

## **An irreversible thermodynamic description of analytical ultracentrifugation (AUC) applied to a solution of the time- and gravitational-potential-space-dependent Lamm equation**

### **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 analytical ultracentrifugation (AUC). (The cgs system is typically used to express all parameters in AUC, and is the default system used here.)

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. Simpler results of integration are obtained by using one-half the square of the radial position, rather than the radial position, as the spatial parameter of the continuity equation. 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.

## References

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## **Section A: An application of irreversible thermodynamics to analytical ultracentrifugation (AUC)**

The application of irreversible thermodynamics [Onsager, 1931a; Onsager, 1931b; de Groot and Mazur, 1962; Katchalsky and Curran, 1965] to AUC yields the flow equation. Given the flow equation, the coupled flow diffusion and sedimentation coefficients can be defined. The flow equation requires a description of the conjugate molar forces in the system. For AUC, those forces are due to gravitational and chemical potential gradients.

### **The sum of the gravitational and chemical potential gradients equals $\nabla U_k$**

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

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

(A1)

where  $\vec{J}_k^S$  is the molar flow of component k in the solvent frame of reference,  $\vec{v}_0$  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 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**), where  $v_0$  is shown to be negligibly small in AUC. The molar mass of a component is discussed below, and described in detail in Section I.

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

$$\nabla U_q = -\vec{X}_q = \nabla \mu_q - M_q \omega^2 \nabla \xi + M_q \nabla g_E h ,$$

(A2)

where  $U_q$  is the total molar potential of solute component q,  $\mu_q$  is the chemical potential of solute component q,  $M_q$  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,  $h$  is the height above the Earth's surface,  $\omega$  is the angular velocity of the centrifuge rotor, and  $\xi = r^2/2$ , for which  $r$  is the radial position in the centrifuge. The component parameter  $\mu_q$  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,  $M_q$  is equal to  $(M_q)_g$ , which is the  $\xi$ -dependent molar mass of component q. (For the definitions of  $\mu_q$  and  $M_q$  in the general case, see **Section I: Calculating 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,  $\nabla \mu_q$  and  $M_q$  become the number averages of the corresponding species parameters of component q. A detailed examination of  $M_q$  is presented in **Section M: Effects of solvent density on (apparent) reduced buoyant mass**.) The molar gravitational potentials of component q due to angular acceleration and the Earth's gravitational acceleration are  $-M_q \omega^2 \xi$  and  $M_q g_E h$ , respectively. It will be shown that  $M_q \nabla g_E h$  is negligible in most cases in AUC. (See **Section H: The contribution of the Earth's gravitational field to transport in AUC**.)

(It is assumed that the system has sufficient concentrations of small, rapidly diffusing ions

that no significant electrical fields develop due to charge separation, which the redistribution of macro-ions in experimentally attainable gravitational fields might otherwise be expected to produce. Thus, in Equation A2,  $\nabla U_q$  does not include any contribution from  $z_q F \nabla \Psi$ , where  $z_q$  is the valence of solute component  $q$ ,  $F$  is the cgs Faraday, and  $\Psi$  is the cgs electrical potential, as  $\nabla \Psi$  is assumed to equal zero everywhere at all times.)

Each chemical potential is a function of time,  $t$ , and spatial position. Each molar gravitational potential, whether arising from angular acceleration or the Earth's gravitational acceleration, is dependent on spatial position. In the case of  $M_q g_E h$ , the potential varies spatially with  $h$ , but as  $(\partial h / \partial t)_{\text{space}} = 0$ , can only vary temporally if  $M_q$  varies temporally. In the case of  $-M_q \omega^2 \xi$ , the potential varies spatially with  $\xi$ , but as  $(\partial \xi / \partial t)_h = 0$  (aside from negligible rotor deformation when  $(\partial \omega / \partial t)_{\text{space}} \neq 0$ ),  $-M_q \omega^2 \xi$  can only vary temporally if  $\omega$  or  $M_q$  vary temporally, and except for periods of rotor acceleration or deceleration,  $(\partial \omega / \partial t)_{\text{space}} = 0$ . Thus, at constant  $\omega$ , the time dependence of each molar gravitational potential is proportional to the time dependence of  $M_q$ . For a single-species component,  $(\partial M_q / \partial t)_{\text{space}} = 0$ . For a multi-species component in a system that has not yet reached equilibrium, if  $\nabla \mu_q \neq 0$ ,  $\mu_q$  is almost certain to vary with time, in which case, where  $(\partial \mu_q / \partial t)_{\text{space}} \neq 0$ ,  $(\partial M_q / \partial t)_{\text{space}} \neq 0$ . (See **Section I: Calculating molar mass, chemical potential and partial specific volume for a multi-species component**. Also see **Equilibrium** at the end of this section.)

The gravitational field due to angular acceleration in the centrifuge is

$$-\nabla(-\omega^2 \xi) = \omega^2 \nabla \xi = \omega^2 \vec{r},$$

(A3)

where  $\vec{r}$  is the radial vector, and  $-\omega^2 \xi$  is the gravitational potential due to angular acceleration.

In AUC, the sample occupies a closed system with the geometry of a cylindrical sector, which usually ensures that all flows of solute components within the system are laminar and, assuming that  $M_q \nabla g_E h$  is negligible, radially directed. Thus, each  $\nabla U_q$  is significant in

the radial direction only, and vector notation can be neglected. This permits a single spatial variable, such as  $r$  or  $\xi$ , to be used to describe all spatial dependencies of interest in the system. Henceforth, therefore, with a few exceptions,  $v_k$ ,  $J_k$ ,  $I_k$  and  $r$  are used in place of  $\vec{v}_k$ ,  $\vec{J}_k$ ,  $\vec{I}_k$  and  $\vec{r}$ , respectively, where  $\vec{v}_k$  is the velocity of component  $k$  in the system frame of reference.

By convention, the meniscus of the solution is defined as the innermost point of the system, and its radial position is denoted as  $r_m$ . (If the location of the innermost wall at the top (with respect to  $\omega^2\vec{r}$ ) of the assembly containing the sample is defined as  $r_t$ , then  $r_t < r_m$ . The space between  $r_t$  and  $r_m$  is typically occupied by air.) The outermost point of the solution is defined as the base of the system, and its radial position, denoted as  $r_b$ , is located at the outermost wall at the bottom (with respect to  $\omega^2\vec{r}$ ) of the assembly containing the sample. As the radial position of the axis of rotation is 0,  $0 < r_m \leq r$  within the system  $\leq r_b$ . In terms of one-half the radial position squared, the system is located within the range of  $\xi_m$  to  $\xi_b$ , where  $\xi_m = r_m^2/2$  and  $\xi_b = r_b^2/2$ .

On the basis of the relationship described by Equation A3,  $\xi$  can be considered the natural independent variable of choice in AUC, as the derivative of the gravitational potential with respect to  $\xi$  is a constant:  $d(-\omega^2\xi)/d\xi = -\omega^2$ . In contrast, the derivative of the gravitational potential with respect to  $r$  is a function of  $r$ :  $d(-\omega^2\xi)/dr = d(-\omega^2r^2/2)/dr = -\omega^2r$ . Hence,  $\xi$  is the parameter associated with the gravitational-potential-space in the title of this work.

## 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,  $\gamma_k$  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  $\mu_k$  is a function of the temperature of the system, the

pressure of the system and the concentrations of all solute components in the system,

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

(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  $\xi$ -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 AUC system, which, despite the flow of matter within it, is treated as if it were hydrostatic, yields

$$P = P_0 + \omega^2 \int_{\xi_m}^{\xi_a} \rho d\xi,$$

(A8)

where  $\rho$  is the solution density, P is the pressure at  $\xi = \xi_a$ , and  $P_0$  is the pressure at  $\xi_m = r_m^2/2$ . Given that  $(\partial\omega^2/\partial\xi)_t = 0$  throughout the system,

$$\left(\frac{\partial P}{\partial \xi}\right)_t = \rho \omega^2.$$

(A9)

Thus,

$$\left(\frac{\partial \mu_k}{\partial P}\right)_{t,T,c} \left(\frac{\partial P}{\partial \xi}\right)_t = M_k \bar{v}_k \rho \omega^2,$$

(A10)

where  $\rho$  is a function of  $\xi$  and  $t$ . Contributions to  $\rho$  include gradients in solute concentrations and  $\xi$ -dependent compression of the solvent, which can be expressed as  $(\partial \rho_0 / \partial \xi)_t \neq 0$ , where  $\rho_0$  is the solvent density. Expectations for a system with a compressible solvent include the likelihood that, when  $d\omega/dt \neq 0$ ,  $(\partial \rho_0 / \partial t)_\xi \neq 0$  and  $d\xi_m/dt \neq 0$ .

Given that  $(\partial \xi / \partial r)_t = r$  throughout the system,

$$\left(\frac{\partial \mu_k}{\partial P}\right)_{t,P,c} \left(\frac{\partial P}{\partial r}\right)_t = \left(\frac{\partial \mu_k}{\partial P}\right)_{t,T,c} \left(\frac{\partial P}{\partial \xi}\right)_t \left(\frac{\partial \xi}{\partial r}\right)_t = M_k \bar{v}_k \rho \omega^2 r.$$

(A11)

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

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

(A12)

The term in square brackets describes the deviation of  $\mu_k$  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,

$$\nabla \mu_k = \left(\frac{\partial \mu_k}{\partial \xi}\right)_t \left(\frac{\partial \xi}{\partial r}\right)_t = M_k \bar{v}_k \rho \omega^2 r + RT \left(\frac{\partial \ln c_k}{\partial r}\right)_t \left[ 1 + c_k \sum_{w=1}^n \left(\frac{\partial c_w}{\partial c_k}\right)_t \left(\frac{\partial \ln \gamma_k}{\partial c_w}\right)_{t,T,P,c_{a \neq w}} \right].$$



(A13)

Applying the above descriptions of the various parts of  $\nabla U_k$ , the gradient of the total molar potential of solute component  $k$  in an AUC system can be written as

$$\nabla U_k = -\vec{X}_k = -M_k(1 - \bar{v}_k\rho)\omega^2r + RT \left( \frac{\partial \ln c_k}{\partial r} \right)_t \left[ 1 + c_k \sum_{w=1}^n \left( \frac{\partial c_w}{\partial c_k} \right)_t \left( \frac{\partial \ln \gamma_k}{\partial c_w} \right)_{t,T,P,c_{a \neq w}} \right],$$

(A14)

where  $\vec{X}_k$  is the conjugate molar force (Equations A2 and I16) of solute component  $k$ . Using Equation A14 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

$$J_k = \sum_{q=1}^n L_{k,q} \left\{ M_q(1 - \bar{v}_q\rho)\omega^2r - RT \left( \frac{\partial \ln c_q}{\partial r} \right)_t \left[ 1 + c_q \sum_{w=1}^n \left( \frac{\partial c_w}{\partial c_q} \right)_t \left( \frac{\partial \ln \gamma_q}{\partial c_w} \right)_{t,T,P,c_{a \neq w}} \right] \right\}.$$

(A15)

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

$$s_{k,q} = \frac{M_q}{c_q} L_{k,q} M_q (1 - \bar{v}_q\rho),$$

(A16)

and the coupled-flow-diffusion coefficient is defined as

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

(A17)

so that

$$J_k = \sum_{q=1}^n \frac{c_q}{M_q} \left[ s_{k,q} \omega^2 r - D_{k,q} \left( \frac{\partial \ln c_q}{\partial r} \right)_t \right].$$

(A18)

Like  $L_{k,q}$ ,  $s_{k,q}$  and  $D_{k,q}$  link the molar flow of solute component  $k$  to the conjugate molar force of solute component  $q$ . Unlike  $L_{k,q}$ ,  $s_{k,q} \neq s_{q,k}$  and  $D_{k,q} \neq D_{q,k}$ .

## An application of irreversible thermodynamics to the Lamm equation

Equation A18 describes the molar flow of one solute component in a multi-component system in the analytical ultracentrifuge, and derives from the application of irreversible thermodynamics to AUC [Williams et al., 1958; Fujita, 1962; Fujita, 1975].

Each coupled-flow-sedimentation (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  $L_{k,k}$ ,

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

(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  $\eta$ , the solution viscosity, are known. The applicability of the Stokes equation, however, is questionable except as  $c_k$  approaches zero, at which point,  $\eta$  becomes identical to the solvent viscosity. Given the restricted applicability of Equation A19, the prospects for calculating  $\mathbf{D}_{k,q}$  or  $\mathbf{s}_{k,q}$  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 AUC.**) 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  $n > 3$  at least (see the discussion following Equation N44),  $L_{k,q}$ ,  $\mathbf{D}_{k,q}$  and  $\mathbf{s}_{k,q}$  cannot be calculated from other experimentally determinable parameters, and cannot be determined directly by any practical or routine approach. Informative parameters derived from  $L_{k,q}$ ,  $\mathbf{D}_{k,q}$  and  $\mathbf{s}_{k,q}$  can be determined experimentally, however. These experimentally determinable parameters are the apparent diffusion coefficient, the apparent sedimentation coefficient, and the apparent reduced molar mass 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

$$\begin{aligned}
 D_k &= \frac{M_k}{c_k \left( \frac{\partial \ln c_k}{\partial r} \right)_t} \sum_{q=1}^n \frac{c_q}{M_q} \left( \frac{\partial \ln c_q}{\partial r} \right)_t \mathbf{D}_{k,q} = \frac{M_k}{\left( \frac{\partial c_k}{\partial r} \right)_t} \sum_{q=1}^n \frac{1}{M_q} \left( \frac{\partial c_q}{\partial r} \right)_t \mathbf{D}_{k,q} \\
 &= \frac{M_k}{\left( \frac{\partial c_k}{\partial r} \right)_t} RT \sum_{q=1}^n L_{k,q} \left( \frac{\partial \ln c_q}{\partial r} \right)_t \left[ 1 + c_q \sum_{w=1}^n \left( \frac{\partial c_w}{\partial c_q} \right)_t \left( \frac{\partial \ln \gamma_q}{\partial c_w} \right)_{t,T,P,c_a \neq w} \right] \\
 &= \frac{M_k RT \sum_{q=1}^n L_{k,q} \frac{1}{r} \left( \frac{\partial \ln c_q}{\partial r} \right)_t \left[ 1 + c_q \sum_{w=1}^n \left( \frac{\partial c_w}{\partial c_q} \right)_t \left( \frac{\partial \ln \gamma_q}{\partial c_w} \right)_{t,T,P,c_a \neq w} \right]}{\frac{1}{r} \left( \frac{\partial c_k}{\partial r} \right)_t} \\
 &= \frac{M_k}{\left( \frac{\partial c_k}{\partial \xi} \right)_t} RT \sum_{q=1}^n L_{k,q} \left( \frac{\partial \ln c_q}{\partial \xi} \right)_t \left[ 1 + c_q \sum_{w=1}^n \left( \frac{\partial c_w}{\partial c_q} \right)_t \left( \frac{\partial \ln \gamma_q}{\partial c_w} \right)_{t,T,P,c_a \neq w} \right],
 \end{aligned}$$

(A21)

and the (apparent) sedimentation coefficient of solute component  $k$  is

$$s_k = \frac{M_k}{c_k} \sum_{q=1}^n \frac{1}{M_q} c_q s_{k,q} = \frac{M_k}{c_k} \sum_{q=1}^n L_{k,q} M_q (1 - \bar{v}_q \rho),$$

(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 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.

The (apparent) reduced molar mass coefficient of solute component  $k$  is defined as

$$\begin{aligned}
 \sigma_k &= \frac{\omega^2 s_k}{D_k} = \frac{\omega^2 \frac{1}{c_k} \sum_{q=1}^n \frac{1}{M_q} c_q s_{k,q}}{\left(\frac{\partial c_k}{\partial r}\right)_t \sum_{q=1}^n \frac{1}{M_q} \left(\frac{\partial c_q}{\partial r}\right)_t D_{k,q}} = \frac{\frac{1}{r} \omega^2 \left(\frac{\partial \ln c_k}{\partial r}\right)_t \sum_{q=1}^n \frac{1}{M_q} c_q s_{k,q}}{\frac{1}{r} \sum_{q=1}^n \frac{1}{M_q} \left(\frac{\partial c_q}{\partial r}\right)_t D_{k,q}} \\
 &= \frac{\left(\frac{\partial \ln c_k}{\partial \xi}\right)_t \omega^2 \sum_{q=1}^n \frac{1}{M_q} c_q s_{k,q}}{\sum_{q=1}^n \frac{1}{M_q} \left(\frac{\partial c_q}{\partial \xi}\right)_t D_{k,q}} = \frac{\left(\frac{\partial \ln c_k}{\partial \xi}\right)_t \sum_{q=1}^n \frac{1}{M_q} c_q \sigma_{k,q} D_{k,q}}{\sum_{q=1}^n \frac{1}{M_q} \left(\frac{\partial c_q}{\partial \xi}\right)_t D_{k,q}} = \\
 &= \frac{\left(\frac{\partial \ln c_k}{\partial \xi}\right)_t \omega^2 \sum_{q=1}^n L_{k,q} M_q (1 - \bar{v}_q \rho)}{RT \sum_{q=1}^n L_{k,q} \left(\frac{\partial \ln c_q}{\partial \xi}\right)_t \left[1 + c_q \sum_{w=1}^n \left(\frac{\partial c_w}{\partial c_q}\right)_t \left(\frac{\partial \ln \gamma_q}{\partial c_w}\right)_{t,T,P,c_{\alpha \neq w}}\right]}
 \end{aligned}$$

(A23)

where, for the effect of component  $q$  on component  $k$ ,  $\sigma_{k,q}$  is the coupled-flow analogue of  $\sigma_k$ . As shown in Section N,  $\sigma_{k,q} = \omega^2 s_{k,q} / D_{k,q}$  (Equation N10). Like  $s_{k,q}$  and  $D_{k,q}$ ,  $\sigma_{k,q}$  links the molar flow of solute component  $k$  to the conjugate molar force of solute component  $q$ . Also like  $s_{k,q}$  and  $D_{k,q}$ ,  $\sigma_{k,q} \neq \sigma_{q,k}$ . While  $\sigma_k$  cannot be completely defined without specifying  $\omega^2$ , on which it explicitly depends, this might be viewed as a virtue, as unlike  $s_k$ ,  $\sigma_k$  preserves information regarding the field dependence of transport, including some effects that might be expected in cases of field-dependent solvent compression.

Because  $\sigma_k$  is proportional to the ratio of  $s_k$  and  $D_k$ , and because both  $s_k$  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  $\sigma_k$ . 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  $\xi$ -dependent Lamm equation in terms of species**), with species rather than components.

Along with  $D_k$ , either  $s_k$  or  $\sigma_k$  are the transport coefficients needed to describe AUC results or simulate transport in AUC. 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  $\mathbf{s}_{k,q}$ , are distinct from  $D_{k,j}$  and  $s_{k,j}$ , respectively, which, respectively, are the  $t$ -dependent,  $\xi$ -independent scalar coefficients derived from  $D_k$  and  $s_k$  in Section B (**Steps taken to solve the  $t$ - and  $\xi$ -dependent Lamm equation**), and are also distinct from  $D_{k,e}$  and  $s_{k,e}$ , respectively, which, respectively, are the diffusion and sedimentation coefficients of species  $e$  of component  $k$  in Section C. To highlight their distinction from similarly denoted parameters,  $\mathbf{D}_{k,q}$  and  $\mathbf{s}_{k,q}$  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 molar mass, chemical potential and partial specific volume for a multi-species component**). Thus, in terms of  $D_k$  and  $s_k$ , or  $D_k$  and  $\sigma_k$ , the mass flow of solute component  $k$  can be written as

$$J_k M_k = I_k = c_k \left[ s_k \omega^2 r - D_k \left( \frac{\partial \ln c_k}{\partial r} \right)_t \right],$$

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

or

$$J_k M_k = I_k = c_k D_k \left[ \sigma_k - \left( \frac{\partial \ln c_k}{\partial \xi} \right)_t \right] \sqrt{2\xi}.$$

(A24)

The total mass flow is

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

(A25)

As a function of  $t$  and  $r$ , the Lamm equation [Williams et al., 1958], which is the continuity equation for sedimentation, can be written as

$$\left( \frac{\partial c}{\partial t} \right)_r = -\frac{1}{r} \left( \frac{\partial r I}{\partial r} \right)_t$$

or

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

and as a function of t and  $\xi$ , the Lamm equation can be written as

$$\left( \frac{\partial c}{\partial t} \right)_\xi = - \left( \frac{\partial \sqrt{2\xi} I}{\partial \xi} \right)_t$$

or

$$\sum_{k=1}^n \left( \frac{\partial c_k}{\partial t} \right)_\xi = - \sum_{k=1}^n \left( \frac{\partial \sqrt{2\xi} I_k}{\partial \xi} \right)_t,$$

(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 r-dependent form or the t- and  $\xi$ -dependent form of the Lamm equation can be obtained. (See **Section B: Steps taken to solve the t- and  $\xi$ -dependent Lamm equation.**)

### Averages

Equations A24 and A25 can be combined to yield

$$I = \sqrt{2\xi} \sum_{k=1}^n \left[ c_k D_k \sigma_k - D_k \left( \frac{\partial c_k}{\partial \xi} \right)_t \right]$$

or

$$I = \sqrt{2\xi} \sum_{k=1}^n \left[ c_k s_k \omega^2 - D_k \left( \frac{\partial c_k}{\partial \xi} \right)_t \right],$$

(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 sedimentation coefficient,  $s_w$ . The diffusion coefficients and concentration gradients of all solute components are used to calculate  $D_G$ , while the sedimentation coefficients and concentrations of all solute components are used to calculate  $s_w$ . Respectively, these averages can be calculated as

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

(A29)

and, in terms of its product with  $\omega^2$ ,

$$\omega^2 s_w = \frac{\omega^2 \sum_{k=1}^n s_k c_k}{\sum_{k=1}^n c_k} = \frac{\sum_{k=1}^n \sigma_k D_k c_k}{\sum_{k=1}^n c_k} = (\sigma D)_w,$$

(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  $s_w$  yield

$$I = \sqrt{2\xi} \left[ c s_w \omega^2 - D_G \left( \frac{\partial c}{\partial \xi} \right)_t \right].$$

(A31)

In general, at any time up to and including equilibrium,



$$\begin{aligned} \omega^2 \frac{s_w}{D_G} &= \left[ \frac{\omega^2 \sum_{k=1}^n s_k c_k}{\sum_{k=1}^n c_k} \right] \left[ \frac{\sum_{k=1}^n \left( \frac{\partial c_k}{\partial \xi} \right)_t}{\sum_{k=1}^n D_k \left( \frac{\partial c_k}{\partial \xi} \right)_t} \right] = \left( \frac{\partial \ln c}{\partial \xi} \right)_t \left[ \frac{\omega^2 \sum_{k=1}^n s_k c_k}{\sum_{k=1}^n D_k \left( \frac{\partial c_k}{\partial \xi} \right)_t} \right] \\ &= \left( \frac{\partial \ln c}{\partial \xi} \right)_t \left[ \frac{\sum_{k=1}^n \sigma_k D_k c_k}{\sum_{k=1}^n D_k \left( \frac{\partial c_k}{\partial \xi} \right)_t} \right]. \end{aligned}$$

(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 equilibrium at zero field, provided that a field has been applied long enough to perturb  $(\partial c_k / \partial \xi)_t$  from zero. Equilibrium is dealt with next.

## Equilibrium

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

$$\sum_{k=1}^n \left[ c_k D_k \sigma_k - D_k \frac{dc_k}{d\xi} \right] = \sum_{k=1}^n I_{k,\infty} = I_\infty = 0,$$

or, applying the definition of  $\sigma_k$  in Equation A23,

$$\sum_{k=1}^n \left[ c_k s_k \omega^2 - D_k \frac{dc_k}{d\xi} \right] = \sum_{k=1}^n I_{k,\infty} = I_\infty = 0,$$

(A33)

where the expression in square brackets is equal to  $I_{k,\infty}$ , which is the mass flow of solute component  $k$  at equilibrium. Due to conservation of mass, at equilibrium, throughout the system, each  $I_{k,\infty} = 0$  and each  $dI_{k,\infty}/d\xi = 0$ . (Conservation of mass ensures that  $(\partial c_k/\partial t)_\xi = -(\partial[2\xi]^{0.5}I_k/\partial\xi)_t$ . Thus, when  $(\partial c_k/\partial t)_\xi = 0$ , as it does at equilibrium,  $(\partial[2\xi]^{0.5}I_k/\partial\xi)_t = 0$ .) Nevertheless, as a consequence of their concentration dependence, each  $D_k$ ,  $\sigma_k$  and  $s_k$ , can, and most likely will, be  $\xi$ -dependent at equilibrium, except for the zero-field case where each  $dc_k/d\xi = 0$  at all  $\xi$ .

Although the mass flow of each solute component is zero at equilibrium, the mass flows of individual species of a solute component may be nonzero at equilibrium. In general, throughout the system, the mass flows of the species of a solute component sum to zero at equilibrium. (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 equilibrium.)

In the limit as equilibrium, or infinite time, is approached,  $I$  approaches zero. Applying this limit to a re-arrangement of Equation A31 results in

$$\lim_{t \rightarrow \infty} \omega^2 \frac{s_w}{D_G} = \lim_{t \rightarrow \infty} \left( \frac{\partial \ln c}{\partial \xi} \right)_t = \frac{d \ln c}{d \xi}.$$

(A34)

Applying the equilibrium condition, in which each  $I_k = 0$ , to Equation A28 (expressed in terms of  $\sigma_k$  and  $D_k$ ) shows that, for each solute component,  $k$ ,

$$\lim_{t \rightarrow \infty} \left[ c_k D_k \sigma_k - D_k \left( \frac{\partial c_k}{\partial \xi} \right)_t \right] = 0.$$

(A35)

Dividing this equation by  $D_k$  yields

$$\lim_{t \rightarrow \infty} \left[ c_k \sigma_k - \left( \frac{\partial c_k}{\partial \xi} \right)_t \right] = 0.$$

(A36)

Taking the sum over all k results in

$$\begin{aligned} \lim_{t \rightarrow \infty} \sum_{k=1}^n \left[ c_k \sigma_k - \left( \frac{\partial c_k}{\partial \xi} \right)_t \right] &= \lim_{t \rightarrow \infty} \left[ \sum_{k=1}^n c_k \sigma_k - \sum_{k=1}^n \left( \frac{\partial c_k}{\partial \xi} \right)_t \right] = \lim_{t \rightarrow \infty} \left[ c \frac{\sum_{k=1}^n c_k \sigma_k}{\sum_{k=1}^n c_k} - \sum_{k=1}^n \left( \frac{\partial c_k}{\partial \xi} \right)_t \right] \\ &= \lim_{t \rightarrow \infty} \left[ c \sigma_w - \left( \frac{\partial c}{\partial \xi} \right)_t \right] = 0. \end{aligned}$$

(A37)

Division by c yields

$$\lim_{t \rightarrow \infty} \left[ \sigma_w - \left( \frac{\partial \ln c}{\partial \xi} \right)_t \right] = 0.$$

(A38)

Thus,

$$\lim_{t \rightarrow \infty} \sigma_w = \lim_{t \rightarrow \infty} \left( \frac{\partial \ln c}{\partial \xi} \right)_t = \frac{d \ln c}{d \xi}.$$

(A39)

Combining the results of Equations A34 and A39 shows that

$$\lim_{t \rightarrow \infty} \omega^2 \frac{S_w}{D_G} = \lim_{t \rightarrow \infty} \sigma_w.$$

(A40)

Equation A40 only applies at equilibrium. Solving Equation A40 for  $D_G$  shows that, at equilibrium,  $D_G = \omega^2 S_w / \sigma_w$ . Furthermore, Equation A30 shows that, in general,  $\omega^2 s_w = (\sigma D)_w$ . Thus, at equilibrium,  $D_G = (\sigma D)_w / \sigma_w$ . Neither of these expressions for  $D_G$  is especially well defined for the case of equilibrium at zero field, however. Nevertheless, information about that system state can be gained from Equation A40 via Equation A39. As  $d \ln c / d \xi = 0$  at zero field at equilibrium, Equation A39 shows that, at zero field at equilibrium,  $\sigma_w = 0$ . Applying this result to Equation A40 shows that  $\omega^2 s_w / D_G = 0$  at zero field at equilibrium. For all of this to hold, as the field approaches zero and the system approaches equilibrium at zero field,  $\omega^2 s_w$  must approach zero faster than  $D_G$ . Expressed as limits applied to  $D_G = (\sigma D)_w / \sigma_w$ ,

$$\lim_{\omega^2 r \rightarrow 0} \left( \lim_{t \rightarrow \infty} D_G \right) = \lim_{\omega^2 r \rightarrow 0} \left[ \lim_{t \rightarrow \infty} \frac{(\sigma D)_w}{\sigma_w} \right] = \frac{\sigma_w D_w}{\sigma_w} = D_w$$

(A41)

is obtained at equilibrium at zero field. (As the system approaches equilibrium at zero field, each  $\sigma_k$  approaches zero, as does  $\sigma_w$ , so that  $(\sigma D)_w$  can be equated to  $\sigma_w D_w$  as  $\omega^2 r$  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

$$\lim_{\left(\frac{\partial c_k}{\partial \xi}\right)_t \rightarrow 0} I = \sqrt{2\xi} \sum_{k=1}^n c_k D_k \sigma_k = c(\sigma D)_w \sqrt{2\xi}$$

or

$$\lim_{\left(\frac{\partial c_k}{\partial \xi}\right)_t \rightarrow 0} I = \sqrt{2\xi} \sum_{k=1}^n c_k s_k \omega^2 = c s_w \omega^2 \sqrt{2\xi}.$$

(A42)

Thus, using  $r$  in place of  $(2\xi)^{0.5}$ ,  $I = c(\sigma D)_w r = c \omega^2 s_w r$  in plateau regions.

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## **Section B: Steps taken to solve the $t$ - and $\xi$ -dependent Lamm equation**

The following finite-element method for solving the  $t$ - and  $\xi$ -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,  $\xi_m$  and  $\xi_b$ . As the flow of each component is expected to meet this boundary condition in a properly enclosed AUC system, the finite-element solution shown can be applied to all components, with solute components treated explicitly, and the solvent component treated implicitly.

