Generalized Principles of Unchanging Total Concentration

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We consider the transport of multiple reacting species under the continuum assumption in situations such as those that frequently arise in electroanalytical chemistry. Under certain limitations, it has been shown that the total species concentration (as defined by Oldham and Feldberg[1]) of such a system is uniform and constant. In this work, we extend the limits of the previous analysis to enable greater applicability. This is accomplished by using either of two new dependent variables, which are generalizations of the concept of total concentration. Then, conditions are determined under which the dependent variable will be uniform and constant in time. From a practical viewpoint, the described formalism allows one to simplify the multispecies transport problem formulation by eliminating one equation from the system of governing equations.

1. Introduction

When modeling multispecies reaction transport systems, there is often a need to solve systems of coupled nonlinear transport equations in order to predict the temporal and spatial variation of species concentrations and fluxes. We are concerned with isothermal problems in which the coupling occurs through homogeneous and heterogeneous reactions. For the transport of ionic species, in problems of electrochemistry, for example, the coupling can also occur through the electric field. Solving the appropriate system of coupled nonlinear partial differential equations can be difficult, or at least computationally expensive. Therefore, any method that can reduce the complexity of the governing system of equations is beneficial. In this work, we present a general method for the elimination of the need to solve for the unknown concentration of one of the species in many such problems. Although we have considered the simplification with problems of electroanalytical chemistry in mind, its use is not so narrowly limited. The presentation is mathematically rigorous and kept as general as possible so that the method can find broad use, and specific examples and illustrations of application are used to enhance the clarity of the results.

The simplification is found by writing the governing equation and boundary conditions for the deviation of a diffusivity weighted total concentration, as defined later in the paper, from its uniform initial value. Then, conditions are found under which the boundary conditions and the governing equation become homogeneous. Under these conditions, the solution of the governing equation is the trivial solution; the dependent variable is always and everywhere zero. This implies that there is no temporal or spatial variation of the weighted total concentration.

Oldham and Feldberg have previously addressed the case of an unweighted total species concentration, $\sum_{i=1}^{N} c_i$, in the context of transport modeling of voltammetry.[1] These authors found their result was valid under the following restrictions:

(1) all species have the same diffusivity;

(2) all reactions, both heterogeneous and homogeneous, must "preserve the total number of solute particles"; and

(3) the velocity vanishes on all model domain boundaries.

They called their result the "principle of unchanging total concentration", and they sought to make the principle, forms of which had been used in earlier literature,[2−4] general and rigorously justified. It is our purpose to broaden this principle further by demonstrating two related principles of unchanging concentration. One, the principle of unchanging diffusivity weighted total *species* concentration, which includes the principle presented by Oldham and Feldberg as a large subset, is typically more useful when the migration of charged species is important. The other, the principle of unchanging diffusivity weighted total *atomic* concentration, has applicability in cases of more general heterogeneous and bulk reactions. The applicability of the two principles overlaps slightly.

Our results extend the principle of unchanging total concentration by finding those situations for which some of the three restrictions enumerated above are unnecessary. For instance, there are conditions under which this methodology can be used for any homogeneous reactions in the governing equations and any heterogeneous reactions in the boundary conditions, so that restriction 2 is not needed. Conditions are also identified under which no restriction of equality is placed on the species' diffusivities. Furthermore, when such a restriction is needed, it is shown often to be limited to the diffusivities of ionic species. Therefore, restriction 1 is frequently too strict. Finally, restriction 3, the requirement that velocities vanish on the boundaries, is relaxed in all cases to a requirement that only the normal component of velocities vanishes, and only on all no-penetration boundaries. Table 1 summarizes the applicability of the two new principles, and simple examples illustrate the implementation, limitations, and advantages of the method.

