξ_j is made equivalent to the set of all ξ_h.

Using Eu_k in place of $\sigma_k D_k$ (from a re-arrangement of Equation A23a) results in

$$\sum_{k=1}^{n}\sum_{h=1}^{N} \frac{dc_{k,h}}{dt} \int_{\xi_m}^{\xi_b} P_h H d\xi = \sum_{k=1}^{n}\sum_{h=1}^{N} c_{k,h} \int_{\xi_m}^{\xi_b} Eu_k P_h \frac{dH}{d\xi} d\xi - \sum_{k=1}^{n}\sum_{h=1}^{N} c_{k,h} \int_{\xi_m}^{\xi_b} D_k \frac{dP_h}{d\xi}\frac{dH}{d\xi} d\xi.$$

(B13)

Replacing Eu_k with the expression in terms of $Eu_{k,j}$, and replacing D_k with the expression in terms of $D_{k,j}$, yields

$$\sum_{k=1}^{n}\sum_{h=1}^{N} \frac{dc_{k,h}}{dt} \int_{\xi_m}^{\xi_b} P_h H d\xi$$

$$= \sum_{k=1}^{n}\sum_{h=1}^{N} c_{k,h} \int_{\xi_m}^{\xi_b} \sum_{j=1}^{N} Eu_{k,j} P_j \, P_h \frac{dH}{d\xi} d\xi - \sum_{k=1}^{n}\sum_{h=1}^{N} c_{k,h} \int_{\xi_m}^{\xi_b} \sum_{j=1}^{N} D_{k,j} P_j \frac{dP_h}{d\xi}\frac{dH}{d\xi} d\xi,$$

and permits the ξ-independent parameters, $D_{k,j}$ and $Eu_{k,j}$, to be factored out of the integrals. Thus,

$$\sum_{k=1}^{n}\sum_{h=1}^{N}\frac{dc_{k,h}}{dt}\int_{\xi_m}^{\xi_b}P_h H d\xi$$
$$=\sum_{k=1}^{n}\sum_{h=1}^{N}c_{k,h}\sum_{j=1}^{N}Eu_{k,j}\left[\int_{\xi_m}^{\xi_b}P_j P_h\frac{dH}{d\xi}d\xi\right]$$
$$-\sum_{k=1}^{n}\sum_{h=1}^{N}c_{k,h}\sum_{j=1}^{N}D_{k,j}\left[\int_{\xi_m}^{\xi_b}P_j\frac{dP_h}{d\xi}\frac{dH}{d\xi}d\xi\right].$$

(B14)

Letting

$$\sigma_{k,j}=\frac{Eu_{k,j}}{D_{k,j}},$$

(B15)

where $\sigma_{k,j}$ is ξ-independent by virtue of $D_{k,j}$ and $Eu_{k,j}$ being ξ-independent, the solution can now be expressed, after some re-arrangement, as

$$\sum_{k=1}^{n}\sum_{h=1}^{N}\left(\frac{dc_{k,h}}{dt}\int_{\xi_m}^{\xi_b}P_h H d\xi-c_{k,h}\sum_{j=1}^{N}D_{k,j}\left[\sigma_{k,j}\int_{\xi_m}^{\xi_b}P_j P_h\frac{dH}{d\xi}d\xi-\int_{\xi_m}^{\xi_b}P_j\frac{dP_h}{d\xi}\frac{dH}{d\xi}d\xi\right]\right)=0.$$

(B16)

At all ξ, each of the N scalar coefficients, $\sigma_{k,j}$ (defined in Equation B15) is equal to σ_k at ξ_j. As a result of using Equation B15 in Equation B16, the product, $D_k\sigma_k$, has been expressed as the sum of N products, each consisting of a ξ-dependent function, P_j, multiplied by a ξ-independent coefficient, $D_{k,j}\sigma_{k,j}$, which nevertheless remains a function of t. Additionally, the coefficient $D_{k,j}\sigma_{k,j}$ is itself the product of the previously defined coefficients, $D_{k,j}$ and $\sigma_{k,j}$.

Dividing Equation B16 by 2, and expressing $dc_{k,h}/dt$ as $\Delta c_{k,h}/\Delta t$, where $\Delta c_{k,h}$ and Δt are finite increments, yields

$$\frac{1}{2}\sum_{k=1}^{n}\sum_{h=1}^{N}\left(\frac{\Delta c_{k,h}}{\Delta t}\int_{\xi_m}^{\xi_b}P_h H d\xi - c_{k,h}\sum_{j=1}^{N}D_{k,j}\left[\sigma_{k,j}\int_{\xi_m}^{\xi_b}P_j P_h\frac{dH}{d\xi}d\xi - \int_{\xi_m}^{\xi_b}P_j\frac{dP_h}{d\xi}\frac{dH}{d\xi}d\xi\right]\right) = 0.$$

(B17)

The difference between the unknown concentration, $c_{k,h+} = c_{k,h}$ at [t + Δt], and the known concentration, $c_{k,h-} = c_{k,h}$ at t, is the change in concentration, $\Delta c_{k,h}$, during the time increment, Δt = [t + Δt] - t. Using $\Delta c_{k,h} = c_{k,h+} - c_{k,h-}$, and multiplying by Δt, yields

$$\frac{1}{2}\sum_{k=1}^{n}\sum_{h=1}^{N}\left(\left[c_{k,h+} - c_{k,h-}\right]\int_{\xi_m}^{\xi_b}P_h H d\xi \right.$$
$$\left. - c_{k,h}\sum_{j=1}^{N}D_{k,j}\left[\sigma_{k,j}\int_{\xi_m}^{\xi_b}P_j P_h\frac{dH}{d\xi}d\xi - \int_{\xi_m}^{\xi_b}P_j\frac{dP_h}{d\xi}\frac{dH}{d\xi}d\xi\right]\Delta t\right) = 0.$$

(B18)

The remaining $c_{k,h}$ term can be replaced with either $c_{k,h-}$, which would yield the less stable explicit solution, or $c_{k,h+}$, which would yield the more stable implicit solution. In the Crank-Nicholson approach [Schuck et al., 1998] used here, both substitutions are made, resulting in two forms of Equation 18. Additionally, $\sigma_{k,j+}$ and $D_{k,j+}$, which, respectively, represent $\sigma_{k,j}$ and $D_{k,j}$ at time [t + Δt], are used in conjunction with the explicit form of Equation B18, where $c_{k,h}$ is expressed in terms of $c_{k,h+}$. Finally, $\sigma_{k,j-}$ and $D_{k,j-}$, which, respectively, represent $\sigma_{k,j}$ and $D_{k,j}$ at time t, are used in conjunction with the implicit form of Equation B18, where $c_{k,h}$ is expressed in terms of $c_{k,h-}$. The two resulting versions of Equation B18 are summed to yield, by virtue of the previous division by 2, their average. The average, like any sum of the two solutions, is considered stable, and is expected to permit the use of larger Δt values than either the explicit or implicit solution alone would.

Applying the Crank-Nicholson approach yields, after some rearrangement,

$$\sum_{k=1}^{n}\sum_{h=1}^{N} c_{k,h+}\left(\int_{\xi_m}^{\xi_b} P_h H d\xi - \sum_{j=1}^{N} D_{k,j+}\left[\sigma_{k,j+}\int_{\xi_m}^{\xi_b} P_j P_h \frac{dH}{d\xi} d\xi - \int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi}\frac{dH}{d\xi} d\xi\right]\Delta t\right)$$
$$= \sum_{k=1}^{n}\sum_{h=1}^{N} c_{k,h-}\left(\int_{\xi_m}^{\xi_b} P_h H d\xi\right.$$
$$\left. + \sum_{j=1}^{N} D_{k,j-}\left[\sigma_{k,j-}\int_{\xi_m}^{\xi_b} P_j P_h \frac{dH}{d\xi} d\xi - \int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi}\frac{dH}{d\xi} d\xi\right]\Delta t\right).$$

(B19)

As σ_k and D_k are functions of all c_k (see Equations A21 to A23), and as each c_k is time dependent (see Equation A26), σ_k and D_k are also time dependent. Thus, for the purpose of obtaining a general solution, $\sigma_{k,j-}$ and $D_{k,j-}$ must be expressed as functions of parameters equal to all $c_{k,h-}$ for which h = j, while $\sigma_{k,j+}$ and $D_{k,j+}$ must be expressed as functions of parameters equal to all $c_{k,h+}$ for which h = j. General expressions of this sort are presented shortly. (See **Evaluating the ξ-independent coefficients of the basis functions indexed by j.**)

At this point, there are n equations and nN unknown values of $c_{k,h+}$. To obtain the nN equations needed to solve for all values of $c_{k,h+}$, H is replaced by N functions,

$$H = \sum_{i=1}^{N} P_i\,,$$

(B20)

where each P_i has the same functional form as each corresponding P_h. (For i = h, $P_i = P_h$.) Applying Equation B20, the set of equations describing the solution is given by

$$\sum_{k=1}^{n}\sum_{h=1}^{N}\sum_{i=1}^{N} c_{k,h+}\left(\int_{\xi_m}^{\xi_b} P_h P_i d\xi - \sum_{j=1}^{N} D_{k,j+}\left[\sigma_{k,j+}\int_{\xi_m}^{\xi_b} P_j P_h \frac{dP_i}{d\xi} d\xi - \int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi}\frac{dP_i}{d\xi} d\xi\right]\Delta t\right)$$
$$= \sum_{k=1}^{n}\sum_{h=1}^{N}\sum_{i=1}^{N} c_{k,h-}\left(\int_{\xi_m}^{\xi_b} P_h P_i d\xi\right.$$
$$\left. + \sum_{j=1}^{N} D_{k,j-}\left[\sigma_{k,j-}\int_{\xi_m}^{\xi_b} P_j P_h \frac{dP_i}{d\xi} d\xi - \int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi}\frac{dP_i}{d\xi} d\xi\right]\Delta t\right).$$

(B21)

The result is solved for $c_{k,h+}$ using the process described below. (See **Solving for $c_{k,h+}$.**) Interactions between solute components and within each solute component (involving its species) are handled separately between time steps. (See **Section C: A solution to the t- and ξ-dependent continuity equation for MCE in terms of species.**)

Evaluating the ξ-independent coefficients of the basis functions indexed by j

Truncated virial expansions are used to approximate the dependence of $D_{k,j-}$, $D_{k,j+}$, $\sigma_{k,j-}$ and $\sigma_{k,j+}$ on the concentration of each explicitly included solute component. To evaluate the ξ-independent coefficients of the ξ-dependent functions indexed by j (see Equations B10 and B11), prior to each time increment, $D_{k,j-}$, $D_{k,j+}$, $\sigma_{k,j-}$ and $\sigma_{k,j+}$ are, to the extent possible, approximated by

$$D_{k,j-} = D^\circ{}_{k,j-}\left(\frac{\sum_{b=1}^{\infty}\sum_{q=1}^{n} y_{b,k,q}\frac{dc_{q,j-}{}^{b}}{dc_{q,j-}}}{\sum_{b=1}^{\infty}\sum_{q=1}^{n} h_{b,k,q}\frac{dc_{q,j-}{}^{b}}{dc_{q,j-}}}\right),$$

(B22-)

$$D_{k,j+} = D^\circ{}_{k,j+}\left(\frac{\sum_{b=1}^{\infty}\sum_{q=1}^{n} y_{b,k,q}\frac{dc_{q,j+}{}^{b}}{dc_{q,j+}}}{\sum_{b=1}^{\infty}\sum_{q=1}^{n} h_{b,k,q}\frac{dc_{q,j+}{}^{b}}{dc_{q,j+}}}\right),$$

(B22+)

$$\sigma_{k,j-} = \frac{Eu_{k,j-}}{D_{k,j-}} = \frac{Eu^\circ{}_{k,j-}}{D^\circ{}_{k,j-}}\frac{\left(\frac{\sum_{b=1}^{\infty}\sum_{q=1}^{n} p_{b,k,q}\frac{dc_{q,j-}{}^{b}}{dc_{q,j-}}}{\sum_{b=1}^{\infty}\sum_{q=1}^{n} h_{b,k,q}\frac{dc_{q,j-}{}^{b}}{dc_{q,j-}}}\right)}{\left(\frac{\sum_{b=1}^{\infty}\sum_{q=1}^{n} y_{b,k,q}\frac{dc_{q,j-}{}^{b}}{dc_{q,j-}}}{\sum_{b=1}^{\infty}\sum_{q=1}^{n} h_{b,k,q}\frac{dc_{q,j-}{}^{b}}{dc_{q,j-}}}\right)} = \sigma^\circ{}_{k,j-}\left(\frac{\sum_{b=1}^{\infty}\sum_{q=1}^{n} p_{b,k,q}\frac{dc_{q,j-}{}^{b}}{dc_{q,j-}}}{\sum_{b=1}^{\infty}\sum_{q=1}^{n} y_{b,k,q}\frac{dc_{q,j-}{}^{b}}{dc_{q,j-}}}\right)$$

(B23-)

and

$$\sigma_{k,j+} = \frac{Eu_{k,j+}}{D_{k,j+}} = \frac{Eu^{\circ}{}_{k,j+}}{D^{\circ}{}_{k,j+}} \frac{\left(\frac{\sum_{b=1}^{\infty}\sum_{q=1}^{n} p_{b,k,q} \frac{dc_{q,j+}{}^{b}}{dc_{q,j+}}}{\sum_{b=1}^{\infty}\sum_{q=1}^{n} h_{b,k,q} \frac{dc_{q,j+}{}^{b}}{dc_{q,j+}}}\right)}{\left(\frac{\sum_{b=1}^{\infty}\sum_{q=1}^{n} y_{b,k,q} \frac{dc_{q,j+}{}^{b}}{dc_{q,j+}}}{\sum_{b=1}^{\infty}\sum_{q=1}^{n} h_{b,k,q} \frac{dc_{q,j+}{}^{b}}{dc_{q,j+}}}\right)} = \sigma^{\circ}{}_{k,j+} \left(\frac{\sum_{b=1}^{\infty}\sum_{q=1}^{n} p_{b,k,q} \frac{dc_{q,j+}{}^{b}}{dc_{q,j+}}}{\sum_{b=1}^{\infty}\sum_{q=1}^{n} y_{b,k,q} \frac{dc_{q,j+}{}^{b}}{dc_{q,j+}}}\right),$$

(B23+)

respectively, where n is the number of solute components, $D^{\circ}_{k,j-}$ at all ξ equals D_k at ξ_j at time t in the limit as c approaches 0, $D^{\circ}_{k,j+}$ at all ξ equals D_k at ξ_j at time [t + Δt] in the limit as c approaches 0, $\sigma^{\circ}_{k,j-}$ at all ξ equals σ_k at ξ_j at time t in the limit as c approaches 0, $\sigma^{\circ}_{k,j+}$ at all ξ equals σ_k at ξ_j at time [t + Δt] in the limit as c approaches 0, $Eu^{\circ}_{k,j-}$ at all ξ equals Eu_k at ξ_j at time t in the limit as c approaches 0, $Eu^{\circ}_{k,j+}$ at all ξ equals Eu_k at ξ_j at time [t + Δt] in the limit as c approaches 0, $c_{q,j-}$ is the ξ-independent concentration coefficient of solute component q at time t (at time t, $c_{q,j-}$, at all ξ, equals c_q at ξ_j, just as $c_{k,h}$, at all ξ, equals c_k at ξ_h in Equation B6), $c_{q,j+}$ is the ξ-independent concentration coefficient of solute component q at time [t + Δt] (at time [t + Δt], $c_{q,j+}$, at all ξ, equals c_q at ξ_j, just as $c_{k,h}$, at all ξ, equals c_k at ξ_h in Equation B6), and where $p_{b,k,q}$, $y_{b,k,q}$ and $h_{b,k,q}$ are the bth of up to an infinite number of coefficients of proportionality for the electrophoretic/asymmetry, thermodynamic nonideality, and viscosity effects, respectively. By definition, $\sum_{q=1}^{n} p_{1,k,q}$, $\sum_{q=1}^{n} y_{1,k,q}$ and $\sum_{q=1}^{n} h_{1,k,q}$ are each equal to 1. Each of the $p_{b,k,q}$, $y_{b,k,q}$ and $h_{b,k,q}$ coefficients couples the concentration of component q to an effect on the transport of component k. (See Section D for more details regarding these component-based virial expansions.)

With ∓ representing either – or +, the component-equivalents of Equations N23∓ and N24∓ can be used in place of Equations B22∓ and B23∓, respectively. Henceforth, c_q is used to denote the concentration of solute component q at either time t or time [t + Δt], and some unspecified position, ξ_j.

Individually, the product of $b(c_q)^{b-1}$ with the corresponding coefficient of proportionality $p_{b,k,q}$ yields the b^th term for the contribution of c_q to the electrophoretic/asymmetry effect of the system as it affects the transport of component k, the product of $b(c_q)^{b-1}$ with the corresponding coefficient of proportionality $y_{b,k,q}$ yields the b^th term for the contribution of c_q to the thermodynamic nonideality of the system as it affects the transport of component k, and the product of $b(c_q)^{b-1}$ with the corresponding coefficient of proportionality $h_{b,k,q}$ yields the b^th term for the contribution of c_q to the viscosity of the system as it affects the transport of component k, where $b(c_q)^{b-1} = d(c_q)^b/dc_q$.

Collectively, the sum of products given by $\sum_{b=2}^{\infty} p_{b,k,q} b {c_q}^{b-1}$ is a measure of the total contribution of c_q to the electrophoretic/asymmetry effect of the system as it affects the transport of component k, the sum of products given by $\sum_{b=2}^{\infty} y_{b,k,q} b {c_q}^{b-1}$ is a measure of the total contribution of c_q to the thermodynamic nonideality of the system as it affects the transport of component k, and the sum of products given by $\sum_{b=2}^{\infty} h_{b,k,q} b {c_q}^{b-1}$ is a measure of the total contribution of c_q to the viscosity of the system as it affects the transport of component k.

Henceforth, $\sigma_{k,j}$, $D_{k,j}$ and $Eu_{k,j}$ are used to denote the ξ-independent transport coefficients at either time t or time [t + Δt], and $\sigma°_{k,j}$, $D°_{k,j}$ and $Eu°_{k,j}$ are used to denote the ξ-independent transport coefficients at either time t or time [t + Δt] in the limit at c approaches zero.

By definition, $\sigma°_{k,j}$, $D°_{k,j}$ and $Eu°_{k,j}$, are ξ-independent, and for a given t-independent electrical current, may also be t-independent. In the case of solvent compressibility however, the expectation is that $\Delta\sigma°_{k,j}/\Delta j \neq 0$ and $\Delta D°_{k,j}/\Delta j \neq 0$, from which it follows that $\Delta Eu°_{k,j}/\Delta j \neq 0$. The condition that, for all solute components, $\Delta\sigma°_{k,j}/\Delta j = 0$ and $\Delta D°_{k,j}/\Delta j = 0$, from which it would follow that $\Delta Eu°_{k,j}/\Delta j = 0$, can only apply to a system with an incompressible solvent, in which case, $\sigma°_{k,j}$, $D°_{k,j}$ and $Eu°_{k,j}$ can be replaced with their respective, system-wide constants, $\sigma°_k$, $D°_k$ and $Eu°_k$. (In writing Equations B22 and B23, it was assumed that $\Delta p_{b,k,q}/\Delta j = 0$, $\Delta y_{b,k,q}/\Delta j = 0$ and $\Delta h_{b,k,q}/\Delta j = 0$ for any given pair of components k and q, even in the case of solvent compressibility. If required to deal adequately with the case of solvent compressibility, $p_{b,k,q}$, $y_{b,k,q}$ and $h_{b,k,q}$ can be replaced with their respective j- and t-dependent coefficients, which would be $p_{b,k,q,j-}$, $y_{b,k,q,j-}$ and $h_{b,k,q,j-}$ at time t, and would be $p_{b,k,q,j+}$, $y_{b,k,q,j+}$ and $h_{b,k,q,j+}$ at time [t + Δt], where, denoting a coefficient at either time by dropping the – or + suffix, $\Delta p_{b,k,q,j}/\Delta j \neq 0$, $\Delta y_{b,k,q,j}/\Delta j \neq 0$ and $\Delta h_{b,k,q,j}/\Delta j \neq 0$ for any given pair of components k and q.)

(As $Eu°_{k,j}$ and $\sigma°_{k,j}$ only apply in the limit as c approaches zero, and thus, where E is ξ-independent, it would be incorrect to incorporate the ξ-dependence of E into the j-dependence of $Eu°_{k,j}$ or $\sigma°_{k,j}$. Practically speaking, however, it may be useful to do just that, especially for the analysis of systems at steady state, when the ξ-dependence of E is time-invariant. When applied to experimental results, such analysis would best be attempted only after acquiring steady-state data at multiple current strengths for multiple systems that differ solely with respect to the total, net concentration of membrane-confined solute components. Extrapolation of σ_w (see Equation A39) to zero current and zero solute concentration should yield $\sigma_w = 0$. The dependence of σ_w on current and solute concentration could then be used to find functions describing the ξ-dependence of such apparent $Eu°_{k,j}$ or $\sigma°_{k,j}$.)

To avoid quadratic and higher-order terms in $c_{q,j-}$ or $c_{q,j+}$, along with other complicated terms arising from the presence of a truncated virial expansion in the denominators of $\sigma_{k,j}$ and $D_{k,j}$ in Equations B22 and B23, no effort is made, initially, to solve Equation B21 as written. Instead, Equation B21 is solved as if $\sigma_{k,j+}$ and $D_{k,j+}$ were independent of all $c_{q,j+}$, and as if $\sigma_{k,j-}$ and $D_{k,j-}$ were independent of all $c_{q,j-}$. Furthermore, because $c_{q,j+}$ values are not known prior to their use in $\sigma_{k,j+}$ and $D_{k,j+}$, $\sigma_{k,j-}$ and $D_{k,j-}$ are used in place of $\sigma_{k,j+}$ and $D_{k,j+}$, respectively. The resulting solution is that referred to as the second approximate solution. (As previously mentioned, the first approximate solution that pertains to the case of $(\partial D_k/\partial \xi)_t = 0$ and $(\partial \sigma_k/\partial \xi)_t = 0$ at all ξ will be derived from the second approximate solution.) The discussion of this issue is continued following Equation B24.

Equations B22 and B23 use a set of power series of each solute component concentration to describe the thermodynamic nonideality, viscosity and electrophoretic/asymmetry effects of the solution. For solutions that are too concentrated to permit the use of highly truncated virial expansions in the description of parameters such as D_k, σ_k and Eu_k, additional terms from the infinite series can be retained. (See **Section D: Expressions for the deviation from van 't Hoff behaviour and other virial expansions.**) It is, however, incorrect to treat $\sigma_{k,j}$, $D_{k,j}$ and $Eu_{k,j}$ as if they were functions of any terms involving solute concentrations in the second approximate solution, unless that solution is applied iteratively within each time increment. The general solution presented in Section J (**Form of the general solution from Equation C32**) does apply the second approximate solution iteratively, and thus permits the concentration dependence of $\sigma_{k,j}$, $D_{k,j}$ and $Eu_{k,j}$ at times t and [t + Δt] to be treated correctly.

Solving for $c_{k,h+}$

There are now three sets of space-dependent, time-independent basis functions (the set of all P_h, P_i and P_j), and there are N functions per set of such basis functions ($1 \leq h \leq N$, $1 \leq i \leq N$, and $1 \leq j \leq N$). For each solute component, k, at either time t or [t + Δt]: there are N space-independent, time-dependent, concentration coefficients, $c_{k,h}$; there are N space-independent, time-dependent, diffusion coefficients, $D_{k,j}$; and there are N space-independent, time-dependent, electrophoretic mobility coefficients, $u_{k,j}$, which are related to the N space-independent, time-dependent, reduced valence coefficients through $Eu_{k,j} = D_{k,j}\sigma_{k,j}$. For the case of each P_h, P_i and P_j being a hat function (as described by Equations B58 to B63), for each solute component, k, at either time t or [t + Δt]: each product, $c_{k,h}P_h$, is maximal at spatial element h, and is zero below spatial element [h – 1] or above spatial element [h + 1]; while each of the products, $D_{k,j}P_j$ and $D_{k,j}\sigma_{k,j}P_j$, is maximal at spatial element j, and is zero below spatial element [j – 1] or above spatial element [j + 1].

Let

$$F_{k,h,i+} = \int_{\xi_m}^{\xi_b} P_h P_i d\xi - \sum_{j=1}^{N} D_{k,j+}\left[\sigma_{k,j+}\int_{\xi_m}^{\xi_b} P_j P_h \frac{dP_i}{d\xi} d\xi - \int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi}\frac{dP_i}{d\xi} d\xi\right]\Delta t$$

and

$$F_{k,h,i-} = \int_{\xi_m}^{\xi_b} P_h P_i d\xi + \sum_{j=1}^{N} D_{k,j-} \left[\sigma_{k,j-} \int_{\xi_m}^{\xi_b} P_j P_h \frac{dP_i}{d\xi} d\xi - \int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi} \frac{dP_i}{d\xi} d\xi \right] \Delta t\,.$$

(B24)

Equations B22 and B23 are used to calculate $D_{k,j}$ and $\sigma_{k,j}$, respectively. Despite their dependence on all $c_{q,j+}$, for each iteration (see Section J) of the second approximate solution, $\sigma_{k,j+}$ and $D_{k,j+}$ are treated as if they were independent of all $c_{k,j+}$, and in the first iteration of any given time increment, $\sigma_{k,j+}$ and $D_{k,j+}$ are replaced with $\sigma_{k,j-}$ and $D_{k,j-}$, respectively, all of which permits the set of solutions to be written as

$$\sum_{k=1}^{n} \sum_{h=1}^{N} \sum_{i=1}^{N} c_{k,h+} F_{k,h,i+} = \sum_{k=1}^{n} \sum_{h=1}^{N} \sum_{i=1}^{N} c_{k,h-} F_{k,h,i-}\,,$$

(B25)

where each $F_{k,h,i+}$ is treated as independent of all $c_{k,j+}$. In the second approximate solution, it is permissible to treat $F_{k,h,i-}$, $\sigma_{k,j-}$ and $D_{k,j-}$ as dependent of all $c_{q,j-}$. In the general solution (Section J), the dependence of $F_{k,h,i+}$, $\sigma_{k,j+}$ and $D_{k,j+}$ on all $c_{q,j+}$ is repeatedly approximated, with the errors in those approximations approaching zero with a sufficient number of iterations.

Letting

$$Z_{k,i-} = \sum_{h=1}^{N} c_{k,h-} F_{k,h,i-}$$

then results in

$$\sum_{k=1}^{n} \sum_{i=1}^{N} Z_{k,i-} = \sum_{k=1}^{n} \sum_{h=1}^{N} \sum_{i=1}^{N} c_{k,h+} F_{k,h,i+}.$$

(B26)

As can be seen from Figure B3 and Equations B39 to B53, the use of the hat function for P_h and P_i results in most of the terms indexed by i and h being zero:

$F_{k,h,1+} = 0$ and $F_{k,h,1-} = 0$ for $h > 2$;

$F_{k,h,N+} = 0$ and $F_{k,h,N-} = 0$ for $h < [N - 1]$; and

$F_{k,h,[1 < i < N]+} = 0$ and $F_{k,h,[1 < i < N]-} = 0$ for $[i - 2] < h < [i + 2]$.

Consequently,

$$\sum_{k=1}^{n} Z_{k,1-} = \sum_{k=1}^{n} \left(c_{k,1+}F_{k,1,1+} + c_{k,2+}F_{k,2,1+}\right),$$

$$\sum_{k=1}^{n} Z_{k,i-} = \sum_{k=1}^{n} \left(c_{k,[i-1]+}F_{k,[i-1],i+} + c_{k,i+}F_{k,i,i+} + c_{k,[i+1]+}F_{k,[i+1],i+}\right)$$

for $1 < i < N$, and

$$\sum_{k=1}^{n} Z_{k,N-} = \sum_{k=1}^{n} \left(c_{k,[N-1]+}F_{k,[N-1],N+} + c_{k,N+}F_{k,N,N+}\right).$$

(B27)

Equation B27 is derived from Equation A26, according to which, $(\partial c/\partial t)_\xi = -(\partial I/\partial \xi)_t$. Equation A26 does not state that each $(\partial c_k/\partial t)_\xi = -(\partial I_k/\partial \xi)_t$, but where this condition holds, each $Z_{k,i-}$ will equal the sum over all h of $c_{k,h+}F_{k,h,i+}$. As each k refers to a solute component, conservation of mass ensures that each $(\partial c_k/\partial t)_\xi$ does equal $-(\partial I_k/\partial \xi)_t$. Thus, equating corresponding terms indexed by k in Equation B27 is permissible, and results in

$$Z_{k,1-} = c_{k,1+}F_{k,1,1+} + c_{k,2+}F_{k,2,1+},$$

$$Z_{k,i-} = c_{k,[i-1]+}F_{k,[i-1],i+} + c_{k,i+}F_{k,i,i+} + c_{k,[i+1]+}F_{k,[i+1],i+}$$

for $1 < i < N$, and

$$Z_{k,N-} = c_{k,[N-1]+}F_{k,[N-1],N+} + c_{k,N+}F_{k,N,N+}.$$

(B28)

(Mass is conserved, but molarity is not, in general. Consequently, in the case of a species, e, of a solute component, k, it is possible for $(\partial c_{k,e}/\partial t)_\xi$ and $-(\partial I_{k,e}/\partial \xi)_t$ to differ, where $c_{k,e}$ is the concentration and $I_{k,e}$ is the mass flow, respectively, of species e of solute component k. Section C deals with the transport of species in detail.)

Equations C74 to C75 show the fully expanded forms of Equation C39, which is the species-by-species equivalent of Equation B28.

Equation B28 permits the continuity equation to be solved component-by-component. For each component, the solution proceeds one concentration coefficient at a time. Solving first for $c_{k,1+}$ yields

$$c_{k,1+} = Y_{k,1} - X_{k,1} c_{k,2+} \,,$$

where

$$Y_{k,1} = \frac{Z_{k,1-}}{F_{k,1,1+}}$$

and

$$X_{k,1} = \frac{F_{k,2,1+}}{F_{k,1,1+}} \,.$$

(B29)

For i < N, the solution for each subsequent $c_{k,i+}$, in ascending order from $2 \leq i < N$, takes the form of

$$c_{k,i+} = Y_{k,i} - X_{k,i} c_{k,[i+1]+} \,,$$

where

$$Y_{k,i} = \frac{Z_{k,i-} - Y_{k,[i-1]} F_{k,[i-1],i+}}{F_{k,i,i+} - X_{k,[i-1]} F_{k,[i-1],i+}}$$

and

$$X_{k,i} = \frac{F_{k,[i+1],i+}}{F_{k,i,i+} - X_{k,[i-1]} F_{k,[i-1],i+}} \,.$$

(B30)

At i = N, the solution for $c_{k,N+}$ is obtained. In terms of $c_{k,[N-1]+}$, the solution for $c_{k,N+}$ is

$$c_{k,N+} = Y_{k,N} - X_{k,N} c_{k,[N-1]+} \,,$$

where

$$Y_{k,N} = \frac{Z_{k,N-}}{F_{k,N,N+}}$$

and

$$X_{k,N} = \frac{F_{k,[N-1],N+}}{F_{k,N,N+}}.$$

(B31)

The solution for $c_{k,[N-1]+}$ can now be substituted into the solution for $c_{k,N+}$ to yield

$$c_{k,N+} = Y_{k,N} - X_{k,N}\left(Y_{k,[N-1]} - X_{k,[N-1]}c_{k,N+}\right),$$

(B32)

which, solved for $c_{k,N+}$, is

$$c_{k,N+} = \frac{Y_{k,N} - X_{k,N}Y_{k,[N-1]}}{1 - X_{k,N}X_{k,[N-1]}},$$

(B33a)

alternative expressions of which are

$$c_{k,N+} = \frac{Y_{k,N}F_{k,N,N+} - F_{k,[N-1],N+}Y_{k,[N-1]}}{F_{k,N,N+} - F_{k,[N-1],N+}X_{k,[N-1]}}$$

(B33b)

and

$$c_{k,N+} = \frac{Z_{k,N-} - Y_{k,[N-1]}F_{k,[N-1],N+}}{F_{k,N,N+} - X_{k,[N-1]}F_{k,[N-1],N+}}.$$

(B33c)

The above solution for $c_{k,N+}$ does not require knowledge of $c_{k,[N-1]+}$ or any other unknowns. This solution for $c_{k,N+}$ can now be used, therefore, to solve the previously obtained expression for $c_{k,[N-1]+}$ in terms of $c_{k,N+}$ and other known parameters. Subsequently, using $c_{k,[N-1]+}$, the previously obtained expression for $c_{k,[N-2]+}$ can be solved in terms of $c_{k,[N-1]+}$ and other known parameters. Thus, once $c_{k,N+}$ is known, each preceding $c_{k,i+}$ is calculated in descending order from i = [N - 1] to i = 2 using Equation B30 until, upon reaching i = 1, $c_{k,1+}$ is calculated using Equation B29, at which point, the entire array of $c_{k,i+}$ values has been determined. For i = h, $c_{k,i+} = c_{k,h+}$, so that the array of $c_{k,i+}$ values obtained equals the array of $c_{k,h+}$ values sought.

This process is carried out for each solute component, k, at each addition of a time increment. These new $c_{k,h+}$ values are then used as the next $c_{k,h-}$ values after the addition of the next time increment, and the process is repeated until the desired time point is reached, at least in a noniterative application of the second approximate solution. (The general solution presented in Section J (**Form of the general solution from Equation C32**) applies the second approximate solution iteratively, with the result that $c_{k,h+}$ is repeatedly recalculated within each time increment until a convergence criterion (Equation J6) is met, or a maximum number of iterations is reached.)

It has been found that the process is made more robust by first calculating all $c_{k,h+}$ in the forward direction starting from $c_{k,1+}$, then recalculating all $c_{k,h+}$ in reverse order (starting from $c_{k,N+}$), and averaging the results. The calculation of all $c_{k,h+}$ in reverse order is implemented by obtaining a solution to the t- and ξ-dependent continuity equation for MCE with the set of all ξ_h reversed, so that $\xi_1 = \xi_b$ and $\xi_N = \xi_m$. The solution obtained is backwards in the sense that $c_{k,1+}$ at all ξ is equal to the value of c_k at ξ_b, while $c_{k,N+}$ at all ξ is equal to the value of c_k at ξ_m. In general, ξ_h, $c_{k,h+}$, $c_{k,h-}$, $D_{k,j+}$, $\sigma_{k,j+}$, $D_{k,j-}$ and $\sigma_{k,j-}$, of the backwards solution are equal to $\xi_{[N-h+1]}$, $c_{k,[N-h+1]+}$, $c_{k,[N-h+1]-}$, $D_{k,[N-j+1]+}$, $\sigma_{k,[N-j+1]+}$, $D_{k,[N-j+1]-}$ and $\sigma_{k,[N-j+1]-}$, respectively, of the forward solution, which is the solution described above for the original orientation. Solving for $c_{k,h+}$ using the backwards solution then proceeds as described for the forward solution. Averaging is weighted toward the starting point of each solution, were artefacts appear to be minimal, so that, subscripting all concentration and spatial parameters by h as that index applies to the forward solution, the average value of $c_{k,h+}$ is $(c_{k,h+})_{avg} = [(\xi_h - \xi_m)(c_{k,h+})_R + (\xi_b - \xi_h)(c_{k,h+})_F]/(\xi_b - \xi_m)$, where $(c_{k,h+})_F$ and $(c_{k,h+})_R$ are values of $c_{k,h+}$ obtained from the forward and backwards solutions, respectively.

Time

In terms of an unvarying time increment, Δt, the time after Ω time increments is

$$t_{\Omega} = t_0 + \Omega\Delta t\ ,$$

(B34)

where t_0 is the initial time. In general, for Ω time increments, where each time increment, Δt_ε, may be different from some or all the rest,

$$t_{\Omega} = \sum_{\varepsilon=0}^{\Omega} \Delta t_{\varepsilon} = \sum_{\varepsilon=0}^{\Omega} (t_{\varepsilon} - t_{\varepsilon-1})\ ,$$

(B35)

where t_{-1} is defined as equal to zero, and $t_0 \geq t_{-1}$.

Space

Defining ξ_0 as equal to zero makes

$$\xi_{\mathrm{h}} = \sum_{\alpha=1}^{\mathrm{h}} \Delta\xi_{\alpha} = \sum_{\alpha=1}^{\mathrm{h}} (\xi_{\alpha} - \xi_{\alpha-1})$$

(B36)

a general formula for calculating ξ_h. This equation does not require Δξ to be the same for all spatial increments between two adjacent points.

Where Δξ is the same for all spatial increments between two adjacent points,

$$\xi_{\mathrm{h}} = \xi_1 + [h-1]\Delta\xi\ ,$$

(B37)

from which it follows, given $\xi_N = \xi_b$ and $\xi_1 = \xi_m$, that

$$\Delta\xi = \frac{\xi_{\mathrm{b}} - \xi_{\mathrm{m}}}{N-1}\,.$$

(B38)

Reactions

As discussed in Section C (**A solution to the t- and ξ-dependent continuity equation for MCE in terms of species**), it is more practical to explicitly include each solute species as if it were a solute component. In such implementations, prior to each addition of a time increment and the subsequent determination of the new $c_{k,h+}$, each solute component's current species concentrations (the sum of which equals $c_{k,h-}$) are adjusted to account for the effects of any chemical reactions in the system, including any mass-action associations or dissociations between the species of an individual solute component. Thus, at each time point, the re-calculation of concentration takes place in two distinct steps: first, the effects of reaction flows are determined; second, the effects of mass transport flows are determined. Calculating concentration changes due to reaction flows is discussed in Section G (**The dissipation function and the Curie-Prigogine principle**). Calculating concentration changes due to transport flows is described in this section (Equations B24 to B33) for the second approximate solution in terms of components, in Sections C (Equations C35 to C44) for the second approximate solution in terms of species, and in Section J (**Form of the general solution from Equation C32**) for the general solution to the second approximate solution in terms of species.

The solutions to the ξ–dependent integrals

In the notation used for the solutions to the ξ-dependent integrals that follow, a spatial increment from ξ_{h-1} to ξ_h is indicated by appending a subscripted minus sign to Δξ, a spatial increment from ξ_h to ξ_{h+1} is indicated by appending a subscripted plus sign to Δξ, ξ_m denotes ξ at the top of the system, and ξ_b denotes ξ at the base of the system. (In open systems, such as those encountered in MCE, both the top and the base of the system are in contact with dialysate. In closed systems, such as those encountered in AUC, the top of the system would coincide with its meniscus, hence the subscript of ξ_m.) The integrals are solved for the forward solution, in which $\xi_{h-1} < \xi_h < \xi_{h+1}$.

A minus sign, a letter x, or a plus sign is appended to a single equation number for each member of any set of two or three equations that reduces to a single equation in the case of

$(\partial\sigma_k/\partial\xi)_t = 0$ and $(\partial D_k/\partial\xi)_t = 0$ at all ξ. Where one exists, an equation with a subscripted minus sign precedes one with a subscripted x, and, where one exists, an equation with a subscripted plus sign follows one with a subscripted x, for a given equation number.

With the hat functions (see Figure B3, above, and Equations B58 to B63, below) used for P_h, P_i and P_j, the only nonzero solutions of the integrals in Equation B21 are:

$$\int_{\xi_m}^{\xi_b} P_1 P_1 d\xi = \int_{\xi_1}^{\xi_{1+1}} P_1 P_1 d\xi = \frac{\Delta\xi_{1+}}{3} \;;$$

(B39)

$$\int_{\xi_m}^{\xi_b} P_{h-1} P_h d\xi = \int_{\xi_{h-1}}^{\xi_h} P_{h-1} P_h d\xi = \frac{\Delta\xi_{h-}}{6} \;;$$

(B40)

$$\int_{\xi_m}^{\xi_b} P_h P_h d\xi = \int_{\xi_{h-1}}^{\xi_{h+1}} P_h P_h d\xi = 2\left(\int_{\xi_m}^{\xi_b} P_{h-1} P_h d\xi + \int_{\xi_m}^{\xi_b} P_{h+1} P_h d\xi\right) \;;$$

(B41)

$$\int_{\xi_m}^{\xi_b} P_{h+1} P_h d\xi = \int_{\xi_h}^{\xi_{h+1}} P_{h+1} P_h d\xi = \frac{\Delta\xi_{h+}}{6} \;;$$

(B42)

$$\int_{\xi_m}^{\xi_b} P_N P_N d\xi = \int_{\xi_{N-1}}^{\xi_N} P_N P_N d\xi = \frac{\Delta\xi_{N-}}{3} \;;$$

(B43)

$$\int_{\xi_m}^{\xi_b} P_1 P_1 \frac{dP_1}{d\xi} d\xi = \int_{\xi_1}^{\xi_{1+1}} P_1 P_1 \frac{dP_1}{d\xi} d\xi = -\frac{1}{3} \;;$$

(B44)

$$\int_{\xi_m}^{\xi_b} P_{h-1} P_{h-1} \frac{dP_h}{d\xi} d\xi = \int_{\xi_{h-1}}^{\xi_h} P_{h-1} P_{h-1} \frac{dP_h}{d\xi} d\xi = \frac{1}{3};$$

(B45$_x$)

$$\int_{\xi_m}^{\xi_b} P_h P_{h-1} \frac{dP_h}{d\xi} d\xi = \int_{\xi_{h-1}}^{\xi_h} P_h P_{h-1} \frac{dP_h}{d\xi} d\xi = \frac{1}{6} = \frac{1}{2}\int_{\xi_m}^{\xi_b} P_{h-1} P_{h-1} \frac{dP_h}{d\xi} d\xi \;;$$

(B45$_+$)

$$\int_{\xi_m}^{\xi_b} P_{h-1}P_h\frac{dP_h}{d\xi}d\xi = \int_{\xi_{h-1}}^{\xi_h} P_{h-1}P_h\frac{dP_h}{d\xi}d\xi = \frac{1}{6} = \int_{\xi_m}^{\xi_b} P_hP_{h-1}\frac{dP_h}{d\xi}d\xi \;\; ;$$

(B46$_-$)

$$\int_{\xi_m}^{\xi_b} P_hP_h\frac{dP_h}{d\xi}d\xi = \int_{\xi_{h-1}}^{\xi_h} P_hP_h\frac{dP_h}{d\xi}d\xi + \int_{\xi_h}^{\xi_{h+1}} P_hP_h\frac{dP_h}{d\xi}d\xi = 0$$

$$= \int_{\xi_{h-1}}^{\xi_h} P_{h-1}P_{h-1}\frac{dP_h}{d\xi}d\xi + \int_{\xi_h}^{\xi_{h+1}} P_{h+1}P_{h+1}\frac{dP_h}{d\xi}d\xi \;\; ;$$

(B46$_x$)

$$\int_{\xi_m}^{\xi_b} P_{h+1}P_h\frac{dP_h}{d\xi}d\xi = \int_{\xi_h}^{\xi_{h+1}} P_{h+1}P_h\frac{dP_h}{d\xi}d\xi = -\frac{1}{6} = \int_{\xi_m}^{\xi_b} P_hP_{h+1}\frac{dP_h}{d\xi}d\xi\,;$$

(B46$_+$)

$$\int_{\xi_m}^{\xi_b} P_hP_{h+1}\frac{dP_h}{d\xi}d\xi = \int_{\xi_h}^{\xi_{h+1}} P_hP_{h+1}\frac{dP_h}{d\xi}d\xi = -\frac{1}{6} = \frac{1}{2}\int_{\xi_m}^{\xi_b} P_{h+1}P_{h+1}\frac{dP_h}{d\xi}d\xi \;\; ;$$

(B47$_-$)

$$\int_{\xi_m}^{\xi_b} P_{h+1}P_{h+1}\frac{dP_h}{d\xi}d\xi = \int_{\xi_h}^{\xi_{h+1}} P_{h+1}P_{h+1}\frac{dP_h}{d\xi}d\xi = -\frac{1}{3};$$

(B47$_x$)

$$\int_{\xi_m}^{\xi_b} P_NP_N\frac{dP_N}{d\xi}d\xi = \int_{\xi_{N-1}}^{\xi_N} P_NP_N\frac{dP_N}{d\xi}d\xi = \frac{1}{3};$$

(B48)

$$\int_{\xi_m}^{\xi_b} P_1\frac{dP_1}{d\xi}\frac{dP_1}{d\xi}d\xi = \int_{\xi_1}^{\xi_{1+1}} P_1\frac{dP_1}{d\xi}\frac{dP_1}{d\xi}d\xi = \frac{1}{2\Delta\xi_{1+}} \;\; ;$$

(B49)

$$\int_{\xi_m}^{\xi_b} P_{h-1}\frac{dP_{h-1}}{d\xi}\frac{dP_h}{d\xi}d\xi = \int_{\xi_{h-1}}^{\xi_h} P_{h-1}\frac{dP_{h-1}}{d\xi}\frac{dP_h}{d\xi}d\xi = -\frac{1}{2\Delta\xi_{h-}} = \int_{\xi_m}^{\xi_b} P_h\frac{dP_{h-1}}{d\xi}\frac{dP_h}{d\xi}d\xi\,;$$

(B50$_x$)

$$\int_{\xi_m}^{\xi_b} P_h\frac{dP_{h-1}}{d\xi}\frac{dP_h}{d\xi}d\xi = \int_{\xi_{h-1}}^{\xi_h} P_{h-1}\frac{dP_{h-1}}{d\xi}\frac{dP_h}{d\xi}d\xi = -\frac{1}{2\Delta\xi_{h-}} = -\int_{\xi_m}^{\xi_b} P_{h-1}\frac{dP_h}{d\xi}\frac{dP_h}{d\xi}d\xi \;\; ;$$

(B50$_+$)

$$\int_{\xi_m}^{\xi_b} P_{h-1}\frac{dP_h}{d\xi}\frac{dP_h}{d\xi}d\xi = \int_{\xi_{h-1}}^{\xi_h} P_{h-1}\frac{dP_h}{d\xi}\frac{dP_h}{d\xi}d\xi = \frac{1}{2\Delta\xi_{h-}}\ ;$$

(B51$_{-}$)

$$\int_{\xi_m}^{\xi_b} P_h\frac{dP_h}{d\xi}\frac{dP_h}{d\xi}d\xi = \int_{\xi_{h-1}}^{\xi_{h+1}} P_h\frac{dP_h}{d\xi}\frac{dP_h}{d\xi}d\xi = \frac{1}{2}\left(\frac{1}{\Delta\xi_{h-}} + \frac{1}{\Delta\xi_{h+}}\right)$$
$$= \left(\int_{\xi_m}^{\xi_b} P_{h-1}\frac{dP_h}{d\xi}\frac{dP_h}{d\xi}d\xi + \int_{\xi_m}^{\xi_b} P_{h+1}\frac{dP_h}{d\xi}\frac{dP_h}{d\xi}d\xi\right)\ ;$$

(B51$_{x}$)

$$\int_{\xi_m}^{\xi_b} P_{h+1}\frac{dP_h}{d\xi}\frac{dP_h}{d\xi}d\xi = \int_{\xi_h}^{\xi_{h+1}} P_{h+1}\frac{dP_h}{d\xi}\frac{dP_h}{d\xi}d\xi = \frac{1}{2\Delta\xi_{h+}}\ ;$$

(B51$_{+}$)

$$\int_{\xi_m}^{\xi_b} P_h\frac{dP_{h+1}}{d\xi}\frac{dP_h}{d\xi}d\xi = \int_{\xi_h}^{\xi_{h+1}} P_h\frac{dP_{h+1}}{d\xi}\frac{dP_h}{d\xi}d\xi = -\frac{1}{2\Delta\xi_{h+}} = -\int_{\xi_m}^{\xi_b} P_{h+1}\frac{dP_h}{d\xi}\frac{dP_h}{d\xi}d\xi\ ;$$

(B52$_{-}$)

$$\int_{\xi_m}^{\xi_b} P_{h+1}\frac{dP_{h+1}}{d\xi}\frac{dP_h}{d\xi}d\xi = \int_{\xi_h}^{\xi_{h+1}} P_{h+1}\frac{dP_{h+1}}{d\xi}\frac{dP_h}{d\xi}d\xi = -\frac{1}{2\Delta\xi_{h+}} = \int_{\xi_m}^{\xi_b} P_h\frac{dP_{h+1}}{d\xi}\frac{dP_h}{d\xi}d\xi\ ;$$

(B52$_{x}$)

and

$$\int_{\xi_m}^{\xi_b} P_N\frac{dP_N}{d\xi}\frac{dP_N}{d\xi}d\xi = \int_{\xi_{N-1}}^{\xi_N} P_N\frac{dP_N}{d\xi}\frac{dP_N}{d\xi}d\xi = \frac{1}{2\Delta\xi_{N-}},$$

(B53)

where

$$\Delta\xi_{1+} = \xi_{1+1} - \xi_1\ ,$$

(B54)

$$\Delta\xi_{h-} = \xi_h - \xi_{h-1}\ ,$$

(B55)

$$\Delta\xi_{h+} = \xi_{h+1} - \xi_h\ ,$$

(B56)

and

$$\Delta\xi_{N-} = \xi_N - \xi_{N-1}\,.$$

(B57)

The hat functions and their derivatives can be described as follows:

For $\xi < \xi_{h-1}$ or $\xi > \xi_{h+1}$,

$$P_h = 0$$

(B58)

and

$$\frac{dP_h}{d\xi} = 0\,;$$

(B59)

for $\xi_{h-1} \leq \xi \leq \xi_h$,

$$P_h = \frac{(\xi - \xi_{h-1})}{\Delta\xi_{h-}}$$

(B60)

and

$$\frac{dP_h}{d\xi} = \frac{1}{\Delta\xi_{h-}}\;;$$

(B61)

and for $\xi_h \leq \xi \leq \xi_{h+1}$,

$$P_h = 1 - \frac{(\xi - \xi_h)}{\Delta\xi_{h+}}$$

(B62)

and

$$\frac{dP_h}{d\xi} = -\frac{1}{\Delta\xi_{h+}}\,.$$

(B63)

Replacing the subscript, h, with i or j in Equations B58 to B63 yields the equations that describe P_h, P_j and their derivatives with respect to ξ.

Each integral in Equations B39 to B53 need only be evaluated within the domain where its integrand is not equal to zero.

Where the integrand is P_1P_1, $P_1P_1(dP_1/d\xi)$, or $P_1(dP_1/d\xi)(dP_1/d\xi)$, the integral is evaluated from ξ_1 to ξ_{1+1}. Equations B62 and B63, with h = 1, describe P_1 and $dP_1/d\xi$, respectively.

Where the integrand is $P_{h-1}P_h$, $P_{h-1}P_{h-1}(dP_h/d\xi)$, $P_{h-1}(dP_{h-1}/d\xi)(dP_h/d\xi)$, $P_hP_{h-1}(dP_h/d\xi)$ (identical to $P_{h-1}P_h(dP_h/d\xi)$), $P_h(dP_{h-1}/d\xi)(dP_h/d\xi)$, or $P_{h-1}(dP_h/d\xi)(dP_h/d\xi)$, the integral is evaluated from ξ_{h-1} to ξ_h.

Where the integrand is P_hP_h, $P_hP_h(dP_h/d\xi)$, or $P_h(dP_h/d\xi)(dP_h/d\xi)$, and where $1 < h < N$, the integral is split in two, with one integral evaluated from ξ_{h-1} to ξ_h, and the other integral evaluated from ξ_h to ξ_{h+1}. The two integrals are then summed.

Where the integrand is $P_{h+1}P_h$, $P_{h+1}P_h(dP_h/d\xi)$ (identical to $P_hP_{h+1}(dP_h/d\xi)$), $P_{h+1}(dP_h/d\xi)(dP_h/d\xi)$, $P_h(dP_{h+1}/d\xi)(dP_h/d\xi)$, $P_{h+1}P_{h+1}(dP_h/d\xi)$, or $P_{h+1}(dP_{h+1}/d\xi)(dP_h/d\xi)$, the integral is evaluated from ξ_h to ξ_{h+1}.

Where the integrand is P_NP_N, $P_NP_N(dP_N/d\xi)$, or $P_N(dP_N/d\xi)(dP_N/d\xi)$, the integral is evaluated from ξ_{N-1} to ξ_N. Equations B60 and B61, with h = N, describe P_N and $dP_N/d\xi$, respectively.

Equations B60 and B61 give the functions used for P_h and $dP_h/d\xi$, respectively, in integrals evaluated from ξ_{h-1} to ξ_h. Equations B62 and B63 give the functions used for P_h and $dP_h/d\xi$, respectively, in integrals evaluated from ξ_h to ξ_{h+1}.

Of the 23 types (within 15 groups) of integrals in Equations B39 to B53, 17 (Equations B40 to B42, $B45_x$ to $B47_x$, and $B50_x$ to $B52_x$) apply to $1 < h < N$, so that each one is evaluated for [N - 2] different values of h. Of the remaining 6 types of integrals in Equations B39 to B53, 3 (Equations B39, B44, and B49) apply to h = 1, and 3 (Equations B43, B48, and B53) apply to h = N, so that each one is evaluated for just one value of h.

Of the solutions to the 23 types (within 15 groups) of integrals in Equations B39 to B53, 9 (Equations B44 to B48, each of which is a multiple of 1/6) are independent of ξ_h, 5 (Equations B39 to B43) are multiples of $\Delta\xi_{h-}/6$ and $\Delta\xi_{h+}/6$, and 9 (B49 to B53) are multiples of $1/2\Delta\xi_{h-}$ and $1/2\Delta\xi_{h+}$. For equally spaced points, $\Delta\xi_{1+} = \Delta\xi_{N-} = \Delta\xi_{h+} = \Delta\xi_{h-} = \Delta\xi$ for all h, in which case, the solutions to all 23 of the integrals in Equations B39 to B53 become independent of ξ. Where Equations B40 to B42, $B45_x$ to $B47_x$, and $B50_x$ to $B52_x$ are independent of ξ, each one can be evaluated just one time, and the result applied to all values of h.

The number, N, and therefore the spacing, of spatial elements, ξ_h (Equations B54 to B57) can be changed between time increments. Doing so, however, requires recalculating the basis functions (P_h, P_i and P_j) and their derivatives (Equations B58 to B63), as a consequence of which, the solutions to the integrals (Equations B39 to B53) must also be recalculated. Furthermore, whenever changes in the number or spacing of spatial elements requires the creation of a new, ξ-independent concentration coefficient, that coefficient's value must be interpolated from the values of its most closely related prior concentration coefficients. Exploiting mass conservation can help to ensure that minimal error is introduced in the process of interpolation, but also requires that mass conservation is always enforced between time increments. (As the finite-element method does not inherently ensure mass conservation, other methods must be employed for that purpose.) Despite how all this may appear, changing the number or spacing of spatial elements does not alter the time-independent nature of the basis functions. Instead, the map of the system is altered. Thus, changing the number or spacing of spatial elements requires the application of a wholly new solution of the continuity equation.

The case of $(\partial\sigma_k/\partial\xi)_t = 0$ and $(\partial D_k/\partial\xi)_t = 0$ at all ξ

In the case of $(\partial\sigma_k/\partial\xi)_t = 0$ and $(\partial D_k/\partial\xi)_t = 0$ at all ξ, each $\sigma_{k,j}$ is equal to the ξ-invariant value of σ_k and each $D_{k,j}$ is equal to the ξ-invariant value D_k, which permits $\sigma_{k,j}$ and $D_{k,j}$ to be factored out of the summations indexed by j in Equations B16 to B24. The consequences to

Equations B39 to B53 are described below. The numbering system for the equations of this special case (where σ_k and D_k are constant with ξ) follows that used for the more general case (where σ_k and D_k can vary with ξ) above, with an asterisk appended to the number of each equation that applies to the special case.