The solution begins with an integration that takes advantage of the boundary conditions to eliminate the partial derivatives with respect to  $\xi$ . To that end, the continuity equation (Equation A26) is first multiplied by  $H$ , which is an arbitrary function of  $\xi$ , and then

integrated over the entire range of  $\xi$ . (Ultimately, H will be replaced by a set of N functions of  $\xi$  indexed by i, where  $1 \leq i \leq N$ .) Thus,

$$\sum_{k=1}^n \int_{\xi_m}^{\xi_b} \left( \frac{\partial c_k}{\partial t} \right)_{\xi} H d\xi = - \sum_{k=1}^n \int_{\xi_m}^{\xi_b} \left( \frac{\partial \sqrt{2\xi} I_k}{\partial \xi} \right)_t H d\xi.$$

(B1)

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

$$\begin{aligned} & - \sum_{k=1}^n \int_{\xi_m}^{\xi_b} \left( \frac{\partial \sqrt{2\xi} I_k}{\partial \xi} \right)_t H d\xi \\ & = - \left[ \sum_{k=1}^n [H(\xi_b) \sqrt{2\xi_b} I_k(\xi_b) - H(\xi_m) \sqrt{2\xi_m} I_k(\xi_m)] - \sum_{k=1}^n \int_{\xi_m}^{\xi_b} \left( \frac{\partial H}{\partial \xi} \right)_t \sqrt{2\xi} I_k d\xi \right], \end{aligned}$$

(B2)

where  $I_k(\xi)$  is  $I_k$  at  $\xi$  and  $H(\xi)$  is  $H$  at  $\xi$ . As the boundary conditions in AUC are  $I_k(\xi_m) = 0$  and  $I_k(\xi_b) = 0$ , the preceding equation reduces to

$$- \sum_{k=1}^n \int_{\xi_m}^{\xi_b} \left( \frac{\partial \sqrt{2\xi} I_k}{\partial \xi} \right)_t H d\xi = \sum_{k=1}^n \int_{\xi_m}^{\xi_b} \left( \frac{\partial H}{\partial \xi} \right)_t \sqrt{2\xi} I_k d\xi.$$

(B3)

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

$$\sum_{k=1}^n \int_{\xi_m}^{\xi_b} \left( \frac{\partial H}{\partial \xi} \right)_t \sqrt{2\xi} I_k d\xi = \sum_{k=1}^n \int_{\xi_m}^{\xi_b} \frac{dH}{d\xi} \sqrt{2\xi} I_k d\xi,$$

(B4)

and Equation B1 becomes

$$\sum_{k=1}^n \int_{\xi_m}^{\xi_b} \left( \frac{\partial c_k}{\partial t} \right)_{\xi} H d\xi = \sum_{k=1}^n \int_{\xi_m}^{\xi_b} \frac{dH}{d\xi} \sqrt{2\xi} I_k d\xi.$$

(B5)

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

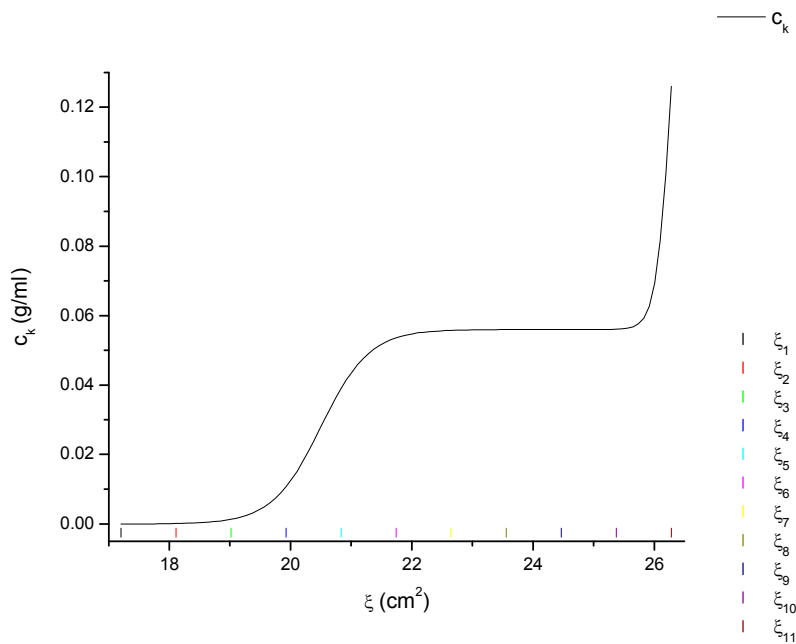


Figure B1. An example of  $c_k$  versus  $\xi$  at a single time,  $t$ . Specific points,  $\xi_h$ , are shown, where  $1 \leq h \leq N$ , and the points are equally spaced. A value of  $N = 11$  was chosen for this example.

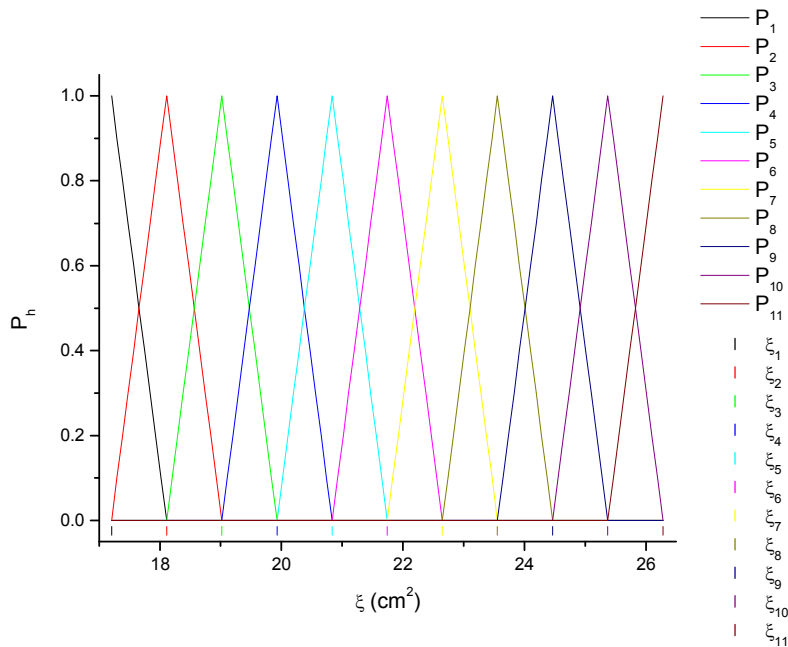


Figure B2. An example, corresponding to that shown in Figure B1, of  $P_h$  versus  $\xi$ . Each  $P_h$  function is independent of  $t$ . The same  $\xi_h$  values shown in Figure B1 are those applied here to the  $P_h$  functions. (See Equations B58 to B63 for a more general description of the  $P_h$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

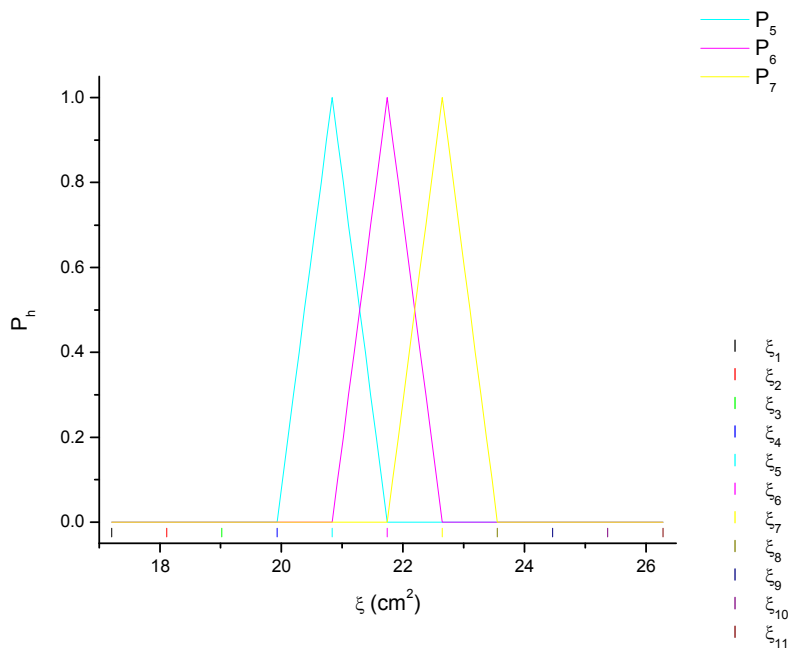




Figure B3. A detail of Figure B2, showing just three of the  $P_h$  functions versus  $\xi$ . The system boundaries are  $\xi_1 = \xi_m = 17.2 \text{ cm}^2$  and  $\xi_N = \xi_{11} = \xi_b = 26.3 \text{ cm}^2$ . In this example, where the points are equally spaced, each  $\Delta\xi_h$  is the same, and is described by Equation B38.

(Equations B53 to B57 describe each  $\Delta\xi_h$  in general.) Calculation of  $\xi_h$  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.

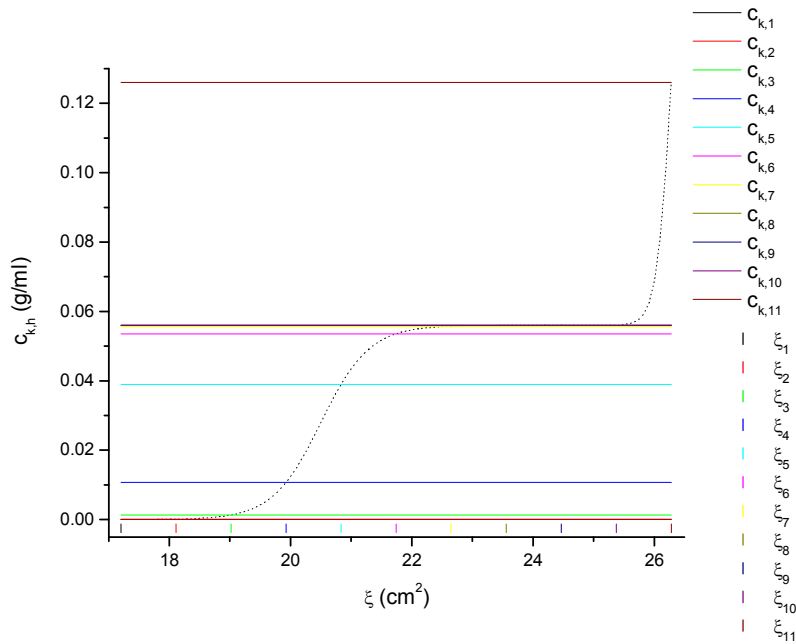


Figure B4. The  $\xi$ -independent concentrations,  $c_{k,h}$ , that describe  $c_k$  at time  $t$ . (Compare this figure with Figure B1, which shows  $c_k$  as a function of  $\xi$  at time  $t$ .) Though each  $c_{k,h}$  is  $\xi$ -independent, this figure shows that the value of each  $c_{k,h}$  at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

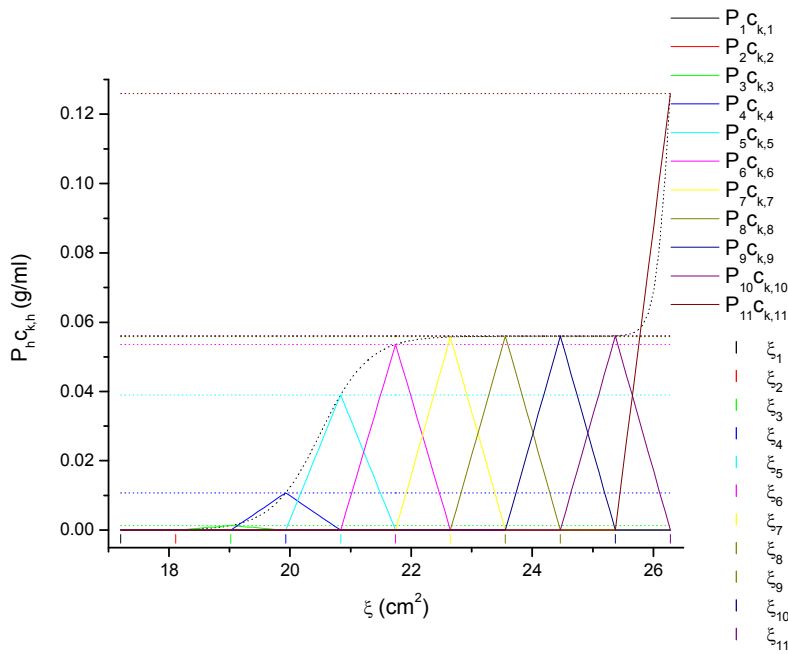


Figure B5.  $P_h c_{k,h}$  versus  $\xi$ , where each  $P_h c_{k,h}$  is obtained by multiplying each  $P_h$  shown in Figure B2 by the corresponding  $c_{k,h}$  shown in Figure B4.

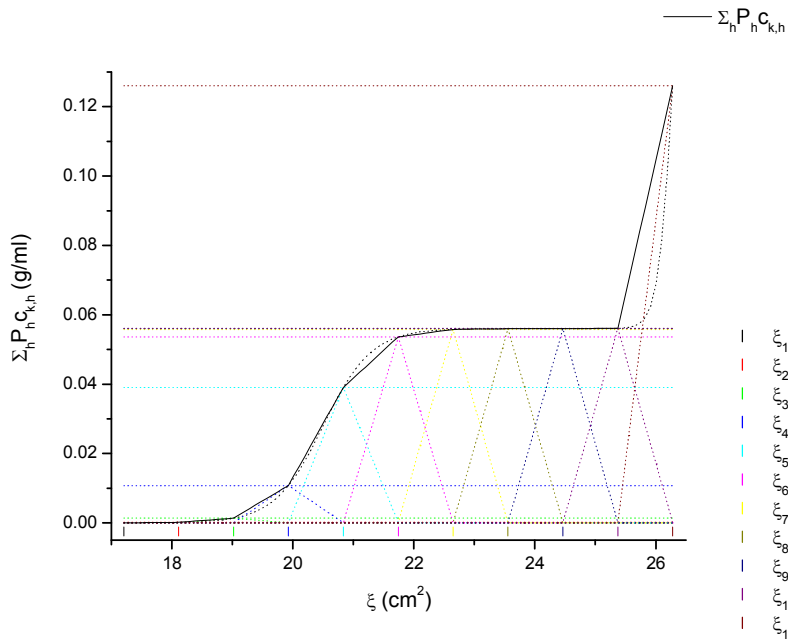


Figure B6. The sum,  $\sum_{h=1}^N P_h c_{k,h}$ , versus  $\xi$ . Each  $P_h c_{k,h}$  used in the sum is shown individually in Figure B5.

For equally spaced points,  $\xi_h = \xi_1 + [h - 1]\Delta\xi$ , where  $\Delta\xi$  is the spatial increment between any two adjacent points. Equations B54 to B57 describe  $\Delta\xi$  for the general case, in which  $\Delta\xi$  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  $\Delta\xi$ .

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

$$\sum_{k=1}^n \sum_{h=1}^N \frac{dc_{k,h}}{dt} \int_{\xi_m}^{\xi_b} P_h H d\xi = \sum_{k=1}^n \int_{\xi_m}^{\xi_b} \frac{dH}{d\xi} \sqrt{2\xi} I_k d\xi.$$

(B7)

Expanding  $I_k$  (Equation A24) as

$$I_k = c_k D_k \left[ \sigma_k - \left( \frac{\partial \ln c_k}{\partial \xi} \right)_t \right] \sqrt{2\xi} = \left[ \sigma_k D_k c_k - D_k \left( \frac{\partial c_k}{\partial \xi} \right)_t \right] \sqrt{2\xi},$$

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

$$I_k = \left[ \sigma_k D_k \sum_{h=1}^N c_{k,h} P_h - D_k \sum_{h=1}^N c_{k,h} \frac{dP_h}{d\xi} \right] \sqrt{2\xi}.$$

(B8)

Substituting this for  $I_k$  in Equation B7 and rearranging slightly yields

$$\begin{aligned} & \sum_{k=1}^n \sum_{h=1}^N \frac{dc_{k,h}}{dt} \int_{\xi_m}^{\xi_b} P_h H d\xi \\ &= 2 \sum_{k=1}^n \int_{\xi_m}^{\xi_b} \frac{dH}{d\xi} \left[ \sigma_k D_k \sum_{h=1}^N c_{k,h} P_h \right] \xi d\xi - 2 \sum_{k=1}^n \int_{\xi_m}^{\xi_b} \frac{dH}{d\xi} \left[ D_k \sum_{h=1}^N c_{k,h} \frac{dP_h}{d\xi} \right] \xi d\xi. \end{aligned}$$

(B9)

The dependence of  $D_k$  (Equation A21) and  $\sigma_k$  (Equation A23) on the concentration,  $c_q$ , of

each explicitly included solute component,  $q$ , renders  $D_k$  and  $\sigma_k$   $\xi$ -dependent in all but special cases, such as  $t = 0$ , when all  $(\partial c_q / \partial \xi)_t = 0$  at all  $\xi$ . (Where the solvent is compressible, once  $\omega$  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.) Previously described, first approximate solutions [Cox and Dale, 1981; Schuck et al., 1998] to the  $r$ - and  $t$ -dependent Lamm equation have been derived by treating  $D_k$  and  $s_k$  as  $r$ -independent. To obtain a second approximate solution to the Lamm equation,  $D_k$  and  $\sigma_k$  are expressed in terms of  $\xi$ -independent coefficients that are separable from  $\xi$ -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  $\xi$  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  $\xi$** ). 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 Lamm equation have been, and in its initial application here, the second approximate solution will be, incorrectly applied to cases in which  $D_k$ ,  $\sigma_k$  and  $s_k$  are  $r$ - or  $\xi$ -dependent. Due to the typically weak  $r$ - or  $\xi$ -dependence of  $D_k$ ,  $\sigma_k$  and  $s_k$ , 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  $\xi$ - and  $t$ -dependent Lamm equation are compared in **Section F ( $\xi$ -dependent functions to approximate  $D_{k,e}$  and  $\sigma_{k,e}$ )**.

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

$$s_k = \sum_{j=1}^N s_{k,j} P_j ,$$

(B10)

where each  $s_{k,j}$  at all  $\xi$  is equal to  $s_k$  at  $\xi_j$ . The result expresses  $s_k$  as separable  $\xi$ -independent and  $\xi$ -dependent terms.

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

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

(B11)

where each  $D_{k,j}$  at all  $\xi$  is equal to  $D_k$  at  $\xi_j$ .

Equations A23, B10 and B11 are combined to express  $\sigma_k$  in terms of previously defined (Equations B10 and B11), separable  $\xi$ -independent and  $\xi$ -dependent terms. Thus,

$$\sigma_k = \frac{\omega^2 s_k}{D_k} = \frac{\omega^2 \sum_{j=1}^N s_{k,j} P_j}{\sum_{j=1}^N D_{k,j} P_j} .$$

(B12)

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

Using  $\omega^2 s_k$  in place of  $\sigma_k D_k$  (from a re-arrangement of Equation A23) results in

$$\begin{aligned} & \sum_{k=1}^n \sum_{h=1}^N \frac{dc_{k,h}}{dt} \int_{\xi_m}^{\xi_b} P_h H d\xi \\ &= 2\omega^2 \sum_{k=1}^n \sum_{h=1}^N c_{k,h} \int_{\xi_m}^{\xi_b} s_k P_h \frac{dH}{d\xi} \xi d\xi - 2 \sum_{k=1}^n \sum_{h=1}^N c_{k,h} \int_{\xi_m}^{\xi_b} D_k \frac{dP_h}{d\xi} \frac{dH}{d\xi} \xi d\xi. \end{aligned}$$

(B13)

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

$$\begin{aligned} & \sum_{k=1}^n \sum_{h=1}^N \frac{dc_{k,h}}{dt} \int_{\xi_m}^{\xi_b} P_h H d\xi \\ &= 2\omega^2 \sum_{k=1}^n \sum_{h=1}^N c_{k,h} \int_{\xi_m}^{\xi_b} \sum_{j=1}^N s_{k,j} P_j P_h \frac{dH}{d\xi} \xi d\xi \\ &\quad - 2 \sum_{k=1}^n \sum_{h=1}^N c_{k,h} \int_{\xi_m}^{\xi_b} \sum_{j=1}^N D_{k,j} P_j \frac{dP_h}{d\xi} \frac{dH}{d\xi} \xi d\xi, \end{aligned}$$

and permits the  $\xi$ -independent parameters,  $D_{k,j}$  and  $s_{k,j}$ , to be factored out of the integrals.

Thus,

$$\begin{aligned} & \sum_{k=1}^n \sum_{h=1}^N \frac{dc_{k,h}}{dt} \int_{\xi_m}^{\xi_b} P_h H d\xi \\ &= 2\omega^2 \sum_{k=1}^n \sum_{h=1}^N c_{k,h} \sum_{j=1}^N s_{k,j} \left[ \int_{\xi_m}^{\xi_b} P_j P_h \frac{dH}{d\xi} \xi d\xi \right] \\ &\quad - 2 \sum_{k=1}^n \sum_{h=1}^N c_{k,h} \sum_{j=1}^N D_{k,j} \left[ \int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi} \frac{dH}{d\xi} \xi d\xi \right]. \end{aligned}$$

(B14)

Letting

$$\sigma_{k,j} = \frac{\omega^2 s_{k,j}}{D_{k,j}},$$

(B15)

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

$$\sum_{k=1}^n \sum_{h=1}^N \left( \frac{dc_{k,h}}{dt} \int_{\xi_m}^{\xi_b} P_h H d\xi - 2c_{k,h} \sum_{j=1}^N D_{k,j} \left[ \sigma_{k,j} \int_{\xi_m}^{\xi_b} P_j P_h \frac{dH}{d\xi} \xi d\xi - \int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi} \frac{dH}{d\xi} \xi d\xi \right] \right) = 0. \quad (\text{B16})$$

At all  $\xi$ , each of the  $N$  scalar coefficients,  $\sigma_{k,j}$  (defined in Equation B15) is equal to  $\sigma_k$  at  $\xi_j$ .

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  $\xi$ -dependent function,  $P_j$ , multiplied by a  $\xi$ -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  $\Delta t$  are finite increments, yields

$$\sum_{k=1}^n \sum_{h=1}^N \left( \frac{1}{2} \frac{\Delta c_{k,h}}{\Delta t} \int_{\xi_m}^{\xi_b} P_h H d\xi - c_{k,h} \sum_{j=1}^N D_{k,j} \left[ \sigma_{k,j} \int_{\xi_m}^{\xi_b} P_j P_h \frac{dH}{d\xi} \xi d\xi - \int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi} \frac{dH}{d\xi} \xi d\xi \right] \right) = 0. \quad (\text{B17})$$

The difference between the unknown concentration,  $c_{k,h+} = c_{k,h}$  at  $[t + \Delta t]$ , 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,  $\Delta t = [t + \Delta t] - t$ . Using  $\Delta c_{k,h} = c_{k,h+} - c_{k,h-}$ , and multiplying by  $\Delta t$ , yields

$$\sum_{k=1}^n \sum_{h=1}^N \left( \frac{c_{k,h+} - c_{k,h-}}{2} \int_{\xi_m}^{\xi_b} P_h H d\xi - c_{k,h} \sum_{j=1}^N D_{k,j} \left[ \sigma_{k,j} \int_{\xi_m}^{\xi_b} P_j P_h \frac{dH}{d\xi} \xi d\xi - \int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi} \frac{dH}{d\xi} \xi d\xi \right] \Delta t \right) = 0. \quad (\text{B18})$$

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  $[t + \Delta t]$ , 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  $\Delta t$  values than either the explicit or implicit solution alone would.

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

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

(B19)

As  $\sigma_k$  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),  $\sigma_k$  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  $\xi$ -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

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

(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  $\xi$ -dependent Lamm equation in terms of species.**)

### Evaluating the $\xi$ -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  $\xi$ -independent coefficients of the  $\xi$ -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+)

$$\sigma_{k,j-} = \frac{\omega^2 S_{k,j-}}{D_{k,j-}} = \frac{\omega^2 S^{\circ}_{k,j-}}{D^{\circ}_{k,j-}} \left( \frac{\sum_{b=1}^{\infty} \sum_{q=1}^n p_{b,k,q} \frac{dc_{q,j-}^b}{dc_{q,j-}}}{\sum_{b=1}^{\infty} \sum_{q=1}^n h_{b,k,q} \frac{dc_{q,j-}^b}{dc_{q,j-}}} \right) = \sigma^{\circ}_{k,j-} \left( \frac{\sum_{b=1}^{\infty} \sum_{q=1}^n p_{b,k,q} \frac{dc_{q,j-}^b}{dc_{q,j-}}}{\sum_{b=1}^{\infty} \sum_{q=1}^n y_{b,k,q} \frac{dc_{q,j-}^b}{dc_{q,j-}}} \right)$$

(B23-)

and

$$\sigma_{k,j+} = \frac{\omega^2 S_{k,j+}}{D_{k,j+}} = \frac{\omega^2 S^{\circ}_{k,j+}}{D^{\circ}_{k,j+}} \left( \frac{\sum_{b=1}^{\infty} \sum_{q=1}^n p_{b,k,q} \frac{dc_{q,j+}^b}{dc_{q,j+}}}{\sum_{b=1}^{\infty} \sum_{q=1}^n h_{b,k,q} \frac{dc_{q,j+}^b}{dc_{q,j+}}} \right) = \sigma^{\circ}_{k,j+} \left( \frac{\sum_{b=1}^{\infty} \sum_{q=1}^n p_{b,k,q} \frac{dc_{q,j+}^b}{dc_{q,j+}}}{\sum_{b=1}^{\infty} \sum_{q=1}^n y_{b,k,q} \frac{dc_{q,j+}^b}{dc_{q,j+}}} \right),$$

(B23+)

respectively, where n is the number of solute components,  $D^{\circ}_{k,j-}$  at all  $\xi$  equals  $D_k$  at  $\xi_j$  at time t in the limit as c approaches 0,  $D^{\circ}_{k,j+}$  at all  $\xi$  equals  $D_k$  at  $\xi_j$  at time [t +  $\Delta t$ ] in the limit as c approaches 0,  $\sigma^{\circ}_{k,j-}$  at all  $\xi$  equals  $\sigma_k$  at  $\xi_j$  at time t in the limit as c approaches 0,  $\sigma^{\circ}_{k,j+}$  at all  $\xi$  equals  $\sigma_k$  at  $\xi_j$  at time [t +  $\Delta t$ ] in the limit as c approaches 0,  $s^{\circ}_{k,j-}$  at all  $\xi$  equals  $s_k$  at  $\xi_j$  at time t in the limit as c approaches 0,  $s^{\circ}_{k,j+}$  at all  $\xi$  equals  $s_k$  at  $\xi_j$  at time [t +  $\Delta t$ ] in the limit as c approaches 0,  $c_{q,j-}$  is the  $\xi$ -independent concentration coefficient of solute component q at time t (at time t,  $c_{q,j-}$  at all  $\xi$ , equals  $c_q$  at  $\xi_j$ , just as  $c_{k,h}$  at all  $\xi$ , equals  $c_k$  at  $\xi_h$  in Equation B6),  $c_{q,j+}$  is the  $\xi$ -independent concentration coefficient of solute component q at time [t +  $\Delta t$ ] (at

time  $[t + \Delta t]$ ,  $c_{q,j+}$ , at all  $\xi$ , equals  $c_q$  at  $\xi_j$ , just as  $c_{k,h}$ , at all  $\xi$ , equals  $c_k$  at  $\xi_h$  in Equation B6), and where  $p_{b,k,q}$ ,  $y_{b,k,q}$  and  $h_{b,k,q}$  are the  $b^{\text{th}}$  of up to an infinite number of coefficients of proportionality for the density increment, 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  $\bar{\phantom{x}}$  representing either  $-$  or  $+$ , the component-equivalents of Equations N23 $\bar{\phantom{x}}$  and N24 $\bar{\phantom{x}}$  can be used in place of Equations B22 $\bar{\phantom{x}}$  and B23 $\bar{\phantom{x}}$ , respectively. Henceforth,  $c_q$  is used to denote the concentration of solute component  $q$  at either time  $t$  or time  $[t + \Delta t]$ , and some unspecified position,  $\xi_j$ .

Individually, the product of  $b(c_q)^{b-1}$  with the corresponding coefficient of proportionality  $p_{b,k,q}$  yields the  $b^{\text{th}}$  term for the contribution of  $c_q$  to the density increment 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  $b^{\text{th}}$  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  $b^{\text{th}}$  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 density increment 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  $s_{k,j}$  are used to denote the  $\xi$ -independent transport coefficients at

either time  $t$  or time  $[t + \Delta t]$ , and  $\sigma^{\circ}_{k,j}$ ,  $D^{\circ}_{k,j}$  and  $s^{\circ}_{k,j}$  are used to denote the  $\xi$ -independent transport coefficients at either time  $t$  or time  $[t + \Delta t]$  in the limit at  $c$  approaches zero.

By definition,  $\sigma^{\circ}_{k,j}$ ,  $D^{\circ}_{k,j}$  and  $s^{\circ}_{k,j}$ , are  $\xi$ -independent, and for a given  $t$ -independent field strength, may also be  $t$ -independent. In the case of solvent compressibility however, the expectation is that  $\Delta\sigma^{\circ}_{k,j}/\Delta j \neq 0$  and  $\Delta D^{\circ}_{k,j}/\Delta j \neq 0$ , from which it follows that  $\Delta s^{\circ}_{k,j}/\Delta j \neq 0$ . The condition that, for all solute components,  $\Delta\sigma^{\circ}_{k,j}/\Delta j = 0$  and  $\Delta D^{\circ}_{k,j}/\Delta j = 0$ , from which it would follow that  $\Delta s^{\circ}_{k,j}/\Delta j = 0$ , can only apply to a system with an incompressible solvent, in which case,  $\sigma^{\circ}_{k,j}$ ,  $D^{\circ}_{k,j}$  and  $s^{\circ}_{k,j}$  can be replaced with their respective, system-wide constants,  $\sigma^{\circ}_k$ ,  $D^{\circ}_k$  and  $s^{\circ}_k$ . (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  $[t + \Delta t]$ , 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  $q$ .)

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  $\xi$  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, density and viscosity 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  $D_k$ ,  $\sigma_k$  and  $s_k$ , 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  $s_{k,j}$  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  $s_{k,j}$  at times  $t$  and  $[t + \Delta t]$  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  $[t + \Delta t]$ : 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, sedimentation coefficients,  $s_{k,j}$ , which are related to the  $N$  space-independent, time-dependent, reduced molar mass coefficients through  $\omega^2 s_{k,j} = D_{k,j} \sigma_{k,j}$ . 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  $[t + \Delta t]$ : 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

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

and

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

(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:

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

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

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

Consequently,

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

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

for  $1 < i < N$ , and

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

(B27)

Equation B27 is derived from Equation A26, according to which,  $(\partial c/\partial t)_\xi = -(\partial[2\xi]^{0.5}I/\partial\xi)_t$ . Equation A26 does not state that each  $(\partial c_k/\partial t)_\xi = -(\partial[2\xi]^{0.5}I_k/\partial\xi)_t$ , 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  $-(\partial[2\xi]^{0.5}I_k/\partial\xi)_t$ . 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  $-(\partial[2\xi]^{0.5}I_{k,e}/\partial\xi)_t$  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

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

(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  $\xi$ -dependent Lamm equation with the set of all  $\xi_h$  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  $\xi$  is equal to the value of  $c_k$  at  $\xi_b$ , while  $c_{k,N+}$  at all  $\xi$  is equal to the value of  $c_k$  at  $\xi_m$ . In general,  $\xi_h$ ,  $c_{k,h+}$ ,  $c_{k,h-}$ ,  $D_{k,j+}$ ,  $\sigma_{k,j+}$ ,  $D_{k,j-}$  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 the values of  $c_{k,h+}$  obtained from the forward and backwards solutions, respectively.

## Time

In terms of an unvarying time increment,  $\Delta t$ , the time after  $\Omega$  time increments is

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

(B34)

where  $t_0$  is the initial time. In general, for  $\Omega$  time increments, where each time increment,  $\Delta t_{\varepsilon}$ , 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  $\xi_0$  as equal to zero makes

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

(B36)

a general formula for calculating  $\xi_h$ . This equation does not require  $\Delta \xi$  to be the same for all spatial increments between two adjacent points.