2. Background

We consider species transport in the continuum limit, using the Nernst−Einstein relationship, so that the local molar flux of species i is given by

$$\vec{J}_i = -\frac{D_i c_i}{RT} \nabla \tilde{\mu}_i + \vec{u} c_i \qquad (1)$$

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TABLE 1: Guide to the Applicability of the Principles of Unchanging Total Concentrations

Basic Assumptions: isothermal; uniform D_i; binary Fickian diffusion (dilute, ideal solution)
General Requirements: all c_i^∞ uniform and constant on $\partial\Omega_\infty$; uniform initial condition $c_i = c_i^\infty$;
$u_n = 0$ on $\partial\Omega_s$; $\partial\Omega_s$ serves as neither source nor sink of any element

Principle of Unchanging Diffusivity Weighted Total Atomic Concentration	**Principle of Unchanging Diffusivity Weighted Total Species Concentration**
$$\Sigma_{i=1}^{N} \Sigma_{j=1}^{M} D_i \nu_{ij} c_i = \Sigma_{i=1}^{N} \Sigma_{j=1}^{M} D_i \nu_{ij} c_i^\infty$$	$$\Sigma_{i=1}^{N} D_i c_i = \Sigma_{i=1}^{N} D_i c_i^\infty$$
Applies for general bulk and heterogeneous reactions as long as one of the groups of the conditions listed below is fulfilled: 1. Steady state (eq 11) with migration and advection negligible (eqs 6 and 12). Appendix B example 1 meets these criteria. 2. Migration negligible (eq 6), all D_i equal. Appendix B example 2 meets these criteria. 3. Steady state (eq 11) with advection negligible (eq 12), D_i of all ionic species equal (eq 29), electroneutrality condition applicable (eq 10), same number of atoms in all ions (eq 30). 4. All D_i equal, electroneutrality condition applicable (eq 10), same number of atoms in all ions (eq 30).	Applies as long as all reactions preserve the number of solute particles and one of the groups of conditions listed below is fulfilled: 1. Steady state (eq 11) with migration and advection negligible (eqs 6 and 12). The example in Appendix C meets these criteria. 2. Migration negligible (eq 6), all D_i equal. 3. Steady state (eq 11) with advection negligible (eq 12), D_i of all ionic species equal (eq 29), electroneutrality condition applicable (eq 10). 4. All D_i equal, electroneutrality condition applicable (eq 10).

where D_i is the diffusion coefficient of species i in the mixture or solution, c_i is the molar concentration, R is the universal gas constant, T is the absolute temperature, and $\vec{u}$ is the local bulk velocity. In the ideal solution approximation, the electrochemical potential, $\tilde{\mu}_i$, is given by

$$\tilde{\mu}_i = \tilde{\mu}_{i0} + RT \ln c_i + z_i F \phi \qquad (2)$$

where $\tilde{\mu}_{i0}$ is the reference electrochemical potential, z_i is the valence, F is Faraday's constant, and ϕ is the electric potential. We further assume isothermal conditions, so that the local molar flux of species i becomes

$$\vec{J}_i = -\underbrace{D_i \nabla c_i}_{\text{diffusion}} - \underbrace{\frac{D_i c_i}{RT} z_i F \nabla \phi}_{\text{migration}} + \underbrace{\vec{u} c_i}_{\text{advection}} \qquad (3)$$

The terms on the right-hand side of eq 3 are the diffusion, migration, and advection terms, respectively. We use the term *advection* instead of *convection* to differentiate between transport of mass solely by bulk fluid flow (advection) and transport by both bulk fluid flow and diffusion (convection). Implicit throughout our approach is the assumption that the diffusion term is always significant, while sometimes the effects of advection or migration may be neglected.

Considering N species, the conservation of mass requires each of them to satisfy

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \vec{J}_i + S_i, \quad i = 1, ..., N \qquad (4)$$

within the problem domain Ω. In eq 4, S_i is a species generation term, present due to the possibility of homogeneous chemical reactions of arbitrary mechanism and mathematical form, and can result in either a local increase or a local decrease in the concentration of the ith species. The species generation term cannot, however, lead to the production or destruction of any chemical element.