Equations B39* to B43* are unchanged from Equations B39 to B43, but can now be expressed in terms of four of the other integrals:

$$\int_{\xi_m}^{\xi_b} P_1 P_1 d\xi = \int_{\xi_1}^{\xi_{1+1}} P_1 P_1 d\xi = \frac{\Delta\xi_{1+}}{3} = \frac{1}{3\int_{\xi_m}^{\xi_b} \frac{dP_1}{d\xi}\frac{dP_1}{d\xi} d\xi} \;;$$

(B39*)

$$\int_{\xi_m}^{\xi_b} P_{h-1} P_h d\xi = \int_{\xi_{h-1}}^{\xi_h} P_{h-1} P_h d\xi = \frac{\Delta\xi_{h-}}{6} = -\frac{1}{6\int_{\xi_m}^{\xi_b} \frac{dP_{h-1}}{d\xi}\frac{dP_h}{d\xi} d\xi} \;;$$

(B40*)

$$\int_{\xi_m}^{\xi_b} P_h P_h d\xi = \int_{\xi_{h-1}}^{\xi_{h+1}} P_h P_h d\xi = 2\left(\int_{\xi_m}^{\xi_b} P_{h-1} P_h d\xi + \int_{\xi_m}^{\xi_b} P_{h+1} P_h d\xi\right) \;;$$

(B41*)

$$\int_{\xi_m}^{\xi_b} P_{h+1} P_h d\xi = \int_{\xi_h}^{\xi_{h+1}} P_{h+1} P_h d\xi = \frac{\Delta\xi_{h+}}{6} = -\frac{1}{6\int_{\xi_m}^{\xi_b} \frac{dP_{h+1}}{d\xi}\frac{dP_h}{d\xi} d\xi};$$

(B42*)

$$\int_{\xi_m}^{\xi_b} P_N P_N d\xi = \int_{\xi_{N-1}}^{\xi_N} P_N P_N d\xi = \frac{\Delta\xi_{N-}}{3} = \frac{1}{3\int_{\xi_m}^{\xi_b} \frac{dP_N}{d\xi}\frac{dP_N}{d\xi} d\xi} \;;$$

(B43*)

$$\sum_{j=1}^{N}\left[\int_{\xi_m}^{\xi_b} P_j P_1 \frac{dP_1}{d\xi} d\xi\right] = \int_{\xi_m}^{\xi_b} P_1 \frac{dP_1}{d\xi} d\xi = \int_{\xi_1}^{\xi_{1+1}} P_1 \frac{dP_1}{d\xi} d\xi = -\frac{1}{2}$$

(B44*)

replaces Equation B44;

$$\sum_{j=1}^{N}\left[\int_{\xi_m}^{\xi_b} P_j P_{h-1}\frac{dP_h}{d\xi}d\xi\right] = \int_{\xi_m}^{\xi_b} P_{h-1}\frac{dP_h}{d\xi}d\xi = \int_{\xi_{h-1}}^{\xi_h} P_{h-1}\frac{dP_h}{d\xi}d\xi = \frac{1}{2}$$

(B45*)

replaces the sum of Equations B45$_{x}$ and B45$_{+}$;

$$\sum_{j=1}^{N}\left[\int_{\xi_m}^{\xi_b} P_j P_h\frac{dP_h}{d\xi}d\xi\right] = \int_{\xi_m}^{\xi_b} P_h\frac{dP_h}{d\xi}d\xi = \int_{\xi_{h-1}}^{\xi_{h+1}} P_h\frac{dP_h}{d\xi}d\xi = 0$$

(B46*)

replaces the sum of Equations B46$_{-}$, B46$_{x}$ and B46$_{+}$;

$$\sum_{j=1}^{N}\left[\int_{\xi_m}^{\xi_b} P_j P_{h+1}\frac{dP_h}{d\xi}d\xi\right] = \int_{\xi_m}^{\xi_b} P_{h+1}\frac{dP_h}{d\xi}d\xi = \int_{\xi_h}^{\xi_{h+1}} P_{h+1}\frac{dP_h}{d\xi}d\xi = -\frac{1}{2}$$

(B47*)

replaces the sum of Equations B47$_{-}$ and B47$_{x}$;

$$\sum_{j=1}^{N}\left[\int_{\xi_m}^{\xi_b} P_j P_N\frac{dP_N}{d\xi}d\xi\right] = \int_{\xi_m}^{\xi_b} P_N\frac{dP_N}{d\xi}d\xi = \int_{\xi_{N-1}}^{\xi_N} P_N\frac{dP_N}{d\xi}d\xi = \frac{1}{2}$$

(B48*)

replaces Equation B48;

$$\sum_{j=1}^{N}\left[\int_{\xi_m}^{\xi_b} P_j\frac{dP_1}{d\xi}\frac{dP_1}{d\xi}d\xi\right] = \int_{\xi_m}^{\xi_b}\frac{dP_1}{d\xi}\frac{dP_1}{d\xi}d\xi = \int_{\xi_1}^{\xi_{1+1}}\frac{dP_1}{d\xi}\frac{dP_1}{d\xi}d\xi = \frac{1}{\Delta\xi_{1+}}$$

(B49*)

replaces Equation B49;

$$\sum_{j=1}^{N}\left[\int_{\xi_m}^{\xi_b} P_j\frac{dP_{h-1}}{d\xi}\frac{dP_h}{d\xi}d\xi\right] = \int_{\xi_m}^{\xi_b}\frac{dP_{h-1}}{d\xi}\frac{dP_h}{d\xi}d\xi = \int_{\xi_{h-1}}^{\xi_h}\frac{dP_{h-1}}{d\xi}\frac{dP_h}{d\xi}d\xi = -\frac{1}{\Delta\xi_{h-}}$$

(B50*)

replaces the sum of Equations B50$_{x}$ and B50$_{+}$;

$$\sum_{j=1}^{N}\left[\int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi}\frac{dP_h}{d\xi}\,d\xi\right] = \int_{\xi_m}^{\xi_b} \frac{dP_h}{d\xi}\frac{dP_h}{d\xi}\,d\xi = \int_{\xi_{h-1}}^{\xi_{h+1}} \frac{dP_h}{d\xi}\frac{dP_h}{d\xi}\,d\xi$$

$$= -\left(\int_{\xi_m}^{\xi_b} \frac{dP_{h-1}}{d\xi}\frac{dP_h}{d\xi}\,d\xi + \int_{\xi_m}^{\xi_b} \frac{dP_{h+1}}{d\xi}\frac{dP_h}{d\xi}\,d\xi\right)$$

(B51*)

replaces the sum of Equations $B51_-$, $B51_x$ and $B51_+$;

$$\sum_{j=1}^{N}\left[\int_{\xi_m}^{\xi_b} P_j \frac{dP_{h+1}}{d\xi}\frac{dP_h}{d\xi}\,d\xi\right] = \int_{\xi_m}^{\xi_b} \frac{dP_{h+1}}{d\xi}\frac{dP_h}{d\xi}\,d\xi = \int_{\xi_h}^{\xi_{h+1}} \frac{dP_{h+1}}{d\xi}\frac{dP_h}{d\xi}\,d\xi = -\frac{1}{\Delta\xi_{h+}}$$

(B52*)

replaces the sum of Equations $B52_-$, $B52_x$; and

$$\sum_{j=1}^{N}\left[\int_{\xi_m}^{\xi_b} P_j \frac{dP_N}{d\xi}\frac{dP_N}{d\xi}\,d\xi\right] = \int_{\xi_m}^{\xi_b} \frac{dP_N}{d\xi}\frac{dP_N}{d\xi}\,d\xi = \int_{\xi_{N-1}}^{\xi_N} \frac{dP_N}{d\xi}\frac{dP_N}{d\xi}\,d\xi = \frac{1}{\Delta\xi_{N-}}$$

(B53*)

replaces Equation B53.

Each integral in Equations B39* to B53* need only be evaluated within the domain where its integrand is not equal to zero.

Where the integrand is P_1P_1, $P_1(dP_1/d\xi)$, or $(dP_1/d\xi)(dP_1/d\xi)$, the integral is evaluated from ξ_1 to ξ_{1+1}. Equations B62 and B63, with h = 1, describe P_1 and $dP_1/d\xi$, respectively.

Where the integrand is $P_{h-1}P_h$, $P_{h-1}(dP_h/d\xi)$, or $(dP_{h-1}/d\xi)(dP_h/d\xi)$, the integral is evaluated from ξ_{h-1} to ξ_h.

Where the integrand is P_hP_h, $P_h(dP_h/d\xi)$, or $(dP_h/d\xi)(dP_h/d\xi)$, and where $1 < h < N$, the integral is split in two, with one integral evaluated from ξ_{h-1} to ξ_h, and the other integral evaluated from ξ_h to ξ_{h+1}. The two integrals are then summed.

Where the integrand is $P_{h+1}P_h$, $P_{h+1}(dP_h/d\xi)$, or $(dP_{h+1}/d\xi)(dP_h/d\xi)$, the integral is evaluated from ξ_h to ξ_{h+1}.

Where the integrand is P_NP_N, $P_N(dP_N/d\xi)$, or $(dP_N/d\xi)(dP_N/d\xi)$, the integral is evaluated from ξ_{N-1} to ξ_N. Equations B60 and B61, with h = N, describe P_N and $dP_N/d\xi$, respectively.

Equations B60 and B61 give the functions used for P_h and $dP_h/d\xi$, respectively, in integrals evaluated from ξ_{h-1} to ξ_h. Equations B62 and B63 give the functions used for P_h and $dP_h/d\xi$, respectively, in integrals evaluated from ξ_h to ξ_{h+1}.

Of the fifteen types of integrals in Equations B39* to B53*, nine (Equations B40* to B42*, B45* to B47*, and B50* to B52*) apply to $1 < h < N$, so that each one is evaluated for [N - 2] different values of h. Of the remaining six types of integrals in Equations B39* to B53*, three (Equations B39*, B44*, and B49*) apply to h = 1, and three (Equations B43*, B48*, and B53*) apply to h = N, so that each one is evaluated for just one value of h.

Of the solutions to the fifteen types of integrals in Equations B39* to B53*, five (Equations B44* to B48*, each of which is a multiple of 1/2) are independent of ξ_h, and six (Equations B39* to B43* and Equation B51*) can be defined in terms of one or two of the remaining four (Equations B49*, B50*, B52* and B53*). For equally spaced points, $\Delta\xi_{1+} = \Delta\xi_{N-} = \Delta\xi_{h+} = \Delta\xi_{h-} = \Delta\xi$ for all h, in which case, the solutions to all 15 of the integrals in Equations B39* to B53* become independent of ξ. Where Equations B40* to B42*, B45* to B47*, and B50* to B52* are independent of ξ, each one can be evaluated just one time, and the result applied to all values of h.

Equations B39* to B53* are equivalent to the integrals obtained by treating D_k and the equivalent to Eu_k as ξ-independent in a previously obtained solution to an MCE-like continuity equation [Cox and Dale, 1981]. That equivalence is further evidence that the first approximate solution can be derived from the second.

Tests of different solutions

The integrals in the solution to the t- and ξ-dependent continuity equation for MCE (Equation B21) have been replaced with their evaluations shown in Equations B39 to B53 or Equations B39* to B53*, and those expanded forms of the solution to the continuity equation for MCE have been used in finite-element simulations. Simulations of MCE based on the second approximate solution (using Equations B39 to B53) have been found to perform at least as well as simulations based on the first approximate solution (using Equations B39* to B53*). (Highly contrived results for comparison can be found in **Section F: ξ-dependent functions to approximate $D_{k,e}$ and $\sigma_{k,e}$.**)

First approximate solution

To express σ_k and D_k in terms of pseudo-ξ-independent parameters, each one is initially approximated as a set of N scalar coefficients that can be a function of t but must be invariant with ξ. For σ_k, at all ξ_h, where $1 \leq h \leq N$, those coefficients are

$$\sigma_{k,h} = \sigma_k \ at \ \xi_h,$$

(B64)

and for D_k, at all ξ_h, where $1 \leq h \leq N$, those coefficients are

$$D_{k,h} = D_k \ at \ \xi_h.$$

(B65)

When it temporarily becomes more convenient to work with Eu_k and D_k instead of σ_k and D_k, Eu_k is also initially approximated as a set of N scalar coefficients that can be a function of t but must be invariant with ξ. At all ξ_h, where $1 \leq h \leq N$, those coefficients are

$$Eu_{k,h} = Eu_k \ at \ \xi_h.$$

(B66)

Equations B64 to B66 define $\sigma_{k,h}$, $D_{k,h}$ and $Eu_{k,h}$ as constants with respect to ξ, and in the first approximate solution, are used in place of Equations B10 to B12. The resulting first approximate solution to the continuity equation for MCE can be written as

$$\sum_{k=1}^{n}\sum_{h=1}^{N}\sum_{i=1}^{N} c_{k,h+}\left(\int_{\xi_m}^{\xi_b} P_h P_i d\xi - D_{k,h+}\left[\sigma_{k,h+}\int_{\xi_m}^{\xi_b} P_h \frac{dP_i}{d\xi} d\xi - \int_{\xi_m}^{\xi_b} \frac{dP_h}{d\xi}\frac{dP_i}{d\xi} d\xi\right]\Delta t\right)$$
$$= \sum_{k=1}^{n}\sum_{h=1}^{N}\sum_{i=1}^{N} c_{k,h-}\left(\int_{\xi_m}^{\xi_b} P_h P_i d\xi \right.$$
$$\left. + D_{k,h-}\left[\sigma_{k,h-}\int_{\xi_m}^{\xi_b} P_h \frac{dP_i}{d\xi} d\xi - \int_{\xi_m}^{\xi_b} \frac{dP_h}{d\xi}\frac{dP_i}{d\xi} d\xi\right]\Delta t\right).$$

(B67)

As usual, a minus or plus subscript refers to time t or [t + Δt], respectively. Equation B67 of the first approximate solution is obtained by applying Equations B64 and B65 to Equation B21 of the second approximate solution in the case of $(\partial\sigma_k/\partial\xi)_t = 0$ and $(\partial D_k/\partial\xi)_t = 0$ at all ξ. Thus, when $\sigma_{k,h}$ and $D_{k,h}$ are used as they are in Equation B67, each $\sigma_{k,h}$ should equal ξ-independent σ_k, each $D_{k,h}$ should equal ξ-independent D_k and, given that $(\partial Eu_k/\partial\xi)_t = 0$ when $(\partial\sigma_k/\partial\xi)_t = 0$ and $(\partial D_k/\partial\xi)_t = 0$, each $Eu_{k,h}$ should equal ξ-independent Eu_k. Furthermore, these conditions make it highly likely that $(\partial D_k/\partial t)_\xi = 0$ in general, and that $(\partial Eu_k/\partial t)_\xi = 0$ and $(\partial\sigma_k/\partial t)_\xi = 0$ at constant field. Therefore, $D_{k,h}$ is likely to be t-independent in general, and $Eu_{k,h}$ and $\sigma_{k,h}$ are likely to be t-independent at constant field. All such constraints are purposefully violated in the following treatment of the first approximate solution.

As typically, but incorrectly, applied, the constants, $\sigma_{k,h}$, $D_{k,h}$ and $Eu_{k,h}$, of the first approximate solution are treated as if they were functions of solute concentration. Thus, $\sigma_{k,h}$, $D_{k,h}$ and $Eu_{k,h}$ become pseudoconstants with respect to ξ. Truncated virial expansions are used to approximate the dependence of $\sigma_{k,h}$ and $D_{k,h}$ on the concentration, c_q, of each explicitly included solute component, q. To evaluate these pseudo-ξ-independent constants indexed by h, prior to each time increment, $D_{k,h}$ and $\sigma_{k,h}$ are approximated by

$$D_{k,h} = D°_k \left(\frac{\sum_{b=1}^{\infty} \sum_{q=1}^{n} y_{b,k,q} \frac{dc_{q,h}{}^b}{dc_{q,h}}}{\sum_{b=1}^{\infty} \sum_{q=1}^{n} h_{b,k,q} \frac{dc_{q,h}{}^b}{dc_{q,h}}} \right)$$

(B68)

and

$$\sigma_{k,h} = \sigma°_k \left(\frac{\sum_{b=1}^{\infty} \sum_{q=1}^{n} p_{b,k,q} \frac{dc_{q,h}{}^b}{dc_{q,h}}}{\sum_{b=1}^{\infty} \sum_{q=1}^{n} y_{b,k,q} \frac{dc_{q,h}{}^b}{dc_{q,h}}} \right),$$

(B69)

respectively, where n is the number of solute components, $D°_k$ at all ξ equals D_k at ξ_h at time t in the limit as c approaches 0, $\sigma°_k$ at all ξ equals σ_k at ξ_h at time t in the limit as c approaches 0, $c_{q,h}$ is the ξ-independent concentration coefficient of solute component q at time t or [t + Δt] ($c_{q,h}$, at all ξ, equals c_q at ξ_h, just as $c_{k,h}$, at all ξ, equals c_k at ξ_h in Equation B6), and where $p_{b,k,q}$, $y_{b,k,q}$ and $h_{b,k,q}$ are the b^{th} of up to an infinite number of coefficients of proportionality for the electrophoretic/asymmetry, thermodynamic nonideality, and viscosity effects, respectively. By definition, $\sum_{q=1}^{n} p_{1,k,q}$, $\sum_{q=1}^{n} y_{1,k,q}$ and $\sum_{q=1}^{n} h_{1,k,q}$ are each equal to 1. (Each of the $p_{b,k,q}$, $y_{b,k,q}$ and $h_{b,k,q}$ coefficients couples the concentration of component q to an effect on the transport of component k. See Section D for more details regarding these component-based virial expansions.)

Both $\sigma°_k$ and $D°_k$ are ξ-independent by definition. Furthermore, the first approximate solution cannot be applied to systems in which changes in solvent density cause $(\partial\rho_0/\partial\xi)_t$ to differ from zero. (Strictly speaking, the first approximate solution cannot even be applied to systems in which solute concentration gradients cause $(\partial\rho/\partial\xi)_t$ to differ from zero.) As discussed in the definitions of $D°_{k,j}$ (Equation B22) and $\sigma°_{k,j}$ (Equation B23), the condition that $\Delta D°_{k,j}/\Delta j = 0$ and $\Delta\sigma°_{k,j}/\Delta j = 0$ for all solute components can only apply to a system with an incompressible solvent, in which case, $D°_{k,j}$ and $\sigma°_{k,j}$ can be replaced with $D°_k$, and

$\sigma°_k$, respectively. Hence, the use of $D°_k$ and $\sigma°_k$ in the first approximate solution.

As noted, when $\sigma_{k,h}$ and $D_{k,h}$ are used as they are in Equation B67, each $\sigma_{k,h}$ should equal ξ-independent σ_k, and each $D_{k,h}$ should equal ξ-independent D_k. Thus, the use of Equations B68 and B69 is incorrect, except where all coefficients of $b(c_q)^{b-1}$ for $b > 1$, which is to say all $p_{b,k,q}$, $y_{b,k,q}$ and $h_{b,k,q}$ for $b > 1$, equal zero, and where, as previously noted, the solvent is incompressible and $(\partial\rho/\partial\xi)_t = 0$ at all ξ and t. (Compare the properties and uses of Equations B68 and B69, with those of Equations B22 and B23, respectively.)

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Section C: A solution to the t- and ξ-dependent continuity equation for MCE in terms of species

In a completely proper application of irreversible thermodynamics, the summations in the equations for concentration, flow and continuity, and hence the summations in any solution to the continuity equation for MCE, would be over solute components rather than solute species, and at a given spatial position (expressed as ξ) and time, it might be expected that the transport coefficients needed for each solute component, k, would be its weight-average (over all species of component k) electrophoretic mobility coefficient multiplied by E, $E(u_k)_w$, and its gradient-average (over all species of component k) diffusion coefficient [Johnson et al., 1973], $(D_k)_G$, the expectation being that $E(u_k)_w = Eu_k$ and $(D_k)_G = D_k$. To account for the t- and ξ-dependent changes in the concentrations of the individual species that sum to c_k, in addition to the aforementioned transport coefficients, $E(u_k)_w$ and $(D_k)_G$, the chemical equations that describe mass-action associations, dissociations or other reaction flows linking any of the species of a solute component would be needed. (See **Section G: The dissipation function and the Curie-Prigogine principle**.)

If the diffusion and electrophoretic mobility coefficients of a solute component's individual species could be defined, $(D_k)_G$ and $E(u_k)_w$ could be calculated. (The diffusion coefficients and concentration gradients of a solute component's individual species would be used to calculate $(D_k)_G$, and the electrophoretic mobility coefficients and concentrations of a solute component's individual species would be used to calculate $(u_k)_w$.) The reduced valence coefficients of a solute component's individual species could then be defined in terms of the diffusion and electrophoretic mobility coefficients of a solute component's individual species. Finally, on the basis of the above expectations and Equation A23a, the relationship of σ_k to the reduced valence coefficients of a solute component's individual species could be determined using $\sigma_k = E(u_k)_w/(D_k)_G$. What follows is an approach to defining these transport coefficients for each solute component's individual species. The transport coefficients obtained are then applied to the solution of the continuity equation expressed in terms of species.

Letting n_k represent the number of species that constitute solute component k, and indexing the species by e,

$$D_k = (D_k)_G = \frac{\sum_{e=1}^{n_k} D_{k,e}\left(\frac{\partial c_{k,e}}{\partial \xi}\right)_t}{\sum_{e=1}^{n_k}\left(\frac{\partial c_{k,e}}{\partial \xi}\right)_t}$$

(C1)

and

$$D_k\sigma_k = Eu_k = E(u_k)_w = E\,\frac{\sum_{e=1}^{n_k} u_{k,e}c_{k,e}}{\sum_{e=1}^{n_k} c_{k,e}} = \frac{\sum_{e=1}^{n_k} D_{k,e}\sigma_{k,e}c_{k,e}}{\sum_{e=1}^{n_k} c_{k,e}} = (\sigma_k D_k)_w\ ,$$

(C2)

where $c_{k,e}$ is the concentration of species e of solute component k, $D_{k,e}$ is the diffusion coefficient of species e of solute component k, $\sigma_{k,e}$ is the reduced valence coefficient of species e of solute component k, $u_{k,e}$ is the electrophoretic mobility coefficient of species e of solute component k, $\sigma_{k,e}D_{k,e}$ is defined (by analogy with Equation A23a) as equal to $Eu_{k,e}$, and $(\sigma_k D_k)_w$ is the weight average of the product, $\sigma_{k,e}D_{k,e}$, for all species of solute component k. The concentration of component k is equal to the sum of the concentrations of all species of solute component k. Thus,

$$c_k = \sum_{e=1}^{n_k} c_{k,e} \,.$$

(C3)

The definitions above permit Equation A24 to be rewritten as

$$I_k = \sum_{e=1}^{n_k} I_{k,e} = \sum_{e=1}^{n_k} c_{k,e}D_{k,e}\left[\sigma_{k,e} - \left(\frac{\partial lnc_{k,e}}{\partial \xi}\right)_t\right] = c_k\left[E(u_k)_w - (D_k)_G\left(\frac{\partial lnc_k}{\partial \xi}\right)_t\right]$$
$$= c_k D_k\left[\sigma_k - \left(\frac{\partial lnc_k}{\partial \xi}\right)_t\right],$$

(C4)

where $I_{k,e}$ is the mass flow of species e of solute component k. A comparison of Equations A24 and C4 shows that, if Equation C4 is valid, $(D_k)_G = D_k$ and $(u_k)_w = u_k$, and thus,

$$\sigma_k = \frac{Eu_k}{D_k} = \frac{E(u_k)_w}{(D_k)_G} = \left(\frac{\partial lnc_k}{\partial \xi}\right)_t \left[\frac{\sum_{e=1}^{n_k} D_{k,e}\sigma_{k,e}c_{k,e}}{\sum_{e=1}^{n_k} D_{k,e}\left(\frac{\partial c_{k,e}}{\partial \xi}\right)_t}\right].$$

(C5)

Note that $(D_k)_G$ and $(u_k)_w$ are averages for all species of a single solute component, k, while D_G and u_w (described in Section A) are averages for all solute components. (Equations A30 and C1 describe D_G and $(D_k)_G$, respectively. Equations A31 and C3 describe u_w and $(u_k)_w$, respectively.) There is no simple relationship between σ_w and any average of the $\sigma_{k,e}$

coefficients. (See Equations A36 to A40, which show the relationships between σ_w, the σ_k coefficients, and the steady-state value of Eu_w/D_G.)

The diffusion coefficients and concentration gradients of all solute species can now be used to calculate the overall gradient-average diffusion coefficient,

$$D_G = \frac{\sum_{k=1}^{n}\left(\frac{\partial c_k}{\partial \xi}\right)_t D_k}{\sum_{k=1}^{n}\left(\frac{\partial c_k}{\partial \xi}\right)_t} = \frac{\sum_{k=1}^{n}\left(\frac{\partial c_k}{\partial \xi}\right)_t (D_k)_G}{\sum_{k=1}^{n}\left(\frac{\partial c_k}{\partial \xi}\right)_t} = \frac{\sum_{k=1}^{n}\left[\left(\frac{\partial c_k}{\partial \xi}\right)_t \frac{\sum_{e=1}^{n_k} D_{k,e}\left(\frac{\partial c_{k.e}}{\partial \xi}\right)_t}{\sum_{e=1}^{n_k}\left(\frac{\partial c_{k.e}}{\partial \xi}\right)_t}\right]}{\sum_{k=1}^{n}\left(\frac{\partial c_k}{\partial \xi}\right)_t}$$
$$= \frac{\sum_{k=1}^{n}\sum_{e=1}^{n_k} D_{k,e}\left(\frac{\partial c_{k.e}}{\partial \xi}\right)_t}{\sum_{k=1}^{n}\sum_{e=1}^{n_k}\left(\frac{\partial c_{k.e}}{\partial \xi}\right)_t}$$

(C6)

(see Equations A29 and C1). The electrophoretic mobility coefficients and concentrations of all solute species can now be used to calculate the overall weight-average electrophoretic mobility coefficient, which, multiplied by E, is

$$Eu_w = \frac{E\sum_{k=1}^{n} c_k u_k}{\sum_{k=1}^{n} c_k} = \frac{E\sum_{k=1}^{n} c_k (u_k)_w}{\sum_{k=1}^{n} c_k} = \frac{E\sum_{k=1}^{n}\left[c_k \frac{\sum_{e=1}^{n_k} u_{k,e} c_{k,e}}{\sum_{e=1}^{n_k} c_{k,e}}\right]}{\sum_{k=1}^{n} c_k} = \frac{E\sum_{k=1}^{n}\sum_{e=1}^{n_k} u_{k,e} c_{k,e}}{\sum_{k=1}^{n}\sum_{e=1}^{n_k} c_{k,e}}$$

(C7)

(see Equations A30 and C2).

The reduced valence coefficients, concentrations and concentration gradients of all membrane-confined solute species are related to Eu_w/D_G through

$$\frac{Eu_w}{D_G} = \frac{(\sigma D)_w}{D_G} = \frac{\frac{\sum_{k=1}^{n} c_k(\sigma_k D_k)_w}{\sum_{k=1}^{n} c_k}}{D_G} = \frac{\frac{\sum_{k=1}^{n}\sum_{e=1}^{n_k} \sigma_{k,e} D_{k,e} c_{k,e}}{\sum_{k=1}^{n} c_k}}{D_G} = \frac{\frac{\sum_{k=1}^{n}\sum_{e=1}^{n_k} \sigma_{k,e} D_{k,e} c_{k,e}}{\sum_{k=1}^{n} c_k}}{\frac{\sum_{k=1}^{n}\sum_{e=1}^{n_k} D_{k,e}\left(\frac{\partial c_{k.e}}{\partial \xi}\right)_t}{\sum_{k=1}^{n}\left(\frac{\partial c_k}{\partial \xi}\right)_t}}$$

$$= \left(\frac{\partial lnc}{\partial \xi}\right)_t \left[\frac{\sum_{k=1}^{n}\sum_{e=1}^{n_k} \sigma_{k,e} D_{k,e} c_{k,e}}{\sum_{k=1}^{n}\sum_{e=1}^{n_k} D_{k,e}\left(\frac{\partial c_{k.e}}{\partial \xi}\right)_t}\right]$$

(C8)

(see Equations A30, A32 and A40).

A comparison of Equations A32 and C8 shows that

$$\frac{\sum_{k=1}^{n} \sigma_k D_k c_k}{\sum_{k=1}^{n} D_k\left(\frac{\partial c_k}{\partial \xi}\right)_t} = \frac{\sum_{k=1}^{n}\sum_{e=1}^{n_k} \sigma_{k,e} D_{k,e} c_{k,e}}{\sum_{k=1}^{n}\sum_{e=1}^{n_k} D_{k,e}\left(\frac{\partial c_{k.e}}{\partial \xi}\right)_t}.$$

(C9)

Using Equation C5, Equation A40, which describes the concentration distribution of membrane-confined solute components at steady state in MCE, can be rewritten in terms of solute species as

$$\sigma_w = \frac{\sum_{k=1}^{n} \sigma_k c_k}{\sum_{k=1}^{n} c_k} = \frac{\sum_{k=1}^{n}\left[\left(\frac{\partial c_k}{\partial \xi}\right)_t \frac{\sum_{e=1}^{n_k} D_{k,e}\sigma_{k,e}c_{k,e}}{\sum_{e=1}^{n_k} D_{k,e}\left(\frac{\partial c_{k,e}}{\partial \xi}\right)_t}\right]}{\sum_{k=1}^{n} c_k} = \frac{\sum_{k=1}^{n}\left[\frac{\sum_{e=1}^{n_k} D_{k,e}\sigma_{k,e}c_{k,e}}{D_k}\right]}{\sum_{k=1}^{n} c_k},$$

(C10)

where, as in Equation C5, use has been made of the equivalence, assuming Equation C4 is valid, of D_k and $(D_k)_G$. As a comparison of Equations A39 and C10 shows, at steady state, the numerator in each expression on the right-hand side of Equation C10 is equal to $dc_{mc}/d\xi$, where c_{mc} is the total membrane-confined solute concentration.

Transport and reaction flows

If a mass flow changes the concentration of a component that chemically reacts with other components, a reaction flow may further change the concentrations of all participating components. (See reference to the Curie-Prigogine principle, below.) Thus, reaction flows describe how the local concentration of each component depends on the local concentrations of any reactively linked components. (The change in the concentration of a component, in turn, will tend to be the main factor determining how the concentrations of that component's solute species change, at least in the absence of a mass flow.) The irreversible thermodynamic expressions for D_k, u_k, and σ_k (Equations A21 to A23a) describe how the transport coefficients change as local properties of the system (mainly solute component concentrations) change. These transport coefficients, then, pertain to the transport flows. If these transport coefficients were sufficiently sophisticated, they could be used to adequately treat any system on a component-by-component basis, so that the values of D_k and u_k calculated for each solute component would be the appropriate average values, $(D_k)_G$ and $(u_k)_w$, respectively, again assuming Equation C4 is valid. Such an approach would accurately reflect the underlying irreversible thermodynamic theory, but at a cost of much effort to determine and evaluate the required functions.

In the actual application of the finite-element method described here, the transport of each species of a multi-species solute component is, in fact, treated as if it were the transport of a single-species solute component. Thus, the transport of a solute component is handled species-by-species, and any reactive interaction (typically mass-action association/dissociation) between species is implemented as a distinct operation conducted prior to, and separately from, the set of transport operations for all species for a given, finite time increment. (See **Section B: Steps taken to solve the t- and ξ-dependent continuity equation for MCE.**) The reaction forces and flows are scalars (tensorial order 0), while transport forces and flows are vectors (tensorial order 1), and the Curie-Prigogine principle states that there is no coupling between flows and forces of different tensorial order [de Groot and Mazur, 1962; Katchalsky and Curran, 1965]. As such, reaction flows are not expected to drive transport flows when the system is isotropic, and there are no phenomenological coefficients linking reaction forces to transport flows, or transport forces to reaction flows. (See **Section G: The dissipation function and the Curie-Prigogine principle**.) Thus, treating the transport and reaction flows separately is theoretically sound. Furthermore, much that applies to solving the continuity equation in terms of components (Section B) can be applied to solving the continuity equation in terms of species (this section).

Using the above parameters described in terms of solute species (Equations C1 to C10), the solution to the continuity equation for MCE in terms of solute components, which is derived in Section B (Equations B1 to B33), can be revised to obtain a solution to the continuity equation for MCE in terms of solute species. Near the end of this section (**Consequences for average parameters**), evidence will be presented in support of the hypothesis that the finite-element solution to the t- and ξ-dependent continuity equation in terms of solute components can be obtained from the finite-element solution to the t- and ξ-dependent continuity equation in terms of solute species. To the extent that this hypothesis is valid, the practicality that led to the following solution in terms of species can be said to yield a solution that can be properly cast in terms of components.

Steps taken to solve the t- and ξ-dependent continuity equation for MCE in terms of solute species

As in Section B (**Steps taken to solve the t- and ξ-dependent continuity equation for MCE**), the following finite-element method for solving the t- and ξ-dependent continuity equation in terms of species requires a resort to discrete spatial elements and a finite time increment. Here, too, this method for solving the continuity equation further requires the flow of each solute species to be zero at the system boundaries, ξ_m and ξ_b. Thus, except for the implicitly treated and presumably membrane-permeant solvent component, the finite-element solution shown is applied to membrane-confined species only. Also as in Section B, a virtually infinite system that includes the membrane-bound system, and extends well beyond both membranes, can be defined. For the virtually infinite system, at some appropriately distant points far from the membranes, the zero-flow boundary conditions can be imposed on membrane-permeant species, so that the same finite-element method can be used to solve the continuity equation for both membrane-confined and membrane-permeant species, albeit with different systems, which have different boundary positions, applied to the different types of species. (For simplicity, except for its much longer length, the virtually infinite system can be treated as having the same geometry as the membrane-bound system.) For each partially-confined species, both the membrane-bound and the virtually infinite system can be applied, with the proportion of time increments for which the virtually infinite system is applied set equal to the proportion of the partially-confined species that exhibits membrane-permeant behaviour. For both the membrane-bound and the virtually infinite systems, the solute species are treated explicitly, while the solvent component is treated implicitly.

Using Equations C3 and C4, the continuity equation (Equation A26) is re-written in terms of species to yield

$$\sum_{k=1}^{n}\sum_{e=1}^{n_k}\left(\frac{\partial c_{k,e}}{\partial t}\right)_{\xi} = -\sum_{k=1}^{n}\sum_{e=1}^{n_k}\left(\frac{\partial I_{k,e}}{\partial \xi}\right)_{t}.$$

(C11)

The solution begins with an integration that takes advantage of the boundary conditions to eliminate the partial derivatives with respect to ξ. To that end, the above form of the continuity equation is multiplied by H, which is an arbitrary function of ξ, and then integrated over the entire range of ξ. (Ultimately, H will be replaced by a set of N functions of ξ indexed by i, where 1 ≤ i ≤ N.) Thus,

$$\sum_{k=1}^{n}\sum_{e=1}^{n_k}\int_{\xi_m}^{\xi_b}\left(\frac{\partial c_{k,e}}{\partial t}\right)_{\xi} H d\xi = -\sum_{k=1}^{n}\sum_{e=1}^{n_k}\int_{\xi_m}^{\xi_b}\left(\frac{\partial I_{k,e}}{\partial \xi}\right)_{t} H d\xi.$$

(C12)

Integrating the right hand side of this equation by parts results in

$$-\sum_{k=1}^{n}\sum_{e=1}^{n_k}\int_{\xi_m}^{\xi_b}\left(\frac{\partial I_{k,e}}{\partial \xi}\right)_{t} H d\xi$$

$$= -\left[\sum_{k=1}^{n}\sum_{e=1}^{n_k}\left[H(\xi_b)I_{k,e}(\xi_b) - H(\xi_m)I_{k,e}(\xi_m)\right] - \sum_{k=1}^{n}\sum_{e=1}^{n_k}\int_{\xi_m}^{\xi_b}\left(\frac{\partial H}{\partial \xi}\right)_{t} I_{k,e} d\xi\right],$$

(C13)

where $I_{k,e}(\xi)$ is $I_{k,e}$ at ξ and $H(\xi)$ is H at ξ. As the boundary conditions in MCE are $I_{k,e}(\xi_m) = 0$ and $I_{k,e}(\xi_b) = 0$, the preceding equation reduces to

$$-\sum_{k=1}^{n}\sum_{e=1}^{n_k}\int_{\xi_m}^{\xi_b}\left(\frac{\partial I_{k,e}}{\partial \xi}\right)_t H d\xi = \sum_{k=1}^{n}\sum_{e=1}^{n_k}\int_{\xi_m}^{\xi_b}\left(\frac{\partial H}{\partial \xi}\right)_t I_{k,e} d\xi\ .$$

(C14)

Furthermore, as H is independent of t, $(\partial H/\partial \xi)_t = dH/d\xi$. Thus,

$$\sum_{k=1}^{n}\sum_{e=1}^{n_k}\int_{\xi_m}^{\xi_b}\left(\frac{\partial H}{\partial \xi}\right)_t I_{k,e} d\xi = \sum_{k=1}^{n}\sum_{e=1}^{n_k}\int_{\xi_m}^{\xi_b}\frac{dH}{d\xi} I_{k,e} d\xi,$$

(C15)

and Equation C12 becomes

$$\sum_{k=1}^{n}\sum_{e=1}^{n_k}\int_{\xi_m}^{\xi_b}\left(\frac{\partial c_{k,e}}{\partial t}\right)_\xi H d\xi = \sum_{k=1}^{n}\sum_{e=1}^{n_k}\int_{\xi_m}^{\xi_b}\frac{dH}{d\xi} I_{k,e} d\xi.$$

(C16)

Next, $c_{k,e}$ is approximated as the sum of N products, each of which consists of a ξ-dependent function, P_h, multiplied by a corresponding ξ-independent coefficient, $c_{k,e,h}$, which nevertheless remains a function of t. With both P_h and $c_{k,e,h}$ indexed by h, where $1 \le h \le N$,

$$c = \sum_{k=1}^{n} c_k = \sum_{k=1}^{n}\sum_{e=1}^{n_k} c_{k,e} = \sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N} c_{k,e,h} P_h.$$

(C17)

Each element, h, corresponds to a point, ξ_h. By convention, $\xi_1 = \xi_m$ and $\xi_N = \xi_b$. Despite the association of h with spatial parameters such as ξ_h, $c_{k,e,h}$ is independent of ξ, so that $(\partial c_{k,e,h}/\partial \xi)_t = dc_{k,e,h}/d\xi = 0$ at all ξ. (Each $c_{k,e,h}$ is ξ-independent, and at all ξ is equal to the value of $c_{k,e}$ at ξ_h.) See Figures B1 through B6, which, for the case of equal spacing between adjacent ξ_h, show the consequences of using the hat function (also known as the triangular function) for each P_h, along with the corresponding set of ξ-independent solute species concentration coefficients, $c_{k,e,h}$. (Equations B54 to B57 describe Δξ for the general case, in which Δξ can be different for different pairs of adjacent points. Equations B58 to B63 describe P_h and $dP_h/d\xi$ for P_h in the form of the hat function, and the case of potentially variable Δξ.)

As $c_{k,e,h}$ is independent of ξ, $(\partial c_{k,e,h}/\partial t)_\xi = dc_{k,e,h}/dt$, so that

$$\sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}\frac{dc_{k,e,h}}{dt}\int_{\xi_m}^{\xi_b}P_h H d\xi = \sum_{k=1}^{n}\sum_{e=1}^{n_k}\int_{\xi_m}^{\xi_b}\frac{dH}{d\xi}I_{k,e}d\xi.$$

(C18)

Expanding I_k (Equation C4) as

$$I_k = \sum_{e=1}^{n_k} I_{k,e} = \sum_{e=1}^{n_k} c_{k,e}D_{k,e}\left[\sigma_{k,e} - \left(\frac{\partial \ln c_{k,e}}{\partial \xi}\right)_t\right] = \sum_{e=1}^{n_k}\left[\sigma_{k,e}c_{k,e}D_{k,e} - D_{k,e}\left(\frac{\partial c_{k,e}}{\partial \xi}\right)_t\right],$$

and re-writing each $I_{k,e}$ in terms of the ξ-independent species concentration coefficients and corresponding ξ-dependent functions results in

$$I_k = \sum_{e=1}^{n_k} I_{k,e} = \sum_{e=1}^{n_k}\left[\sigma_{k,e}D_{k,e}\sum_{h=1}^{N}c_{k,e,h}P_h - D_{k,e}\sum_{h=1}^{N}c_{k,e,h}\frac{dP_h}{d\xi}\right].$$

(C19)

Using Equation C19 to substituting for $I_{k,e}$ in Equation C18 yields

$$\sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}\frac{dc_{k,e,h}}{dt}\int_{\xi_m}^{\xi_b}P_h H d\xi = \sum_{k=1}^{n}\sum_{e=1}^{n_k}\int_{\xi_m}^{\xi_b}\frac{dH}{d\xi}\left[\sigma_{k,e}D_{k,e}\sum_{h=1}^{N}c_{k,e,h}P_h - D_{k,e}\sum_{h=1}^{N}c_{k,e,h}\frac{dP_h}{d\xi}\right]d\xi,$$

which expands to

$$\sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}\frac{dc_{k,e,h}}{dt}\int_{\xi_m}^{\xi_b}P_h H d\xi$$
$$=\sum_{k=1}^{n}\sum_{e=1}^{n_k}\int_{\xi_m}^{\xi_b}\frac{dH}{d\xi}\left[\sigma_{k,e}D_{k,e}\sum_{h=1}^{N}c_{k,e,h}P_h\right]d\xi$$
$$-\sum_{k=1}^{n}\sum_{e=1}^{n_k}\int_{\xi_m}^{\xi_b}\frac{dH}{d\xi}\left[D_{k,e}\sum_{h=1}^{N}c_{k,e,h}\frac{dP_h}{d\xi}\right]d\xi,$$

and rearranges to

$$\sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}\frac{dc_{k,e,h}}{dt}\int_{\xi_m}^{\xi_b}P_h H d\xi$$
$$=\sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}c_{k,e,h}\int_{\xi_m}^{\xi_b}\sigma_{k,e}D_{k,e}P_h\frac{dH}{d\xi}d\xi-\sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}c_{k,e,h}\int_{\xi_m}^{\xi_b}D_{k,e}\frac{dP_h}{d\xi}\frac{dH}{d\xi}d\xi.$$

(C20)

The dependence of D_k (Equation A21) and σ_k (Equation A23) on the concentration, c_q, of each explicitly included solute component, q, renders $D_{k,e}$ and $\sigma_{k,e}$ dependent on the concentration, $c_{q,a}$, of each species, a, of each explicitly included solute component, q. This concentration dependence, in turn, makes $D_{k,e}$ and $\sigma_{k,e}$ ξ-dependent in all but special cases, such as $t = 0$, when all $(\partial c_{q,a}/\partial\xi)_t = 0$ at all ξ. (Where the solvent is compressible, it is remotely possible that, once |E| exceeds zero, $(\partial\rho_0/\partial\xi)_t \neq 0$, in which case, in all likelihood, $(\partial c_{q,a}/\partial\xi)_t$ will not equal zero at any position at any subsequent time.) To obtain a second approximate solution to the continuity equation for MCE, $D_{k,e}$ and $\sigma_{k,e}$ are expressed in terms of ξ-independent coefficients that are separable from ξ-dependent functions. In Section F (**ξ-dependent functions to approximate $D_{k,e}$ and $\sigma_{k,e}$**), the second approximate solution is compared with a first approximate solution that pertains to the case of $(\partial D_{k,e}/\partial\xi)_t = 0$ and $(\partial\sigma_{k,e}/\partial\xi)_t = 0$ at all ξ. The solutions of the integrals of first approximate solution were derived from those of the second approximate solution in Section B (**The case of $(\partial\sigma_k/\partial\xi)_t = 0$ and $(\partial D_k/\partial\xi)_t = 0$ at all ξ**).

As it temporarily becomes more convenient to work with $Eu_{k,e}$ and $D_{k,e}$ instead of $\sigma_{k,e}$ and $D_{k,e}$, $Eu_{k,e}$ is approximated as the sum of N products, each of which consists of a ξ-dependent function, P_j, multiplied by a corresponding ξ-independent coefficient, $Eu_{k,e,j}$, which nevertheless remains a function of t. With both P_j and $Eu_{k,e,j}$ indexed by j, where $1 \leq j \leq N$,

$$Eu_{k,e} = \sum_{j=1}^{N} Eu_{k,e,j} P_j \ ,$$

(C21)

where each $Eu_{k,e,j}$ at all ξ is equal to $Eu_{k,e}$ at ξ_j. The result expresses $Eu_{k,e}$ as separable ξ-independent and ξ-dependent terms. Here, E and $u_{k,e}$, each of which is t- and ξ-dependent, are combined to implicitly form a single, t- and ξ-dependent parameter, $Eu_{k,e} = \upsilon_{k,e}$, where $\upsilon_{k,e}$ is the t- and ξ-dependent electrophoretic velocity of species e of component k. (The total velocity is equal to that due to diffusion plus that due to electrophoresis, which includes the effect of solvent flow.) Thus, $Eu_{k,e,j} = \upsilon_{k,e,j}$, where $\upsilon_{k,e}$ is approximated as the sum of N products, each consisting of a ξ-dependent function, P_j, multiplied by a ξ-independent coefficient, $\upsilon_{k,e,j}$, which nevertheless remains a function of t.

To express $D_{k,e}$ as separable ξ-independent and ξ-dependent terms, this transport coefficient is also approximated as the sum of N products, each of which consists of a ξ-dependent function, P_j, multiplied by a corresponding ξ-independent coefficient, $D_{k,e,j}$, which nevertheless remains a function of t. With both P_j and $D_{k,e,j}$ indexed by j, where $1 \leq j \leq N$,

$$D_{k,e} = \sum_{j=1}^{N} D_{k,e,j} P_j \ ,$$

(C22)

where each $D_{k,e,j}$ at all ξ is equal to $D_{k,e}$ at ξ_j.

Equations C21 and C22 are combined to define $\sigma_{k,e}$ in terms of separable ξ-independent and ξ-dependent terms, which results in the species analogue of Equation A23a,

$$\sigma_{k,e} = \frac{Eu_{k,e}}{D_{k,e}} = \frac{\sum_{j=1}^{N} Eu_{k,e,j} P_j}{\sum_{j=1}^{N} D_{k,e,j} P_j} \ .$$

(C23)

While the same approach has been used to express $c_{k,e}$, $D_{k,e}$ and $Eu_{k,e}$ in terms of ξ-independent coefficients of ξ-dependent functions, those ξ-independent coefficients and ξ-dependent functions are indexed by h in the case of $c_{k,e}$, but indexed by j in the case of $D_{k,e}$ or $Eu_{k,e}$. At any given time, then, the ξ-dependent functions used in the description of $c_{k,e}$ are expressed in terms of ξ_h, while the ξ-dependent functions used in the descriptions of $D_{k,e}$ and $Eu_{k,e}$ are expressed in terms of ξ_j. To use these parameters together in the same solution of the continuity equation, at each time point, the set of all ξ_j is made equivalent to the set of all ξ_h.

Using $Eu_{k,e}$ in place of $\sigma_{k,e}D_{k,e}$ (from a re-arrangement of Equation C23) results in

$$\sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}\frac{dc_{k,e,h}}{dt}\int_{\xi_m}^{\xi_b}P_hHd\xi$$
$$=\sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}c_{k,e,h}\int_{\xi_m}^{\xi_b}Eu_{k,e}P_h\frac{dH}{d\xi}d\xi-\sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}c_{k,e,h}\int_{\xi_m}^{\xi_b}D_{k,e}\frac{dP_h}{d\xi}\frac{dH}{d\xi}d\xi.$$

(C24)

Replacing $Eu_{k,e}$ with the expression in terms of $Eu_{k,e,j}$, and replacing $D_{k,e}$ with the expression in terms of $D_{k,e,j}$, yields

$$\sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}\frac{dc_{k,e,h}}{dt}\int_{\xi_m}^{\xi_b}P_hHd\xi$$
$$=\sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}c_{k,e,h}\int_{\xi_m}^{\xi_b}\sum_{j=1}^{N}Eu_{k,e,j}P_j\,P_h\frac{dH}{d\xi}d\xi$$
$$-\sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}c_{k,e,h}\int_{\xi_m}^{\xi_b}\sum_{j=1}^{N}D_{k,e,j}P_j\frac{dP_h}{d\xi}\frac{dH}{d\xi}d\xi,$$

and permits the ξ-independent parameters, $D_{k,e,j}$ and $Eu_{k,e,j}$, to be factored out of the integrals. Thus,

$$\sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}\frac{dc_{k,e,h}}{dt}\int_{\xi_m}^{\xi_b}P_h H d\xi$$
$$= \sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}c_{k,e,h}\sum_{j=1}^{N}Eu_{k,e,j}\left[\int_{\xi_m}^{\xi_b}P_j P_h\frac{dH}{d\xi}d\xi\right]$$
$$-\sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}c_{k,e,h}\sum_{j=1}^{N}D_{k,e,j}\left[\int_{\xi_m}^{\xi_b}P_j\frac{dP_h}{d\xi}\frac{dH}{d\xi}d\xi\right].$$

(C25)

Letting

$$\sigma_{k,e,j} = \frac{Eu_{k,e,j}}{D_{k,e,j}},$$

(C26)

where $\sigma_{k,e,j}$ is ξ-independent by virtue of $D_{k,e,j}$ and $Eu_{k,e,j}$ being ξ-independent, the solution can now be expressed, after some rearrangement, as

$$\sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}\left(\frac{dc_{k,e,h}}{dt}\int_{\xi_m}^{\xi_b}P_h H d\xi - c_{k,e,h}\sum_{j=1}^{N}D_{k,e,j}\left[\sigma_{k,e,j}\int_{\xi_m}^{\xi_b}P_j P_h\frac{dH}{d\xi}d\xi - \int_{\xi_m}^{\xi_b}P_j\frac{dP_h}{d\xi}\frac{dH}{d\xi}d\xi\right]\right)$$
$$= 0.$$

(C27)

At all ξ, each of the N scalar coefficients, $\sigma_{k,e,j}$ (defined in Equation C26) is equal to $\sigma_{k,e}$ at ξ_j. As a result of using Equation C26 in Equation C27, the product, $D_{k,e}\sigma_{k,e}$, has been expressed as the sum of N products, each consisting of a ξ-dependent function, P_j, multiplied by a ξ-independent coefficient, $D_{k,e,j}\sigma_{k,e,j}$, which nevertheless remains a function of t. Additionally, the coefficient $D_{k,e,j}\sigma_{k,e,j}$ is itself the product of the previously defined coefficients, $D_{k,e,j}$ and $\sigma_{k,e,j}$.

Dividing Equation C27 by 2, and expressing $dc_{k,e,h}/dt$ as $\Delta c_{k,e,h}/\Delta t$, where $\Delta c_{k,e,h}$ and Δt are finite increments, yields

$$\frac{1}{2}\sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}\left(\frac{\Delta c_{k,e,h}}{\Delta t}\int_{\xi_m}^{\xi_b} P_h H d\xi - c_{k,e,h}\sum_{j=1}^{N} D_{k,e,j}\left[\sigma_{k,e,j}\int_{\xi_m}^{\xi_b} P_j P_h \frac{dH}{d\xi} d\xi - \int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi}\frac{dH}{d\xi} d\xi\right]\right) = 0.$$

(C28)

The difference between the unknown concentration, $c_{k,e,h+} = c_{k,e,h}$ at $[t + \Delta t]$, and the known concentration, $c_{k,e,h-} = c_{k,e,h}$ at t, is the change in concentration, $\Delta c_{k,e,h}$, during the time increment, $\Delta t = [t + \Delta t] - t$. Using $\Delta c_{k,e,h} = c_{k,e,h+} - c_{k,e,h-}$, and multiplying by Δt, yields

$$\frac{1}{2}\sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}\left(\left[c_{k,e,h+} - c_{k,e,h-}\right]\int_{\xi_m}^{\xi_b} P_h H d\xi - c_{k,e,h}\sum_{j=1}^{N} D_{k,e,j}\left[\sigma_{k,e,j}\int_{\xi_m}^{\xi_b} P_j P_h \frac{dH}{d\xi} d\xi - \int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi}\frac{dH}{d\xi} d\xi\right]\Delta t\right) = 0.$$

(C29)

The remaining $c_{k,e,h}$ term can be replaced with either $c_{k,e,h-}$, which would yield the less stable explicit solution, or $c_{k,e,h+}$, which would yield the more stable implicit solution. In the Crank-Nicholson approach [Schuck et al., 1998] used here, both substitutions are made, resulting in two forms of Equation C29. Additionally, $\sigma_{k,e,j+}$ and $D_{k,e,j+}$, which, respectively, represent $\sigma_{k,e,j}$ and $D_{k,e,j}$ at time $[t + \Delta t]$, are used in conjunction with the explicit form of Equation C29, where $c_{k,e,h}$ is expressed in terms of $c_{k,e,h+}$. Finally, $\sigma_{k,e,j-}$ and $D_{k,e,j-}$, which, respectively, represent $\sigma_{k,e,j}$ and $D_{k,e,j}$ at time t, are used in conjunction with the implicit form of Equation C29, where $c_{k,e,h}$ is expressed in terms of $c_{k,e,h-}$. The two resulting versions of Equation C29 are summed to yield, by virtue of the previous division by 2, their average. The average, like any sum of the two solutions, is considered stable, and is expected to permit the use of larger Δt values than either the explicit or implicit solution alone would.

Applying the Crank-Nicholson approach yields, after some rearrangement,

$$\sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N} c_{k,e,h+}\left(\int_{\xi_m}^{\xi_b} P_h H d\xi - \sum_{j=1}^{N} D_{k,e,j+}\left[\sigma_{k,e,j+}\int_{\xi_m}^{\xi_b} P_j P_h \frac{dH}{d\xi} d\xi - \int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi}\frac{dH}{d\xi} d\xi\right]\Delta t\right)$$

$$= \sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N} c_{k,e,h-}\left(\int_{\xi_m}^{\xi_b} P_h H d\xi\right.$$

$$\left. + \sum_{j=1}^{N} D_{k,e,j-}\left[\sigma_{k,e,j-}\int_{\xi_m}^{\xi_b} P_j P_h \frac{dH}{d\xi} d\xi - \int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi}\frac{dH}{d\xi} d\xi\right]\Delta t\right).$$

(C30)

As σ_k and D_k are functions of all c_k (see Equations A21 to A23), and as each c_k is time dependent (see Equation A26), σ_k and D_k are also time dependent. Thus, for the purpose of obtaining a general solution, $\sigma_{k,e,j-}$ and $D_{k,e,j-}$ must be expressed as functions of parameters equal to all $c_{k,e,h-}$ for which h = j, while $\sigma_{k,e,j+}$ and $D_{k,e,j+}$ must be expressed as functions of parameters equal to all $c_{k,e,h+}$ for which h = j. General expressions of this sort are presented shortly. (See **Evaluating the ξ-independent coefficients of the basis functions indexed by j**.)

At this point, there are n equations and nN unknown values of $c_{k,e,h+}$. To obtain the nN equations needed to solve for all values of $c_{k,e,h+}$, H is replaced by N functions,

$$H = \sum_{i=1}^{N} P_i\,,$$

(C31)

where each P_i has the same functional form as each corresponding P_h. (For i = h, $P_i = P_h$.) Applying Equation C31, the set of equations describing the solution is given by

$$\sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}\sum_{i=1}^{N} c_{k,e,h+}\left(\int_{\xi_m}^{\xi_b} P_h P_i d\xi \right.$$
$$\left. - \sum_{j=1}^{N} D_{k,e,j+}\left[\sigma_{k,e,j+}\int_{\xi_m}^{\xi_b} P_j P_h \frac{dP_i}{d\xi} d\xi - \int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi}\frac{dP_i}{d\xi} d\xi\right]\Delta t\right)$$
$$= \sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}\sum_{i=1}^{N} c_{k,e,h-}\left(\int_{\xi_m}^{\xi_b} P_h P_i d\xi \right.$$
$$\left. + \sum_{j=1}^{N} D_{k,e,j-}\left[\sigma_{k,e,j-}\int_{\xi_m}^{\xi_b} P_j P_h \frac{dP_i}{d\xi} d\xi - \int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi}\frac{dP_i}{d\xi} d\xi\right]\Delta t\right).$$

(C32)

The result is solved for $c_{k,e,h+}$ using the process described below. (See **Solving for $c_{k,e,h+}$.**) Interactions between solute components are handled separately between time steps. (Also see **Solving for $c_{k,e,h+}$.**)

Evaluating the ξ-independent coefficients of the basis functions indexed by j

Truncated virial expansions are used to approximate the dependence of $D_{k,e,j-}$, $D_{k,e,j+}$, $\sigma_{k,e,j-}$ and $\sigma_{k,e,j+}$ on the concentration of each explicitly included species of each explicitly included solute component. To evaluate the ξ-independent coefficients of ξ-dependent functions indexed by j (see Equations C21 and C22), prior to each time increment, $D_{k,e,j-}$, $D_{k,e,j+}$, $\sigma_{k,e,j-}$ and $\sigma_{k,e,j+}$ are, to the extent possible, approximated by

$$D_{k,e,j-} = D^{\circ}{}_{k,e,j-}\left(\frac{\sum_{b=1}^{\infty}\sum_{q=1}^{n}\sum_{a=1}^{n_q} y_{b,k,e,q,a}\frac{dc_{q,a,j-}{}^{b}}{dc_{q,a,j-}}}{\sum_{b=1}^{\infty}\sum_{q=1}^{n}\sum_{a=1}^{n_q} h_{b,k,e,q,a}\frac{dc_{q,a,j-}{}^{b}}{dc_{q,a,j-}}}\right),$$

(C33-)

$$D_{k,e,j+} = D^{\circ}{}_{k,e,j+}\left(\frac{\sum_{b=1}^{\infty}\sum_{q=1}^{n}\sum_{a=1}^{n_q} y_{b,k,e,q,a}\,\frac{dc_{q,a,j+}{}^{b}}{dc_{q,a,j+}}}{\sum_{b=1}^{\infty}\sum_{q=1}^{n}\sum_{a=1}^{n_q} h_{b,k,e,q,a}\,\frac{dc_{q,a,j+}{}^{b}}{dc_{q,a,j+}}}\right),$$

(C33+)

$$\sigma_{k,e,j-} = \frac{Eu_{k,e,j-}}{D_{k,e,j-}} = \frac{Eu^{\circ}{}_{k,e,j-}}{D^{\circ}{}_{k,e,j-}}\frac{\left(\frac{\sum_{b=1}^{\infty}\sum_{q=1}^{n}\sum_{a=1}^{n_q} p_{b,k,e,q,a}\,\frac{dc_{q,a,j-}{}^{b}}{dc_{q,a,j-}}}{\sum_{b=1}^{\infty}\sum_{q=1}^{n}\sum_{a=1}^{n_q} h_{b,k,e,q,a}\,\frac{dc_{q,a,j-}{}^{b}}{dc_{q,a,j-}}}\right)}{\left(\frac{\sum_{b=1}^{\infty}\sum_{q=1}^{n}\sum_{a=1}^{n_q} y_{b,k,e,q,a}\,\frac{dc_{q,a,j-}{}^{b}}{dc_{q,a,j-}}}{\sum_{b=1}^{\infty}\sum_{q=1}^{n}\sum_{a=1}^{n_q} h_{b,k,e,q,a}\,\frac{dc_{q,a,j-}{}^{b}}{dc_{q,a,j-}}}\right)}$$

$$= \sigma^{\circ}{}_{k,e,j-}\left(\frac{\sum_{b=1}^{\infty}\sum_{q=1}^{n}\sum_{a=1}^{n_q} p_{b,k,e,q,a}\,\frac{dc_{q,a,j-}{}^{b}}{dc_{q,a,j-}}}{\sum_{b=1}^{\infty}\sum_{q=1}^{n}\sum_{a=1}^{n_q} y_{b,k,e,q,a}\,\frac{dc_{q,a,j-}{}^{b}}{dc_{q,a,j-}}}\right)$$

(C34-)

and

$$\sigma_{k,e,j+} = \frac{Eu_{k,e,j+}}{D_{k,e,j+}} = \frac{Eu^{\circ}{}_{k,e,j+}}{D^{\circ}{}_{k,e,j+}}\frac{\left(\frac{\sum_{b=1}^{\infty}\sum_{q=1}^{n}\sum_{a=1}^{n_q} p_{b,k,e,q,a}\,\frac{dc_{q,a,j+}{}^{b}}{dc_{q,a,j+}}}{\sum_{b=1}^{\infty}\sum_{q=1}^{n}\sum_{a=1}^{n_q} h_{b,k,e,q,a}\,\frac{dc_{q,a,j+}{}^{b}}{dc_{q,a,j+}}}\right)}{\left(\frac{\sum_{b=1}^{\infty}\sum_{q=1}^{n}\sum_{a=1}^{n_q} y_{b,k,e,q,a}\,\frac{dc_{q,a,j+}{}^{b}}{dc_{q,a,j+}}}{\sum_{b=1}^{\infty}\sum_{q=1}^{n}\sum_{a=1}^{n_q} h_{b,k,e,q,a}\,\frac{dc_{q,a,j+}{}^{b}}{dc_{q,a,j+}}}\right)}$$

$$= \sigma^{\circ}{}_{k,e,j+}\left(\frac{\sum_{b=1}^{\infty}\sum_{q=1}^{n}\sum_{a=1}^{n_q} p_{b,k,e,q,a}\,\frac{dc_{q,a,j+}{}^{b}}{dc_{q,a,j+}}}{\sum_{b=1}^{\infty}\sum_{q=1}^{n}\sum_{a=1}^{n_q} y_{b,k,e,q,a}\,\frac{dc_{q,a,j+}{}^{b}}{dc_{q,a,j+}}}\right),$$

(C34+)

respectively, where n is the number of solute components, n_q is the number of species that constitute solute component q, $D^{\circ}{}_{k,e,j-}$ at all ξ equals $D_{k,e}$ at ξ_j at time t in the limit as c approaches 0, $D^{\circ}_{k,e,j+}$ at all ξ equals $D_{k,e}$ at ξ_j at time [t + Δt] in the limit as c approaches 0, $\sigma^{\circ}_{k,e,j-}$ at all ξ equals $\sigma_{k,e}$ at ξ_j at time t in the limit as c approaches 0, $\sigma^{\circ}_{k,e,j+}$ at all ξ equals $\sigma_{k,e}$ at ξ_j at time [t + Δt] in the limit as c approaches 0, $Eu^{\circ}_{k,e,j-}$ at all ξ equals $Eu_{k,e}$ at ξ_j at time t in the limit as c approaches 0, $Eu^{\circ}_{k,e,j+}$ at all ξ equals $Eu_{k,e}$ at ξ_j at time [t + Δt] in the limit as c approaches 0, $c_{q,a,j-}$ is the ξ-independent concentration coefficient of species a of solute component q at time t (at time t, $c_{q,a,j-}$, at all ξ, equals $c_{q,a}$ at ξ_j, just as $c_{k,e,h}$, at all ξ, equals $c_{k,e}$ at ξ_h in Equation C17), $c_{q,a,j+}$ is the ξ-independent concentration coefficient of species a of solute component q at time [t + Δt] (at time [t + Δt], $c_{q,a,j+}$, at all ξ, equals $c_{q,a}$ at ξ_j, just as $c_{k,e,h}$, at all ξ, equals $c_{k,e}$ at ξ_h in Equation C17), and where $p_{b,k,e,q,a}$, $y_{b,k,e,q,a}$ and $h_{b,k,e,q,a}$ are the b^{th} of up to an infinite number of coefficients of proportionality for the electrophoretic/asymmetry, thermodynamic nonideality, and viscosity effects, respectively. By definition, $\sum_{q=1}^{n}\sum_{a=1}^{n_q} p_{1,k,e,q,a}$, $\sum_{q=1}^{n}\sum_{a=1}^{n_q} y_{1,k,e,q,a}$ and $\sum_{q=1}^{n}\sum_{a=1}^{n_q} h_{1,k,e,q,a}$ are each equal to 1. Each of the $p_{b,k,e,q,a}$, $y_{b,k,e,q,a}$ and $h_{b,k,e,q,a}$ coefficients couples the concentration of species a of component q to an effect on the transport of species e of component k. (See Section D for the component-based equivalents of these virial expansions.)