Where  $\Delta \xi$  is the same for all spatial increments between two adjacent points,

$$\xi_h = \xi_1 + [h - 1] \Delta \xi ,$$

(B37)

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

$$\Delta \xi = \frac{\xi_b - \xi_m}{N - 1} .$$

(B38)

## Reactions

As discussed in Section C (**A solution to the  $t$ - and  $\xi$ -dependent Lamm equation 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 $\xi$ -dependent integrals

In the notation used for the solutions to the  $\xi$ -dependent integrals that follow, a spatial increment from  $\xi_{h-1}$  to  $\xi_h$  is indicated by appending a subscripted minus sign to  $\Delta\xi$ , a spatial increment from  $\xi_h$  to  $\xi_{h+1}$  is indicated by appending a subscripted plus sign to  $\Delta\xi$ ,  $\xi_m$  denotes  $\xi$  at the meniscus, and  $\xi_b$  denotes  $\xi$  at the base of the system. 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  $\xi$ . 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)

$$\int_{\xi_m}^{\xi_b} P_1 P_1 \frac{dP_1}{d\xi} \xi d\xi = \int_{\xi_1}^{\xi_{1+1}} P_1 P_1 \frac{dP_1}{d\xi} \xi d\xi = -\frac{\xi_1}{3} - \frac{\int_{\xi_m}^{\xi_b} P_1 P_1 d\xi}{4} ;$$

(B44)

$$\int_{\xi_m}^{\xi_b} P_{h-1} P_{h-1} \frac{dP_h}{d\xi} \xi d\xi = \int_{\xi_{h-1}}^{\xi_h} P_{h-1} P_{h-1} \frac{dP_h}{d\xi} \xi d\xi = \frac{\xi_h}{3} - \frac{3}{2} \int_{\xi_m}^{\xi_b} P_{h-1} P_h d\xi ;$$

(B45<sub>x</sub>)

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

(B45<sub>+</sub>)

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

(B46<sub>-</sub>)

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

(B46<sub>x</sub>)

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

(B46<sub>+</sub>)

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

(B47<sub>-</sub>)

$$\int_{\xi_m}^{\xi_b} P_{h+1} P_{h+1} \frac{dP_h}{d\xi} \xi d\xi = \int_{\xi_h}^{\xi_{h+1}} P_{h+1} P_{h+1} \frac{dP_h}{d\xi} \xi d\xi = -\frac{\xi_h}{3} - \frac{3}{2} \int_{\xi_m}^{\xi_b} P_{h+1} P_h d\xi;$$

(B47<sub>x</sub>)

$$\int_{\xi_m}^{\xi_b} P_N P_N \frac{dP_N}{d\xi} \xi d\xi = \int_{\xi_{N-1}}^{\xi_N} P_N P_N \frac{dP_N}{d\xi} \xi d\xi = \frac{\xi_N}{3} - \frac{\int_{\xi_m}^{\xi_b} P_N P_N d\xi}{4};$$

(B48)

$$\int_{\xi_m}^{\xi_b} P_1 \frac{dP_1}{d\xi} \frac{dP_1}{d\xi} \xi d\xi = \int_{\xi_1}^{\xi_{1+1}} P_1 \frac{dP_1}{d\xi} \frac{dP_1}{d\xi} \xi d\xi = \frac{1}{6} \left( \frac{3\xi_1}{\Delta\xi_{1+}} + 1 \right);$$

(B49)

$$\begin{aligned} \int_{\xi_m}^{\xi_b} P_{h-1} \frac{dP_{h-1}}{d\xi} \frac{dP_h}{d\xi} \xi d\xi &= \int_{\xi_{h-1}}^{\xi_h} P_{h-1} \frac{dP_{h-1}}{d\xi} \frac{dP_h}{d\xi} \xi d\xi = -\frac{1}{6} \left( \frac{3\xi_h}{\Delta\xi_{h-}} - 2 \right) \\ &= - \int_{\xi_m}^{\xi_b} P_{h-1} \frac{dP_h}{d\xi} \frac{dP_h}{d\xi} \xi d\xi; \end{aligned}$$

(B50<sub>x</sub>)

$$\begin{aligned} \int_{\xi_m}^{\xi_b} P_h \frac{dP_{h-1}}{d\xi} \frac{dP_h}{d\xi} \xi d\xi &= \int_{\xi_{h-1}}^{\xi_h} P_{h-1} \frac{dP_{h-1}}{d\xi} \frac{dP_h}{d\xi} \xi d\xi = -\frac{1}{6} \left( \frac{3\xi_h}{\Delta\xi_{h-}} - 1 \right) \\ &= -\frac{1}{6} - \int_{\xi_m}^{\xi_b} P_{h-1} \frac{dP_h}{d\xi} \frac{dP_h}{d\xi} \xi d\xi ; \end{aligned}$$

(B50+)

$$\int_{\xi_m}^{\xi_b} P_{h-1} \frac{dP_h}{d\xi} \frac{dP_h}{d\xi} \xi d\xi = \int_{\xi_{h-1}}^{\xi_h} P_{h-1} \frac{dP_h}{d\xi} \frac{dP_h}{d\xi} \xi d\xi = \frac{1}{6} \left( \frac{3\xi_h}{\Delta\xi_{h-}} - 2 \right) ;$$

(B51.)

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

(B51x)

$$\int_{\xi_m}^{\xi_b} P_{h+1} \frac{dP_h}{d\xi} \frac{dP_h}{d\xi} \xi d\xi = \int_{\xi_h}^{\xi_{h+1}} P_{h+1} \frac{dP_h}{d\xi} \frac{dP_h}{d\xi} \xi d\xi = \frac{1}{6} \left( \frac{3\xi_h}{\Delta\xi_{h+}} + 2 \right) ;$$

(B51+)

$$\begin{aligned} \int_{\xi_m}^{\xi_b} P_h \frac{dP_{h+1}}{d\xi} \frac{dP_h}{d\xi} \xi d\xi &= \int_{\xi_h}^{\xi_{h+1}} P_h \frac{dP_{h+1}}{d\xi} \frac{dP_h}{d\xi} \xi d\xi = -\frac{1}{6} \left( \frac{3\xi_h}{\Delta\xi_{h+}} + 1 \right) \\ &= \frac{1}{6} - \int_{\xi_m}^{\xi_b} P_{h+1} \frac{dP_h}{d\xi} \frac{dP_h}{d\xi} \xi d\xi ; \end{aligned}$$

(B52.)

$$\begin{aligned} \int_{\xi_m}^{\xi_b} P_{h+1} \frac{dP_{h+1}}{d\xi} \frac{dP_h}{d\xi} \xi d\xi &= \int_{\xi_h}^{\xi_{h+1}} P_{h+1} \frac{dP_{h+1}}{d\xi} \frac{dP_h}{d\xi} \xi d\xi = -\frac{1}{6} \left( \frac{3\xi_h}{\Delta\xi_{h+}} + 2 \right) \\ &= - \int_{\xi_m}^{\xi_b} P_{h+1} \frac{dP_h}{d\xi} \frac{dP_h}{d\xi} \xi d\xi ; \end{aligned}$$

(B52x)

and

$$\int_{\xi_m}^{\xi_b} P_N \frac{dP_N}{d\xi} \frac{dP_N}{d\xi} \xi d\xi = \int_{\xi_{N-1}}^{\xi_N} P_N \frac{dP_N}{d\xi} \frac{dP_N}{d\xi} \xi d\xi = \frac{1}{6} \left( \frac{3\xi_N}{\Delta\xi_{N-}} - 1 \right),$$

(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  $\xi$ .

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  $P_1 P_1$ ,  $P_1 P_1 (dP_1/d\xi)\xi$ , or  $P_1 (dP_1/d\xi)(dP_1/d\xi)\xi$ , the integral is evaluated from  $\xi_1$  to  $\xi_{1+1}$ . Equations B62 and B63, with  $h = 1$ , describe  $P_1$  and  $dP_1/d\xi$ , respectively.

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

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

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

Where the integrand is  $P_N P_N$ ,  $P_N P_N (dP_N/d\xi)\xi$ , or  $P_N (dP_N/d\xi)(dP_N/d\xi)\xi$ , the integral is

evaluated from  $\xi_{N-1}$  to  $\xi_N$ . 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  $\xi_{h-1}$  to  $\xi_h$ . Equations B62 and B63 give the functions used for  $P_h$  and  $dP_h/d\xi$ , respectively, in integrals evaluated from  $\xi_h$  to  $\xi_{h+1}$ .

Of the 23 types (within 15 groups) of integrals in Equations B39 to B53, 17 (Equations B40 to B42, B45<sub>x</sub> to B47<sub>x</sub>, and B50<sub>x</sub> to B52<sub>x</sub>) 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: 5 (Equations B39 to B43) are multiples of  $\Delta\xi_{h-}/6$  and  $\Delta\xi_{h+}/6$ ; 2 (Equations B44 and B48) are equal to  $-\xi_1/3 - B39/4$  or  $\xi_N/3 - B43/4$ ; 7 (Equations B45<sub>x</sub> to B47<sub>x</sub>) are multiples of  $\xi_h/6$ ,  $B44/2$  and  $B42/2$ ; 2 (B49 and B53) are equal to  $\xi_1/2\Delta\xi_{1+} + 1/6$  or  $\xi_N/2\Delta\xi_{N-} - 1/6$ ; and 7 (B50<sub>x</sub> to B52<sub>x</sub>) are multiples of  $B51_-$  and  $B51_+$ . 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 the 14 integrals in Equations B39 to B48 become independent of  $\xi$ . Where Equations B40 to B42 and B45<sub>x</sub> to B47<sub>x</sub> are independent of  $\xi$ , 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,  $\xi_h$  (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,  $\xi$ -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 $\xi$

In the case of  $(\partial\sigma_k/\partial\xi)_t = 0$  and  $(\partial D_k/\partial\xi)_t = 0$  at all  $\xi$ , each  $\sigma_{k,j}$  is equal to the  $\xi$ -invariant value of  $\sigma_k$  and each  $D_{k,j}$  is equal to the  $\xi$ -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  $\sigma_k$  and  $D_k$  are constant with  $\xi$ ) follows that used for the more general case (where  $\sigma_k$  and  $D_k$  can vary with  $\xi$ ) 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:

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

(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\*)

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

(B44\*)

replaces Equation B44;

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

(B45\*)

replaces the sum of Equations B45<sub>x</sub> and B45<sub>+</sub>;

$$\begin{aligned} \sum_{j=1}^N \left[ \int_{\xi_m}^{\xi_b} P_j P_h \frac{dP_h}{d\xi} \xi d\xi \right] &= \int_{\xi_m}^{\xi_b} P_h \frac{dP_h}{d\xi} \xi d\xi = \int_{\xi_{h-1}}^{\xi_{h+1}} P_h \frac{dP_h}{d\xi} \xi d\xi \\ &= -\frac{1}{2} \int_{\xi_m}^{\xi_b} P_h P_h d\xi = - \left( \int_{\xi_m}^{\xi_b} P_{h-1} P_h d\xi + \int_{\xi_m}^{\xi_b} P_{h+1} P_h d\xi \right) \end{aligned}$$

(B46\*)

replaces the sum of Equations B46<sub>-</sub>, B46<sub>x</sub> and B46<sub>+</sub>;

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

(B47\*)

replaces the sum of Equations B47<sub>-</sub> and B47<sub>x</sub>;

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

(B48\*)

replaces Equation B48;

$$\begin{aligned} \sum_{j=1}^N \left[ \int_{\xi_m}^{\xi_b} P_j \frac{dP_1}{d\xi} \frac{dP_1}{d\xi} \xi d\xi \right] &= \int_{\xi_m}^{\xi_b} \frac{dP_1}{d\xi} \frac{dP_1}{d\xi} \xi d\xi = \int_{\xi_1}^{\xi_{1+1}} \frac{dP_1}{d\xi} \frac{dP_1}{d\xi} \xi d\xi = \frac{\xi_1}{\Delta\xi_{1+}} + \frac{1}{2} \\ &= \frac{\xi_1}{3 \int_{\xi_m}^{\xi_b} P_1 P_1 d\xi} + \frac{1}{2} \end{aligned}$$

(B49\*)

replaces Equation B49;

$$\begin{aligned} \sum_{j=1}^N \left[ \int_{\xi_m}^{\xi_b} P_j \frac{dP_{n-1}}{d\xi} \frac{dP_n}{d\xi} \xi d\xi \right] &= \int_{\xi_m}^{\xi_b} \frac{dP_{n-1}}{d\xi} \frac{dP_n}{d\xi} \xi d\xi = \int_{\xi_{n-1}}^{\xi_n} \frac{dP_{n-1}}{d\xi} \frac{dP_n}{d\xi} \xi d\xi = -\frac{\xi_n}{\Delta\xi_{n-}} + \frac{1}{2} \\ &= \frac{\xi_n}{-6 \int_{\xi_m}^{\xi_b} P_{n-1} P_n d\xi} + \frac{1}{2} \end{aligned}$$

(B50\*)

replaces the sum of Equations B50<sub>x</sub> and B50<sub>+</sub>;

$$\begin{aligned} \sum_{j=1}^N \left[ \int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi} \frac{dP_h}{d\xi} \xi d\xi \right] &= \int_{\xi_m}^{\xi_b} \frac{dP_h}{d\xi} \frac{dP_h}{d\xi} \xi d\xi = \int_{\xi_{n-1}}^{\xi_{n+1}} \frac{dP_h}{d\xi} \frac{dP_h}{d\xi} \xi d\xi \\ &= -\left( \int_{\xi_m}^{\xi_b} \frac{dP_{n-1}}{d\xi} \frac{dP_n}{d\xi} \xi d\xi + \int_{\xi_m}^{\xi_b} \frac{dP_{n+1}}{d\xi} \frac{dP_n}{d\xi} \xi d\xi \right) \end{aligned}$$

(B51\*)

replaces the sum of Equations B51<sub>-</sub>, B51<sub>x</sub> and B51<sub>+</sub>;

$$\begin{aligned} \sum_{j=1}^N \left[ \int_{\xi_m}^{\xi_b} P_j \frac{dP_{h+1}}{d\xi} \frac{dP_h}{d\xi} \xi d\xi \right] &= \int_{\xi_m}^{\xi_b} \frac{dP_{h+1}}{d\xi} \frac{dP_h}{d\xi} \xi d\xi = \int_{\xi_n}^{\xi_{n+1}} \frac{dP_{h+1}}{d\xi} \frac{dP_h}{d\xi} \xi d\xi = -\frac{\xi_n}{\Delta\xi_{n+}} - \frac{1}{2} \\ &= \frac{\xi_n}{-6 \int_{\xi_m}^{\xi_b} P_{h+1} P_h d\xi} - \frac{1}{2} \end{aligned}$$

(B52\*)

replaces the sum of Equations B52<sub>-</sub>, B52<sub>x</sub>; and

$$\begin{aligned} \sum_{j=1}^N \left[ \int_{\xi_m}^{\xi_b} P_j \frac{dP_N}{d\xi} \frac{dP_N}{d\xi} \xi d\xi \right] &= \int_{\xi_m}^{\xi_b} \frac{dP_N}{d\xi} \frac{dP_N}{d\xi} \xi d\xi = \int_{\xi_{N-1}}^{\xi_N} \frac{dP_N}{d\xi} \frac{dP_N}{d\xi} \xi d\xi = \frac{\xi_N}{\Delta \xi_{N-}} - \frac{1}{2} \\ &= \frac{\xi_N}{3 \int_{\xi_m}^{\xi_b} P_N P_N d\xi} - \frac{1}{2} \end{aligned}$$

(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  $P_1 P_1$ ,  $P_1 (dP_1/d\xi) \xi$ , or  $(dP_1/d\xi) (dP_1/d\xi) \xi$ , the integral is evaluated from  $\xi_1$  to  $\xi_{1+1}$ . Equations B62 and B63, with  $h = 1$ , describe  $P_1$  and  $dP_1/d\xi$ , respectively.

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

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

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

Where the integrand is  $P_N P_N$ ,  $P_N (dP_N/d\xi) \xi$ , or  $(dP_N/d\xi) (dP_N/d\xi) \xi$ , the integral is evaluated from  $\xi_{N-1}$  to  $\xi_N$ . 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  $\xi_{h-1}$  to  $\xi_h$ . Equations B62 and B63 give the functions used for  $P_h$  and  $dP_h/d\xi$ , respectively, in integrals evaluated from  $\xi_h$  to  $\xi_{h+1}$ .

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\*, eleven (Equation B41\* and Equations B44\* to B53\*) can be defined in terms of one or two of the other four (Equations B39\*, B40\*, B42\* and B43\*, each of which is a multiple of  $\Delta\xi_{h-}/6$  and  $\Delta\xi_{h+}/6$ ). For equally spaced points,  $\Delta\xi_{1+} = \Delta\xi_{N-} = \Delta\xi_{h+} = \Delta\xi_{h-} = \Delta\xi$  for all  $h$ , in which case Equations B39\* to B43\* would be independent of  $\xi$ . Where Equations B40\* to B42\* are independent of  $\xi$ , 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 when Equation A26 in terms of  $t$  and  $\xi$  is solved for the case of  $(\partial\sigma_k/\partial\xi)_t = 0$  and  $(\partial D_k/\partial\xi)_t = 0$  at all  $\xi$ . (Details not shown). 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  $\xi$ -dependent Lamm equation (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 AUC have been used in finite-element simulations. Simulations of AUC 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:  $\xi$ -dependent functions to approximate  $D_{k,e}$  and  $\sigma_{k,e}$** .) Additionally, finite-element simulations of sedimentation based on the first approximate solution to the  $t$ - and  $\xi$ -dependent Lamm equation have been found to perform at least as well as finite-element simulations based on the first approximate solution to the  $t$ - and  $r$ -dependent Lamm equation [Cox and Dale, 1981; Schuck et al., 1998].

(Results not shown.)

### First approximate solution

To express  $\sigma_k$  and  $D_k$  in terms of pseudo- $\xi$ -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  $\xi$ . For  $\sigma_k$ , at all  $\xi_h$ , where  $1 \leq h \leq N$ , those coefficients are

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

(B64)

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

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

(B65)

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

$$s_{k,h} = s_k \text{ at } \xi_h.$$

(B66)

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

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



(B67)

As usual, a minus or plus subscript refers to time  $t$  or  $[t + \Delta t]$ , 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  $\xi$ . Thus, when  $\sigma_{k,h}$  and  $D_{k,h}$  are used as they are in Equation B67, each  $\sigma_{k,h}$  should equal  $\xi$ -independent  $\sigma_k$ , each  $D_{k,h}$  should equal  $\xi$ -independent  $D_k$  and, given that  $(\partial s_k/\partial\xi)_t = 0$  when  $(\partial\sigma_k/\partial\xi)_t = 0$  and  $(\partial D_k/\partial\xi)_t = 0$ , each  $s_{k,h}$  should equal  $\xi$ -independent  $s_k$ . Furthermore, these conditions make it highly likely that  $(\partial s_k/\partial t)_\xi = 0$  and  $(\partial D_k/\partial t)_\xi = 0$  in general, and that  $(\partial\sigma_k/\partial t)_\xi = 0$  at constant field. Therefore,  $s_{k,h}$  and  $D_{k,h}$  are likely to be  $t$ -independent in general, and  $\sigma_{k,h}$  is 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  $s_{k,h}$ , of the first approximate solution are treated as if they were functions of solute concentration. Thus,  $\sigma_{k,h}$ ,  $D_{k,h}$  and  $s_{k,h}$  become pseudoconstants with respect to  $\xi$ . 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- $\xi$ -independent constants indexed by  $h$ , prior to each time increment,  $D_{k,h}$  and  $\sigma_{k,h}$  are approximated by

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

(B68)

and

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

(B69)

respectively, where  $n$  is the number of solute components,  $D^{\circ}_k$  at all  $\xi$  equals  $D_k$  at  $\xi_h$  at time

t in the limit as c approaches 0,  $\sigma_k^\circ$  at all  $\xi$  equals  $\sigma_k$  at  $\xi_h$  at time t in the limit as c approaches 0,  $c_{q,h}$  is the  $\xi$ -independent concentration coefficient of solute component q at time t or [t +  $\Delta t$ ] ( $c_{q,h}$ , at all  $\xi$ , equals  $c_q$  at  $\xi_h$ , just as  $c_{k,h}$ , at all  $\xi$ , equals  $c_k$  at  $\xi_h$  in Equation B6), and where  $p_{b,k,q}$ ,  $y_{b,k,q}$  and  $h_{b,k,q}$  are the  $b^{\text{th}}$  of up to an infinite number of coefficients of proportionality for the density increment, 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  $\sigma_k^\circ$  and  $D_k^\circ$  are  $\xi$ -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  $(\partial\rho_0/\partial\xi)_t$  to differ from zero.) As discussed in the definitions of  $D_{k,j}^\circ$  (Equation B22) and  $\sigma_{k,j}^\circ$  (Equation B23), the condition that  $\Delta D_{k,j}^\circ/\Delta j = 0$  and  $\Delta\sigma_{k,j}^\circ/\Delta j = 0$  for all solute components can only apply to a system with an incompressible solvent, in which case,  $D_{k,j}^\circ$  and  $\sigma_{k,j}^\circ$  can be replaced with  $D_k^\circ$ , and  $\sigma_k^\circ$ , respectively. Hence, the use of  $D_k^\circ$  and  $\sigma_k^\circ$  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  $\xi$ -independent  $\sigma_k$ , and each  $D_{k,h}$  should equal  $\xi$ -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  $\xi$  and t. (Compare the properties and uses of Equations B68 and B69, with those of Equations B22 and B23, respectively.)

### **Possible advantages to working in equi-gravitational-potential space**

There are two possible advantages of the finite-element solution to the t- and  $\xi$ -dependent Lamm equation: the resulting integrals have simpler solutions than the t- and r-dependent equivalent, making recalculation of the integral solutions less computationally costly; and

the element spacing, in terms of  $r$ , decreases in proportion to the increase in the gravitational potential from the innermost to the outermost point, with the result that, where  $\Delta\xi$  is the same for all spatial increments between two adjacent points, simulated transport takes place over equi-gravitational-potential steps with the  $t$ - and  $\xi$ -dependent Lamm equation solution and may, therefore, be more computationally stable than simulated transport using the  $t$ - and  $r$ -dependent Lamm equation solution in the case of  $\Delta r$  being the same for all spatial increments between two adjacent points.

## References

[B1] Cox, D., and Dale, R. (1981) Simulation of Transport Experiments for Interacting Systems. *In* "Protein-Protein Interactions." (C. Frieden, and L. Nichol, editors.) pp. 173-211. John Wiley and Sons, New York.

[B2] Schuck, P., McPhee, C. E., and Howlett, G. J. (1998) Determination of sedimentation coefficients for small peptides. *Biophys J.* **74** 466-474.

## Section C: A solution to the $t$ - and $\xi$ -dependent Lamm equation 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 Lamm equation, would be over solute components rather than solute species, and at a given spatial position (expressed as  $r$  or  $\xi$ ) 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  $k$ ) sedimentation coefficient,  $(s_k)_w$ , and its gradient-average (over all species of component  $k$ ) diffusion coefficient [Johnson et al., 1973],  $(D_k)_G$ , the expectation being that  $(s_k)_w = s_k$  and  $(D_k)_G = D_k$ . To account for the  $t$ - and  $\xi$ -dependent changes in the concentrations of the individual species that sum to  $c_k$ , in addition to the aforementioned transport coefficients,  $(s_k)_w$  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 sedimentation coefficients of a solute component's individual species could be defined,  $(D_k)_G$  and  $(s_k)_w$  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 sedimentation coefficients and concentrations of a solute component's individual species would be used to calculate  $(s_k)_w$ .) The reduced molar mass coefficients of a solute component's individual species could then be defined in terms of the diffusion and sedimentation coefficients of a solute component's individual species. Finally, on the basis of the above expectations and Equation A23, the relationship of  $\sigma_k$  to the reduced molar mass coefficients of a solute component's individual species could be determined using  $\sigma_k = \omega^2(s_k)_w/(D_k)_G$ . 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

$$D_k \sigma_k = \omega^2 s_k = \omega^2 (s_k)_w = \frac{\omega^2 \sum_{e=1}^{n_k} s_{k,e} c_{k,e}}{\sum_{e=1}^{n_k} c_{k,e}} = \frac{\sum_{e=1}^{n_k} D_{k,e} \sigma_{k,e} c_{k,e}}{\sum_{e=1}^{n_k} c_{k,e}} = (\sigma_k D_k)_w,$$

(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 molar mass coefficient of species  $e$  of solute component  $k$ ,  $s_{k,e}$  is the sedimentation coefficient of species  $e$  of solute component  $k$ ,  $\sigma_{k,e}D_{k,e}$  is defined (by analogy with Equation A23) as equal to  $\omega^2 s_{k,e}$ , 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

$$\begin{aligned} I_k &= \sum_{e=1}^{n_k} I_{k,e} = \sum_{e=1}^{n_k} c_{k,e} D_{k,e} \left[ \sigma_{k,e} - \left( \frac{\partial \ln c_{k,e}}{\partial \xi} \right)_t \right] \sqrt{2\xi} = c_k \left[ \omega^2 (s_k)_w - (D_k)_G \left( \frac{\partial \ln c_k}{\partial \xi} \right)_t \right] \sqrt{2\xi} \\ &= c_k D_k \left[ \sigma_k - \left( \frac{\partial \ln c_k}{\partial \xi} \right)_t \right] \sqrt{2\xi} , \end{aligned}$$

(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  $(s_k)_w = s_k$ , and thus,

$$\sigma_k = \frac{\omega^2 s_k}{D_k} = \frac{\omega^2 (s_k)_w}{(D_k)_G} = \left( \frac{\partial \ln c_k}{\partial \xi} \right)_t \left[ \frac{\sum_{e=1}^{n_k} D_{k,e} \sigma_{k,e} c_{k,e}}{\sum_{e=1}^{n_k} D_{k,e} \left( \frac{\partial c_{k,e}}{\partial \xi} \right)_t} \right] .$$

(C5)

Note that  $(D_k)_G$  and  $(s_k)_w$  are averages for all species of a single solute component,  $k$ , while  $D_G$  and  $s_w$  (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  $s_w$  and  $(s_k)_w$ , respectively.) There is no simple relationship between  $\sigma_w$  and any average of the  $\sigma_{k,e}$

coefficients. (See Equations A36 to A40, which show the relationships between  $\sigma_w$ , the  $\sigma_k$  coefficients, and the equilibrium value of  $\omega^2 s_w/D_G$ .)

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 sedimentation coefficients and concentrations of all solute species can now be used to calculate the overall weight-average sedimentation coefficient, which, multiplied by  $\omega^2$ , is

$$\omega^2 s_w = \frac{\omega^2 \sum_{k=1}^n c_k s_k}{\sum_{k=1}^n c_k} = \frac{\omega^2 \sum_{k=1}^n c_k (s_k)_w}{\sum_{k=1}^n c_k} = \frac{\omega^2 \sum_{k=1}^n \left[ c_k \frac{\sum_{e=1}^{n_k} s_{k,e} c_{k,e}}{\sum_{e=1}^{n_k} c_{k,e}} \right]}{\sum_{k=1}^n c_k}$$

$$= \frac{\omega^2 \sum_{k=1}^n \sum_{e=1}^{n_k} s_{k,e} c_{k,e}}{\sum_{k=1}^n \sum_{e=1}^{n_k} c_{k,e}}$$

(C7)

(see Equations A30 and C2).

The reduced molar mass coefficients, concentrations and concentration gradients of all solute species are related to  $\omega^2 s_w/D_G$  through

$$\begin{aligned} \frac{\omega^2 s_w}{D_G} &= \frac{(\sigma D)_w}{D_G} = \frac{\sum_{k=1}^n c_k (\sigma_k D_k)_w}{\sum_{k=1}^n c_k} = \frac{\sum_{k=1}^n \sum_{e=1}^{n_k} \sigma_{k,e} D_{k,e} c_{k,e}}{\sum_{k=1}^n c_k} = \frac{\sum_{k=1}^n \sum_{e=1}^{n_k} \sigma_{k,e} D_{k,e} c_{k,e}}{\sum_{k=1}^n c_k} \\ &= \frac{\sum_{k=1}^n \sum_{e=1}^{n_k} D_{k,e} \left( \frac{\partial c_{k,e}}{\partial \xi} \right)_t}{\sum_{k=1}^n \left( \frac{\partial c_k}{\partial \xi} \right)_t} \\ &= \left( \frac{\partial \ln c}{\partial \xi} \right)_t \left[ \frac{\sum_{k=1}^n \sum_{e=1}^{n_k} \sigma_{k,e} D_{k,e} c_{k,e}}{\sum_{k=1}^n \sum_{e=1}^{n_k} D_{k,e} \left( \frac{\partial c_{k,e}}{\partial \xi} \right)_t} \right] \end{aligned}$$

(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 solute components at equilibrium in AUC, 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 equilibrium, the numerator in each expression on the right-hand side of Equation C10 is equal to  $dc/d\xi$ .

## 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  $D_k$ ,  $s_k$ , and  $\sigma_k$  (Equations A21 to A23) 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  $s_k$  calculated for each solute component would be the appropriate average values,  $(D_k)_G$  and  $(s_k)_w$ , 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  $\xi$ -dependent Lamm equation.**) 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 Lamm equation in terms of solute components, which is derived in Section B (Equations B1 to B33), can be revised to obtain a solution to the Lamm equation 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  $\xi$ -dependent Lamm equation in terms of solute components can be obtained from the finite-element solution to the  $t$ - and  $\xi$ -dependent Lamm 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 $\xi$ -dependent Lamm equation in terms of solute species**

As in Section B (**Steps taken to solve the  $t$ - and  $\xi$ -dependent continuity equation for AUC**), the following finite-element method for solving the  $t$ - and  $\xi$ -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,  $\xi_m$  and  $\xi_b$ . As the flow of each species is expected to meet this boundary condition in a properly enclosed AUC system, the finite-element solution shown can be applied to all species, with solute species treated explicitly, and the solvent component treated implicitly.