The terms species, element, and atom can often be glossed over due to their mundane nature. As the principles of unchanging total concentration are at heart nothing more than simple accounting, close attention must be paid to what items are being counted, and the species generation term provides a good opportunity for exposition. Each of the N

species can be written in terms of a chemical formula, $(\beta_1)_{\nu_{i1}}(\beta_2)_{\nu_{i2}}(\beta_3)_{\nu_{i3}}, ...$, where each mole of the ith species has ν_{ij} moles of atoms of chemical element β_j. For example, ferrocyanide $[Fe(CN)_6]^{4-}$ and ferricyanide $[Fe(CN)_6]^{3-}$ are two different species (different i) but both consist of the same elements, β_j, with identical atomic contents and therefore identical coefficients, ν_{ij}:

$$\beta_1 = \text{Fe}, \ \nu_{i1} = 1$$

$$\beta_2 = \text{C}, \ \nu_{i2} = 6$$

$$\beta_3 = \text{N}, \ \nu_{i3} = 6 \qquad (5)$$

The atomic concentration of a given element is simply the sum over the contribution from each species concentration, $\Sigma_{i=1}^{N} \nu_{ij} c_i$, and the prohibition on destruction or production of any chemical element (in the absence of nuclear reactions) is mathematically given by $\Sigma_{i=1}^{N} \nu_{ij} S_i = 0$ for all elements, β_j. In light of the example above, it is worth recognizing that the choice of atomic concentration is motivated by the generality of the assumption that the atom is an indivisible unit. If there is a more convenient unit that remains undivided in a particular example, for example, (CN), then that unit can be treated as an "atom" but the calculation procedure remains unchanged.

It is necessary to identify the set of N species that must be included in the analysis. This can be done by using the following simple procedure to identify several subsets. We define N_1 as the number of species of interest, by which we mean the species whose transport provides the motivation for developing the model. We next define a broader set that contains the N_1 species of interest and all species linked through bulk or heterogeneous reactions to the species of interest, directly or indirectly (i.e., through intermediate reactions). We let N_2 be the number of species in this set. We continue by noting that if any of these N_2 species are ionic, then another set must be defined. This set, which contains N_3 species, consists of all ionic species present, even those not linked through reactions to the species of interest. The set of N_3 ionic species must be identified in order to determine whether the effect of migration on the transport of the ionic components of the set of the N_2 species of interest and species linked by reaction is negligible. In other words, we

General Principles of Unchanging Total Concentration

J. Phys. Chem. B, Vol. 109, No. 35, 2005 **16813**

must identify all ionic species to determine whether it is reasonable to state that

$$\underbrace{\left|\nabla\cdot\left(D_i\nabla c_i\right)\right|}_{\text{diffusion}} \gg \underbrace{\left|\frac{z_iF_i}{RT}\nabla\cdot\left(D_ic\nabla\phi\right)\right|}_{\text{migration}} \quad i=1..N_2 \qquad (6)$$

We fill the set of all N species that must be considered first with species $1, \dots, N_2$, where species $1, \dots, N_1$ are the species of interest and species $N_1 + 1, \dots, N_2$ are the species not initially deemed of interest but linked to the species of interest by reactions. If eq 6 is satisfied, then $N = N_2$; otherwise, species $N_2 + 1, \dots, N$ are those of the N_3 ionic species not included in $1, \dots, N_2$. The conditions under which eq 6 may be considered satisfied are discussed next, and an example demonstrating the determination of the N species that must be included in the analyses is provided in Appendix A.

In problems of electroanalytical chemistry, the determination that the migration of the N_2 species is negligible, that is, that eq 6 is satisfied, is based on satisfying two conditions. The first is that the transference numbers, $\tau_k = D_k|z_k|c_k^\infty/(\Sigma_{i=1}^{N_3} D_i|z_i|c_i^\infty)$, of the species involved in reactions are small:[5]

$$\tau_k \ll 1, \quad k = 1, \dots, N_2 \qquad (7)$$

The second condition is that the minimum relevant characteristic diffusion length, L_{diff}, is large compared to the double layer thickness. Usually, the double layer thickness is of the order of the Debye length for the electrolyte, $\lambda_D = \sqrt{\epsilon RT/(2F^2\Sigma_{i=1}^{N_3} z_i^2 c_i^\infty)}$, where ϵ is the electric permittivity, and this second condition becomes[6]

$$\lambda_D \ll L_{\text{diff}} \qquad (8)$$

Note that in the denominators of the transference number definition as well as in the Debye length definition, the index runs to N_3, indicating that all ionic species are included, whereas eq 7 only applies a condition on the ionic species in the set of N_2 species that are of interest or linked by chemical reaction. Both requirements, eqs 7 and 8, are typically satisfied when an excess of supporting electrolyte is present in solution, provided the electrode (whose size sets the diffusion length, L_{diff}) is not of nanometric size. The Debye length, even in the absence of supporting electrolyte, is smaller than 100 nm in nearly all cases.