With ∓ representing either – or +, Equations N23∓ and N24∓ can be used in place of Equations C33∓ and C34∓, respectively. Henceforth, $c_{q,a}$ is used to denote the concentration of species a of solute component q at either time t or time [t + Δt], and some unspecified position, ξ_j.

Individually, the product of $b(c_{q,a})^{b-1}$ with the corresponding coefficient of proportionality $p_{b,k,e,q,a}$ yields the b^{th} term for the contribution of $c_{q,a}$ to the electrophoretic/asymmetry effect of the system as it affects the transport of species e of component k, the product of $b(c_{q,a})^{b-1}$ with the corresponding coefficient of proportionality $y_{b,k,e,q,a}$ yields the b^{th} term for the contribution of $c_{q,a}$ to the thermodynamic nonideality of the system as it affects the transport of species e of component k, and the product of $b(c_{q,a})^{b-1}$ with the corresponding coefficient of proportionality $h_{b,k,e,q,a}$ yields the b^{th} term for the contribution of $c_{q,a}$ to the viscosity of the system as it affects the transport of species e of component k, where $b(c_{q,a})^{b-1} = d(c_{q,a})^b/dc_{q,a}$.

Collectively, the sum of products given by $\sum_{b=2}^{\infty}\sum_{a=1}^{n_q} p_{b,k,e,q,a} bc_{q,a}{}^{b-1}$ is a measure of the total contribution of $c_{q,a}$ to the electrophoretic/asymmetry effect of the system as it affects the transport of species e of component k, the sum of products given by $\sum_{b=2}^{\infty}\sum_{a=1}^{n_q} y_{b,k,e,q,a} bc_{q,a}{}^{b-1}$ is a measure of the total contribution of $c_{q,a}$ to the thermodynamic nonideality of the system as it affects the transport of species e of component k, and the sum of products given by $\sum_{b=2}^{\infty}\sum_{a=1}^{n_q} h_{b,k,e,q,a} bc_{q,a}{}^{b-1}$ is a measure of the total contribution of $c_{q,a}$ to the viscosity of the system as it affects the transport of species e of component k.

Henceforth, $\sigma_{k,e,j}$, $D_{k,e,j}$ and $Eu_{k,e,j}$ are used to denote the ξ-independent transport coefficients at either time t or time [t + Δt], and $\sigma^{\circ}_{k,e,j}$, $D^{\circ}_{k,e,j}$ and $Eu^{\circ}_{k,e,j}$ are used to denote the ξ-independent transport coefficients at either time t or time [t + Δt] in the limit at c approaches zero.

By definition, $\sigma^{\circ}_{k,e,j}$, $D^{\circ}_{k,e,j}$ and $Eu^{\circ}_{k,e,j}$, are ξ-independent, and for a given t-independent electrical current, may also be t-independent. In the case of solvent compressibility however, the expectation is that $\Delta\sigma^{\circ}_{k,e,j}/\Delta j \neq 0$ and $\Delta D^{\circ}_{k,e,j}/\Delta j \neq 0$, from which it follows that $\Delta Eu^{\circ}_{k,e,j}/\Delta j \neq 0$. The condition that, for all solute species, $\Delta\sigma^{\circ}_{k,e,j}/\Delta j = 0$ and $\Delta D^{\circ}_{k,e,j}/\Delta j = 0$, from which it would follow that $\Delta Eu^{\circ}_{k,e,j}/\Delta j = 0$, can only apply to a system with an incompressible solvent, in which case, $\sigma^{\circ}_{k,e,j}$, $D^{\circ}_{k,e,j}$ and $Eu^{\circ}_{k,e,j}$ can be replaced with their respective, system-wide constants, $\sigma^{\circ}_{k,e}$, $D^{\circ}_{k,e}$ and $Eu^{\circ}_{k,e}$. (In writing Equations C33 and C34, it was assumed that $\Delta p_{b,k,e,q,a}/\Delta j = 0$, $\Delta y_{b,k,e,q,a}/\Delta j = 0$ and $\Delta h_{b,k,e,q,a}/\Delta j = 0$ for any given pair of species e and a of their respective components k and q, even in the case of solvent compressibility. If required to deal adequately with the case of solvent compressibility, $p_{b,k,e,q,a}$, $y_{b,k,e,q,a}$ and $h_{b,k,e,q,a}$ can be replaced with their respective j- and t-dependent coefficients, which would be $p_{b,k,e,q,a,j-}$, $y_{b,k,e,q,a,j-}$ and $h_{b,k,e,q,a,j-}$ at time t, and would be $p_{b,k,e,q,a,j+}$, $y_{b,k,e,q,a,j+}$ and $h_{b,k,e,q,a,j+}$ at time [t + Δt], where, denoting a coefficient at either time by dropping the – or + suffix, $\Delta p_{b,k,e,q,a,j}/\Delta j \neq 0$, $\Delta y_{b,k,e,q,a,j}/\Delta j \neq 0$ and $\Delta h_{b,k,e,q,a,j}/\Delta j \neq 0$ for any given pair of species e and a of their respective components k and q.)

(As $Eu°_{k,e,j}$ and $\sigma°_{k,e,j}$ only apply in the limit as c approaches zero, and thus, where E is ξ-independent, it would be incorrect to incorporate the ξ-dependence of E into the j-dependence of $Eu°_{k,e,j}$ or $\sigma°_{k,e,j}$. Practically speaking, however, it may be useful to do just that, especially for the analysis of systems at steady state, when the ξ-dependence of E is time-invariant. When applied to experimental results, such analysis would best be attempted only after acquiring steady-state data at multiple current strengths for multiple systems that differ solely with respect to the total, net concentration of membrane-confined solute components. Extrapolation of σ_w (see Equation A39) to zero current and zero solute concentration should yield $\sigma_w = 0$. The dependence of σ_w on current and solute concentration could then be used to find functions describing the ξ-dependence of such apparent $Eu°_{k,e,j}$ or $\sigma°_{k,e,j}$.)

To avoid quadratic and higher-order terms in $c_{q,a,j-}$ or $c_{q,a,j+}$, along with other complicated terms arising from the presence of a truncated virial expansion in the denominators of $\sigma_{k,e,j}$ and $D_{k,e,j}$ in Equations C33 and C34, no effort is made, initially, to solve Equation C32 as written. Instead, Equation C32 is solved as if $\sigma_{k,e,j+}$ and $D_{k,e,j+}$ were independent of all $c_{q,a,j+}$, and as if $\sigma_{k,e,j-}$ and $D_{k,e,j-}$ were independent of all $c_{q,a,j-}$. Furthermore, because $c_{q,a,j+}$ values are not known prior to their use in $\sigma_{k,e,j+}$ and $D_{k,e,j+}$, $\sigma_{k,e,j-}$ and $D_{k,e,j-}$ are used in place of $\sigma_{k,e,j+}$ and $D_{k,e,j+}$, respectively. The resulting solution is that referred to as the second approximate solution. (As previously mentioned, the first approximate solution that pertains to the case of $(\partial D_{k,e}/\partial \xi)_t = 0$ and $(\partial \sigma_{k,e}/\partial \xi)_t = 0$ at all ξ will be derived from the second approximate solution.) The discussion of this issue is continued following Equation C35.

Equations C33 and C34 use a set of power series of each solute species concentration to describe the thermodynamic nonideality, viscosity and electrophoretic/asymmetry effects of the solution. For solutions that are too concentrated to permit the use of highly truncated virial expansions in the description of parameters such as $D_{k,e}$, $\sigma_{k,e}$ and $Eu_{k,e}$, additional terms from the infinite series can be retained. (See **Section D: Expressions for the deviation from van 't Hoff behaviour and other virial expansions**. The expressions shown in Section D are based on a component-by-component description of the system, but by extension, corresponding expressions based on a species-by-species description of the system can be obtained.) It is, however, incorrect to treat $\sigma_{k,e,j}$, $D_{k,e,j}$ and $Eu_{k,e,j}$ as if they were functions of any terms involving solute concentrations in the second approximate solution, unless that solution is applied iteratively within each time increment. The general solution presented in Section J (**Form of the general solution from Equation C32**) does apply the second approximate solution iteratively, and thus permits the concentration dependence of $\sigma_{k,e,j}$, $D_{k,e,j}$ and $Eu_{k,e,j}$ at times t and [t + Δt] to be treated correctly.

Solving for $c_{k,e,h+}$

There are now three sets of space-dependent, time-independent basis functions (the set of all P_h, P_i and P_j), and there are N functions per set of such basis functions ($1 \leq h \leq N$, $1 \leq i \leq N$, and $1 \leq j \leq N$). For each species e of solute component k, at either time t or [t + Δt]: there are N space-independent, time-dependent, concentration coefficients, $c_{k,e,h}$; there are N space-independent, time-dependent, diffusion coefficients, $D_{k,e,j}$; and there are N space-independent, time-dependent, electrophoretic mobility coefficients, $u_{k,e,j}$, which are related to the N space-independent, time-dependent, reduced valence coefficients through $Eu_{k,e,j} = D_{k,e,j}\sigma_{k,e,j}$. For the case of each P_h, P_i and P_j being a hat function (as described by Equations B58 to B63), for each species e of solute component k, at either time t or [t + Δt]: each product, $c_{k,e,h}P_h$, is maximal at spatial element h, and is zero below spatial element [h – 1] or above spatial element [h + 1]; while each of the products, $D_{k,e,j}P_j$ and $D_{k,e,j}\sigma_{k,e,j}P_j$, is maximal at spatial element j, and is zero below spatial element [j – 1] or above spatial element [j + 1].

Let

$$F_{k,e,h,i+} = \int_{\xi_m}^{\xi_b} P_h P_i d\xi - \sum_{j=1}^{N} D_{k,e,j+}\left[\sigma_{k,e,j+}\int_{\xi_m}^{\xi_b} P_j P_h \frac{dP_i}{d\xi} d\xi - \int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi}\frac{dP_i}{d\xi} d\xi\right]\Delta t$$

and

$$F_{k,e,h,i-} = \int_{\xi_m}^{\xi_b} P_h P_i d\xi + \sum_{j=1}^{N} D_{k,e,j-}\left[\sigma_{k,e,j-}\int_{\xi_m}^{\xi_b} P_j P_h \frac{dP_i}{d\xi} d\xi - \int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi}\frac{dP_i}{d\xi} d\xi\right]\Delta t\,.$$

(C35)

Equations B33 and B34 are used to calculate $D_{k,e,j}$ and $\sigma_{k,e,j}$, respectively. Despite their dependence on all $c_{q,a,j+}$, for each iteration (see Section J) of the second approximate solution, $\sigma_{k,e,j+}$ and $D_{k,e,j+}$ are treated as if they were independent of all $c_{k,e,j+}$, and in the first iteration of any given time increment, $\sigma_{k,e,j+}$ and $D_{k,e,j+}$ are replaced with $\sigma_{k,e,j-}$ and $D_{k,e,j-}$, respectively, all of which permits the set of solutions to be written as

$$\sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}\sum_{i=1}^{N} c_{k,e,h+}F_{k,e,h,i+} = \sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}\sum_{i=1}^{N} c_{k,e,h-}F_{k,e,h,i-}\ ,$$

(C36)

where each $F_{k,e,h,i+}$ is treated as independent of all $c_{k,e,j+}$. In the second approximate solution, it is permissible to treat $F_{k,e,h,i-}$, $\sigma_{k,e,j-}$ and $D_{k,e,j-}$ as dependent of all $c_{q,a,j-}$. In the general solution (Section J), the dependence of $F_{k,e,h,i+}$, $\sigma_{k,e,j+}$ and $D_{k,e,j+}$ on all $c_{q,a,j+}$ is repeatedly approximated, with the errors in those approximations approaching zero with a sufficient number of iterations.

Letting

$$Z_{k,e,i-} = \sum_{h=1}^{N} c_{k,e,h-}F_{k,e,h,i-}$$

then results in

$$\sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{i=1}^{N} Z_{k,e,i-} = \sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}\sum_{i=1}^{N} c_{k,e,h+}F_{k,e,h,i+}.$$

(C37)

As can be seen from Figure B3 and Equations B39 to B53, the use of the hat function for P_h and P_i results in most of the terms indexed by i and h being zero:

$F_{k,e,h,1+} = 0$ and $F_{k,e,h,1-} = 0$ for $h > 2$;

$F_{k,e,h,N+} = 0$ and $F_{k,e,h,N-} = 0$ for $h < [N - 1]$; and

$F_{k,e,h,[1<i<N]+} = 0$ and $F_{k,e,h,[1<i<N]-} = 0$ for $[i - 2] < h < [i + 2]$.

Consequently,

$$\sum_{k=1}^{n}\sum_{e=1}^{n_k} Z_{k,e,1-} = \sum_{k=1}^{n}\sum_{e=1}^{n_k}\left(c_{k,e,1+}F_{k,e,1,1+} + c_{k,e,2+}F_{k,e,2,1+}\right),$$

$$\sum_{k=1}^{n}\sum_{e=1}^{n_k} Z_{k,e,i-} = \sum_{k=1}^{n}\sum_{e=1}^{n_k}\left(c_{k,e,[i-1]+}F_{k,e,[i-1],i+} + c_{k,e,i+}F_{k,e,i,i+} + c_{k,e,[i+1]+}F_{k,e,[i+1],i+}\right)$$

for 1 < i < N, and

$$\sum_{k=1}^{n}\sum_{e=1}^{n_k} Z_{k,e,N-} = \sum_{k=1}^{n}\sum_{e=1}^{n_k}\left(c_{k,e,[N-1]+}F_{k,e,[N-1],N+} + c_{k,e,N+}F_{k,e,N,N+}\right).$$

(C38)

Equating corresponding terms indexed by e results in

$$Z_{k,e,1-} = c_{k,e,1+}F_{k,e,1,1+} + c_{k,e,2+}F_{k,e,2,1+},$$

$$Z_{k,e,i-} = c_{k,e,[i-1]+}F_{k,e,[i-1],i+} + c_{k,e,i+}F_{k,e,i,i+} + c_{k,e,[i+1]+}F_{k,e,[i+1],i+}$$

for 1 < i < N, and

$$Z_{k,e,N-} = c_{k,e,[N-1]+}F_{k,e,[N-1],N+} + c_{k,e,N+}F_{k,e,N,N+}.$$

(C39)

The equalities in Equation C39 are permissible by virtue of the Curie-Prigogine principle. (See **Section G: The dissipation function and the Curie-Prigogine principle.**) In the case here, where e is a solute species, it is possible for $(\partial c_{k,e}/\partial t)_\xi$ and $-(\partial I_{k,e}/\partial \xi)_t$ to differ. This would appear to invalidate the step of equating each $Z_{k,e,i-}$ to the sum over all h of $c_{k,e,h+}F_{k,e,h,i+}$. As mentioned with respect to Equations B26 to B28, for the case of a solute component, k, $(\partial c_k/\partial t)_\xi$ does equal $-(\partial I_k/\partial \xi)_t$, which makes each $Z_{k,i-}$ equal the sum over all h of $c_{k,h+}F_{k,h,i+}$ in those equations. Therefore,

$$z_{k,1-} = \sum_{e=1}^{n_k} z_{k,e,1-} = \sum_{e=1}^{n_k}\left(c_{k,e,1+}F_{k,e,1,1+} + c_{k,e,2+}F_{k,e,2,1+}\right),$$

$$z_{k,i-} = \sum_{e=1}^{n_k} z_{k,e,i-} = \sum_{e=1}^{n_k} \left(c_{k,e,[i-1]+}F_{k,e,[i-1],i+} + c_{k,e,i+}F_{k,e,i,i+} + c_{k,e,[i+1]+}F_{k,e,[i+1],i+}\right)$$

for 1 < i < N, and

$$z_{k,N-} = \sum_{e=1}^{n_k} z_{k,e,N-} = \sum_{e=1}^{n_k} \left(c_{k,e,[N-1]+}F_{k,e,[N-1],N+} + c_{k,e,N+}F_{k,e,N,N+}\right)$$

(C40)

are valid equations. The fact that there are no phenomenological coefficients linking reaction forces to transport flows, or transport forces to reaction flows, permits the transport and reaction flows to be dealt with separately, however. Furthermore, the reaction flow is the sole source of the potential inequality between $(\partial c_{k,e}/\partial t)_\xi$ and $-(\partial I_{k,e}/\partial \xi)_t$. Thus, when the reaction flow is handled separately, the transport flow can be handled as it would be for a solute component. As reaction flows are, in fact, handled separately from transport flows in this method, it is valid to equate each $Z_{k,e,i-}$ to the sum over all h of $c_{k,e,i+}F_{k,e,h,i+}$ (as shown in Equation C39), which is the approach taken to obtain a solution here.

Equations C74 to C75 show the fully expanded forms of Equation C39.

Equation C39 permits the continuity equation to be solved species-by-species and component-by-component. For each species of a given component, the solution proceeds one concentration coefficient at a time. Solving first for $c_{k,e,1+}$ yields

$$c_{k,e,1+} = Y_{k,e,1} - X_{k,e,1}c_{k,e,2+}\ ,$$

where

$$Y_{k,e,1} = \frac{Z_{k,e,1-}}{F_{k,e,1,1+}}$$

and

$$X_{k,e,1} = \frac{F_{k,e,2,1+}}{F_{k,e,1,1+}}.$$

(C41)

For i < N, the solution for each subsequent $c_{k,e,i+}$, in ascending order from $2 \leq i < N$, takes the form of

$$c_{k,e,i+} = Y_{k,e,i} - X_{k,e,i} c_{k,e,[i+1]+},$$

where

$$Y_{k,e,i} = \frac{Z_{k,e,i-} - Y_{k,e,[i-1]} F_{k,e,[i-1],i+}}{F_{k,e,i,i+} - X_{k,e,[i-1]} F_{k,e,[i-1],i+}}$$

and

$$X_{k,e,i} = \frac{F_{k,e,[i+1],i+}}{F_{k,e,i,i+} - X_{k,e,[i-1]} F_{k,e,[i-1],i+}}.$$

(C42)

At i = N, the solution for $c_{k,e,N+}$ is obtained. In terms of $c_{k,e,[N-1]+}$, the solution for $c_{k,e,N+}$ is

$$c_{k,e,N+} = Y_{k,e,N} - X_{k,e,N} c_{k,e,[N-1]+},$$

where

$$Y_{k,e,N} = \frac{Z_{k,e,N-}}{F_{k,e,N,N+}}$$

and

$$X_{k,e,N} = \frac{F_{k,e,[N-1],N+}}{F_{k,e,N,N+}}.$$

(C43)

The solution for $c_{k,e,[N-1]+}$ can now be substituted into the solution for $c_{k,e,N+}$ to obtain

$$c_{k,e,N+} = Y_{k,e,N} - X_{k,e,N}\left(Y_{k,e,[N-1]} - X_{k,e,[N-1]}c_{k,e,N+}\right),$$

(C44)

which, solved for $c_{k,e,N+}$, is

$$c_{k,e,N+} = \frac{Y_{k,e,N} - X_{k,e,N}Y_{k,e,[N-1]}}{1 - X_{k,e,N}X_{k,e,[N-1]}},$$

(C45a)

alternative expressions of which are

$$c_{k,e,N+} = \frac{Y_{k,e,N}F_{k,e,N,N+} - F_{k,e,[N-1],N+}Y_{k,e,[N-1]}}{F_{k,e,N,N+} - F_{k,e,[N-1],N+}X_{k,e,[N-1]}}$$

(C45b)

and

$$c_{k,e,N+} = \frac{Z_{k,e,N-} - Y_{k,e,[N-1]}F_{k,e,[N-1],N+}}{F_{k,e,N,N+} - X_{k,e,[N-1]}F_{k,e,[N-1],N+}}.$$

(C45c)

The above solution for $c_{k,e,N+}$ does not require knowledge of $c_{k,e,[N-1]+}$ or any other unknowns. This solution for $c_{k,e,N+}$ can now be used, therefore, to solve the previously obtained expression for $c_{k,e,[N-1]+}$ in terms of $c_{k,e,N+}$ and other known parameters. Subsequently, using $c_{k,[N-1]+}$, the previously obtained expression for $c_{k,e,[N-2]+}$ can be solved in terms of $c_{k,e,[N-1]+}$ and other known parameters. Thus, once $c_{k,e,N+}$ is known, each preceding $c_{k,e,i+}$ is calculated in descending order from i = [N - 1] to i = 2 using Equation C42 until, upon reaching i = 1, $c_{k,e,1+}$ is calculated using Equation C41, at which point, the entire array of $c_{k,e,i+}$ values has been determined. For i = h, $c_{k,e,i+} = c_{k,e,h+}$, so that the array of $c_{k,e,i+}$ values obtained equals the array of $c_{k,e,h+}$ values sought.

This process is carried out for each species, e, of each solute component, k, at each addition of a time increment. These new $c_{k,e,h+}$ values are then used as the next $c_{k,e,h-}$ values after the addition of the next time increment, and the process is repeated until the desired time point is reached, at least in a noniterative application of the second approximate solution. (The general solution presented in Section J (**Form of the general solution from Equation C32**) applies the second approximate solution iteratively, with the result that $c_{k,e,h+}$ is repeatedly recalculated within each time increment until a convergence criterion (Equation J6) is met, or a maximum number of iterations is reached.)

It has been found that the process is made more robust by first calculating all $c_{k,e,h+}$ in the forward direction starting from $c_{k,e,1+}$, then recalculating all $c_{k,e,h+}$ in reverse order (starting from $c_{k,e,N+}$), and averaging the results. The calculation of all $c_{k,e,h+}$ in reverse order is implemented by obtaining a solution to the t- and ξ-dependent continuity equation for MCE with the set of all ξ_h reversed, so that $\xi_1 = \xi_b$ and $\xi_N = \xi_m$. The solution obtained is backwards in the sense that $c_{k,e,1+}$ at all ξ is equal to the value of $c_{k,e}$ at ξ_b, while $c_{k,e,N+}$ at all ξ is equal to the value of $c_{k,e}$ at ξ_m. In general, ξ_h, $c_{k,e,h+}$, $c_{k,e,h-}$, $D_{k,e,j+}$, $\sigma_{k,e,j+}$, $D_{k,e,j-}$ and $\sigma_{k,e,j-}$, of the backwards solution are equal to $\xi_{[N-h+1]}$, $c_{k,e,[N-h+1]+}$, $c_{k,e,[N-h+1]-}$, $D_{k,e,[N-j+1]+}$, $\sigma_{k,e,[N-j+1]+}$, $D_{k,e,[N-j+1]-}$ and $\sigma_{k,e,[N-j+1]-}$, respectively, of the forward solution, which is the solution described above for the original orientation. Solving for $c_{k,e,h+}$ using the backwards solution then proceeds as described for the forward solution. Averaging is weighted toward the starting point of each solution, were artefacts appear to be minimal, so that, subscripting all concentration and spatial parameters by h as that index applies to the forward solution, the average value of $c_{k,e,h+}$ is $(c_{k,e,h+})_{avg} = [(\xi_h - \xi_m)(c_{k,e,h+})_R + (\xi_b - \xi_h)(c_{k,e,h+})_F]/(\xi_b - \xi_m)$, where $(c_{k,e,h+})_F$ and $(c_{k,e,h+})_R$ are the values of $c_{k,e,h+}$ obtained from the forward and backwards solutions, respectively.

For the remainder of the solution, Equations B34 to B63 apply as written, except that the case of $(\partial\sigma_k/\partial\xi)_t = 0$ and $(\partial D_k/\partial\xi)_t = 0$ at all ξ is replaced with the case of $(\partial\sigma_{k,e}/\partial\xi)_t = 0$ and $(\partial D_{k,e}/\partial\xi)_t = 0$ at all ξ, which is covered in Section F (**ξ-dependent functions to approximate $D_{k,e}$ and $\sigma_{k,e}$**).

Consequences for average parameters

Examining whether $(F_{k,h,i+})_w = F_{k,h,i+}$ and $(F_{k,h,i-})_w = F_{k,h,i-}$

Given that

$$\sum_{k=1}^{n}\sum_{h=1}^{N}\sum_{i=1}^{N}\sum_{e=1}^{n_k} c_{k,e,h-}F_{k,e,h,i-} = \sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}\sum_{i=1}^{N} c_{k,e,h-}F_{k,e,h,i-}$$

and

$$\sum_{k=1}^{n}\sum_{h=1}^{N}\sum_{i=1}^{N}\sum_{e=1}^{n_k} c_{k,e,h+}F_{k,e,h,i+} = \sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}\sum_{i=1}^{N} c_{k,e,h+}F_{k,e,h,i+}$$

(C46)

(see Equation C36), weight averages of $F_{k,e,h,i+}$ and $F_{k,e,h,i-}$ can be calculated for all species of a given solute component. Averaging the terms indexed by e in Equation C46 results in

$$\sum_{k=1}^{n}\sum_{h=1}^{N}\sum_{i=1}^{N}\left(\sum_{e=1}^{n_k} c_{k,e,h+}\right)\frac{\sum_{e=1}^{n_k} c_{k,e,h+}F_{k,e,h,i+}}{\sum_{e=1}^{n_k} c_{k,e,h+}} = \sum_{k=1}^{n}\sum_{h=1}^{N}\sum_{i=1}^{N}\left(\sum_{e=1}^{n_k} c_{k,e,h-}\right)\frac{\sum_{e=1}^{n_k} c_{k,e,h-}F_{k,e,h,i-}}{\sum_{e=1}^{n_k} c_{k,e,h-}},$$

(C47)

which yields

$$\sum_{k=1}^{n}\sum_{h=1}^{N}\sum_{i=1}^{N} c_{k,h+}\left(F_{k,h,i+}\right)_w = \sum_{k=1}^{n}\sum_{h=1}^{N}\sum_{i=1}^{N} c_{k,h-}\left(F_{k,h,i-}\right)_w,$$

(C48)

where $(F_{k,h,i+})_w$ and $(F_{k,h,i-})_w$ are the weight-average values of $F_{k,e,h,i+}$ and $F_{k,e,h,i-}$, respectively, for all species e of solute component k. Using Equation C35 to express $F_{k,e,h,i+}$ and $F_{k,e,h,i-}$ in expanded form results, after some re-arrangement, in

$$c_{k,h+}\left(F_{k,h,i+}\right)_w = c_{k,h+}\left(\int_{\xi_m}^{\xi_b} P_h P_i d\xi - \sum_{j=1}^{N}\left\{\left(\left[D_{k,j+}\sigma_{k,j+}\right]_h\right)_w \int_{\xi_m}^{\xi_b} P_j P_h \frac{dP_i}{d\xi} d\xi - \left(\left[D_{k,j+}\right]_h\right)_w \int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi}\frac{dP_i}{d\xi} d\xi\right\}\Delta t\right)$$

(C49)

and

$$c_{k,h-}\left(F_{k,h,i-}\right)_w = c_{k,h-}\left(\int_{\xi_m}^{\xi_b} P_h P_i d\xi + \sum_{j=1}^{N}\left\{\left(\left[D_{k,j-}\sigma_{k,j-}\right]_h\right)_w \int_{\xi_m}^{\xi_b} P_j P_h \frac{dP_i}{d\xi} d\xi - \left(\left[D_{k,j-}\right]_h\right)_w \int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi}\frac{dP_i}{d\xi} d\xi\right\}\Delta t\right),$$

(C50)

where

$$\left(\left[D_{k,j-}\sigma_{k,j-}\right]_h\right)_w = \frac{\sum_{e=1}^{n_k} c_{k,e,h-}\, D_{k,e,j-}\sigma_{k,e,j-}}{\sum_{e=1}^{n_k} c_{k,e,h-}},$$

(C51)

$$\left(\left[D_{k,j-}\right]_h\right)_w = \frac{\sum_{e=1}^{n_k} c_{k,e,h-}\, D_{k,e,j-}}{\sum_{e=1}^{n_k} c_{k,e,h-}},$$

(C52)

$$\left(\left[D_{k,j+}\sigma_{k,j+}\right]_h\right)_w = \frac{\sum_{e=1}^{n_k} c_{k,e,h+}\, D_{k,e,j+}\sigma_{k,e,j+}}{\sum_{e=1}^{n_k} c_{k,e,h+}}$$

(C53)

and

$$\left(\left[D_{k,j+}\right]_h\right)_w = \frac{\sum_{e=1}^{n_k} c_{k,e,h+}\, D_{k,e,j+}}{\sum_{e=1}^{n_k} c_{k,e,h+}}.$$

(C54)

Equations C51 and C52, respectively, show that $([\sigma_{k,j-}D_{k,j-}]_h)_w$ and $([D_{k,j-}]_h)_w$ are $c_{k,e,h-}$-weighted averages of all $\sigma_{k,e,j-}D_{k,e,j-}$ and $D_{k,e,j-}$, respectively, of component k. Equations C53 and C54, respectively, show that $([\sigma_{k,j+}D_{k,j+}]_h)_w$ and $([D_{k,j+}]_h)_w$ are $c_{k,e,h+}$-weighted averages of all $\sigma_{k,e,j+}D_{k,e,j+}$ and $D_{k,e,j+}$, respectively, of component k. Based on the gradient average, $(D_k)_G$, obtained in Equation C1, however, gradient averages of $D_{k,e,j-}$ and $D_{k,e,j+}$ might have been expected in place of the weight averages obtained in Equations C52 and C54, respectively. (Equation C1 yields one of the averages, $(D_k)_G$, required to express I_k in terms of component parameters in Equation C4. Equation C2 yields the other, which can be expressed as $(\sigma_k D_k)_w$.)

In Equations C52 and C54 , the occurrence of weight averages in place of gradient averages is due to there being no derivatives of $c_{k,e,h-}$ and $c_{k,e,h+}$ with respect to ξ in Equation C36 (as expanded using Equation C35), because $c_{k,e,h-}$ and $c_{k,e,h+}$ are ξ-independent. Instead, the partial derivatives of $c_{k,e}$ and c_k with respect to ξ in Equation C4 give rise to ordinary derivatives of P_h with respect to ξ in Equations C35, B24 and anyplace else where the continuity equation has been solved by separation of variables and integration with respect to ξ. The situation is akin to Equations A40 and A41, where D_G approaches D_w in the limit as t approaches infinity at zero field, at which point, the concentration of each component becomes ξ-independent and thus indistinguishable from $c_{k,h-}$ and $c_{k,h+}$.

As noted where Equation C38 is obtained from Equation C37, and as shown in the next section, for $j < [h - 1]$ or $j > [h + 1]$, the integrals in the summations indexed by j are equal to zero. As $([\sigma_{k,j-}D_{k,j-}]_h)_w$, $([D_{k,j-}]_h)_w$, $([\sigma_{k,j+}D_{k,j+}]_h)_w$ and $([D_{k,j+}]_h)_w$ are multiplied by such integrals, only $([\sigma_{k,j-}D_{k,j-}]_h)_w$ and $([D_{k,j-}]_h)_w$ for which $[h - 1] \leq j \leq [h + 1]$ contribute to $(F_{k,h,i-})_w$, and only $([\sigma_{k,j+}D_{k,j+}]_h)_w$ and $([D_{k,j+}]_h)_w$ for which $[h - 1] \leq j \leq [h + 1]$ contribute to $(F_{k,h,i+})_w$.

The transport coefficients associated with the left-hand ($F_{k,e,h,i+}$) side of Equation C47 are $D_{k,e,j+}\sigma_{k,e,j+}$ and $D_{k,e,j+}$, while the transport coefficients associated with the right-hand ($F_{k,e,h,i-}$) side of Equation C47 are $D_{k,e,j-}\sigma_{k,e,j-}$ and $D_{k,e,j-}$. Thus, as described by Equations C49 to C54, $D_{k,e,j+}\sigma_{k,e,j+}$ and $D_{k,e,j+}$ are averaged with respect to $c_{k,e,h+}$ on the left-hand side of Equations C47 and C48, while $D_{k,e,j-}\sigma_{k,e,j-}$ and $D_{k,e,j-}$ are averaged with respect to $c_{k,e,h-}$ on the right-hand side of Equations C47 and C48. As discussed with respect to Equations C32, C33 and C34, in the second approximate solution used initially, $D_{k,e,j+}\sigma_{k,e,j+}$ and $D_{k,e,j+}$ are replaced, respectively, with $D_{k,e,j-}\sigma_{k,e,j-}$ and $D_{k,e,j-}$. Hence, in the initial iteration within a given time increment, $(F_{k,h,i+})_w$, the average obtained for the $[t + \Delta t]$ part of the second approximate solution, would be incorrect. Within a given time increment, the correct value of $(F_{k,h,i+})_w$ would be obtained by the iterative approach of the general solution (Section J), but only after $c_{k,e,h+}$ had ceased to change significantly with continued iterations of the second approximate solution.

Using Equations C49 and C50, Equation C48 can now be written as

$$\sum_{k=1}^{n}\sum_{h=1}^{N}\sum_{i=1}^{N} c_{k,h+}\left(\int_{\xi_m}^{\xi_b} P_h P_i d\xi \right.$$
$$\left. - \sum_{j=1}^{N}\left\{\left(\left[D_{k,j+}\sigma_{k,j+}\right]_h\right)_w \int_{\xi_m}^{\xi_b} P_j P_h \frac{dP_i}{d\xi} d\xi - \left(\left[D_{k,j+}\right]_h\right)_w \int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi}\frac{dP_i}{d\xi} d\xi\right\}\Delta t\right)$$
$$= \sum_{k=1}^{n}\sum_{h=1}^{N}\sum_{i=1}^{N} c_{k,h-}\left(\int_{\xi_m}^{\xi_b} P_h P_i d\xi \right.$$
$$\left. + \sum_{j=1}^{N}\left\{\left(\left[D_{k,j-}\sigma_{k,j-}\right]_h\right)_w \int_{\xi_m}^{\xi_b} P_j P_h \frac{dP_i}{d\xi} d\xi - \left(\left[D_{k,j-}\right]_h\right)_w \int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi}\frac{dP_i}{d\xi} d\xi\right\}\Delta t \right).$$

(C55)

This equation corresponds to Equation B21, which is the solution to the continuity equation with respect to components. If

$$\sum_{k=1}^{n}\sum_{h=1}^{N}\sum_{i=1}^{N} c_{k,h+}\left(F_{k,h,i+}\right)_w = \sum_{k=1}^{n}\sum_{h=1}^{N}\sum_{i=1}^{N}\left(\sum_{e=1}^{n_k} c_{k,e,h+}\right)\frac{\sum_{e=1}^{n_k} c_{k,e,h+}F_{k,e,h,i+}}{\sum_{e=1}^{n_k} c_{k,e,h+}}$$
$$= \sum_{k=1}^{n}\sum_{h=1}^{N}\sum_{i=1}^{N}\sum_{e=1}^{n_k} c_{k,e,h+}F_{k,e,h,i+} = \sum_{k=1}^{n}\sum_{h=1}^{N}\sum_{i=1}^{N} c_{k,h+}F_{k,h,i+}$$

(C56)

and if

$$\sum_{k=1}^{n}\sum_{h=1}^{N}\sum_{i=1}^{N} c_{k,h-}\left(F_{k,h,i-}\right)_w = \sum_{k=1}^{n}\sum_{h=1}^{N}\sum_{i=1}^{N}\left(\sum_{e=1}^{n_k} c_{k,e,h-}\right)\frac{\sum_{e=1}^{n_k} c_{k,e,h-}F_{k,e,h,i-}}{\sum_{e=1}^{n_k} c_{k,e,h-}}$$
$$= \sum_{k=1}^{n}\sum_{h=1}^{N}\sum_{i=1}^{N}\sum_{e=1}^{n_k} c_{k,e,h-}F_{k,e,h,i-} = \sum_{k=1}^{n}\sum_{h=1}^{N}\sum_{i=1}^{N} c_{k,h-}F_{k,h,i-}\ ,$$

(C57)

then Equations B21 and C55 are identical, in which case, $(F_{k,h,i+})_w = F_{k,h,i+}$, $(F_{k,h,i-})_w = F_{k,h,i-}$ and $\sigma_{k,j-}D_{k,j-}$, $D_{k,j-}$, $\sigma_{k,j+}D_{k,j+}$ and $D_{k,j+}$, respectively, of Equation B21 equal $([\sigma_{k,j-}D_{k,j-}]_h)_w$, $([D_{k,j-}]_h)_w$, $([\sigma_{k,j+}D_{k,j+}]_h)_w$ and $([D_{k,j+}]_h)_w$, respectively, of Equation C55. The equivalence of

Equations B21 and C55 would indicate that the solution in terms of components can be derived from the solution in terms of species. The question of whether Equations B21 and C55 are identical is revisited after calculating the weight averages of $F_{k,h,i+}$ and $F_{k,h,i-}$ for all solute components.

Defining $(F_{h,i+})_w = F_{h,i+}$ and $(F_{h,i-})_w = F_{h,i-}$

Given that

$$\sum_{i=1}^{N}\sum_{h=1}^{N}\sum_{k=1}^{n} c_{k,h-}\left(F_{k,h,i-}\right)_w = \sum_{k=1}^{n}\sum_{h=1}^{N}\sum_{i=1}^{N} c_{k,h-}\left(F_{k,h,i-}\right)_w$$

and

$$\sum_{i=1}^{N}\sum_{h=1}^{N}\sum_{k=1}^{n} c_{k,h+}\left(F_{k,h,i+}\right)_w = \sum_{k=1}^{n}\sum_{h=1}^{N}\sum_{i=1}^{N} c_{k,h+}\left(F_{k,h,i+}\right)_w$$

(C58)

(see Equation C48), weight averages of $F_{k,h,i+}$ and $F_{k,h,i-}$ can be calculated for all solute components. First, however, it is useful to define the total solute concentration before and after the time increment as c_+ and c_-, respectively. Next, the sums of $c_{k,h+}$ and $c_{k,h-}$ over all solute components are defined as c_{h+} and c_{h-}, respectively, through

$$c_+ = \sum_{h=1}^{N} c_{h+}P_h = \sum_{h=1}^{N}\sum_{k=1}^{n} c_{k,h+}P_h = \sum_{k=1}^{n}\sum_{h=1}^{N} c_{k,h+}P_h$$

and

$$c_- = \sum_{h=1}^{N} c_{h-}P_h = \sum_{h=1}^{N}\sum_{k=1}^{n} c_{k,h-}P_h = \sum_{k=1}^{n}\sum_{h=1}^{N} c_{k,h-}P_h\ ,$$

(C59)

respectively. (Each c_h, either as c_{h+} or c_{h-}, is ξ-independent, and at all ξ is equal to the value of c at ξ_h. Equation B6 describes $c_{k,h}$ and P_h.) Penultimately, Equation C58 and C59 are used to obtain

$$\sum_{i=1}^{N}\sum_{h=1}^{N}\left(\sum_{k=1}^{n} c_{k,h+}\right)\frac{\sum_{k=1}^{n} c_{k,h+}\left(F_{k,h,i+}\right)_w}{\sum_{k=1}^{n} c_{k,h+}} = \sum_{i=1}^{N}\sum_{h=1}^{N}\left(\sum_{k=1}^{n} c_{k,h-}\right)\frac{\sum_{e=1}^{n_k} c_{k,h-}\left(F_{k,h,i-}\right)_w}{\sum_{k=1}^{n} c_{k,h-}},$$

which, finally, yields

$$\sum_{i=1}^{N}\sum_{h=1}^{N} c_{h+}\left(F_{h,i+}\right)_w = \sum_{i=1}^{N}\sum_{h=1}^{N} c_{h-}\left(F_{h,i-}\right)_w ,$$

(C60)

where $(F_{h,i+})_w$ and $(F_{h,i-})_w$ are the weight-average values of $F_{k,h,i+}$ and $F_{k,h,i-}$, respectively, for all solute components.

In the general solution (Section J) in terms of components, $D_{k,j}\sigma_{k,j+}$ and $D_{k,j+}$ are the transport coefficients associated with the left-hand side of Equation C60 (expressed in terms of $F_{k,h,i+}$ on a component basis, or $(F_{h,i+})_w$ on a weight-average basis), while $D_{k,j-}\sigma_{k,j-}$ and $D_{k,j-}$ are the transport coefficients associated with the right-hand side of Equation C60 (expressed in terms of $F_{k,h,i-}$ on a component basis, or $(F_{h,i-})_w$ on a weight-average basis). Thus, in the general solution in terms of components, $D_{k,j+}\sigma_{k,j+}$ and $D_{k,j+}$ are averaged with respect to $c_{k,h+}$ on the left-hand side of Equation C60, while $D_{k,j-}\sigma_{k,j-}$ and $D_{k,j-}$ are averaged with respect to $c_{k,h-}$ on the right-hand side of Equation C60. As discussed with respect to Equations B21, B22 and B23, in the second approximate solution used initially, $D_{k,j+}\sigma_{k,j+}$ and $D_{k,j+}$ are replaced, respectively, with $D_{k,j-}\sigma_{k,j-}$ and $D_{k,j-}$. Hence, in the initial iteration within a given time increment, the average obtained for the [t + Δt] part of the second approximate solution, $(F_{h,i+})_w$, would be incorrect. Within a given time increment, the correct value of $(F_{h,i+})_w$ would be obtained by the iterative approach of the general solution (Section J), but only after $c_{k,h+}$ had ceased to change significantly with continued iterations of the second approximate solution.

Using Equation B24 to express $F_{k,h,i+}$ and $F_{k,h,i-}$ in expanded form results, after some re-arrangement, in

$$c_{h+}\left(F_{h,i+}\right)_w = c_{h+}\left(\int_{\xi_m}^{\xi_b} P_h P_i d\xi \right.$$

$$\left. - \sum_{j=1}^{N}\left\{\left(\left[D_{j+}\sigma_{j+}\right]_h\right)_w \int_{\xi_m}^{\xi_b} P_j P_h \frac{dP_i}{d\xi} d\xi - \left(\left[D_{j+}\right]_h\right)_w \int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi}\frac{dP_i}{d\xi} d\xi\right\}\Delta t\right)$$

(C61)

and

$$c_{h-}\left(F_{h,i-}\right)_w = c_{h-}\left(\int_{\xi_m}^{\xi_b} P_h P_i d\xi \right.$$

$$\left. + \sum_{j=1}^{N}\left\{\left(\left[D_{j-}\sigma_{j-}\right]_h\right)_w \int_{\xi_m}^{\xi_b} P_j P_h \frac{dP_i}{d\xi} d\xi - \left(\left[D_{j-}\right]_h\right)_w \int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi}\frac{dP_i}{d\xi} d\xi\right\}\Delta t \right),$$

(C62)

where

$$\left(\left[D_{j-}\sigma_{j-}\right]_h\right)_w = \frac{\sum_{e=1}^{n_k} c_{k,h-}\, D_{k,j-}\sigma_{k,j-}}{\sum_{e=1}^{n_k} c_{k,h-}},$$

(C63)

$$\left(\left[D_{j-}\right]_h\right)_w = \frac{\sum_{e=1}^{n_k} c_{k,h-}\, D_{k,j-}}{\sum_{e=1}^{n_k} c_{k,h-}},$$

(C64)

$$\left(\left[D_{j+}\sigma_{j+}\right]_h\right)_w = \frac{\sum_{e=1}^{n_k} c_{k,h+}\, D_{k,j+}\sigma_{k,j+}}{\sum_{e=1}^{n_k} c_{k,h+}}$$

(C65)

and

$$\left(\left[D_{j+}\right]_h\right)_w = \frac{\sum_{e=1}^{n_k} c_{k,h+}\, D_{k,j+}}{\sum_{e=1}^{n_k} c_{k,h+}}.$$

(C66)

Equations C63 and C64, respectively, show that $([\sigma_{j-}D_{j-}]_h)_w$ and $([D_{j-}]_h)_w$ are $c_{k,h-}$-weighted averages of all $\sigma_{k,j-}D_{k,j-}$ and $D_{k,j-}$, respectively. Equations C65 and C66, respectively, show that $([\sigma_{j+}D_{j+}]_h)_w$ and $([D_{j+}]_h)_w$ are $c_{k,h+}$-weighted averages of all $\sigma_{k,j+}D_{k,j+}$ and $D_{k,j+}$, respectively.

Using Equations C61 and C62, Equation C60 can now be written as

$$\sum_{h=1}^{N}\sum_{i=1}^{N} c_{h+}\left(\int_{\xi_m}^{\xi_b} P_h P_i\, d\xi - \sum_{j=1}^{N}\left\{\left(\left[D_{j+}\sigma_{j+}\right]_h\right)_w \int_{\xi_m}^{\xi_b} P_j P_h \frac{dP_i}{d\xi}\, d\xi - \left(\left[D_{j+}\right]_h\right)_w \int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi}\frac{dP_i}{d\xi}\, d\xi\right\}\Delta t\right)$$
$$= \sum_{h=1}^{N}\sum_{i=1}^{N} c_{h-}\left(\int_{\xi_m}^{\xi_b} P_h P_i\, d\xi + \sum_{j=1}^{N}\left\{\left(\left[D_{j-}\sigma_{j-}\right]_h\right)_w \int_{\xi_m}^{\xi_b} P_j P_h \frac{dP_i}{d\xi}\, d\xi - \left(\left[D_{j-}\right]_h\right)_w \int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi}\frac{dP_i}{d\xi}\, d\xi\right\}\Delta t\right).$$

(C67)

This equation corresponds to a solution of the continuity equation with respect to total concentration and total mass flow. (See Equation A26.) Defining $F_{h,i+}$ and $F_{h,i-}$ as $(F_{h,i+})_w$ and $(F_{h,i-})_w$, respectively, results in

$$\sum_{h=1}^{N}\sum_{i=1}^{N} c_{h+}\left(F_{h,i+}\right)_w = \sum_{h=1}^{N}\sum_{i=1}^{N}\left(\sum_{k=1}^{n} c_{k,h+}\right)\frac{\sum_{k=1}^{n} c_{k,h+}F_{k,h,i+}}{\sum_{k=1}^{n} c_{k,h+}} = \sum_{h=1}^{N}\sum_{i=1}^{N}\sum_{k=1}^{n} c_{k,h+}F_{k,h,i+}$$
$$= \sum_{h=1}^{N}\sum_{i=1}^{N} c_{h+}F_{h,i+}$$

(C68)

which is analogous to Equation C56, and

$$\sum_{h=1}^{N}\sum_{i=1}^{N} c_{h-}\left(F_{h,i-}\right)_w = \sum_{h=1}^{N}\sum_{i=1}^{N}\left(\sum_{k=1}^{n} c_{k,h-}\right)\frac{\sum_{k=1}^{n} c_{k,h-}F_{k,h,i-}}{\sum_{k=1}^{n} c_{k,h-}} = \sum_{h=1}^{N}\sum_{i=1}^{N}\sum_{k=1}^{n} c_{k,h-}F_{k,h,i-}$$
$$= \sum_{h=1}^{N}\sum_{i=1}^{N} c_{h-}F_{h,i-}\ ,$$

(C69)

which is analogous to Equation C57. Defining $\sigma_{j-}D_{j-}$, D_{j-}, $\sigma_{j+}D_{j+}$ and D_{j+}, respectively, as $([\sigma_{j-}D_{j-}]_h)_w$, $([D_{j-}]_h)_w$, $([\sigma_{j+}D_{j+}]_h)_w$ and $([D_{j+}]_h)_w$, respectively, Equation C67 can be written as

$$\sum_{h=1}^{N}\sum_{i=1}^{N} c_{h+}\left(\int_{\xi_m}^{\xi_b} P_h P_i d\xi - \sum_{j=1}^{N}\left\{D_{j+}\sigma_{j+}\int_{\xi_m}^{\xi_b} P_j P_h \frac{dP_i}{d\xi} d\xi - D_{j+}\int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi}\frac{dP_i}{d\xi} d\xi\right\}\Delta t\right)$$

$$= \sum_{h=1}^{N}\sum_{i=1}^{N} c_{h-}\left(\int_{\xi_m}^{\xi_b} P_h P_i d\xi\right.$$

$$\left. + \sum_{j=1}^{N}\left\{D_{j-}\sigma_{j-}\int_{\xi_m}^{\xi_b} P_j P_h \frac{dP_i}{d\xi} d\xi - D_{j-}\int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi}\frac{dP_i}{d\xi} d\xi\right\}\Delta t\right),$$

(C70)

where

$$D_w = \sum_{j=1}^{N} D_j P_j \,,$$

(C71)

$$(\sigma D)_w = \sum_{j=1}^{N} \sigma_j D_j P_j \,,$$

(C72)

D_j and $\sigma_j D_j$ at time t are denoted as D_{j-} and $\sigma_{j-}D_{j-}$, respectively, and D_j and $\sigma_j D_j$ at time [t + Δt] are denoted as D_{j+} and $\sigma_{j+}D_{j+}$, respectively. Rather than yielding D_G, as in Equation A29, Equation C71 expresses the weight-average diffusion coefficient, D_w, as the sum of N products, each of which consists of a ξ-dependent function, P_j, multiplied by a corresponding ξ-independent coefficient, D_j, which nevertheless remains a function of t. Each D_j at all ξ is equal to D_w at ξ_j. Similarly, Equation C72 expresses $(\sigma D)_w$ of Equation A30 as the sum of N products, each of which consists of a ξ-dependent function, P_j, multiplied by a corresponding ξ-independent coefficient, $\sigma_j D_j$, which nevertheless remains a function of t. Each $\sigma_j D_j$ at all ξ is equal to $(\sigma D)_w$ at ξ_j.

In Equation C70, D_{j-} and D_{j+} are weight-average parameters for the same reason that $([D_{k,j-}]_h)_w$ and $([D_{k,j+}]_h)_w$ are weight-average parameters in Equation C55. It should be expected that weight-average diffusion coefficients would be calculated from the solution of the continuity equation obtained by separation of variables and integration with respect to

ξ, and it should be expected that gradient-average diffusion coefficients would be calculated from the continuity equation itself.

In using the continuity equation, something akin to a frame-of-reference problem arises when determining whether D_k, which is the diffusion coefficient of solute component k, should be viewed as representing $(D_k)_G$, which is the gradient average of the diffusion coefficients of all the constituent species of component k (Equation C1), or whether D_k itself represents the defining measure of the diffusion coefficient of solute component k. As the implicit solvent and the explicit solutes are quantified component-by-component in an irreversible thermodynamic context, all species-specific parameters can be considered improper, which would mean that D_k represents a measure of the diffusion coefficient of solute component k that is properly dependent on component concentrations (including component k) only. At best, then, species-specific parameters such as $c_{k,e}$, $D_{k,e}$, $\sigma_{k,e}$, etcetera, are improper means to a proper end. The proper end being sought is a solution to the continuity equation in terms of components. As developed here, that proper solution to the continuity equation in terms of components can be derived from the improper solution to the continuity equation in terms of species, but only to the extent that improper species-specific parameters can be chosen so that $([\sigma_{k,j-}D_{k,j-}]_h)_w$, $([D_{k,j-}]_h)_w$, $([\sigma_{k,j+}D_{k,j+}]_h)_w$ and $([D_{k,j+}]_h)_w$ of Equation C55 equal $\sigma_{k,j-}D_{k,j-}$, $D_{k,j-}$, $\sigma_{k,j+}D_{k,j+}$ and $D_{k,j+}$, respectively, of Equation B21, in which case, Equations C55 and B21 are identical.

As there is nothing improper about component-specific parameters in an irreversible thermodynamic context, there should be no doubt that D_G, the gradient-average diffusion coefficient for all solute components, is the correct average of all D_k to use in the continuity equation expressed in terms of the total solute concentration, as is the case when Equation A31 is used to expand the total-solute-concentration form of Equation A26. Nevertheless, D_w would be the correct average to use in Equation C70 or any other form of the integral solution to the continuity equation expressed in terms of the total solute concentration. The fact that Equations C55 and C70 both yield analogous weight-average parameters is evidence in support of the hypothesis that Equation C55 is identical to Equation B21.

Expanded solution from Equation C32

The solution to the continuity equation for MCE can be written as

$$\begin{aligned}
&\sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}\sum_{i=1}^{N} c_{k,e,h+}\left(\int_{\xi_m}^{\xi_b} P_h P_i d\xi\right.\\
&\qquad \left. -\sum_{j=1}^{N} D_{k,e,j+}\left[\sigma_{k,e,j+}\int_{\xi_m}^{\xi_b} P_j P_h \frac{dP_i}{d\xi} d\xi - \int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi}\frac{dP_i}{d\xi} d\xi\right]\Delta t\right)\\
&\qquad = \sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}\sum_{i=1}^{N} c_{k,e,h-}\left(\int_{\xi_m}^{\xi_b} P_h P_i d\xi\right.\\
&\qquad \left. +\sum_{j=1}^{N} D_{k,e,j-}\left[\sigma_{k,e,j-}\int_{\xi_m}^{\xi_b} P_j P_h \frac{dP_i}{d\xi} d\xi - \int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi}\frac{dP_i}{d\xi} d\xi\right]\Delta t\right).
\end{aligned}$$

(See Equation C32.)