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

$$\sum_{k=1}^n \sum_{e=1}^{n_k} \left( \frac{\partial c_{k,e}}{\partial t} \right)_{\xi} = - \sum_{k=1}^n \sum_{e=1}^{n_k} \left( \frac{\partial \sqrt{2\xi} I_{k,e}}{\partial \xi} \right)_t.$$

(C11)

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

$$\sum_{k=1}^n \sum_{e=1}^{n_k} \int_{\xi_m}^{\xi_b} \left( \frac{\partial c_{k,e}}{\partial t} \right)_{\xi} H d\xi = - \sum_{k=1}^n \sum_{e=1}^{n_k} \int_{\xi_m}^{\xi_b} \left( \frac{\partial \sqrt{2\xi} I_{k,e}}{\partial \xi} \right)_t H d\xi.$$

(C12)

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

$$\begin{aligned} & - \sum_{k=1}^n \sum_{e=1}^{n_k} \int_{\xi_m}^{\xi_b} \left( \frac{\partial \sqrt{2\xi} I_{k,e}}{\partial \xi} \right)_t H d\xi \\ & = - \left[ \sum_{k=1}^n \sum_{e=1}^{n_k} [H(\xi_b) \sqrt{2\xi_b} I_{k,e}(\xi_b) - H(\xi_m) \sqrt{2\xi_m} I_{k,e}(\xi_m)] \right. \\ & \quad \left. - \sum_{k=1}^n \sum_{e=1}^{n_k} \int_{\xi_m}^{\xi_b} \left( \frac{\partial H}{\partial \xi} \right)_t \sqrt{2\xi} I_{k,e} d\xi \right], \end{aligned}$$

(C13)

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

$$- \sum_{k=1}^n \sum_{e=1}^{n_k} \int_{\xi_m}^{\xi_b} \left( \frac{\partial \sqrt{2\xi} I_{k,e}}{\partial \xi} \right)_t H d\xi = \sum_{k=1}^n \sum_{e=1}^{n_k} \int_{\xi_m}^{\xi_b} \left( \frac{\partial H}{\partial \xi} \right)_t \sqrt{2\xi} I_{k,e} d\xi.$$

(C14)

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

$$\sum_{k=1}^n \sum_{e=1}^{n_k} \int_{\xi_m}^{\xi_b} \left( \frac{\partial H}{\partial \xi} \right)_t \sqrt{2\xi} I_{k,e} d\xi = \sum_{k=1}^n \sum_{e=1}^{n_k} \int_{\xi_m}^{\xi_b} \frac{dH}{d\xi} \sqrt{2\xi} I_{k,e} d\xi,$$

(C15)

and Equation C12 becomes

$$\sum_{k=1}^n \sum_{e=1}^{n_k} \int_{\xi_m}^{\xi_b} \left( \frac{\partial c_{k,e}}{\partial t} \right)_{\xi} H d\xi = \sum_{k=1}^n \sum_{e=1}^{n_k} \int_{\xi_m}^{\xi_b} \frac{dH}{d\xi} \sqrt{2\xi} I_{k,e} d\xi.$$

(C16)

Next,  $c_{k,e}$  is approximated as the sum of  $N$  products, each of which consists of a  $\xi$ -dependent function,  $P_h$ , multiplied by a corresponding  $\xi$ -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  $1 \leq h \leq N$ ,

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

(C17)

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

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

$$\sum_{k=1}^n \sum_{e=1}^{n_k} \sum_{h=1}^N \frac{dc_{k,e,h}}{dt} \int_{\xi_m}^{\xi_b} P_h H d\xi = \sum_{k=1}^n \sum_{e=1}^{n_k} \int_{\xi_m}^{\xi_b} \frac{dH}{d\xi} \sqrt{2\xi} I_{k,e} d\xi.$$

(C18)

Expanding  $I_k$  (Equation C4) as

$$I_k = \sum_{e=1}^{n_k} I_{k,e} = \sum_{e=1}^{n_k} c_{k,e} D_{k,e} \left[ \sigma_{k,e} - \left( \frac{\partial \ln c_{k,e}}{\partial \xi} \right)_t \right] \sqrt{2\xi} = \sum_{e=1}^{n_k} \left[ \sigma_{k,e} c_{k,e} D_{k,e} - D_{k,e} \left( \frac{\partial c_{k,e}}{\partial \xi} \right)_t \right] \sqrt{2\xi},$$

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

$$I_k = \sum_{e=1}^{n_k} I_{k,e} = \sum_{e=1}^{n_k} \left[ \sigma_{k,e} D_{k,e} \sum_{h=1}^N c_{k,e,h} P_h - D_{k,e} \sum_{h=1}^N c_{k,e,h} \frac{dP_h}{d\xi} \right] \sqrt{2\xi}.$$

(C19)

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

$$\begin{aligned} \sum_{k=1}^n \sum_{e=1}^{n_k} \sum_{h=1}^N \frac{dc_{k,e,h}}{dt} \int_{\xi_m}^{\xi_b} P_h H d\xi \\ = 2 \sum_{k=1}^n \sum_{e=1}^{n_k} \int_{\xi_m}^{\xi_b} \frac{dH}{d\xi} \left[ \sigma_{k,e} D_{k,e} \sum_{h=1}^N c_{k,e,h} P_h - D_{k,e} \sum_{h=1}^N c_{k,e,h} \frac{dP_h}{d\xi} \right] \xi d\xi, \end{aligned}$$

which expands to

$$\begin{aligned} \sum_{k=1}^n \sum_{e=1}^{n_k} \sum_{h=1}^N \frac{dc_{k,e,h}}{dt} \int_{\xi_m}^{\xi_b} P_h H d\xi \\ = 2 \sum_{k=1}^n \sum_{e=1}^{n_k} \int_{\xi_m}^{\xi_b} \frac{dH}{d\xi} \left[ \sigma_{k,e} D_{k,e} \sum_{h=1}^N c_{k,e,h} P_h \right] \xi d\xi \\ - 2 \sum_{k=1}^n \sum_{e=1}^{n_k} \int_{\xi_m}^{\xi_b} \frac{dH}{d\xi} \left[ D_{k,e} \sum_{h=1}^N c_{k,e,h} \frac{dP_h}{d\xi} \right] \xi d\xi, \end{aligned}$$

and rearranges to

$$\begin{aligned} \sum_{k=1}^n \sum_{e=1}^{n_k} \sum_{h=1}^N \frac{dc_{k,e,h}}{dt} \int_{\xi_m}^{\xi_b} P_h H d\xi \\ = 2 \sum_{k=1}^n \sum_{e=1}^{n_k} \sum_{h=1}^N c_{k,e,h} \int_{\xi_m}^{\xi_b} \sigma_{k,e} D_{k,e} P_h \frac{dH}{d\xi} \xi d\xi \\ - 2 \sum_{k=1}^n \sum_{e=1}^{n_k} \sum_{h=1}^N c_{k,e,h} \int_{\xi_m}^{\xi_b} D_{k,e} \frac{dP_h}{d\xi} \frac{dH}{d\xi} \xi d\xi. \end{aligned}$$

(C20)

The dependence of  $D_k$  (Equation A21) and  $\sigma_k$  (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  $\sigma_{k,e}$   $\xi$ -dependent in all but special cases, such as  $t = 0$ , when all  $(\partial c_{q,a}/\partial \xi)_t = 0$  at all  $\xi$ . (Where the solvent is compressible, once  $\omega$  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.) In Section F ( **$\xi$ -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  $\xi$ . 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  $\xi$** ).

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

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

(C21)

where each  $s_{k,e,j}$  at all  $\xi$  is equal to  $s_{k,e}$  at  $\xi_j$ . The result expresses  $s_{k,e}$  as separable  $\xi$ -independent and  $\xi$ -dependent terms.

To express  $D_{k,e}$  as separable  $\xi$ -independent and  $\xi$ -dependent terms, this transport coefficient is also approximated as the sum of  $N$  products, each of which consists of a  $\xi$ -dependent function,  $P_j$ , multiplied by a corresponding  $\xi$ -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  $\xi$  is equal to  $D_{k,e}$  at  $\xi_j$ .

Equations C21 and C22 are combined to define  $\sigma_{k,e}$  in terms of separable  $\xi$ -independent and  $\xi$ -dependent terms, which results in the species analogue of Equation A23,

$$\sigma_{k,e} = \frac{\omega^2 s_{k,e}}{D_{k,e}} = \frac{\omega^2 \sum_{j=1}^N s_{k,e,j} P_j}{\sum_{j=1}^N D_{k,e,j} P_j} .$$

(C23)

While the same approach has been used to express  $c_{k,e}$ ,  $D_{k,e}$  and  $s_{k,e}$  in terms of  $\xi$ -independent coefficients of  $\xi$ -dependent functions, those  $\xi$ -independent coefficients and  $\xi$ -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  $s_{k,e}$ . At any given time, then, the  $\xi$ -dependent functions used in the description of  $c_{k,e}$  are expressed in terms of  $\xi_h$ , while the  $\xi$ -dependent functions used in the descriptions of  $D_{k,e}$  and  $s_{k,e}$  are expressed in terms of  $\xi_j$ . To use these parameters together in the same solution of the continuity equation, at each time point, the set of all  $\xi_j$  is made equivalent to the set of all  $\xi_h$ .

Using  $\omega^2 s_{k,e}$  in place of  $\sigma_{k,e} D_{k,e}$  (from a re-arrangement of Equation C23) results in

$$\begin{aligned} & \sum_{k=1}^n \sum_{e=1}^{n_k} \sum_{h=1}^N \frac{dc_{k,e,h}}{dt} \int_{\xi_m}^{\xi_b} P_h H d\xi \\ & = 2\omega^2 \sum_{k=1}^n \sum_{e=1}^{n_k} \sum_{h=1}^N c_{k,e,h} \int_{\xi_m}^{\xi_b} s_{k,e} P_h \frac{dH}{d\xi} \xi d\xi \\ & - 2 \sum_{k=1}^n \sum_{e=1}^{n_k} \sum_{h=1}^N c_{k,e,h} \int_{\xi_m}^{\xi_b} D_{k,e} \frac{dP_h}{d\xi} \frac{dH}{d\xi} \xi d\xi . \end{aligned}$$

(C24)

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

terms of  $D_{k,e,j}$ , yields

$$\begin{aligned} & \sum_{k=1}^n \sum_{e=1}^{n_k} \sum_{h=1}^N \frac{dc_{k,e,h}}{dt} \int_{\xi_m}^{\xi_b} P_h H d\xi \\ &= 2\omega^2 \sum_{k=1}^n \sum_{e=1}^{n_k} \sum_{h=1}^N c_{k,e,h} \int_{\xi_m}^{\xi_b} \sum_{j=1}^N s_{k,e,j} P_j P_h \frac{dH}{d\xi} \xi d\xi \\ & \quad - 2 \sum_{k=1}^n \sum_{e=1}^{n_k} \sum_{h=1}^N c_{k,e,h} \int_{\xi_m}^{\xi_b} \sum_{j=1}^N D_{k,e,j} P_j \frac{dP_h}{d\xi} \frac{dH}{d\xi} \xi d\xi, \end{aligned}$$

and permits the  $\xi$ -independent parameters,  $D_{k,e,j}$  and  $s_{k,e,j}$ , to be factored out of the integrals.

Thus,

$$\begin{aligned} & \sum_{k=1}^n \sum_{e=1}^{n_k} \sum_{h=1}^N \frac{dc_{k,e,h}}{dt} \int_{\xi_m}^{\xi_b} P_h H d\xi \\ &= 2\omega^2 \sum_{k=1}^n \sum_{e=1}^{n_k} \sum_{h=1}^N c_{k,e,h} \sum_{j=1}^N s_{k,e,j} \left[ \int_{\xi_m}^{\xi_b} P_j P_h \frac{dH}{d\xi} \xi d\xi \right] \\ & \quad - 2 \sum_{k=1}^n \sum_{e=1}^{n_k} \sum_{h=1}^N c_{k,e,h} \sum_{j=1}^N D_{k,e,j} \left[ \int_{\xi_m}^{\xi_b} P_j \frac{dP_h}{d\xi} \frac{dH}{d\xi} \xi d\xi \right]. \end{aligned}$$

(C25)

Letting

$$\sigma_{k,e,j} = \frac{\omega^2 s_{k,e,j}}{D_{k,e,j}},$$

(C26)

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

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

(C27)

At all  $\xi$ , each of the N scalar coefficients,  $\sigma_{k,e,j}$  (defined in Equation C26) is equal to  $\sigma_{k,e}$  at  $\xi_j$ . 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  $\xi$ -dependent function,  $P_j$ , multiplied by a  $\xi$ -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  $\Delta t$  are finite increments, yields

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

(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  $\Delta t$ , yields



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

(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  $\Delta t$  values than either the explicit or implicit solution alone would.

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

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

(C30)

As  $\sigma_k$  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),  $\sigma_k$  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  $\xi$ -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

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

(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 $\xi$ -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  $\xi$ -independent coefficients of  $\xi$ -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+)

$$\begin{aligned} \sigma_{k,e,j-} &= \frac{\omega^2 S_{k,e,j-}}{D_{k,e,j-}} = \frac{\omega^2 S^{\circ}_{k,e,j-}}{D^{\circ}_{k,e,j-}} \left( \frac{\sum_{b=1}^{\infty} \sum_{q=1}^n \sum_{a=1}^{n_q} p_{b,k,e,q,a} \frac{dc_{q,a,j-}^b}{dc_{q,a,j-}}}{\sum_{b=1}^{\infty} \sum_{q=1}^n \sum_{a=1}^{n_q} h_{b,k,e,q,a} \frac{dc_{q,a,j-}^b}{dc_{q,a,j-}}} \right) \\ &= \sigma^{\circ}_{k,e,j-} \left( \frac{\sum_{b=1}^{\infty} \sum_{q=1}^n \sum_{a=1}^{n_q} p_{b,k,e,q,a} \frac{dc_{q,a,j-}^b}{dc_{q,a,j-}}}{\sum_{b=1}^{\infty} \sum_{q=1}^n \sum_{a=1}^{n_q} y_{b,k,e,q,a} \frac{dc_{q,a,j-}^b}{dc_{q,a,j-}}} \right) \end{aligned}$$

(C34-)

and

$$\begin{aligned} \sigma_{k,e,j+} &= \frac{\omega^2 S_{k,e,j+}}{D_{k,e,j+}} = \frac{\omega^2 S^{\circ}_{k,e,j+}}{D^{\circ}_{k,e,j+}} \frac{\left( \frac{\sum_{b=1}^{\infty} \sum_{q=1}^n \sum_{a=1}^{n_q} p_{b,k,e,q,a} \frac{dc_{q,a,j+}^b}{dc_{q,a,j+}}}{\sum_{b=1}^{\infty} \sum_{q=1}^n \sum_{a=1}^{n_q} h_{b,k,e,q,a} \frac{dc_{q,a,j+}^b}{dc_{q,a,j+}}} \right)}{\left( \frac{\sum_{b=1}^{\infty} \sum_{q=1}^n \sum_{a=1}^{n_q} y_{b,k,e,q,a} \frac{dc_{q,a,j+}^b}{dc_{q,a,j+}}}{\sum_{b=1}^{\infty} \sum_{q=1}^n \sum_{a=1}^{n_q} h_{b,k,e,q,a} \frac{dc_{q,a,j+}^b}{dc_{q,a,j+}}} \right)} \\ &= \sigma^{\circ}_{k,e,j+} \frac{\left( \frac{\sum_{b=1}^{\infty} \sum_{q=1}^n \sum_{a=1}^{n_q} p_{b,k,e,q,a} \frac{dc_{q,a,j+}^b}{dc_{q,a,j+}}}{\sum_{b=1}^{\infty} \sum_{q=1}^n \sum_{a=1}^{n_q} y_{b,k,e,q,a} \frac{dc_{q,a,j+}^b}{dc_{q,a,j+}}} \right)}{\left( \frac{\sum_{b=1}^{\infty} \sum_{q=1}^n \sum_{a=1}^{n_q} y_{b,k,e,q,a} \frac{dc_{q,a,j+}^b}{dc_{q,a,j+}}}{\sum_{b=1}^{\infty} \sum_{q=1}^n \sum_{a=1}^{n_q} h_{b,k,e,q,a} \frac{dc_{q,a,j+}^b}{dc_{q,a,j+}}} \right)}, \end{aligned}$$

(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  $\xi$  equals  $D_{k,e}$  at  $\xi_j$  at time  $t$  in the limit as  $c$  approaches 0,  $D^{\circ}_{k,e,j+}$  at all  $\xi$  equals  $D_{k,e}$  at  $\xi_j$  at time  $[t + \Delta t]$  in the limit as  $c$  approaches 0,  $\sigma^{\circ}_{k,e,j-}$  at all  $\xi$  equals  $\sigma_{k,e}$  at  $\xi_j$  at time  $t$  in the limit as  $c$  approaches 0,  $\sigma^{\circ}_{k,e,j+}$  at all  $\xi$  equals  $\sigma_{k,e}$  at  $\xi_j$  at time  $[t + \Delta t]$  in the limit as  $c$  approaches 0,  $s^{\circ}_{k,e,j-}$  at all  $\xi$  equals  $s_{k,e}$  at  $\xi_j$  at time  $t$  in the limit as  $c$  approaches 0,  $s^{\circ}_{k,e,j+}$  at all  $\xi$  equals  $s_{k,e}$  at  $\xi_j$  at time  $[t + \Delta t]$  in the limit as  $c$  approaches 0,  $c_{q,a,j-}$  is the  $\xi$ -independent concentration coefficient of species  $a$  of solute component  $q$  at time  $t$  (at time  $t$ ,  $c_{q,a,j-}$  at all  $\xi$ , equals  $c_{q,a}$  at  $\xi_j$ , just as  $c_{k,e,h}$  at all  $\xi$ , equals  $c_{k,e}$  at  $\xi_h$  in Equation C17),  $c_{q,a,j+}$  is the  $\xi$ -independent concentration coefficient of species  $a$  of solute component  $q$  at time  $[t + \Delta t]$  (at time  $[t + \Delta t]$ ,  $c_{q,a,j+}$  at all  $\xi$ , equals  $c_{q,a}$  at  $\xi_j$ , just as  $c_{k,e,h}$  at all  $\xi$ , equals  $c_{k,e}$  at  $\xi_h$  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  $b^{\text{th}}$  of up to an infinite number of coefficients of proportionality for the density increment, 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  $\mp$  representing either  $-$  or  $+$ , Equations N23 $\mp$  and N24 $\mp$  can be used in place of

Equations C33 $\bar{r}$  and C34 $\bar{r}$ , 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 +  $\Delta t$ ].

Individually, the product of  $b(c_{q,a})^{b-1}$  with the corresponding coefficient of proportionality  $p_{b,k,e,q,a}$  yields the  $b^{\text{th}}$  term for the contribution of  $c_{q,a}$  to the density increment 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  $b^{\text{th}}$  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  $b^{\text{th}}$  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  $\sum_{b=2}^{\infty} \sum_{a=1}^{n_q} p_{b,k,e,q,a} b c_{q,a}^{b-1}$  is a measure of the total contribution of  $c_{q,a}$  to the density increment 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.

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

By definition,  $\sigma^{\circ}_{k,e,j}$ ,  $D^{\circ}_{k,e,j}$  and  $s^{\circ}_{k,e,j}$ , are  $\xi$ -independent, and for a given t-independent field strength, 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  $\Delta s^{\circ}_{k,e,j}/\Delta j \neq 0$ . 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  $\Delta s^{\circ}_{k,e,j}/\Delta j = 0$ , can only apply to a system with an incompressible solvent, in which case,  $\sigma^{\circ}_{k,e,j}$ ,  $D^{\circ}_{k,e,j}$  and  $s^{\circ}_{k,e,j}$  can be replaced with their respective, system-wide constants,  $\sigma^{\circ}_{k,e}$ ,  $D^{\circ}_{k,e}$  and  $s^{\circ}_{k,e}$ . (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  $[t + \Delta t]$ , 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.)

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  $\xi$  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, density and viscosity 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  $S_{k,e}$ , 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  $s_{k,e,j}$  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  $s_{k,e,j}$  at times  $t$  and  $[t + \Delta t]$  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  $[t + \Delta t]$ : 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, sedimentation coefficients,  $s_{k,e,j}$ , which are related to the  $N$  space-independent, time-dependent, reduced molar mass coefficients through  $\omega^2 s_{k,e,j} = D_{k,e,j} \sigma_{k,e,j}$ . 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  $[t + \Delta t]$ : 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

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

and

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

(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:

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

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

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

Consequently,

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



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

for  $1 < i < N$ , and

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

(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  $-(\partial[2\xi]^{0.5}I_{k,e}/\partial \xi)_t$  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  $-(\partial[2\xi]^{0.5}I_k/\partial \xi)_t$ , which makes each  $Z_{k,i-}$  equal the sum over all h of  $c_{k,h+} F_{k,h,i+}$  in those equations. Therefore,

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

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

for  $1 < i < N$ , and

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

(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  $-(\partial[2\xi]^{0.5} I_{k,e}/\partial \xi)_t$ . 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

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

(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  $c_{k,e,[N-1]+}$ , 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  $\xi$ -dependent Lamm equation with the set of all  $\xi_h$  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  $\xi$  is equal to the value of  $c_{k,e}$  at  $\xi_b$ , while  $c_{k,e,N+}$  at all  $\xi$  is equal to the value of  $c_{k,e}$  at  $\xi_m$ . In general,  $\xi_h$ ,  $c_{k,e,h+}$ ,  $c_{k,e,h-}$ ,  $D_{k,e,j+}$ ,  $\sigma_{k,e,j+}$ ,  $D_{k,e,j-}$  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, where 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  $(c_{k,e,h+})_{\text{avg}} = [(\xi_h - \xi_m)(c_{k,e,h+})_R + (\xi_b - \xi_h)(c_{k,e,h+})_F]/(\xi_b - \xi_m)$ , 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  $\xi$  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  $\xi$ , which is covered in Section F ( **$\xi$ -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

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

(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

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

(C49)

and

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

(C50)

where

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

(C51)

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

(C52)

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

(C53)

and

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

(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  $\xi$  in Equation C36 (as expanded using Equation C35), because  $c_{k,e,h-}$  and  $c_{k,e,h+}$  are  $\xi$ -independent. Instead, the partial derivatives of  $c_{k,e}$  and  $c_k$  with respect to  $\xi$  in Equation C4 give rise to ordinary derivatives of  $P_h$  with respect to  $\xi$  in Equations C35, B24 and anywhere else where the continuity equation has been solved by separation of variables and integration with respect to  $\xi$ . 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  $\xi$ -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

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

(C55)

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

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

(C56)

and if

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

(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

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

and

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

(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  $\xi$ -independent, and at all  $\xi$  is equal to the value of  $c$  at  $\xi_h$ . Equation B6 describes  $c_{k,h}$  and  $P_h$ .) Penultimately, Equation C58 and C59 are used to obtain

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

which, finally, yields

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

(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  $[t + \Delta t]$  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

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

(C61)

and

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

(C62)

where

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

(C63)

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

(C64)

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

(C65)

and

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

(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

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

(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

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

(C68)

which is analogous to Equation C56, and

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

(C69)

which is analogous to Equation C57. Next, 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

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

(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  $[t + \Delta t]$  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  $\xi$ -dependent function,  $P_j$ , multiplied by a corresponding  $\xi$ -independent coefficient,  $D_j$ , which nevertheless remains a function of  $t$ . Each  $D_j$  at all  $\xi$  is equal to  $D_w$  at  $\xi_j$ . Similarly, Equation C72 expresses  $(\sigma D)_w$  of Equation A30 as the sum of  $N$  products, each of which consists of a  $\xi$ -dependent function,  $P_j$ , multiplied by

a corresponding  $\xi$ -independent coefficient,  $\sigma_j D_j$ , which nevertheless remains a function of  $t$ . Each  $\sigma_j D_j$  at all  $\xi$  is equal to  $(\sigma D)_w$  at  $\xi_j$ .

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  $\xi$ , 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 Lamm equation can be written as

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

(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



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

(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

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

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

(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

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

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

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

(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  $b^{\text{th}}$  of an infinite number of coefficients accounting for the thermodynamic nonideality effect of component  $q$  on the transport of component  $k$ , and

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

(D2)

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

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

(D3)

where

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

(D4)

As with the van 't Hoff expression, density increment and viscosity expressions can be expanded as infinite series, so that  $\sigma_k$  (the reduced molar mass coefficient of component k) and  $D_k$  (the diffusion coefficient of component k) can be described, respectively, by

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

(D5)

and

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

(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  $b^{\text{th}}$  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 density increment coefficient of  $dc_q^b/dc_q$ , which makes  $p_{b,k,q}$  the  $b^{\text{th}}$  of an infinite number of coefficients accounting for the density increment effect of component  $q$  on the transport of component  $k$ .

From the above equations, it follows that

$$s_k = \frac{\sigma_k^{\circ} D_k^{\circ}}{\omega^2} \left( \frac{\sum_{b=1}^{\infty} \left[ \sum_{q=1}^n p_{b,k,q} \frac{dc_q^b}{dc_q} \right]}{\sum_{b=1}^{\infty} \left[ \sum_{q=1}^n h_{b,k,q} \frac{dc_q^b}{dc_q} \right]} \right),$$

(D7)

where

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

(D8)

and

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

(D9)

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



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

(D10)

where

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

(D11)

and

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

(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

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

(D14)

where

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

(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 fringe displacement data

To present results that are comparable to the fringe displacement data observed experimentally, at each time  $t$ , at each point  $\xi$ , 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 fringe displacement [Gray et al., 1995] for species  $e$  of solute component  $k$  at wavelength  $\lambda$ . For species  $e$  of solute component  $k$  at a concentration of  $c_{k,e}$  in an AUC experiment using an optical pathlength of  $L$  and a wavelength of  $\lambda$  (in cm), the specific fringe displacement (in fringe·cm<sup>2</sup>/g) is

$$k_{\lambda,k,e} = \left( \frac{\partial n_{\lambda}}{\partial c_{k,e}} \right)_{\mu} \frac{\text{fringe}}{\lambda} = \frac{\Delta J_{\lambda,k,e}}{L c_{k,e}}.$$

(E1)

where  $(\partial n_{\lambda} / \partial c_{k,e})_{\mu}$  is the refractive index increment (in cm<sup>3</sup>/g) at wavelength  $\lambda$  for a solution of species  $e$  of solute component  $k$  at dialysis equilibrium with the solvent, and  $\Delta J_{\lambda,k,e}$  is the observed fringe displacement for species  $e$  of solute component  $k$  at wavelength  $\lambda$ . As  $\Delta J_{\lambda,k,e} = L k_{\lambda,k,e} c_{k,e}$ , the total fringe displacement, which is equal to the sum of all  $\Delta J_{\lambda,k,e}$ , is dependent on the concentration of each species of each solute component.

## 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: $\xi$ -dependent functions to approximate $D_{k,e}$ and $\sigma_{k,e}$

### Tests of different solutions

The integrals in the solution to the  $t$ - and  $\xi$ -dependent Lamm equation (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 AUC have been used in finite-element simulations. Simulations of AUC 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\*). Additionally, finite-element simulations of sedimentation based on the first approximate solution to the  $t$ - and  $\xi$ -dependent Lamm equation have been found to perform at least as well as finite-element simulations based on the first approximate solution to the  $t$ - and  $r$ -dependent Lamm equation [Cox and Dale, 1981; Schuck et al., 1998]. (Results not shown.)

### First approximate solution

To express  $\sigma_{k,e}$  and  $D_{k,e}$  in terms of pseudo- $\xi$ -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  $\xi$ . For  $\sigma_{k,e}$ , at all  $\xi_h$ , where  $1 \leq h \leq N$ , those coefficients are

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

(F1)

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

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

(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  $\xi$ -independent coefficients ( $D_{k,e,j}$  and  $\sigma_{k,e,j}$ , respectively) and  $\xi$ -dependent basis functions ( $P_j$ ). It is the  $\xi$ -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  $s_{k,e}$  and  $D_{k,e}$  instead of  $\sigma_{k,e}$  and  $D_{k,e}$ ,  $s_{k,e}$  is also approximated as a set of  $N$  scalar coefficients that can be a function of  $t$  but must be invariant with  $\xi$ . At all  $\xi_h$ , where  $1 \leq h \leq N$ , those coefficients are

$$s_{k,e,h} = s_{k,e} \text{ at } \xi_h.$$

(F3)

(Compare Equation F3 with Equation C21.)

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

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

(F4)

As usual, a minus or plus subscript refers to time  $t$  or  $[t + \Delta t]$ , 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  $\xi$ . 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  $\xi$ -independent  $\sigma_{k,e}$ , each  $D_{k,e,h}$  should equal  $\xi$ -independent  $D_{k,e}$  and, given that  $(\partial s_{k,e}/\partial\xi)_t = 0$

when  $(\partial\sigma_{k,e}/\partial\xi)_t = 0$  and  $(\partial D_{k,e}/\partial\xi)_t = 0$ , each  $s_{k,e,h}$  should equal  $\xi$ -independent  $s_{k,e}$ .

Furthermore, these conditions make it highly likely that  $(\partial s_{k,e}/\partial t)_\xi = 0$  and  $(\partial D_{k,e}/\partial t)_\xi = 0$  in general, and that  $(\partial\sigma_{k,e}/\partial t)_\xi = 0$  at constant field. Therefore,  $s_{k,e,h}$  and  $D_{k,e,h}$  are likely to be  $t$ -independent in general, and  $\sigma_{k,e,h}$  is 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  $s_{k,e,h}$ , 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  $s_{k,e,h}$  become pseudoconstants with respect to  $\xi$ . 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- $\xi$ -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  $\xi$  equals  $D_{k,e}$  at  $\xi_h$  at time  $t$  or  $[t + \Delta t]$  in the limit as  $c$  approaches 0,  $\sigma^{\circ}_{k,e}$  at all  $\xi$  equals  $\sigma_{k,e}$  at  $\xi_h$  at time  $t$  or  $[t + \Delta t]$  in the limit as  $c$  approaches 0,  $c_{q,a,h}$  is the  $\xi$ -independent concentration coefficient of species  $a$  of solute component  $q$  at time  $t$  or  $[t + \Delta t]$  ( $c_{q,a,h}$ , at all  $\xi$ , equals  $c_{q,a}$  at  $\xi_h$ , just as  $c_{k,e,h}$ , at all  $\xi$ , equals  $c_{k,e}$  at  $\xi_h$  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  $b^{\text{th}}$  of up to an infinite

number of coefficients of proportionality for the density increment, 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  $\sigma_{k,e}^\circ$  and  $D_{k,e}^\circ$  are  $\xi$ -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  $D_{k,e,j}^\circ$ , (Equation C33) and  $\sigma_{k,e,j}^\circ$  (Equation C34), the condition that  $\Delta D_{k,e,j}^\circ/\Delta j = 0$  and  $\Delta\sigma_{k,e,j}^\circ/\Delta j = 0$  for all species of all solute components can only apply to a system with an incompressible solvent, in which case,  $D_{k,e,j}^\circ$  and  $\sigma_{k,e,j}^\circ$  can be replaced with  $D_{k,e}^\circ$ , and  $\sigma_{k,e}^\circ$ , respectively. Hence, the use of  $D_{k,e}^\circ$  and  $\sigma_{k,e}^\circ$  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  $\xi$ -independent  $\sigma_{k,e}$ , and each  $D_{k,e,h}$  should equal  $\xi$ -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  $\xi$  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**

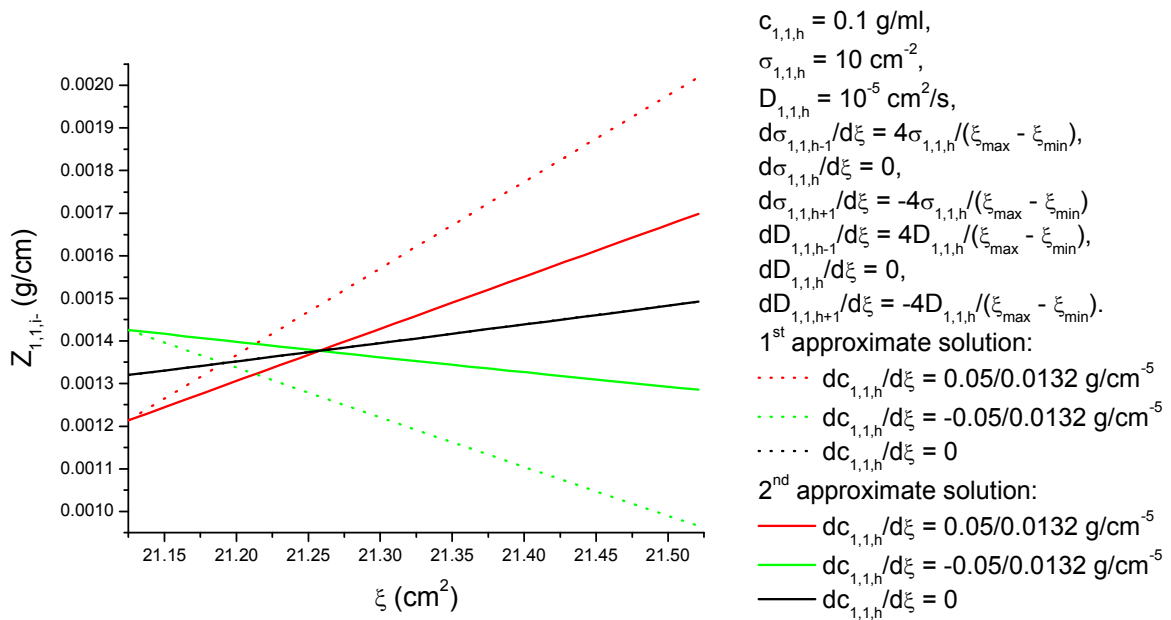


Figure F1. Results, as  $Z_{k,e,i-} = Z_{1,1,i-}$  versus  $\xi$ , from the first approximate and second approximate solutions, compared after a 1 s time increment for 87 three-element, single solute component ( $k = 1$ ), single solute species ( $e = 1$ ) systems. (Each system consists of 3 adjacent spatial elements,  $[h - 1]$ ,  $h$  and  $[h + 1]$ , where  $1 < h < 31$ ,  $\xi_{\min} = \xi_1 = 21.1250 \text{ cm}^2$ ,  $\xi_{\max} = \xi_{31} = 21.5210 \text{ cm}^2$ ,  $\Delta\xi_{h-} = \Delta\xi_{h+} = \Delta\xi = 0.0132 \text{ cm}^2$ , and each system is characterised by one of three concentration gradients,  $dc_{1,1,h}/d\xi$ , in which  $(c_{1,1,[h-1]} + c_{1,1,h} + c_{1,1,[h+1]})/3 = 0.1 \text{ g/ml}$ .) 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 indistinguishable. (See Section C in general, and Equations C39 and C74 in particular, for details regarding  $Z_{k,e,i-}$ .)