The conditions of applicability of our method depend considerably upon the ability to neglect the contribution of certain components in the molar flux expressions, eq 3. We have addressed the neglect of the migration term and shortly address the advection and transient terms. First, we introduce a common simplification in problems with ionic species for which the migration effect cannot be neglected. Generally, under the continuum assumption, the gradient of the electric potential can be found by solving Poisson's equation in the domain Ω (subject to appropriate boundary conditions):

$$\nabla\cdot(\epsilon\nabla\phi) = -(\rho_f + F\sum_i z_ic_i) \qquad (9)$$

where ϵ is the electric permittivity and ρ_f is the fixed local volumetric charge density. Problems frequently have $\rho_f = 0$, and the permittivity is typically assumed to be a constant given by the permittivity of the bulk solvent. In electrochemistry

problems, eq 9 is often replaced by the local electroneutrality condition[3,6,7]

$$\sum_i z_ic_i = 0 \qquad (10)$$

The electroneutrality condition, eq 10, is typically used when, although the ratio of the Debye length to the characteristic diffusion length is much less than unity, not all necessary transference numbers are small, and hence, migration will affect the fluxes of some species. The electroneutrality condition will be useful, when migration effects cannot be ignored, for finding conditions under which the principles of diffusivity weighted total concentration can be used.

The conditions of applicability of our method are less restrictive when the problem can be treated as steady, or at least quasi-steady, and when advective effects are negligible. Recall that we limit consideration to problems for which diffusion is a dominant mode of transport. For such a problem, the determination that a steady state formulation can be applied is made when the observation time scale, t_{obs}, is much greater than the longest characteristic time for diffusion

$$t_{\text{obs}} \gg L_{\text{diff}}^2/D_i, \quad i = 1, \dots, N \qquad (11)$$

Note that the characteristic length scale for diffusion, L_{diff}, generally depends on the effects of advection and migration, as, for instance, when forced convection leads to boundary layer formation. A fairly general criterion for neglecting advection is that the highest Peclet number based on the characteristic velocity in the diffusion layer, u_{char}, be much less than unity

$$Pe_i = \frac{u_{\text{char}}L_{\text{diff}}}{D_i} \ll 1, \quad i = 1, \dots, N \qquad (12)$$

For our purposes, it is convenient to divide the boundary of the problem domain Ω into two parts: a no-penetration boundary, $\partial\Omega_s$, across which there is no net mass flux, and a far-field boundary, $\partial\Omega_\infty$, on which the concentrations of species are specified. The boundary conditions for the latter are

$$c_i = c_i^\infty \text{ on } \partial\Omega_\infty, \quad i = 1, \dots, N \qquad (13)$$

The no-penetration boundary condition, when heterogeneous reactions are possible, must generally be formulated in terms of the normal flux of each chemical *element*

$$\tilde{J}_j = 0 \text{ on } \partial\Omega_s, \quad j = 1, \dots, M \qquad (14)$$

In eq 14, the tilde ($\sim$) above J is meant to emphasize that the flux is of the jth element, not of a species. Furthermore, note that $\tilde{J}_j$ is a scalar; it is the normal component of the elemental flux vector. If each mole of the ith species has ν_{ij} moles of atoms of the jth chemical element, then

$$\tilde{J}_j = \sum_{i=1}^N \nu_{ij}\left(-D_i\frac{\partial c_i}{\partial n} - \frac{D_ic_i}{RT}z_iF\frac{\partial\phi}{\partial n} + u_nc_i\right) = 0 \text{ on } \partial\Omega_s \qquad (15)$$

where $\partial/\partial n = \hat{n}\cdot\nabla$ is a projection of the gradient operator on the unit normal vector on the boundary pointing into the domain. Equation 15 is a statement of no penetration of the boundary