For species e of solute component k, at a specific value of index i (other than 1 or N), the nonzero terms are

$$\begin{aligned}
Z_{k,e,i-} = c_{k,e,[i-1]-}\Bigg(& \int_{\xi_m}^{\xi_b} P_{[i-1]} P_i d\xi \\
& + \sum_{j=1}^{N} D_{k,e,j-} \left[\sigma_{k,e,j-} \int_{\xi_m}^{\xi_b} P_j P_{[i-1]} \frac{dP_i}{d\xi} d\xi - \int_{\xi_m}^{\xi_b} P_j \frac{dP_{[i-1]}}{d\xi} \frac{dP_i}{d\xi} d\xi \right] \Delta t \Bigg) \\
& + c_{k,e,i-} \Bigg(\int_{\xi_m}^{\xi_b} P_i P_i d\xi \\
& + \sum_{j=1}^{N} D_{k,e,j-} \left[\sigma_{k,e,j-} \int_{\xi_m}^{\xi_b} P_j P_i \frac{dP_i}{d\xi} d\xi - \int_{\xi_m}^{\xi_b} P_j \frac{dP_i}{d\xi} \frac{dP_i}{d\xi} d\xi \right] \Delta t \Bigg) \\
& + c_{k,e,[i+1]-} \Bigg(\int_{\xi_m}^{\xi_b} P_{[i+1]} P_i d\xi \\
& + \sum_{j=1}^{N} D_{k,e,j-} \left[\sigma_{k,e,j-} \int_{\xi_m}^{\xi_b} P_j P_{[i+1]} \frac{dP_i}{d\xi} d\xi - \int_{\xi_m}^{\xi_b} P_j \frac{dP_{[i+1]}}{d\xi} \frac{dP_i}{d\xi} d\xi \right] \Delta t \Bigg) \\
& = c_{k,e,[i-1]+} \Bigg(\int_{\xi_m}^{\xi_b} P_{[i-1]} P_i d\xi \\
& + \sum_{j=1}^{N} D_{k,e,j+} \left[\sigma_{k,e,j+} \int_{\xi_m}^{\xi_b} P_j P_{[i-1]} \frac{dP_i}{d\xi} d\xi - \int_{\xi_m}^{\xi_b} P_j \frac{dP_{[i-1]}}{d\xi} \frac{dP_i}{d\xi} d\xi \right] \Delta t \Bigg) \\
& + c_{k,e,i+} \Bigg(\int_{\xi_m}^{\xi_b} P_i P_i d\xi \\
& + \sum_{j=1}^{N} D_{k,e,j+} \left[\sigma_{k,e,j+} \int_{\xi_m}^{\xi_b} P_j P_i \frac{dP_i}{d\xi} d\xi - \int_{\xi_m}^{\xi_b} P_j \frac{dP_i}{d\xi} \frac{dP_i}{d\xi} d\xi \right] \Delta t \Bigg) \\
& + c_{k,e,[i+1]+} \Bigg(\int_{\xi_m}^{\xi_b} P_{[i+1]} P_i d\xi \\
& + \sum_{j=1}^{N} D_{k,e,j+} \left[\sigma_{k,e,j+} \int_{\xi_m}^{\xi_b} P_j P_{[i+1]} \frac{dP_i}{d\xi} d\xi - \int_{\xi_m}^{\xi_b} P_j \frac{dP_{[i+1]}}{d\xi} \frac{dP_i}{d\xi} d\xi \right] \Delta t \Bigg),
\end{aligned}$$

(C73)

as shown in Equations C37 to C40. Expanded fully, for species e of solute component k, at a specific value of index i (other than 1 or N), the nonzero terms of $Z_{k,e,i-}$ are

$$
\begin{aligned}
Z_{k,e,i-} = c_{k,e,[i-1]-}\Bigg(&\int_{\xi_m}^{\xi_b} P_{[i-1]}P_i d\xi \\
&+ \Bigg\{D_{k,e,[i-1]-}\left[\sigma_{k,e,[i-1]-}\int_{\xi_m}^{\xi_b} P_{[i-1]}P_{[i-1]}\frac{dP_i}{d\xi}d\xi - \int_{\xi_m}^{\xi_b} P_{[i-1]}\frac{dP_{[i-1]}}{d\xi}\frac{dP_i}{d\xi}d\xi\right] \\
&+ D_{k,e,i-}\left[\sigma_{k,e,i-}\int_{\xi_m}^{\xi_b} P_iP_{[i-1]}\frac{dP_i}{d\xi}d\xi - \int_{\xi_m}^{\xi_b} P_i\frac{dP_{[i-1]}}{d\xi}\frac{dP_i}{d\xi}d\xi\right]\Bigg\}\Delta t\Bigg) \\
&+ c_{k,e,i-}\Bigg(\int_{\xi_m}^{\xi_b} P_iP_i d\xi \\
&+ \Bigg\{D_{k,e,[i-1]-}\left[\sigma_{k,e,[i-1]-}\int_{\xi_m}^{\xi_b} P_{[i-1]}P_i\frac{dP_i}{d\xi}d\xi - \int_{\xi_m}^{\xi_b} P_{[i-1]}\frac{dP_i}{d\xi}\frac{dP_i}{d\xi}d\xi\right] \\
&+ D_{k,e,i-}\left[\sigma_{k,e,i-}\int_{\xi_m}^{\xi_b} P_iP_i\frac{dP_i}{d\xi}d\xi - \int_{\xi_m}^{\xi_b} P_i\frac{dP_i}{d\xi}\frac{dP_i}{d\xi}d\xi\right] \\
&+ D_{k,e,[i+1]-}\left[\sigma_{k,e,[i+1]-}\int_{\xi_m}^{\xi_b} P_{[i+1]}P_i\frac{dP_i}{d\xi}d\xi - \int_{\xi_m}^{\xi_b} P_{[i+1]}\frac{dP_i}{d\xi}\frac{dP_i}{d\xi}d\xi\right]\Bigg\}\Delta t\Bigg) \\
&+ c_{k,e,[i+1]-}\Bigg(\int_{\xi_m}^{\xi_b} P_{[i+1]}P_i d\xi \\
&+ \Bigg\{D_{k,e,i-}\left[\sigma_{k,e,i-}\int_{\xi_m}^{\xi_b} P_iP_{[i+1]}\frac{dP_i}{d\xi}d\xi - \int_{\xi_m}^{\xi_b} P_i\frac{dP_{[i+1]}}{d\xi}\frac{dP_i}{d\xi}d\xi\right] \\
&+ D_{k,e,[i+1]-}\left[\sigma_{k,e,[i+1]-}\int_{\xi_m}^{\xi_b} P_{[i+1]}P_{[i+1]}\frac{dP_i}{d\xi}d\xi - \int_{\xi_m}^{\xi_b} P_{[i+1]}\frac{dP_{[i+1]}}{d\xi}\frac{dP_i}{d\xi}d\xi\right]\Bigg\}\Delta t\Bigg) \\
&=
\end{aligned}
$$

$$
\begin{aligned}
c_{k,e,[i-1]+} & \Bigg(\int_{\xi_m}^{\xi_b} P_{[i-1]} P_i \, d\xi \\
& + \Bigg\{ D_{k,e,[i-1]+} \Bigg[\sigma_{k,e,[i-1]+} \int_{\xi_m}^{\xi_b} P_{[i-1]} P_{[i-1]} \frac{dP_i}{d\xi} \, d\xi - \int_{\xi_m}^{\xi_b} P_{[i-1]} \frac{dP_{[i-1]}}{d\xi} \frac{dP_i}{d\xi} \, d\xi \Bigg] \\
& + D_{k,e,i+} \Bigg[\sigma_{k,e,i+} \int_{\xi_m}^{\xi_b} P_i P_{[i-1]} \frac{dP_i}{d\xi} \, d\xi - \int_{\xi_m}^{\xi_b} P_i \frac{dP_{[i-1]}}{d\xi} \frac{dP_i}{d\xi} \, d\xi \Bigg] \Bigg\} \Delta t \Bigg) \\
& + c_{k,e,i+} \Bigg(\int_{\xi_m}^{\xi_b} P_i P_i \, d\xi \\
& + \Bigg\{ D_{k,e,[i-1]+} \Bigg[\sigma_{k,e,[i-1]+} \int_{\xi_m}^{\xi_b} P_{[i-1]} P_i \frac{dP_i}{d\xi} \, d\xi - \int_{\xi_m}^{\xi_b} P_{[i-1]} \frac{dP_i}{d\xi} \frac{dP_i}{d\xi} \, d\xi \Bigg] \\
& + D_{k,e,i+} \Bigg[\sigma_{k,e,i+} \int_{\xi_m}^{\xi_b} P_i P_i \frac{dP_i}{d\xi} \, d\xi - \int_{\xi_m}^{\xi_b} P_i \frac{dP_i}{d\xi} \frac{dP_i}{d\xi} \, d\xi \Bigg] \\
& + D_{k,e,[i+1]+} \Bigg[\sigma_{k,e,[i+1]+} \int_{\xi_m}^{\xi_b} P_{[i+1]} P_i \frac{dP_i}{d\xi} \, d\xi - \int_{\xi_m}^{\xi_b} P_{[i+1]} \frac{dP_i}{d\xi} \frac{dP_i}{d\xi} \, d\xi \Bigg] \Bigg\} \Delta t \Bigg) \\
& + c_{k,e,[i+1]+} \Bigg(\int_{\xi_m}^{\xi_b} P_{[i+1]} P_i \, d\xi \\
& + \Bigg\{ D_{k,e,i+} \Bigg[\sigma_{k,e,i+} \int_{\xi_m}^{\xi_b} P_i P_{[i+1]} \frac{dP_i}{d\xi} \, d\xi - \int_{\xi_m}^{\xi_b} P_i \frac{dP_{[i+1]}}{d\xi} \frac{dP_i}{d\xi} \, d\xi \Bigg] \\
& + D_{k,e,[i+1]+} \Bigg[\sigma_{k,e,[i+1]+} \int_{\xi_m}^{\xi_b} P_{[i+1]} P_{[i+1]} \frac{dP_i}{d\xi} \, d\xi \\
& - \int_{\xi_m}^{\xi_b} P_{[i+1]} \frac{dP_{[i+1]}}{d\xi} \frac{dP_i}{d\xi} \, d\xi \Bigg] \Bigg\} \Delta t \Bigg),
\end{aligned}
$$

(C74)

Equation C74 shows that for a given i within $1 < i < N$, there are 17 integrals to evaluate.

Expanded fully, for species e of solute component k, at $i = 1$, the nonzero terms of $Z_{k,e,i-}$ are

$$
\begin{aligned}
Z_{k,e,1-} = c_{k,e,1-}\Bigg(\int_{\xi_m}^{\xi_b} P_1P_1\,d\xi \\
&+ \Bigg\{D_{k,e,1-}\left[\sigma_{k,e,1-}\int_{\xi_m}^{\xi_b} P_1P_1\frac{dP_1}{d\xi}\,d\xi - \int_{\xi_m}^{\xi_b} P_1\frac{dP_1}{d\xi}\frac{dP_1}{d\xi}\,d\xi\right] \\
&+ D_{k,e,2-}\left[\sigma_{k,e,2-}\int_{\xi_m}^{\xi_b} P_2P_1\frac{dP_1}{d\xi}\,d\xi - \int_{\xi_m}^{\xi_b} P_2\frac{dP_1}{d\xi}\frac{dP_1}{d\xi}\,d\xi\right]\Bigg\}\Delta t\Bigg) \\
&+ c_{k,e,2-}\Bigg(\int_{\xi_m}^{\xi_b} P_2P_1\,d\xi \\
&+ \Bigg\{D_{k,e,1-}\left[\sigma_{k,e,1-}\int_{\xi_m}^{\xi_b} P_1P_2\frac{dP_1}{d\xi}\,d\xi - \int_{\xi_m}^{\xi_b} P_1\frac{dP_2}{d\xi}\frac{dP_1}{d\xi}\,d\xi\right] \\
&+ D_{k,e,2-}\left[\sigma_{k,e,2-}\int_{\xi_m}^{\xi_b} P_2P_2\frac{dP_1}{d\xi}\,d\xi - \int_{\xi_m}^{\xi_b} P_2\frac{dP_2}{d\xi}\frac{dP_1}{d\xi}\,d\xi\right]\Bigg\}\Delta t\Bigg) \\
&= c_{k,e,1+}\Bigg(\int_{\xi_m}^{\xi_b} P_1P_1\,d\xi \\
&+ \Bigg\{D_{k,e,1+}\left[\sigma_{k,e,1+}\int_{\xi_m}^{\xi_b} P_1P_1\frac{dP_1}{d\xi}\,d\xi - \int_{\xi_m}^{\xi_b} P_1\frac{dP_1}{d\xi}\frac{dP_1}{d\xi}\,d\xi\right] \\
&+ D_{k,e,2+}\left[\sigma_{k,e,2+}\int_{\xi_m}^{\xi_b} P_2P_1\frac{dP_1}{d\xi}\,d\xi - \int_{\xi_m}^{\xi_b} P_2\frac{dP_1}{d\xi}\frac{dP_1}{d\xi}\,d\xi\right]\Bigg\}\Delta t\Bigg) \\
&+ c_{k,e,2+}\Bigg(\int_{\xi_m}^{\xi_b} P_2P_1\,d\xi \\
&+ \Bigg\{D_{k,e,1+}\left[\sigma_{k,e,1+}\int_{\xi_m}^{\xi_b} P_1P_2\frac{dP_1}{d\xi}\,d\xi - \int_{\xi_m}^{\xi_b} P_1\frac{dP_2}{d\xi}\frac{dP_1}{d\xi}\,d\xi\right] \\
&+ D_{k,e,2+}\left[\sigma_{k,e,2+}\int_{\xi_m}^{\xi_b} P_2P_2\frac{dP_1}{d\xi}\,d\xi - \int_{\xi_m}^{\xi_b} P_2\frac{dP_2}{d\xi}\frac{dP_1}{d\xi}\,d\xi\right]\Bigg\}\Delta t\Bigg).
\end{aligned}
$$

(C75)

Equation C75 shows that for i = 1, there are 10 integrals to evaluate.

Expanded fully, for species e of solute component k, at i = N, the nonzero terms of $Z_{k,e,i-}$ are

$$
\begin{aligned}
Z_{k,e,N-} = {} & c_{k,e,[N-1]-}\Bigg(\int_{\xi_m}^{\xi_b} P_{[N-1]}P_N d\xi \\
& + \Bigg\{D_{k,e,[N-1]-}\Bigg[\sigma_{k,e,[N-1]-}\int_{\xi_m}^{\xi_b} P_{[N-1]}P_{[N-1]}\frac{dP_N}{d\xi}d\xi \\
& - \int_{\xi_m}^{\xi_b} P_{[N-1]}\frac{dP_{[N-1]}}{d\xi}\frac{dP_N}{d\xi}d\xi\Bigg] \\
& + D_{k,e,N-}\Bigg[\sigma_{k,e,N-}\int_{\xi_m}^{\xi_b} P_N P_{[N-1]}\frac{dP_N}{d\xi}d\xi - \int_{\xi_m}^{\xi_b} P_N\frac{dP_{[N-1]}}{d\xi}\frac{dP_N}{d\xi}d\xi\Bigg]\Bigg\}\Delta t\Bigg) \\
& + c_{k,e,N-}\Bigg(\int_{\xi_m}^{\xi_b} P_N P_N d\xi \\
& + \Bigg\{D_{k,e,[N-1]-}\Bigg[\sigma_{k,e,[N-1]-}\int_{\xi_m}^{\xi_b} P_{[N-1]}P_N\frac{dP_N}{d\xi}d\xi - \int_{\xi_m}^{\xi_b} P_{[N-1]}\frac{dP_N}{d\xi}\frac{dP_N}{d\xi}d\xi\Bigg] \\
& + D_{k,e,N-}\Bigg[\sigma_{k,e,N-}\int_{\xi_m}^{\xi_b} P_N P_N\frac{dP_N}{d\xi}d\xi - \int_{\xi_m}^{\xi_b} P_N\frac{dP_N}{d\xi}\frac{dP_N}{d\xi}d\xi\Bigg]\Bigg\}\Delta t\Bigg) \\
& = c_{k,e,[N-1]+}\Bigg(\int_{\xi_m}^{\xi_b} P_{[N-1]}P_N d\xi \\
& + \Bigg\{D_{k,e,[N-1]+}\Bigg[\sigma_{k,e,[N-1]+}\int_{\xi_m}^{\xi_b} P_{[N-1]}P_{[N-1]}\frac{dP_N}{d\xi}d\xi \\
& - \int_{\xi_m}^{\xi_b} P_{[N-1]}\frac{dP_{[N-1]}}{d\xi}\frac{dP_N}{d\xi}d\xi\Bigg] \\
& + D_{k,e,N+}\Bigg[\sigma_{k,e,N+}\int_{\xi_m}^{\xi_b} P_N P_{[N-1]}\frac{dP_N}{d\xi}d\xi - \int_{\xi_m}^{\xi_b} P_N\frac{dP_{[N-1]}}{d\xi}\frac{dP_N}{d\xi}d\xi\Bigg]\Bigg\}\Delta t\Bigg) \\
& + c_{k,e,N+}\Bigg(\int_{\xi_m}^{\xi_b} P_N P_N d\xi \\
& + \Bigg\{D_{k,e,[N-1]+}\Bigg[\sigma_{k,e,[N-1]+}\int_{\xi_m}^{\xi_b} P_{[N-1]}P_N\frac{dP_N}{d\xi}d\xi - \int_{\xi_m}^{\xi_b} P_{[N-1]}\frac{dP_N}{d\xi}\frac{dP_N}{d\xi}d\xi\Bigg] \\
& + D_{k,e,N+}\Bigg[\sigma_{k,e,N+}\int_{\xi_m}^{\xi_b} P_N P_N\frac{dP_N}{d\xi}d\xi - \int_{\xi_m}^{\xi_b} P_N\frac{dP_N}{d\xi}\frac{dP_N}{d\xi}d\xi\Bigg]\Bigg\}\Delta t\Bigg).
\end{aligned}
$$

(C76)

Equation C76 shows that for i = N, there are 10 integrals to evaluate.

References

[C1] Johnson, M. L., Yphantis, D. A., and Weiss, G. H. (1973) Instability in Pressure Dependent Sedimentation of Monomer-Polymer Systems. *Biopolymers* 12 2477-2490.

[C2] de Groot, S. R., and Mazur, P. (1962) "Nonequilibrium Thermodynamics." North Holland Publishing Company, Amsterdam.

[C3] Katchalsky, A., and Curran, P. F. (1965) "Nonequilibrium Thermodynamics in Biophysics." Harvard University Press, Cambridge, MA.

Section D: Expressions for the deviation from van 't Hoff behaviour and other virial expansions

A minimally restrictive expression of the deviation from van 't Hoff behaviour can be written as

$$1+\sum_{b=2}^{\infty} b\left(\sum_{q=1}^{n} y_{b,k,q}{c_q}^{b-1}\right)=\sum_{b=1}^{\infty}\left(\sum_{q=1}^{n} y_{b,k,q}\frac{d{c_q}^{b}}{dc_q}\right),$$

(D1)

where b is the index of the virial expansion, c_q is the concentration of component q, $y_{b,k,q}$ is the component-k affecting thermodynamic nonideality coefficient of dc_q^b/dc_q, which makes $y_{b,k,q}$ the b^{th} of an infinite number of coefficients accounting for the thermodynamic nonideality effect of component q on the transport of component k, and

$$\lim_{c\to 0}\sum_{b=1}^{\infty}\left(\sum_{q=1}^{n} y_{b,k,q}\frac{d{c_q}^{b}}{dc_q}\right)=\sum_{q=1}^{n} y_{1,k,q}=1\,.$$

(D2)

A truncated, linear equation is restricted to solutions that are sufficiently dilute to permit use of an approximation, such as,

$$\lim_{dilute\ solution} \sum_{b=1}^{\infty} \left(\sum_{q=1}^{n} y_{b,k,q} \frac{d{c_q}^b}{dc_q} \right) \cong 1 + 2 \sum_{q=1}^{n} y_{2,k,q} c_q = 1 + \sum_{q=1}^{n} y_{k,q} c_q \ ,$$

(D3)

where

$$y_{k,q} = 2y_{2,k,q} \ .$$

(D4)

As with the van 't Hoff expression, electrophoretic/asymmetry and viscosity expressions can be expanded as infinite series, so that σ$_k$ (the reduced valence coefficient of component k) and D$_k$ (the diffusion coefficient of component k) can be described, respectively, by

$$\sigma_k = {\sigma^\circ}_k \left(\frac{\sum_{b=1}^{\infty} \left[\sum_{q=1}^{n} p_{b,k,q} \frac{d{c_q}^b}{dc_q} \right]}{\sum_{b=1}^{\infty} \left[\sum_{q=1}^{n} y_{b,k,q} \frac{d{c_q}^b}{dc_q} \right]} \right)$$

(D5)

and

$$D_k = {D^\circ}_k \left(\frac{\sum_{b=1}^{\infty} \left[\sum_{q=1}^{n} y_{b,k,q} \frac{d{c_q}^b}{dc_q} \right]}{\sum_{b=1}^{\infty} \left[\sum_{q=1}^{n} h_{b,k,q} \frac{d{c_q}^b}{dc_q} \right]} \right),$$

(D6)

where $y_{b,k,q}$ is the component-k affecting thermodynamic nonideality coefficient of dc_q^b/dc_q defined as for Equation D1; $h_{b,k,q}$ is the component-k affecting viscosity coefficient of dc_q^b/dc_q, which makes $h_{b,k,q}$ the bth of an infinite number of coefficients accounting for the viscosity effect of component q on the transport of component k; and $p_{b,k,q}$ is the component-k affecting electrophoretic/asymmetry coefficient of dc_q^b/dc_q, which makes $p_{b,k,q}$ the bth of an infinite number of coefficients accounting for the electrophoretic/asymmetry effect of component q on the transport of component k.

From the above equations, it follows that

$$Eu_k = \sigma^\circ{}_k D^\circ{}_k \left(\frac{\sum_{b=1}^{\infty} \left[\sum_{q=1}^{n} p_{b,k,q} \frac{d{c_q}^b}{dc_q} \right]}{\sum_{b=1}^{\infty} \left[\sum_{q=1}^{n} h_{b,k,q} \frac{d{c_q}^b}{dc_q} \right]} \right),$$

(D7)

where

$$\lim_{c \to 0} \sum_{b=1}^{\infty} \left(\sum_{q=1}^{n} p_{b,k,q} \frac{d{c_q}^b}{dc_q} \right) = \sum_{q=1}^{n} p_{1,k,q} = 1$$

(D8)

and

$$\lim_{c \to 0} \sum_{b=1}^{\infty} \left(\sum_{q=1}^{n} h_{b,k,q} \frac{d{c_q}^b}{dc_q} \right) = \sum_{q=1}^{n} h_{1,k,q} = 1 .$$

(D9)

Truncated, linear equations are restricted to solutions that are sufficiently dilute to permit use of approximations, such as,

$$\lim_{dilute\ solution} \sum_{b=1}^{\infty} \left(\sum_{q=1}^{n} p_{b,k,q} \frac{d{c_q}^b}{dc_q} \right) \cong 1 + 2 \sum_{q=1}^{n} p_{2,k,q} c_q = 1 + \sum_{q=1}^{n} p_{k,q} c_q \ ,$$

(D10)

where

$$p_{k,q} = 2p_{2,k,q} \ ,$$

(D11)

and

$$\lim_{dilute\ solution} \sum_{b=1}^{\infty} \left(\sum_{q=1}^{n} h_{b,k,q} \frac{d{c_q}^b}{dc_q} \right) \cong 1 + 2 \sum_{q=1}^{n} h_{2,k,q} c_q = 1 + \sum_{q=1}^{n} h_{k,q} c_q \ ,$$

(D12)

where

$$h_{k,q} = 2h_{2,k,q} \ .$$

(D13)

Equations D3, D10 and D12 are virial expressions that are truncated at b = 2. Equations D4, D11 and D13 are the second virial coefficients that apply to Equations D3, D10 and D12, respectively.

In some cases [Johnson et al., 1981], the deviation from van 't Hoff behaviour can be described by a virial expansion in terms of c, M_w, and an infinite series of global nonideality coefficients, each denoted by B_b, where b is the index of the summation. That virial expansion can be written as

$$1 + \sum_{q=1}^{m} y_{k,q} c_q = 1 + M_w \sum_{b=2}^{\infty} bB_b c^{b-1} = M_w \sum_{b=1}^{\infty} B_b \frac{dc^b}{dc} \ ,$$

(D14)

where

$$\lim_{c \to 0} M_w \sum_{b=1}^{\infty} B_b \frac{dc^b}{dc} = M_w B_1 = 1\,.$$

(D15)

References

[D1] Johnson, M. L., Correia, J. J., Yphantis, D. A., and Halvorson, H. R. (1981) Analysis of data from the analytical ultracentrifuge by nonlinear least squares techniques. *Biophys. J.* **36** 575-588.

Section E: Presenting concentration data from calculations as optical density data

To present results that are comparable to the optical density data observed experimentally, at each time t, at each point ξ, the concentration, $c_{k,e}$ (in g/ml) of each species, e, of each solute component, k, is multiplied by L and $k_{\lambda,k,e}$, where L is the optical pathlength (in cm), and $k_{\lambda,k,e}$ is an estimate of the specific optical density for species e of solute component k at wavelength λ. For species e of solute component k at a concentration of $c_{k,e}$ in an MCE experiment using an optical pathlength of L and a wavelength of λ, the specific optical density (in [optical density]cm^2/g) is

$$k_{\lambda,k,e} = \left(\epsilon_{\lambda,k,e,\mu}\right)OD = \frac{OD_{\lambda,k,e}}{Lc_{k,e}}\,.$$

(E1)

where $\epsilon_{\lambda,k,e,\mu}$ is the apparent mass extinction coefficient (in cm^2/g) at wavelength λ for a solution of species e of solute component k at dialysis equilibrium with the solvent, and $OD_{\lambda,k,e}$ is the observed optical density for species e of solute component k at wavelength λ. As $OD_{\lambda,k,e} = Lk_{\lambda,k,e}c_{k,e}$, the total optical density, which is equal to the sum of all $OD_{\lambda,k,e}$, is dependent on the concentration of each species of each solute component.

For the fringe-displacement analogue to the preceding description of experimentally observable signal as a function of solute concentrations, see Gray et al. [1995].

References

[E1] Gray, R. A., Stern, A., Bewley, T., and Shire, S. J. (1995) Rapid Determination of Spectrophotometric Absorptivity by Analytical Ultracentrifugation. Fullerton, CA: Beckman Instruments.

Section F: ξ-dependent functions to approximate $D_{k,e}$ and $\sigma_{k,e}$

Tests of different solutions

The integrals in the solution to the t- and ξ-dependent continuity equation for MCE (Equation B21) have been replaced with their evaluations shown in Equations B39 to B53 or Equations B39* to B53*, and those expanded forms of the solution to the continuity equation for MCE have been used in finite-element simulations. Simulations of MCE based on the second approximate solution (using Equations B39 to B53) have been found to perform at least as well as simulations based on the first approximate solution (using Equations B39* to B53*).

First approximate solution

To express $\sigma_{k,e}$ and $D_{k,e}$ in terms of pseudo-ξ-independent parameters, each one is approximated as a set of N scalar coefficients that can be a function of t but must be invariant with ξ. For $\sigma_{k,e}$, at all ξ_h, where $1 \leq h \leq N$, those coefficients are

$$\sigma_{k,e,h} = \sigma_{k,e} \; at \; \xi_h,$$

(F1)

and for $D_{k,e}$, at all ξ_h, where $1 \leq h \leq N$, those coefficients are

$$D_{k,e,h} = D_{k,e} \; at \; \xi_h.$$

(F2)

(Compare Equations F1 and F2 with Equations C22 and C23, which describe the functions that express $D_{k,e}$ and $\sigma_{k,e}$ in terms of sums of products of ξ-independent coefficients ($D_{k,e,j}$ and $\sigma_{k,e,j}$, respectively) and ξ-dependent basis functions (P_j). It is the ξ-independence of the coefficients that permits their being factored out of the summations indexed by j in Equations C25 to C35.)

When it temporarily becomes more convenient to work with $Eu_{k,e}$ and $D_{k,e}$ instead of $\sigma_{k,e}$ and $D_{k,e}$, $Eu_{k,e}$ is also approximated as a set of N scalar coefficients that can be a function of t but must be invariant with ξ. At all ξ_h, where $1 \le h \le N$, those coefficients are

$$Eu_{k,e,h} = Eu_{k,e} \; at \; \xi_h.$$

(F3)

(Compare Equation F3 with Equation C21.)

Equations F1 to F3 define $\sigma_{k,e,h}$, $D_{k,e,h}$ and $Eu_{k,e,h}$ as constants with respect to ξ, and in the first approximate solution, are used in place of Equations C21 to C23. The resulting first approximate solution to the continuity equation for MCE can be written as

$$\sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}\sum_{i=1}^{N} c_{k,e,h+}\left(\int_{\xi_m}^{\xi_b} P_h P_i d\xi - D_{k,e,h+}\left[\sigma_{k,e,h+}\int_{\xi_m}^{\xi_b} P_h \frac{dP_i}{d\xi} d\xi - \int_{\xi_m}^{\xi_b} \frac{dP_h}{d\xi}\frac{dP_i}{d\xi} d\xi\right]\Delta t\right)$$
$$= \sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}\sum_{i=1}^{N} c_{k,e,h-}\left(\int_{\xi_m}^{\xi_b} P_h P_i d\xi\right.$$
$$\left. + D_{k,e,h-}\left[\sigma_{k,e,h-}\int_{\xi_m}^{\xi_b} P_h \frac{dP_i}{d\xi} d\xi - \int_{\xi_m}^{\xi_b} \frac{dP_h}{d\xi}\frac{dP_i}{d\xi} d\xi\right]\Delta t\right).$$

(F4)

As usual, a minus or plus subscript refers to time t or [t + Δt], respectively. Equation F4 of the first approximate solution is obtained by applying Equations F1 and F2 to Equation C32 of the second approximate solution in the case of $(\partial\sigma_{k,e}/\partial\xi)_t = 0$ and $(\partial D_{k,e}/\partial\xi)_t = 0$ at all ξ. Thus, when $\sigma_{k,e,h}$ and $D_{k,e,h}$ are used as they are in Equation F4, each $\sigma_{k,e,h}$ should equal ξ-independent $\sigma_{k,e}$, each $D_{k,e,h}$ should equal ξ-independent $D_{k,e}$ and, given that $(\partial Eu_{k,e}/\partial\xi)_t = 0$ when $(\partial\sigma_{k,e}/\partial\xi)_t = 0$ and $(\partial D_{k,e}/\partial\xi)_t = 0$, each $Eu_{k,e,h}$ should equal ξ-independent $Eu_{k,e}$.

Furthermore, these conditions make it highly likely that $(\partial D_{k,e}/\partial t)_\xi = 0$ in general, and that $(\partial Eu_{k,e}/\partial t)_\xi = 0$ and $(\partial \sigma_{k,e}/\partial t)_\xi = 0$ at constant field. Therefore, $D_{k,e,h}$ is likely to be t-independent in general, and $Eu_{k,e,h}$ and $\sigma_{k,e,h}$ are likely to be t-independent at constant field. All such constraints are purposefully violated in the following treatment of the first approximate solution.

As typically, but incorrectly, applied, the constants, $\sigma_{k,e,h}$, $D_{k,e,h}$ and $Eu_{k,e,h}$, of the first approximate solution are treated as if they were functions of solute concentration. Thus, $\sigma_{k,e,h}$, $D_{k,e,h}$ and $Eu_{k,e,h}$ become pseudoconstants with respect to ξ. Truncated virial expansions are used to approximate the dependence of $\sigma_{k,e,h}$ and $D_{k,e,h}$ on the concentration, $c_{q,a}$, of each explicitly included species, a, of each explicitly included solute component, q. To evaluate these pseudo-ξ-independent constants indexed by h, prior to each time increment, $D_{k,e,h}$ and $\sigma_{k,e,h}$ are approximated by

$$D_{k,e,h} = D^\circ{}_{k,e}\left(\frac{\sum_{b=1}^{\infty}\sum_{q=1}^{n}\sum_{a=1}^{n_q} y_{b,k,e,q,a}\,\frac{dc_{q,a,h}{}^{b}}{dc_{q,a,h}}}{\sum_{b=1}^{\infty}\sum_{q=1}^{n}\sum_{a=1}^{n_q} h_{b,k,e,q,a}\,\frac{dc_{q,a,h}{}^{b}}{dc_{q,a,h}}}\right)$$

(F5)

and

$$\sigma_{k,e,h} = \sigma^\circ{}_{k,e}\left(\frac{\sum_{b=1}^{\infty}\sum_{q=1}^{n}\sum_{a=1}^{n_q} p_{b,k,e,q,a}\,\frac{dc_{q,a,h}{}^{b}}{dc_{q,a,h}}}{\sum_{b=1}^{\infty}\sum_{q=1}^{n}\sum_{a=1}^{n_q} y_{b,k,e,q,a}\,\frac{dc_{q,a,h}{}^{b}}{dc_{q,a,h}}}\right),$$

(F6)

respectively, where n is the number of solute components, n_q is the number of species that constitute solute component q, $D^\circ{}_{k,e}$ at all ξ equals $D_{k,e}$ at ξ_h at time t or [t + Δt] in the limit as c approaches 0, $\sigma^\circ{}_{k,e}$ at all ξ equals $\sigma_{k,e}$ at ξ_h at time t or [t + Δt] in the limit as c approaches 0, $c_{q,a,h}$ is the ξ-independent concentration coefficient of species a of solute component q at time t or [t + Δt] ($c_{q,a,h}$, at all ξ, equals $c_{q,a}$ at ξ_h, just as $c_{k,e,h}$, at all ξ, equals $c_{k,e}$ at ξ_h in Equation C17), and where $p_{b,k,e,q,a}$, $y_{b,k,e,q,a}$ and $h_{b,k,e,q,a}$ are the bth of up to an infinite number of coefficients of proportionality for the electrophoretic/asymmetry, thermodynamic nonideality, and viscosity effects, respectively. By definition, $\sum_{q=1}^{n}\sum_{a=1}^{n_q} p_{1,k,e,q,a}$, $\sum_{q=1}^{n}\sum_{a=1}^{n_q} y_{1,k,e,q,a}$ and $\sum_{q=1}^{n}\sum_{a=1}^{n_q} h_{1,k,e,q,a}$ are each equal to 1. (Each of the $p_{b,k,e,q,a}$, $y_{b,k,e,q,a}$ and $h_{b,k,e,q,a}$ coefficients couples the concentration of species a of component q to an effect on the transport of species e of component k. See Section D for the component-based equivalents of these virial expansions.)

Both $\sigma°_{k,e}$ and $D°_{k,e}$ are ξ-independent by definition. Furthermore, the first approximate solution cannot be applied to systems in which changes in solvent density cause $(\partial\rho_0/\partial\xi)_t$ to differ from zero. (Strictly speaking, the first approximate solution cannot even be applied to systems in which solute concentration gradients cause $(\partial\rho/\partial\xi)_t$ to differ from zero.) As discussed in the definitions of $D°_{k,e,j}$, (Equation C33) and $\sigma°_{k,e,j}$ (Equation C34), the condition that $\Delta D°_{k,e,j}/\Delta j = 0$ and $\Delta\sigma°_{k,e,j}/\Delta j = 0$ for all species of all solute components can only apply to a system with an incompressible solvent, in which case, $D°_{k,e,j}$ and $\sigma°_{k,e,j}$ can be replaced with $D°_{k,e}$, and $\sigma°_{k,e}$, respectively. Hence, the use of $D°_{k,e}$ and $\sigma°_{k,e}$ in the first approximate solution.

As noted, when $\sigma_{k,e,h}$ and $D_{k,e,h}$ are used as they are in Equation F4, each $\sigma_{k,e,h}$ should equal ξ-independent $\sigma_{k,e}$, and each $D_{k,e,h}$ should equal ξ-independent $D_{k,e}$. Thus, the use of Equations F5 and F6 is incorrect, except where all coefficients of $b(c_{q,a})^{b-1}$ for $b > 1$, which is to say all $p_{b,k,e,q,a}$, $y_{b,k,e,q,a}$ and $h_{b,k,e,q,a}$ for $b > 1$, equal zero, and where, as previously noted, the solvent is incompressible and $(\partial\rho/\partial\xi)_t = 0$ at all ξ and t. (Compare the properties and uses of Equations F5 and F6, with those of Equations C33 and C34, respectively.)

Results of the first approximate solution compared with those of the second approximate solution

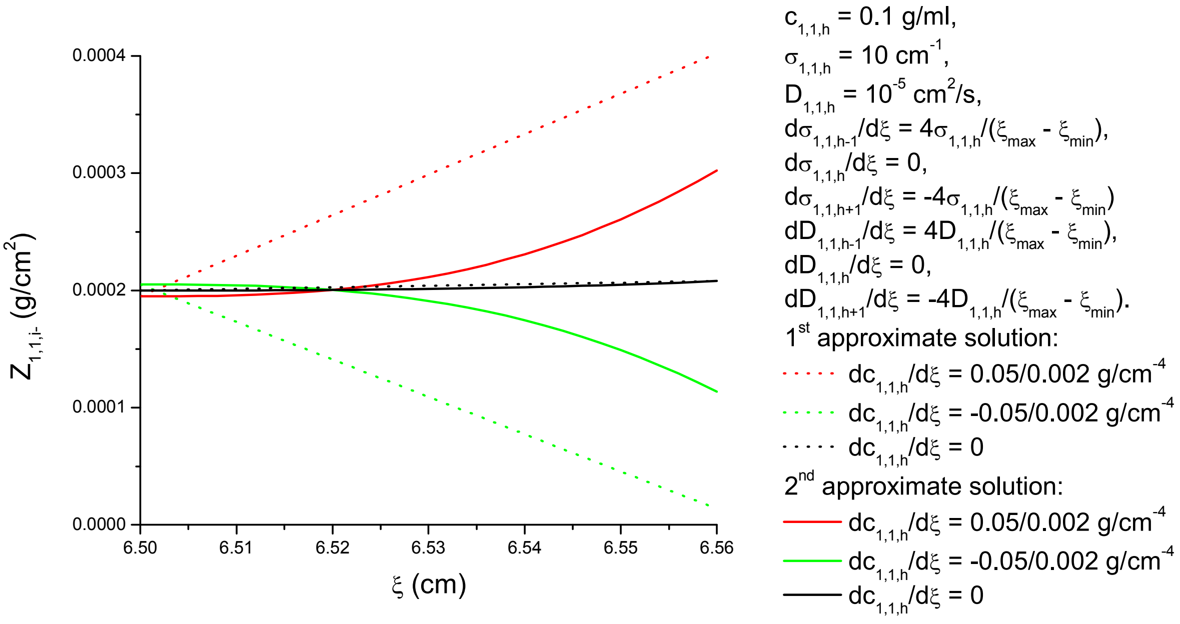

Figure F1. Results, as $Z_{k,e,i-} = Z_{1,1,i-}$ versus ξ, from the first approximate and second approximate solutions, compared after a 1 s time increment for 87 three-element, single solute component ($k = 1$), single solute species ($e= 1$) systems. (Each system consists of 3 adjacent spatial elements, [h - 1], h and [h + 1], where $1 < h < 31$, $\xi_{min} = \xi_1 = 6.500$ cm, $\xi_{max} = \xi_{31} = 6.560$ cm, $\Delta\xi_{h-} = \Delta\xi_{h+} = \Delta\xi = 0.002$ cm, and each system is characterised by one of three concentration gradients, $dc_{1,1,h}/d\xi$, in which $(c_{1,1,[h-1]} + c_{1,1,h} + c_{1,1,[h+1]})/3 = 0.1$ g/ml.) The central values of, and gradients in $c_{1,1,h}$, $\sigma_{1,1,h}$ and $D_{1,1,h}$ are given to the right of the graph. At the scale shown, $Z_{1,1,i-}$ from the first approximate and second approximate solutions for the case of $dc_{1,1,h}/d\xi = 0$ are nearly indistinguishable. (See Section C in general, and Equations C39 and C74 in particular, for details regarding $Z_{k,e,i-}$.)

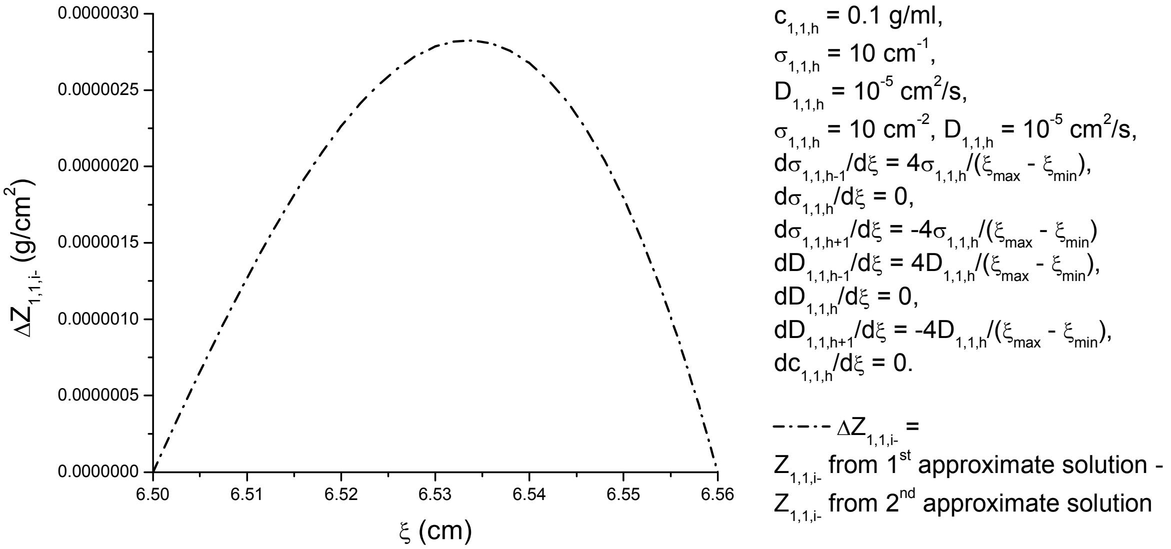

Figure F2. Results, as $\Delta Z_{k,e,i-} = \Delta Z_{1,1,i-}$ versus ξ, from $Z_{1,1,i-}$ of the first approximate solution minus $Z_{1,1,i-}$ of the second approximate solution after a 1 s time increment for the 29 $dc_{1,1,h}/d\xi = 0$ systems shown in Figure F1. The central values of, and gradients in $c_{1,1,h}$, $\sigma_{1,1,h}$ and $D_{1,1,h}$ are given to the right of the graph. This figure shows that $Z_{1,1,i-}$ from the first approximate and second approximate solutions differ, even for the case of $dc_{1,1,h}/d\xi = 0$.

References

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Section G: The dissipation function and the Curie-Prigogine principle

The formalism of irreversible thermodynamics applies when flows can be expressed as linear functions of the forces present [de Groot and Mazur, 1962; Tanford, 1961]. The forces that give rise to flows in the MCE instrument are assumed to be small enough that this formalism is applicable. Given this assumption, and denoting the solvent as component 0, the equation for $\overrightarrow{J_k^S}$, the molar flow of component k in the solvent frame of reference, can be written as

$$\overrightarrow{J_k^S} = \sum_{q=1}^{n} L_{k,q}\vec{X}_q = \vec{J}_k - \frac{c_k}{M_k}\frac{M_0}{c_0}\vec{J}_0 = \vec{J}_k - \frac{c_k}{M_k}\vec{v}_0 \ ,$$

(G1)

where $L_{k,q}$ is the phenomenological coefficient linking the transport of component k to $\vec{X}_q$ [Tanford, 1961], and $\vec{X}_q$ is the conjugate molar force (Equations A2, A14 and I16) of $\vec{J}_q$, which is the molar flow of component q in the system frame of reference [Katchalsky and Curran, 1965]. (See the dissipation function, Equation G2, which shows how a conjugate force is assigned to each flow through the system [Katchalsky and Curran, 1965]. Also see Equations I6 to I14 for further discussion of $\vec{J}_q$.) The sum over all q is taken over all linearly independent forces [Katchalsky and Curran, 1965]. Each conjugate molar force is a vector, $\vec{X}_q = -\nabla U_q$, where U_q is the total molar potential of solute component q. In the MCE instrument, however, $\vec{X}_q$ has no component along the x- or y-axis of the system, so that $X_q = (X_q)_z$, which is the z-component of $\vec{X}_q$, can be used in place of the vector. In total, there are n + 1 conjugate molar forces, but X_0, that of the solvent, has been expressed in terms of the others in Equation G1. The bulk fluid velocity in the system frame of reference is described by v_0, the nonvector representation of $\vec{v}_o$, which is the velocity of the solvent flow through the system in the frame of reference of the system. In the absence of any forces other than that associated with solvent flow, $X_{q\neq 0} = 0$, and the system-frame-of-reference velocity of solute component q, v_q, equals v_0, from which it follows, in such cases, that $J_k = (c_k/M_k)v_0$.

The phenomenological coefficients are functions of system properties, such as temperature, pressure, and the concentrations of solute components, but are independent of the magnitudes of any forces present, provided that those forces are sufficiently small [Tanford, 1961]. The phenomenological coefficients pertaining to coupled flows are the $L_{k,q}$ terms for which $q \neq k$. By a statistical mechanical treatment of microscopically reversible processes, Onsager showed that these cross terms are symmetric in the absence of magnetic fields or

Coriolis forces in the system, in which case, the reciprocal relations are $L_{k,q} = L_{q,k}$ for all k and q [Onsager, 1931a; Onsager, 1931b; de Groot and Mazur, 1962]. Denoting any magnetic fields or Coriolis forces by $\vec{G}$, the most general expression of the reciprocal relations is $L_{k,q}(\vec{G}) = \epsilon_q\epsilon_k L_{q,k}(-\vec{G})$, where $L_{k,q}(\vec{G})$ is $L_{k,q}$ in the presence of $\vec{G}$, $L_{q,k}(-\vec{G})$ is $L_{q,k}$ in the presence of $-\vec{G}$, ϵ_q is the indicator of time parity for $\vec{X}_q$ and ϵ_k is the indicator of time parity for $\vec{X}_k$ [Jou, Casas-Vázquez and Lebon, 2010; Jou, Casas-Vázquez and Criado-Sancho, 2011]. If a conjugate molar force, such as $\vec{X}_q$ or $\vec{X}_k$, is even under time reversal, its indicator of time parity, ϵ_q or ϵ_k, respectively, is equal to 1. If a conjugate molar force is odd under time reversal, its indicator of time parity is equal to -1.

In the MCE instrument, under the usual operating conditions, $\vec{G}$ may well be negligible, but as neither $L_{k,q}$ nor $L_{q,k}$ is likely to be known or experimentally determinable, data analysis and simulations generally take place at the next highest level of abstraction, for which D_k (Equation A21) and either u_k (Equation A22) or σ_k (Equation A23) are the accessible parameters. As such, details regarding the applicable forms of $L_{k,q}(\vec{G}) = \epsilon_q\epsilon_k L_{q,k}(-\vec{G})$ are not explored here, except in the latter part of Section N (**A simple coupled-flow equation for MCE**). Nevertheless, a large body of experimental evidence suggests that the applicability of the reciprocal relations is broader than might be expected, given that their theoretical basis deals only with processes that are close to equilibrium [Katchalsky and Curran, 1965].

The dissipation function,

$$\Phi = \sum_{k=0}^{n} \vec{J}_k \cdot \vec{X}_k + \sum_{g=1}^{n_R} J_g^R A_g = \vec{J}_0 \cdot \vec{X}_0 + \sum_{k=1}^{n} \vec{J}_k \cdot \vec{X}_k + \sum_{g=1}^{n_R} J_g^R A_g = \sum_{k=1}^{n} \overrightarrow{J_k^S} \cdot \vec{X}_k + \sum_{g=1}^{n_R} J_g^R A_g,$$

(G2)

measures the local rate of free energy dissipation per unit volume [Katchalsky and Curran, 1965]. This equation is used to determine the proper flows and forces to include in Equation G1. In the MCE instrument, all significant flows are either those of transport (the molar flows and mass flows discussed throughout this work) or those of chemical reactions.

The summation indexed by k gives the contribution of independent particle flows to Φ. The summation indexed by g gives the contribution of independent chemical reaction flows to Φ. Each term in the summation indexed by g is the product of the molar reaction flow, J_g^R, of reaction g, times the conjugate molar affinity, A_g, of reaction g.

The total number of all possible flows is $1 + n + n_R$, where $1 + n$ is the number of possible molar flows, and $n_R = n$ is the number of possible independent chemical reaction flows [de Groot and Mazur, 1962]. The total number of all possible forces is also $1 + n + n_R$. As J_g^R and A_g are scalars, their tensorial order is 0. As $\vec{J}_k$ and $\vec{X}_k$ are vectors, their tensorial order is 1. Given that reaction flows are not expected to produce molar flows when the system is isotropic, it is assumed that the Curie-Prigogine principle [de Groot and Mazur, 1962; Katchalsky and Curran, 1965] applies in the MCE system. Accordingly, there is assumed to be no coupling between flows and forces of different tensorial order, with the result that no phenomenological coefficients link the molar affinities of any chemical reactions to the conjugate molar forces in Equation G1.

Without the n_R molar affinities to contend with in Equation G1, there remain $n + 1$ conjugate molar forces, one of which may be expressed in terms of the others, so that only n linearly independent forces appear in Equation G1. The Gibbs-Duhem relation is used to express $\vec{X}_0$ in terms of the other conjugate molar forces, each of which is associated with one solute component.

Conjugate molar forces

The rectangular coordinate system, where z is the vertical coordinate, and the planar coordinates are x and y, is well suited to describing the geometry of an MCE system. It is assumed that an MCE system develops gradients in the electrical potential and chemical potentials mainly, and these potentials are expected to be invariant with respect to x and y in most systems. In general, where gravitational potential gradients are negligible, $\vec{X}_q = -Fz_q\nabla\Psi - \nabla\mu_q$, where, as discussed with respect to Equation A2, μ_q is the chemical potential of solute component q, z_q is the valence of solute component q, F is the cgs Faraday, and Ψ is the cgs electrical potential. In cases where $\nabla\Psi$ and $\nabla\mu_q$ vary with respect to z only, $(\partial\mu_q/\partial z)_{t,x,y} = (\partial\mu_q/\partial z)_t$ and $(\partial\Psi/\partial z)_{t,y,x} = (\partial\Psi/\partial z)_t$, as a result of which, $\vec{X}_q$ can be described by $X_q = - Fz_q(\partial\Psi/\partial z)_t - (\partial\mu_q/\partial z)_t$.

In cases where the molar gravitational potential gradient, $-M_q\nabla g_E h$, is significant, a resort to $\vec{X}_q = -M_q\nabla g_E h - Fz_q\nabla\Psi - \nabla\mu_q$ may be necessary, but as $\nabla g_E h$ is directed vertically in a properly levelled MCE instrument, $\vec{X}_q$ will still be expected to vary with respect to z only. (As discussed with respect to Equation A2, M_q is the molar mass of solute component q, g_E is the magnitude of the gravitational field at the Earth's surface, and h is the height above the Earth's surface.) As z and h are oppositely directed, where the dimensionality of z and h is the same, dz/dh = -1. Thus, $(\partial g_E h/\partial z)_{t,x,y} = -(\partial g_E z/\partial z)_t = -g_E$, so that $\vec{X}_q$ can be described by $X_q = M_q g_E - Fz_q(\partial\Psi/\partial z)_t - (\partial\mu_q/\partial z)_t$. For definitions of μ_q, z_q and M_q, see Section I (**Calculating molar mass, chemical potential and partial specific volume for a multi-species component**).

Chemical reactions

The contribution of the chemical molar flows to the dissipation function (Equation G2) is

$$\Phi_R = \sum_{g=1}^{n_R} J_g^R A_g ,$$

(G3)

where $n_R = n$ is the number of possible independent chemical reaction flows [de Groot and Mazur, 1962], which are indexed by g. Each term in the summation is the product of the molar reaction flow, J_g^R, of reaction g, times the conjugate molar affinity, A_g, of reaction g.

Following Equation G20, the molar reaction flow and molar affinity are discussed further, utilising some of the results that are obtained between here and there. What follows immediately is the development of the equations that, in Section K (**Reaction flow**

algorithms), are applied to the practical problem of calculating the concentrations of solutes that participate in a chemical reaction. The examples of the various types of reactions presented in Section K painstakingly illustrate, and may thus help clarify, some of the considerably tedious material that is covered next.

A chemical reaction involving components $1 \leq k \leq n$ can be cast in terms of $S_{k,e}$, where $S_{k,e}$ represents the formula notation of species e of component k. The sum over all of the independent chemical reactions that are possible yields

$$\sum_{g=1}^{n_R} \sum_{k=1}^{n} \sum_{e=1}^{n_k} |\nu_{R,g,k,e}| \mathrm{S}_{k,e} \rightleftharpoons \sum_{g=1}^{n_R} \sum_{k=1}^{n} \sum_{e=1}^{n_k} |\nu_{P,g,k,e}| \mathrm{S}_{k,e} \, ,$$

(G4)

where $\nu_{R,g,k,e}$ is the signed stoichiometry of reactant species e of component k in reaction g, and $\nu_{P,g,k,e}$ is the signed stoichiometry of product species e of component k in reaction g. A convention is employed where, by definition, $\nu_{R,g,k,e} \leq 0$ and $\nu_{P,g,k,e} \geq 0$. Furthermore, by definition, $\nu_{R,g,k,e} = 0$ if species e of component k is not a reactant in reaction g, and $\nu_{P,g,k,e} = 0$ if species e of component k is not a product in reaction g.

Throughout the equations and examples that follow, the activity of species e of solute component k will be given by $\gamma_{k,e}c_{k,e}$, where $\gamma_{k,e}$ is the activity coefficient of that species, the concentration of which is $c_{k,e}$, as usual. Furthermore, if species e of solute component k is a product or reactant of a chemical reaction, $\tilde{\gamma}_{k,e}$ and $\tilde{c}_{k,e}$ will denote the activity coefficient and the concentration, respectively, that the species would exhibit if the chemical reaction were at equilibrium.

The association constant of independent chemical reaction g is given by

$$K_{A,g} = \frac{k_{f,g}}{k_{r,g}} = \frac{\prod_{k=1}^{n} \prod_{e=1}^{n_k} \left(\tilde{\gamma}_{k,e}\tilde{c}_{k,e}\right)^{|\nu_{P,g,k,e}|}}{\prod_{k=1}^{n} \prod_{e=1}^{n_k} \left(\tilde{\gamma}_{k,e}\tilde{c}_{k,e}\right)^{|\nu_{R,g,k,e}|}} = \prod_{k=1}^{n} \prod_{e=1}^{n_k} \left(\tilde{\gamma}_{k,e}\tilde{c}_{k,e}\right)^{(\nu_{P,g,k,e}+\nu_{R,g,k,e})} \, ,$$

(G5)

where, for independent chemical reaction g, $k_{f,g}$ is the forward rate constant and $k_{r,g}$ is the reverse rate constant. Letting ϒ represent the unit solute concentration (with dimensions such as 1 g/cm^3), the dimensions of $k_{f,g}$ are given by

$$\frac{1}{s}\Upsilon^{1-\sum_{k=1}^{n}\sum_{e=1}^{n_k}|\nu_{R,g,k,e}|} ,$$

(G6)

and the dimensions of $k_{r,g}$ are given by

$$\frac{1}{s}\Upsilon^{1-\sum_{k=1}^{n}\sum_{e=1}^{n_k}|\nu_{P,g,k,e}|} .$$

(G7)

The net stoichiometry of species e of component k in independent chemical reaction g is defined as $\nu_{g,k,e} = \nu_{R,g,k,e} + \nu_{P,g,k,e}$, so that, due to conservation of mass,

$$\sum_{k=1}^{n}\sum_{e=1}^{n_k}\nu_{g,k,e}\mathrm{M}_{k,e} = 0 .$$

(G8)

The net rate of independent chemical reaction g, given by

$$k_{f,g}\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\gamma_{k,e}\mathrm{c}_{k,e}\right)^{|\nu_{R,g,k,e}|} - k_{r,g}\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\gamma_{k,e}\mathrm{c}_{k,e}\right)^{|\nu_{P,g,k,e}|} ,$$

(G9)

is zero when the reaction is at equilibrium.

Explicitly including the forward and reverse reactions of each component, the continuity equation for all components is

$$\sum_{k=1}^{n}\left(\frac{\partial c_k}{\partial t}\right)_{\xi} = -\sum_{k=1}^{n}\left(\frac{\partial I_k}{\partial \xi}\right)_{t} - \sum_{g=1}^{n_R=n}\left(k_{f,g}\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\gamma_{k,e}\mathrm{c}_{k,e}\right)^{|\nu_{R,g,k,e}|} - k_{r,g}\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\gamma_{k,e}\mathrm{c}_{k,e}\right)^{|\nu_{P,g,k,e}|}\right),$$

(G10)

where the sum of the net reaction rates,

$$\sum_{g=1}^{n_R=n}\left(k_{f,g}\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\gamma_{k,e}c_{k,e}\right)^{\left|\nu_{R,g,k,e}\right|}-k_{r,g}\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\gamma_{k,e}c_{k,e}\right)^{\left|\nu_{P,g,k,e}\right|}\right),$$

(G11)

is zero when all reactions are at equilibrium.

A convention is now adopted in which the simplest species of each component is assigned the lowest number, 1, of the species index, e. Higher-order species of component k are thus those for which $2 \leq e \leq n_k$. Furthermore, in view of the fact that there are as many independent chemical reactions (n_R) as there are components (n), the reaction index, g, can be reused as an additional component index. Thus, the composition of each higher-order species ($e > 1$) of component k is given by the set of $\nu_{g,k,e}$ for which $1 \leq g \leq n$, where $\nu_{g,k,e}$ is defined as the stoichiometry of species 1 of component g, with the constraint that $1 \leq \nu_{g=k,k,e} < \infty$ for $g = k$, while $0 \leq \nu_{g\neq k,k,e} < \infty$ for $g \neq k$.

To describe the reactions that form each higher-order species ($e > 1$) of each component ($1 \leq k \leq n$), an additional species index, a, is applied to the association constant, forward rate constant and reverse rate constant of these reactions. To describe reactions in which the reactants or products include higher-order species ($e > 1$) of any components ($1 \leq k \leq n$), the additional species index (a) is also applied to the stoichiometries of each species. Henceforth, the reaction that produces species a of component g is referred to as reaction a/g.