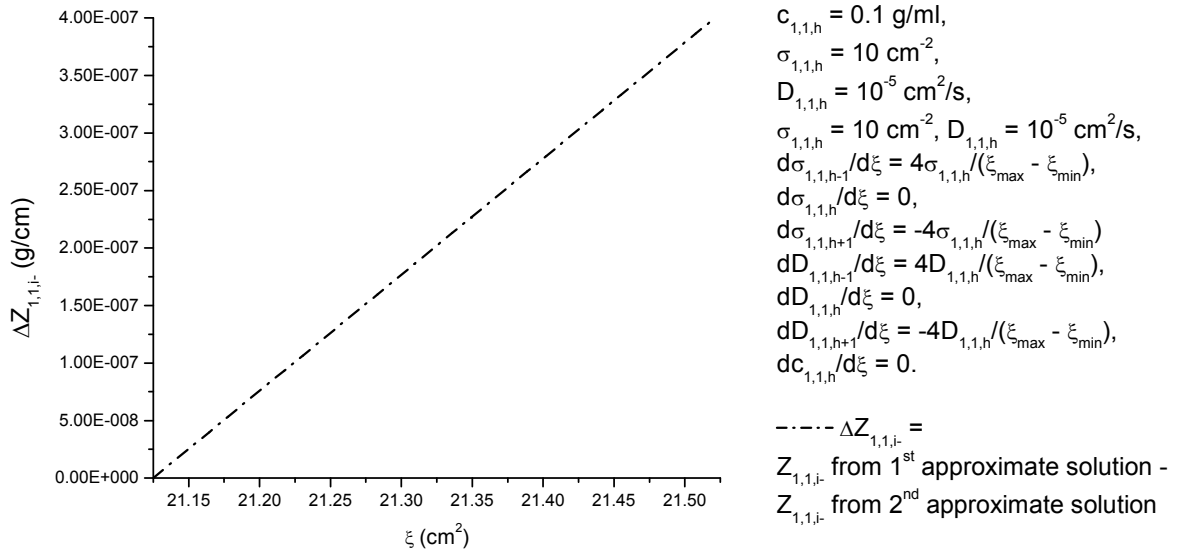


Figure F2. Results, as  $\Delta Z_{k,e,i} = \Delta Z_{1,1,i}$  versus  $\xi$ , from  $Z_{1,1,i}$  of the first approximate solution minus  $Z_{1,1,i}$  of the second approximate solution after a 1 s time increment for the 29  $dc_{1,1,h}/d\xi = 0$  systems shown in Figure F1. The central values of, and 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 AUC 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  $\vec{J}_k^S$ , the molar flow of component k in the solvent frame of reference, can be written as

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

(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 AUC instrument, in cases where the Earth's gravitational acceleration makes no significant contribution the molar gravitational potential of any component,  $\vec{X}_q$  has no component along the  $\varphi$ - or z-axis of the system, so that  $X_q = (X_q)_r$ , which is the r-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  $\vec{v}_0$ , 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  $J_k = (c_k/M_k)v_0$ . As the AUC system is closed,  $v_0$  must be zero at the boundaries, and is likely to be negligibly small elsewhere.

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  $-\vec{G}$ ,  $\epsilon_q$  is the indicator of time parity for  $\vec{X}_q$  and  $\epsilon_k$  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,  $\epsilon_q$  or  $\epsilon_k$ , 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 AUC instrument, under the usual operating conditions,  $\vec{G}$  may not 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  $s_k$  (Equation A22) or  $\sigma_k$  (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 AUC**). 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,

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

(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 AUC 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  $\Phi$ . The summation indexed by  $g$  gives the contribution of independent chemical reaction flows to  $\Phi$ . 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 AUC 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 cylindrical coordinate system, where  $r$  is the radial coordinate,  $z$  is the longitudinal coordinate, and  $\varphi$  is the angular coordinate (the segment of arc), is well suited to describing

the geometry of an AUC system. It is assumed that an AUC system develops gradients in the gravitational potential and chemical potentials mainly, and these potentials are expected to be invariant with respect to  $\varphi$  in most systems. Furthermore, in many systems, the gravitational potential and chemical potentials are expected to be invariant with respect to  $z$ . In general,  $\vec{X}_q = M_q(\omega^2 \nabla \xi - \nabla g_E h) - \nabla \mu_q$ , where, as discussed with respect to Equation A2,  $\mu_q$  is the chemical potential of solute component  $q$ ,  $M_q$  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.

In cases where the Earth's contribution to the molar gravitational potential gradient,  $-M_q \nabla g_E h$ , is significant,  $-\nabla g_E h$  will not be negligible, and  $\vec{X}_q$  will vary significantly with respect to  $r$  and  $z$ , but is still likely to be invariant with respect to  $\varphi$ . (For further details about the consequences of significant values of  $-M_q \nabla g_E h$ , see **Section H: The contribution of the Earth's gravitational field to transport in AUC.**) In general,  $(\partial \xi / \partial r)_{t,\varphi,z} = (\partial \xi / \partial r)_t$ . Thus, where  $-g_E \nabla h$  is negligible, in all likelihood,  $(\partial \mu_q / \partial r)_{t,\varphi,z} = (\partial \mu_q / \partial r)_t$  as a result of which,  $\vec{X}_q$  can be described by  $X_q = M_q \omega^2 (\partial \xi / \partial r)_t - (\partial \mu_q / \partial r)_t$ . For definitions of  $\mu_q$  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

$$\sum_{g=1}^{n_R} \sum_{k=1}^n \sum_{e=1}^{n_k} |v_{R,g,k,e}| S_{k,e} \rightleftharpoons \sum_{g=1}^{n_R} \sum_{k=1}^n \sum_{e=1}^{n_k} |v_{P,g,k,e}| S_{k,e} ,$$

(G4)

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

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

(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  $Y$  represent the unit solute concentration (with dimensions such as  $1 \text{ g/cm}^3$ ), the dimensions of  $k_{f,g}$  are given by

$$\frac{1}{S} Y^{1 - \sum_{k=1}^n \sum_{e=1}^{n_k} |v_{R,g,k,e}|},$$

(G6)

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

$$\frac{1}{S} Y^{1 - \sum_{k=1}^n \sum_{e=1}^{n_k} |v_{P,g,k,e}|}.$$

(G7)

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

$$\sum_{k=1}^n \sum_{e=1}^{n_k} v_{g,k,e} M_{k,e} = 0.$$

(G8)

The net rate of independent chemical reaction  $g$ , given by

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

(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

$$\sum_{k=1}^n \left( \frac{\partial c_k}{\partial t} \right)_{\xi} = - \sum_{k=1}^n \left( \frac{\partial \sqrt{2\xi} I_k}{\partial \xi} \right)_t - \sum_{g=1}^{n_R=n} \left( k_{f,g} \prod_{k=1}^n \prod_{e=1}^{n_k} (\gamma_{k,e} c_{k,e})^{|\nu_{R,g,k,e}|} - k_{r,g} \prod_{k=1}^n \prod_{e=1}^{n_k} (\gamma_{k,e} c_{k,e})^{|\nu_{P,g,k,e}|} \right),$$

(G10)

where the sum of the net reaction rates,

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

(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

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

(G12)

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

The association constant of reaction a/g is given by

$$K_{A,g,a} = \frac{k_{f,g,a}}{k_{r,g,a}} = \frac{\prod_{k=1}^n \prod_{e=1}^{n_k} (\tilde{Y}_{k,e} \tilde{C}_{k,e})^{|v_{P,g,a,k,e}|}}{\prod_{k=1}^n \prod_{e=1}^{n_k} (\tilde{Y}_{k,e} \tilde{C}_{k,e})^{|v_{R,g,a,k,e}|}} = \prod_{k=1}^n \prod_{e=1}^{n_k} (\tilde{Y}_{k,e} \tilde{C}_{k,e})^{(v_{P,g,a,k,e} + v_{R,g,a,k,e})} ,$$

(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

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

(G14)

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

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

(G15)

where  $\Upsilon$  is the unit solute concentration.

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



$$\sum_{k=1}^n \sum_{e=1}^{n_k} v_{g,a,k,e} M_{k,e} = 0 .$$

(G16)

The net rate of reaction a/g, given by

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

(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

$$\begin{aligned} & \sum_{k=1}^n \sum_{e=1}^{n_k} \left( \frac{\partial c_{k,e}}{\partial t} \right)_{\xi} \\ &= - \sum_{k=1}^n \sum_{e=1}^{n_k} \left( \frac{\partial \sqrt{2\xi} I_{k,e}}{\partial \xi} \right)_t - \sum_{g=1}^{n_R=n} \sum_{a=1}^{n_g} \left( k_{f,g,a} \prod_{k=1}^n \prod_{e=1}^{n_k} (\gamma_{k,e} c_{k,e})^{|v_{R,g,a,k,e}|} \right. \\ & \quad \left. - k_{r,g,a} \prod_{k=1}^n \prod_{e=1}^{n_k} (\gamma_{k,e} c_{k,e})^{|v_{P,g,a,k,e}|} \right) , \end{aligned}$$

(G18)

where the sum of the net reaction rates,

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

(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  $\xi$ -dependent,  $K_{A,g,a}$ ,  $k_{f,g,a}$  and  $k_{r,g,a}$  may be functions of  $\xi$ , and may be worth treating as such. A  $\xi$ -dependence in pressure may also

give rise to an additional  $\xi$ -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  $\xi$ -dependence is discussed in connection with the species-e-of-component-k affecting density increment, 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

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

(G20)

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

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

(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

$$K_{A,g,a}^{\text{collig}} = \frac{\left( \frac{\prod_{k=1}^n \prod_{e=1}^{n_k} M_{k,e} |v_{R,g,a,k,e}|}{\sum_{k=1}^n \sum_{e=1}^{n_k} M_{k,e} |v_{R,g,a,k,e}|} \right) k_{f,g,a}}{\left( \frac{\prod_{k=1}^n \prod_{e=1}^{n_k} M_{k,e} |v_{P,g,a,k,e}|}{\sum_{k=1}^n \sum_{e=1}^{n_k} M_{k,e} |v_{P,g,a,k,e}|} \right) k_{r,g,a}} = \frac{\left( \frac{\sum_{k=1}^n \sum_{e=1}^{n_k} M_{k,e} |v_{P,g,a,k,e}|}{\sum_{k=1}^n \sum_{e=1}^{n_k} M_{k,e} |v_{R,g,a,k,e}|} \right) k_{f,g,a}}{\left( \frac{\prod_{k=1}^n \prod_{e=1}^{n_k} M_{k,e} |v_{P,g,a,k,e}|}{\prod_{k=1}^n \prod_{e=1}^{n_k} M_{k,e} |v_{R,g,a,k,e}|} \right) k_{r,g,a}} \\ = \frac{\left( \frac{\sum_{k=1}^n \sum_{e=1}^{n_k} M_{k,e} |v_{P,g,a,k,e}|}{\sum_{k=1}^n \sum_{e=1}^{n_k} M_{k,e} |v_{R,g,a,k,e}|} \right) k_{f,g,a}}{\prod_{k=1}^n \prod_{e=1}^{n_k} M_{k,e}^{(v_{P,g,a,k,e} + v_{R,g,a,k,e})}}$$

(G22)

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

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

(G23)

where  $\tilde{\gamma}$  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

$$\begin{aligned}\Delta G^\circ &= -RT \ln \left( \frac{K_{eq,g,a}}{collig} \right) = -RT \ln \left[ \prod_{k=1}^n \prod_{e=1}^{n_k} \left( \frac{\tilde{Y}_{k,e} \tilde{C}_{k,e}}{YM_{k,e}} \right)^{(v_{P,g,a,k,e} + v_{R,g,a,k,e})} \right] \\ &= -RT \sum_{k=1}^n \sum_{e=1}^{n_k} (v_{P,g,a,k,e} + v_{R,g,a,k,e}) \ln \left( \frac{\tilde{Y}_{k,e} \tilde{C}_{k,e}}{YM_{k,e}} \right).\end{aligned}$$

(G24)

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

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT \ln \left[ \prod_{k=1}^n \prod_{e=1}^{n_k} \left( \frac{\gamma_{k,e} c_{k,e}}{YM_{k,e}} \right)^{(v_{P,g,a,k,e} + v_{R,g,a,k,e})} \right] \\ &= \Delta G^\circ + RT \sum_{k=1}^n \sum_{e=1}^{n_k} (v_{P,g,a,k,e} + v_{R,g,a,k,e}) \ln \left( \frac{\gamma_{k,e} c_{k,e}}{YM_{k,e}} \right) \\ &= RT \sum_{k=1}^n \sum_{e=1}^{n_k} (v_{P,g,a,k,e} + v_{R,g,a,k,e}) \ln \left( \frac{\gamma_{k,e} c_{k,e}}{\tilde{Y}_{k,e} \tilde{C}_{k,e}} \right) \\ &= RT \sum_{k=1}^n \sum_{e=1}^{n_k} (v_{P,g,a,k,e} + v_{R,g,a,k,e}) \ln(x_{k,e}) \\ &= RT \ln \left[ \prod_{k=1}^n \prod_{e=1}^{n_k} x_{k,e}^{(v_{P,g,a,k,e} + v_{R,g,a,k,e})} \right],\end{aligned}$$

(G25)

where

$$x_{k,e} = \frac{\gamma_{k,e} c_{k,e}}{\tilde{Y}_{k,e} \tilde{C}_{k,e}}$$

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

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

(G28)

Thus,

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

(G29)

More importantly for what follows,  $\Delta G$  is divided into two parts,

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

(G30)

where

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

(G31)

and

$$\begin{aligned} \Delta G_f &= RT \ln \left[ \prod_{k=1}^n \prod_{e=1}^{n_k} x_{k,e}^{v_{R,g,a,k,e}} \right] = RT \ln \left[ \prod_{k=1}^n \prod_{e=1}^{n_k} x_{k,e}^{-|v_{R,g,a,k,e}|} \right] \\ &= -RT \ln \left[ \prod_{k=1}^n \prod_{e=1}^{n_k} x_{k,e}^{|v_{R,g,a,k,e}|} \right], \end{aligned}$$

(G32)

so that

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

(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

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

(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} M_{k,e}^{|\nu_{R,g,a,k,e}|}}{\sum_{k=1}^n \sum_{e=1}^{n_k} 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{Y}_{k,e} \tilde{C}_{k,e}}{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} M_{k,e}^{|\nu_{P,g,a,k,e}|}}{\sum_{k=1}^n \sum_{e=1}^{n_k} 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{Y}_{k,e} \tilde{C}_{k,e}}{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} M_{k,e}^{|\nu_{R,g,a,k,e}|}}{\sum_{k=1}^n \sum_{e=1}^{n_k} 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{Y}_{k,e} \tilde{C}_{k,e}}{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} M_{k,e}^{|\nu_{P,g,a,k,e}|}}{\sum_{k=1}^n \sum_{e=1}^{n_k} 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{Y}_{k,e} \tilde{C}_{k,e}}{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} M_{k,e}^{|\nu_{R,g,a,k,e}|}}{\sum_{k=1}^n \sum_{e=1}^{n_k} 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{Y}_{k,e} \tilde{C}_{k,e}}{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} M_{k,e}^{|\nu_{P,g,a,k,e}|}}{\sum_{k=1}^n \sum_{e=1}^{n_k} 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{Y}_{k,e} \tilde{C}_{k,e}}{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

$$\begin{aligned}
 J_{g,a}^R &= \frac{1}{RT} \left( \frac{\prod_{k=1}^n \prod_{e=1}^{n_k} M_{k,e}^{|\nu_{R,g,a,k,e}|}}{\sum_{k=1}^n \sum_{e=1}^{n_k} M_{k,e}^{|\nu_{R,g,a,k,e}|}} \right) k_{f,g,a} \prod_{k=1}^n \prod_{e=1}^{n_k} \left( \frac{\tilde{Y}_{k,e} \tilde{C}_{k,e}}{M_{k,e}} \right)^{|\nu_{R,g,a,k,e}|} [RT - \Delta G_f] \\
 &- \frac{1}{RT} \left( \frac{\prod_{k=1}^n \prod_{e=1}^{n_k} M_{k,e}^{|\nu_{P,g,a,k,e}|}}{\sum_{k=1}^n \sum_{e=1}^{n_k} M_{k,e}^{|\nu_{P,g,a,k,e}|}} \right) k_{r,g,a} \prod_{k=1}^n \prod_{e=1}^{n_k} \left( \frac{\tilde{Y}_{k,e} \tilde{C}_{k,e}}{M_{k,e}} \right)^{|\nu_{P,g,a,k,e}|} [RT + \Delta G_r] \\
 &= L_{P,R}^{g,a} X_R^{g,a} + L_{R,P}^{g,a} X_P^{g,a},
 \end{aligned}$$

(G37)

where

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

(G38)

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

$$L_{P,R}^{g,a} = \frac{1}{RT} \left( \frac{\prod_{k=1}^n \prod_{e=1}^{n_k} M_{k,e}^{|v_{R,g,a,k,e}|}}{\sum_{k=1}^n \sum_{e=1}^{n_k} M_{k,e}^{|v_{R,g,a,k,e}|}} \right) k_{f,g,a} \prod_{k=1}^n \prod_{e=1}^{n_k} \left( \frac{\tilde{Y}_{k,e} \tilde{C}_{k,e}}{M_{k,e}} \right)^{|v_{R,g,a,k,e}|}$$

(G39)

is the coupled-flow-phenomenological coefficient linking  $J_P^{g,a}$  to  $X_R^{g,a}$ ,

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

(G40)

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

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

(G41)

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

$$L_{R,P}^{g,a} = -\frac{1}{RT} \left( \frac{\prod_{k=1}^n \prod_{e=1}^{n_k} M_{k,e}^{|v_{P,g,a,k,e}|}}{\sum_{k=1}^n \sum_{e=1}^{n_k} M_{k,e}^{|v_{P,g,a,k,e}|}} \right) k_{r,g,a} \prod_{k=1}^n \prod_{e=1}^{n_k} \left( \frac{\tilde{Y}_{k,e} \tilde{C}_{k,e}}{M_{k,e}} \right)^{|v_{P,g,a,k,e}|}$$

(G42)

is the coupled-flow-phenomenological coefficient linking  $J_R^{g,a}$  to  $X_P^{g,a}$ , and

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

(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

$$\Phi_R = \sum_{g=1}^{n_R=n} \Phi_g.$$

(G48)

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

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

(G49)

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

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

(G50)

Assuming that, by definition,

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

(G51)

then

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

(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  $X_P^{g,a}$  (Equation G40) or  $X_R^{g,a}$  (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,  $\Phi$ . 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,  $J_g^R A_g$ ,  $J_g^R U_q$ ,  $(\nabla \cdot \vec{J}_k) A_g$ , 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,  $[(\nabla \cdot)^{-1} J_g^R] \cdot (-\nabla A_g)$ ,  $[(\nabla \cdot)^{-1} J_g^R] \cdot \vec{X}_q$ ,  $\vec{J}_k \cdot (-\nabla A_g)$ , 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  $-\nabla A_g$  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  $-\nabla A_g$  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: The contribution of the Earth's gravitational field to transport in AUC

The gravitational potential due to angular acceleration is  $-\omega^2\xi$ , and the gravitational field due to angular acceleration is  $\omega^2\nabla\xi = \omega^2\vec{r}$ , where  $\vec{r}$  is the radial vector. In a vertically mounted rotor, in the absence of precession,  $\omega^2\vec{r} \cdot \vec{g}_E = 0$ , as such designs make  $\omega^2\vec{r}$  orthogonal to the gravitational field of the Earth, which, expressed as a vector, is  $\vec{g}_E$ . If the rotor were mounted horizontally, as in the oil-turbine ultracentrifuge built by Lysholm and Svedberg [Svedberg, 1927], then, in the absence of precession,  $\omega^2\vec{r} \cdot \vec{g}_E$  would, on a time-average basis, be zero for each point in the rotor, though for any given point in the rotor,  $\omega^2\vec{r} \cdot \vec{g}_E$  would only actually be zero at the two times per revolution when the angle between  $\vec{r}$  and  $\vec{g}_E$  was either  $\pi/2$  or  $-\pi/2$ . Thus, in a horizontally mounted rotor, the Earth's gravity cannot significantly contribute to a concentration gradient in the system, as the sum of its contributions per revolution is zero.

Rotors are vertically mounted in Beckman-Coulter XL-A/I analytical ultracentrifuges, and viewed from above, those rotors spin clockwise, so that the rotor's axis of rotation,  $\vec{\Omega}$ , is directed downward, according to the right-hand rule. For a height change of  $\Delta h$  (equal to a chosen final height minus a chosen initial height) in an XL-A/I AUC system, the difference in the Earth's gravitational potential is  $g_E\Delta h$ . In a properly levelled AUC instrument with a vertically mounted rotor, in the absence of rotor precession, the acceleration due to gravity is directed downward along  $\vec{\Omega}$ , and the drop in height in the direction of  $\vec{g}_E$  is typically no greater than -1.2 cm (equal to the lowest possible height minus the highest possible height). More importantly for what follows, in a properly levelled AUC instrument with a vertically mounted rotor, the instrument's vertical axis,  $\vec{z}$ , is defined as being directed downward, with its reference position,  $z_0$ , arbitrarily assigned a value of 0, which is arbitrarily chosen to coincide with the maximum height,  $h_{\max}$ , of the AUC system in the absence of precession. As  $z$  and  $h$  are oppositely directed, where the dimensionality of  $z$  and  $h$  is the same,  $dz/dh$

= -1.

Calculating the contribution of the Earth's gravitational field to AUC is similar to calculating the contribution of angular acceleration to AUC. The same standard thermodynamic relation,

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

(H1, from A7, which see)

applies to the chemical potential gradient both cases. In both cases, Bernoulli's equation also applies, but for the case of the contribution of the Earth's gravitational field, the form used, neglecting vector notation, is

$$P = P_0 + g_E \int_{z_0}^{z_a} \rho dz,$$

(H2)

where, at a given value of  $\xi$ ,  $P$  is the pressure at  $z = z_a$ ,  $P_0$  is the pressure at  $z = z_0$ , and the rest of the parameters have been defined previously.

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

$$\left(\frac{\partial P}{\partial z}\right)_{\xi,t} \cong \rho g_E,$$

(H3)

so that

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

(H4)

As shown in Equation A2, the gradient of the molar gravitational potential of component k due to the Earth's gravitational acceleration is equal to  $M_k \nabla g_E h$ , which, given  $dz/dh = -1$ , makes  $-M_k \nabla g_{EZ} = M_k \nabla g_E h$ . Thus,  $-M_k \nabla g_{EZ} = -M_k g_E$ , and for component k, the sum of the gravitational and chemical potential gradient terms involving  $g_E$  is  $-M_k \nabla g_{EZ} + (\partial \mu / \partial P)_{\xi, t, T, c} (\partial P / \partial z)_{\xi, t} = -M_k (1 - \bar{v}_k \rho) g_E$ .

For  $M_k \bar{v}_k \rho \leq 10^7$  g/mol (approximately),  $(\partial \mu / \partial P)_{\xi, t, T, c} (\partial P / \partial z)_{\xi, t} \leq 10^{10}$  g·cm/mol·s<sup>2</sup>. While the upper range of this value may seem significant, it is still less than 0.2% of  $M_k \bar{v}_k \rho \omega_{\min}^2 r_{\min}$ , 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 ( $2\pi[3,000 \text{ RPM}]/[60 \text{ s/min}]$ ),  $\omega_{\min}$ , in the XL-A/I. Thus, the gravitational force term,  $M_k \bar{v}_k \rho g_E$ , is usually negligible ( $M_k \bar{v}_k \rho g_E < 0.002 \cdot M_k \bar{v}_k \rho \omega_{\min}^2 r_{\min}$ ). In general, with a vertically mounted rotor, the height of an AUC system would have to be much greater than the typical maximum of 1.2 cm, or  $|M_k (1 - \bar{v}_k \rho)|$  would have to exceed approximately  $3 \cdot 10^7$  g/mol, before  $M_k (1 - \bar{v}_k \rho) g_E$  would make a substantial contribution to a vertically oriented concentration gradient.

For  $|M_k (1 - \bar{v}_k \rho)| \gg 3 \cdot 10^7$  g/mol, reducing  $\Delta h$  (by using a 0.3 cm or shorter optical pathlength centrepiece, for example) could reduce the ultimate extent of the difference in  $c_k$  across  $\Delta h$ . The main problem with significant vertical concentration gradients is the extent to which the correspondingly significant vertical mass flows would couple with radial mass flows. For any system in which  $|M_k (1 - \bar{v}_k \rho)| \gg 3 \cdot 10^7$  g/mol, coupled vertical and radial flows would likely render the data highly challenging to analyse properly. Furthermore, the  $(\partial c / \partial z)_{\xi, t}$  portion of the data that would be needed to analyse such systems cannot yet be collected in the XL-A/I.

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## Section I: Calculating 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 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

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



(15)

The total molar flow of all species of solute component k is given by

$$\begin{aligned}
 (\vec{J}_k)_{total} &= \sum_{e=1}^{n_k} \vec{J}_{k,e} = \sum_{e=1}^{n_k} m_{k,e} \vec{v}_{k,e} = (m_k)_{total} \frac{\sum_{e=1}^{n_k} m_{k,e} \vec{v}_{k,e}}{\sum_{e=1}^{n_k} m_{k,e}} = (m_k)_{total} \frac{\sum_{e=1}^{n_k} \frac{N_{k,e}}{N_A V} \vec{v}_{k,e}}{\sum_{e=1}^{n_k} \frac{N_{k,e}}{N_A V}} \\
 &= (m_k)_{total} \frac{\sum_{e=1}^{n_k} N_{k,e} \vec{v}_{k,e}}{\sum_{e=1}^{n_k} N_{k,e}} = (m_k)_{total} (\vec{v}_k)_N,
 \end{aligned}$$

(16)

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

$$(m_k)_{total} = \sum_{e=1}^{n_k} m_{k,e} = \sum_{e=1}^{n_k} \frac{c_{k,e}}{M_{k,e}} = c_k \frac{\sum_{e=1}^{n_k} \frac{c_{k,e}}{M_{k,e}}}{\sum_{e=1}^{n_k} c_{k,e}} = \frac{c_k}{(M_k)_N},$$

(17)

where  $(M_k)_N$  is the number-average molar mass for all species of component k, so that

$$(\vec{J}_k)_{total} = (m_k)_{total} (\vec{v}_k)_N = \frac{c_k (\vec{v}_k)_N}{(M_k)_N}.$$

(18)

Similarly, the mass flow of solute component k can be related to the mass and molar flows of all species of component k by

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

(19)

where  $(\vec{v}_k)_w$  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.  $(\vec{J}_k)_{total}$  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

$$\vec{I}_k = c_k(\vec{v}_k)_w = c_k(\vec{v}_k)_N \frac{(\vec{v}_k)_w}{(\vec{v}_k)_N} = (M_k)_N \frac{(\vec{v}_k)_w}{(\vec{v}_k)_N} \vec{J}_k = (M_k)_X \vec{J}_k,$$

(110)

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 110 for  $(M_k)_X$  in terms of the mass and molar flows of component k yields

$$(M_k)_X = \frac{\vec{I}_k}{\vec{J}_k}.$$

(111)

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

$$(M_k)_X = \frac{\vec{I}_k}{\vec{J}_k} = \frac{\sum_{e=1}^{n_k} M_{k,e}\vec{J}_{k,e}}{\vec{J}_k} = \frac{\sum_{e=1}^{n_k} M_{k,e}\vec{J}_{k,e}}{\sum_{e=1}^{n_k} \vec{J}_{k,e}} = (M_k)_J,$$

(112)

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

$$(M_k)_J = \frac{\sum_{e=1}^{n_k} M_{k,e}\vec{J}_{k,e}}{\sum_{e=1}^{n_k} \vec{J}_{k,e}} = \frac{\sum_{e=1}^{n_k} M_{k,e}m_{k,e}\vec{v}_{k,e}}{\sum_{e=1}^{n_k} m_{k,e}\vec{v}_{k,e}},$$

(113)

the limit as the velocity of each species of solute component k approaches zero is

$$\lim_{all \vec{v}_{k,e} \rightarrow 0} (M_k)_J = \lim_{all \vec{v}_{k,e} \rightarrow 0} \frac{\sum_{e=1}^{n_k} M_{k,e}m_{k,e}\vec{v}_{k,e}}{\sum_{e=1}^{n_k} m_{k,e}\vec{v}_{k,e}} = \frac{\sum_{e=1}^{n_k} M_{k,e}m_{k,e}}{\sum_{e=1}^{n_k} m_{k,e}} = (M_k)_N,$$

(114)

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  $D_k$ ,  $s_k$  and  $I_k$  in Section A.