16814 *J. Phys. Chem. B, Vol. 109, No. 35, 2005*

Kottke and Fedorov

by any element, and summing over all elements results in a statement of no mass penetration across $\partial\Omega_s$

$$\sum_{j=1}^{M}\sum_{i=1}^{N}\nu_{ij}\left(-D_i\frac{\partial c_i}{\partial n}-\frac{D_ic_i}{RT}z_iF\frac{\partial\phi}{\partial n}+u_nc_i\right)=0 \text{ on } \partial\Omega_s \quad (16)$$

A special case occurs when the total normal *species* flux is zero on the no-penetration boundaries, $\partial\Omega_s$. Oldham and Feldberg recognized that this must be the case when the net effect of the surface reactions does not change the total number of ions and molecules.[1] For instance, if no species participates in more than one reaction at a surface, then as long as each reaction has an equal number of reactants and products, this condition of preserving the total number of solute particles will be met. In such circumstances, we find it useful to replace eq 16 with a statement of species balance

$$J_n=\sum_{i=1}^{N}\left(-D_i\frac{\partial c_i}{\partial n}-\frac{D_ic_i}{RT}z_iF\frac{\partial\phi}{\partial n}+u_nc_i\right)=0 \text{ on } \partial\Omega_s \quad (17)$$

Finally, the transient problem requires initial conditions, which we make

$$c_i=c_i^{\infty} \text{ in } \Omega \text{ for } t=0, \quad i=1,\dots,N \quad (18)$$

Although the initial and boundary conditions described above, eqs 13−18, are applicable for many problems, their applicability is clearly not universal. For transient problems, the initial conditions require that the concentrations of all species are uniform and consistent with their values on $\partial\Omega_\infty$. We assume that the value of c_i^{∞} does not vary with position on $\partial\Omega_\infty$, nor does it vary with time, so our conclusions are not applicable if, for instance, the domain has far-field boundaries with different species concentrations (e.g., if the problem domain is a channel connecting two large containers holding different solutions). We emphasize that although the no-penetration boundary, $\partial\Omega_s$, can either be inert or be participating (i.e., electroactive or catalytic), $\partial\Omega_s$ cannot serve as a net mass source or sink. This last restriction prevents use of the principles of unchanging total concentration in analyses where dissolution of a solid into the solvent occurs, or, as frequently is the case in electroanalytical techniques using amalgam or mercury electrodes, where a species crosses a phase boundary at the electrode.

3. Weighted Total Concentration Deviations

We define two rescaled concentrations. The diffusivity weighted total atomic concentration deviation, α, is defined as

$$\alpha\equiv\sum_{i=1}^{N}\sum_{j=1}^{M}D_i\nu_{ij}(c_i-c_i^{\infty}) \quad (19)$$

and the diffusivity weighted total species concentration deviation, σ, is defined as

$$\sigma\equiv\sum_{i=1}^{N}D_i(c_i-c_i^{\infty}) \quad (20)$$

The initial conditions, eq 18, and the boundary conditions on $\partial\Omega_\infty$, eq 13, from the original problem, can be used to construct a new initial condition and boundary condition for α or σ:

$$\alpha=0 \text{ or } \sigma=0 \text{ in } \Omega \text{ for } t=0 \quad (21)$$

and

$$\alpha=0 \text{ or } \sigma=0 \text{ on } \partial\Omega_\infty \quad (22)$$

The no-penetration boundary condition, eq 16, is rewritten using the definition of the diffusivity weighted total atomic concentration deviation to obtain

$$\frac{\partial\alpha}{\partial n}=u_n\sum_{j=1}^{M}\sum_{i=1}^{N}\nu_{ij}c_i-\frac{F}{RT}\frac{\partial\phi}{\partial n}\sum_{j=1}^{M}\sum_{i=1}^{N}z_i\nu_{ij}D_ic_i \text{ on } \partial\Omega_s \quad (23)$$

Alternatively, the net balance of normal fluxes of species, eq 17, is written using the definition of the diffusivity weighted total species concentration deviation

$$\frac{\partial\sigma}{\partial n}=u_n\sum_{i=1}^{N}c_i-\frac{F}{RT}\frac{\partial\phi}{\partial n}\sum_{i=1}^{N}D_ic_iz_i \text{ on } \partial\Omega_s \quad (24)$$