For components indexed by g, species are indexed by a. As n_g is the number of species that constitute solute component g, for $g = k$, $n_g = n_k$. After further indexing the stoichiometries by a, Equation G4 is summed over all species to obtain

$$\sum_{g=1}^{n_R=n}\sum_{a=1}^{n_g}\sum_{k=1}^{n}\sum_{e=1}^{n_k}\left|\nu_{R,g,a,k,e}\right|S_{k,e} \rightleftharpoons \sum_{g=1}^{n_R=n}\sum_{a=1}^{n_g}\sum_{k=1}^{n}\sum_{e=1}^{n_k}\left|\nu_{P,g,a,k,e}\right|S_{k,e}\ ,$$

(G12)

where $\nu_{R,g,a,k,e}$ is the signed stoichiometry of reactant species e of component k in reaction a/g, and $\nu_{P,g,a,k,e}$ is the signed stoichiometry of product species e of component k in reaction a/g. By definition, $\nu_{R,g,a,k,e} \leq 0$ and $\nu_{P,g,a,k,e} \geq 0$, where $\nu_{R,g,a,k,e} = 0$ if species e of component k is not a reactant in reaction a/g, and $\nu_{P,g,a,k,e} = 0$ if species e of component k is not a product in reaction a/g.

The association constant of reaction a/g is given by

$$K_{A,g,a} = \frac{k_{f,g,a}}{k_{r,g,a}} = \frac{\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\tilde{\gamma}_{k,e}\tilde{c}_{k,e}\right)^{|\nu_{P,g,a,k,e}|}}{\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\tilde{\gamma}_{k,e}\tilde{c}_{k,e}\right)^{|\nu_{R,g,a,k,e}|}} = \prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\tilde{\gamma}_{k,e}\tilde{c}_{k,e}\right)^{(\nu_{P,g,a,k,e}+\nu_{R,g,a,k,e})} ,$$

(G13)

where $k_{f,g,a}$ is the forward rate constant and $k_{r,g,a}$ is the reverse rate constant of reaction a/g. The dimensions of $k_{f,g,a}$ are given by

$$\frac{1}{s}\Upsilon^{1-\sum_{k=1}^{n}\sum_{e=1}^{n_k}|\nu_{R,g,a,k,e}|} ,$$

(G14)

and the dimensions of $k_{r,g,a}$ are given by

$$\frac{1}{s}\Upsilon^{1-\sum_{k=1}^{n}\sum_{e=1}^{n_k}|\nu_{P,g,a,k,e}|} ,$$

(G15)

where Υ is the unit solute concentration.

The net stoichiometry of species e of component k in reaction a/g is defined as $\nu_{g,a,k,e} = \nu_{R,g,a,k,e} + \nu_{P,g,a,k,e}$, so that, due to conservation of mass,

$$\sum_{k=1}^{n}\sum_{e=1}^{n_k}\nu_{g,a,k,e}\mathrm{M}_{k,e} = 0 .$$

(G16)

The net rate of reaction a/g, given by

$$k_{f,g,a}\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\gamma_{k,e}c_{k,e}\right)^{|\nu_{R,g,a,k,e}|} - k_{r,g,a}\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\gamma_{k,e}c_{k,e}\right)^{|\nu_{P,g,a,k,e}|} ,$$

(G17)

is zero when the reaction is at equilibrium.

Explicitly including the forward and reverse reactions of each species, the continuity equation for all species is

$$\sum_{k=1}^{n}\sum_{e=1}^{n_k}\left(\frac{\partial c_{k,e}}{\partial t}\right)_{\xi} = -\sum_{k=1}^{n}\sum_{e=1}^{n_k}\left(\frac{\partial I_{k,e}}{\partial \xi}\right)_{t} - \sum_{g=1}^{n_R=n}\sum_{a=1}^{n_g}\left(k_{f,g,a}\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\gamma_{k,e}c_{k,e}\right)^{\left|\nu_{R,g,a,k,e}\right|} - k_{r,g,a}\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\gamma_{k,e}c_{k,e}\right)^{\left|\nu_{P,g,a,k,e}\right|}\right),$$

(G18)

where the sum of the net reaction rates,

$$\sum_{g=1}^{n_R=n}\sum_{a=1}^{n_g}\left(k_{f,g,a}\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\gamma_{k,e}c_{k,e}\right)^{\left|\nu_{R,g,a,k,e}\right|} - k_{r,g,a}\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\gamma_{k,e}c_{k,e}\right)^{\left|\nu_{P,g,a,k,e}\right|}\right),$$

(G19)

is zero when all reactions are at equilibrium.

Equation G18 applies to simulations based on the solution to the continuity equation in terms of species. Where the pressure in the system is ξ-dependent, $K_{A,g,a}$, $k_{f,g,a}$ and $k_{r,g,a}$ may be functions of ξ, and may be worth treating as such. A ξ-dependence in pressure may also give rise to an additional ξ-dependence in $\gamma_{k,e}$, beyond that which may result from gradients in the concentrations of any solute species. Following Equations J2 to J5, the topic of how to model a pressure-induced ξ-dependence is discussed in connection with the species-e-of-component-k affecting electrophoretic/asymmetry, thermodynamic nonideality, and viscosity coefficients.

Equilibrium constant

Properly speaking, the association constant should be defined in such a way that it is dimensionless. It is convenient, however, to preserve the dimensionality of $K_{A,g,a}$ as defined by Equation G13. To deal with situations where the numerically equivalent but dimensionless constant is needed, the dimensionless equilibrium constant of reaction a/g is defined as

$$K_{eq,g,a} = \frac{\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\frac{\tilde{\gamma}_{k,e}\tilde{c}_{k,e}}{\Upsilon}\right)^{|\nu_{P,g,a,k,e}|}}{\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\frac{\tilde{\gamma}_{k,e}\tilde{c}_{k,e}}{\Upsilon}\right)^{|\nu_{R,g,a,k,e}|}} = \prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\frac{\tilde{\gamma}_{k,e}\tilde{c}_{k,e}}{\Upsilon}\right)^{(\nu_{P,g,a,k,e}+\nu_{R,g,a,k,e})},$$

(G20)

where Υ is the unit solute concentration. The dimensionless aspect of the equilibrium constant makes it suitable for calculations that require its logarithm, such as $\Delta G° = -RT\ln K_{eq,g,a}$, and is the parameter obtained from exponential operations, such as $K_{eq,g,a} = e^{-\Delta G°/RT}$, where ΔG° is the standard Gibbs free energy change of reaction a/g.

Obtaining conjugate molar affinities from the molar reaction flows

The molar reaction flow on an independent reaction is equal to the portion of the time-derivative of molar concentration that is a direct result of a chemical reaction [Onsager, 1931a]. Thus, for reaction g/a, the molar reaction flow can be defined as

$$J_{g,a}^{R} = \left(\frac{\prod_{k=1}^{n}\prod_{e=1}^{n_k} \mathrm{M}_{k,e}{}^{|\nu_{R,g,a,k,e}|}}{\sum_{k=1}^{n}\sum_{e=1}^{n_k} \mathrm{M}_{k,e}|\nu_{R,g,a,k,e}|}\right) k_{f,g,a}\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\gamma_{k,e}\frac{c_{k,e}}{\mathrm{M}_{k,e}}\right)^{|\nu_{R,g,a,k,e}|} - \left(\frac{\prod_{k=1}^{n}\prod_{e=1}^{n_k} \mathrm{M}_{k,e}{}^{|\nu_{P,g,a,k,e}|}}{\sum_{k=1}^{n}\sum_{e=1}^{n_k} \mathrm{M}_{k,e}|\nu_{P,g,a,k,e}|}\right) k_{r,g,a}\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\gamma_{k,e}\frac{c_{k,e}}{\mathrm{M}_{k,e}}\right)^{|\nu_{P,g,a,k,e}|},$$

(G21)

which is the molar equivalent of Expression G17. Wherever and whenever reaction g/a is at chemical equilibrium, $J_{g,a}^{R} = 0$ and each $\gamma_{k,e}c_{k,e} = \tilde{\gamma}_{k,e}\tilde{c}_{k,e}$, in which case, the association constant of reaction a/g can be redefined as

$$K_{\frac{A,g,a}{collig}} = \frac{\left(\frac{\prod_{k=1}^{n}\prod_{e=1}^{n_k} \mathrm{M}_{k,e}{}^{|\nu_{R,g,a,k,e}|}}{\sum_{k=1}^{n}\sum_{e=1}^{n_k} \mathrm{M}_{k,e}|\nu_{R,g,a,k,e}|}\right) k_{f,g,a}}{\left(\frac{\prod_{k=1}^{n}\prod_{e=1}^{n_k} \mathrm{M}_{k,e}{}^{|\nu_{P,g,a,k,e}|}}{\sum_{k=1}^{n}\sum_{e=1}^{n_k} \mathrm{M}_{k,e}|\nu_{P,g,a,k,e}|}\right) k_{r,g,a}} = \frac{\left(\frac{\sum_{k=1}^{n}\sum_{e=1}^{n_k} \mathrm{M}_{k,e}|\nu_{P,g,a,k,e}|}{\sum_{k=1}^{n}\sum_{e=1}^{n_k} \mathrm{M}_{k,e}|\nu_{R,g,a,k,e}|}\right) k_{f,g,a}}{\left(\frac{\prod_{k=1}^{n}\prod_{e=1}^{n_k} \mathrm{M}_{k,e}{}^{|\nu_{P,g,a,k,e}|}}{\prod_{k=1}^{n}\prod_{e=1}^{n_k} \mathrm{M}_{k,e}{}^{|\nu_{R,g,a,k,e}|}}\right) k_{r,g,a}}$$

$$= \frac{\left(\frac{\sum_{k=1}^{n}\sum_{e=1}^{n_k} \mathrm{M}_{k,e}|\nu_{P,g,a,k,e}|}{\sum_{k=1}^{n}\sum_{e=1}^{n_k} \mathrm{M}_{k,e}|\nu_{R,g,a,k,e}|}\right) \frac{k_{f,g,a}}{k_{r,g,a}}}{\prod_{k=1}^{n}\prod_{e=1}^{n_k} \mathrm{M}_{k,e}{}^{(\nu_{P,g,a,k,e}+\nu_{R,g,a,k,e})}}$$

(G22)

(compare with Equation G13), while the dimensionless equilibrium constant of reaction a/g can be redefined as

$$K_{\frac{eq,g,a}{collig}} = \frac{\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\frac{\tilde{\gamma}_{k,e}\tilde{c}_{k,e}}{\Upsilon \mathrm{M}_{k,e}}\right)^{|\nu_{P,g,a,k,e}|}}{\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\frac{\tilde{\gamma}_{k,e}\tilde{c}_{k,e}}{\Upsilon \mathrm{M}_{k,e}}\right)^{|\nu_{R,g,a,k,e}|}} = \prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\frac{\tilde{\gamma}_{k,e}\tilde{c}_{k,e}}{\Upsilon \mathrm{M}_{k,e}}\right)^{(\nu_{P,g,a,k,e}+\nu_{R,g,a,k,e})},$$

(G23)

where Υ is now the molar unit solute concentration. (Compare this result with Equation G20.) The addition of "collig" in their subscripts indicates that these association and equilibrium constants are defined colligatively, and distinguishes them from their respective counterparts of Equations G13 and G20, which are defined using mass concentrations.

As calculated from the colligative equilibrium constant (Equation G23), the standard Gibbs free energy change of reaction a/g is thus

$$\Delta G^{\circ} = -RTln\left(K_{\frac{eq,g,a}{collig}}\right) = -RTln\left[\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\frac{\tilde{\gamma}_{k,e}\tilde{c}_{k,e}}{\Upsilon \mathrm{M}_{k,e}}\right)^{(\nu_{P,g,a,k,e}+\nu_{R,g,a,k,e})}\right]$$

$$= -RT\sum_{k=1}^{n}\sum_{e=1}^{n_k}(\nu_{P,g,a,k,e}+\nu_{R,g,a,k,e})ln\left(\frac{\tilde{\gamma}_{k,e}\tilde{c}_{k,e}}{\Upsilon \mathrm{M}_{k,e}}\right).$$

(G24)

For values of $\gamma_{k,e}c_{k,e}$ that differ from their corresponding values of $\tilde{\gamma}_{k,e}\tilde{c}_{k,e}$,

$$\begin{aligned}\Delta G &= \Delta G^{\circ} + RTln\left[\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\frac{\gamma_{k,e}\mathrm{c}_{k,e}}{\Upsilon\mathrm{M}_{k,e}}\right)^{(\nu_{P,g,a,k,e}+\nu_{R,g,a,k,e})}\right] \\ &= \Delta G^{\circ} + RT\sum_{k=1}^{n}\sum_{e=1}^{n_k}(\nu_{P,g,a,k,e}+\nu_{R,g,a,k,e})ln\left(\frac{\gamma_{k,e}\mathrm{c}_{k,e}}{\Upsilon\mathrm{M}_{k,e}}\right) \\ &= RT\sum_{k=1}^{n}\sum_{e=1}^{n_k}(\nu_{P,g,a,k,e}+\nu_{R,g,a,k,e})ln\left(\frac{\gamma_{k,e}\mathrm{c}_{k,e}}{\tilde{\gamma}_{k,e}\tilde{\mathrm{c}}_{k,e}}\right) \\ &= RT\sum_{k=1}^{n}\sum_{e=1}^{n_k}(\nu_{P,g,a,k,e}+\nu_{R,g,a,k,e})ln(x_{k,e}) \\ &= RTln\left[\prod_{k=1}^{n}\prod_{e=1}^{n_k}x_{k,e}{}^{(\nu_{P,g,a,k,e}+\nu_{R,g,a,k,e})}\right],\end{aligned}$$

(G25)

where

$$x_{k,e} = \frac{\gamma_{k,e}\mathrm{c}_{k,e}}{\tilde{\gamma}_{k,e}\tilde{\mathrm{c}}_{k,e}}$$

(G26)

is the equilibrium-normalised activity of species e of component k. For irreversible thermodynamics to be applicable, all points of the system must be near equilibrium at all times. Thus, at any time and place in the system,

$$x_{k,e} = 1 + \delta x_{k,e},$$

(G27)

where $\left|\delta x_{k,e}\right|$ is not much greater than zero. Furthermore, it is assumed that $\left|\delta x_{k,e}\right|$ is always near enough to zero that, to a good approximation,

$$\Delta G = RTln\left[\prod_{k=1}^{n}\prod_{e=1}^{n_k}x_{k,e}{}^{(\nu_{P,g,a,k,e}+\nu_{R,g,a,k,e})}\right] \approx RT\left[\prod_{k=1}^{n}\prod_{e=1}^{n_k}x_{k,e}{}^{(\nu_{P,g,a,k,e}+\nu_{R,g,a,k,e})} - 1\right].$$

(G28)

Thus,

$$\prod_{k=1}^{n}\prod_{e=1}^{n_k}x_{k,e}{}^{(\nu_{P,g,a,k,e}+\nu_{R,g,a,k,e})} \approx 1 + ln\left[\prod_{k=1}^{n}\prod_{e=1}^{n_k}x_{k,e}{}^{(\nu_{P,g,a,k,e}+\nu_{R,g,a,k,e})}\right] = 1 + \frac{\Delta G}{RT}.$$

(G29)

More importantly for what follows, ΔG is divided into two parts,

$$\Delta G = \Delta G_r + \Delta G_f,$$

(G30)

where

$$\Delta G_r = RTln\left[\prod_{k=1}^{n}\prod_{e=1}^{n_k} {x_{k,e}}^{\nu_{P,g,a,k,e}}\right] = RTln\left[\prod_{k=1}^{n}\prod_{e=1}^{n_k} {x_{k,e}}^{|\nu_{P,g,a,k,e}|}\right]$$

(G31)

and

$$\Delta G_f = RTln\left[\prod_{k=1}^{n}\prod_{e=1}^{n_k} {x_{k,e}}^{\nu_{R,g,a,k,e}}\right] = RTln\left[\prod_{k=1}^{n}\prod_{e=1}^{n_k} {x_{k,e}}^{-|\nu_{R,g,a,k,e}|}\right]$$

$$= -RTln\left[\prod_{k=1}^{n}\prod_{e=1}^{n_k} {x_{k,e}}^{|\nu_{R,g,a,k,e}|}\right],$$

(G32)

so that

$$\prod_{k=1}^{n}\prod_{e=1}^{n_k} {x_{k,e}}^{|\nu_{P,g,a,k,e}|} \approx 1 + ln\left[\prod_{k=1}^{n}\prod_{e=1}^{n_k} {x_{k,e}}^{|\nu_{P,g,a,k,e}|}\right] = 1 + \frac{\Delta G_r}{RT}$$

(G33)

and

$$\prod_{k=1}^{n}\prod_{e=1}^{n_k} {x_{k,e}}^{|\nu_{R,g,a,k,e}|} \approx 1 + ln\left[\prod_{k=1}^{n}\prod_{e=1}^{n_k} {x_{k,e}}^{|\nu_{R,g,a,k,e}|}\right] = 1 - \frac{\Delta G_f}{RT}.$$

(G34)

Given the definition of $x_{k,e}$, the molar reaction flow of reaction g/a can be rewritten as

$$
\begin{aligned}
&J_{g,a}^{R} \\
&= \left(\frac{\prod_{k=1}^{n}\prod_{e=1}^{n_k}\mathrm{M}_{k,e}{}^{|\nu_{R,g,a,k,e}|}}{\sum_{k=1}^{n}\sum_{e=1}^{n_k}\mathrm{M}_{k,e}|\nu_{R,g,a,k,e}|}\right)k_{f,g,a}\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\frac{\tilde{\gamma}_{k,e}\tilde{c}_{k,e}x_{k,e}}{\mathrm{M}_{k,e}}\right)^{|\nu_{R,g,a,k,e}|} \\
&- \left(\frac{\prod_{k=1}^{n}\prod_{e=1}^{n_k}\mathrm{M}_{k,e}{}^{|\nu_{P,g,a,k,e}|}}{\sum_{k=1}^{n}\sum_{e=1}^{n_k}\mathrm{M}_{k,e}|\nu_{P,g,a,k,e}|}\right)k_{r,g,a}\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\frac{\tilde{\gamma}_{k,e}\tilde{c}_{k,e}x_{k,e}}{\mathrm{M}_{k,e}}\right)^{|\nu_{P,g,a,k,e}|} \\
&= \left(\frac{\prod_{k=1}^{n}\prod_{e=1}^{n_k}\mathrm{M}_{k,e}{}^{|\nu_{R,g,a,k,e}|}}{\sum_{k=1}^{n}\sum_{e=1}^{n_k}\mathrm{M}_{k,e}|\nu_{R,g,a,k,e}|}\right)k_{f,g,a}\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\frac{\tilde{\gamma}_{k,e}\tilde{c}_{k,e}}{\mathrm{M}_{k,e}}\right)^{|\nu_{R,g,a,k,e}|}\prod_{k=1}^{n}\prod_{e=1}^{n_k}x_{k,e}{}^{|\nu_{R,g,a,k,e}|} \\
&- \left(\frac{\prod_{k=1}^{n}\prod_{e=1}^{n_k}\mathrm{M}_{k,e}{}^{|\nu_{P,g,a,k,e}|}}{\sum_{k=1}^{n}\sum_{e=1}^{n_k}\mathrm{M}_{k,e}|\nu_{P,g,a,k,e}|}\right)k_{r,g,a}\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\frac{\tilde{\gamma}_{k,e}\tilde{c}_{k,e}}{\mathrm{M}_{k,e}}\right)^{|\nu_{P,g,a,k,e}|}\prod_{k=1}^{n}\prod_{e=1}^{n_k}x_{k,e}{}^{|\nu_{P,g,a,k,e}|}.
\end{aligned}
$$

(G35)

Given the expected characteristics of $x_{k,e}$, the molar reaction flow of reaction g/a can be rewritten as

$$
\begin{aligned}
&J_{g,a}^{R} \\
&= \left(\frac{\prod_{k=1}^{n}\prod_{e=1}^{n_k}\mathrm{M}_{k,e}{}^{|\nu_{R,g,a,k,e}|}}{\sum_{k=1}^{n}\sum_{e=1}^{n_k}\mathrm{M}_{k,e}|\nu_{R,g,a,k,e}|}\right)k_{f,g,a}\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\frac{\tilde{\gamma}_{k,e}\tilde{c}_{k,e}}{\mathrm{M}_{k,e}}\right)^{|\nu_{R,g,a,k,e}|}\prod_{k=1}^{n}\prod_{e=1}^{n_k}x_{k,e}{}^{|\nu_{R,g,a,k,e}|} \\
&- \left(\frac{\prod_{k=1}^{n}\prod_{e=1}^{n_k}\mathrm{M}_{k,e}{}^{|\nu_{P,g,a,k,e}|}}{\sum_{k=1}^{n}\sum_{e=1}^{n_k}\mathrm{M}_{k,e}|\nu_{P,g,a,k,e}|}\right)k_{r,g,a}\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\frac{\tilde{\gamma}_{k,e}\tilde{c}_{k,e}}{\mathrm{M}_{k,e}}\right)^{|\nu_{P,g,a,k,e}|}\prod_{k=1}^{n}\prod_{e=1}^{n_k}x_{k,e}{}^{|\nu_{P,g,a,k,e}|} \\
&\approx \left(\frac{\prod_{k=1}^{n}\prod_{e=1}^{n_k}\mathrm{M}_{k,e}{}^{|\nu_{R,g,a,k,e}|}}{\sum_{k=1}^{n}\sum_{e=1}^{n_k}\mathrm{M}_{k,e}|\nu_{R,g,a,k,e}|}\right)k_{f,g,a}\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\frac{\tilde{\gamma}_{k,e}\tilde{c}_{k,e}}{\mathrm{M}_{k,e}}\right)^{|\nu_{R,g,a,k,e}|}\left[1+ln\left[\prod_{k=1}^{n}\prod_{e=1}^{n_k}x_{k,e}{}^{|\nu_{R,g,a,k,e}|}\right]\right] \\
&- \left(\frac{\prod_{k=1}^{n}\prod_{e=1}^{n_k}\mathrm{M}_{k,e}{}^{|\nu_{P,g,a,k,e}|}}{\sum_{k=1}^{n}\sum_{e=1}^{n_k}\mathrm{M}_{k,e}|\nu_{P,g,a,k,e}|}\right)k_{r,g,a}\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\frac{\tilde{\gamma}_{k,e}\tilde{c}_{k,e}}{\mathrm{M}_{k,e}}\right)^{|\nu_{P,g,a,k,e}|}\left[1+ln\left[\prod_{k=1}^{n}\prod_{e=1}^{n_k}x_{k,e}{}^{|\nu_{P,g,a,k,e}|}\right]\right] \\
&= \left(\frac{\prod_{k=1}^{n}\prod_{e=1}^{n_k}\mathrm{M}_{k,e}{}^{|\nu_{R,g,a,k,e}|}}{\sum_{k=1}^{n}\sum_{e=1}^{n_k}\mathrm{M}_{k,e}|\nu_{R,g,a,k,e}|}\right)k_{f,g,a}\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\frac{\tilde{\gamma}_{k,e}\tilde{c}_{k,e}}{\mathrm{M}_{k,e}}\right)^{|\nu_{R,g,a,k,e}|}\left[1-\frac{\Delta G_f}{RT}\right] \\
&- \left(\frac{\prod_{k=1}^{n}\prod_{e=1}^{n_k}\mathrm{M}_{k,e}{}^{|\nu_{P,g,a,k,e}|}}{\sum_{k=1}^{n}\sum_{e=1}^{n_k}\mathrm{M}_{k,e}|\nu_{P,g,a,k,e}|}\right)k_{r,g,a}\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\frac{\tilde{\gamma}_{k,e}\tilde{c}_{k,e}}{\mathrm{M}_{k,e}}\right)^{|\nu_{P,g,a,k,e}|}\left[1+\frac{\Delta G_r}{RT}\right].
\end{aligned}
$$

(G36)

Multiplying this equation by $\frac{RT}{RT}$ yields

$$\begin{aligned} J^{R}_{g,a} &= \frac{1}{RT}\left(\frac{\prod_{k=1}^{n}\prod_{e=1}^{n_k}\mathrm{M}_{k,e}{}^{|\nu_{R,g,a,k,e}|}}{\sum_{k=1}^{n}\sum_{e=1}^{n_k}\mathrm{M}_{k,e}|\nu_{R,g,a,k,e}|}\right)k_{f,g,a}\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\frac{\tilde{\gamma}_{k,e}\tilde{c}_{k,e}}{\mathrm{M}_{k,e}}\right)^{|\nu_{R,g,a,k,e}|}\left[RT-\Delta G_f\right] \\ &\quad -\frac{1}{RT}\left(\frac{\prod_{k=1}^{n}\prod_{e=1}^{n_k}\mathrm{M}_{k,e}{}^{|\nu_{P,g,a,k,e}|}}{\sum_{k=1}^{n}\sum_{e=1}^{n_k}\mathrm{M}_{k,e}|\nu_{P,g,a,k,e}|}\right)k_{r,g,a}\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\frac{\tilde{\gamma}_{k,e}\tilde{c}_{k,e}}{\mathrm{M}_{k,e}}\right)^{|\nu_{P,g,a,k,e}|}\left[RT+\Delta G_r\right] \\ &= L^{g,a}_{P,R}X^{g,a}_{R} + L^{g,a}_{R,P}X^{g,a}_{P}\ , \end{aligned}$$

(G37)

where

$$J^{g,a}_{P} = L^{g,a}_{P,R}X^{g,a}_{R}$$

(G38)

is the molar reaction flow of the products (P) of reaction g/a,

$$L^{g,a}_{P,R} = \frac{1}{RT}\left(\frac{\prod_{k=1}^{n}\prod_{e=1}^{n_k}\mathrm{M}_{k,e}{}^{|\nu_{R,g,a,k,e}|}}{\sum_{k=1}^{n}\sum_{e=1}^{n_k}\mathrm{M}_{k,e}|\nu_{R,g,a,k,e}|}\right)k_{f,g,a}\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\frac{\tilde{\gamma}_{k,e}\tilde{c}_{k,e}}{\mathrm{M}_{k,e}}\right)^{|\nu_{R,g,a,k,e}|}$$

(G39)

is the coupled-flow-phenomenological coefficient linking $J^{g,a}_{P}$ to $X^{g,a}_{R}$,

$$X^{g,a}_{R} = RT\prod_{k=1}^{n}\prod_{e=1}^{n_k}x_{k,e}{}^{|\nu_{R,g,a,k,e}|} \approx RT\left[1+ln\left[\prod_{k=1}^{n}\prod_{e=1}^{n_k}x_{k,e}{}^{|\nu_{R,g,a,k,e}|}\right]\right] = RT-\Delta G_f$$

(G40)

is the conjugate molar affinity of the reactants (R) of reaction g/a,

$$J^{g,a}_{R} = L^{g,a}_{R,P}X^{g,a}_{P}$$

(G41)

is the molar reaction flow of the reactants (R) of reaction g/a,

$$L^{g,a}_{R,P} = -\frac{1}{RT}\left(\frac{\prod_{k=1}^{n}\prod_{e=1}^{n_k}\mathrm{M}_{k,e}{}^{|\nu_{P,g,a,k,e}|}}{\sum_{k=1}^{n}\sum_{e=1}^{n_k}\mathrm{M}_{k,e}|\nu_{P,g,a,k,e}|}\right)k_{r,g,a}\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\frac{\tilde{\gamma}_{k,e}\tilde{c}_{k,e}}{\mathrm{M}_{k,e}}\right)^{|\nu_{P,g,a,k,e}|}$$

(G42)

is the coupled-flow-phenomenological coefficient linking $J^{g,a}_{R}$ to $X^{g,a}_{P}$, and

$$X_P^{g,a} = RT\prod_{k=1}^{n}\prod_{e=1}^{n_k} x_{k,e}{}^{|\nu_{P,g,a,k,e}|} \approx RT\left[1 + ln\left[\prod_{k=1}^{n}\prod_{e=1}^{n_k} x_{k,e}{}^{|\nu_{P,g,a,k,e}|}\right]\right] = RT + \Delta G_r$$

(G43)

is the conjugate molar affinity of the products (P) of reaction g/a.

Taking Equations G21 to G23 into consideration together with Equations G37 to G43, it can be seen that

$$L_{P,R}^{g,a} = L_{R,P}^{g,a}$$

(G44)

is a reciprocal relationship. Thus, the phenomenological coefficients ($L_{P,R}^{g,a}$ of Equation G39 and $L_{R,P}^{g,a}$ of Equation G42) of the reaction flows ($J_P^{g,a}$ of Equation G38 and $J_R^{g,a}$ of Equation G41) included within $J_{g,a}^R$ (Equation 37) yield identical results upon evaluation. In part, splitting $J_{g,a}^R$ into two reactions flows,

$$J_{g,a}^R = J_P^{g,a} + J_R^{g,a},$$

(G45)

was justified on the basis of $L_{P,R}^{g,a}$ and $L_{R,P}^{g,a}$ being reciprocal. The split was also motivated by the search for the two molar reaction flows that, in the dissipation function (Equations G2 and G3), are needed to complement the conjugate molar affinities, $X_R^{g,a}$ and $X_P^{g,a}$, that Equation G37 was contrived to yield. Having split Equation G37 as shown, it is now possible to write the dissipation function for reaction g/a as

$$\Phi_{g,a} = J_P^{g,a}X_P^{g,a} + J_R^{g,a}X_R^{g,a}.$$

(G46)

Equation G46 is a dissipation function for two directionally distinct reactions, which are the forward reaction that produces species a of component g, and the corresponding reverse reaction. The dissipation function that includes all such pairs of reactions for all species of component g can thus be written as

$$\Phi_g = \sum_{a=1}^{n_g}\Phi_{g,a}.$$

(G47)

Likewise, the dissipation function that includes all such pairs of reactions for all species of all components can be written as

$$\Phi_{\mathrm{R}} = \sum_{g=1}^{n_R=n} \Phi_g.$$

(G48)

Thus, the right-hand sides of Equations G48 and G3 can be equated to obtain

$$\Phi_{\mathrm{R}} = \sum_{g=1}^{n_R=n} J_g^R A_g = \sum_{g=1}^{n_R=n} \Phi_g.$$

(G49)

Using first Equation 47 and then Equation 46, the right-most summation of this result can be expanded to yield

$$\Phi_{\mathrm{R}} = \sum_{g=1}^{n_R=n} J_g^R A_g = \sum_{g=1}^{n_R=n} \Phi_g = \sum_{g=1}^{n_R=n} \sum_{a=1}^{n_g} \Phi_{g,a} = \sum_{g=1}^{n_R=n} \sum_{a=1}^{n_g} \left(J_P^{g,a} X_P^{g,a} + J_R^{g,a} X_R^{g,a}\right).$$

(G50)

Assuming that, by definition,

$$A_g = \sum_{a=1}^{n_g} \left(X_P^{g,a} + X_R^{g,a}\right) = RT \sum_{a=1}^{n_g} \left(\prod_{k=1}^{n} \prod_{e=1}^{n_k} x_{k,e}{}^{|\nu_{P,g,a,k,e}|} + \prod_{k=1}^{n} \prod_{e=1}^{n_k} x_{k,e}{}^{|\nu_{R,g,a,k,e}|} \right),$$

(G51)

then

$$J_g^R = \frac{\sum_{a=1}^{n_g} \left(J_P^{g,a} X_P^{g,a} + J_R^{g,a} X_R^{g,a}\right)}{\sum_{a=1}^{n_g} \left(X_P^{g,a} + X_R^{g,a}\right)},$$

(G52)

which would make J_g^R the conjugate-molar-affinity-average of the species-level molar reaction flows of component g.

Dimensionality and tensorial order

The dimensions of A_g are those of chemical potential, and A_g (Equation G51), the conjugate molar affinity of component g, can be considered a measure of the chemical potential of component g. (To be liberally flippant, one could say that the conjugate molar affinity quantifies how reactionary a component is at any given place and time.) As would be expected of a chemical potential, A_g is a scalar, as are the species-level conjugate molar affinities denoted as $X_R^{g,a}$ (Equation G40) or $X_P^{g,a}$ (Equation G43). Hence, although Onsager referred to A_g as a force, he tended to put quotation marks about the word when doing so [Onsager, 1931a]. In contrast, as noted in the discussion of Equation G1, $\vec{X}_q$, the conjugate molar force (Equations A2, A14 and I16) of solute component q, is a vector equal to $-\nabla U_q$, where U_q is the total molar potential of solute component q. Thus, A_g and U_q are dimensionally and tensorially equivalent, as are $-\nabla A_g$ and $\vec{X}_q$.

Similarly, despite their being referred to as flows, reaction flows, such as J_g^R at the component level or $J_P^{g,a}$ (Equation G38) and $J_R^{g,a}$ (Equation G41) at the species level, are scalars, and are dimensionally distinct from the molar flows of components, such as $\vec{J}_k$ (Equation G2), which are vectors. The reaction flows have the dimensions that would be obtained from a divergence of a molar flow. Thus, $\nabla \cdot \vec{J}_k$ and J_g^R are dimensionally and tensorially equivalent, as are $\vec{J}_k$ and $(\nabla \cdot)^{-1} J_g^R$, where $(\nabla \cdot)^{-1}$ is the inverse divergence operator (Sahoo, 2008).

In the dissipation function (Equation G2), products of pairs of vectors, $\vec{J}_k$ and $\vec{X}_k$, are added to products of pairs of scalars, J_g^R and A_g, to obtain a scalar, Φ. Dimensionally, the product of any $\vec{J}_k$ and any $\vec{X}_k$ is the same as the product of any J_g^R and any A_g. However, while the product of two scalars yields a scalar, the product of two vectors can yield a scalar (tensorial order 0), a vector (tensorial order 1) or a dyad (tensorial order 2), depending on how the two vectors are multiplied (Kolecki, 2005). Thus, to ensure that each product in the dissipation function yields a scalar, each such product that involves two vectors must be an inner product. (As it happens, the inner product between two vectors will not yield a result of the standard form unless one of the vectors is represented covariantly and the other vector is represented contravariantly (Kolecki, 2005).)

Given the above, it can be stated that the following products between scalars, J_g^RA$_g$, J_g^RU$_q$, $(\nabla \cdot \vec{J}_k)$A$_g$, and $(\nabla \cdot \vec{J}_k)$U$_q$, are dimensionally and tensorially equivalent, both to each other, and to the following inner products between vectors, $\left[(\nabla \cdot)^{-1} J_g^R\right] \cdot$ (-∇A$_g$), $\left[(\nabla \cdot)^{-1} J_g^R\right] \cdot \vec{X}_q$, $\vec{J}_k \cdot$ (-∇A$_g$), and $\vec{J}_k \cdot \vec{X}_q$. It would seem, then, that the divergence of a molar flow might be a molar reaction flow, and the inverse divergence of a molar reaction flow might be a molar flow. It seems clear, though, that $\nabla \cdot \vec{J}_k$ does not equal J_g^R, and $\vec{J}_k$ does not equal $(\nabla \cdot)^{-1} J_g^R$. Likewise, in general, A$_g$ cannot be equated to U$_q$, and -∇A$_g$ cannot be equated to $\vec{X}_q$. It may, however, be alright to say that, in general, A$_g$ is part of U$_q$ and thus -∇A$_g$ is part of $\vec{X}_q$.

(See Moody and Shepard, 2004, for a previous version of the material in this section.)

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Section H: Factors affecting the electrical field in MCE

It is convenient to describe an MCE system in rectangular coordinates, where the previously defined spatial vector, $\vec{\xi}$, equals $\vec{z}$. As such, the plane cross-sectional area, A, of the system is perpendicular to the downwardly directed z-axis of the MCE system, and independent of the vertical position, ξ = z. As A is also time-independent, the ordinary derivative, dA/dz = 0, can be used to describe this geometric characteristic of the system.

The current density can be written as

$$\vec{j} = \frac{F}{\Theta}\sum_{k=1}^{n}\sum_{e=1}^{n_k} z_{k,e}\vec{J}_{k,e} ,$$

(H1)

where $z_{k,e}$ is the valence of species e of component k, $\vec{J}_{k,e}$ is the molar flow vector of species e of component k, F is the Faraday, and Θ is a conversion constant. As $\vec{j}$ is assumed to be invariant with position over any horizontal cross-section, and as dA/dz = 0, $\vec{j}$ should be independent of position in the system. That is, everywhere in the system, at all times, $\nabla \cdot \vec{j} = 0$, and in particular, $(\partial j_z/\partial z)_{x,y} = 0$, where j_z is the z-component of $\vec{j}$. During the normal operation of the MCE instrument, for $\vec{j}$ not equal to zero, j_z is expected to be the only nonzero component of $\vec{j}$.

(For detailed descriptions of system geometry and construction, plus methods to detect solute concentration as a function of vertical position, see the first three references listed at the end of this section.)

A flow of electrical current through the system in the MCE instrument results in a flow of mass (that of the membrane-permeant ions) into and out of the system. Furthermore, as an electrical current passes through the system, power is dissipated, and in the process of maintaining a constant system temperature (by such means as a re-circulating water bath or a Peltier system), heat flows from the system to the surroundings. (At the currents and ionic strengths used in MCE experiments, the resistive heating of the system is unlikely to tax the capacity of a surrounding heat sink to maintain a stable system temperature [Ridgeway et al., 1998; Godfrey, 1989; Laue et al., 1989].) Due to the current flowing through it, a system in the MCE instrument can never achieve equilibrium, but it can reach steady state. The appropriate thermodynamic description of such a system is one based on irreversible thermodynamics, the theoretical basis of which was greatly advanced by Onsager [1931a; 1931b].

The MCE system is composed of an implicitly treated solvent component, plus n solute components. Each solute component, k, is composed of n_k solute species. Applying the irreversible thermodynamic framework to this system, the net transport of matter within it can be described in terms of the total molar flow vector, $\vec{J}$, which, in turn, is described by

$$\vec{J} = \sum_{k=1}^{n} \vec{J}_k = \sum_{k=1}^{n} \sum_{e=1}^{n_k} \vec{J}_{k,e} = \sum_{k=1}^{n} \sum_{e=1}^{n_k} \frac{\vec{I}_{k,e}}{M_{k,e}} = \sum_{k=1}^{n} \sum_{e=1}^{n_k} \frac{c_{k,e} \vec{v}_{k,e}}{M_{k,e}},$$

(H2)

where $M_{k.e}$ is the molar mass, $c_{k.e}$ is the mass concentration, $\vec{I}_{k,e}$ is the mass flow vector, and $\vec{v}_{k,e}$ is the transport velocity vector of species e of solute component k.

It is assumed that the electrical fields present in the system are weak enough, and the thermal motion of each species is great enough, that, on average, all species of all components are randomly oriented. As a result, no net transport along the y- or x-axis is expected to result from forces directed along the z-axis, so that, in the absence of turbulent flow, $\vec{J}_{k,e}$ and $\vec{v}_{k,e}$ have no component along the y- or x-axis of the system. As no turbulent flows are expected in the normal operation of the MCE instrument, only the z-components of these vectors need to be considered. Thus, $\vec{J}_{k,e} = \hat{e}_z(J_{k,e})_z$, where $\hat{e}_z$ is the unit vector in the direction of the positive z-axis, and $(J_{k,e})_z$ is the z-component of $\vec{J}_{k,e}$.This allows the vector notation to be dropped, so that $J_{k,e} = (J_{k,e})_z$ can be used in place of $\vec{J}_{k,e}$. Similarly, $I_{k,e} = (I_{k,e})_z$ can be used in place of $\vec{I}_{k,e}$, and $v_{k,e} = (v_{k,e})_z$ can be used in place of $\vec{v}_{k,e}$.

Chemical potential gradients in any of the species, the electrical potential gradient acting on the charge of any of the species, the gravitational potential gradient acting on the mass of any of the species, and solvent flow determine $\vec{J}_{k,e}$. Chemical potential gradients in charged species are constrained by the requirement of charge neutrality [Onsager and Fuoss, 1932], which is described by

$$\sum_{k=1}^{n}\sum_{e=1}^{n_k}\frac{z_{k,e}c_{k,e}}{M_{k,e}} = 0\,,$$

(H3)

where $z_{k,e}$ is a signed parameter. Charge neutrality holds from macroscopic volumes down to some minimum volume that includes some minimum number of charged particles. Such minimum volumes can become electrostatically polarised by transport processes, however, giving rise to the electrophoretic/asymmetry effect.

Other than A, the most easily controlled variable in an MCE experiment is i, which is equal to the sum of the currents of all species. During an experiment, i is typically held constant with time.

Due to conservation of current, and because there are no sources or sinks of current within the system,$\nabla i = 0$ everywhere at all times in the system. Although i is a not a vector, $\vec{j}$, from which i is obtained, is. (See Equations H1 and H4.) In the MCE instrument, $\vec{j}$ has no component along the y- or x-axis of the system, so that $\vec{j}= \hat{e}_z j_z$. Thus, j can be used in place of the vector.

Provided that, as should be the case in the MCE instrument, each $\vec{J}_{k,e}$ is everywhere perpendicular to, and invariant with position over, the horizontal cross-section,

$$i = \int \vec{j} \cdot d\vec{S} = j \int_{y_0}^{\frac{\sqrt{A}}{\varsigma}+y_0} \int_{x_0}^{\varsigma\sqrt{A}+x_0} dxdy = jA = \frac{AF}{\Theta} \sum_{k=1}^{n} \sum_{e=1}^{n_k} z_{k,e} \frac{I_{k,e}}{M_{k,e}},$$

(H4)

where $d\vec{S}$ is a vector equal to $\vec{n}dS$. The magnitude, dS, is the differential element of cross-sectional surface area. The direction, $\vec{n}$, is the unit normal vector that is outwardly directed from dS. As $\vec{n}$ is everywhere equal to $\hat{e}_z$, and as $\vec{j}$ is everywhere equal to $\hat{e}_z j_z = \hat{e}_z j$, the integrand of Equation H4 is everywhere equal to $jdS = j$dxdy. In the upper limits of integration with respect to x and y, the cross-sectional scaling factor, ς, must be greater than 0 and less than infinity. The lower limits of integration with respect to x and y, x_0 and y_0, respectively, can be equated to zero.

(With L_x defined as the width of the system, and with L_y defined as the depth of the system, $A = L_x L_y$. With ς defined as $\sqrt{\frac{L_x}{L_y}}$, $\varsigma\sqrt{A} = L_x$ and $\frac{\sqrt{A}}{\varsigma} = L_y$. When, as is often the case in practice, L_x is equal to L_y, $\varsigma = 1$. Given that L_y is equal to the optical pathlength of Equation E1, it would be useful to have access to systems that are identical in all respects except L_y. Thus, there is some motivation to construct systems for which $\varsigma \neq 1$.)

The sum on the right-hand side of Equation H4 is taken over all species of all components.

The current carried by species e of component k is $i_{k,e} = (AF/\Theta)z_{k,e}I_{k,e}/M_{k,e}$. As each product, $z_{k,e}I_{k,e}$, is signed, each $i_{k,e}$ is a signed parameter. In the absence of overwhelming, opposing chemical potential gradients, species that differ with respect to the sign of $z_{k,e}$ will differ with respect to the sign of $I_{k,e}$. Consequently, when no such chemical potential gradients are present, the sign of $i_{k,e}$ is the same for all charged species.

The conductivity of the solution is described by

$$\kappa = \frac{F}{\Theta}\sum_{k=1}^{n}\sum_{e=1}^{n_k}\frac{z_{k,e}c_{k,e}u_{k,e}}{M_{k,e}},$$

(H5)

where $u_{k,e}$ is the electrophoretic mobility of species e of solute component k. Provided that E is everywhere perpendicular to A, and does not vary across A,

$$E = \frac{i}{A\kappa} + \frac{F}{\Theta\kappa}\sum_{k=1}^{n}\sum_{e=1}^{n_k}\frac{z_{k,e}D_{k,e}}{M_{k,e}}\left(\frac{\partial c_{k,e}}{\partial \xi}\right)_t,$$

(H6)

which result is obtained by substituting the expression for $I_{k,e}$ from Equation C4 into Equation H4, using $Eu_{k,e}$ in place of $\sigma_{k,e}D_{k,e}$, solving for E, and using Equation H5 to simplify the denominators on the right-hand side. Equation H6 holds even if κ varies with ξ.

In the MCE instrument, A, i and κ are exploited to control the electrical field, $\vec{E}$. In general,

$$\vec{E} = -\varpi\nabla\Psi,$$

(H7)

where Ψ is the electrical potential, and ϖ is a conversion constant. Both Ψ and $\vec{E}$ can be functions of spatial position and time. The design of the MCE instrument, however, results in ∇Ψ having no component along the y- or x-axis of the system. Consequently, $(\partial\Psi/\partial z)_{t,y,x} = \nabla\Psi_z$ and $E = E_z$ can be used in place of ∇Ψ and $\vec{E}$, respectively.

As A is fixed and i can be held constant, E varies with ξ as a function of κ, concentration gradients, and solute properties. (See Equation H6.) As κ is a function of the ionic strength of the solution, Γ, κ can be controlled to the extent that Γ can be controlled. In general, κ increases as Γ increases, but κ is not linearly proportional to Γ [Castellan, 1983]. For example, in a sufficiently dilute, aqueous solution of a uni-univalent salt at a fixed temperature, κ can be estimated by $\kappa = o_1\Gamma - o_2\Gamma^{3/2}$, which is a rearrangement of the Onsager equation. The coefficients o_1 and o_2 can be calculated [Castellan, 1983], or can be obtained by fitting experimentally determined conductivity data. As $d\kappa/d\Gamma = o_1 - 3o_2(\Gamma^{1/2})/2$, $d\kappa/d\Gamma$ is diminished from o_1 by $3o_2(\Gamma^{1/2})/2$. The source of this diminution is thought to be an increase in flow effects, and thus a decrease in the electrophoretic mobility of each ion, as Γ increases.

In the presence of membrane-confined components, when $i \neq 0$, Γ is likely to vary with ξ and t, resulting in variations of κ and E with ξ and t. Neglecting the second term on the right-hand side of Equation H6, E can be estimated by $E_{ref}\kappa_{ref}/\kappa$, where κ is a function of ξ and t, such that $\kappa_{ref} = \kappa$ at reference position ξ_{ref} and reference time t_{ref}. For steady-state experiments, infinite time, t_∞, is a practical reference time, in which case, at $\xi = \xi_{ref}$ and $t = t_\infty$, $E = E_{ref}$. (When the system is at steady state, the time elapsed since the start of the experiment can be considered to be t_∞.) For moving boundary experiments, the time at which current flow is started, $t_0 = 0$, is the most practical reference time, in which case, at $\xi = \xi_{ref}$ and $t = t_0$, $E = E_{ref}$. In either case, $E_{ref} \approx i/A\kappa_{ref}$, and any convenient reference position can be chosen for ξ_{ref}. In the simplest systems, Γ is not expected to vary significantly with ξ or t, with the result that, for all practical purposes, $\kappa \approx \kappa_{ref}$, and $E \approx E_{ref}$, at all ξ and all t.

Along gradients in Γ, liquid junction (diffusion) potentials can arise from local polarisation [Castellan, 1983]. The development of diffusion potentials would cause E to vary with ξ and t. In the case of a uni-univalent electrolyte, PX, for which the cation, P^+, and anion, X^-, have closely matched transference numbers, $v_{PX,P+}$ (the velocity of the cation) is approximately equal to $-v_{PX,X-}$, (-1 times the velocity of the anion). (Representing the transference number of current-carrying species e of component k by $\tau_{k,e}$, $v_{k,e} = i\tau_{k,e}M_{k,e}\Theta/FAz_{k,e}c_{k,e}$.) For such an electrolyte, little, if any, polarisation is expected to occur in the system [Castellan, 1983]. Also, for any electrolyte, such polarisation is minimised if the system is designed so that gradients in the mean ionic activity (the geometric mean of the individual ion activities) are negligible [Castellan, 1983].

(See Moody and Shepard, 2004, for a previous version of the material in this section).

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Section I: Calculating valence, molar mass, chemical potential and partial specific volume for a multi-species component

The molar mass of species e of component k is represented by $M_{k,e}$, the valence of species e of component k is represented by $z_{k,e}$, the chemical potential of species e of component k is represented by $\mu_{k,e}$, and the number of molecules of species e of component k is represented by $N_{k,e}$. The number of moles of species e of component k is equal to $N_{k,e}/N_A$, where N_A is Avogadro's number. Defining V as the volume within which the $N_{k,e}$ molecules are found, and representing the molar concentration of species e of component k by $m_{k,e}$, the relationship,

$$m_{k,e} = \frac{N_{k,e}}{N_A V} ,$$

(I1)

is obtained. The mass concentration of species e of component k is thus given by

$$c_{k,e} = M_{k,e} m_{k,e} .$$

(I2)

Letting n_k represent the number of species that constitute solute component k, and indexing the species by e, the number of molecules of all species of component k is given by

$$N_k = \sum_{e=1}^{n_k} N_{k,e} ,$$

(I3)

the total molar concentration of all species of component k is given by

$$(m_k)_{total} = \sum_{e=1}^{n_k} m_{k,e} ,$$

(I4)

and the mass concentration of all species of component k is given by

$$c_k = \sum_{e=1}^{n_k} c_{k,e} .$$

(I5)

The total molar flow of all species of solute component k is given by

$$\left(\vec{J}_k\right)_{total} = \sum_{e=1}^{n_k} \vec{J}_{k,e} = \sum_{e=1}^{n_k} m_{k,e}\vec{v}_{k,e} = (m_k)_{total}\frac{\sum_{e=1}^{n_k} m_{k,e}\vec{v}_{k,e}}{\sum_{e=1}^{n_k} m_{k,e}} = (m_k)_{total}\frac{\sum_{e=1}^{n_k}\frac{N_{k,e}}{N_A V}\vec{v}_{k,e}}{\sum_{e=1}^{n_k}\frac{N_{k,e}}{N_A V}}$$

$$= (m_k)_{total}\frac{\sum_{e=1}^{n_k} N_{k,e}\vec{v}_{k,e}}{\sum_{e=1}^{n_k} N_{k,e}} = (m_k)_{total}(\vec{v}_k)_N\,,$$

(I6)

where $\vec{v}_{k,e}$ is the velocity of species e of component k in the system frame of reference, $(\vec{v}_k)_N$ is the number-average velocity for all species of component k in the system frame of reference, and use has been made of the definition of a component's molar flow as the product of its molar concentration and its velocity in the system frame of reference, which for component k is denoted as $\vec{v}_k$.

The total molar concentration of all species of component k can be expressed as

$$(m_k)_{total} = \sum_{e=1}^{n_k} m_{k,e} = \sum_{e=1}^{n_k}\frac{c_{k,e}}{M_{k,e}} = c_k\frac{\sum_{e=1}^{n_k}\frac{c_{k,e}}{M_{k,e}}}{\sum_{e=1}^{n_k} c_{k,e}} = \frac{c_k}{(M_k)_N}\,,$$

(I7)

where $(M_k)_N$ is the number-average molar mass for all species of component k, so that

$$\left(\vec{J}_k\right)_{total} = (m_k)_{total}(\vec{v}_k)_N = \frac{c_k(\vec{v}_k)_N}{(M_k)_N}\,.$$

(I8)

Similarly, the mass flow of solute component k can be related to the mass and molar flows of all species of component k by

$$\vec{I}_k = \sum_{e=1}^{n_k}\vec{I}_{k,e} = \sum_{e=1}^{n_k} M_{k,e}\vec{J}_{k,e} = \sum_{e=1}^{n_k} c_{k,e}\vec{v}_{k,e} = c_k\frac{\sum_{e=1}^{n_k} c_{k,e}\vec{v}_{k,e}}{\sum_{e=1}^{n_k} c_{k,e}} = c_k(\vec{v}_k)_w\,,$$

(I9)

where $(v_k)_w$ is the weight-average velocity for all species of component k, and use has been made of the definition of a component's mass flow as the product of its mass concentration and its velocity in the system frame of reference. $\left(\vec{J}_k\right)_{total}$ is now defined as $\vec{J}_k$, the molar flow of component k, and from the previous two equations, the relationship between $\vec{I}_k$ and $\vec{J}_k$ is given by

$$\vec{I}_k = c_k(\vec{v}_k)_w = c_k(\vec{v}_k)_N \frac{(\vec{v}_k)_w}{(\vec{v}_k)_N} = (M_k)_N \frac{(\vec{v}_k)_w}{(\vec{v}_k)_N} \vec{J}_k = (M_k)_X \vec{J}_k \,,$$

(I10)

where $(M_k)_X$ is the coefficient needed to convert from the molar flow of component k to the mass flow of component k. Solving Equation I10 for $(M_k)_X$ in terms of the mass and molar flows of component k yields

$$(M_k)_X = \frac{\vec{I}_k}{\vec{J}_k} \,.$$

(I11)

Using Equation I9 to express $\vec{I}_k$ as the sum of all $M_{k,e}\vec{J}_{k,e}$ of component k results in

$$(M_k)_X = \frac{\vec{I}_k}{\vec{J}_k} = \frac{\sum_{e=1}^{n_k} M_{k,e}\vec{J}_{k,e}}{\vec{J}_k} = \frac{\sum_{e=1}^{n_k} M_{k,e}\vec{J}_{k,e}}{\sum_{e=1}^{n_k} \vec{J}_{k,e}} = (M_k)_J \,,$$

(I12)

where $(M_k)_J$ is the molar-flow-average molar mass of solute component k. This equation is undefined for the case of $\vec{J}_k = 0$, but the limit as $\vec{J}_k$ approaches zero, the limit as all $\vec{J}_{k,e}$ approach zero, or the limit as all $\vec{v}_{k,e}$ approach zero, can be used to evaluate $(M_k)_J$ in these zero-flow-in-component-k cases.

As

$$(M_k)_J = \frac{\sum_{e=1}^{n_k} M_{k,e}\vec{J}_{k,e}}{\sum_{e=1}^{n_k} \vec{J}_{k,e}} = \frac{\sum_{e=1}^{n_k} M_{k,e} m_{k,e} \vec{v}_{k,e}}{\sum_{e=1}^{n_k} m_{k,e} \vec{v}_{k,e}} \,,$$

(I13)

the limit as the velocity of each species of solute component k approaches zero is

$$\lim_{all\ \vec{v}_{k,e} \to 0} (M_k)_J = \lim_{all\ \vec{v}_{k,e} \to 0} \frac{\sum_{e=1}^{n_k} M_{k,e} m_{k,e} \vec{v}_{k,e}}{\sum_{e=1}^{n_k} m_{k,e} \vec{v}_{k,e}} = \frac{\sum_{e=1}^{n_k} M_{k,e} m_{k,e}}{\sum_{e=1}^{n_k} m_{k,e}} = (M_k)_N \,,$$

(I14)

which is the number-average molar mass of solute component k. As $(M_k)_J$ is simpler to describe than its equivalent, $(M_k)_X$, $(M_k)_J$ is used in the definitions of D_k, u_k and I_k in Section A.

Equations A1, A2, I10 and I12 can be combined to yield

$$\vec{I}_k = (M_k)_J \left[\sum_{q=1}^{n} L_{k,q} \vec{X}_q + \frac{c_k}{M_k} \vec{v}_0 \right] = (M_k)_J \left[\sum_{q=1}^{n} L_{k,q} \left(-M_q g_E \nabla h - z_q F \nabla \Psi - \nabla \mu_q \right) + \frac{c_k}{M_k} \vec{v}_0 \right].$$

(I15)

Using Equation A2, the gradient of the total molar potential of solute component q can be written as

$$\nabla U_q = -\vec{X}_q = -\left(-M_q \nabla g_E h - z_q F \nabla \Psi - \nabla \mu_q \right),$$

(I16)

in which $\vec{X}_q$ is the conjugate molar force (Equations A2 and A14a) of component q.

As U_q is a molar quantity, it can be calculated from the number average of its species-specific parts. Thus,

$$\begin{aligned} U_q &= \frac{\sum_{a=1}^{n_q} m_{q,a} U_{q,a}}{\sum_{a=1}^{n_q} m_{q,a}} = \frac{\sum_{a=1}^{n_q} N_{q,a} U_{q,a}}{\sum_{a=1}^{n_q} N_{q,a}} \\ &= \frac{\sum_{a=1}^{n_q} N_{q,a} \mu_{q,a}}{\sum_{a=1}^{n_q} N_{q,a}} + F\Psi \frac{\sum_{a=1}^{n_q} N_{q,a} z_{q,a}}{\sum_{a=1}^{n_q} N_{q,a}} + g_E h \frac{\sum_{a=1}^{n_q} N_{q,a} M_{q,a}}{\sum_{a=1}^{n_q} N_{q,a}} \\ &= \left(\mu_q\right)_N + F\Psi\left(z_q\right)_N + g_E h \left(M_q\right)_N, \end{aligned}$$

(I17)

where the n_q species of component q are indexed by a, so that, for species a of component q, $U_{q,a}$, $\mu_{q,a}$, $M_{q,a}$ and $z_{q,a}$ are, respectively, the total molar potential, the chemical potential, the molar mass, and the valence; while for component q, U_q, $(\mu_q)_N$, $(M_q)_N$ and $(z_q)_N$ are, respectively, the number average of the total molar potential, the number average of the chemical potential, the number average of the molar mass, and the number average of the valence, with each number average being for all species of component q. (Equation M21 shows $(z_q)_N$.)