Equations A1, A2, I10 and I12 can be combined to yield

$$\vec{I}_k = (M_k)_J \left[ \sum_{q=1}^n L_{k,q} \vec{X}_q + \frac{c_k}{M_k} \vec{v}_0 \right] = (M_k)_J \left[ \sum_{q=1}^n L_{k,q} (M_q [\omega^2 \vec{r} - \nabla g_E h] - \nabla \mu_q) + \frac{c_k}{M_k} \vec{v}_0 \right]. \quad (115)$$

Using Equation A2, the gradient of  $U_q$ , the total molar potential of solute component q, can be written as

$$\nabla U_q = -\vec{X}_q = -(M_q [\omega^2 \vec{r} - \nabla g_E h] - \nabla \mu_q), \quad (116)$$

in which  $\vec{X}_q$  is the conjugate molar force (Equations A2 and A14) of component q. (As noted in **Section A (An application of irreversible thermodynamics to analytical ultracentrifugation)**, and again in **Section H (The contribution of the Earth's gravitational field to transport in AUC)**, the gravitational potential due to angular acceleration is  $-\omega^2 \xi$ , and the gravitational field due to angular acceleration is  $\omega^2 \nabla \xi = \omega^2 \vec{r}$ , where  $\vec{r}$  is the radial vector.)

As  $U_q$  is a molar quantity, it can be calculated from the number average of its species-specific parts. Thus,

$$U_q = \frac{\sum_{a=1}^{n_q} m_{q,a} U_{q,a}}{\sum_{a=1}^{n_q} m_{q,a}} = \frac{\sum_{a=1}^{n_q} N_{q,a} U_{q,a}}{\sum_{a=1}^{n_q} N_{q,a}} = \frac{\sum_{a=1}^{n_q} N_{q,a} \mu_{q,a}}{\sum_{a=1}^{n_q} N_{q,a}} - [\omega^2 \xi - g_E h] \frac{\sum_{a=1}^{n_q} N_{q,a} M_{q,a}}{\sum_{a=1}^{n_q} N_{q,a}} = (\mu_q)_N - [\omega^2 \xi - g_E h] (M_q)_N, \quad (117)$$

where the  $n_q$  species of component q are indexed by a, so that so that, for species a of component q,  $U_{q,a}$ ,  $\mu_{q,a}$  and  $M_{q,a}$  are, respectively, the total molar potential, the chemical potential, and the molar mass; while for component q,  $U_q$ ,  $(\mu_q)_N$  and  $(M_q)_N$  are, respectively, the number average of the total molar potential, the number average of the chemical

potential, and the number average of the molar mass, with each number average being for all species of component q. (Equation M15 shows  $(M_q)_N$ .)

In what follows,  $(\nabla M_q)_N$  is the number-average gradient of the molar mass for all species of component q (Equation M19), 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,  $\nabla(M_q)_N$  (Equation M18) 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 it equals zero,  $\nabla(M_q)_N = (\nabla M_q)_N = 0$ , and  $\nabla(\mu_q)_N = (\nabla \mu_q)_N$ .

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

$$\begin{aligned} \nabla U_q &= \sum_{a=1}^{n_q} \nabla U_{q,a} = - \sum_{a=1}^{n_q} \vec{X}_{q,a} = \nabla(\mu_q)_N - (M_q)_N \nabla[\omega^2 \xi - g_E h] - [\omega^2 \xi - g_E h] \nabla(M_q)_N \\ &= \nabla(\mu_q)_N - [\omega^2 \vec{r} - \nabla g_E h] (M_q)_N - [\omega^2 \xi - g_E h] \nabla(M_q)_N, \end{aligned}$$

(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

$$(M_q)_g = \frac{(M_q)_N \nabla[\omega^2 \xi - g_E h] + [\omega^2 \xi - g_E h] \nabla(M_q)_N}{\nabla[\omega^2 \xi - g_E h]},$$

(I19)

the gradient of the total molar potential of solute component q becomes

$$\nabla U_q = \nabla(\mu_q)_N - [\omega^2 \vec{r} - \nabla g_E h] (M_q)_g .$$

(I20)

A comparison of Equations A2 and I20 shows that  $\nabla \mu_q = \nabla(\mu_q)_N$  and  $M_q = (M_q)_g$ . Equation I19 (of which Equation M17 is an alternative form) shows that

$$\lim_{\nabla(M_q)_N \rightarrow 0} (M_q)_g = (M_q)_N.$$

(I21)

This result is a consequence of

$$\lim_{\text{all } \nabla N_{q,a} \rightarrow 0} \nabla(M_q)_N = \lim_{\text{all } \nabla N_{q,a} \rightarrow 0} \nabla \left( \frac{\sum_{a=1}^{n_q} N_{q,a} M_{q,a}}{\sum_{a=1}^{n_q} N_{q,a}} \right) = \lim_{\text{all } \nabla N_{q,a} \rightarrow 0} \frac{\sum_{a=1}^{n_q} N_{q,a} \nabla M_{q,a}}{\sum_{a=1}^{n_q} N_{q,a}} = 0,$$

(I22)

which, as described previously, is applicable for any value of  $n_q$ . For the case of  $n_q = 1$ ,  $\nabla(M_q)_N$  is always equal to zero. (A more detailed examination of  $(M_q)_N$ ,  $(\nabla M_q)_N$ ,  $\nabla(M_q)_N$  and  $(M_q)_g$  is presented in **Section M: Effects of solvent density on (apparent) reduced buoyant mass.**)

In contrast,

$$\lim_{\text{all } \nabla N_{q,a} \rightarrow 0} \nabla(\mu_q)_N = \lim_{\text{all } \nabla N_{q,a} \rightarrow 0} \nabla \left( \frac{\sum_{a=1}^{n_q} N_{q,a} \mu_{q,a}}{\sum_{a=1}^{n_q} N_{q,a}} \right) = \lim_{\text{all } \nabla N_{q,a} \rightarrow 0} \frac{\sum_{a=1}^{n_q} N_{q,a} \nabla \mu_{q,a}}{\sum_{a=1}^{n_q} N_{q,a}} = (\nabla \mu_q)_N,$$

(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

$$\begin{aligned} \nabla(\mu_q)_N = \nabla \mu_q &= \left( \frac{\partial \mu_q}{\partial \xi} \right)_t \left( \frac{\partial \xi}{\partial r} \right)_t \\ &= \left[ \left( \frac{\partial \mu_q}{\partial T} \right)_{t,P,c} \left( \frac{\partial T}{\partial \xi} \right)_t + \left( \frac{\partial \mu_q}{\partial P} \right)_{t,T,c} \left( \frac{\partial P}{\partial \xi} \right)_t + \sum_{w=1}^n \left( \frac{\partial \mu_q}{\partial c_w} \right)_{t,T,P,c_{q \neq w}} \left( \frac{\partial c_w}{\partial \xi} \right)_t \right] \left( \frac{\partial \xi}{\partial r} \right)_t, \end{aligned}$$

(I24)

where gradients in dimensions other than  $\xi$  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

$$\begin{aligned} \left(\frac{\partial \mu_q}{\partial P}\right)_{t,T,c} \left(\frac{\partial P}{\partial \xi}\right)_t &= \left(\frac{\partial (\mu_q)_N}{\partial P}\right)_{t,T,c} \left(\frac{\partial P}{\partial \xi}\right)_t = \left(\frac{\partial \left[\frac{\sum_{a=1}^{n_q} N_{q,a} \mu_{q,a}}{\sum_{a=1}^{n_q} N_{q,a}}\right]}{\partial P}\right)_{t,T,c} \left(\frac{\partial P}{\partial \xi}\right)_t \\ &= \left\{ \frac{\sum_{a=1}^{n_q} N_{q,a} \left(\frac{\partial \mu_{q,a}}{\partial P}\right)_{t,T,c}}{\sum_{a=1}^{n_q} N_{q,a}} + \frac{\sum_{a=1}^{n_q} \mu_{q,a} \left(\frac{\partial N_{q,a}}{\partial P}\right)_{t,T,c}}{\sum_{a=1}^{n_q} N_{q,a}} \right. \\ &\quad \left. - (\mu_q)_N \left[ \frac{\sum_{a=1}^{n_q} \left(\frac{\partial N_{q,a}}{\partial P}\right)_{t,T,c}}{\sum_{a=1}^{n_q} N_{q,a}} \right] \right\} \left(\frac{\partial P}{\partial \xi}\right)_t \\ &= \left\{ (M_q \bar{v}_q)_N + [(\mu_q)_P - (\mu_q)_N] \left(\frac{\partial \ln N_q}{\partial P}\right)_{t,T,c} \right\} \left(\frac{\partial P}{\partial \xi}\right)_t \end{aligned}$$

(I25)

where:

$$(M_q \bar{v}_q)_N = \left[ \left(\frac{\partial \mu_q}{\partial P}\right)_{t,T,c} \right]_N = \frac{\sum_{a=1}^{n_q} N_{q,a} \left(\frac{\partial \mu_{q,a}}{\partial P}\right)_{t,T,c}}{\sum_{a=1}^{n_q} N_{q,a}} = \frac{\sum_{a=1}^{n_q} N_{q,a} M_{q,a} \bar{v}_{q,a}}{\sum_{a=1}^{n_q} N_{q,a}}$$

(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;

$$(\mu_q)_P = \frac{\sum_{a=1}^{n_q} \mu_{q,a} \left( \frac{\partial N_{q,a}}{\partial P} \right)_{t,T,c}}{\sum_{a=1}^{n_q} \left( \frac{\partial N_{q,a}}{\partial P} \right)_{t,T,c}}$$

(127)

is defined as the pressure-gradient average of  $\mu_q$ ;

$$\left( \frac{\partial \ln N_q}{\partial P} \right)_{t,T,c} = \frac{\left( \frac{\partial N_q}{\partial P} \right)_{t,T,c}}{N_q} = \frac{\sum_{a=1}^{n_q} \left( \frac{\partial N_{q,a}}{\partial P} \right)_{t,T,c}}{\sum_{a=1}^{n_q} N_{q,a}};$$

(128)

and  $(\mu_q)_N$  is previously defined. Using  $(M_q)_g$  to define

$$(\bar{v}_q)_{Pg} = \frac{(M_q \bar{v}_q)_N + [(\mu_q)_P - (\mu_q)_N] \left( \frac{\partial \ln N_q}{\partial P} \right)_{t,T,c}}{(M_q)_g},$$

(129)

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

$$\left( \frac{\partial \mu_q}{\partial P} \right)_{t,T,c} \left( \frac{\partial P}{\partial \xi} \right)_t = \left\{ (M_q \bar{v}_q)_N + [(\mu_q)_P - (\mu_q)_N] \left( \frac{\partial \ln N_q}{\partial P} \right)_{t,T,c} \right\} \left( \frac{\partial P}{\partial \xi} \right)_t = (M_q)_g (\bar{v}_q)_{Pg} \left( \frac{\partial P}{\partial \xi} \right)_t.$$

(130)

## Section J: Form of the general solution from Equation C32

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

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

(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  $[t + \Delta t]$ , 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  $\xi$  equals  $D_{k,e}$  at  $\xi_j$  at time  $t$  in the limit as  $c$  approaches 0,  $D^{\circ}_{k,e,j+}$  at all  $\xi$  equals  $D_{k,e}$  at  $\xi_j$  at time  $[t + \Delta t]$  in the limit as  $c$  approaches 0,  $\sigma^{\circ}_{k,e,j-}$  at all  $\xi$  equals  $\sigma_{k,e}$  at  $\xi_j$  at time  $t$  in the limit as  $c$  approaches 0,  $\sigma^{\circ}_{k,e,j+}$  at all  $\xi$  equals  $\sigma_{k,e}$  at  $\xi_j$  at time  $[t + \Delta t]$  in the limit as  $c$  approaches 0,  $c_{q,a,j-}$  is the  $\xi$ -independent concentration coefficient of species  $a$  of solute component  $q$  at time  $t$ ,  $c_{q,a,j+}$  is the  $\xi$ -independent concentration coefficient of species  $a$  of solute component  $q$  at time  $[t + \Delta t]$ , and where  $p_{b,k,e,q,a}$ ,  $y_{b,k,e,q,a}$  and  $h_{b,k,e,q,a}$  are the  $b^{\text{th}}$  of up to an infinite number of species-e-of-component-k affecting density increment, 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  $[t + \Delta t]$ , and some unspecified position,  $\xi_j$ .

Individually, the product of  $b(c_{q,a})^{b-1}$  with the corresponding coefficient of proportionality  $p_{b,k,e,q,a}$  yields the  $b^{\text{th}}$  term for the contribution of  $c_{q,a}$  to the density increment 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  $b^{\text{th}}$  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  $b^{\text{th}}$  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  $\sum_{b=2}^{\infty} \sum_{a=1}^{n_q} p_{b,k,e,q,a} b c_{q,a}^{b-1}$  is a measure of the total contribution of  $c_{q,a}$  to the density increment 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  $[t + \Delta t]$ , 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  $m^{\text{th}}$  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  $\Xi_{\min}$ , which is repeatedly compared against

$$\Xi_m = \frac{\sum_{k=1}^n \sum_{e=1}^{n_k} \sum_{h=1}^N \left\{ \left[ (c_{k,e,h+})_m - (c_{k,e,h+})_{m-1} \right] \frac{V_h}{V} \right\}^2}{\left( \sum_{k=1}^n \sum_{e=1}^{n_k} \sum_{h=1}^N \frac{V_h}{V} c_{k,e,h-} \right)^2} = \frac{(c_{RSS})_m}{(c_-)^2},$$

(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 height of the spatial element given by  $\Delta z$  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  $\Delta \xi_{1-} = \Delta \xi_{N+} = 0$ ),  $V_h = \varphi(\Delta z)\Delta \xi_h$ , where  $\varphi$  is the angular coordinate (the segment of arc) of the system, which has the geometry of a cylindrical sector.) 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,  $\nu_{total}$ , for which  $\nu_{R,g,a,k,e} \neq 0$ . (See Equation G12.) Thus, at each spatial element,  $\xi_h$  (Equation B36), for each time increment,  $\Delta t_\epsilon$  (Equation B35), the flow of each reaction, a/g, is calculated at least  $\nu_{total}$  times. In each of the  $\nu_{total}$  iterations, the reaction flow throughout the system is calculated for all reactions. Additionally, in each of the  $\nu_{total}$  iterations, the flow of reaction a/g at each  $\xi_h$  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,  $R_{a/g} \leq \nu_{total}$ . If there is more than one reaction,  $R_{a/g} < \nu_{total}$ . 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  $\Delta t_\epsilon$  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  $\xi_h$  within  $\Delta t_\epsilon$  is denoted as  $c_{a/g}$ . At a given  $\xi_h$ , within  $\Delta t_\epsilon$ ,  $c_{a/g}$  remains constant, but the concentration of each species of reaction  $a/g$  may change over  $\Delta t_\epsilon$ . Henceforth, a minus subscript is used to denote a concentration at the start of  $\Delta t_\epsilon$ , and a plus subscript is used to denote a concentration at the end of  $\Delta t_\epsilon$ . 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  $\xi_h$  within  $\Delta t_\epsilon$  can be expressed as

$$c_{a/g} = c_{g,a-} + c_{g,r1-} + c_{q,r2-} = c_{g,a+} + c_{g,r1+} + c_{q,r2+} .$$

(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  $\xi_h$  within  $\Delta t_\epsilon$ . Thus, the concentration of species  $r1$  of component  $g$  that would be present if the product completely dissociated to reactants can be expressed as

$$c_{g1} = \frac{|v_{R,g,a,g,r1}|M_{g,r1}}{|v_{P,g,a,g,a}|M_{g,a}} c_{g,a-} + c_{g,r1-} = \frac{|v_{R,g,a,g,r1}|M_{g,r1}}{|v_{P,g,a,g,a}|M_{g,a}} c_{g,a+} + c_{g,r1+} ,$$

(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

$$c_{q2} = \frac{|v_{R,g,a,q,r2}|M_{q,r2}}{|v_{P,g,a,g,a}|M_{g,a}} c_{g,a-} + c_{q,r2-} = \frac{|v_{R,g,a,q,r2}|M_{q,r2}}{|v_{P,g,a,g,a}|M_{g,a}} c_{g,a+} + c_{q,r2+} .$$

(K3)

(See Equation K13.) Respectively, Equations K2 and K3 reflect the fact that  $c_{g1}$  and  $c_{q2}$  are conserved at a given  $\xi_h$  within  $\Delta t_\varepsilon$ . 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  $\xi_h$ , the concentration changes per  $\Delta t_\varepsilon$  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  $\Delta t_\varepsilon$  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 $\Delta t_\varepsilon$**

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  $\Delta t_\epsilon$ ,

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

(K8)

which is just Expression G17 multiplied by the reduced time increment,  $\Delta t_\tau = \Delta t_\epsilon / \tau_{\text{total}}$ , where  $\tau_{\text{total}} = v_{\text{total}} R_{a/g}$ , and  $\tau$  is an index for which  $1 \leq \tau \leq \tau_{\text{total}}$ . Expression K8 describes the flow of reaction a/g during  $\Delta t_\tau$ , and is applied  $\tau_{\text{total}}$  times per  $\Delta t_\epsilon$ , thereby yielding the flow of reaction a/g during  $\Delta t_\epsilon$ . Here, the concentration,  $c_{k,e}$ , is that which applies to species e of component k at the start of  $\Delta t_\tau$ . (At the start of  $\Delta t_\epsilon$ ,  $c_{k,e} = c_{k,e-}$ )

For reaction a/g, the portion of the products that dissociates to form reactants during  $\Delta t_\tau$ , expressed as a concentration, is

$$C_{r,g,a} = \left[ k_{r,g,a} \prod_{k=1}^n \prod_{e=1}^{n_k} (\gamma_{k,e} c_{k,e})^{|v_{P,g,a,k,e}|} \right] \Delta t_\tau,$$

(K9)

and the portion of the reactants that associates to form products during  $\Delta t_\tau$ , expressed as a concentration, is

$$C_{f,g,a} = \left[ k_{f,g,a} \prod_{k=1}^n \prod_{e=1}^{n_k} (\gamma_{k,e} c_{k,e})^{|v_{R,g,a,k,e}|} \right] \Delta t_\tau,$$

(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  $v_{P,g,a,g,a}$ , and with  $v_{P,g,a,g,a}$  being the only nonzero product stoichiometry of reaction a/g, Equation K9 simplifies to



$$C_{r,g,a} = \left[ k_{r,g,a} (\gamma_{g,a} c_{g,a})^{|v_{P,g,a,g,a}|} \right] \Delta t_{\tau},$$

(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  $\Delta t_{\tau}$ . (At the start of  $\Delta t_{\tau}$ ,  $c_{g,a} = c_{g,a-}$ .)

Of the reactant species,  $v_{R,g,a,g,r1}$  and  $v_{R,g,a,q,r2}$  are the only nonzero stoichiometries of reaction a/g, as a result of which, Equation K10 simplifies to

$$C_{f,g,a} = \left[ k_{f,g,a} (\gamma_{g,r1} c_{g,r1})^{|v_{R,g,a,g,r1}|} (\gamma_{q,r2} c_{q,r2})^{|v_{R,g,a,q,r2}|} \right] \Delta t_{\tau},$$

(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  $\Delta t_{\tau}$ . (At the start of  $\Delta t_{\tau}$ ,  $c_{g,r1} = c_{g,r1-}$  and  $c_{q,r2} = c_{q,r2-}$ .)

Given that

$$|v_{P,g,a,g,a}| M_{g,a} = |v_{R,g,a,g,r1}| M_{g,r1} + |v_{R,g,a,q,r2}| M_{q,r2},$$

(K13)

the portion of  $C_{f,g,a}$  that consists of species r1 of component g is given by

$$C_{f,g,r1} = \frac{|v_{R,g,a,g,r1}| M_{g,r1}}{|v_{P,g,a,g,a}| M_{g,a}} C_{f,g,a},$$

(K14)

and the portion of  $C_{f,g,a}$  that consists of species r2 of component q is given by

$$C_{f,q,r2} = \frac{|v_{R,g,a,q,r2}| M_{q,r2}}{|v_{P,g,a,g,a}| M_{g,a}} C_{f,g,a} = C_{f,g,a} - C_{f,g,r1}.$$

(K15)

The change in  $c_{g,a}$  per  $\Delta t_\tau$  is

$$(\Delta c_{g,a})_\tau = C_{f,g,a} - C_{r,g,a} ,$$

(K16)

the change in  $c_{g,r1}$  per  $\Delta t_\tau$  is

$$(\Delta c_{g,r1})_\tau = \frac{|v_{R,g,a,g,r1}|M_{g,r1}}{|v_{P,g,a,g,a}|M_{g,a}} (C_{r,g,a} - C_{f,g,a})$$

(K17)

and the change in  $c_{q,r2}$  per  $\Delta t_\tau$  is

$$\begin{aligned} (\Delta c_{q,r2})_\tau &= -(\Delta c_{g,a})_\tau - (\Delta c_{g,r1})_\tau = \left(1 - \frac{|v_{R,g,a,g,r1}|M_{g,r1}}{|v_{P,g,a,g,a}|M_{g,a}}\right) (C_{r,g,a} - C_{f,g,a}) \\ &= \frac{|v_{R,g,a,q,r2}|M_{q,r2}}{|v_{P,g,a,g,a}|M_{g,a}} (C_{r,g,a} - C_{f,g,a}) . \end{aligned}$$

(K18)

Equations K16 to K18 form the basis of a test to determine whether reaction a/g is slow relative to  $\Delta t_\tau$ . 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  $\Delta t_\epsilon$ . If

$$\gamma_{g,a}c_{g,a-} > C_{r,g,a-} ,$$

(K19)

$$\gamma_{g,r1}c_{g,r1-} > \frac{|v_{R,g,a,g,r1}|M_{g,r1}}{|v_{P,g,a,g,a}|M_{g,a}} C_{f,g,a-}$$

(K20)

and

$$\gamma_{q,r2}c_{q,r2-} > \frac{|v_{R,g,a,q,r2}|M_{q,r2}}{|v_{P,g,a,g,a}|M_{g,a}} C_{f,g,a-} ,$$

(K21)

from which it follows that

$$(\gamma_{g,a}c_{g,a-} + \gamma_{g,r1}c_{g,r1-} + \gamma_{q,r2}c_{q,r2-}) - (C_{r,g,a-} + C_{f,g,a-}) > 0 ,$$

(K22)

then reaction a/g is judged to equilibrate slowly enough, relative to  $\Delta t_\tau$ , 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  $\Delta t_\tau$ , 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  $\Delta t_\varepsilon$  can be calculated as

$$c_{g,a+} = c_{g,a-} + \sum_{\tau=1}^{\tau_{\text{total}}} (\Delta c_{g,a})_\tau = c_{g,a-} + \Delta c_{g,a} ,$$

(K23)

$$c_{q,r1+} = c_{q,r1-} + \sum_{\tau=1}^{\tau_{\text{total}}} (\Delta c_{q,r1})_\tau = c_{q,r1-} + \Delta c_{q,r1}$$

(K24)

and

$$c_{q,r2+} = c_{q,r2-} + \sum_{\tau=1}^{\tau_{\text{total}}} (\Delta c_{q,r2})_\tau = c_{q,r2-} + \Delta c_{q,r2} .$$

(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 $\Delta t_\varepsilon$**

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  $\Delta t_\varepsilon$ , 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  $N_{\text{equil}}$  more iterations, where  $N_{\text{equil}}$ , an empirically determined parameter, may be a number in the low thousands. (At present, the routinely used values of  $N_{\text{equil}}$  are 5,000 for the initial equilibration at  $t = 0$ , and 2,500 for all

equilibrations after  $t = 0$ .)

During  $\Delta t_\epsilon$ , up to  $N_{\text{equil}}$  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  $v_{\text{total}}$  iterations. Thus, for reaction  $a/g$ , within  $\Delta t_\epsilon$ , the maximum number of iterations is equal to  $v_{\text{total}}R_{a/g}N_{\text{equil}}$ . (The main purpose of imposing a maximum of  $N_{\text{equil}}$  iterations is to prevent the occurrence of infinite loops, but it is usually best to set  $N_{\text{equil}}$  higher than necessary to ensure equilibration. Spurious spikes and dips in the concentration data are evidence that  $N_{\text{equil}}$  is too low to consistently achieve equilibration, but such low values of  $N_{\text{equil}}$  might sometimes be useful for quickly testing a complicated model system.)

The innermost iterations are indexed by  $w$ , where  $1 \leq w \leq w_{\text{final}}$ , and  $w_{\text{final}} \leq N_{\text{equil}}$ . The last iteration,  $w_{\text{final}}$ , occurs when the equilibration criterion (Inequality K29) has been met, or when  $w$  reaches  $N_{\text{equil}}$ , whichever comes first. Thus, for reaction  $a/g$ , within  $\Delta t_\epsilon$ , the total number of iterations is equal to  $v_{\text{total}}R_{a/g}w_{\text{final}}$ . At each of the  $w_{\text{final}}$  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  $\Delta t_\epsilon$** ), 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,

$$Q_{P,w} = (\gamma_{g,a} c_{g,a,w-})^{|\nu_{P,g,a,g,a}|} \quad (\text{K27})$$

and

$$Q_{R,w} = K_{A,g,a} (\gamma_{g,r1} c_{g,r1,w-})^{|\nu_{R,g,a,g,r1}|} (\gamma_{q,r2} c_{q,r2,w-})^{|\nu_{R,g,a,q,r2}|}, \quad (\text{K28})$$

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,  $\zeta$ , 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  $\zeta$  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

$$\zeta K_{A,g,a} \leq \frac{(\gamma_{g,a} c_{g,a+})^{|\nu_{P,g,a,g,a}|}}{(\gamma_{g,r1} c_{g,r1+})^{|\nu_{R,g,a,g,r1}|} (\gamma_{q,r2} c_{q,r2+})^{|\nu_{R,g,a,q,r2}|}} \leq \frac{1}{\zeta} K_{A,g,a}, \quad (\text{K29})$$

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

$$(\Delta c_{g,r1})_{w^{**}} = (\Delta c_{g,r1})_{F,w} = -k_w c_{g,r1-}, \quad (K30)$$

$$(\Delta c_{q,r2})_{w^{**}} = (\Delta c_{q,r2})_{F,w} = -k_w c_{q,r2-} \quad (K31)$$

and

$$(\Delta c_{g,a})_{w^{**}} = (\Delta c_{g,a})_{F,w} = - \left[ (\Delta c_{g,r1})_{F,w} + (\Delta c_{q,r2})_{F,w} \right] = k_w (c_{g,r1-} + c_{q,r2-}).$$

(K32)

At iteration  $w$ , if  $\zeta Q_{P,w} > Q_{R,w}$ , the preliminary concentration changes per iteration  $w$  are given by

$$(\Delta c_{g,r1})_{w^{**}} = (\Delta c_{g,r1})_{R,w} = k_w \frac{|v_{R,g,a,g,r1}| M_{g,r1}}{|v_{P,g,a,g,a}| M_{g,a}} c_{g,a-},$$

(K33)

$$(\Delta c_{q,r2})_{w^{**}} = (\Delta c_{q,r2})_{R,w} = k_w \frac{|v_{R,g,a,q,r2}| M_{q,r2}}{|v_{P,g,a,g,a}| M_{g,a}} c_{g,a-}$$

(K34)

and

$$(\Delta c_{g,a})_{w^{**}} = (\Delta c_{g,a})_{R,w} = - \left[ (\Delta c_{g,r1})_{R,w} + (\Delta c_{q,r2})_{R,w} \right] = -k_w c_{g,a-}.$$

(K35)

The functions used to calculate the intermediate differences of iteration  $w$  are

$$(\Delta c_{g,r1})_{w^*} = \frac{1}{2} \left[ (\Delta c_{g,r1})_{w^{**}} + \frac{M_{g,r1}}{M_{q,r2}} (\Delta c_{q,r2})_{w^{**}} \right],$$

(K36)

$$(\Delta c_{q,r2})_{w^*} = \frac{1}{2} \left[ (\Delta c_{q,r2})_{w^{**}} + \frac{M_{q,r2}}{M_{g,r1}} (\Delta c_{g,r1})_{w^{**}} \right]$$

(K37)

and

$$(\Delta c_{g,a})_{w^*} = - \left[ (\Delta c_{g,r1})_{w^*} + (\Delta c_{q,r2})_{w^*} \right].$$

(K38)

The final differences of iteration  $w$  are determined when mass conservation is enforced. If

$$(\Delta c_{g,r1})_{w^*} < (\Delta c_{g,r1})_{\max} = \frac{|v_{R,g,a,g,r1}| M_{g,r1}}{|v_{P,g,a,g,a}| M_{g,a}} c_{g,a-},$$

(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

$$(\Delta c_{q,r2})_{w*} < (\Delta c_{q,r2})_{\max} = \frac{|v_{R,g,a,q,r2}| M_{q,r2}}{|v_{P,g,a,g,a}| M_{g,a}} c_{g,a-} ,$$

(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,

$$(\Delta c_{g,a})_w = - \left[ (\Delta c_{g,r1})_w + (\Delta c_{q,r2})_w \right] .$$

(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  $N_{\text{equil}}$ , 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  $N_{\text{equil}}$ , then the end of iteration  $w$  is the end of the chemical equilibration process for reaction,  $a/g$  within  $\Delta t_\epsilon$ , 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  $\Delta t_\epsilon$ , and the flow calculations for the next  $\Delta t_\epsilon$  are begun. (Otherwise, without incrementing  $\Delta t_\epsilon$ , 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  $\Delta t_\epsilon$ .)

## 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,  $\alpha$  and  $\beta$ , 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,  $\Upsilon$  represents the unit solute concentration (with dimensions such as  $1 \text{ g/cm}^3$ ), just as it does in Equations G6, G7, G14, G15 and G20.

The first parameter,  $\alpha$ , is used to test whether the concentration of one or both reactants is approaching zero. If

$$\left(\frac{\Upsilon_{g,r1} c_{g,r1,w-}}{\Upsilon}\right)^{|v_{R,g,a,g,r1}|} > \alpha \left[ \left(\frac{\Upsilon_{g,a} c_{g,a,w-}}{\Upsilon}\right)^{|v_{P,g,a,g,a}|} + \left(\frac{\Upsilon_{q,r2} c_{q,r2,w-}}{\Upsilon}\right)^{|v_{R,g,a,q,r2}|} \right]$$

(K42)

or

$$\left(\frac{\Upsilon_{q,r2} c_{q,r2,w-}}{\Upsilon}\right)^{|v_{R,g,a,q,r2}|} > \alpha \left[ \left(\frac{\Upsilon_{g,a} c_{g,a,w-}}{\Upsilon}\right)^{|v_{P,g,a,g,a}|} + \left(\frac{\Upsilon_{g,r1} c_{g,r1,w-}}{\Upsilon}\right)^{|v_{R,g,a,g,r1}|} \right],$$

(K43)

then the algorithm for a fast (relative to  $\Delta t_\epsilon$ ) 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  $\Delta t_\epsilon$ ) reaction flow is used, regardless of the test results from Equations K42 and K43. At present, the routinely used value of  $\alpha$  is  $(10^{-13} \text{ erg}\cdot\text{s})/h$ ,

where  $h$  is the cgs Planck constant.

The second parameter,  $\beta$ , tests whether the concentrations of all reactant and product species are approaching zero. If

$$\beta > \left( \frac{Y_{g,a} C_{g,a,w-}}{Y} \right)^{|v_{P,g,a,g,a}|}, \quad (K44)$$

$$\beta > \left( \frac{Y_{g,r1} C_{g,r1,w-}}{Y} \right)^{|v_{R,g,a,g,r1}|} \quad (K45)$$

and

$$\beta > \left( \frac{Y_{q,r2} C_{q,r2,w-}}{Y} \right)^{|v_{R,g,a,q,r2}|}, \quad (K46)$$

neither the algorithm for a fast (relative to  $\Delta t_\varepsilon$ ) reaction flow, nor the algorithm for a slow (relative to  $\Delta t_\varepsilon$ ) 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  $\beta$  is  $h(10^{10}/\text{erg}\cdot\text{s})$ .