We will be seeking conditions for which the boundary conditions and governing equation for α or σ are homogeneous. From eqs 23 and 24, one can see that this requires that on all parts of $\partial\Omega_s$ the normal component of velocity is zero. Importantly, this restriction allows purely tangential motion, such as that which occurs on rotating disk electrodes or at free surfaces under steady state flow conditions. Thus, the requirement reported by Oldham and Feldberg,[1] that the velocity must vanish on all boundaries, needs to be relaxed to a requirement that the normal velocity component at no-penetration boundaries vanishes. Furthermore, this condition is not needed at all on the far-field boundary, on which the fixed species concentration condition is specified.

4. Unchanging Total Atomic Concentration

We will first determine the conditions under which the diffusivity weighted total atomic concentration is everywhere uniform and remains unchanging in time. To start, both sides of each of the N governing equations, eq 4, are multiplied by $\Sigma_{j=1}^{M}\nu_{ij}$, and then, they are combined to obtain

$$\frac{\partial}{\partial t}\left[\sum_{i=1}^{N}\sum_{j=1}^{M}\frac{1}{D_i}D_i\nu_{ij}(c_i-c_i^{\infty})\right]=$$

$$\nabla^2\alpha-\vec{u}\cdot\nabla\left[\sum_{i=1}^{N}\sum_{j=1}^{M}\frac{1}{D_i}D_i\nu_{ij}(c_i-c_i^{\infty})\right]+\sum_{i=1}^{N}\sum_{j=1}^{M}\nu_{ij}S_i+$$

$$\frac{F}{RT}\nabla\cdot[\nabla\phi\sum_{i=1}^{N}\sum_{j=1}^{M}\nu_{ij}D_ic_iz_i]-(\nabla\cdot\vec{u})\sum_{i=1}^{N}\sum_{j=1}^{M}\nu_{ij}c_i \quad (25)$$

where uniform diffusivities, D_i, have been assumed. Equation 25 is simplified by assuming an incompressible flow, $\nabla\cdot\vec{u}=0$. Considering the source term $\Sigma_{j=1}^{M}\Sigma_{i=1}^{N}\nu_{ij}S_i$, as noted earlier, the local rate of generation of the jth chemical element, $\Sigma_{i=1}^{N}\nu_{ij}S_i$, must be zero, so this source term vanishes.

With the simplifications and assumptions described in this and the previous section, the governing equation for α becomes

$$\nabla^2\alpha = \frac{\partial}{\partial t}\left[\sum_{i=1}^{N}\sum_{j=1}^{M}\frac{1}{D_i}D_i\nu_{ij}(c_i - c_i^\infty)\right] +$$

$$\vec{u}\cdot\nabla\left[\sum_{i=1}^{N}\sum_{j=1}^{M}\frac{1}{D_i}D_i\nu_{ij}(c_i - c_i^\infty)\right] - \frac{F}{RT}\nabla\cdot[\nabla\phi\sum_{i=1}^{N}\sum_{j=1}^{M}\nu_{ij}D_ic_iz_i] \quad (26)$$

where the source terms on the right-hand side are the transient term, the advective term, and the migration term. The initial condition for eq 26 is given by eq 21, and the boundary conditions are

$$\frac{\partial\alpha}{\partial n} = -\frac{F}{RT}\frac{\partial\phi}{\partial n}\sum_{j=1}^{M}\sum_{i=1}^{N}z_i\nu_{ij}D_ic_i \text{ on } \partial\Omega_s \quad (27)$$

and eq 22.

Our method reduces to finding conditions such that the governing equation, eq 26, and the boundary condition, eq 27, become homogeneous. Equations 21 and 22 are already homogeneous and need no further consideration. When eqs 26 and 27 are also homogeneous, the solution of the problem is given by $\alpha = 0$, which, from eq 19, implies

$$\sum_{i=1}^{N}\sum_{j=1}^{M}D_i\nu_{ij}c_i = \sum_{i=1}^{N}\sum_{j=1}^{M}D_i\nu_{ij}c_i^\infty \quad (28)$$

Equation 28 is thus the principle of unchanging diffusivity weighted total atomic concentration.