As noted with respect to Equation H3, charge neutrality holds from macroscopic volumes down to some minimum volume that includes some minimum number of charged particles. Based on an expectation of charge neutrality except at fairly small spatial scales, then, for each charged species of component q, there must be one or more oppositely charged species of component q such that $(z_q)_N = 0$ in Equation I17, and, it could be argued, in general. As also noted with respect to Equation H3, however, the minimum volumes that are charge-neutral in the absence of transport processes can become electrostatically polarised in the presence of transport processes. Such polarisation gives rise to the electrophoretic/asymmetry effect, and it argued here, without proof, that where the electrophoretic/asymmetry effect is present, it is possible that $|(z_q)_N| > 0$. (Conditions in which $(z_q)_N$ can be nonzero examined more deeply in **Section M: Effects of ionic strength on (apparent) reduced valence and zeta potential.**)

In what follows, $(\nabla z_q)_N$ is the number-average gradient of the valence for all species of component q (Equation M25), $(\nabla M_q)_N$ is the number-average gradient of the molar mass for all species of component q, and $(\nabla \mu_q)_N$ is the number-average gradient of the chemical potential for all species of component q.

If each $N_{q,a}$ were invariant with space, each $\nabla N_{q,a}$ would equal zero everywhere, in which case, throughout the system, $\nabla(z_q)_N$ (Equation M24) would equal $(\nabla z_q)_N = 0$, $\nabla(M_q)_N$ would equal $(\nabla M_q)_N = 0$, and $\nabla(\mu_q)_N$ would equal $(\nabla \mu_q)_N$. This result holds for any value of n_q. For the special case of $n_q = 1$, at each point in space, there is only one $\nabla N_{q,a}$, and regardless of whether $\nabla N_{q,a}$ equals zero, $\nabla(z_q)_N = (\nabla z_q)_N = 0$, $\nabla(M_q)_N = (\nabla M_q)_N = 0$, and $\nabla(\mu_q)_N = (\nabla \mu_q)_N$. When $n_q = 1$, charge neutrality also requires that $z_q = 0$.

Without assuming that each $\nabla N_{q,a}$ is equal to zero, the gradient of the total molar potential of solute component q must be expressed in a more general form, such as

$$\nabla U_q = \sum_{a=1}^{n_q} \nabla U_{q,a} = -\sum_{a=1}^{n_q} \vec{X}_{q,a}$$

$$= \nabla(\mu_q)_N + (z_q)_N F \nabla \Psi + F \Psi \nabla (z_q)_N + (M_q)_N \nabla g_E h + g_E h \nabla (M_q)_N ,$$

(I18)

where $\vec{X}_{q,a}$ denotes the conjugate molar force of species a of component q. Defining a gradient-modified-average molar mass for all species of component q as

$$\left(M_q\right)_g = \frac{\left(M_q\right)_N \nabla g_E h + g_E h \nabla \left(M_q\right)_N}{\nabla g_E h} ,$$

(I19a)

and defining a gradient-modified-average valence for all species of component q as

$$\left(z_q\right)_g = \frac{\left(z_q\right)_N F \nabla \Psi + F \Psi \nabla \left(z_q\right)_N}{F \nabla \Psi} ,$$

(I19b)

the gradient of the total molar potential of solute component q becomes

$$\nabla U_q = \nabla \left(\mu_q\right)_N + \left(z_q\right)_g F \nabla \Psi + \left(M_q\right)_g \nabla g_E h .$$

(I20)

A comparison of Equations A2 and I20 shows that $\nabla\mu_q = \nabla(\mu_q)_N$, $z_q = (z_q)_g$ and $M_q = (M_q)_g$. Equation I19a shows that

$$\lim_{\nabla\left(M_q\right)_N \longrightarrow 0} \left(M_q\right)_g = \left(M_q\right)_N ,$$

(I21a)

and Equation I19b (of which Equation M23 is an alternative form) shows that

$$\lim_{\nabla\left(z_q\right)_N \longrightarrow 0} \left(z_q\right)_g = \left(z_q\right)_N .$$

(I21b)

These results are a consequence of

$$\lim_{\text{all } \nabla N_{q,a} \longrightarrow 0} \nabla \left(M_q\right)_N = \lim_{\text{all } \nabla N_{q,a} \longrightarrow 0} \nabla \left(\frac{\sum_{a=1}^{n_q} N_{q,a} M_{q,a}}{\sum_{a=1}^{n_q} N_{q,a}} \right) = \lim_{\text{all } \nabla N_{q,a} \longrightarrow 0} \frac{\sum_{a=1}^{n_q} N_{q,a} \nabla M_{q,a}}{\sum_{a=1}^{n_q} N_{q,a}} = 0 ,$$

(I22a)

and

$$\lim_{\text{all } \nabla N_{q,a} \rightarrow 0} \nabla \left(z_q\right)_N = \lim_{\text{all } \nabla N_{q,a} \rightarrow 0} \nabla \left(\frac{\sum_{a=1}^{n_q} N_{q,a} z_{q,a}}{\sum_{a=1}^{n_q} N_{q,a}} \right) = \lim_{\text{all } \nabla N_{q,a} \rightarrow 0} \frac{\sum_{a=1}^{n_q} N_{q,a} \nabla z_{q,a}}{\sum_{a=1}^{n_q} N_{q,a}} = 0 ,$$

(I22b)

which, as described previously, are applicable for any value of n_q. For the case of $n_q = 1$,

$\nabla(z_q)_N$ and $\nabla(M_q)_N$ are always equal to zero.

In contrast,

$$\lim_{\text{all } \nabla N_{q,a} \to 0} \nabla\left(\mu_q\right)_N = \lim_{\text{all } \nabla N_{q,a} \to 0} \nabla\left(\frac{\sum_{a=1}^{n_q} N_{q,a}\mu_{q,a}}{\sum_{a=1}^{n_q} N_{q,a}}\right) = \lim_{\text{all } \nabla N_{q,a} \to 0} \frac{\sum_{a=1}^{n_q} N_{q,a}\nabla\mu_{q,a}}{\sum_{a=1}^{n_q} N_{q,a}} = \left(\nabla\mu_q\right)_N ,$$

(I23)

which reflects the fact that, even when each $\nabla N_{q,a}$ equals zero, under some conditions, some or all $\nabla\mu_{q,a}$ may differ from zero, as a result of which, $(\nabla\mu_q)_N$ may also differ from zero. (For example, concentration gradients in components other than q may result in $(\nabla\mu_q)_N$ being nonzero despite all $\nabla N_{q,a}$ being equal to zero.) Equation I23 is applicable for any value of n_q. For the case of $n_q = 1$, $\nabla(\mu_q)_N$ is always equal to $(\nabla\mu_q)_N$.

In addition to its utility in Equation A2, the description of $\nabla\mu_q$ as $\nabla(\mu_q)_N$ is directly applicable to Equations A5 to A14, and thence, to every subsequent description of the continuity equation. The derivation of Equation A5 from $\nabla\mu_q$ begins with

$$\nabla\left(\mu_q\right)_N = \nabla\mu_q = \left(\frac{\partial\mu_q}{\partial\xi}\right)_t$$
$$= \left(\frac{\partial\mu_q}{\partial T}\right)_{t,P,c}\left(\frac{\partial T}{\partial\xi}\right)_t + \left(\frac{\partial\mu_q}{\partial P}\right)_{t,T,c}\left(\frac{\partial P}{\partial\xi}\right)_t + \sum_{w=1}^{n}\left(\frac{\partial\mu_q}{\partial c_w}\right)_{t,T,P,c_{q\neq w}}\left(\frac{\partial c_w}{\partial\xi}\right)_t ,$$

(I24)

where gradients in dimensions other than ξ are assumed equal to zero. As $\left(\frac{\partial T}{\partial\xi}\right)_t$ is assumed to equal zero, the product, $\left(\frac{\partial\mu_q}{\partial T}\right)_{t,P,c}\left(\frac{\partial T}{\partial\xi}\right)_t = 0$. Furthermore, as each $\left(\frac{\partial\mu_q}{\partial c_w}\right)_{t,T,P,c_{q\neq w}}\left(\frac{\partial c_w}{\partial\xi}\right)_t$ is adequately treated in terms of component concentrations and activity coefficients (Equation A12), it is not necessary to expand these parts of Equation I24 in terms of all the $N_{q,a}$ and $\mu_{q,a}$ parameters that comprise $(\mu_q)_N$. Thus, the only part of Equation I24 that must be dealt with in fully expanded form is

$$\left(\frac{\partial \mu_q}{\partial P}\right)_{t,T,c}\left(\frac{\partial P}{\partial \xi}\right)_t = \left(\frac{\partial \left(\mu_q\right)_N}{\partial P}\right)_{t,T,c}\left(\frac{\partial P}{\partial \xi}\right)_t = \left(\frac{\partial\left[\frac{\sum_{a=1}^{n_q} N_{q,a}\mu_{q,a}}{\sum_{a=1}^{n_q} N_{q,a}}\right]}{\partial P}\right)_{t,T,c}\left(\frac{\partial P}{\partial \xi}\right)_t$$

$$= \left\{\frac{\sum_{a=1}^{n_q} N_{q,a}\left(\frac{\partial \mu_{q,a}}{\partial P}\right)_{t,T,c}}{\sum_{a=1}^{n_q} N_{q,a}} + \frac{\sum_{a=1}^{n_q} \mu_{q,a}\left(\frac{\partial N_{q,a}}{\partial P}\right)_{t,T,c}}{\sum_{a=1}^{n_q} N_{q,a}}\right.$$

$$\left. - \left(\mu_q\right)_N\left[\frac{\sum_{a=1}^{n_q}\left(\frac{\partial N_{q,a}}{\partial P}\right)_{t,T,c}}{\sum_{a=1}^{n_q} N_{q,a}}\right]\right\}\left(\frac{\partial P}{\partial \xi}\right)_t$$

$$= \left\{\left(M_q\bar{v}_q\right)_N + \left[\left(\mu_q\right)_P - \left(\mu_q\right)_N\right]\left(\frac{\partial lnN_q}{\partial P}\right)_{t,T,c}\right\}\left(\frac{\partial P}{\partial \xi}\right)_t,$$

(I25)

where:

$$\left(M_q\bar{v}_q\right)_N = \left[\left(\frac{\partial \mu_q}{\partial P}\right)_{t,T,c}\right]_N = \frac{\sum_{a=1}^{n_q} N_{q,a}\left(\frac{\partial \mu_{q,a}}{\partial P}\right)_{t,T,c}}{\sum_{a=1}^{n_q} N_{q,a}} = \frac{\sum_{a=1}^{n_q} N_{q,a}M_{q,a}\bar{v}_{q,a}}{\sum_{a=1}^{n_q} N_{q,a}}$$

(I26)

is the number average of the product, $M_{q,a}\bar{v}_{q,a}$, for all species of component q, with $\bar{v}_{q,a}$ being the partial specific volume of the system with respect to species a of solute component q;

$$\left(\mu_q\right)_P = \frac{\sum_{a=1}^{n_q} \mu_{q,a}\left(\frac{\partial N_{q,a}}{\partial P}\right)_{t,T,c}}{\sum_{a=1}^{n_q}\left(\frac{\partial N_{q,a}}{\partial P}\right)_{t,T,c}}$$

(I27)

is defined as the pressure-gradient average of μ_q;

$$\left(\frac{\partial lnN_q}{\partial P}\right)_{t,T,c} = \frac{\left(\frac{\partial N_q}{\partial P}\right)_{t,T,c}}{N_q} = \frac{\sum_{a=1}^{n_q}\left(\frac{\partial N_{q,a}}{\partial P}\right)_{t,T,c}}{\sum_{a=1}^{n_q} N_{q,a}}\ ;$$

(I28)

and $(\mu_q)_N$ is previously defined. Using $(M_q)_g$ to define

$$\left(\bar{v}_q\right)_{Pg} = \frac{\left(M_q \bar{v}_q\right)_N + \left[\left(\mu_q\right)_P - \left(\mu_q\right)_N\right]\left(\frac{\partial lnN_q}{\partial P}\right)_{t,T,c}}{\left(M_q\right)_g},$$

(I29)

which is a pressure-and-gradient-modified-average partial specific volume of the system with respect to component q, permits $\left(\frac{\partial \mu_q}{\partial P}\right)_{t,T,c}\left(\frac{\partial P}{\partial \xi}\right)_t$ to be described as

$$\left(\frac{\partial \mu_q}{\partial P}\right)_{t,T,c}\left(\frac{\partial P}{\partial \xi}\right)_t = \left\{\left(M_q \bar{v}_q\right)_N + \left[\left(\mu_q\right)_P - \left(\mu_q\right)_N\right]\left(\frac{\partial lnN_q}{\partial P}\right)_{t,T,c}\right\}\left(\frac{\partial P}{\partial \xi}\right)_t = \left(M_q\right)_g \left(\bar{v}_q\right)_{Pg}\left(\frac{\partial P}{\partial \xi}\right)_t.$$

(I30)

Section J: Form of the general solution from Equation C32

The solution to the continuity equation for MCE can be written as

$$\sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}\sum_{i=1}^{N} c_{k,e,h+}\left(\int_{\xi_m}^{\xi_b} P_h P_i d\xi - \sum_{j=1}^{N}\left[\sigma_{k,e,j+} D_{k,e,j+}\int_{\xi_m}^{\xi_b} P_j P_h \frac{dP_i}{d\xi} d\xi - D_{k,e,j+}\int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi}\frac{dP_i}{d\xi} d\xi\right]\Delta t\right)$$
$$= \sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}\sum_{i=1}^{N} c_{k,e,h-}\left(\int_{\xi_m}^{\xi_b} P_h P_i d\xi + \sum_{j=1}^{N}\left[\sigma_{k,e,j-} D_{k,e,j-}\int_{\xi_m}^{\xi_b} P_j P_h \frac{dP_i}{d\xi} d\xi - D_{k,e,j-}\int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi}\frac{dP_i}{d\xi} d\xi\right]\Delta t\right).$$

(J1, from Equation C32)

General virial expansions of the transport coefficients can be defined as

$$\sigma_{k,e,j-} = \sigma^{\circ}{}_{k,e,j-}\left(\frac{\sum_{b=1}^{\infty}\sum_{q=1}^{n}\sum_{a=1}^{n_q} p_{b,k,e,q,a}\frac{dc_{q,a,j-}{}^{b}}{dc_{q,a,j-}}}{\sum_{b=1}^{\infty}\sum_{q=1}^{n}\sum_{a=1}^{n_q} y_{b,k,e,q,a}\frac{dc_{q,a,j-}{}^{b}}{dc_{q,a,j-}}}\right)$$

(J2)

and

$$D_{k,e,j-} = D^{\circ}{}_{k,e,j-}\left(\frac{\sum_{b=1}^{\infty}\sum_{q=1}^{n}\sum_{a=1}^{n_q} y_{b,k,e,q,a}\,\frac{dc_{q,a,j-}{}^{b}}{dc_{q,a,j-}}}{\sum_{b=1}^{\infty}\sum_{q=1}^{n}\sum_{a=1}^{n_q} h_{b,k,e,q,a}\,\frac{dc_{q,a,j-}{}^{b}}{dc_{q,a,j-}}}\right),$$

(J3)

for time t, while for time [t + Δt], they can be defined as

$$\sigma_{k,e,j+} = \sigma^{\circ}{}_{k,e,j+}\left(\frac{\sum_{b=1}^{\infty}\sum_{q=1}^{n}\sum_{a=1}^{n_q} p_{b,k,e,q,a}\,\frac{dc_{q,a,j+}{}^{b}}{dc_{q,a,j+}}}{\sum_{b=1}^{\infty}\sum_{q=1}^{n}\sum_{a=1}^{n_q} y_{b,k,e,q,a}\,\frac{dc_{q,a,j+}{}^{b}}{dc_{q,a,j+}}}\right)$$

(J4)

and

$$D_{k,e,j+} = D^{\circ}{}_{k,e,j+}\left(\frac{\sum_{b=1}^{\infty}\sum_{q=1}^{n}\sum_{a=1}^{n_q} y_{b,k,e,q,a}\,\frac{dc_{q,a,j+}{}^{b}}{dc_{q,a,j+}}}{\sum_{b=1}^{\infty}\sum_{q=1}^{n}\sum_{a=1}^{n_q} h_{b,k,e,q,a}\,\frac{dc_{q,a,j+}{}^{b}}{dc_{q,a,j+}}}\right),$$

(J5)

where n is the number of solute components, n_q is the number of species that constitute solute component q, $D^{\circ}{}_{k,e,j-}$ at all ξ equals $D_{k,e}$ at ξ_j at time t in the limit as c approaches 0, $D^{\circ}{}_{k,e,j+}$ at all ξ equals $D_{k,e}$ at ξ_j at time [t + Δt] in the limit as c approaches 0, $\sigma^{\circ}{}_{k,e,j-}$ at all ξ equals $\sigma_{k,e}$ at ξ_j at time t in the limit as c approaches 0, $\sigma^{\circ}{}_{k,e,j+}$ at all ξ equals $\sigma_{k,e}$ at ξ_j at time [t + Δt] in the limit as c approaches 0, $c_{q,a,j-}$ is the ξ-independent concentration coefficient of species a of solute component q at time t, $c_{q,a,j+}$ is the ξ-independent concentration coefficient of species a of solute component q at time [t + Δt], and where $p_{b,k,e,q,a}$, $y_{b,k,e,q,a}$ and $h_{b,k,e,q,a}$ are the b^{th} of up to an infinite number of species-e-of-component-k affecting electrophoretic/asymmetry, thermodynamic nonideality, and viscosity coefficients, respectively. By definition, $\sum_{q=1}^{n}\sum_{a=1}^{n_q} p_{1,k,e,q,a}$, $\sum_{q=1}^{n}\sum_{a=1}^{n_q} y_{1,k,e,q,a}$ and $\sum_{q=1}^{n}\sum_{a=1}^{n_q} h_{1,k,e,q,a}$ are each equal to 1. (See Section D for the component-based equivalents of these virial expansions.)

Henceforth, $c_{q,a}$ is used to denote the concentration of species a of solute component q at either time t or time [t + Δt], and some unspecified position, ξ_j.

Individually, the product of $b(c_{q,a})^{b-1}$ with the corresponding coefficient of proportionality $p_{b,k,e,q,a}$ yields the bth term for the contribution of $c_{q,a}$ to the electrophoretic/asymmetry effect of the system as it affects the transport of species e of component k, the product of $b(c_{q,a})^{b-1}$ with the corresponding coefficient of proportionality $y_{b,k,e,q,a}$ yields the bth term for the contribution of $c_{q,a}$ to the thermodynamic nonideality of the system as it affects the transport of species e of component k, and the product of $b(c_{q,a})^{b-1}$ with the corresponding coefficient of proportionality $h_{b,k,e,q,a}$ yields the bth term for the contribution of $c_{q,a}$ to the viscosity of the system as it affects the transport of species e of component k, where $b(c_{q,a})^{b-1} = d(c_{q,a})^{b}/dc_{q,a}$.

Collectively, the sum of products given by $\sum_{b=2}^{\infty}\sum_{a=1}^{n_q} p_{b,k,e,q,a} b {c_{q,a}}^{b-1}$ is a measure of the total contribution of $c_{q,a}$ to the electrophoretic/asymmetry effect of the system as it affects the transport of species e of component k, the sum of products given by $\sum_{b=2}^{\infty}\sum_{a=1}^{n_q} y_{b,k,e,q,a} b {c_{q,a}}^{b-1}$ is a measure of the total contribution of $c_{q,a}$ to the thermodynamic nonideality of the system as it affects the transport of species e of component k, and the sum of products given by $\sum_{b=2}^{\infty}\sum_{a=1}^{n_q} h_{b,k,e,q,a} b {c_{q,a}}^{b-1}$ is a measure of the total contribution of $c_{q,a}$ to the viscosity of the system as it affects the transport of species e of component k.

In writing Equations J2 to J5, it was assumed that $\Delta p_{b,k,e,q,a}/\Delta j = 0$, $\Delta y_{b,k,e,q,a}/\Delta j = 0$ and $\Delta h_{b,k,e,q,a}/\Delta j = 0$ for any given pair of species e and a of their respective components k and q, even in the case of solvent compressibility. If required to deal adequately with the case of solvent compressibility, $p_{b,k,e,q,a}$, $y_{b,k,e,q,a}$ and $h_{b,k,e,q,a}$ can be replaced with their respective j-and t-dependent coefficients, which would be $p_{b,k,e,q,a,j-}$, $y_{b,k,e,q,a,j-}$ and $h_{b,k,e,q,a,j-}$ at time t, and would be $p_{b,k,e,q,a,j+}$, $y_{b,k,e,q,a,j+}$ and $h_{b,k,e,q,a,j+}$ at time [t + Δt], where, denoting a coefficient at either time by dropping the – or + suffix, $\Delta p_{b,k,e,q,a,j}/\Delta j \neq 0$, $\Delta y_{b,k,e,q,a,j}/\Delta j \neq 0$ and $\Delta h_{b,k,e,q,a,j}/\Delta j \neq 0$ for any given pair of species e and a of their respective components k and q.

In the general solution, Equation J1 is solved iteratively as follows:

1. Using $c_{k,e,h-}$ for $c_{q,a,j+}$ (where k = q, e = a and h = j) in Equations J4 and J5, the second approximate solution (Section C) is used to calculate all $(c_{k,e,h+})_0$, which are the initial approximations of the true $c_{k,e,h+}$ values;
2. Using $(c_{k,e,h+})_0$ for $c_{q,a,j+}$ (where k = q, e = a and h = j) in Equations J4 and J5, the second approximate solution (Section C) is used to calculate all $(c_{k,e,h+})_1$, which are the first approximations of the true $c_{k,e,j+}$ values that can be tested against an acceptance criterion of convergence (see Equation J6, below);
3. Step 2 is iterated until the acceptance criterion of convergence (Equation J6) is met, so that, at iteration m, using $(c_{k,e,h+})_{m-1}$ for $c_{q,a,j+}$ (where k = q, e = a and h = j) in Equations J4 and J5, the second approximate solution (Section C) is used to calculate all $(c_{k,e,h+})_m$, which are the m^th^ approximations of the true $c_{k,e,h+}$ values that can be tested against an acceptance criterion of convergence (Equation J6).

An example of an acceptance criterion of convergence would be a chosen value of Ξ_{min}, which is repeatedly compared against

$$\Xi_m = \frac{\sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}\left\{\left[\left(c_{k,e,h+}\right)_m - \left(c_{k,e,h+}\right)_{m-1}\right]\frac{V_h}{V}\right\}^2}{\left(\sum_{k=1}^{n}\sum_{e=1}^{n_k}\sum_{h=1}^{N}\frac{V_h}{V}c_{k,e,h-}\right)^2} = \frac{(c_{RSS})_m}{(c_-)^2},$$

(J6)

where $(c_{RSS})_m$ is the residual sum of squares for the final total solute concentration at iteration m relative to iteration (m - 1), V_h is the volume of spatial element h, V is the total solution volume, and $(c_-)^2$ is the square of the initial (time t) total solute concentration. (With the width of the system given by Δx, the depth of the spatial element given by Δy, and the length of the spatial element given by $\Delta\xi_h = (\Delta\xi_{h-} + \Delta\xi_{h+})/2$ (see Equations B54 to B57, and let $\Delta\xi_{1-} = \Delta\xi_{N+} = 0$), $V_h = (\Delta x)(\Delta y)\Delta\xi_h$, where ξ is the vertical coordinate, and x and y are the planar coordinates of the system, which has the geometry of a rectangular cuboid.) The squared raw sum of all initial solute mass values is identical to $V(c_-)^2$. Convergence is considered to be adequate if $\Xi_m \leq \Xi_{min}$. Once this convergence criterion is met, $(c_{k,e,h+})_m$ is considered to be equal to $c_{k,e,h+}$.

Section K: Reaction flow algorithms

Notation and other common features

An iterative process is used to calculate the concentrations of solutes that participate in each chemical reaction, a/g. As noted in the discussion preceding Equation G12, reaction a/g is defined as the sole explicit reaction that produces species a of component g. In addition to the restriction of just one product species per reaction, the algorithms presented here are restricted to just 1 or 2 reactants per reaction.

The constraint of just one reaction per product could be cheated by giving identical characteristics to multiple species of a component, and summing the concentrations of the identical species, each of which is the product of a unique reaction. In principle, it should also be possible to model more complicated reactions by linking multiple reactions. (For example, if two reactions share one product, the shared product could be considered an intermediate, and the reactants of the second reaction could be viewed as the ultimate products of the first reaction.) The algorithms presented here are not well optimised for linked reactions, however.

Throughout this section, the concentration, activity coefficient and molar mass of species e of solute component k are denoted as $c_{k,e}$, $\gamma_{k,e}$ and $M_{k,e}$, respectively. As with the definition of reaction a/g, much of the reaction-specific notation here follows that of Section G. Thus, $k_{f,g,a}$ is the forward rate constant (hence the subscript f) and $k_{r,g,a}$ is the reverse rate constant (hence the subscript r) of reaction a/g. Additionally, $\nu_{X,g,a,k,e}$ is the stoichiometry of species e of component k in reaction a/g, where X = R if species e of component k is a reactant, and X

= P if species e of component k is a product. As in Section G, the reactant stoichiometries are negatively signed, and the product stoichiometries are positively signed. (See Equations G13 and G16.)

As there is only one product per reaction, it must consist solely of species a of component g. Thus, the stoichiometry of the product species is $\nu_{P,g,a,g,a}$, and $\nu_{P,g,a,g,a}$ is the only nonzero product stoichiometry of reaction a/g. By the convention adopted in Section G, the species index is greater than 1 for any higher-order species, and as the product is a higher-order species by definition, $a > 1$. (See the discussion preceding Equation G12, where the simplest species of each component is assigned the lowest number, 1, of the species index.) The concentration, activity coefficient and molar mass of the product are denoted as $c_{g,a}$, $\gamma_{g,a}$ and $M_{g,a}$, respectively.

A minimum of one reactant must be something other than species a of component g. Thus, one reactant species is denoted as species r1 of component g, where r1 may equal 1, but r1 cannot equal a. The stoichiometry of reactant species r1 of component g in reaction a/g is $\nu_{R,g,a,g,r1}$. The concentration, activity coefficient and molar mass of species r1 of component g are denoted as $c_{g,r1}$, $\gamma_{g,r1}$ and $M_{g,r1}$, respectively.

There may be a second reactant species, which could be any species other than species a or species r1 of component g. If present, then, the second reactant species is denoted as species r2 of component q. If $q \neq g$, r2 may be any species of component q. If $q = g$, however, r2 cannot equal r1 or a. The stoichiometry of reactant species r2 of component q in reaction a/g is $\nu_{R,g,a,q,r2}$. The concentration, activity coefficient and molar mass of species r2 of component q are denoted as $c_{q,r2}$, $\gamma_{q,r2}$ and $M_{q,r2}$, respectively.

In typical usage, each stoichiometry is integral, but integral values are not required for the algorithms. As currently implemented [Moody, 2012a; Moody, 2012b], $\gamma_{k,e}$ is always equal to 1 in all reaction flow calculations. To show how to work with values of $\gamma_{k,e}$ other than 1, however, $\gamma_{k,e}$ is retained in many of the expressions presented here. Similarly, to present the most general case possible, some of the expressions shown are applicable to reactions in which more than 2 reactants form more than 1 product.

The minimum number of iterations is equal to the total number of reactant stoichiometries, ν_{total}, for which $\nu_{R,g,a,k,e} \neq 0$. (See Equation G12.) Thus, at each spatial element, ξ_h (Equation B36), for each time increment, Δt_ε (Equation B35), the flow of each reaction, a/g, is calculated at least ν_{total} times. In each of the ν_{total} iterations, the reaction flow throughout the system is calculated for all reactions. Additionally, in each of the ν_{total} iterations, the flow of reaction a/g at each ξ_h is calculated $R_{a/g}$ times, where $R_{a/g}$ is the total number of all reactant species for reaction a/g. (With the algorithms restricted to a two-reactant maximum, $R_{a/g}$ is either 1 or 2.)

In general, $R_{a/g} \leq \nu_{\text{total}}$. If there is more than one reaction, $R_{a/g} < \nu_{\text{total}}$. Where multiple reactions are present, the order in which their reaction flows are calculated may affect the outcome. The multiple iterations of the full sequence of reaction flow calculations within Δt_ε are meant to minimise such order-specific effects. Toward that end, where possible, species indices are chosen to ensure that the $R_{a/g}$ iterations of a given reaction are not consecutive. (The $R_{a/g}$ iterations will be consecutive if the species indices of the corresponding reactants do not encompass the species index of a reactant from another reaction. Conventions adopted for the species index, e, are described in the discussion preceding Equation G12.)

Mass conservation

The total concentration of all species of reaction a/g at a given ξ_h within Δt_ε is denoted as $c_{a/g}$. At a given ξ_h, within Δt_ε, $c_{a/g}$ remains constant, but the concentration of each species of reaction a/g may change over Δt_ε. Henceforth, a minus subscript is used to denote a concentration at the start of Δt_ε, and a plus subscript is used to denote a concentration at the end of Δt_ε. Thus, in terms of the total concentration, in the case of a two-reactant, one-product reaction, the mass conservation of all species of reaction a/g at a given ξ_h within Δt_ε can be expressed as

$$c_{a/g} = \mathrm{c}_{g,a-} + \mathrm{c}_{g,r1-} + \mathrm{c}_{q,r2-} = \mathrm{c}_{g,a+} + \mathrm{c}_{g,r1+} + \mathrm{c}_{q,r2+}\,.$$

(K1)

Additionally, in the case of a two-reactant, one-product reaction, the total mass of each reactant, expressed as the mass of that species that would be present if the product completely dissociated, is conserved at a given ξ_h within Δt_ε. Thus, the concentration of species r1 of component g that would be present if the product completely dissociated to reactants can be expressed as

$$c_{g1} = \frac{|\nu_{R,g,a,g,r1}|M_{g,r1}}{|\nu_{P,g,a,g,a}|M_{g,a}} c_{g,a-} + c_{g,r1-} = \frac{|\nu_{R,g,a,g,r1}|M_{g,r1}}{|\nu_{P,g,a,g,a}|M_{g,a}} c_{g,a+} + c_{g,r1+} \,,$$

(K2)

and the concentration of species r2 of component q that would be present if the product completely dissociated to reactants can be expressed as

$$c_{q2} = \frac{|\nu_{R,g,a,q,r2}|M_{q,r2}}{|\nu_{P,g,a,g,a}|M_{g,a}} c_{g,a-} + c_{q,r2-} = \frac{|\nu_{R,g,a,q,r2}|M_{q,r2}}{|\nu_{P,g,a,g,a}|M_{g,a}} c_{g,a+} + c_{q,r2+} \,.$$

(K3)

(See Equation K13.) Respectively, Equations K2 and K3 reflect the fact that $c_{g1}$and c_{q2} are conserved at a given ξ_h within Δt_ε. The sum of Equations K2 and K3 yields $c_{a/g} = c_{g1} + c_{q2}$.

Finally, in the case of a two-reactant, one-product reaction, at a given ξ_h, the concentration changes per Δt_ε are

$$\Delta c_{g,a} = c_{g,a+} - c_{g,a-} \,,$$

(K4)

$$\Delta c_{g,r1} = c_{g,r1+} - c_{g,r1-}$$

(K5)

and

$$\Delta c_{q,r2} = c_{q,r2+} - c_{q,r2-} \,,$$

(K6)

where, by conservation of mass,

$$\Delta c_{g,a} + \Delta c_{g,r1} + \Delta c_{q,r2} = 0 \,.$$

(K7)

Once $c_{g,a+}$, $c_{g,r1+}$, $c_{q,r2+}$ and all other species concentrations pertaining to the end of Δt_ε have been determined, they become, respectively, $c_{g,a-}$, $c_{g,r1-}$, $c_{q,r2-}$ and all other species concentrations pertaining to the start of $\Delta t_{\varepsilon+1}$, during which they are likely to change again due, as in prior time increments, to mass flows and reaction flows.

In the following discussions of reaction flows, products are described as being formed from the association of reactants, and reactants are described as being formed from the dissociation of products. Such descriptions apply well to mass-action interactions, but are not well suited for some other types of reactions, such as conformational changes. Once the subject of two-reactant, one-product reactions has been thoroughly covered, however, the application of the algorithms will be generalised to include one-reactant, one-product reactions.

Algorithm for reaction flows that are slow, relative to Δt_ε

When a reaction does not fully equilibrate within a given period of time, its net reaction flow is nonzero for that time. Thus, if a reaction, a/g, is judged too slow to equilibrate within some time increment of interest, its reactant and product concentrations can be calculated on the basis of the product of the net reaction flow and Δt_ε,

$$\left[k_{f,g,a}\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\gamma_{k,e}c_{k,e}\right)^{|\nu_{R,g,a,k,e}|} - k_{r,g,a}\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\gamma_{k,e}c_{k,e}\right)^{|\nu_{P,g,a,k,e}|}\right]\Delta t_\tau\,,$$

(K8)

which is just Expression G17 multiplied by the reduced time increment, $\Delta t_\tau = \Delta t_\varepsilon/\tau_{total}$, where $\tau_{total} = \nu_{total}R_{a/g}$, and τ is an index for which $1 \leq \tau \leq \tau_{total}$. Expression K8 describes the flow of reaction a/g during Δt_τ, and is applied τ_{total} times per Δt_ε, thereby yielding the flow of reaction a/g during Δt_ε. Here, the concentration, $c_{k,e}$, is that which applies to species e of component k at the start of Δt_τ. (At the start of Δt_ε, $c_{k,e} = c_{k,e-}$.)

For reaction a/g, the portion of the products that dissociates to form reactants during Δt_τ, expressed as a concentration, is

$$C_{r,g,a} = \left[k_{r,g,a}\prod_{k=1}^{n}\prod_{e=1}^{n_k}\left(\gamma_{k,e}c_{k,e}\right)^{|\nu_{P,g,a,k,e}|}\right]\Delta t_\tau\,,$$

(K9)

and the portion of the reactants that associates to form products during Δt_τ, expressed as a concentration, is

$$C_{f,g,a} = \left[k_{f,g,a} \prod_{k=1}^{n} \prod_{e=1}^{n_k} \left(\gamma_{k,e} c_{k,e} \right)^{\left| \nu_{R,g,a,k,e} \right|} \right] \Delta t_\tau \, ,$$

(K10)

where the subscript r refers to the reverse reaction, and the subscript f refers to the forward reaction.

The current algorithm is restricted to reactions in which 1 or 2 reactants form just 1 product. As there is only one product per reaction, it must consist solely of species a of component g. Thus, the stoichiometry of the product species is $\nu_{P,g,a,g,a}$, and with $\nu_{P,g,a,g,a}$ being the only nonzero product stoichiometry of reaction a/g, Equation K9 simplifies to

$$C_{r,g,a} = \left[k_{r,g,a} \left(\gamma_{g,a} c_{g,a} \right)^{\left| \nu_{P,g,a,g,a} \right|} \right] \Delta t_\tau \, ,$$

(K11)

where $C_{r,g,a}$ is the portion of the concentration of the product, species a of component g, that dissociates to form the reactants, species r1 of component g and species r2 of component q. Here, the concentration, $c_{g,a}$, is that which applies to species a of component g at the start of Δt_τ. (At the start of Δt_ε, $c_{g,a} = c_{g,a\text{-}}$.)

Of the reactant species, $\nu_{R,g,a,g,r1}$ and $\nu_{R,g,a,q,r2}$ are the only nonzero stoichiometries of reaction a/g, as a result of which, Equation K10 simplifies to

$$C_{f,g,a} = \left[k_{f,g,a} \left(\gamma_{g,r1} c_{g,r1} \right)^{\left| \nu_{R,g,a,g,r1} \right|} \left(\gamma_{q,r2} c_{q,r2} \right)^{\left| \nu_{R,g,a,q,r2} \right|} \right] \Delta t_\tau \, ,$$

(K12)

where $C_{f,g,a}$ is the portion of the concentration of the reactants, species r1 of component g and species r2 of component q, that associates to form the product, species a of component g. Here, the concentrations, $c_{g,r1}$ and $c_{q,r2}$, are those which apply, respectively, to species r1 of component g and species r2 of component q at the start of Δt_τ. (At the start of Δt_ε, $c_{g,r1} = c_{g,r1\text{-}}$ and $c_{q,r2} = c_{q,r2\text{-}}$.)

Given that

$$\left|\nu_{P,g,a,g,a}\right|M_{g,a}=\left|\nu_{R,g,a,g,r1}\right|M_{g,r1}+\left|\nu_{R,g,a,q,r2}\right|M_{q,r2}\ ,$$

(K13)

the portion of $C_{f,g,a}$ that consists of species r1 of component g is given by

$$C_{f,g,r1}=\frac{\left|\nu_{R,g,a,g,r1}\right|M_{g,r1}}{\left|\nu_{P,g,a,g,a}\right|M_{g,a}}C_{f,g,a}\ ,$$

(K14)

and the portion of $C_{f,g,a}$ that consists of species r2 of component q is given by

$$C_{f,q,r2}=\frac{\left|\nu_{R,g,a,q,r2}\right|M_{q,r2}}{\left|\nu_{P,g,a,g,a}\right|M_{g,a}}C_{f,g,a}=C_{f,g,a}-C_{f,g,r1}\ .$$

(K15)

The change in $c_{g,a}$ per Δt_τ is

$$\left(\Delta c_{g,a}\right)_\tau=C_{f,g,a}-C_{r,g,a}\ ,$$

(K16)

the change in $c_{g,r1}$ per Δt_τ is

$$\left(\Delta c_{g,r1}\right)_\tau=\frac{\left|\nu_{R,g,a,g,r1}\right|M_{g,r1}}{\left|\nu_{P,g,a,g,a}\right|M_{g,a}}\left(C_{r,g,a}-C_{f,g,a}\right)$$

(K17)

and the change in $c_{q,r2}$ per Δt_τ is

$$\left(\Delta c_{q,r2}\right)_\tau=-\left(\Delta c_{g,a}\right)_\tau-\left(\Delta c_{g,r1}\right)_\tau=\left(1-\frac{\left|\nu_{R,g,a,g,r1}\right|M_{g,r1}}{\left|\nu_{P,g,a,g,a}\right|M_{g,a}}\right)\left(C_{r,g,a}-C_{f,g,a}\right)$$
$$=\frac{\left|\nu_{R,g,a,q,r2}\right|M_{q,r2}}{\left|\nu_{P,g,a,g,a}\right|M_{g,a}}\left(C_{r,g,a}-C_{f,g,a}\right).$$

(K18)

Equations K16 to K18 form the basis of a test to determine whether reaction a/g is slow relative to Δt_τ. The test employs $C_{r,g,a-}$ and $C_{f,g,a-}$, which, respectively, are the values of $C_{r,g,a}$ and $C_{f,g,a}$ at the start of Δt_ε. If

$$\gamma_{g,a}c_{g,a-}>C_{r,g,a-}\ ,$$

(K19)

$$\gamma_{g,r1}\mathrm{c}_{g,r1-} > \frac{\left|\nu_{R,g,a,g,r1}\right| M_{g,r1}}{\left|\nu_{P,g,a,g,a}\right| M_{g,a}} C_{f,g,a-}$$

(K20)

and

$$\gamma_{q,r2}\mathrm{c}_{q,r2-} > \frac{\left|\nu_{R,g,a,q,r2}\right| M_{q,r2}}{\left|\nu_{P,g,a,g,a}\right| M_{g,a}} C_{f,g,a-} \,,$$

(K21)

from which it follows that

$$\left(\gamma_{g,a}\mathrm{c}_{g,a-} + \gamma_{g,r1}\mathrm{c}_{g,r1-} + \gamma_{q,r2}\mathrm{c}_{q,r2-}\right) - \left(C_{r,g,a-} + C_{f,g,a-}\right) > 0 \,,$$

(K22)

then reaction a/g is judged to equilibrate slowly enough, relative to Δt_τ, that Equations K11 and K12, or more generally, Equations K9 and K10, can be used to calculate the changes in the reactant and product concentrations. If, relative to Δt_τ, reaction a/g is slow enough that Equations K19 to K21 hold, then, relative to $\Delta t_\varepsilon = \tau_{\text{total}}\Delta t_\tau$, reaction a/g is considered slow enough that its product and reactant concentrations after Δt_ε can be calculated as

$$\mathrm{c}_{g,a+} = \mathrm{c}_{g,a-} + \sum_{\tau=1}^{\tau_{\text{total}}} \left(\Delta\mathrm{c}_{g,a}\right)_\tau = \mathrm{c}_{g,a-} + \Delta\mathrm{c}_{g,a} \,,$$

(K23)

$$\mathrm{c}_{q,r1+} = \mathrm{c}_{q,r1-} + \sum_{\tau=1}^{\tau_{\text{total}}} \left(\Delta\mathrm{c}_{g,r1}\right)_\tau = \mathrm{c}_{q,r1-} + \Delta\mathrm{c}_{g,r1}$$

(K24)

and

$$\mathrm{c}_{q,r2+} = \mathrm{c}_{q,r2-} + \sum_{\tau=1}^{\tau_{\text{total}}} \left(\Delta\mathrm{c}_{q,r2}\right)_\tau = \mathrm{c}_{q,r2-} + \Delta\mathrm{c}_{q,r2} \,.$$

(K25)

The test (Equations K19 to K21) ensures that Equations K23 to K25 will not be applied if their use would violate mass conservation. Essentially, Equations K19 to K21 test the applicability of the slow equilibration method by testing whether the method conserves mass.

Algorithm for reaction flows that are fast, relative to Δt_ε

When a reaction fully equilibrates within a given period of time, its net reaction flow is zero for that time. If one or more of Equations K19 to K21 do not hold, then reaction a/g is judged rapid enough to fully equilibrate within Δt_ε, in which case, the product and reactant concentrations of reaction a/g are iteratively recalculated until their values yield the association constant of the reaction, within a chosen level of tolerance. Compared to the method for a slowly equilibrating reaction, the method for a rapidly equilibrating reaction is more computationally intensive, as it involves up to N_{equil} more iterations, where N_{equil}, an empirically determined parameter, may be a number in the low thousands. (At present, the routinely used values of N_{equil} are 5,000 for the initial equilibration at $t = 0$, and 2,500 for all equilibrations after $t = 0$.)

During Δt_ε, up to N_{equil} iterations take place within each of the previously discussed $R_{a/g}$ iterations, and those $R_{a/g}$ iterations, in turn, take place within each of the previously discussed ν_{total} iterations. Thus, for reaction a/g, within Δt_ε, the maximum number of iterations is equal to $\nu_{total}R_{a/g}N_{equil}$. (The main purpose of imposing a maximum of N_{equil} iterations is to prevent the occurrence of infinite loops, but it is usually best to set N_{equil} higher than necessary to ensure equilibration. Spurious spikes and dips in the concentration data are evidence that N_{equil} is too low to consistently achieve equilibration, but such low values of N_{equil} might sometimes be useful for quickly testing a complicated model system.)

The innermost iterations are indexed by w, where $1 \leq w \leq w_{final}$, and $w_{final} \leq N_{equil}$. The last iteration, w_{final}, occurs when the equilibration criterion (Inequality K29) has been met, or when w reaches N_{equil}, whichever comes first. Thus, for reaction a/g, within Δt_ε, the total number of iterations is equal to $\nu_{total}R_{a/g}w_{final}$. At each of the w_{final} iterations, a concentration-change factor,

$$k_w = \frac{k_0}{k_0 + (w - w_0)},$$

(K26)

is calculated, where k_0 is a real number greater than zero, and w_0 is a real number equal to or greater than 1. Both k_0 and w_0 are empirically determined parameters. For $w_0 = 1$, at $w = 1$, $k_w = 1$, which is its maximum possible value. As w increases, k_w decreases. The smaller k_0 is, the faster k_w decreases as w increases. The larger k_0 is, the closer k_w is to zero at $w = 1$. (At present, the routinely used value of k_0 is 3, while the routinely used values of w_0 are 1 for the initial equilibration at $t = 0$, and 4 for all equilibrations after $t = 0$.)

As in the discussion of slowly equilibrating reactions (**Algorithm for reaction flows that are slow, relative to Δt_ε**), a minus subscript is used to indicate a concentration before equilibration, and a plus subscript indicates a concentration after equilibration. Also, henceforth, concentrations that are in use during iteration w are subscripted by w, and further subscripted with a minus sign to indicate a concentration at the start of iteration w, or a plus sign to indicate a concentration at the end of iteration w. Thus, $c_{g,a,w-}$, $c_{g,r1,w-}$ and $c_{q,r2,w-}$ are, respectively, the values of $c_{g,a}$, $c_{g,r1}$ and $c_{q,r2}$ at the start of iteration w, and for $w = 1$, are equal to $c_{g,a-}$, $c_{g,r1-}$ and $c_{q,r2-}$, respectively. Likewise, $c_{g,a,w+}$, $c_{g,r1,w+}$ and $c_{q,r2,w+}$ are, respectively, the values of $c_{g,a}$, $c_{g,r1}$ and $c_{q,r2}$ at the end of iteration w, and for $w = w_{\text{final}}$, are equal to $c_{g,a+}$, $c_{g,r1+}$ and $c_{q,r2+}$, respectively.

At each iteration, two test parameters,

$$Q_{P,w} = \left(\gamma_{g,a} c_{g,a,w-}\right)^{|\nu_{P,g,a,g,a}|}$$

(K27)

and

$$Q_{R,w} = K_{A,g,a}\left(\gamma_{g,r1} c_{g,r1,w-}\right)^{|\nu_{R,g,a,g,r1}|}\left(\gamma_{q,r2} c_{q,r2,w-}\right)^{|\nu_{R,g,a,q,r2}|},$$

(K28)

are calculated, where $Q_{P,w}$ derives from the product concentration (hence the subscript P), and $Q_{R,w}$ derives from the reactant concentrations (hence the subscript R). At chemical equilibrium, $Q_{P,w} = Q_{R,w}$. To test whether $Q_{P,w}$ is acceptably close to $Q_{R,w}$, a tolerance level, ζ, is chosen, where $0 < \zeta < 1$ in principle, though values as close to 1 as practical are preferred. (At present, the routinely used values of ζ are 0.999 for the initial equilibration at

$t = 0$, and 0.995 for all equilibrations after $t = 0$.)

If $\zeta Q_{P,w} \leq Q_{R,w}$ and $\zeta Q_{R,w} \leq Q_{P,w}$, the reaction is considered equilibrated, and the new concentrations are equated to the old concentrations: $c_{g,a+} = c_{g,a-}$, $c_{g,r1+} = c_{g,r1-}$, and $c_{q,r2+} = c_{q,r2-}$. Thus, the criterion for adequate equilibration of reaction a/g is

$$\zeta K_{A,g,a} \leq \frac{\left(\gamma_{g,a} c_{g,a+}\right)^{|\nu_{P,g,a,g,a}|}}{\left(\gamma_{g,r1} c_{g,r1+}\right)^{|\nu_{R,g,a,g,r1}|}\left(\gamma_{q,r2} c_{q,r2+}\right)^{|\nu_{R,g,a,q,r2}|}} \leq \frac{1}{\zeta} K_{A,g,a} \text{ ,}$$

(K29)

where the central value of Inequality K29 has the form of the simplified association constant of reaction a/g (Equation G13) that pertains to the case of 1 product species and 2 reactant species per reaction.

If $\zeta Q_{P,w} > Q_{R,w}$ or $\zeta Q_{R,w} > Q_{P,w}$, the reaction is not considered equilibrated, and to meet the criterion for adequate equilibration (Inequality K29), the new concentrations must be altered from their old concentrations, with the constraint that mass must be conserved. (If $\zeta Q_{P,w} > Q_{R,w}$, $c_{g,a,w+}$ must be made smaller than $c_{g,a,w-}$, $c_{g,r1,w+}$ must be made larger than $c_{g,r1,w-}$, and $c_{q,r2,w+}$ must be made larger than $c_{q,r2,w-}$. If $\zeta Q_{R,w} > Q_{P,w}$, $c_{g,a,w+}$ must be made larger than $c_{g,a,w-}$, $c_{g,r1,w+}$ must be made smaller than $c_{g,r1,w-}$, and $c_{q,r2,w+}$ must be made smaller than $c_{q,r2,w-}$.)

The concentration changes per iteration w are defined as $(\Delta c_{g,a})_w = c_{g,a,w+} - c_{g,a,w-}$, $(\Delta c_{g,r1})_w = c_{g,r1,w+} - c_{g,r1,w-}$, and $(\Delta c_{q,r2})_w = c_{q,r2,w+} - c_{q,r2,w-}$, which, in this algorithm, are also subject to mass conservation. Thus, $(\Delta c_{g,a})_w + (\Delta c_{g,r1})_w + (\Delta c_{q,r2})_w = 0$. The algorithm also enforces mass conservation for c_{g1} and c_{q2} at each w. Thus, Equations K1 to K3, and Equation K7, must hold when $c_{g,a+}$, $c_{g,r1+}$ and $c_{q,r2+}$ in those equations are replaced with $c_{g,a,w+}$, $c_{g,r1,w+}$ and $c_{q,r2,w+}$, respectively.

For each iteration, w, the calculation of the concentration changes is divided into three parts, the first of which yields the preliminary differences, $(\Delta c_{g,a})_{w^{**}}$, $(\Delta c_{g,r1})_{w^{**}}$ and $(\Delta c_{q,r2})_{w^{**}}$; the second of which yields the intermediate differences, $(\Delta c_{g,a})_{w^{*}}$, $(\Delta c_{g,r1})_{w^{*}}$ and

$(\Delta c_{q,r2})_{w*}$; and the third of which yields the final differences, $(\Delta c_{g,a})_w$, $(\Delta c_{g,r1})_w$ and $(\Delta c_{q,r2})_w$.

The functions used to calculate the preliminary differences of iteration w depend on whether $\zeta Q_{R,w} > Q_{P,w}$ or $\zeta Q_{P,w} > Q_{R,w}$. At iteration w, if $\zeta Q_{R,w} > Q_{P,w}$, the preliminary concentration changes per iteration w are given by

$$\left(\Delta c_{g,r1}\right)_{w**} = \left(\Delta c_{g,r1}\right)_{F,w} = -k_w c_{g,r1-} ,$$

(K30)

$$\left(\Delta c_{q,r2}\right)_{w**} = \left(\Delta c_{q,r2}\right)_{F,w} = -k_w c_{q,r2-}$$

(K31)

and

$$\left(\Delta c_{g,a}\right)_{w**} = \left(\Delta c_{g,a}\right)_{F,w} = -\left[\left(\Delta c_{g,r1}\right)_{F,w} + \left(\Delta c_{q,r2}\right)_{F,w}\right] = k_w\left(c_{g,r1-} + c_{q,r2-}\right) .$$

(K32)

At iteration w, if $\zeta Q_{P,w} > Q_{R,w}$, the preliminary concentration changes per iteration w are given by

$$\left(\Delta c_{g,r1}\right)_{w**} = \left(\Delta c_{g,r1}\right)_{R,w} = k_w \frac{\left|\nu_{R,g,a,g,r1}\right| M_{g,r1}}{\left|\nu_{P,g,a,g,a}\right| M_{g,a}} c_{g,a-} ,$$

(K33)

$$\left(\Delta c_{q,r2}\right)_{w**} = \left(\Delta c_{q,r2}\right)_{R,w} = k_w \frac{\left|\nu_{R,g,a,q,r2}\right| M_{q,r2}}{\left|\nu_{P,g,a,g,a}\right| M_{g,a}} c_{g,a-}$$

(K34)

and

$$\left(\Delta c_{g,a}\right)_{w**} = \left(\Delta c_{g,a}\right)_{R,w} = -\left[\left(\Delta c_{g,r1}\right)_{R,w} + \left(\Delta c_{q,r2}\right)_{R,w}\right] = -k_w c_{g,a-} .$$

(K35)

The functions used to calculate the intermediate differences of iteration w are

$$\left(\Delta c_{g,r1}\right)_{w*} = \frac{1}{2}\left[\left(\Delta c_{g,r1}\right)_{w**} + \frac{M_{g,r1}}{M_{q,r2}}\left(\Delta c_{q,r2}\right)_{w**}\right],$$

(K36)

$$\left(\Delta c_{q,r2}\right)_{w*} = \frac{1}{2}\left[\left(\Delta c_{q,r2}\right)_{w**} + \frac{M_{q,r2}}{M_{g,r1}}\left(\Delta c_{g,r1}\right)_{w**}\right]$$

(K37)

and

$$\left(\Delta c_{g,a}\right)_{w*} = -\left[\left(\Delta c_{g,r1}\right)_{w*} + \left(\Delta c_{q,r2}\right)_{w*}\right].$$

(K38)

The final differences of iteration w are determined when mass conservation is enforced. If

$$\left(\Delta c_{g,r1}\right)_{w*} < \left(\Delta c_{g,r1}\right)_{\max} = \frac{\left|\nu_{R,g,a,g,r1}\right| M_{g,r1}}{\left|\nu_{P,g,a,g,a}\right| M_{g,a}}\, c_{g,a-}\,,$$

(K39)

then $(\Delta c_{g,r1})_w$ is set equal to $(\Delta c_{g,r1})_{w*}$, but if the condition described by Equation K39 is not met, $(\Delta c_{g,r1})_w$ is set equal to $(\Delta c_{g,r1})_{\max}$. Likewise, if

$$\left(\Delta c_{q,r2}\right)_{w*} < \left(\Delta c_{q,r2}\right)_{\max} = \frac{\left|\nu_{R,g,a,q,r2}\right| M_{q,r2}}{\left|\nu_{P,g,a,g,a}\right| M_{g,a}}\, c_{g,a-}\,,$$

(K40)

then $(\Delta c_{q,r2})_w$ is set equal to $(\Delta c_{q,r2})_{w*}$, but if the condition described by Equation K40 is not met, $(\Delta c_{q,r2})_w$ is set equal to $(\Delta c_{q,r2})_{\max}$. Finally,

$$\left(\Delta c_{g,a}\right)_{w} = -\left[\left(\Delta c_{g,r1}\right)_{w} + \left(\Delta c_{q,r2}\right)_{w}\right].$$

(K41)

At this point, it can be seen that Equations K32, K35 or K38, which are included for completeness, are not needed to obtain the results given by Equations K39 to K41.

If w is less than N_{equil}, and if the criterion for adequate equilibration (Inequality K29) has not been met, then the end of iteration w is the start of iteration [w + 1], in which case, $c_{g,a,[w+1]-} = c_{g,a,w+} = c_{g,a,w-} + (\Delta c_{g,a})_w$, $c_{g,r1,[w+1]-} = c_{g,r1,w+} = c_{g,r1,w-} + (\Delta c_{g,r1})_w$, and $c_{q,r2,[w+1]-} = c_{q,r2,w+} = c_{q,r2,w-} + (\Delta c_{q,r2})_w$. If the criterion for adequate equilibration is met, or if w reaches N_{equil}, then the end of iteration w is the end of the chemical equilibration process for reaction, a/g within Δt_ε, in which case, $c_{g,a+} = c_{g,a,w-} + (\Delta c_{g,a})_w$, $c_{g,r1+} = c_{g,r1,w-} + (\Delta c_{g,r1})_w$, and $c_{q,r2+} = c_{q,r2,w-} + (\Delta c_{q,r2})_w$.

The iterative application of the second approximate solution

As noted in Section C (**Transport and reaction flows**), the reaction flow and the mass flow are calculated in separate, consecutive steps within a given time increment. Thus, the values of $c_{g,a+}$, $c_{g,r1+}$ and $c_{q,r2+}$ obtained from the reaction flow calculations are used to re-initialise $c_{g,a-}$, $c_{g,r1-}$ and $c_{q,r2-}$, respectively, after which, $c_{g,a-}$, $c_{g,r1-}$ and $c_{q,r2-}$ are subjected to the mass flow calculations described in Section C. Following those mass flow calculations, mass conservation is enforced, as described in Section L. Finally, if the convergence criterion (Equation J6) has been met, or a set limit on the maximum number of iterations has been reached, the time is incremented by Δt_ε, and the flow calculations for the next Δt_ε are begun. (Otherwise, without incrementing Δt_ε, the values of $c_{k,e,h+}$ obtained, which pertain to iteration m and are thus denoted as $(c_{k,e,h+})_m$, are used to calculate $(c_{k,e,h+})_{m+1}$, which denotes the next iteration of $c_{k,e,h+}$ at the end of Δt_ε.)

Limits

For a given chemical reaction, as the concentration of any of its reactants approaches zero, the computational intensity of the reaction flow calculation rises, while the significance of the information gained from the calculation falls. Avoiding such calculations, therefore, reduces the time required to model a system, without adversely affecting the accuracy of the results to a significant extent. To this end, two methods are used to place appropriate limits on the application of the reaction flow algorithms. These methods employ two dimensionless parameters, α and β, that, when properly set, identify conditions in which there is little or no need to calculate a reaction flow.

As with the flow calculations themselves, the methods to limit reaction flow calculations are described in terms of a two-reactant, one-product reaction. In the inequalities used to limit reaction flow calculations, ϒ represents the unit solute concentration (with dimensions such as 1 g/cm^3), just as it does in Equations G6, G7, G14, G15 and G20.

The first parameter, α, is used to test whether the concentration of one or both reactants is approaching zero. If

$$\left(\frac{\gamma_{g,r1}c_{g,r1,w-}}{\Upsilon}\right)^{|\nu_{R,g,a,g,r1}|} > \alpha\left[\left(\frac{\gamma_{g,a}c_{g,a,w-}}{\Upsilon}\right)^{|\nu_{P,g,a,g,a}|} + \left(\frac{\gamma_{q,r2}c_{q,r2,w-}}{\Upsilon}\right)^{|\nu_{R,g,a,q,r2}|}\right]$$

(K42)

or

$$\left(\frac{\gamma_{q,r2}c_{q,r2,w-}}{\Upsilon}\right)^{|\nu_{R,g,a,q,r2}|} > \alpha\left[\left(\frac{\gamma_{g,a}c_{g,a,w-}}{\Upsilon}\right)^{|\nu_{P,g,a,g,a}|} + \left(\frac{\gamma_{g,r1}c_{g,r1,w-}}{\Upsilon}\right)^{|\nu_{R,g,a,g,r1}|}\right],$$

(K43)

then the algorithm for a fast (relative to Δt_ε) reaction flow is not used, even if one or more of Equations K19 to K21 do not hold. If Equations K19 to K21 do hold, however, the algorithm for a slow (relative to Δt_ε) reaction flow is used, regardless of the test results from Equations K42 and K43. At present, the routinely used value of α is (10^{-13} erg·s)/h, where h is the cgs Planck constant.