### One-reactant, one-product reactions

Expressions for one-reactant, one-product reactions are obtained by letting  $v_{R,g,a,q,r2} = 0$ ,  $M_{q,r2} = 0$ ,  $c_{q,r2-} = 0$ ,  $c_{q,r2+} = 0$  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  $v_{R,g,a,g,r1} = 1$  and  $v_{P,g,a,g,a} = 1$ , wherein one species simply changes into another. Such reactions would include conformational changes.

For all other one-reactant, one-product reactions,  $v_{R,g,a,g,r1} > 1$  and  $v_{P,g,a,g,a} = 1$ . Such

reactions would include any oligomerisation that can be described as an event in which  $v_{R,g,a,g,r1}$  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/>.

[K2] Moody, T. P. (2012b) The apparent sedimentation coefficient,  $s^*$ , and its distribution function,  $g(s^*)$ , within  $-\infty < s^* < \infty$ . <http://moodybiophysicalconsulting.blogspot.com/>.

## 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  $\xi$ -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,  $\xi_h$ . (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

$$m_{k,e-} = \sum_{h=1}^N V_h c_{k,e,h-} ,$$

(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,  $\Delta t_\varepsilon$ , 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  $\Delta t_\varepsilon$ , 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

$$m_{k,e+} = \sum_{h=1}^N V_h c_{k,e,h+} ,$$

(L2)

where the plus subscript indicates a concentration at the end of  $\Delta t_\varepsilon$ . Thus,  $c_{k,e,h+}$  is the concentration of species  $e$  of component  $k$  at the end of  $\Delta t_\varepsilon$ , 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  $\Delta t_\varepsilon$ , 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,  $\Delta t_\varepsilon$  is not incremented until the

convergence criterion (Equation J6) is met, or a set limit on the maximum number of iterations is reached. Within  $\Delta t_\epsilon$ , 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  $\Delta t_\epsilon$ . 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  $\Delta t_\epsilon$ ,  $c_{k,e,h+}$  multiplied by a mass-conservation-correction factor,  $K_{k,e,h+}$ , to obtain

$$c_{k,e,h^*} = c_{k,e,h+} K_{k,e,h+} ,$$

(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

$$K_{k,e,h+} = 1 - \delta_{k,e,h+} .$$

(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

$$\Lambda_{k,e,h+} = |\Delta c_{k,e,h+}|^\Lambda ,$$

(L8)

where  $\Lambda$ , the exponential term of  $\Lambda_{k,e,h+}$ , is an empirically chosen parameter. As Equation L8 is only applied if  $|\Delta c_{k,e,h+}| > 0$ ,  $\Lambda$  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,

$$N_{k,e+} = \sum_{h=1}^N V_h c_{k,e,h+} \Lambda_{k,e,h+} ,$$

(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  $N_{k,e+}$ , as it will if all  $c_{k,e,h+}$  equal zero or all  $\Lambda_{k,e,h+}$  equal zero,  $N_{k,e+}$  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  $N_{k,e+}$  to nought.)

Given the definitions and exceptions above,  $\delta_{k,e,h+}$  can be defined as

$$\delta_{k,e,h+} = \frac{(m_{k,e+} - m_{k,e-}) \Lambda_{k,e,h+}}{N_{k,e,h+}} .$$

(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  $(m_{k,e+} - m_{k,e-}) > 0$ , and  $\delta_{k,e,h+} < 0$  if  $(m_{k,e+} - m_{k,e-}) < 0$ .

For  $\Lambda \geq 1$ , as  $\Lambda$  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  $\Lambda$  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  $\Lambda$  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,  $\Lambda$  is typically set equal to 1.

### **Adjustments of the time increment**

If, at the end of  $\Delta t_\epsilon$ , 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  $\Delta t_\epsilon$ , and the flow calculations for the next  $\Delta t_\epsilon$  are begun. (Otherwise, without incrementing  $\Delta t_\epsilon$ , 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  $\Delta t_\epsilon$ .)

If, however, at the end of  $\Delta t_\epsilon$ , 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  $\Delta t_\epsilon$ . In that case, the time is not incremented by  $\Delta t_\epsilon$ ,  $\Delta t_\epsilon$  is halved, and the flows are recalculated using the shorter time increment.

Evidence of instability practically requires that  $\Delta t_\epsilon$  be decreased. Evidence of stability does not require that  $\Delta t_\epsilon$  be increased, but may justify testing whether  $\Delta t_\epsilon$  can be increased without jeopardising stability. To that end, an algorithm has been implemented that can raise  $\Delta t_\epsilon$  under conditions where it may be appropriate to do so. The evidence to raise  $\Delta t_\epsilon$  is less definitive than the evidence to lower it, however. Thus, limiting parameters, such as a maximum  $\Delta t_\epsilon$  value, are used to regulate the  $\Delta t_\epsilon$ -raising algorithm.

If permitted by the relevant limits,  $\Delta t_\epsilon$  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  $\Delta t$ ,  $\Lambda$ , 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

[L1] Claverie, J.-M., Dreux, H., and Cohen, R. (1975) Sedimentation of generalized systems of interacting particles. I. Solution of systems of complete Lamm equations. *Biopolymers*. **14** 1685-1700.

## Section M: Effects of solvent density on (apparent) reduced buoyant mass

The (apparent) reduced molar mass coefficient of solute component  $k$  is

$$\begin{aligned}\sigma_k &= \frac{\omega^2 s_k}{D_k} = \frac{\omega^2 \frac{1}{c_k} \sum_{q=1}^n \frac{c_q}{M_q} s_{k,q}}{\left(\frac{\partial c_k}{\partial r}\right)_t} \frac{1}{\sum_{q=1}^n \frac{D_{k,q}}{M_q} \left(\frac{\partial c_q}{\partial r}\right)_t} \\ &= \frac{\left(\frac{\partial \ln c_k}{\partial r}\right)_t \omega^2 \sum_{q=1}^n L_{k,q} M_q (1 - \bar{v}_q \rho)}{RT \sum_{q=1}^n \left(\frac{\partial \ln c_q}{\partial r}\right)_t L_{k,q} \left[1 + c_q \sum_{w=1}^n \left(\frac{\partial c_w}{\partial c_q}\right)_t \left(\frac{\partial \ln \gamma_q}{\partial c_w}\right)_{t,T,P,c_{a \neq w}}\right]},\end{aligned}$$

(M1 = A23)

and the reduced buoyant molar mass of solute component  $k$  is defined as

$$\begin{aligned}M_k^* &= \frac{RT}{\omega^2} \sigma_k = RT \frac{s_k}{D_k} = \frac{RT \frac{1}{c_k} \sum_{q=1}^n \frac{c_q}{M_q} s_{k,q}}{\left(\frac{\partial c_k}{\partial r}\right)_t} \frac{1}{\sum_{q=1}^n \frac{D_{k,q}}{M_q} \left(\frac{\partial c_q}{\partial r}\right)_t} \\ &= \frac{\left(\frac{\partial \ln c_k}{\partial r}\right)_t \sum_{q=1}^n L_{k,q} M_q (1 - \bar{v}_q \rho)}{\sum_{q=1}^n \left(\frac{\partial \ln c_q}{\partial r}\right)_t L_{k,q} \left[1 + c_q \sum_{w=1}^n \left(\frac{\partial c_w}{\partial c_q}\right)_t \left(\frac{\partial \ln \gamma_q}{\partial c_w}\right)_{t,T,P,c_{a \neq w}}\right]},\end{aligned}$$



(M2)

where  $R$  is the cgs ideal gas constant,  $\rho$  is the density of the solution,  $\xi = r^2/2$  ( $r$  being the radial position in the centrifuge),  $\xi_m = r_m^2/2$  ( $r_m$  being the innermost radial position of the system),  $T$  is the absolute temperature,  $t$  is time,  $P$  is the pressure of the system,  $\omega$  is the angular velocity of the centrifuge rotor,  $n$  is the total number of solute components,  $s_k$  is the (apparent) sedimentation 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  $k$ ,  $\bar{v}_q$  is the partial specific volume of solute component  $q$ ,  $c_q$  is the mass concentration of solute component  $q$ ,  $M_q$  is the molar mass of solute component  $q$ ,  $\gamma_q$  is the activity coefficient of solute component  $q$ ,  $c_w$  is the mass concentration of solute component  $w$ ,  $s_{k,q}$  is the coupled-flow-sedimentation coefficient of solute component  $k$  as affected by solute component  $q$ ,  $D_{k,q}$  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.

For further information about the parameters in Equations M1 and M2, see **Section A: An application of irreversible thermodynamics to analytical ultracentrifugation**. Most of the details regarding  $M_q$ , one of the parameters of Equations M1 and M2, are presented in **Section I: Calculating molar mass, chemical potential and partial specific volume for a multi-species component**. (Equation I19 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 M15 to M19) regarding  $M_q$  are presented in the last part of this section (**An examination of whether  $(M_q)_N$  and  $M_q$  can be regarded as molecular parameters**).

There are a number of obstacles to calculating  $M_k^*$ , 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

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

(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  $\eta$ , the solution viscosity, are known. The applicability of the Stokes equation, however, is questionable except as  $c_k$  approaches zero, at which point,  $\eta$  becomes identical to the solvent viscosity.

### **Reduced buoyant molar mass as a function of solution density**

In special cases,  $M_k^*$  can be calculated, and one such case is used here to examine the trends

exhibited by  $M_k^*$  as the density of the solution approaches its extrema. In the absence of all components other than the solvent and solute component  $k$ , and in the limit as  $c_k$  approaches zero, Equation M2 reduces to

$$M_k^0 = \lim_{c \rightarrow 0} \left( \lim_{c_{q \neq k} \rightarrow 0} M_k^* \right) = M_k \left( 1 - \frac{\rho_0}{\rho_k} \right), \quad (\text{M5})$$

where  $c$  is the total solute concentration,  $\rho_0$  is the density of the solvent, and  $\rho_k$  is the density of solute component  $k$ . This simplified form of Equation M2 stems first from the absence of any solute components other than  $k$ , which reduces Equation M2 to

$$\lim_{c_{q \neq k} \rightarrow 0} M_k^* = \frac{L_{k,k} M_k (1 - \bar{v}_k \rho)}{\left( \frac{\partial \ln c_k}{\partial \ln c_k} \right)_t L_{k,k} \left[ 1 + \left( \frac{\partial \ln \gamma_k}{\partial \ln c_k} \right)_{t,T,P} \right]} = \frac{M_k (1 - \bar{v}_k \rho)}{\left[ 1 + \left( \frac{\partial \ln \gamma_k}{\partial \ln c_k} \right)_{t,T,P} \right]}. \quad (\text{M6})$$

Further simplification stems from the application of the subsequent limit,

$$\lim_{c \rightarrow 0} \left( \lim_{c_{q \neq k} \rightarrow 0} M_k^* \right) = \lim_{c \rightarrow 0} \left\{ \frac{M_k (1 - \bar{v}_k \rho)}{\left[ 1 + \left( \frac{\partial \ln \gamma_k}{\partial \ln c_k} \right)_{t,T,P} \right]} \right\} = M_k \left( 1 - \frac{\rho_0}{\rho_k} \right), \quad (\text{M7})$$

to which the individual limits,

$$\lim_{c \rightarrow 0} \rho = \rho_0, \quad (\text{M8})$$

$$\lim_{c \rightarrow 0} \bar{v}_k = \frac{1}{\rho_k} \quad (\text{M9})$$

and

$$\lim_{c \rightarrow 0} \left( \frac{\partial \ln \gamma_k}{\partial \ln c_k} \right)_{t,T,P} = 0 \quad (\text{M10})$$

have been applied to obtain  $M_k^0$  as shown in Equation M5. If the solvent is incompressible, it also follows that

$$\lim_{c \rightarrow 0} \left( \frac{\partial \rho}{\partial \xi} \right)_t = \lim_{c \rightarrow 0} \left( \frac{\partial \rho_0}{\partial \xi} \right)_t = 0.$$

(M11)

At a given  $M_k$  and a given  $\rho_k$ ,

$$\lim_{\rho_0 \rightarrow \infty} M_k^0 = -\infty$$

(M12)

describes the buoyant molar mass of an infinitesimally dilute solute component  $k$  in a singularly dense black hole of a solvent.

At a given  $M_k$  and a given  $\rho_k$ ,

$$\lim_{\rho_0 \rightarrow \rho_k} M_k^0 = 0$$

(M13)

describes the buoyant molar mass of an infinitesimally dilute solute component  $k$  in a solvent with a density that is equal to the density of solute component  $k$ .

At a given  $M_k$  and a given  $\rho_k$ ,

$$\lim_{\rho_0 \rightarrow 0} M_k^0 = M_k$$

(M14)

describes the buoyant molar mass of an infinitesimally dilute solute component  $k$  in an otherwise perfect vacuum.

While it is not possible to achieve the extreme conditions applied in Equations M12 and M14, as hypothetical conditions, they nonetheless help to illustrate the trends sought regarding  $M_k^*$  over the range of possible solvent densities. Those trends show a dependence of  $M_k^*$  on  $\rho_0$ , and that dependence renders  $M_k^*$  a system parameter, rather than a molecular parameter.

**An examination of whether  $(M_q)_N$  and  $M_q$  can be regarded as molecular parameters**

The number average of the molar mass,  $(M_q)_N$ , is given, as in Equation I17, by

$$(M_q)_N = \frac{\sum_{a=1}^{n_q} N_{q,a} M_{q,a}}{\sum_{a=1}^{n_q} N_{q,a}},$$

(M15)

where the  $n_q$  species of component  $q$  are indexed by  $a$ , so that, for species  $a$  of component  $q$ ,  $M_{q,a}$  is the molar mass and  $N_{q,a}$  is the number of molecules (Equation I1). Each  $M_{q,a}$  can be considered independent of system properties by definition, as  $M_{q,a}$  is a defining molecular parameter. (For a given species, molar mass cannot change. Within a component, a change in molar mass requires an association of more than one species, or a dissociation into more than one species.) In the absence of a gravitational field, each  $N_{q,a}$  may change with such system properties as  $T$ ,  $P$  and solute concentrations at any given point in the system. Thus, in the absence of an gravitational field,  $(M_q)_N$  is a system parameter.

In the presence of a gravitational field, the gradient of the total molar potential of solute component  $q$  includes a gravitational contribution given, as in Equations I15 to I19, by

$$(M_q)_g \nabla[\omega^2 \xi - g_E h] = (M_q)_N \nabla[\omega^2 \xi - g_E h] + [\omega^2 \xi - g_E h] \nabla(M_q)_N,$$

(M16)

where  $(M_q)_g$  is the gradient-modified-average molar mass for all species of component  $q$ ,  $g_E$  is the magnitude of the gravitational field at the Earth's surface,  $h$  is the height above the Earth's surface,  $-\omega^2 \xi$  is the gravitational potential due to angular acceleration, and  $\omega^2 \nabla \xi$  is the gravitational field due to angular acceleration (Equation A3; Section H).

Dividing both sides of Equation M16 by  $\nabla[\omega^2 \xi - g_E h]$  yields

$$(M_q)_g = (M_q)_N + \frac{\nabla(M_q)_N}{\nabla \ln[\omega^2 \xi - g_E h]},$$

(M17)

where

$$\nabla(M_q)_N = \nabla \left( \frac{\sum_{a=1}^{n_q} N_{q,a} M_{q,a}}{\sum_{a=1}^{n_q} N_{q,a}} \right) = \frac{\sum_{a=1}^{n_q} M_{q,a} \nabla N_{q,a}}{\sum_{a=1}^{n_q} N_{q,a}} - (M_q)_N \frac{\sum_{a=1}^{n_q} \nabla N_{q,a}}{\sum_{a=1}^{n_q} N_{q,a}}.$$

(M18)

Equation M17 is an alternative form of Equation I19. As a comparison of Equations A2 and I20 shows,  $(M_q)_g$  is identical to  $M_q$ . As such, Equation M17 shows that  $M_q = (M_q)_N$  where  $\nabla(M_q)_N = 0$ .

In what follows,

$$(\nabla M_q)_N = \frac{\sum_{a=1}^{n_q} N_{q,a} \nabla M_{q,a}}{\sum_{a=1}^{n_q} N_{q,a}} = \frac{\sum_{a=1}^{n_q} N_{q,a}(0)}{\sum_{a=1}^{n_q} N_{q,a}} = 0,$$

(M19)

is the number-average gradient of the molar mass for all species of component  $q$ , and  $(\nabla M_q)_N = 0$  because each  $\nabla M_{q,a} = 0$ .

For a system at equilibrium, in the absence of a gravitational 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 M18 would equal zero everywhere, in which case, throughout the system,  $\nabla(M_q)_N$  would equal  $(\nabla M_q)_N = 0$ . 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,  $\nabla(M_q)_N = (\nabla M_q)_N = 0$ .

Regardless of whether a system is at equilibrium, in the presence of a gravitational 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 M18 will be nonzero, and wherever  $\nabla N_{q,a}$  is nonzero,  $\nabla(M_q)_N$  will be nonzero. According to Equation M17,  $M_q$  will differ from  $(M_q)_N$  where  $\nabla(M_q)_N$  differs from zero. Compared to  $(M_q)_N$ , then,  $M_q$  is especially dependent on gravitational field.

The discussion surrounding Equations M15 to M19 constitutes the argument that, regardless of whether a gravitational field is present,  $(M_q)_N$  and  $M_q = (M_q)_g$  are system parameters, in that they depend on system properties, such as  $T$ ,  $P$  and component concentrations.

## References

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### Section N: A simple coupled-flow equation for AUC

Equation A24 can be expressed as

$$I_k = c_k \left[ s_k^0 \left( \frac{1 + \sum_{a=1}^n p_{k,a} c_a}{1 + \sum_{a=1}^n h_{k,a} c_a} \right) \omega^2 r - D_k^0 \left( \frac{1 + \sum_{a=1}^n y_{k,a} c_a}{1 + \sum_{a=1}^n h_{k,a} c_a} \right) \left( \frac{\partial \ln c_k}{\partial r} \right)_t \right]$$

or

$$I_k = c_k D_k^0 \left( \frac{1 + \sum_{a=1}^n y_{k,a} c_a}{1 + \sum_{a=1}^n h_{k,a} c_a} \right) \left[ \sigma_k^0 \left( \frac{1 + \sum_{a=1}^n p_{k,a} c_a}{1 + \sum_{a=1}^n y_{k,a} c_a} \right) - \left( \frac{\partial \ln c_k}{\partial \xi} \right)_t \right] \sqrt{2\xi},$$

(N1)

where the expressions for  $\sigma_k$ ,  $D_k$  and  $s_k$ ,

$$\sigma_k = \sigma_k^0 \left( \frac{1 + \sum_{a=1}^n p_{k,a} c_a}{1 + \sum_{a=1}^n y_{k,a} c_a} \right),$$

(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

$$s_k = \frac{\sigma_k D_k}{\omega^2} = \frac{\sigma_k^0 D_k^0}{\omega^2} \left( \frac{1 + \sum_{a=1}^n p_{k,a} c_a}{1 + \sum_{a=1}^n h_{k,a} c_a} \right) = s_k^0 \left( \frac{1 + \sum_{a=1}^n p_{k,a} c_a}{1 + \sum_{a=1}^n h_{k,a} c_a} \right),$$

(N4)

respectively, were obtained by applying the truncated linear equations (3, 10 and 12) of Section D to Equations D5, D6 and D7, respectively.

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 molar mass, chemical potential and partial specific volume for a multi-species component**), yields

$$J_k M_k = I_k = M_k \sum_{q=1}^n \frac{c_q}{M_q} \left[ s_{k,q} \omega^2 r - D_{k,q} \left( \frac{\partial \ln c_q}{\partial r} \right)_t \right].$$

(N5)

For  $q = k$ , the right-hand-side of Equation N3 can be used to approximate  $D_{k,q}$  and the right-hand-side of Equation N4 can be used to approximate  $s_{k,q}$ . More generally,  $D_{k,q}$  can be approximated as

$$D_{k,q} = X_{k,q}^D D_q^0 \left( \frac{1 + \sum_{a=1}^n y_{q,a} c_a}{1 + \sum_{a=1}^n h_{q,a} c_a} \right)$$

(N6)

and  $s_{k,q}$  can be approximated as

$$s_{k,q} = X_{k,q}^S s_q^0 \left( \frac{1 + \sum_{a=1}^n p_{q,a} c_a}{1 + \sum_{a=1}^n h_{q,a} c_a} \right),$$

(N7)

where  $X_{k,q}^D$  and  $X_{k,q}^S$  are constants. Thus, Equations N6 and N7 become equivalent to the truncated forms of  $X_{k,q}^D$  times Equation D6 and  $X_{k,q}^S$  times Equation D7, respectively, when  $q = k$ . Applying Equations N6 and N7 to Equation N5 yields



$$\begin{aligned}
 I_k &= M_k \sum_{q=1}^n \frac{c_q}{M_q} \left[ X_{k,q}^S S_q^0 \left( \frac{1 + \sum_{a=1}^n p_{q,a} c_a}{1 + \sum_{a=1}^n h_{q,a} c_a} \right) \omega^2 r - X_{k,q}^D D_q^0 \left( \frac{1 + \sum_{a=1}^n y_{q,a} c_a}{1 + \sum_{a=1}^n h_{q,a} c_a} \right) \left( \frac{\partial \ln c_q}{\partial r} \right)_t \right] \\
 &= M_k \left\{ \omega^2 r \left[ \sum_{q=1}^n \frac{c_q}{M_q} X_{k,q}^S S_q^0 \left( \frac{1 + \sum_{a=1}^n p_{q,a} c_a}{1 + \sum_{a=1}^n h_{q,a} c_a} \right) \right] \right. \\
 &\quad \left. - \left[ \sum_{q=1}^n \left( \frac{\partial c_q}{\partial r} \right)_t \frac{X_{k,q}^D D_q^0}{M_q} \left( \frac{1 + \sum_{a=1}^n y_{q,a} c_a}{1 + \sum_{a=1}^n h_{q,a} c_a} \right) \right] \right\}.
 \end{aligned}$$

(N8)

For  $n = 2$ , Equation N8 yields

$$\begin{aligned}
 I_1 &= M_1 \left\{ \omega^2 r \left[ \frac{c_1}{M_1} X_{1,1}^S S_1^0 \left( \frac{1 + p_{1,1} c_1 + p_{1,2} c_2}{1 + h_{1,1} c_1 + h_{1,2} c_2} \right) + \frac{c_2}{M_2} X_{1,2}^S S_2^0 \left( \frac{1 + p_{2,1} c_1 + p_{2,2} c_2}{1 + h_{2,1} c_1 + h_{2,2} c_2} \right) \right] \right. \\
 &\quad - \left[ \frac{1}{M_1} \left( \frac{\partial c_1}{\partial r} \right)_t X_{1,1}^D D_1^0 \left( \frac{1 + y_{1,1} c_1 + y_{1,2} c_2}{1 + h_{1,1} c_1 + h_{1,2} c_2} \right) \right. \\
 &\quad \left. \left. + \frac{1}{M_2} \left( \frac{\partial c_2}{\partial r} \right)_t X_{1,2}^D D_2^0 \left( \frac{1 + y_{2,1} c_1 + y_{2,2} c_2}{1 + h_{2,1} c_1 + h_{2,2} c_2} \right) \right] \right\}
 \end{aligned}$$

and

$$\begin{aligned}
 I_2 &= M_2 \left\{ \omega^2 r \left[ \frac{c_1}{M_1} X_{2,1}^S S_1^0 \left( \frac{1 + p_{1,1} c_1 + p_{1,2} c_2}{1 + h_{1,1} c_1 + h_{1,2} c_2} \right) + \frac{c_2}{M_2} X_{2,2}^S S_2^0 \left( \frac{1 + p_{2,1} c_1 + p_{2,2} c_2}{1 + h_{2,1} c_1 + h_{2,2} c_2} \right) \right] \right. \\
 &\quad - \left[ \frac{1}{M_1} \left( \frac{\partial c_1}{\partial r} \right)_t X_{2,1}^D D_1^0 \left( \frac{1 + y_{1,1} c_1 + y_{1,2} c_2}{1 + h_{1,1} c_1 + h_{1,2} c_2} \right) \right. \\
 &\quad \left. \left. + \frac{1}{M_2} \left( \frac{\partial c_2}{\partial r} \right)_t X_{2,2}^D D_2^0 \left( \frac{1 + y_{2,1} c_1 + y_{2,2} c_2}{1 + h_{2,1} c_1 + h_{2,2} c_2} \right) \right] \right\}.
 \end{aligned}$$

(N9)

The coupled-flow analogue of the (apparent) reduced molar mass coefficient (Equation A23) is defined as

$$\sigma_{k,q} = \frac{\omega^2 \mathbf{s}_{k,q}}{\mathbf{D}_{k,q}} = \frac{\omega^2 M_q (1 - \bar{v}_q \rho)}{RT \left[ 1 + c_q \sum_{w=1}^n \left( \frac{\partial c_w}{\partial c_q} \right)_t \left( \frac{\partial \ln \gamma_q}{\partial c_w} \right)_{t,T,P,c_{a \neq w}} \right]},$$

(N10)

where  $\mathbf{D}_{k,q}$  and  $\mathbf{s}_{k,q}$  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  $\mathbf{s}_{k,q}$  cancels  $L_{k,q}$  from  $\mathbf{D}_{k,q}$ . (See the discussion following Equation A20.) Using Equations N6 and N7 to express  $\mathbf{D}_{k,q}$  and  $\mathbf{s}_{k,q}$  respectively, and introducing a set of constants denoted by  $X_{k,q}^\sigma$ ,  $\sigma_{k,q}$  can be approximated as

$$\sigma_{k,q} = \frac{\omega^2 \mathbf{s}_{k,q}}{\mathbf{D}_{k,q}} = \frac{\omega^2 X_{k,q}^s s_q^0 \left( \frac{1 + \sum_{a=1}^n p_{q,a} c_a}{1 + \sum_{a=1}^n h_{q,a} c_a} \right)}{X_{k,q}^D D_q^0 \left( \frac{1 + \sum_{a=1}^n y_{q,a} c_a}{1 + \sum_{a=1}^n h_{q,a} c_a} \right)} = X_{k,q}^\sigma \sigma_q^0 \left( \frac{1 + \sum_{a=1}^n p_{q,a} c_a}{1 + \sum_{a=1}^n y_{q,a} c_a} \right),$$

(N11)

where, by virtue of  $X_{k,q}^\sigma$ ,  $X_{k,q}^D$ ,  $X_{k,q}^s$ ,  $\sigma_q^0$ ,  $D_q^0$  and  $s_q^0$  being constants,

$$X_{k,q}^\sigma \sigma_q^0 = \frac{\omega^2 X_{k,q}^s s_q^0}{X_{k,q}^D D_q^0}$$

(N12)

is a constant to the extent that  $\omega$  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

$$I_k = M_k \sum_{q=1}^n \frac{c_q}{M_q} \mathbf{D}_{k,q} \left[ \sigma_{k,q} r - \left( \frac{\partial \ln c_q}{\partial r} \right)_t \right] = M_k \sum_{q=1}^n \frac{c_q}{M_q} \mathbf{D}_{k,q} \left[ \sigma_{k,q} - \left( \frac{\partial \ln c_q}{\partial \xi} \right)_t \right] \sqrt{2\xi},$$

(N13)

where, as defined in Section A,  $\xi = r^2/2$ . For  $q = k$ , the right-hand-side of Equation N2 can be used to approximate  $\sigma_{k,q}$  and the right-hand-side of Equation N3 can be used to approximate  $\mathbf{D}_{k,q}$ . More generally,  $\mathbf{D}_{k,q}$  can be approximated by Equation N6, and  $\sigma_{k,q}$  can be approximated by Equation N11. Applying Equations N6 and N11 to Equation N13 yields

$$I_k = M_k \sqrt{2\xi} \sum_{q=1}^n \frac{c_q}{M_q} X_{k,q}^D D_q^0 \left( \frac{1 + \sum_{a=1}^n y_{q,a} c_a}{1 + \sum_{a=1}^n h_{q,a} c_a} \right) \left[ X_{k,q}^\sigma \sigma_q^0 \left( \frac{1 + \sum_{a=1}^n p_{q,a} c_a}{1 + \sum_{a=1}^n y_{q,a} c_a} \right) - \left( \frac{\partial \ln c_q}{\partial \xi} \right)_t \right].$$

(N14)

For  $n = 2$ , Equation N14 yields

$$I_1 = M_1\sqrt{2\xi} \left\{ \left[ \frac{c_1}{M_1} X_{1,1}^D X_{1,1}^\sigma D_1^0 \sigma_1^0 \left( \frac{1 + p_{1,1}c_1 + p_{1,2}c_2}{1 + h_{1,1}c_1 + h_{1,2}c_2} \right) \right] \right. \\ \left. - \left[ \frac{1}{M_1} \left( \frac{\partial c_1}{\partial \xi} \right)_t X_{1,1}^D D_1^0 \left( \frac{1 + y_{1,1}c_1 + y_{1,2}c_2}{1 + h_{1,1}c_1 + h_{1,2}c_2} \right) \right] \right. \\ \left. + \left[ \frac{c_2}{M_2} X_{1,2}^D X_{1,2}^\sigma D_2^0 \sigma_2^0 \left( \frac{1 + p_{2,1}c_1 + p_{2,2}c_2}{1 + h_{2,1}c_1 + h_{2,2}c_2} \right) \right] \right. \\ \left. - \left[ \frac{1}{M_2} \left( \frac{\partial c_2}{\partial \xi} \right)_t X_{1,2}^D D_2^0 \left( \frac{1 + y_{2,1}c_1 + y_{2,2}c_2}{1 + h_{2,1}c_1 + h_{2,2}c_2} \right) \right] \right\}$$

and

$$I_2 = M_2\sqrt{2\xi} \left\{ \left[ \frac{c_1}{M_1} X_{2,1}^D X_{2,1}^\sigma D_1^0 \sigma_1^0 \left( \frac{1 + p_{1,1}c_1 + p_{1,2}c_2}{1 + h_{1,1}c_1 + h_{1,2}c_2} \right) \right] \right. \\ \left. - \left[ \frac{1}{M_1} \left( \frac{\partial c_1}{\partial \xi} \right)_t X_{2,1}^D D_1^0 \left( \frac{1 + y_{1,1}c_1 + y_{1,2}c_2}{1 + h_{1,1}c_1 + h_{1,2}c_2} \right) \right] \right. \\ \left. + \left[ \frac{c_2}{M_2} X_{2,2}^D X_{2,2}^\sigma D_2^0 \sigma_2^0 \left( \frac{1 + p_{2,1}c_1 + p_{2,2}c_2}{1 + h_{2,1}c_1 + h_{2,2}c_2} \right) \right] \right. \\ \left. - \left[ \frac{1}{M_2} \left( \frac{\partial c_2}{\partial \xi} \right)_t X_{2,2}^D D_2^0 \left( \frac{1 + y_{2,1}c_1 + y_{2,2}c_2}{1 + h_{2,1}c_1 + h_{2,2}c_2} \right) \right] \right\}.$$

(N15)

### Re-evaluating $s_k$ , $D_k$ and $\sigma_k$

In terms of  $D_k$  and  $s_k$ , or  $D_k$  and  $\sigma_k$ , the mass flow of solute component  $k$  can be written as

$$I_k = J_k M_k = c_k \left[ s_k \omega^2 r - D_k \left( \frac{\partial \ln c_k}{\partial r} \right)_t \right]$$

(N16)

or

$$I_k = J_k M_k = c_k D_k \left[ \sigma_k - \left( \frac{\partial \ln c_k}{\partial \xi} \right)_t \right] \sqrt{2\xi},$$

(N17)

both forms of which are shown in Equation A24.