4.1. Conditions due to the No-Penetration Boundary. Our goal is to find conditions under which the boundary condition given by eq 27 becomes homogeneous. We find no meaningful conditions such that the right-hand side of eq 27 becomes a nontrivial homogeneous function of α; therefore, to make the boundary condition homogeneous, we seek conditions for which the right-hand side vanishes.

Considering eq 27, the right-hand side is the flux due to migration; therefore, it can be neglected whenever the effect of migration is negligible. If this condition is not satisfied, then one other situation arises for which the boundary condition will be homogeneous. It relies on the assumption of local electroneutrality, given in eq 10. In addition to local electroneutrality, we must require that the diffusivities of all ionic species be equal.

$$D_i = D, \quad i{:}z_i \neq 0 \quad (29)$$

Finally, we must further require that the number of atoms in all ions be the same.

$$\sum_{j=1}^{M}\nu_{ij} = \nu \neq f(i), \quad i{:}z_i \neq 0 \quad (30)$$

It should be noted that eq 29 applies to ionic species only, and no restriction has been placed on the diffusivities of nonionic species at this point. Likewise, eq 30 does not limit the atomic content of nonionic species. With eqs 10, 29, and 30, eq 27 becomes

$$\frac{\partial\alpha}{\partial n} = 0 \text{ on } \partial\Omega_s \quad (31)$$

4.2. Conditions due to the Governing Equation. In the analysis of the no-penetration boundary condition, obtaining a homogeneous boundary condition required making the migration term vanish at the boundary. In dealing with the governing equation, eq 26, the same is true. Therefore, the migration term does not prevent the governing equation from being homogeneous if migration is negligible for all N species, or under conditions of local electroneutrality with the further restrictions on ionic species provided by eqs 29 and 30.

In the case that all diffusivities are the same, that is,

$$D_i = D, \quad i = 1, \dots, N \quad (32)$$

then once the migration term has been dealt with, the governing equation becomes homogeneous

$$\nabla^2\alpha = \frac{1}{D}\left(\frac{\partial\alpha}{\partial t} + \vec{u}\cdot\nabla\alpha\right) \quad (33)$$

If all diffusivities are not equal, that is, eq 32 is not satisfied, then the governing equation becomes homogeneous under steady state conditions with negligible advection. Note that, although this leads to a simple Laplace equation for α, the underlying species transport equations can still be Poisson equations with general source terms due to homogeneous reactions.

The various conditions under which the application of the principle of unchanging diffusivity weighted total atomic concentration is valid are summarized in the left column of Table 1, and Appendix B contains two examples.

5. Unchanging Total Species Concentration

The diffusivity weighted total species concentration deviation, σ, is a better choice for the dependent variable when all reactions are particle number preserving. This condition was required by Oldham and Feldberg in their principle of unchanging total concentration.[1] We next determine the additional conditions under which the diffusivity weighted total species concentration is unchanging ($\sigma = 0$). As before, the governing equations, eq 4, are combined and simplified through the application of assumptions of uniform diffusivities and incompressible flow. The source term due to bulk reactions in the resulting equation is $\sum_{i=1}^{N} S_i$, which vanishes if all homogeneous reactions preserve the total number of solute particles.[1] The resulting governing equation is

$$\nabla^2\sigma = \frac{\partial}{\partial t}\left[\sum_{i=1}^{N}\frac{1}{D_i}D_i(c_i - c_i^\infty)\right] +$$

$$\vec{u}\cdot\nabla\left[\sum_{i=1}^{N}\frac{1}{D_i}D_i(c_i - c_i^\infty)\right] - \frac{F}{RT}\nabla\cdot[\nabla\phi\sum_{i=1}^{N}D_ic_iz_i] \quad (34)$$

We continue the restriction of reaction types to $\partial\Omega_s$ so that the species normal flux boundary condition holds:

$$\frac{\partial\sigma}{\partial n} = -\frac{F}{RT}\frac{\partial\phi}{\partial n}\sum_{i=1}^{N}D_ic_iz_i \text{ on } \partial\Omega_s \quad (35)$$

where we have maintained the requirement of zero normal velocity at the no-penetration boundaries.