The second parameter, β, tests whether the concentrations of all reactant and product species are approaching zero. If

$$\beta > \left(\frac{\gamma_{g,a}c_{g,a,w-}}{\Upsilon}\right)^{|\nu_{P,g,a,g,a}|},$$

(K44)

$$\beta > \left(\frac{\gamma_{g,r1}c_{g,r1,w-}}{\Upsilon}\right)^{|\nu_{R,g,a,g,r1}|}$$

(K45)

and

$$\beta > \left(\frac{\gamma_{q,r2}c_{q,r2,w-}}{\Upsilon}\right)^{|\nu_{R,g,a,q,r2}|},$$

(K46)

neither the algorithm for a fast (relative to Δt_ε) reaction flow, nor the algorithm for a slow (relative to Δt_ε) reaction flow, are used, regardless of the test results from Equations K19 to K21. Instead, whenever Equations K44 to K46 prove true, any remaining product is converted to reactants. At present, the routinely used value of β is h(10^{10}/erg·s).

One-reactant, one-product reactions

Expressions for one-reactant, one-product reactions are obtained by letting $\nu_{R,g,a,q,r2} = 0$, $M_{q,r2} = 0$, $c_{q,r2-} = 0$, $c_{q,r2+} = 0$ and $\Delta c_{q,r2} = 0$, wherever they appear in Equations/Inequalities K1 to K35. For one-reactant, one-product reactions, Equations/Inequalities K36 to K46 are either superfluous or inapplicable, and are not used.

A special case of one-reactant, one-product reactions is that for which $\nu_{R,g,a,g,r1} = 1$ and $\nu_{P,g,a,g,a} = 1$, wherein one species simply changes into another. Such reactions would include conformational changes.

For all other one-reactant, one-product reactions, $\nu_{R,g,a,g,r1} > 1$ and $\nu_{P,g,a,g,a} = 1$. Such reactions would include any oligomerisation that can be described as an event in which $\nu_{R,g,a,g,r1}$ monomers form 1 oligomer. A polymerisation, or complex formation, that must be described by the successive addition of monomeric or oligomeric subunits, in which each addition may have unique rate and association constants, would have to be modelled as multiple reactions on a one-addition-one-reaction basis.

References

[K1] Moody, T. P. (2012a) Johnston-Ogston effects in AUC simulations of two model systems based on polystyrene beads that are polydisperse with respect to specific gravity. http://moodybiophysicalconsulting.blogspot.com/.

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Section L: Algorithms to conserve mass and adjust the time increment

Neither the finite-element approach of Claverie [Claverie et al., 1975; Cox and Dale, 1981], nor similar numerical solutions to the t- and r-dependent or the t- and ξ-dependent forms of the continuity equation (Sections B, C, F and J), conserve mass. Computational instabilities appear to worsen the failure of such approaches to conserve mass. Thus, the severity of the mass-conservation failure can be exploited to measure computational stability. When instabilities develop, as evidenced by severe deviations from mass conservation, parameters, such as the time increment, can be adjusted to restore stability. Algorithms to enforce mass conservation, and to decrease the time increment when computational instability is judged to be excessive, are described here. The description of these algorithms uses parameters and notation found in Sections C, J and K. As in Sections C and J, the subscript h corresponds to a spatial element, ξ_h. (See Equation C17.)

The total mass, throughout the system, of species e of component k after the calculation of all reaction flows (Section K), but prior to the calculation of the mass flows (Section C), is

$$\mathrm{m}_{k,e-} = \sum_{h=1}^{N} V_h c_{k,e,h-} ,$$

(L1)

where V_h is the volume of spatial element h, and the minus subscript indicates a concentration at the start of the time increment, Δt_ε, already used in the reaction flow calculations, and yet to be used in the impending mass flow calculations. Thus, $c_{k,e,h-}$ is the concentration of species e of component k at the start of Δt_ε, after application of the reaction flow algorithms described in Section K, but before application of the mass flow algorithms described in Section C. Any mass of species e of component k that is associated with any boundary of the system is included in $c_{k,e,h-}$.

The total mass, throughout the system, of species e of component k after the calculation of all reaction flows (Section K), and after the calculation of all mass flows (Section C), is

$$\mathrm{m}_{k,e+} = \sum_{h=1}^{N} V_h c_{k,e,h+} ,$$

(L2)

where the plus subscript indicates a concentration at the end of Δt_ε. Thus, $c_{k,e,h+}$ is the concentration of species e of component k at the end of Δt_ε, after application of the reaction flow algorithms described in Section K, and after application of the mass flow algorithms described in Section C. Any mass of species e of component k that is associated with any boundary of the system is included in $c_{k,e,h+}$. If there is a flow of species e of component k through the system during Δt_ε, the set of all $c_{k,e,h+}$ accounts for any resulting change in the mass of that species. Prior to calculating $m_{k,e+}$, and prior to using the set of all $c_{k,e,h+}$ in any of the equations that follow in this section, any negative values of $c_{k,e,h+}$ are set equal to zero.

As described in Section K (**The iterative application of the second approximate solution**), within each iteration of the general solution of the continuity equation (Section J), the reaction flow, mass flow, and mass-conservation algorithms are applied consecutively. When the iterative solution of Section J is applied, Δt_ε is not incremented until the convergence criterion (Equation J6) is met, or a set limit on the maximum number of iterations is reached. Within Δt_ε, at the end of each iteration, m, the values of $c_{k,e,h+}$ obtained, which are denoted as $(c_{k,e,h+})_m$, are used to calculate $(c_{k,e,h+})_{m+1}$, which denotes the next iteration of $c_{k,e,h+}$ at the end of Δt_ε. In this section, for simplicity, the subscript associated with the iterative solution of Section J is not appended to $c_{k,e,h+}$ unless needed to distinguish values pertaining to different iterations.

At the end of Δt_ε, $c_{k,e,h+}$ multiplied by a mass-conservation-correction factor, $K_{k,e,h+}$, to obtain

$$c_{k,e,h*} = c_{k,e,h+}\mathrm{K}_{k,e,h+} \, ,$$

(L3)

where $c_{k,e,h*}$ is equal to $c_{k,e,h+}$ corrected for mass-conservation errors, and where $K_{k,e,h+}$ is given by

$$\mathrm{K}_{k,e,h+} = 1 - \delta_{k,e,h+} \, .$$

(L4)

To define the fractional-change parameter, $\delta_{k,e,h+}$, the concentration-gradient parameter, $\Lambda_{k,e,h+}$, and the normalisation factor, $N_{k,e+}$, must first be defined.

For all h, the default value of $\Lambda_{k,e,h+}$ is zero. Nonzero values of $\Lambda_{k,e,h+}$ are obtained if $c_{k,e,h+} > 0$ and $|\Delta c_{k,e,h+}| > 0$, where

$$\Delta c_{k,e,h+} = \frac{c_{k,e,[h+1]+} - c_{k,e,[h-1]+}}{2}$$

(L5)

for $1 < h < N$,

$$\Delta c_{k,e,1+} = c_{k,e,2+} - c_{k,e,1+}$$

(L6)

for $h = 1$, and

$$\Delta c_{k,e,N+} = c_{k,e,N+} - c_{k,e,[N-1]+}$$

(L7)

for $h = N$. With $\Delta c_{k,e,h+}$ thus defined for all h, $\Lambda_{k,e,h+}$ can be defined as

$$\Lambda_{k,e,h+} = \left|\Delta c_{k,e,h+}\right|^{\Lambda},$$

(L8)

where Λ, the exponential term of $\Lambda_{k,e,h+}$, is an empirically chosen parameter. As Equation L8 is only applied if $|\Delta c_{k,e,h+}| > 0$, Λ can be any real number. (If $|\Delta c_{k,e,h+}| = 0$, $\Lambda_{k,e,h+}$ maintains its default value of zero.)

The normalisation parameter,

$$\mathrm{N}_{k,e+} = \sum_{h=1}^{N} V_h c_{k,e,h+} \Lambda_{k,e,h+},$$

(L9)

must be greater than zero, as it is the denominator in the equation that defines $\delta_{k,e,h+}$. Where Equation L9 yields a value of zero for $\mathrm{N}_{k,e+}$, as it will if all $c_{k,e,h+}$ equal zero or all $\Lambda_{k,e,h+}$ equal zero, $\mathrm{N}_{k,e+}$ is set equal to 1. (As each V_h must be greater than zero, there is no set of V_h values that could cause Equation L9 to bring $\mathrm{N}_{k,e+}$ to nought.)

Given the definitions and exceptions above, $\delta_{k,e,h+}$ can be defined as

$$\delta_{k,e,h+} = \frac{(\mathrm{m}_{k,e+} - \mathrm{m}_{k,e-})\Lambda_{k,e,h+}}{\mathrm{N}_{k,e,h+}}.$$

(L10)

When $\Lambda_{k,e,h+} = 0$, $\delta_{k,e,h+} = 0$. Thus, for $|\Delta c_{k,e,h+}| = 0$ or $c_{k,e,h+} = 0$, $\delta_{k,e,h+} = 0$. For $|\Delta c_{k,e,h+}| > 0$ and $c_{k,e,h+} > 0$, $\delta_{k,e,h+} > 0$ if $(\mathrm{m}_{k,e+} - \mathrm{m}_{k,e-}) > 0$, and $\delta_{k,e,h+} < 0$ if $(\mathrm{m}_{k,e+} - \mathrm{m}_{k,e-}) < 0$.

For $\Lambda \geq 1$, as Λ increases, the difference between the highest and lowest nonzero values of $|\delta_{k,e,h+}|$ increases, while fewer $c_{k,e,h+}$ values bear more of the concentration changes required to enforce mass conservation, as more of the correction affects the nonzero $c_{k,e,h+}$ values that correspond to the largest nonzero $|\Delta c_{k,e,h+}|$ values.

As Λ approaches zero from above($\Lambda \geq 0$) or below ($\Lambda \leq 0$), the difference between the highest and lowest nonzero values of $|\delta_{k,e,h+}|$ decreases toward zero, and at $\Lambda = 0$, the concentration required to enforce mass conservation is the same for each nonzero $c_{k,e,h+}$ value that corresponds to a nonzero $|\Delta c_{k,e,h+}|$ value.

For $\Lambda \leq -1$, as Λ decreases, the difference between the highest and lowest nonzero values of $|\delta_{k,e,h+}|$ increases, while fewer $c_{k,e,h+}$ values bear more of the concentration changes required to enforce mass conservation, as more of the correction affects the nonzero $c_{k,e,h+}$ values that correspond to the smallest nonzero $|\Delta c_{k,e,h+}|$ values.

At present, Λ is typically set equal to 1.

Adjustments of the time increment

If, at the end of Δt_ε, each $c_{k,e,h^*} \geq 0$ after the application of Equation L3, the system is considered computationally stable, in which case, each $c_{k,e,h+}$ is equated to its corresponding c_{k,e,h^*} value. If the convergence criterion (Equation J6) has been met, or a set limit on the maximum number of iterations has been reached, the time is incremented by Δt_ε, and the flow calculations for the next Δt_ε are begun. (Otherwise, without incrementing Δt_ε, the values of $c_{k,e,h+}$ obtained, which pertain to iteration m and are thus denoted as $(c_{k,e,h+})_m$, are used to calculate $(c_{k,e,h+})_{m+1}$, which denotes the next iteration of $c_{k,e,h+}$ at the end of Δt_ε.)

If, however, at the end of Δt_ε, one or more $c_{k,e,h^*} < 0$ after the application of Equation L3, the system is considered computationally unstable, in which case, each $c_{k,e,h+}$ is equated to its corresponding $c_{k,e,h-}$ value that pertains to the start of Δt_ε. In that case, the time is not incremented by Δt_ε, Δt_ε is halved, and the flows are recalculated using the shorter time increment.

Evidence of instability practically requires that Δt_ε be decreased. Evidence of stability does not require that Δt_ε be increased, but may justify testing whether Δt_ε can be increased without jeopardising stability. To that end, an algorithm has been implemented that can raise Δt_ε under conditions where it may be appropriate to do so. The evidence to raise Δt_ε is less definitive than the evidence to lower it, however. Thus, limiting parameters, such as a maximum Δt_ε value, are used to regulate the Δt_ε-raising algorithm.

If permitted by the relevant limits, Δt_ε may be increased if the system is considered computationally stable, provided that a computationally unstable condition has not occurred within a specified time span. A judicious selection of various parameters, such as Δt_ε, Λ, the set of spatial elements, and the limits that govern reaction-flow calculations, can minimise the occurrence of computationally unstable conditions while nearly maximising computational speed.

References

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Section M: Effects of ionic strength on (apparent) reduced valence and zeta potential

The (apparent) reduced valence coefficient of solute component k is

$$\sigma_k = \frac{Eu_k}{D_k} = \frac{\left(\frac{\partial lnc_k}{\partial \xi}\right)_t \left(E \sum_{q=1}^{n} \frac{1}{M_q} c_q \boldsymbol{u}_{k,q} + v_0 \frac{c_k}{M_k}\right)}{\sum_{q=1}^{n} \frac{1}{M_q} \left(\frac{\partial c_q}{\partial \xi}\right)_t \boldsymbol{D}_{k,q}}$$

$$= \frac{\left(\frac{\partial lnc_k}{\partial \xi}\right)_t \left(E \frac{F}{\varpi} \sum_{q=1}^{n} L_{k,q} z_q + v_0 \frac{c_k}{M_k}\right)}{RT \sum_{q=1}^{n} L_{k,q} \left(\frac{\partial lnc_q}{\partial \xi}\right)_t \left[1 + c_q \sum_{w=1}^{n} \left(\frac{\partial c_w}{\partial c_q}\right)_t \left(\frac{\partial ln\gamma_q}{\partial c_w}\right)_{t,T,P,c_{a\neq w}}\right]},$$

(M1 = A23a)

and the reduced valence of solute component *k* is defined as

$$z_k^* = \varpi \frac{RT}{FE} \sigma_k = \varpi \frac{RT}{F} \frac{u_k}{D_k} = \frac{\varpi \frac{RT}{F} \left(\frac{\partial lnc_k}{\partial \xi}\right)_t \left(\sum_{q=1}^{n} \frac{c_q}{M_q} \boldsymbol{u}_{k,q} + \frac{v_0}{E} \frac{c_k}{M_k}\right)}{\sum_{q=1}^{n} \frac{\boldsymbol{D}_{k,q}}{M_q} \left(\frac{\partial c_q}{\partial \xi}\right)_t}$$

$$= \frac{\left(\frac{\partial lnc_k}{\partial \xi}\right)_t \left(\sum_{q=1}^{n} L_{k,q} z_q + \frac{\varpi}{F} \frac{v_0}{E} \frac{c_k}{M_k}\right)}{\sum_{q=1}^{n} \left(\frac{\partial lnc_q}{\partial \xi}\right)_t L_{k,q} \left[1 + c_q \sum_{w=1}^{n} \left(\frac{\partial c_w}{\partial c_q}\right)_t \left(\frac{\partial \ln\gamma_q}{\partial c_w}\right)_{t,T,P,c_{a\neq w}}\right]},$$

(M2)

where ξ is the magnitude of the downwardly directed spatial vector by which position is measured in the MCE system, R is the cgs ideal gas constant, T is the absolute temperature, F is the cgs Faraday, t is time, P is the pressure of the system, ϖ is an electrical-potential conversion factor, E is the electrical field strength (assumed to be expressed in units of volt/cm), v_0 is the magnitude of the velocity of the solvent (component 0) in the system frame of reference, n is the total number of solute components, u_k is the (apparent) electrophoretic mobility coefficient of solute component k, D_k is the (apparent) diffusion coefficient of solute component k, c_k is the mass concentration of solute component k, M_k is the molar mass of solute component k, z_q is the valence of solute component q, c_q is the mass concentration of solute component q, M_q is the molar mass of solute component q, γ_q is the activity coefficient of solute component q, c_w is the mass concentration of solute component w, $\boldsymbol{u}_{k,q}$ is the coupled-flow-electrophoretic mobility coefficient of solute component k as affected by solute component q, $\boldsymbol{D}_{k,q}$ is the coupled-flow-diffusion coefficient of solute component k as affected by solute component q, $L_{k,q}$ is the coupled-flow-phenomenological coefficient linking the molar flow of solute component k to the conjugate molar force (Equations A2, A14 and I16) of solute component q, and where the components are variously indexed by k, q or w, for which $1 \leq k \leq n$, $1 \leq q \leq n$ and $1 \leq w \leq n$, respectively. The apparent charge of solute component k is equal to $z_k^* e$, where e is the elementary charge.

For further information about the parameters in Equations M1 and M2, see **Section A: An application of irreversible thermodynamics to membrane-confined electrophoresis**. (Further information about R, F, ϖ and e is also found in the second note following the **List of selected parameters, their indices, and their cgs, mks or other dimensions**.) Most of the details regarding z_q and M_q, two of the parameters of Equations M1 and M2, are presented in **Section I: Calculating valence, molar mass, chemical potential and partial specific volume for a multi-species component**. (Equation I19b describes $(z_q)_g$, the gradient-modified-average valence of component q, which is found (Equations A2 and I20) to be identical to z_q. Likewise, Equation I19a describes $(M_q)_g$, the gradient-modified-average molar mass of component q, which is found (Equations A2 and I20) to be identical to M_q.) Additional details (Equations M21 to M25) regarding z_q are presented in the last part of this section (**An examination of whether $(z_q)_N$ and z_q can be regarded as molecular parameters**).

There are a number of obstacles to calculating z_k^*, among which is the fact that each $L_{k,q}$ of Equation M2 is generally unknown. Onsager showed that the cross terms $L_{k,q}$ and $L_{q,k}$ are symmetric in the absence of magnetic fields or Coriolis forces in the system, in which case, the reciprocal relations provide $L_{k,q} = L_{q,k}$ for all k and q [Onsager, 1931a; Onsager, 1931b; de Groot and Mazur, 1962]. (In the presence of magnetic fields or Coriolis forces, resort must be made of the more general form of the reciprocal relations mentioned in **Section G: The dissipation function and the Curie-Prigogine principle**.)

Beyond the reciprocal relationships, the most that can be said in general is that each $L_{k,q}$ is a function of system properties (e.g. T, P, and component concentrations), and that each $L_{k,q}$ is independent of the magnitudes of any forces present, provided that those forces are sufficiently small [Tanford, 1961]. For q not equal to k, however, there is no equation that describes $L_{k,q}$ in terms of independently determinable parameters. Even for $q = k$, $L_{k,k}$ is only calculable in the case given by

$$\lim_{c_{q \neq k} \to 0} L_{k,k} = \frac{c_k}{N_A M_k f_k},$$

(M3 = A19)

where N_A is Avogadro's number and f_k is the frictional coefficient of solute component k, but this equation only applies in the limit as all solute concentrations other than that of solute component k approach zero. Nevertheless, if there are no solute components other than k, and if f_k, c_k and M_k are known, $L_{k,k}$ is the one phenomenological coefficient that can be calculated.

Of all the parameters needed to calculate $L_{k,k}$, f_k is the most challenging to determine. In the absence of solute components other than k, f_k can be calculated from the Stokes equation,

$$f_k = 6\pi\eta R_k^*,$$

(M4 = A20)

if R_k^*, the Stokes radius of an equivalent sphere of solute component k, and η, the solution viscosity, are known. The applicability of the Stokes equation, however, is questionable except as c_k approaches zero, at which point, η becomes identical to the solvent viscosity.

Reduced valence as a function of ionic strength

In special cases, z_k^* or a related parameter can be calculated, and one such case is used here to examine the trends exhibited by z_k^* as the ionic strength of the solution approaches its extrema. Toward that end, an applicable model system is first defined, and the calculable parameters of that model system are then compared with the most closely related parameters of Equation M1.

Equations M5 to M20 will apply to a model system in which a macro-ion shares its counter-ion with an electrolyte in solution. The model system comprises a solvent component, $k = 1$, plus two ionic components, $k = 2$ and $k = 3$. Component $k = 1$ is assumed to be water, the ionic species of which need not be specified explicitly in this case. Component $k = 2$ comprises two ionic species, both of which are small. Component $k = 3$ comprises two ionic species, of which one is large and the other is small. As in Equation H1, the valence of species e of component k will be denoted as $z_{k,e}$.

Component 2 is assumed to be a uni-univalent electrolyte of the sort discussed following Equation H7. The large species of component 3 is the macro-ion of the system, and is defined as species 1 of component 3, so that its valence is denoted as $z_{3,1}$. The small species of component 3 is the counter-ion of the system, and is defined as species 2 of component 3, so that its valence is denoted as $z_{3,2}$. With the counter-ion of the system so defined, one species of component 2 must be identical to it. Defining species 2 of component 2 as identical to the counter-ion of the system, its valence, $z_{2,2}$, must be equal to $z_{3,2}$, and as component 2 is uni-univalent, the counter-ion must be univalent. Species 1 of component 2 is thus identified as the co-ion of the system, and as the co-ion is univalent, its valence, $z_{2,1}$, must be equal to $-z_{2,2}$. In terms of magnitude, $|z_{2,1}| = |z_{2,2}| = |z_{3,2}| = 1$, and $|z_{3,1}| \geq 1$. In terms of signed quantities, $z_{3,1} = -|z_{3,1}|z_{3,2} = -|z_{3,1}|z_{2,2} = |z_{3,1}|z_{2,1}$. To conform to the constraints of the Debye-Hückel-Henry model applied below, the macro-ion is assumed to be a spherical molecule with a centrosymmetric charge distribution.

In Equations M5 to M20, the system can be considered identical to that just described. For example, when the valence of the macro-ion is written as $z_{k,1}$, it can be assumed that $k = 3$. Likewise, the counter-ion of the system will be univalent, and will be a species of both component $k = 3$ and component $k = 2$, the latter component being identified as the uni-univalent electrolyte. Furthermore, except where it is taken to the limit of zero concentration, the electrolyte is assumed present in sufficient excess that it alone determines the ionic strength, Γ, of the system, and as the electrolyte is uni-univalent, its molar concentration is identical to Γ. (Where the electrolyte approaches zero concentration, it is also assumed that the concentration of the macro-ion component is infinitesimally low, in which case, Γ can still be equated to the molar concentration of the electrolyte.)

According to the Debye-Hückel-Henry model [Henry, 1931], in the absence of ion relaxation, $z^*_{k,1}$, the reduced valence of a spherical macro-ion with a centrosymmetric charge distribution, is given by

$$z^{*}_{k,1} = z_{k,1} \frac{H\left(\kappa^{-1}_{\Gamma/T} \alpha_{k,1}\right)}{1 + \kappa^{-1}_{\Gamma/T} \alpha_{k,1}},$$

(M5)

where $z_{k,1}$ is the valence of a macro-ion of solute component k within its surface of shear, $\alpha_{k,1}$ is the cgs radial distance to the surface of shear of a macro-ion of solute component k, $\kappa^{-1}_{\Gamma/T}$ is the cgs inverse Debye length for the system, and $H(\kappa^{-1}_{\Gamma/T}, \alpha_{k,1})$ is Henry's function. The sum of the Stokes radii of the equivalent spheres of a macro-ion of solute component k and its counter-ion can be used to approximate $\alpha_{k,1}$. The cgs inverse Debye length for the system is given by

$$\kappa^{-1}_{\Gamma/T} = F \sqrt{\frac{2\Gamma}{\varepsilon \varepsilon_0 RT}} \sqrt{\frac{1000\ \mathrm{l}}{\mathrm{m}^3}} \left(\frac{1\ \mathrm{m}}{100\ \mathrm{cm}}\right),$$

(M6)

where F is the mks Faraday, R is the mks ideal gas constant, ε_0 is the mks permittivity constant, ε is the dielectric constant (the relative permittivity) of the solution (the applicable dielectric material), and Γ is the mol-per-litre ionic strength. For $\kappa^{-1}_{\Gamma/T} \alpha_{k,1} <$ 200,000, Henry's function can be approximated by

$$H\left(\kappa^{-1}_{\Gamma/T} \alpha_{k,1}\right) = \frac{5 - \operatorname{erf}\left(\frac{5}{4}\left[K_0 + K_1\left\{\log\left(\kappa^{-1}_{\Gamma/T} \alpha_{k,1}\right)\right\} + K_2\left\{\log\left(\kappa^{-1}_{\Gamma/T} \alpha_{k,1}\right)\right\}^2\right]\right)}{4},$$

(M7)

where $K_0 = 0.99302$, $K_1 = -1.10094$ and $K_2 = 0.10392$ [Moody *et al.*, 2005]. For $\kappa^{-1}_{\Gamma/T} \alpha_{k,1} \geq$ 200,000, Henry's function can be equated to 1.5, which is the value that the precise form of Henry's function approaches as $\kappa^{-1}_{\Gamma/T} \alpha_{k,1}$ approaches infinity. (Further information about the parameters in Equations M5 and M6 is found in the second note following the **List of selected parameters, their indices, and their cgs, mks or other dimensions**.)

At a given $T > 0$ and a given ε for which $1 \leq \varepsilon < \infty$,

$$\lim_{\Gamma \to 0} \kappa^{-1}_{\Gamma/T} = 0\ \mathrm{cm}^{-1}$$

(M8)

and

$$\lim_{\Gamma\to\infty} \kappa_{\Gamma/T}^{-1} = \infty\ \mathrm{cm}^{-1}.$$

(M9)

Equations M8 and M9 show the behaviour of the cgs inverse Debye length for the system (Equation M6) at the hypothetical extremes of Γ.

At a given $\alpha_{k,1} > 0$, a given $\mathrm{T} > 0$ and a given ε for which $1 \leq \varepsilon < \infty$,

$$\lim_{\Gamma\to 0} H\left(\kappa_{\Gamma/T}^{-1}\alpha_{k,1}\right) = \lim_{\kappa_{\Gamma/T}^{-1}\to\frac{0}{\mathrm{cm}}} H\left(\kappa_{\Gamma/T}^{-1}\alpha_{k,1}\right) = 1$$

(M10)

and

$$\lim_{\Gamma\to\infty} H\left(\kappa_{\Gamma/T}^{-1}\alpha_{k,1}\right) = \lim_{\kappa_{\Gamma/T}^{-1}\to\frac{\infty}{\mathrm{cm}}} H\left(\kappa_{\Gamma/T}^{-1}\alpha_{k,1}\right) = 1.5.$$

(M11)

Equations M10 and M11 show the behaviour of Henry's function (Equation M7) at the hypothetical extremes of Γ.

It is not possible to achieve the upper extreme of ionic strength applied in Equations M9 and M11. Nor is it possible to perform an MCE experiment at the lower extreme of ionic strength applied in Equations M8 and M10. Despite their hypothetical nature, however, these extremes of ionic strength, when applied to Equation M5, reveal the trends sought regarding $z_{k.1}^{*}$ as a function of Γ.

At a given $z_{k,1}$, a given $\alpha_{k,1} > 0$, a given $\mathrm{T} > 0$ and a given ε for which $1 \leq \varepsilon < \infty$,

$$\lim_{\Gamma\to 0} z_{k,1}^{*} = \lim_{\kappa_{\Gamma/T}^{-1}\to\frac{0}{\mathrm{cm}}} z_{k,1}^{*} = z_{k,1}$$

(M12)

and

$$\lim_{\Gamma\to\infty} z_{k,1}^{*} = \lim_{\kappa_{\Gamma/T}^{-1}\to\frac{\infty}{\mathrm{cm}}} z_{k,1}^{*} = 0.$$

(M13)

It is now argued that as $z_{k,1}^{*}$ of Equations M12 and M13 goes, so goes z_{k}^{*} of Equation M2. That is, to the extent that $|z_{k}^{*}|$, the magnitude of z_{k}^{*}, can be nonzero, $|z_{k}^{*}|$ will be greatest when Γ reaches its lowest practical value, while $|z_k^*|$ will be smallest when Γ reaches its highest practical value. According to Equation M2, the extent to which $|z_k^*|$ can be nonzero will partly depend on whether z_q is nonzero for at least one of the n solute components. **An examination of whether (z_q)$_N$ and z_q can be regarded as molecular parameters**, which is the last part of this section (see Equation M21 to M25), addresses the question of whether z_q can be nonzero.

Zeta potential as a function of ionic strength

In a typical MCE experiment, the signal is proportional to the concentration of the membrane-confined species, of which there may be just one in a system like that to which Equation M5 is applied above. In such cases, when Equation M2 is used to calculate z_k^* from σ_k, the result may be equivalent to $z_{k,1}^*$ of Equation M5. The ability to make such selective measurements is exploited in the following consideration of the zeta potential.

Smoluchowski [1903] defined the zeta potential as the electrical potential at the surface of shear of an individual macro-ion. With respect to the macro-ion of solute component k, the zeta potential, $\zeta_{k,1}$, can be related to the coupled-flow-electrophoretic mobility coefficient, $\boldsymbol{u}_{k,1}$ (Equation A16), via

$$\zeta_{k,1} = \frac{\eta \boldsymbol{u}_{k,1}}{\varepsilon\varepsilon_0}\left(\frac{1\ \mathrm{kg}}{1000\ \mathrm{g}}\right)\left(\frac{1\ \mathrm{m}}{100\ \mathrm{cm}}\right),$$

(M14)

where it is assumed that η and $\boldsymbol{u}_{k,1}$ are cgs quantities while ε_0 is an mks quantity. To proceed, it is now necessary to propose that, qualitatively at least, u_k can substitute for $\boldsymbol{u}_{k,1}$ and z_k^* can substitute for $z_{k,1}^*$.

As a rearrangement of Equation M2 shows,

$$u_k = \frac{FD_k z_k^*}{\varpi RT}.$$

(M15)

Equating $\boldsymbol{u}_{k,1}$ to u_k (Equation A22) and combining the previous two equations yields

$$\zeta_{k,1} \cong \frac{\eta F D_k z_k^*}{\varpi R T \varepsilon \varepsilon_0}\left(\frac{1\ \text{kg}}{1000\ \text{g}}\right)\left(\frac{1\ \text{m}}{100\ \text{cm}}\right).$$

(M16)

Next, z_k^* is equated to $z_{k,1}^*$ of Equations M5 to M13, the corresponding results from which are used to determine $\zeta_{k,1}$ at the limits of interest. For $z_k^* = z_{k,1}^*$ of Equation M5, at a given $z_{k,1}$, a given $\alpha_k > 0$, a given $T > 0$ and a given ε for which $1 \leq \varepsilon < \infty$,

$$\lim_{\kappa_{\Gamma/T}^{-1} \to 0} \zeta_{k,1} \cong \frac{\eta F D_k z_{k,1}}{\varpi R T \varepsilon \varepsilon_0}\left(\frac{1\ \text{kg}}{1000\ \text{g}}\right)\left(\frac{1\ \text{m}}{100\ \text{cm}}\right)$$

(M17)

and

$$\lim_{\kappa_{\Gamma/T}^{-1} \to \infty} \zeta_{k,1} \cong 0.$$

(M18)

From the relationship (Equations M6 and M7) of $\kappa_{\Gamma/T}^{-1}$ to Γ, then,

$$\lim_{\Gamma \to 0} \zeta_{k,1} \cong \frac{\eta F D_k z_{k,1}}{\varpi R T \varepsilon \varepsilon_0}\left(\frac{1\ \text{kg}}{1000\ \text{g}}\right)\left(\frac{1\ \text{m}}{100\ \text{cm}}\right)$$

(M19)

and

$$\lim_{\Gamma \to \infty} \zeta_{k,1} \cong 0.$$

(M20)

According to these hypothetical limits, $\zeta_{k,1}$ exhibits the same trends as $z_{k,1}^*$ with respect to a dependence on Γ. The dependence on Γ shown by both $\zeta_{k,1}$ and $z_{k,1}^*$ renders them system parameters, rather than molecular parameters.

Where data have been obtained from MCE experiments in which the signal was proportional to the concentration of a single membrane-confined species, and during which v_0 was negligible, z_k^* (Equation M2) may be equal to $z_{k,1}^*$, in which case, u_k (Equation M15) should be equal to $\boldsymbol{u}_{k,1}$. Where the experimental arrangement would yield $z_k^* = z_{k,1}^*$ upon application of Equation M2, the subsequent application of Equation M16 would yield a valid measure of $\zeta_{k,1}$, and the two sides of each equation from M16 to M20 could be fully, rather than approximately, equatable. To the extent of such equatability, z_k^* is shown to be a system parameter by the same evidence that shows $z_{k,1}^*$ to be a system parameter.

An examination of whether $(z_q)_N$ and z_q can be regarded as molecular parameters

The number average of the valence, $(z_q)_N$, is given, as in Equation I17, by

$$\left(z_q\right)_N = \frac{\sum_{a=1}^{n_q} N_{q,a} z_{q,a}}{\sum_{a=1}^{n_q} N_{q,a}},$$

(M21)

where the n_q species of component q are indexed by a, so that, for species a of component q, $z_{q,a}$ is the valence and $N_{q,a}$ is the number of molecules (Equation I1). Each $z_{q,a}$ can be considered independent of system properties by definition, as $z_{q,a}$ is a defining molecular parameter. (For a given species, valence cannot change. Within a component, a change in valence requires an association of more than one species, or a dissociation into more than one species.) In the absence of an electrical field, each $N_{q,a}$ may change with such system properties as T, P and solute concentrations, but each $N_{q,a}$ should be such that Equation M21 yields $(z_q)_N = 0$ at any given point in the system. Thus, in the absence of an electrical field, $(z_q)_N$ could be viewed as a molecular parameter.

In the presence of an electrical field, the gradient of the total molar potential of solute component q (Equation I20) includes an electrical contribution (Equation I15 to I19b). Division of that electrical contribution by F yields

$$\left(z_q\right)_g \nabla\Psi \ = \left(z_q\right)_N \nabla\Psi + \Psi\nabla\left(z_q\right)_N,$$

(M22)

where $(z_q)_g$ is the gradient-modified-average valence for all species of component q, Ψ is the cgs electrical potential, and $\nabla\Psi$ is proportional to the electrical field (Equations A3, H6 and H7). (The equation for the electrical field can be written as $\vec{E} = -\varpi\nabla\Psi$. Thus, where $|\nabla\Psi| > 0$, $|\vec{E}| > 0$, and where $|\vec{E}| > 0$, an electrical field is present.)

Dividing both sides of Equation M22 by $\nabla\Psi$ yields

$$\left(z_q\right)_g = \left(z_q\right)_N + \frac{\nabla\left(z_q\right)_N}{\nabla \ln \Psi},$$

(M23)

where

$$\nabla\left(z_q\right)_N = \nabla\left(\frac{\sum_{a=1}^{n_q} N_{q,a} z_{q,a}}{\sum_{a=1}^{n_q} N_{q,a}}\right) = \frac{\sum_{a=1}^{n_q} z_{q,a} \nabla N_{q,a}}{\sum_{a=1}^{n_q} N_{q,a}} - \left(z_q\right)_N \frac{\sum_{a=1}^{n_q} \nabla N_{q,a}}{\sum_{a=1}^{n_q} N_{q,a}}.$$

(M24)

Equation M23 is an alternative form of Equation I19b. As a comparison of Equations A2 and I20 shows, $(z_q)_g$ is identical to z_q. As such, Equation M23 shows that $|z_q| > 0$ where $|(z_q)_N| > 0$ only, and $z_q = (z_q)_N$ where $\nabla(z_q)_N = 0$.

In what follows,

$$\left(\nabla z_q\right)_N = \frac{\sum_{a=1}^{n_q} N_{q,a} \nabla z_{q,a}}{\sum_{a=1}^{n_q} N_{q,a}} = \frac{\sum_{a=1}^{n_q} N_{q,a}(0)}{\sum_{a=1}^{n_q} N_{q,a}} = 0$$

(M25)

is the number-average gradient of the valence for all species of component q, and $(\nabla z_q)_N = 0$ because each $\nabla z_{q,a} = 0$.

For a system at steady state, in the absence of an electrical field, each $N_{q,a}$ would be invariant with space. If each $N_{q,a}$ were invariant with space, each $\nabla N_{q,a}$ of Equation M24 would equal zero everywhere, in which case, throughout the system, $\nabla(z_q)_N$ would equal $(\nabla z_q)_N = 0$. This result holds for any value of n_q. For the special case of $n_q = 1$, at each point in space, there is only one $\nabla N_{q,a}$, and regardless of whether $\nabla N_{q,a}$ equals zero, $\nabla(z_q)_N = (\nabla z_q)_N = 0$. When $n_q = 1$, charge neutrality also requires that $z_q = 0$.

Where an electrical field is present, an electrical current flows through the system. Thus, the presence of an electrical field drives transport processes in an MCE system. Where such transport processes result in the development of concentration gradients, diffusion will also contribute to the net transport process. As noted with respect to Equation H3, the minimum volumes that are charge-neutral in the absence of transport processes can become electrostatically polarised in the presence of transport processes. Such polarisation gives rise to the electrophoretic/asymmetry effect, and it is argued here, without proof, that where the electrophoretic/asymmetry effect is present, it is possible that $|(z_q)_N| > 0$. The electrical field and the flow of electrical current would produce the polarisation that gives rise to the electrophoretic/asymmetry effect that, as argued here, can render $|(z_q)_N| > 0$. By Equation M23, $|z_q| > 0$ where $|(z_q)_N| > 0$.

Regardless of whether a system is at steady state, in the presence of an electrical field, some $N_{q,a}$ might not be invariant with space. Wherever $N_{q,a}$ varies with spatial position, the corresponding $\nabla N_{q,a}$ of Equation M24 will be nonzero, and wherever $\nabla N_{q,a}$ is nonzero, $\nabla(z_q)_N$ will be nonzero, provided that the electrophoretic/asymmetry effect can render $|(z_q)_N| > 0$. According to Equation M23, z_q will differ from $(z_q)_N$ where $\nabla(z_q)_N$ differs from zero. Compared to $(z_q)_N$, then, z_q is especially dependent on electrical field.

Equation M21 is now reconsidered for a system in which an electrical field is present. In the presence of an electrical field, each $N_{q,a}$ may change with such system properties as T, P and solute concentrations, and each $N_{q,a}$ may be such that Equation M21 yields $(z_q)_N \neq 0$ at some or all points in the system. Thus, in the presence of an electrical field, $(z_q)_N$ is best viewed as a system parameter. Given the relationship (Equation M23) of $(z_q)_N$ to $z_q = (z_q)_g$, in the presence of an electrical field, z_q is also best viewed as a system parameter.

The discussion surrounding Equations M21 to M25 constitutes the argument that, where an electrical field is present, $(z_q)_N$ and $z_q = (z_q)_g$ are system parameters, in that they depend on system properties, such as T, P, component concentrations in general, and component concentrations that contribute to Γ in particular. In the absence of an electrical field, $(z_q)_N$ and z_q both equal zero regardless of the system properties. Thus, $(z_q)_N$ and z_q can be regarded as molecular parameters in the absence of an electrical field.

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Section N: A simple coupled-flow equation for MCE

Equation A24 can be expressed as

$$I_k = c_k\left[u_k^0\left(\frac{1+\sum_{a=1}^{n} p_{k,a}c_a}{1+\sum_{a=1}^{n} h_{k,a}c_a}\right)E - D_k^0\left(\frac{1+\sum_{a=1}^{n} y_{k,a}c_a}{1+\sum_{a=1}^{n} h_{k,a}c_a}\right)\left(\frac{\partial lnc_k}{\partial \xi}\right)_t\right]$$

or

$$I_k = c_k D_k^0\left(\frac{1+\sum_{a=1}^{n} y_{k,a}c_a}{1+\sum_{a=1}^{n} h_{k,a}c_a}\right)\left[\sigma_k^0\left(\frac{1+\sum_{a=1}^{n} p_{k,a}c_a}{1+\sum_{a=1}^{n} y_{k,a}c_a}\right) - \left(\frac{\partial lnc_k}{\partial \xi}\right)_t\right],$$

(N1)

where the expressions for σ_k, D_k and u_k,

$$\sigma_k = \sigma_k^0 \left(\frac{1 + \sum_{a=1}^{n} p_{k,a} c_a}{1 + \sum_{a=1}^{n} y_{k,a} c_a} \right),$$

(N2)

$$D_k = D_k^0 \left(\frac{1 + \sum_{a=1}^{n} y_{k,a} c_a}{1 + \sum_{a=1}^{n} h_{k,a} c_a} \right)$$

(N3)

and

$$u_k = \frac{\sigma_k D_k}{E} = \frac{\sigma_k^0 D_k^0}{E} \left(\frac{1 + \sum_{a=1}^{n} p_{k,a} c_a}{1 + \sum_{a=1}^{n} h_{k,a} c_a} \right) = u_k^0 \left(\frac{1 + \sum_{a=1}^{n} p_{k,a} c_a}{1 + \sum_{a=1}^{n} h_{k,a} c_a} \right),$$

(N4)

respectively, were obtained by applying the truncated linear equations (3, 10 and 12) of Section D to Equations D5, D6 and D7, respectively. In contrast to Equation D7, however, $\sigma_k^0 D_k^0 / E$has been defined as u_k^0 in Equation N4.

Equation N1 does not account for coupled flows, but can be used as the basis for an equation that does. Multiplying Equation A18 by M_k, which is equated to $(M_k)_J$ in Section I (**Calculating valence, molar mass, chemical potential and partial specific volume for a multi-species component**), yields

$$J_k M_k = I_k = M_k \left\{ \frac{v_0 c_k}{M_k} + \sum_{q=1}^{n} \frac{c_q}{M_q} \left[\boldsymbol{u}_{k,q} E - \boldsymbol{D}_{k,q} \left(\frac{\partial ln c_q}{\partial \xi} \right)_t \right] \right\}.$$

(N5)

For $q = k$, the right-hand-side of Equation N3 can be used to approximate $\boldsymbol{D}_{k,q}$ and the right-hand-side of Equation N4 can be used to approximate $\boldsymbol{u}_{k,q}$. More generally, $\boldsymbol{D}_{k,q}$ can be approximated as

$$\boldsymbol{D}_{k,q} = X_{k,q}^{D} D_k^0 \left(\frac{1 + \sum_{a=1}^{n} y_{q,a} c_a}{1 + \sum_{a=1}^{n} h_{k,a} c_a} \right)$$

(N6)

and $\boldsymbol{u}_{k,q}$ can be approximated as

$$\boldsymbol{u}_{k,q} = X_{k,q}^{u} u_q^0 \left(\frac{1 + \sum_{a=1}^{n} p_{q,a} c_a}{1 + \sum_{a=1}^{n} h_{q,a} c_a} \right),$$

(N7)

where $X_{k,q}^{D}$ and $X_{k,q}^{u}$ are constants. Thus, Equations N6 and N7 become equivalent to the truncated forms of $X_{k,q}^{D}$ times Equation D6 and $X_{k,q}^{u}$ times Equation D7, respectively, when $q = k$. Applying Equations N6 and N7 to Equation N5 yields

$$I_k = M_k\left\{\frac{v_0 c_k}{M_k} + \sum_{q=1}^{n}\frac{c_q}{M_q}\left[X_{k,q}^{u}u_q^0\left(\frac{1+\sum_{a=1}^{n}p_{q,a}c_a}{1+\sum_{a=1}^{n}h_{q,a}c_a}\right)E - X_{k,q}^{D}D_k^0\left(\frac{1+\sum_{a=1}^{n}y_{q,a}c_a}{1+\sum_{a=1}^{n}h_{k,a}c_a}\right)\left(\frac{\partial lnc_q}{\partial\xi}\right)_t\right]\right\}$$

$$= M_k\left\{\frac{v_0 c_k}{M_k} + E\left[\sum_{q=1}^{n}\frac{c_q}{M_q}X_{k,q}^{u}\,u_q^0\left(\frac{1+\sum_{a=1}^{n}p_{q,a}c_a}{1+\sum_{a=1}^{n}h_{q,a}c_a}\right)\right]\right.$$

$$\left. - \left[\sum_{q=1}^{n}\left(\frac{\partial c_q}{\partial\xi}\right)_t\frac{X_{k,q}^{D}D_k^0}{M_q}\left(\frac{1+\sum_{a=1}^{n}y_{q,a}c_a}{1+\sum_{a=1}^{n}h_{k,a}c_a}\right)\right]\right\}.$$

(N8)

For $n = 2$, Equation N8 yields

$$I_1 = M_1\left\{\frac{v_0 c_1}{M_1} + E\left[\frac{c_1}{M_1}X_{1,1}^{u}u_1^0\left(\frac{1+p_{1,1}c_1+p_{1,2}c_2}{1+h_{1,1}c_1+h_{1,2}c_2}\right) + \frac{c_2}{M_2}X_{1,2}^{u}u_2^0\left(\frac{1+p_{2,1}c_1+p_{2,2}c_2}{1+h_{2,1}c_1+h_{2,2}c_2}\right)\right]\right.$$

$$- \left[\frac{1}{M_1}\left(\frac{\partial c_1}{\partial\xi}\right)_t X_{1,1}^{D}D_1^0\left(\frac{1+y_{1,1}c_1+y_{1,2}c_2}{1+h_{1,1}c_1+h_{1,2}c_2}\right)\right.$$

$$\left.\left. + \frac{1}{M_2}\left(\frac{\partial c_2}{\partial\xi}\right)_t X_{1,2}^{D}D_2^0\left(\frac{1+y_{2,1}c_1+y_{2,2}c_2}{1+h_{2,1}c_1+h_{2,2}c_2}\right)\right]\right\}$$

and

$$I_2 = M_2\left\{\frac{v_0 c_2}{M_2} + E\left[\frac{c_1}{M_1}X_{2,1}^{u}u_1^0\left(\frac{1+p_{1,1}c_1+p_{1,2}c_2}{1+h_{1,1}c_1+h_{1,2}c_2}\right) + \frac{c_2}{M_2}X_{2,2}^{u}u_2^0\left(\frac{1+p_{2,1}c_1+p_{2,2}c_2}{1+h_{2,1}c_1+h_{2,2}c_2}\right)\right]\right.$$

$$- \left[\frac{1}{M_1}\left(\frac{\partial c_1}{\partial\xi}\right)_t X_{2,1}^{D}D_1^0\left(\frac{1+y_{1,1}c_1+y_{1,2}c_2}{1+h_{1,1}c_1+h_{1,2}c_2}\right)\right.$$

$$\left.\left. + \frac{1}{M_2}\left(\frac{\partial c_2}{\partial\xi}\right)_t X_{2,2}^{D}D_2^0\left(\frac{1+y_{2,1}c_1+y_{2,2}c_2}{1+h_{2,1}c_1+h_{2,2}c_2}\right)\right]\right\}.$$

(N9)

The coupled-flow analogue of the (apparent) reduced valence coefficient (Equation A23a) is defined as

$$\boldsymbol{\sigma}_{k,q} = \frac{E\boldsymbol{u}_{k,q}}{\boldsymbol{D}_{k,q}} = \frac{E\dfrac{F}{\varpi}z_q}{RT\left[1 + c_q \sum_{w=1}^{n}\left(\dfrac{\partial c_w}{\partial c_q}\right)_t \left(\dfrac{\partial ln\gamma_q}{\partial c_w}\right)_{t,T,P,c_{a\neq w}}\right]},$$

(N10)

where $\boldsymbol{D}_{k,q}$ and $\boldsymbol{u}_{k,q}$ are defined by Equations A17 and A16, respectively, and are approximated by Equations N6 and N7, respectively. This result is noteworthy for the lack of a viscosity term in $\sigma_{k,q}$, presumably because $L_{k,q}$ from $\boldsymbol{u}_{k,q}$ cancels $L_{k,q}$ from $\boldsymbol{D}_{k,q}$. (See the discussion following Equation A20.) Using Equations N6 and N7 to express $\boldsymbol{D}_{k,q}$ and $\boldsymbol{u}_{k,q}$, respectively, and introducing a set of constants denoted by $X_{k,q}^{\sigma}$, $\boldsymbol{\sigma}_{k,q}$ can be approximated as

$$\boldsymbol{\sigma}_{k,q} = \frac{E\boldsymbol{u}_{k,q}}{\boldsymbol{D}_{k,q}} = \frac{EX_{k,q}^{u}u_q^0\left(\dfrac{1+\sum_{a=1}^{n}p_{q,a}c_a}{1+\sum_{a=1}^{n}h_{q,a}c_a}\right)}{X_{k,q}^{D}D_q^0\left(\dfrac{1+\sum_{a=1}^{n}y_{q,a}c_a}{1+\sum_{a=1}^{n}h_{q,a}c_a}\right)} = X_{k,q}^{\sigma}\sigma_q^0\left(\frac{1+\sum_{a=1}^{n}p_{q,a}c_a}{1+\sum_{a=1}^{n}y_{q,a}c_a}\right),$$

(N11)

where, by virtue of $X_{k,q}^{\sigma}$, $X_{k,q}^{D}$, $X_{k,q}^{u}$, σ_q^0, D_q^0 and u_q^0 being constants,

$$X_{k,q}^{\sigma}\sigma_q^0 = \frac{EX_{k,q}^{u}u_q^0}{X_{k,q}^{D}D_q^0}$$

(N12)

is a constant to the extent that E is constant. Thus, Equation N11 becomes equivalent to $X_{k,q}^{\sigma}$ times the truncated form of Equation D5 when $q = k$. Using Equation N10, Equation N5 can be rewritten as

$$I_k = M_k\left\{\frac{v_0c_k}{M_k} + \sum_{q=1}^{n}\frac{c_q}{M_q}\boldsymbol{D}_{k,q}\left[\boldsymbol{\sigma}_{k,q} - \left(\frac{\partial lnc_q}{\partial\xi}\right)_t\right]\right\}.$$

(N13)

For $q = k$, the right-hand-side of Equation N2 can be used to approximate $\boldsymbol{\sigma}_{k,q}$ and the right-hand-side of Equation N3 can be used to approximate $\boldsymbol{D}_{k,q}$. More generally, $\boldsymbol{D}_{k,q}$ can be approximated by Equation N6, and $\boldsymbol{\sigma}_{k,q}$ can be approximated by Equation N11. Applying Equations N6 and N11 to Equation N13 yields

$$I_k = M_k\left\{\frac{v_0c_k}{M_k} + \sum_{q=1}^{n}\frac{c_q}{M_q}X_{k,q}^{D}D_q^0\left(\frac{1+\sum_{a=1}^{n}y_{q,a}c_a}{1+\sum_{a=1}^{n}h_{q,a}c_a}\right)\left[X_{k,q}^{\sigma}\sigma_q^0\left(\frac{1+\sum_{a=1}^{n}p_{q,a}c_a}{1+\sum_{a=1}^{n}y_{q,a}c_a}\right) - \left(\frac{\partial lnc_q}{\partial\xi}\right)_t\right]\right\}.$$

(N14)

For $n = 2$, Equation N14 yields

$$\begin{aligned} I_1 = M_1 \Bigg(\frac{v_0 c_1}{M_1} + \Bigg\{ & \left[\frac{c_1}{M_1} X^D_{1,1} X^\sigma_{1,1} D^0_1 \sigma^0_1 \left(\frac{1 + p_{1,1}c_1 + p_{1,2}c_2}{1 + h_{1,1}c_1 + h_{1,2}c_2} \right) \right] \\ & - \left[\frac{1}{M_1} \left(\frac{\partial c_1}{\partial \xi} \right)_t X^D_{1,1} D^0_1 \left(\frac{1 + y_{1,1}c_1 + y_{1,2}c_2}{1 + h_{1,1}c_1 + h_{1,2}c_2} \right) \right] \\ & + \left[\frac{c_2}{M_2} X^D_{1,2} X^\sigma_{1,2} D^0_2 \sigma^0_2 \left(\frac{1 + p_{2,1}c_1 + p_{2,2}c_2}{1 + h_{2,1}c_1 + h_{2,2}c_2} \right) \right] \\ & - \left[\frac{1}{M_2} \left(\frac{\partial c_2}{\partial \xi} \right)_t X^D_{1,2} D^0_2 \left(\frac{1 + y_{2,1}c_1 + y_{2,2}c_2}{1 + h_{2,1}c_1 + h_{2,2}c_2} \right) \right] \Bigg\} \Bigg) \end{aligned}$$

and

$$\begin{aligned} I_2 = M_2 \Bigg(\frac{v_0 c_2}{M_2} + \Bigg\{ & \left[\frac{c_1}{M_1} X^D_{2,1} X^\sigma_{2,1} D^0_1 \sigma^0_1 \left(\frac{1 + p_{1,1}c_1 + p_{1,2}c_2}{1 + h_{1,1}c_1 + h_{1,2}c_2} \right) \right] \\ & - \left[\frac{1}{M_1} \left(\frac{\partial c_1}{\partial \xi} \right)_t X^D_{2,1} D^0_1 \left(\frac{1 + y_{1,1}c_1 + y_{1,2}c_2}{1 + h_{1,1}c_1 + h_{1,2}c_2} \right) \right] \\ & + \left[\frac{c_2}{M_2} X^D_{2,2} X^\sigma_{2,2} D^0_2 \sigma^0_2 \left(\frac{1 + p_{2,1}c_1 + p_{2,2}c_2}{1 + h_{2,1}c_1 + h_{2,2}c_2} \right) \right] \\ & - \left[\frac{1}{M_2} \left(\frac{\partial c_2}{\partial \xi} \right)_t X^D_{2,2} D^0_2 \left(\frac{1 + y_{2,1}c_1 + y_{2,2}c_2}{1 + h_{2,1}c_1 + h_{2,2}c_2} \right) \right] \Bigg\} \Bigg). \end{aligned}$$

(N15)

Re-evaluating u_k, D_k and σ_k

In terms of D_k and u_k, or D_k and σ_k, the mass flow of solute component k can be written as

$$I_k = J_k M_k = c_k \left[u_k E - D_k \left(\frac{\partial lnc_k}{\partial \xi} \right)_t \right]$$

(N16)

or

$$I_k = J_k M_k = c_k D_k \left[\sigma_k - \left(\frac{\partial lnc_k}{\partial \xi} \right)_t \right]$$

(N17)

both forms of which are shown in Equation A24.

Replacing D_k and u_k of Equation N16 with

$$D_k = \frac{M_k}{c_k\left(\frac{\partial lnc_k}{\partial \xi}\right)_t}\sum_{q=1}^{n}\frac{c_q}{M_q}\left(\frac{\partial lnc_q}{\partial \xi}\right)_t X_{k,q}^{D}D_q^0\left(\frac{1+\sum_{a=1}^{n} y_{q,a}c_a}{1+\sum_{a=1}^{n} h_{q,a}c_a}\right)$$

(N18)

and

$$u_k = \frac{M_k}{c_k}\sum_{q=1}^{n}\frac{c_q}{M_q}X_{k,q}^{u}u_q^0\left(\frac{1+\sum_{a=1}^{n} p_{q,a}c_a}{1+\sum_{a=1}^{n} h_{q,a}c_a}\right)+\frac{v_0}{E},$$

(N19)

respectively, yields Equation N8. Equations N18 and N19 approximate Equations A21 and A22, respectively.

Replacing D_k and σ_k of Equation N17 with

$$D_k = \frac{M_k}{\left(\frac{\partial c_k}{\partial \xi}\right)_t}\sum_{q=1}^{n}\frac{\left(\frac{\partial c_q}{\partial \xi}\right)_t}{M_q}X_{k,q}^{D}D_q^0\left(\frac{1+\sum_{a=1}^{n} y_{q,a}c_a}{1+\sum_{a=1}^{n} h_{q,a}c_a}\right)$$

(N20)

and

$$\sigma_k = \frac{Eu_k}{D_k} = \left(\frac{\partial lnc_k}{\partial \xi}\right)_t \frac{E\sum_{q=1}^{n}\frac{c_q}{M_q}X_{k,q}^{u}u_q^0\left(\frac{1+\sum_{a=1}^{n} p_{q,a}c_a}{1+\sum_{a=1}^{n} h_{q,a}c_a}\right)+v_0\frac{c_k}{M_k}}{\sum_{q=1}^{n}\frac{\left(\frac{\partial c_q}{\partial \xi}\right)_t}{M_q}X_{k,q}^{D}D_q^0\left(\frac{1+\sum_{a=1}^{n} y_{q,a}c_a}{1+\sum_{a=1}^{n} h_{q,a}c_a}\right)}$$

$$= \left(\frac{\partial lnc_k}{\partial \xi}\right)_t \frac{\sum_{q=1}^{n}\frac{c_q}{M_q}X_{k,q}^{\sigma}X_{k,q}^{D}\sigma_q^0D_q^0\left(\frac{1+\sum_{a=1}^{n} p_{q,a}c_a}{1+\sum_{a=1}^{n} h_{q,a}c_a}\right)+v_0\frac{c_k}{M_k}}{\sum_{q=1}^{n}\frac{\left(\frac{\partial c_q}{\partial \xi}\right)_t}{M_q}X_{k,q}^{D}D_q^0\left(\frac{1+\sum_{a=1}^{n} y_{q,a}c_a}{1+\sum_{a=1}^{n} h_{q,a}c_a}\right)}$$

$$= \left(\frac{\partial lnc_k}{\partial \xi}\right)_t \frac{\sum_{q=1}^{n}\frac{c_q}{M_q}X_{k,q}^{u}\sigma_q^0D_q^0\left(\frac{1+\sum_{a=1}^{n} p_{q,a}c_a}{1+\sum_{a=1}^{n} h_{q,a}c_a}\right)+v_0\frac{c_k}{M_k}}{\sum_{q=1}^{n}\frac{\left(\frac{\partial c_q}{\partial \xi}\right)_t}{M_q}X_{k,q}^{D}D_q^0\left(\frac{1+\sum_{a=1}^{n} y_{q,a}c_a}{1+\sum_{a=1}^{n} h_{q,a}c_a}\right)}$$

(N21)

respectively, yields Equation N14. Equations N20 and N21 approximate Equations A21 and A23a, respectively. Multiplying both sides of Equation N12 by $X^D_{k,q}D^0_q$ yields $X^D_{k,q}X^\sigma_{k,q}D^0_q\sigma^0_q =$ $EX^u_{k,q}u^0_q$, the left-hand side of which is used to replace $EX^u_{k,q}u^0_q$ in the numerator of Equation N21. As $D^0_q\sigma^0_q = Eu^0_q$ (Equations A21, B23∓, C34∓), $X^u_{k,q} = X^D_{k,q}X^\sigma_{k,q}$, in which the derived parameter is actually

$$X^\sigma_{k,q} = \frac{X^u_{k,q}}{X^D_{k,q}}.$$

(N22)

Provided that $X^D_{k,q}$ is not equal to zero, $X^\sigma_{k,q}$can be calculated using Equation 26. Where $X^D_{k,q}$ $= 0$, $X^\sigma_{k,q}$ is undefined, except that the product, $X^\sigma_{k,q}X^D_{k,q}$, is nevertheless treated as being equal to $X^u_{k,q}$.