Replacing  $D_k$  and  $s_k$  of Equation N16 with

$$D_k = \frac{M_k}{\left(\frac{\partial c_k}{\partial r}\right)_t} \sum_{q=1}^n \frac{\left(\frac{\partial c_q}{\partial r}\right)_t}{M_q} X_{k,q}^D D_q^0 \left( \frac{1 + \sum_{a=1}^n y_{q,a} c_a}{1 + \sum_{a=1}^n h_{q,a} c_a} \right)$$

(N18)

and

$$S_k = \frac{M_k}{c_k} \sum_{q=1}^n \frac{c_q}{M_q} X_{k,q}^S S_q^0 \left( \frac{1 + \sum_{a=1}^n p_{q,a} c_a}{1 + \sum_{a=1}^n h_{q,a} c_a} \right),$$

(N19)

respectively, yields Equation N8. Equations N18 and N19 approximate Equations A21 and A22, respectively.

Replacing  $D_k$  and  $\sigma_k$  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

$$\begin{aligned} \sigma_k = \frac{\omega^2 S_k}{D_k} &= \left(\frac{\partial \ln c_k}{\partial \xi}\right)_t \frac{\omega^2 \sum_{q=1}^n \frac{c_q}{M_q} X_{k,q}^S S_q^0 \left( \frac{1 + \sum_{a=1}^n p_{q,a} c_a}{1 + \sum_{a=1}^n h_{q,a} c_a} \right)}{\sum_{q=1}^n \frac{\left(\frac{\partial c_q}{\partial \xi}\right)_t}{M_q} X_{k,q}^D D_q^0 \left( \frac{1 + \sum_{a=1}^n y_{q,a} c_a}{1 + \sum_{a=1}^n h_{q,a} c_a} \right)} \\ &= \left(\frac{\partial \ln c_k}{\partial \xi}\right)_t \frac{\sum_{q=1}^n \frac{c_q}{M_q} X_{k,q}^S S_q^0 X_{k,q}^D D_q^0 \left( \frac{1 + \sum_{a=1}^n p_{q,a} c_a}{1 + \sum_{a=1}^n h_{q,a} c_a} \right)}{\sum_{q=1}^n \frac{\left(\frac{\partial c_q}{\partial \xi}\right)_t}{M_q} X_{k,q}^D D_q^0 \left( \frac{1 + \sum_{a=1}^n y_{q,a} c_a}{1 + \sum_{a=1}^n h_{q,a} c_a} \right)} \\ &= \left(\frac{\partial \ln c_k}{\partial \xi}\right)_t \frac{\sum_{q=1}^n \frac{c_q}{M_q} X_{k,q}^S S_q^0 D_q^0 \left( \frac{1 + \sum_{a=1}^n p_{q,a} c_a}{1 + \sum_{a=1}^n h_{q,a} c_a} \right)}{\sum_{q=1}^n \frac{\left(\frac{\partial c_q}{\partial \xi}\right)_t}{M_q} X_{k,q}^D D_q^0 \left( \frac{1 + \sum_{a=1}^n y_{q,a} c_a}{1 + \sum_{a=1}^n h_{q,a} c_a} \right)} \end{aligned}$$

(N21)

respectively, yields Equation N14. Equations N20 and N21 approximate Equations A21 and A23, respectively. Multiplying both sides of Equation N12 by  $X_{k,q}^D D_q^0$  yields  $X_{k,q}^D X_{k,q}^\sigma D_q^0 \sigma_q^0 = \omega^2 X_{k,q}^S s_q^0$ , the left-hand side of which is used to replace  $\omega^2 X_{k,q}^S s_q^0$  in the numerator of Equation N21. As  $D_q^0 \sigma_q^0 = \omega^2 s_q^0$  (Equations A21, B23 $\bar{+}$ , C34 $\bar{+}$ ),  $X_{k,q}^S = X_{k,q}^D X_{k,q}^\sigma$ , in which the derived parameter is actually

$$X_{k,q}^\sigma = \frac{X_{k,q}^S}{X_{k,q}^D}.$$

(N22)

Provided that  $X_{k,q}^D$  is not equal to zero,  $X_{k,q}^\sigma$  can be calculated using Equation 26. Where  $X_{k,q}^D = 0$ ,  $X_{k,q}^\sigma$  is undefined, except that the product,  $X_{k,q}^\sigma X_{k,q}^D$ , is nevertheless treated as being equal to  $X_{k,q}^S$ .

When all  $X_{k,q \neq k}^D$  values are equal to zero, Equation N20 reduces to Equation N1. Similarly, when all  $X_{k,q \neq k}^D$  and  $X_{k,q \neq k}^S$  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  $X_{k,q \neq k}^D$  and  $X_{k,q \neq k}^S$  values are equal to zero, however,  $h_{q,a}$  values can wield some influence on  $\sigma_k$  values, even at equilibrium, unless all  $X_{k,q \neq k}^D$  and  $X_{k,q \neq k}^S$  values are equal to zero. This residual influence of  $h_{q,a}$  is a flaw of the approximation of  $\sigma_k$  by Equation N21, as the equation (A23) that defines  $\sigma_k$  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 $\xi$ -independent coefficients of the basis functions indexed by $j$

Equations 33 $-$ , 33 $+$ , 34 $-$  and 34 $+$  of Section C (**A solution to the  $t$ - and  $\xi$ -dependent continuity equation for AUC 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  $\xi$ -independent, the solute concentrations at each explicitly included spatial element,  $\xi_j$ , were replaced by the corresponding  $\xi$ -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  $\xi$ -dependent continuity equation in terms of species (Section C), Equations C33- and C33+ can be replaced by  $\xi$ -independent diffusion coefficients in the form of

$$D_{k,e,j-} = \frac{M_{k,e}}{\frac{\Delta c_{k,e,j-}}{\Delta \xi}} \sum_{q=1}^n \sum_{a=1}^{n_q} \frac{\Delta c_{q,a,j-}}{\Delta \xi} \frac{1}{M_{q,a}} X_{[k,e],[q,a]}^D D_{q,a,j-}^0 - \left( \frac{\sum_{b=1}^{\infty} \sum_{w=1}^n \sum_{u=1}^{n_w} y_{b,q,a,w,u} \frac{dc_{w,u,j-}^b}{dc_{w,u,j-}}}{\sum_{b=1}^{\infty} \sum_{w=1}^n \sum_{u=1}^{n_w} h_{b,q,a,w,u} \frac{dc_{w,u,j-}^b}{dc_{w,u,j-}}} \right)$$

(N23-)

and

$$D_{k,e,j+} = \frac{M_{k,e}}{\frac{\Delta c_{k,e,j+}}{\Delta \xi}} \sum_{q=1}^n \sum_{a=1}^{n_q} \frac{\Delta c_{q,a,j+}}{\Delta \xi} \frac{1}{M_{q,a}} X_{[k,e],[q,a]}^D D_{q,a,j+}^0 - \left( \frac{\sum_{b=1}^{\infty} \sum_{w=1}^n \sum_{u=1}^{n_w} y_{b,q,a,w,u} \frac{dc_{w,u,j+}^b}{dc_{w,u,j+}}}{\sum_{b=1}^{\infty} \sum_{w=1}^n \sum_{u=1}^{n_w} h_{b,q,a,w,u} \frac{dc_{w,u,j+}^b}{dc_{w,u,j+}}} \right),$$

(N23+)

which are based on the  $\xi$ -dependent function given by Equation N20, while Equations C33- and C33+ can be replaced by  $\xi$ -independent reduced molar mass coefficients in the form of

$$\sigma_{k,e,j-} = \frac{\omega^2 s_{k,e,j-}}{D_{k,e,j-}}$$

$$= \frac{\frac{M_{k,e}}{c_{k,e,j-}} \sum_{q=1}^n \sum_{a=1}^{n_q} \frac{c_{q,a,j-}}{M_{q,a}} X_{[k,e],[q,a]}^S \sigma_{q,a,j-}^0 - D_{q,a,j-}^0}{D_{k,e,j-}} - \left( \frac{\sum_{b=1}^{\infty} \sum_{w=1}^n \sum_{u=1}^{n_w} p_{b,q,a,w,u} \frac{dc_{w,u,j-}^b}{dc_{w,u,j-}}}{\sum_{b=1}^{\infty} \sum_{w=1}^n \sum_{u=1}^{n_w} h_{b,q,a,w,u} \frac{dc_{w,u,j-}^b}{dc_{w,u,j-}}} \right)$$

(N24-)

and

$$\sigma_{k,e,j+} = \frac{\omega^2 s_{k,e,j+}}{D_{k,e,j+}}$$

$$= \frac{\frac{M_{k,e}}{c_{k,e,j+}} \sum_{q=1}^n \sum_{a=1}^{n_q} \frac{c_{q,a,j+}}{M_{q,a}} X_{[k,e],[q,a]}^S \sigma_{q,a,j+}^0 D_{q,a,j+}^0 \left( \frac{\sum_{b=1}^{\infty} \sum_{w=1}^n \sum_{u=1}^{n_w} p_{b,q,a,w,u} \frac{dc_{w,u,j+}^b}{dc_{w,u,j+}}}{\sum_{b=1}^{\infty} \sum_{w=1}^n \sum_{u=1}^{n_w} h_{b,q,a,w,u} \frac{dc_{w,u,j+}^b}{dc_{w,u,j+}}} \right)}{D_{k,e,j+}},$$

(N24+)

which are based on the  $\xi$ -dependent function given by Equation N21.

To define the parameters of Equations N23–, N23+, N24– and N24+, it is convenient to let  $\alpha$  represent component  $k$ ,  $q$  or  $w$ , let  $\beta$  represent species  $e$ ,  $a$  or  $u$ , and let  $j\mp$  represent  $j$ - or  $j+$ , where  $j$  refers to spatial element  $\xi_j$ , 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+,  $n$  is the number of solute components,  $n_\alpha$  is the number of species that constitute solute component  $\alpha$ ,  $c_{\alpha,\beta}$  is the concentration of species  $\beta$  of component  $\alpha$ ,  $D_{\alpha,\beta}$  is the diffusion coefficient of species  $\beta$  of component  $\alpha$ ,  $\sigma_{\alpha,\beta}$  is the reduced molar mass coefficient of species  $\beta$  of component  $\alpha$ ,  $D_{\alpha,\beta}^0$  equals  $D_{\alpha,\beta}$  in the limit as  $c$  approaches 0,  $\sigma_{\alpha,\beta}^0$  equals  $\sigma_{\alpha,\beta}$  in the limit as  $c$  approaches 0,  $c_{\alpha,\beta,j-}$  at all  $\xi$  equals the concentration of species  $\beta$  of solute component  $\alpha$  at  $\xi_j$  at time  $t$ ,  $c_{\alpha,\beta,j+}$  at all  $\xi$  equals the concentration of species  $\beta$  of solute component  $\alpha$  at  $\xi_j$  at time  $[t + \Delta t]$ ,  $D_{\alpha,\beta,j-}$  at all  $\xi$  equals  $D_{\alpha,\beta}$  at  $\xi_j$  at time  $t$ ,  $D_{\alpha,\beta,j+}$  at all  $\xi$  equals  $D_{\alpha,\beta}$  at  $\xi_j$  at time  $[t + \Delta t]$ ,  $\sigma_{\alpha,\beta,j-}$  at all  $\xi$  equals  $\sigma_{\alpha,\beta}$  at  $\xi_j$  at time  $t$ ,  $\sigma_{\alpha,\beta,j+}$  at all  $\xi$  equals  $\sigma_{\alpha,\beta}$  at  $\xi_j$  at time  $[t + \Delta t]$ ,  $D_{\alpha,\beta,j\mp}^0$  equals  $D_{\alpha,\beta,j\mp}$  in the limit as  $c$  approaches 0,  $\sigma_{\alpha,\beta,j\mp}^0$  equals  $\sigma_{\alpha,\beta,j\mp}$  in the limit as  $c$  approaches 0,  $X_{[k,e],[q,a]}^D$  is the coefficient that couples  $D_{q,a,j\mp}^0$  to  $D_{k,e,j\mp}$ ,  $X_{[k,e],[q,a]}^S$  is the coefficient that couples  $\sigma_{q,a,j\mp}^0 D_{q,a,j\mp}^0$  to  $\sigma_{k,e,j\mp}$ ,  $M_{k,e}$  is the molar mass of species  $e$  of solute component  $k$ ,  $s_{k,e}$  is the sedimentation coefficient of species  $e$  of solute component  $k$ ,  $\omega^2 s_{k,e,j-}$  at all  $\xi$  equals  $\omega^2 s_{k,e}$  at  $\xi_j$  at time  $t$ , and  $\omega^2 s_{k,e,j+}$  at all  $\xi$  equals  $\omega^2 s_{k,e}$  at  $\xi_j$  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  $b^{\text{th}}$  of up to an infinite number of coefficients of proportionality for the density increment, 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  $(\partial D^{\circ}_{q,a}/\partial \xi)_t = 0$  and  $(\partial D^{\circ}_{q,a}/\partial t)_\xi = 0$  at all  $\xi$  at all times,  $D^{\circ}_{q,a,j-} = D^{\circ}_{q,a}$  and  $D^{\circ}_{q,a,j+} = D^{\circ}_{q,a}$  at all  $\xi$  at all times. Provided that  $(\partial \sigma^{\circ}_{q,a}/\partial \xi)_t = 0$  and  $(\partial \sigma^{\circ}_{q,a}/\partial t)_\xi = 0$  at all  $\xi$  at all times after a change in the gravitational field is complete,  $\sigma^{\circ}_{q,a,j-} = \sigma^{\circ}_{q,a}$  and  $\sigma^{\circ}_{q,a,j+} = \sigma^{\circ}_{q,a}$  at all  $\xi$  at all times after a change in the gravitational field is complete.

With  $\alpha$  representing component  $k$  or  $q$ ,  $\beta$  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  $\xi$  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  $\xi$  independent result.

Equations N23 $\mp$  and N24 $\mp$  can be used in place of Equations C33 $\mp$  and C34 $\mp$ , 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 $\mp$ , N24 $\mp$  and N25. The component-equivalents of Equations N23 $\mp$  and N24 $\mp$  can be used in place of Equations B22 $\mp$  and B23 $\mp$ , 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 AUC**) for  $L_{k,q}$  yields

$$L_{k,q} = \frac{c_q \mathbf{s}_{k,q}}{M_q M_q (1 - \bar{v}_q \rho)} = \frac{c_q \mathbf{D}_{k,q}}{M_q RT \left[ 1 + c_q \sum_{w=1}^n \left( \frac{\partial c_w}{\partial c_q} \right)_t \left( \frac{\partial \ln \gamma_q}{\partial c_w} \right)_{t,T,P,c_{\alpha \neq w}} \right]}$$

(N26)

Using Equations N6 and N7 to approximate  $\mathbf{D}_{k,q}$  and  $\mathbf{s}_{k,q}$  respectively, results in

$$L_{k,q} = \frac{c_q X_{k,q}^s S_q^0 \left( \frac{1 + \sum_{a=1}^n p_{q,a} c_a}{1 + \sum_{a=1}^n h_{q,a} c_a} \right)}{M_q M_q (1 - \bar{v}_q \rho)} = \frac{c_q X_{k,q}^D D_q^0 \left( \frac{1 + \sum_{a=1}^n y_{q,a} c_a}{1 + \sum_{a=1}^n h_{q,a} c_a} \right)}{M_q RT \left[ 1 + c_q \sum_{w=1}^n \left( \frac{\partial c_w}{\partial c_q} \right)_t \left( \frac{\partial \ln \gamma_q}{\partial c_w} \right)_{t,T,P,c_{a \neq w}} \right]}$$

(N27)

and division by  $c_q / (M_q [1 + \sum_{a=1}^n h_{q,a} c_a])$  yields

$$\frac{X_{k,q}^s S_q^0 (1 + \sum_{a=1}^n p_{q,a} c_a)}{M_q (1 - \bar{v}_q \rho)} = \frac{X_{k,q}^D D_q^0 (1 + \sum_{a=1}^n y_{q,a} c_a)}{RT \left[ 1 + c_q \sum_{w=1}^n \left( \frac{\partial c_w}{\partial c_q} \right)_t \left( \frac{\partial \ln \gamma_q}{\partial c_w} \right)_{t,T,P,c_{a \neq w}} \right]}$$

(N28)

Thus, as the total solute concentration,  $c$ , approaches zero,

$$\lim_{c \rightarrow 0} \frac{X_{k,q}^s S_q^0 (1 + \sum_{a=1}^n p_{q,a} c_a)}{M_q (1 - \bar{v}_q \rho)} = \lim_{c \rightarrow 0} \frac{X_{k,q}^D D_q^0 (1 + \sum_{a=1}^n y_{q,a} c_a)}{RT \left[ 1 + c_q \sum_{w=1}^n \left( \frac{\partial c_w}{\partial c_q} \right)_t \left( \frac{\partial \ln \gamma_q}{\partial c_w} \right)_{t,T,P,c_{a \neq w}} \right]}$$

(N29)

the result of which is

$$\frac{X_{k,q}^s S_q^0}{M_q \left( 1 - \frac{\rho_0}{\rho_q} \right)} = \frac{X_{k,q}^D D_q^0}{RT},$$

(N30)

where  $\rho_0$  is the density of the solvent, and  $\rho_k$  is the density of solute component  $k$

(Equations M5 to M7). Solving for  $X_{k,q}^D$  yields

$$X_{k,q}^D = \frac{X_{k,q}^s S_q^0 RT}{D_q^0 M_q \left( 1 - \frac{\rho_0}{\rho_q} \right)}.$$

(N31)

Applying the limit as  $c$  approaches zero to Equation M2, and comparing the result to the Equation M7, shows that

$$\frac{S_q^0 RT}{D_q^0} = M_q \left( 1 - \frac{\rho_0}{\rho_q} \right).$$

(N32)

Thus,

$$X_{k,q}^D = X_{k,q}^S.$$

(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  $X_{k,q}^S$ , it may be convenient to treat them as independent variables in a simulation program, so that the coupled-flow effects on  $s_q$  can be evaluated separately from the coupled-flow effects on  $D_q$ .

**In the limit as  $t$  approaches  $\infty$**

Equation N21 can be rewritten as

$$\sigma_k = \left( \frac{\partial \ln c_k}{\partial \xi} \right)_t \frac{\sum_{q=1}^n \frac{c_q}{M_q} X_{k,q}^S \sigma_q^0 D_q^0 \left( \frac{1 + \sum_{a=1}^n p_{q,a} c_a}{1 + \sum_{a=1}^n h_{q,a} c_a} \right)}{\sum_{q=1}^n \frac{\left( \frac{\partial c_q}{\partial \xi} \right)_t}{M_q} X_{k,q}^D D_q^0 \left( \frac{1 + \sum_{a=1}^n y_{q,a} c_a}{1 + \sum_{a=1}^n h_{q,a} c_a} \right)}.$$

(N34)

Equation A36 applies to the system at equilibrium, and dividing both sides of that equation by  $c_k$  yields

$$\sigma_k = \left( \frac{\partial \ln c_k}{\partial \xi} \right)_t.$$

(N35)

As such, it must be that

$$\lim_{t \rightarrow \infty} \frac{\sigma_k}{\left( \frac{\partial \ln c_k}{\partial \xi} \right)_t} = \lim_{t \rightarrow \infty} \frac{\sum_{q=1}^n \frac{c_q}{M_q} X_{k,q}^S \sigma_q^0 D_q^0 \left( \frac{1 + \sum_{a=1}^n p_{q,a} c_a}{1 + \sum_{a=1}^n h_{q,a} c_a} \right)}{\sum_{q=1}^n \frac{\left( \frac{\partial c_q}{\partial \xi} \right)_t}{M_q} X_{k,q}^D D_q^0 \left( \frac{1 + \sum_{a=1}^n y_{q,a} c_a}{1 + \sum_{a=1}^n h_{q,a} c_a} \right)} = 1$$

(N36)

at each spatial position,  $\xi$ , in the system at equilibrium.

The more general equation, A23, can be rewritten as

$$\sigma_k = \left( \frac{\partial \ln c_k}{\partial \xi} \right)_t \frac{\omega^2 \sum_{q=1}^n \frac{1}{M_q} c_q \mathbf{S}_{k,q}}{\sum_{q=1}^n \frac{1}{M_q} \left( \frac{\partial c_q}{\partial \xi} \right)_t \mathbf{D}_{k,q}}, \quad (\text{N37})$$

$$\sigma_k = \left( \frac{\partial \ln c_k}{\partial \xi} \right)_t \frac{\sum_{q=1}^n \frac{1}{M_q} c_q \sigma_{k,q} \mathbf{D}_{k,q}}{\sum_{q=1}^n \frac{1}{M_q} \left( \frac{\partial c_q}{\partial \xi} \right)_t \mathbf{D}_{k,q}} \quad (\text{N38})$$

or

$$\sigma_k = \left( \frac{\partial \ln c_k}{\partial \xi} \right)_t \frac{\omega^2 \sum_{q=1}^n L_{k,q} M_q (1 - \bar{v}_q \rho)}{RT \sum_{q=1}^n \left( \frac{\partial \ln c_q}{\partial \xi} \right)_t L_{k,q} \left[ 1 + c_q \sum_{w=1}^n \left( \frac{\partial c_w}{\partial c_q} \right)_t \left( \frac{\partial \ln \gamma_q}{\partial c_w} \right)_{t,T,P,c_{a \neq w}} \right]}, \quad (\text{N39})$$

which, in the limit as  $t$  approaches  $\infty$ , yield

$$\lim_{t \rightarrow \infty} \frac{\sigma_k}{\left( \frac{\partial \ln c_k}{\partial \xi} \right)_t} = \lim_{t \rightarrow \infty} \frac{\omega^2 \sum_{q=1}^n \frac{1}{M_q} c_q \mathbf{S}_{k,q}}{\sum_{q=1}^n \frac{1}{M_q} \left( \frac{\partial c_q}{\partial \xi} \right)_t \mathbf{D}_{k,q}} = 1, \quad (\text{N40})$$

$$\lim_{t \rightarrow \infty} \frac{\sigma_k}{\left( \frac{\partial \ln c_k}{\partial \xi} \right)_t} = \lim_{t \rightarrow \infty} \frac{\sum_{q=1}^n \frac{1}{M_q} c_q \sigma_{k,q} \mathbf{D}_{k,q}}{\sum_{q=1}^n \frac{1}{M_q} \left( \frac{\partial c_q}{\partial \xi} \right)_t \mathbf{D}_{k,q}} = 1 \quad (\text{N41})$$

and

$$\lim_{t \rightarrow \infty} \frac{\sigma_k}{\left( \frac{\partial \ln c_k}{\partial \xi} \right)_t} = \lim_{t \rightarrow \infty} \frac{\omega^2 \sum_{q=1}^n L_{k,q} M_q (1 - \bar{v}_q \rho)}{RT \sum_{q=1}^n \left( \frac{\partial \ln c_q}{\partial \xi} \right)_t L_{k,q} \left[ 1 + c_q \sum_{w=1}^n \left( \frac{\partial c_w}{\partial c_q} \right)_t \left( \frac{\partial \ln \gamma_q}{\partial c_w} \right)_{t,T,P,c_{a \neq w}} \right]} = 1, \quad (\text{N42})$$

respectively, at each spatial position,  $\xi$ . 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

$$\lim_{t \rightarrow \infty} \frac{\omega^2 \sum_{q=1}^n L_{k,q} M_q (1 - \bar{v}_q \rho)}{RT \sum_{q=1}^n L_{k,q} \left( \frac{\partial \ln c_q}{\partial \xi} \right)_t \left[ 1 + \left( \frac{\partial \ln \gamma_q}{\partial \ln c_q} \right)_{t,T,P,c_{a \neq q}} \right]} = 1.$$

(N43)

Thus, at equilibrium, with  $\left( \frac{\partial \ln c_q}{\partial \xi} \right)_t$  being equal to  $\frac{d \ln c_q}{d \xi}$ , and with  $\left( \frac{\partial \ln \gamma_q}{\partial \ln c_q} \right)_{t,T,P,c_{a \neq q}}$  being equal to  $\frac{d \ln \gamma_q}{d \ln c_q}$ ,

$$\sum_{q=1}^n L_{k,q} \left[ \omega^2 M_q (1 - \bar{v}_q \rho) - RT \frac{d \ln c_q}{d \xi} \left( 1 + \frac{d \ln \gamma_q}{d \ln c_q} \right) \right] = 0$$

(N44)

at each spatial position,  $\xi$ , in the system.

Neglecting vector notation (see the discussion following Equation A3), in an AUC system,  $\nabla U_q$  can be reduced to  $\left( \frac{\partial U_q}{\partial r} \right)_t$  (Equations A2, A14, and I16 to I20), and at equilibrium,  $\left( \frac{\partial U_q}{\partial r} \right)_t$  can be expressed as  $\frac{d U_q}{d r}$ . In Equation N44,  $L_{k,q}$  is the coefficient of  $\frac{d U_q}{d \xi} = \frac{1}{r} \frac{d U_q}{d r}$ . Thus, Equation N44 can be written more compactly as

$$\sum_{q=1}^n L_{k,q} \frac{d U_q}{d \xi} = 0,$$

(N45)

where  $U_q$  is the total molar potential of solute component  $q$  (Equation I17). As each  $\frac{d U_q}{d \xi} = 0$  at equilibrium, Equation N45 cannot be used to determine  $L_{k,q}$  values. In the case of membrane-confined electrophoresis (MCE) [Moody, 2011], however, reservoirs of solvent are separated from the top and bottom of the system by semi-permeable membranes through which the solvent and membrane-permeant components can flow at a steady rate, while membrane-confined components that must remain between the membranes form concentration gradients in response to an applied electrical potential difference and the flow of mass through the system. MCE systems approach steady state rather than equilibrium, and in such a system at steady state, each  $\frac{d U_q}{d \xi}$  can be nonzero. Under conditions

in which the  $\frac{dU_q}{d\xi}$  values are nonzero, the MCE-equivalent to Equation N45 can be used to determine  $L_{k,q}$  values. Such determinations are explored in Section N of the MCE document [Moody, 2011] that mirrors this AUC document.

## References

[M1] Moody, T. P. (2011) 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.

<http://moodybiophysicalconsulting.blogspot.com/>.

## List of selected parameters, their indices, and their cgs dimensions

symbol <sub>indices</sub>	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 <sup>3</sup>
$c_{1,2}$	mass concentration	component	spatial element	g/cm <sup>3</sup>
$D_{1,2}$	diffusion coefficient	component	component	cm <sup>2</sup> /s
$s_{1,2}$	sedimentation coefficient	component	component	s
$D_1$	diffusion coefficient	component		cm <sup>2</sup> /s
$s_1$	sedimentation coefficient	component		s
$\sigma_1$	reduced molar mass coefficient	component		cm <sup>-2</sup>
$D_{1,2}$	diffusion coefficient	component	spatial element	cm <sup>2</sup> /s
$s_{1,2}$	sedimentation coefficient	component	spatial element	s
$\sigma_{1,2}$	reduced molar mass coefficient	component	spatial element	cm <sup>-2</sup>
$r$	radial position			cm
$\xi$	half the radial position squared			cm <sup>2</sup>
$\xi_1$	half the radial position squared	spatial element		cm <sup>2</sup>
$\omega$	angular velocity			s <sup>-1</sup>
$t$	time			s

$\bar{v}_1$	partial specific volume	component		$\text{cm}^3/\text{g}$
$\rho$	solution density			$\text{g}/\text{cm}^3$
$\rho_1$	density	component		$\text{g}/\text{cm}^3$
$\gamma_1$	activity coefficient	component		dimensionless
$N_A$	Avogadro's number			$\text{mol}^{-1}$
$f_1$	frictional coefficient	component		$\text{g}/\text{s}$
$\eta$	solution viscosity			$\text{g}/\text{s}\cdot\text{cm}$
$R_1^*$	Stokes radius (equivalent sphere)	component		$\text{cm}$
$P_1$	basis function	spatial element		dimensionless
$P$	pressure			$\text{dyne}/\text{cm}^2$
$R$	ideal gas constant			$\text{erg}/\text{mol}\cdot\text{K}$
$T$	absolute temperature			$\text{K}$
$m_1^*$	reduced buoyant mass	component		$\text{g}$
$p_{1,2}$	density increment coefficient	component	component	$\text{cm}^3/\text{g}$
$y_{1,2}$	nonideality coefficient	component	component	$\text{cm}^3/\text{g}$
$h_{1,2}$	viscosity coefficient	component	component	$\text{cm}^3/\text{g}$
$U_1$	total molar potential	component		$\text{erg}/\text{mol}$
$\mu_1$	chemical potential	component		$\text{erg}/\text{mol}$
$\vec{X}_1$	conjugate molar force	component		$\text{dyne}/\text{mol}$
$\vec{l}_1$	mass flow vector	component		$\text{g}/\text{s}\cdot\text{cm}^2$
$I_1$	mass flow	component		$\text{g}/\text{s}\cdot\text{cm}^2$
$L_{1,2}$	phenomenological coefficient	component	component	$\text{mol}^2\cdot\text{s}/\text{g}\cdot\text{cm}^3$
$L_{P,R}^{g,a}$	phenomenological coefficient	products	reactants	$\text{mol}^2\cdot\text{s}/\text{g}\cdot\text{cm}^5$
$L_{R,P}^{g,a}$	phenomenological coefficient	reactants	products	$\text{mol}^2\cdot\text{s}/\text{g}\cdot\text{cm}^5$
$\vec{J}_1$	molar flow vector	component		$\text{mol}/\text{s}\cdot\text{cm}^2$
$J_1$	molar flow	component		$\text{mol}/\text{s}\cdot\text{cm}^2$
$J_1^R$	molar reaction flow	reaction		$\text{mol}/\text{s}\cdot\text{cm}^3$
$A_1$	conjugate molar affinity	reaction		$\text{erg}/\text{mol}$
$\vec{G}$	magnetic field			tesla, or
$\vec{G}$	Coriolis force			$\text{dyne}/\text{g}$

$\Phi$	free energy dissipation function		erg/cm <sup>3</sup> ·s
$z$	longitudinal coordinate		cm
$\varphi$	angular coordinate		dimensionless
$\vec{v}_1$	velocity vector	component	cm/s
$v_1$	velocity magnitude	component	cm/s
$\hat{e}_r$	unit vector	direction (+r-axis)	dimensionless
$g_E$	gravitational acceleration (See note.)	Earth	cm/s <sup>2</sup>

#### Note

The cgs standard acceleration due to gravity,  $g_E$ , is approximately 981 cm/s<sup>2</sup> (for the Earth at sea level).

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