When all $X^D_{k,q\neq k}$ values are equal to zero, Equation N20 reduces to Equation N1. Similarly, when all $X^D_{k,q\neq k}$ and $X^u_{k,q\neq k}$ values are equal to zero, Equation N21 reduces to Equation N2. As shown by the inability to eliminate the $(1 + \sum_{a=1}^{n} h_{q,a}c_a)$ terms from Equations N21 when not all $X^D_{k,q\neq k}$ and $X^u_{k,q\neq k}$ values are equal to zero, however, $h_{q,a}$ values, which are the second virial coefficients of the viscosity of the system, can wield some influence on σ_k values, even at equilibrium, unless all $X^D_{k,q\neq k}$ and $X^u_{k,q\neq k}$ values are equal to zero. This residual influence of $h_{q,a}$ is a flaw of the approximation of σ_k by Equation N21, as the equation (A23) that defines σ_k is devoid of any viscosity-related terms such as $h_{q,a}$, which represents the species-q-applicable transport coefficient that links c_a to the viscosity of the system (Equations D6, D9 D12 and D13).

Re-evaluating the *ξ*-independent coefficients of the basis functions indexed by *j*

Equations 33−, 33+, 34− and 34+ of Section C (**A solution to the *t*- and *ξ*-dependent continuity equation for MCE in terms of species**) show the functions used to approximate the concentration-dependent transport coefficients of each species, *e*, of each solute component, *k*. To render those functions ξ-independent, the solute concentrations at each explicitly included spatial element, ξ_j, were replaced by the corresponding ξ-independent concentration coefficients of each species of each solute component at each of two times, t or $[t + \Delta t]$, of which, all of the time-dependent parameters at time t are known, while all of the time-dependent parameters at time $[t + \Delta t]$ are in the process of being determined.

To include the effects of coupled flows when solving the t- and ξ-dependent continuity equation in terms of species (Section C), Equations C33– and C33+ can be replaced by ξ-independent diffusion coefficients in the form of

$$D_{k,e,j-} = \frac{M_{k,e}}{\frac{\Delta c_{k,e,j-}}{\Delta \xi}} \sum_{q=1}^{n} \sum_{a=1}^{n_q} \frac{\frac{\Delta c_{q,a,j-}}{\Delta \xi}}{M_{q,a}} X^{D}_{[k,e],[q,a]} D^{0}_{q,a,j-} \left(\frac{\sum_{b=1}^{\infty} \sum_{w=1}^{n} \sum_{u=1}^{n_w} y_{b,q,a,w,u} \frac{d{c_{w,u,j-}}^{b}}{dc_{w,u,j-}}}{\sum_{b=1}^{\infty} \sum_{w=1}^{n} \sum_{u=1}^{n_w} h_{b,q,a,w,u} \frac{d{c_{w,u,j-}}^{b}}{dc_{w,u,j-}}} \right)$$

(N23–)

and

$$D_{k,e,j+} = \frac{M_{k,e}}{\frac{\Delta c_{k,e,j+}}{\Delta \xi}} \sum_{q=1}^{n} \sum_{a=1}^{n_q} \frac{\frac{\Delta c_{q,a,j+}}{\Delta \xi}}{M_{q,a}} X^{D}_{[k,e],[q,a]} D^{0}_{q,a,j+} \left(\frac{\sum_{b=1}^{\infty} \sum_{w=1}^{n} \sum_{u=1}^{n_w} y_{b,q,a,w,u} \frac{d{c_{w,u,j+}}^{b}}{dc_{w,u,j+}}}{\sum_{b=1}^{\infty} \sum_{w=1}^{n} \sum_{u=1}^{n_w} h_{b,q,a,w,u} \frac{d{c_{w,u,j+}}^{b}}{dc_{w,u,j+}}} \right),$$

(N23+)

which are based on the ξ-dependent function given by Equation N20, while Equations C33– and C33+ can be replaced by ξ-independent reduced valence coefficients in the form of

$$\sigma_{k,e,j-} = \frac{Eu_{k,e,j-}}{D_{k,e,j-}}$$

$$= \frac{\frac{M_{k,e}}{c_{k,e,j-}} \sum_{q=1}^{n} \sum_{a=1}^{n_q} \frac{c_{q,a,j-}}{M_{q,a}} X^{u}_{[k,e],[q,a]} \sigma^{0}_{q,a,j-} D^{0}_{q,a,j-} \left(\frac{\sum_{b=1}^{\infty} \sum_{w=1}^{n} \sum_{u=1}^{n_w} p_{b,q,a,w,u} \frac{d{c_{w,u,j-}}^{b}}{dc_{w,u,j-}}}{\sum_{b=1}^{\infty} \sum_{w=1}^{n} \sum_{u=1}^{n_w} h_{b,q,a,w,u} \frac{d{c_{w,u,j-}}^{b}}{dc_{w,u,j-}}} \right)}{D_{k,e,j-}}$$

(N24–)

and

$$\sigma_{k,e,j+} = \frac{Eu_{k,e,j+}}{D_{k,e,j+}}$$

$$= \frac{\frac{M_{k,e}}{c_{k,e,j+}} \sum_{q=1}^{n} \sum_{a=1}^{n_q} \frac{c_{q,a,j+}}{M_{q,a}} X^{u}_{[k,e],[q,a]} \sigma^{0}_{q,a,j+} D^{0}_{q,a,j+} \left(\frac{\sum_{b=1}^{\infty} \sum_{w=1}^{n} \sum_{u=1}^{n_w} p_{b,q,a,w,u} \frac{dc_{w,u,j+}{}^{b}}{dc_{w,u,j+}}}{\sum_{b=1}^{\infty} \sum_{w=1}^{n} \sum_{u=1}^{n_w} h_{b,q,a,w,u} \frac{dc_{w,u,j+}{}^{b}}{dc_{w,u,j+}}} \right)}{D_{k,e,j+}},$$

(N24+)

which are based on the ξ-dependent function given by Equation N21.

To define the parameters of Equations N23–, N23+, N24– and N24+, it is convenient to let α represent component k, q or w, let β represent species e, a or u, and let $j\mp$ represent $j-$ or $j+$, where j refers to spatial element ξ_j, the minus sign refers to time t, and the plus sign refers to time $[t + \Delta t]$. As such, in Equations N23–, N23+, N24– and N24+, n_α is the number of species that constitute solute component α, $c_{\alpha,\beta}$ is the concentration of species β of component α, $D_{\alpha,\beta}$ is the diffusion coefficient of species β of component α, $D_{\alpha,\beta}$ is the diffusion coefficient of species β of component α, $\sigma_{\alpha,\beta}$ is the reduced valence coefficient of species β of component α, $D^{0}_{\alpha,\beta}$ equals $D_{\alpha,\beta}$ in the limit as c approaches 0, $\sigma^{\circ}{}_{\alpha,\beta}$ equals $\sigma_{\alpha,\beta}$ in the limit as c approaches 0, $c_{\alpha,\beta,j-}$ at all ξ equals the concentration of species β of solute component α at ξ_j at time t, $c_{\alpha,\beta,j+}$ at all ξ equals the concentration of species β of solute component α at ξ_j at time $[t + \Delta t]$, $D_{\alpha,\beta,j-}$ at all ξ equals $D_{\alpha,\beta}$ at ξ_j at time t, $D_{\alpha,\beta,j+}$ at all ξ equals $D_{\alpha,\beta}$ at ξ_j at time $[t + \Delta t]$, $\sigma_{\alpha,\beta,j-}$ at all ξ equals $\sigma_{\alpha,\beta}$ at ξ_j at time t, $\sigma_{\alpha,\beta,j+}$ at all ξ equals $\sigma_{\alpha,\beta}$ at ξ_j at time $[t + \Delta t]$, $D^{0}_{\alpha,\beta,j\mp}$ equals $D_{\alpha,\beta,j\mp}$ in the limit as c approaches 0, $\sigma^{\circ}{}_{\alpha,\beta,j\mp}$ equals $\sigma_{\alpha,\beta,j\mp}$ in the limit as c approaches 0, $X^{D}_{[k,e],[q,a]}$ is the coefficient that couples $D^{\circ}{}_{q,a,j\mp}$ to $D_{k,e,j\mp}$, $X^{u}_{[k,e],[q,a]}$ is the coefficient that couples $\sigma^{\circ}{}_{q,a,j\mp} D^{\circ}{}_{q,a,j\mp}$ to $\sigma_{k,e,j\mp}$, $M_{k,e}$ is the molar mass of species e of solute component k, $u_{k,e}$ is the electrophoretic mobility coefficient of species e of solute component k, $Eu_{k,e,j-}$ at all ξ equals $Eu_{k,e}$ at ξ_j at time t, and $Eu_{k,e,j+}$ at all ξ equals $Eu_{k,e}$ at ξ_j at time $[t + \Delta t]$. (See the various forms of Equation N25 for the definitions of $\Delta c_{k,e,j-}/\Delta\xi$, $\Delta c_{k,e,j+}/\Delta\xi$, $\Delta c_{q,a,j-}/\Delta\xi$ and $\Delta c_{q,a,j+}/\Delta\xi$.) The bth of up to an infinite number of coefficients of proportionality for the electrophoretic/asymmetry, thermodynamic nonideality, and viscosity effects are $p_{b,q,a,w,u}$, $y_{b,q,a,w,u}$, and $h_{b,q,a,w,u}$, respectively.

By definition, $\sum_{w=1}^{n}\sum_{u=1}^{n_w} p_{1,q,a,w,u}$, $\sum_{w=1}^{n}\sum_{u=1}^{n_w} y_{1,q,a,w,u}$ and $\sum_{w=1}^{n}\sum_{u=1}^{n_w} h_{1,q,a,w,u}$ are each equal to 1. Each of the $p_{b,q,a,w,u}$, $y_{b,q,a,w,u}$and $h_{b,q,a,w,u}$ coefficients is a constant that couples the concentration of species u of component w to an effect on the transport of species a of component q. (See Section D for the component-based equivalents of these virial expansions.)

Provided that $\left(\partial D^\circ{}_{q,a}/\partial\xi\right)_t = 0$ and $\left(\partial D^\circ{}_{q,a}/\partial t\right)_\xi = 0$ at all ξ at all times, $D^\circ{}_{q,a,j-} = D^\circ{}_{q,a}$ and $D^\circ{}_{q,a,j+} = D^\circ{}_{q,a}$ at all ξ at all times. Provided that $\left(\partial\sigma^\circ{}_{q,a}/\partial\xi\right)_t = 0$ and $\left(\partial\sigma^\circ{}_{q,a}/\partial t\right)_\xi = 0$ at all ξ at all times after a change in the electrical field is complete, $\sigma^\circ{}_{q,a,j-} = \sigma^\circ{}_{q,a}$ and $\sigma^\circ{}_{q,a,j+} = \sigma^\circ{}_{q,a}$ at all ξ at all times after a change in the gravitational field is complete.

With α representing component k or q, β representing species e or a, and $j\mp$ representing $j-$ or $j+$, the approximated derivatives, $\Delta c_{k,e,j-}/\Delta\xi$, $\Delta c_{k,e,j+}/\Delta\xi$, $\Delta c_{q,a,j-}/\Delta\xi$ and $\Delta c_{q,a,j+}/\Delta\xi$, in Equations N23– and N23+, are calculated as

$$\frac{\Delta c_{\alpha,\beta,j\mp}}{\Delta\xi} = \frac{c_{\alpha,\beta,[2]\mp} - c_{\alpha,\beta,[1]\mp}}{\xi_{[2]} - \xi_{[1]}}$$

(N25a)

for $j = 1$,

$$\frac{\Delta c_{\alpha,\beta,j\mp}}{\Delta\xi} = \frac{1}{2}\left(\frac{c_{\alpha,\beta,[j+1]\mp} - c_{\alpha,\beta,[j]\mp}}{\xi_{[j+1]} - \xi_{[j]}} + \frac{c_{\alpha,\beta,[j]\mp} - c_{\alpha,\beta,[j-1]\mp}}{\xi_{[j]} - \xi_{[j-1]}}\right)$$

(N25b)

for $1 < j < N$, and

$$\frac{\Delta c_{\alpha,\beta,j\mp}}{\Delta\xi} = \frac{c_{\alpha,\beta,[N]\mp} - c_{\alpha,\beta,[N-1]\mp}}{\xi_{[N]} - \xi_{[N-1]}}$$

(N25c)

for $j = N$. Provided that $\Delta\xi/\Delta j = 0$, Equations N25a, N25b and N25c, respectively, are equivalent to

$$\frac{\Delta c_{\alpha,\beta,j\mp}}{\Delta\xi} = \frac{c_{\alpha,\beta,[2]\mp} - c_{\alpha,\beta,[1]\mp}}{\Delta\xi}$$

(N25d)

for $j = 1$,

$$\frac{\Delta c_{\alpha,\beta,j\mp}}{\Delta\xi} = \frac{c_{\alpha,\beta,[j+1]\mp} - c_{\alpha,\beta,[j-1]\mp}}{2\Delta\xi}$$

(N25e)

for $1 < j < N$, and

$$\frac{\Delta c_{\alpha,\beta,j\mp}}{\Delta\xi} = \frac{c_{\alpha,\beta,[N]\mp} - c_{\alpha,\beta,[N-1]\mp}}{\Delta\xi}$$

(N25f)

for $j = N$. Thus, for $\Delta\xi/\Delta j = 0$ (as in Equation B37 and B38), it can be argued, given the ξ-independence of $c_{k,e,j-}$, $c_{k,e,j+}$, $c_{q,a,j-}$, $c_{q,a,j+}$ and $\Delta\xi$, that each form of Equation N25 yield a ξ-independent result.

Equations N23∓ and N24∓ can be used in place of Equations C33∓ and C34∓, respectively, where the minus/plus sign refers the equation at either time t or time $[t + \Delta t]$. Eliminating the indices e and a, which apply to species, and the summations with respect to species, yields the component-equivalents of Equations N23∓, N24∓ and N25. The component-equivalents of Equations N23∓ and N24∓ can be used in place of Equations B22∓ and B23∓, respectively.

Evaluating $X_{k,q}^{u}$ and $X_{k,q}^{D}$

Solving Equations A16 and A17 of Section A (**An application of irreversible thermodynamics to MCE**) for $L_{k,q}$ yields

$$L_{k,q} = \frac{c_q \boldsymbol{u}_{k,q}}{M_q z_q \frac{F}{\varpi}} = \frac{c_q \boldsymbol{D}_{k,q}}{M_q RT \left[1 + c_q \sum_{w=1}^{n} \left(\frac{\partial c_w}{\partial c_q}\right)_t \left(\frac{\partial ln\gamma_q}{\partial c_w}\right)_{t,T,P,c_{a\neq w}}\right]}.$$

(N26)

Using Equations N6 and N7 to approximate $\boldsymbol{D}_{k,q}$ and $\boldsymbol{u}_{k,q}$, respectively, results in

$$L_{k,q}=\frac{c_qX_{k,q}^u u_q^0\left(\frac{1+\sum_{a=1}^n p_{q,a}c_a}{1+\sum_{a=1}^n h_{q,a}c_a}\right)}{M_q z_q\frac{F}{\varpi}}=\frac{c_qX_{k,q}^D D_q^0\left(\frac{1+\sum_{a=1}^n y_{q,a}c_a}{1+\sum_{a=1}^n h_{q,a}c_a}\right)}{M_qRT\left[1+c_q\sum_{w=1}^n\left(\frac{\partial c_w}{\partial c_q}\right)_t\left(\frac{\partial ln\gamma_q}{\partial c_w}\right)_{t,T,P,c_{a\neq w}}\right]},$$

(N27)

and division by $c_q/\left(M_q\left[1+\sum_{a=1}^n h_{q,a}c_a\right]\right)$ yields

$$\frac{X_{k,q}^u u_q^0\left(1+\sum_{a=1}^n p_{q,a}c_a\right)}{z_q\frac{F}{\varpi}}=\frac{X_{k,q}^D D_q^0\left(1+\sum_{a=1}^n y_{q,a}c_a\right)}{RT\left[1+c_q\sum_{w=1}^n\left(\frac{\partial c_w}{\partial c_q}\right)_t\left(\frac{\partial ln\gamma_q}{\partial c_w}\right)_{t,T,P,c_{a\neq w}}\right]}.$$

(N28)

Thus, as the total solute concentration, c, approaches zero,

$$\lim_{c\to 0}\frac{X_{k,q}^u u_q^0\left(1+\sum_{a=1}^n p_{q,a}c_a\right)}{z_q\frac{F}{\varpi}}=\lim_{c\to 0}\frac{X_{k,q}^D D_q^0\left(1+\sum_{a=1}^n y_{q,a}c_a\right)}{RT\left[1+c_q\sum_{w=1}^n\left(\frac{\partial c_w}{\partial c_q}\right)_t\left(\frac{\partial ln\gamma_q}{\partial c_w}\right)_{t,T,P,c_{a\neq w}}\right]},$$

(N29)

the result of which is

$$\frac{X_{k,q}^u u_q^0}{z_q^0\frac{F}{\varpi}}=\frac{X_{k,q}^D D_q^0}{RT},$$

(N30)

where z_q^0 is equal to z_q in the limit as c approaches zero. Solving for $X_{k,q}^D$ yields

$$X_{k,q}^D=\frac{X_{k,q}^u u_q^0 RT}{D_q^0 z_q^0\frac{F}{\varpi}}.$$

(N31)

Applying the limit as c approaches zero to Equation M2, and multiplying the result by F/ϖ, shows that

$$\frac{u_q^0 RT}{D_q^0}=z_q^0\frac{F}{\varpi}.$$

(N32)

Thus,

$$X_{k,q}^{D} = X_{k,q}^{u}.$$

(N33)

Applying this result to Equations N12 and N22 shows that $X_{k,q}^{\sigma}$ should be equal to 1. Although this result shows that $X_{k,q}^{D}$ should always have the same value as $X_{k,q}^{u}$, it may be convenient to treat them as independent variables in a simulation program, so that the coupled-flow effects on u_q can be evaluated separately from the coupled-flow effects on D_q.

In the limit as t approaches ∞

Over time, an MCE system approaches steady state. Thus, any MCE system can be deemed to achieve steady state as t is considered to approach infinity. As partial derivatives at constant time become ordinary derivatives at steady state, the steady-state form of Equation N21 can be written as

$$\sigma_k = \frac{dlnc_k}{d\xi} \frac{\sum_{q=1}^{n} \frac{c_q}{M_q} X_{k,q}^{u} \sigma_q^0 D_q^0 \left(\frac{1 + \sum_{a=1}^{n} p_{q,a} c_a}{1 + \sum_{a=1}^{n} h_{q,a} c_a} \right) + v_0 \frac{c_k}{M_k}}{\sum_{q=1}^{n} \frac{dc_q}{d\xi} \frac{1}{M_q} X_{k,q}^{D} D_q^0 \left(\frac{1 + \sum_{a=1}^{n} y_{q,a} c_a}{1 + \sum_{a=1}^{n} h_{q,a} c_a} \right)}.$$

(N34)

Equation A36 applies to the system at steady state, and dividing both sides of that equation by c_k in the case of $I_{k,\infty} = \left(I_{k,\infty}\right)_{mc} = 0$ (where the subscript mc indicates that component k is membrane-confined) yields

$$\lim_{t\to\infty} \sigma_k = \lim_{t\to\infty} \left(\frac{\partial lnc_k}{\partial \xi} \right)_t = \frac{dlnc_k}{d\xi}.$$

(N35)

Applying this relationship to Equation N34 results in

$$\lim_{t\to\infty} \frac{\sigma_k}{\left(\frac{\partial lnc_k}{\partial \xi} \right)_t} = \lim_{t\to\infty} \frac{\sum_{q=1}^{n} \frac{c_q}{M_q} X_{k,q}^{u} \sigma_q^0 D_q^0 \left(\frac{1 + \sum_{a=1}^{n} p_{q,a} c_a}{1 + \sum_{a=1}^{n} h_{q,a} c_a} \right) + v_0 \frac{c_k}{M_k}}{\sum_{q=1}^{n} \frac{\left(\frac{\partial c_k}{\partial \xi} \right)_t}{M_q} X_{k,q}^{D} D_q^0 \left(\frac{1 + \sum_{a=1}^{n} y_{q,a} c_a}{1 + \sum_{a=1}^{n} h_{q,a} c_a} \right)} = 1,$$

(N36a)

or equivalently,

$$\frac{\sigma_k}{\frac{dlnc_k}{d\xi}} = \frac{\sum_{q=1}^{n} \frac{c_q}{M_q} X_{k,q}^{u} \sigma_q^0 D_q^0 \left(\frac{1 + \sum_{a=1}^{n} p_{q,a} c_a}{1 + \sum_{a=1}^{n} h_{q,a} c_a} \right) + v_0 \frac{c_k}{M_k}}{\sum_{q=1}^{n} \frac{dc_q}{d\xi} \frac{1}{M_q} X_{k,q}^{D} D_q^0 \left(\frac{1 + \sum_{a=1}^{n} y_{q,a} c_a}{1 + \sum_{a=1}^{n} h_{q,a} c_a} \right)} = 1,$$

(N36b)

at each spatial position, ξ, in the system at steady state.

The more general equation, A23a, can be written as

$$\sigma_k = \left(\frac{\partial lnc_k}{\partial \xi} \right)_t \frac{E \sum_{q=1}^{n} \frac{1}{M_q} c_q \boldsymbol{u}_{k,q} + v_0 \frac{c_k}{M_k}}{\sum_{q=1}^{n} \frac{1}{M_q} \left(\frac{\partial c_q}{\partial \xi} \right)_t \boldsymbol{D}_{k,q}},$$

(N37)

$$\sigma_k = \left(\frac{\partial lnc_k}{\partial \xi} \right)_t \frac{\sum_{q=1}^{n} \frac{1}{M_q} c_q \boldsymbol{\sigma}_{k,q} \boldsymbol{D}_{k,q} + v_0 \frac{c_k}{M_k}}{\sum_{q=1}^{n} \frac{1}{M_q} \left(\frac{\partial c_q}{\partial \xi} \right)_t \boldsymbol{D}_{k,q}}$$

(N38)

or

$$\sigma_k = \left(\frac{\partial lnc_k}{\partial \xi} \right)_t \frac{E \frac{F}{\varpi} \sum_{q=1}^{n} L_{k,q} z_q + v_0 \frac{c_k}{M_k}}{RT \sum_{q=1}^{n} L_{k,q} \left(\frac{\partial lnc_q}{\partial \xi} \right)_t \left[1 + c_q \sum_{w=1}^{n} \left(\frac{\partial c_w}{\partial c_q} \right)_t \left(\frac{\partial ln\gamma_q}{\partial c_w} \right)_{t,T,P,c_{a \neq w}} \right]},$$

(N39)

which, in the limit as t approaches ∞, yield

$$\lim_{t \to \infty} \frac{\sigma_k}{\left(\frac{\partial lnc_k}{\partial \xi} \right)_t} = \lim_{t \to \infty} \frac{E \sum_{q=1}^{n} \frac{1}{M_q} c_q \boldsymbol{u}_{k,q} + v_0 \frac{c_k}{M_k}}{\sum_{q=1}^{n} \frac{1}{M_q} \left(\frac{\partial c_q}{\partial \xi} \right)_t \boldsymbol{D}_{k,q}} = 1,$$

(N40)

$$\lim_{t \to \infty} \frac{\sigma_k}{\left(\frac{\partial lnc_k}{\partial \xi} \right)_t} = \lim_{t \to \infty} \frac{\sum_{q=1}^{n} \frac{1}{M_q} c_q \boldsymbol{\sigma}_{k,q} \boldsymbol{D}_{k,q} + v_0 \frac{c_k}{M_k}}{\sum_{q=1}^{n} \frac{1}{M_q} \left(\frac{\partial c_q}{\partial \xi} \right)_t \boldsymbol{D}_{k,q}} = 1$$

(N41)

and

$$\lim_{t\to\infty}\frac{\sigma_k}{\left(\frac{\partial lnc_k}{\partial \xi}\right)_t}=\lim_{t\to\infty}\frac{E\frac{F}{\varpi}\sum_{q=1}^{n} L_{k,q}z_q+v_0\frac{c_k}{M_k}}{RT\sum_{q=1}^{n}L_{k,q}\left(\frac{\partial lnc_q}{\partial\xi}\right)_t\left[1+c_q\sum_{w=1}^{n}\left(\frac{\partial c_w}{\partial c_q}\right)_t\left(\frac{\partial ln\gamma_q}{\partial c_w}\right)_{t,T,P,c_{a\neq w}}\right]}=1,$$

(N42)

respectively, at each spatial position, ξ. Assuming that $\left(\frac{\partial c_w}{\partial c_q}\right)_t\left(\frac{\partial ln\gamma_q}{\partial c_w}\right)_{t,T,P,c_{a\neq w}}$ is zero for all $w \neq q$, Equation N42 further simplifies to

$$\lim_{t\to\infty}\frac{\frac{c_k}{M_k}v_0+E\frac{F}{\varpi}\sum_{q=1}^{n} L_{k,q}z_q}{RT\sum_{q=1}^{n}L_{k,q}\left(\frac{\partial lnc_q}{\partial\xi}\right)_t\left[1+\left(\frac{\partial ln\gamma_q}{\partial lnc_q}\right)_{t,T,P,c_{a\neq q}}\right]}=1.$$

(N43)

Thus, at steady state, with $\left(\frac{\partial lnc_q}{\partial\xi}\right)_t$ being equal to $\frac{dlnc_q}{d\xi}$, and with $\left(\frac{\partial ln\gamma_q}{\partial lnc_q}\right)_{t,T,P,c_{a\neq q}}$ being equal to $\frac{dln\gamma_q}{dlnc_q}$,

$$\frac{c_k}{M_k}v_0+\sum_{q=1}^{n}L_{k,q}\left[E\frac{F}{\varpi}\,z_q-RT\frac{dlnc_q}{d\xi}\left(1+\frac{dln\gamma_q}{dlnc_q}\right)\right]=0$$

(N44)

at each spatial position, ξ, in the system.

Neglecting vector notation (see the discussion following Equation A3), in an MCE system, ∇U_q can be reduced to $\left(\frac{\partial U_q}{\partial\xi}\right)_t$ (Equations A2, A14, and I16 to I20), and at steady state, $\left(\frac{\partial U_q}{\partial\xi}\right)_t$ can be expressed as $\frac{dU_q}{d\xi}$. In Equation N44, $L_{k,q}$ is the coefficient of $\frac{dU_q}{d\xi}=\frac{1}{\xi}\frac{dU_q}{d\xi}$. Thus, Equation N44 can be written more compactly as

$$\frac{c_k}{M_k}v_0+\sum_{q=1}^{n}L_{k,q}\frac{dU_q}{d\xi}=0,$$

(N45)

where U_q is the total molar potential of solute component q (Equation I17). Provided that each $\frac{dU_q}{d\xi}$ is not equal to zero at steady state, Equation N45 can be used to determine $L_{k,q}$ values. In the discussion that follows, it is assumed that $\frac{dU_q}{d\xi} \neq 0$ holds for all values of q at steady state if $\frac{c_k}{M_k} v_0 \neq 0$ at steady state.

Determining $L_{k,q}$ values

To use Equations N44 and N45 to determine $L_{k,q}$ values, all the other parameters in Equation N44 must be known. The spatial parameter ξ can be determined with considerable accuracy and precision. The parameters that can be measured include E, T, M_q, c_q, z_q and v_0. Of these, c_q, the concentration of explicit solute q, will tend to vary greatly with ξ. Thus, at each spatial position, ξ, each of the n values of c_q would need to be determined from the various sets of MCE data collected while the system was at steady state.

As z_q (see **An examination of whether $(z_q)_N$ and z_q can be regarded as molecular parameters** in Section M) and E (see **Section H: Factors affecting the electrical field in MCE**) are functions of the concentration of each solute, explicit or otherwise, they too will tend to vary with ξ. Given each of the n values of c_q and all other solute concentrations at each spatial position ξ, the values of z_q and E at any position ξ should be measurable with appropriate instrumentation, albeit at the expense of much time and materials. The activity coefficient, γ_q, of each explicit solute, q, is also a function of the concentration of each explicit solute, and given each of the n values of c_q at each spatial position ξ, its value at any position ξ should also be measurable. It might, however, be more practical to largely rely on estimates of each thermodynamic nonideality term, $1 + \frac{dln\gamma_q}{dlnc_q}$, using applicable functions. (For examples, see Equations D1 and D3.) Applicable functions (such as Equations D5 and D10) could also be used to approximate the electrophoretic/asymmetry effect. (See Equation M23 and the surrounding discussion.)

Though invariant with ξ at steady state, v_0 could be challenging to determine. As the last in each set of steady-state measurements, v_0 could perhaps be measured using a membrane-permeant component with distinguishing optical characteristics and a net charge of zero. (See **Section E: Presenting concentration data from calculations as optical density data**.) If such a membrane-permeant component could be found, it could be repeatedly injected as a narrow band next to the upper or lower membrane (depending on the direction of v_0), and t_L, the time of its passage across the length of the system, L, could be measured. Dividing L by t_L would yield an estimate of v_0.

The remaining parameters of Equation N44 are the n^2 phenomenological coefficients, of which, at each spatial position ξ in the system at steady state, there would be n $L_{k,q=k}$ values and $(n^2 - n)/2$ $L_{k,q\neq k} = L_{q\neq k,k}$ values to determine. (Regarding such reciprocal relations as $L_{k,q\neq k} = L_{q\neq k,k}$, see **Section G: The dissipation function and the Curie-Prigogine principle**.) Assuming that the n $L_{k,q=k}$ values of Equation N44 can be calculated, at each position, ξ, there would be n linearly independent equations and $(n^2 - n)/2$ unknowns in the form of the $L_{k,q\neq k} = L_{q\neq k,k}$ parameters. Equations from different spatial positions in the system cannot be used to augment the number of linearly independent equations because the $L_{k,q=k}$ and the $L_{k,q\neq k} = L_{q\neq k,k}$ parameters, being dependent on all properties of the system, are not constant with spatial position. Thus, the $(n^2 - n)/2$ unknown values of $L_{k,q\neq k} = L_{q\neq k,k}$ could not be solved if n were greater than 3, as for $n > 3$, $n < (n^2 - n)/2$. Furthermore, membrane-permeant components, at least one of which must be present to carry the electrical current through the system, would have to be included when counting the number of components of the system.

As stated in Equation A19, in the limit as $c_{q\neq k}$ approaches zero, the coupled-flow-phenomenological coefficient linking the molar flow of solute component k to the conjugate molar force of solute component k is given by

$$\lim_{c_{q\neq k}\to 0} L_{k,k} = \frac{c_k}{N_A M_k f_k},$$

(N46 = A19)

and as stated in Equation A20, the frictional coefficient of solute component k is given by

$$f_k = 6\pi\eta R_k^*.$$

(N47 = A20)

As Equation N46 (A19) only applies in the limit as the concentrations of all components other than component k approach zero, its usefulness is limited to the case of $n = 1$, unless great, and probably misleading, liberties are taken when defining the implicit solvent. With respect to MCE, those liberties would include defining the implicit solvent as comprising all but one of the components that form significant concentration gradients. Troublingly, such a definition would result in different implicit solvents being applied to different spatial positions in the system. Furthermore, at each spatial position, a different implicit solvent would be defined for each choice of the sole explicit solute. Despite any doubts that such creative accounting should raise, this is exactly the approach taken here to make use of Equations N46 (A19) and N47 (A20).

Calculating f_k by means of the right-hand side of Equation N47 (A20) requires the measurement of η, the solution viscosity, and the determination of R_k^*, the Stokes radius of an equivalent sphere of solute component k. The viscosity of the implicit solvent, which comprises all components save the one that is treated explicitly, is η_0. With c_k being the concentration of the sole explicit solute, η becomes identical to η_0 in the limit as c_k approaches zero. With η_0 defined as $\lim_{c_k \to 0} \eta$, R_k^0 defined as $\lim_{c_k \to 0} R_k^*$, and f_k^0 defined as $\lim_{c_k \to 0} f_k$, it follows that

$$f_k^0 = 6\pi\eta_0 R_k^0,$$

(N48)

but it does not necessarily follow that f_k would equal $6\pi\eta R_k^0$ if the concentration of component k were to rise to experimentally relevant values. Thus, to use Equation N47 (A19) in Equation N46 (A20), R_k^* would need to be determined in the solution used to measure η. Of more concern, given the spatial redistribution of components at steady state in an MCE experiment, in each determination of R_k^* and measurement of η, the implicit solvent, by being defined as comprising all components other than component k, would need to reflect the composition of the so-defined implicit solvent at specific spatial positions in the system.

In all, to create the correct solutions in which to determine R_k^* and measure η, it would be necessary to reproduce the composition of the solution at each selected spatial position, ξ, in the MCE system being analysed. (Additionally, the determination of R_k^* and the measurement of η would need to be conducted at the same temperature at which the MCE data were collected, but this requirement, at least, could easily be met.) Going to such extremes would allow Equation N46 (A19) to be used to calculate the $n\,L_{k,q=k}$ values needed in Equation N44. The confidence in those values might not be great, but with them, the remaining unknowns, which are the $(n^2 - n)/2\ L_{k,q\neq k} = L_{q\neq k,k}$ values, could, for better or worse, be calculated for any part of the system in which n did not exceed 3.

For $n = 3$, solving Equation N45 for $L_{1,2} = L_{2,1}$, $L_{2,3} = L_{3,2}$ and $L_{1,3} = L_{3,1}$ yields

$$L_{1,2} = L_{2,1} = \frac{-L_{1,1}\left(\frac{dU_1}{d\xi}\right)^2 - L_{2,2}\left(\frac{dU_2}{d\xi}\right)^2 + L_{3,3}\left(\frac{dU_3}{d\xi}\right)^2}{2\frac{dU_1}{d\xi}\frac{dU_2}{d\xi}} + v_0\frac{-\frac{c_1}{M_1}\frac{dU_1}{d\xi} - \frac{c_2}{M_2}\frac{dU_2}{d\xi} + \frac{c_3}{M_3}\frac{dU_3}{d\xi}}{2\frac{dU_1}{d\xi}\frac{dU_2}{d\xi}},$$

(N49a)

$$L_{1,3} = L_{3,1} = \frac{-L_{1,1}\left(\frac{dU_1}{d\xi}\right)^2 + L_{2,2}\left(\frac{dU_2}{d\xi}\right)^2 - L_{3,3}\left(\frac{dU_3}{d\xi}\right)^2}{2\frac{dU_1}{d\xi}\frac{dU_3}{d\xi}} + v_0\frac{-\frac{c_1}{M_1}\frac{dU_1}{d\xi} + \frac{c_2}{M_2}\frac{dU_2}{d\xi} - \frac{c_3}{M_3}\frac{dU_3}{d\xi}}{2\frac{dU_1}{d\xi}\frac{dU_3}{d\xi}}$$

(N49b)

and

$$L_{2,3} = L_{3,2} = \frac{L_{1,1}\left(\frac{dU_1}{d\xi}\right)^2 - L_{2,2}\left(\frac{dU_2}{d\xi}\right)^2 - L_{3,3}\left(\frac{dU_3}{d\xi}\right)^2}{2\frac{dU_2}{d\xi}\frac{dU_3}{d\xi}} + v_0\frac{\frac{c_1}{M_1}\frac{dU_1}{d\xi} - \frac{c_2}{M_2}\frac{dU_2}{d\xi} - \frac{c_3}{M_3}\frac{dU_3}{d\xi}}{2\frac{dU_2}{d\xi}\frac{dU_3}{d\xi}},$$

(N49c)

respectively.

For $n = 2$, solving Equation N45 for $L_{1,2}$ and $L_{2,1}$ yields

$$L_{1,2} = \frac{-L_{1,1}\frac{dU_1}{d\xi} - \frac{c_1}{M_1}v_0}{\frac{dU_2}{d\xi}}$$

(N50a)

and

$$L_{2,1} = \frac{-L_{2,2}\dfrac{dU_2}{d\xi} - \dfrac{c_2}{M_2}v_0}{\dfrac{dU_1}{d\xi}},$$

(N50b)

respectively, of which the sum divided by 2 is

$$L_{1,2} = L_{2,1} = \frac{L_{1,2} + L_{2,1}}{2} = \frac{-L_{1,1}\left(\dfrac{dU_1}{d\xi}\right)^2 - L_{2,2}\left(\dfrac{dU_2}{d\xi}\right)^2}{2\dfrac{dU_1}{d\xi}\dfrac{dU_2}{d\xi}} + v_0\frac{-\dfrac{c_1}{M_1}\dfrac{dU_1}{d\xi} - \dfrac{c_2}{M_2}\dfrac{dU_2}{d\xi}}{2\dfrac{dU_1}{d\xi}\dfrac{dU_2}{d\xi}}.$$

(N50c)

Setting Equations N50a and N50b equal to each other results, after some rearrangement, in

$$L_{1,1} = \frac{L_{2,2}\left(\dfrac{dU_2}{d\xi}\right)^2}{\left(\dfrac{dU_1}{d\xi}\right)^2} + v_0\frac{-\dfrac{c_1}{M_1}\dfrac{dU_1}{d\xi} + \dfrac{c_2}{M_2}\dfrac{dU_2}{d\xi}}{\left(\dfrac{dU_1}{d\xi}\right)^2}$$

(N51a)

and

$$L_{2,2} = \frac{L_{1,1}\left(\dfrac{dU_1}{d\xi}\right)^2}{\left(\dfrac{dU_2}{d\xi}\right)^2} + v_0\frac{\dfrac{c_1}{M_1}\dfrac{dU_1}{d\xi} - \dfrac{c_2}{M_2}\dfrac{dU_2}{d\xi}}{\left(\dfrac{dU_2}{d\xi}\right)^2},$$

(N51b)

which, assuming that Equations N50a and N50b are valid, show the relationship between $L_{1,1}$ and $L_{2,2}$ at steady state in the case of $n = 2$. Thus, for $n = 2$, Equations N46 (A19) and N47 (A20) need only be used to determine either $L_{1,1}$ or $L_{2,2}$, as once one is known, the other can be calculated using one or the other form of Equation N51. Given the doubts raised regarding their applicability , however, it might be better to first obtain results using Equations N46 (A19) and N47 (A20), and then use Equation N51 as a test of those results, with the caveat that Equation N51 might hold despite both $L_{1,1}$ and $L_{2,2}$ being invalid.

Taking the limit of Equation N49a as c_3 approaches zero yields

$$\lim_{c_3\to 0} L_{1,2} = \lim_{c_3\to 0} L_{2,1}$$
$$= \lim_{c_3\to 0}\left[\frac{-L_{1,1}\left(\frac{dU_1}{d\xi}\right)^2 - L_{2,2}\left(\frac{dU_2}{d\xi}\right)^2 + L_{3,3}\left(\frac{dU_3}{d\xi}\right)^2}{2\frac{dU_1}{d\xi}\frac{dU_2}{d\xi}}\right.$$
$$\left. + v_0\frac{-\frac{c_1}{M_1}\frac{dU_1}{d\xi} - \frac{c_2}{M_2}\frac{dU_2}{d\xi} + \frac{c_3}{M_3}\frac{dU_3}{d\xi}}{2\frac{dU_1}{d\xi}\frac{dU_2}{d\xi}}\right]$$
$$= \frac{-L_{1,1}\left(\frac{dU_1}{d\xi}\right)^2 - L_{2,2}\left(\frac{dU_2}{d\xi}\right)^2}{2\frac{dU_1}{d\xi}\frac{dU_2}{d\xi}} + v_0\frac{-\frac{c_1}{M_1}\frac{dU_1}{d\xi} - \frac{c_2}{M_2}\frac{dU_2}{d\xi}}{2\frac{dU_1}{d\xi}\frac{dU_2}{d\xi}},$$

(N52)

which is identical to Equation N50c.

At steady state in the case of $n = 1$, Equation N45 yields

$$L_{1,1} = v_0\frac{\frac{c_1}{M_1}}{\frac{dU_1}{d\xi}}$$

(N53a)

and

$$v_0 = \frac{M_1}{c_1}L_{1,1}\frac{dU_1}{d\xi}.$$

(N53b)

The two forms of Equation N53 show that, for $n = 1$, $\frac{dU_1}{d\xi}$ cannot be zero unless v_0 is equal to zero, and that $L_{1,1}$ cannot be calculated if v_0 is equal to zero. With $n = 1$, however, the sole component is either a membrane-permeant current carrier or a membrane-confined component that cannot carry a current through the system. Both possibilities will be considered shortly.

Solving each form of Equations N49 and N50 shows that, for n= 2 or $n = 3$, no more than one value of $\frac{dU_q}{d\xi}$ can zero unless v_0 is equal to zero. The three forms of Equation N50 show that $L_{1,2} = L_{2,1}$ can be calculated if either $\frac{dU_1}{d\xi}$ alone or $\frac{dU_2}{d\xi}$ alone is zero. Equation N49a shows that $L_{1,2} = L_{2,1}$ can be calculated if $\frac{dU_3}{d\xi}$ alone is zero, Equation N49b shows that $L_{1,3} = L_{3,1}$ can be calculated if $\frac{dU_2}{d\xi}$ alone is zero, and Equation N49c shows that $L_{2,3} = L_{3,2}$ can be calculated if $\frac{dU_1}{d\xi}$ alone is zero.

A consideration of v_0

The presence of $\frac{c_k}{M_k} v_0$ in Equation N45 stems from Equation A1, which expresses the molar flow of solute component *k* in the system frame of reference as

$$\vec{J}_k = \overrightarrow{J_k^S} + \frac{c_k}{M_k}\vec{v}_0 = \sum_{q=1}^{n} L_{k,q}\vec{X}_q + \frac{c_k}{M_k}\vec{v}_0\ .$$

(N54 = A1)

The second term on the right-hand side of this equation can be expressed as

$$\frac{c_k}{M_k}\vec{v}_0 = \sum_{q=n+1}^{n+n_{mp}} L_{k,q}\vec{X}_q,$$

(N55)

where n_{mp} is the number of membrane-permeant components that give rise to $\vec{v}_o$, which is the velocity with which the solvent flows through the system. Applying Equation N55, Equation N45 becomes

$$\sum_{q=1}^{n} L_{k,q}\frac{dU_q}{d\xi} + \sum_{q=n+1}^{n+n_{mp}} L_{k,q}\vec{X}_q = 0.$$

(N56)

Thus,

$$\sum_{q=1}^{n+n_{mp}} L_{k,q}\frac{dU_q}{d\xi} = 0,$$

(N57)

which, if the system were closed, could generally be true only if each value of $\frac{dU_q}{d\xi}$ were equal to zero for $1 \leq q \leq n + n_{mp}$. Equations N55 to N57 show, then, that if $\frac{c_k}{M_k} v_0$ were equal to zero at steady state, each value of $\frac{dU_q}{d\xi}$ would be equal to zero, in which case, Equation N44 could not be used to determine any $L_{k,q}$ values. Equations N55 to N57 also show that $n + n_{mp}$ is the number of components that should be counted when trying to determine $L_{k,q}$ values.

For $n + n_{mp} = 1$, if the sole component is a membrane-permeant current carrier, $\frac{dlnc_1}{d\xi} = 0$ at steady state, and if there is no pressure gradient that could drive the flow of solvent through the system, Equations N44, N46 and N47 can be applied to obtain

$$\frac{z_1}{R_1^*} = -6\pi N_A \eta \frac{\varpi v_0}{EF}.$$

(N58)

Assuming only that R_1^* and η have values that are physically plausible for a system of the sort encountered in MCE, this equation states that, in the absence of a pressure gradient that could drive the flow of solvent through the system, if z_1 is equal to zero, v_0 will be equal to zero when $|E|$ is greater than zero. This result perhaps addresses the definition of the valence of a component, as distinct from the definition of the valence of a species. (These definitions are pondered in Section I (**Calculating valence, molar mass, chemical potential and partial specific volume for a multi-species component**) and the latter part of Section M (**An examination of whether $(z_q)_N$ and z_q can be regarded as molecular parameters**)).

Denoting the valence of species a of component 1 as $z_{1,a}$, denoting the stoichiometry of species a of component 1 as $\nu_{1,a}$, and denoting the total number of species of component 1 as n_1,

$$\sum_{a=1}^{n_1} \nu_{1,a} z_{1,a} = 0$$

(N59)

describes the net valence of stoichiometric amounts of the species of component 1. For $n + n_{mp} = 1$,

$$v_0 = E \sum_{a=1}^{n_1} u_{1,a} v_{1,a} \eta_{1,a}$$

(N60)

where $Eu_{1,a}$ is the electrophoretic velocity of species a of component 1, and $\eta_{1,a}$, which has the same dimensions a η (unit mass divided by the product of unit distance and unit time), is the mass of solvent that a particle of species a of component 1 carries for some distance through the system in one unit of time. For a current to be maintained through the system, both $z_{1,a}$ and $Eu_{1,a}$ must be nonzero for two or more of the species that constitute component 1, and when $|E|$ is greater than zero, each such species will probably carry some amount of solvent through the system, but v_0 will be zero if the amount of solvent that the anionic current-carrying species carry through the system in one direction is exactly counterbalanced by the amount of solvent that the cationic current-carrying species carry through the system in the other direction. Thus, for $n + n_{mp} = 1$, a v_0 of zero at $|E| > 0$ means that z_1 is zero, but a z_1 of zero does not mean an absence of electrophoretic transport at $|E| > 0$. In fact, if $|E|$ is greater than zero, there must be electrophoretic transport through the system, in which case, a z_1 of zero cannot mean an absence of electrophoretic transport at $|E| > 0$ for a system in which $n + n_{mp} = 1$.

For $n + n_{mp} = 1$, if the sole component is a membrane-confined component that cannot carry a current through the system, $|E| = 0$, and if there is no pressure gradient that could drive the flow of solvent through the system, v_0 will equal zero and $\frac{dU_1}{d\xi}$ will equal zero (Equation N44). This situation raises the possibility that if a time-invariant pressure gradient were applied to drive a steady flow of solvent through the system, the MCE instrument could be used to determine $L_{k,q}$ values in the absence of an electrical current, in which case, Equation N44 would reduce to

$$\frac{c_k}{M_k} v_0 - RT \sum_{q=1}^{n} L_{k,q} \frac{dlnc_q}{d\xi}\left(1 + \frac{dln\gamma_q}{dlnc_q}\right) = 0$$

(N61)

at each spatial position, ξ, in the system at steady state.

With respect to determining $L_{k,q}$ values via Equations N49 to N53, the use of Equation N61 would only require a knowledge of T and v_0, plus the value of each M_q (along with M_k), plus the value of each c_q (along with c_k) at each spatial position ξ, plus the parameters needed to calculate the $n\, L_{k,q=k}$ values. (See the discussions following Equations N45, N46 and N47.) To ensure that the maintenance of charge neutrality did not prevent the formation of concentration gradients in the membrane-confined components, a supporting electrolyte would need to be included as a membrane-permeant component. Thus, the solution compositions could be such that any one system could be used to acquire both steady-state pressure-gradient and steady-state electrophoretic measurements.

Membrane-confined gravitational redistribution

In an extremely tall MCE system submerged from top to bottom in a single, temperature-controlled reservoir containing the same implicit solvent as that found within the system, there would be no net flow of solvent through the system in the absence of that carried by membrane-permeant solutes that enter or leave the system under the influence of gravity. By virtue of the system being submerged in a single reservoir, there could be no electrical current through the system, because the top and bottom of the system would be at the same electrical potential. The height of the system would be such that there would be a significant difference in the gravitational potential from the top to the bottom, however. In such a system, rather than Equation N44,

$$\frac{c_k}{M_k}v_0+\sum_{q=1}^{n}L_{k,q}\left[M_q\left(1-\bar{v}_q\rho\right)g_E-RT\frac{dlnc_q}{d\xi}\left(1+\frac{dln\gamma_q}{dlnc_q}\right)\right]=0$$

(N61a)

would apply, as shown by Equation A14a. If the full form of Equation A9 were applied,

$$\frac{c_k}{M_k}v_0+\sum_{q=1}^{n}L_{k,q}\left[M_q\left[\left(1-\bar{v}_q\rho\right)g_E-\left(\frac{\partial\rho}{\partial\xi}\right)_t\frac{v_0^2}{2}\right]-RT\frac{dlnc_q}{d\xi}\left(1+\frac{dln\gamma_q}{dlnc_q}\right)\right]=0$$

(N62b)

would be obtained. For $n+n_{mp}=1$, if the sole component were membrane-permeant, both

$\frac{dlnc_1}{d\xi}$ and $\left(\frac{\partial\rho}{\partial\xi}\right)_t$ would equal zero at steady state, and in the hydrostatic case, which is marked by the absence of a pressure gradient that could drive a flow of solvent through the system, Equations N62, N46 and N47 can be applied to obtain

$$\frac{M_1(1-\bar{v}_1\rho)}{R_1^*} = -6\pi N_A\eta\frac{v_0}{g_E}.$$

(N63)

A comparison of Equations N58 and N61 shows that $M_1(1-\bar{v}_1\rho)$ is the gravitational analogue of z_1. Equation N61 states that, in the hydrostatic case, if $M_1(1-\bar{v}_1\rho)$ is equal to zero, v_0 will be equal to zero. Except for the trivial case of $(1-\bar{v}_1\rho)=0$ for each species of component 1, this result addresses the definition of the molar mass of a component, as distinct from the definition of the molar mass of a species. (See **Section I: Calculating valence, molar mass, chemical potential and partial specific volume for a multi-species component.**) In a case analogous to that discussed with respect to N58, an $M_1(1-\bar{v}_1\rho)$ of zero need not mean an absence of gravitational transport, as component 1 could comprise both species that float and species that sink, with those that float having $(1-\bar{v}_1\rho)<0$ and those that sink having $(1-\bar{v}_1\rho)>0$. The sum total of the solvent that these species transported through the system would be zero, and thus v_0 would be zero, if the species that floated carried the same amount of solvent as the species that sank.

An additional flaw

As noted with respect to Equations N46 and N47, the above methods for determining $L_{k,q}$ require multiple abuses of the definition of the solvent. To that flaw can be added another, which is that v_0 only appears in the expression of $\vec{J_k}$, which is the molar flow of solute component k in the system frame of reference. Solving Equation N54 (A1) for $\overrightarrow{J_k^S}$, the molar flow of solute component k in the solvent frame of reference, yields

$$\overrightarrow{J_k^S} = \vec{J_k} - \frac{c_k}{M_k}\vec{v}_0\,.$$

(N64)

Thus, if $L_{k,q} = L_{q,k}$ only holds in the solvent frame of reference, then v_0 must vanish from

Equations N44 to N63, with the result that the $L_{k,q}$ values could not, in fact, be calculated as shown because, except for the n_{mp} membrane-permeant components that give rise to $\vec{v}_o$, each value of $\frac{dU_q}{d\xi}$ would be zero in the solvent frame of reference at steady state (Equation N57).

List of selected parameters, their indices, and their cgs, mks or other dimensions

$\text{symbol}_{\text{indices}}$	parameter	index 1	index 2	dimensions
$\vec{r}$	radial vector			cm
M_1	molar mass	component		g/mol
c_1	mass concentration	component		g/cm^3
$c_{1,2}$	mass concentration	component	spatial element	g/cm^3
E	electrical field strength			volt/cm
$D_{1,2}$	diffusion coefficient	component	component	cm^2/s
$u_{1,2}$	electrophoretic mobility coefficient	component	component	$cm^2/volt{\cdot}s$
D_1	diffusion coefficient	component		cm^2/s
u_1	electrophoretic mobility coefficient	component		$cm^2/volt{\cdot}s$
σ_1	reduced valence coefficient	component		cm^{-1}
$D_{1,2}$	diffusion coefficient	component	spatial element	cm^2/s
$u_{1,2}$	electrophoretic mobility coefficient	component	spatial element	$cm^2/volt{\cdot}s$
$\sigma_{1,2}$	reduced valence coefficient	component	spatial element	cm^{-1}
r	radial position			cm
Ψ	electrical potential			statvolt
ξ	Ψ -space parameter	spatial element		cm
ξ_1	Ψ -space parameter	spatial element		cm
ω	angular velocity			s^{-1}
t	time			s
$\bar{v}_1$	partial specific volume	component		cm^3/g
ρ	solution density			g/cm^3
γ_1	activity coefficient	component		dimensionless
N_A	Avogadro's number			mol^{-1}

f_1	frictional coefficient	component		g/s
η	solution viscosity			g/s·cm
R_1^*	Stokes radius (equivalent sphere)	component		cm
P_1	basis function	spatial element		dimensionless
P	pressure			dyne/cm^2
R	cgs ideal gas constant			erg/mol·K
R	mks ideal gas constant			J/mol·K
T	absolute temperature			K
$p_{1,2}$	asymmetry effects coefficient	component	component	cm^3/g
$y_{1,2}$	nonideality coefficient	component	component	cm^3/g
$h_{1,2}$	viscosity coefficient	component	component	cm^3/g
U_1	total molar potential	component		erg/mol
μ_1	chemical potential	component		erg/mol
$\vec{X}_1$	conjugate molar force	component		dyne/mol
$\vec{I}_1$	mass flow vector	component		g/s·cm^2
I_1	mass flow	component		g/s·cm^2
$L_{1,2}$	phenomenological coefficient	component	component	mol^2·s/g·cm^3
$L_{P,R}^{g,a}$	phenomenological coefficient	products	reactants	mol^2·s/g·cm^5
$L_{R,P}^{g,a}$	phenomenological coefficient	reactants	products	mol^2·s/g·cm^5
$\vec{J}_1$	molar flow vector	component		mol/s·cm^2
J_1	molar flow	component		mol/s·cm^2
J_1^R	molar reaction flow	reaction		mol/s·cm^3
A_1	conjugate molar affinity	reaction		erg/mol
$\vec{G}$	magnetic field			tesla, or
$\vec{G}$	Coriolis force			dyne/g
Φ	free energy dissipation function			erg/cm^3·s
$\vec{S}$	outward-normal surface vector			cm^2
$\vec{j}$	current density			ampere/cm^2
A	cross-sectional area			cm^2
i	current			ampere

$\vec{v}_1$	velocity vector	component		cm/s
v_1	velocity magnitude	component		cm/s
$\hat{e}_z$	unit vector	direction (+z-axis)		dimensionless
κ	conductivity of the solution			siemens/cm
$z_{1,2}$	valence	component	species	H$^+$ equivalent
τ	transference number			dimensionless
z_1	valence	component		H$^+$ equivalent
z_1^*	reduced valence	component		H$^+$ equivalent
g_E	gravitational acceleration (See note 1.)	Earth		cm/s^2
F	Faraday (See note 2.)			statcoulomb/mol
Θ	Faraday conversion factor (See note 2.)			statcoulomb/coulomb
ϖ	electrical-potential conversion factor (See note 2.)			volt/statvolt
ε_0	permittivity constant (See note 2.)			C^2/J·m
ε	dielectric constant			dimensionless
$\kappa_{\Gamma/T}^{-1}$	Debye length			cm^{-1}
$\alpha_{1,2}$	radius of shear surface	component	species	cm
$H\left(\kappa_{\Gamma/T}^{-1}\alpha_{1,2}\right)$	Henry's function	component	species	dimensionless
$\zeta_{1,2}$	zeta potential	component	species	volt

Parameters that include non-cgs, non-mks dimensions

Γ	mol-per-litre ionic strength	mol/l
o_1	1st coefficient of the Onsager equation	siemens/cm·[mol/l]
o_2	2nd coefficient of the Onsager equation	siemens/cm·[mol/l]$^{3/2}$

Notes

1. The cgs standard acceleration due to gravity, g_E, is approximately 981 cm/s^2 (for the Earth at sea level).

2. The cgs Faraday is equal to $N_A e$, where N_A is Avogadro's number ($6.0221413\cdot10^{23}$ mol^{-1}) and e, the cgs elementary charge, is equal to $4.8032354\cdot10^{-10}$ statcoulomb. Thus, the cgs

Faraday is $F = 2.89253 \cdot 10^{14}$ statcoulomb/mol. With F and R in cgs units, $F/\varpi R = 11604.5$ K/volt. This is also equal to the mks Faraday (96484.56 coulomb/mol) divided by the mks ideal gas constant (8.31441 J/mol·K). The electrical-potential conversion factor between cgs and mks dimensions is $\varpi = 299.7925$ volt/statvolt. The charge conversion factor between cgs and mks dimensions is $\Theta = 299.7925 \cdot 10^{7}$ statcoulomb/coulomb. The mks permittivity constant, ε_0, is equal to $8.85419 \cdot 10^{-12}$ C^2/J·m.

Contact Information

Thomas P. Moody
Moody Biophysical Consulting
Vancouver, British Columbia
Canada
E-mail: moodybiophysicalconsulting@gmail.com
Web site: http://moodybiophysicalconsulting.blogspot.com/.