Again, we seek conditions such that the governing equation, eq 34, and the boundary condition on the no-penetration

surfaces, eq 35, are homogeneous, so that $\sigma = 0$ is the solution of the problem, implying

$$\sum_{i=1}^{N} D_i c_i = \sum_{i=1}^{N} D_i c_i^{\infty} \text{ in } \Omega \text{ and on } \partial\Omega \text{ for all } t \quad (36)$$

Equation 36 is the principle of unchanging diffusivity weighted total species concentration.

5.1. Conditions due to the No-Penetration Boundary. Equation 35 becomes homogeneous when the right-hand side vanishes. This occurs under conditions for which migration is negligible, or under conditions for which local electroneutrality can be applied and the diffusivities of all ionic species are equal.

5.2. Conditions due to the Governing Equation. The governing equation, eq 34, has three source terms that can prevent a homogeneous solution. They are readily identifiable as the transient term, the advection term, and the migration term. Each source term must only be considered when the effect that gives rise to its presence is not negligible for the transport of the N species. In the event that the migration term cannot be neglected, then the governing equation can only be homogeneous if all ionic species have the same diffusivities and the electroneutrality principle can be applied. If either the advection or transient term must be considered, then we must require all diffusivities to be the same. It is in this last case that our principle and that of Oldham and Feldberg exhibit the greatest overlap. The only differences in this category would be the less restrictive velocity boundary conditions in our derivation.

6. Conclusions

We have carefully derived the conditions under which either the principle of unchanging diffusivity weighted total species concentration or the principle of unchanging diffusivity weighted total atomic concentration can be applied. The results, which generalize and greatly expand the limit of the previously developed principle of unchanging total concentration,[1] are summarized compactly in Table 1. If either of the new generalized principles can be applied, it can be used to eliminate one of the equations in the system of governing equations describing mass transport of multiple, reacting species, which can result in simpler and speedier solution of the problem.

Appendix A: Example of the Determination of N

To demonstrate the determination of N, we consider a model of the species concentrations near the working electrode during electrochemical titration of 8-quinolinol (C_9H_7NO) using electrogenerated bromine.[8] The titrant, bromine, is produced electrochemically via the oxidation of bromide:

$$2Br^- \rightarrow Br_2 + 2e^- \quad (37)$$

The bromine reacts with 8-quinolinol in a homogeneous reaction

$$C_9H_7ON + 2Br_2 \rightarrow C_9H_5ONBr_2 + 2HBr \quad (38)$$

The bromide must be introduced to the solution as a component of a compound, for instance, KBr, so at least one other ionic species (K^+ in this example) is present.

Following the procedure delineated in the main body of the text, first we identify all species of interest: in this case, there is one, 8-quinolinol, so N_1 is one. Next, we identify the species linked to the N_1 species of interest by reactions: here, we identify four additional species—$C_9H_5ONBr_2$, HBr, Br_2, and Br^-—so N_2, the number of species of interest and reaction-linked species, is five. Next, we identify all ionic species present, and we will consider two possibilities. The first is that the only ionic species present are bromide and its dissociated cation, K^+, while the other possibility is that excess supporting electrolyte is present. For the first possibility, N_3 is two, while for the second possibility it will be at least three. For both possibilities, in determining if migration effects can be neglected, we find it is likely that eq 8 will be satisfied, as the diffusion length, L_{diff}, will be determined by the electrode, whose characteristic dimension will probably not be smaller than 100 nm, a conservative upper bound on Debye lengths, λ_D. The difference is that eq 7 will only be satisfied in the second possibility when additional supporting electrolyte, not participating in any reactions liked to the species of interest, is present. In the absence of supporting electrolyte, N is six and the set of species that must be considered consists of C_9H_7ON, $C_9H_5ONBr_2$, HBr, Br_2, Br^-, and K^+. With the addition of sufficient supporting electrolyte, N becomes five, as K^+ need not be considered.

Appendix B: Examples of the Principle of Unchanging Diffusivity Weighted Atomic Concentration

Example 1. We consider the use of chemical focusing for scanning electrochemical microscopy (SECM) imaging.[9] SECM is a scanning probe microscopy that can be used to spatially characterize the surface kinetics of a substrate.[10] The probe, a small electrode, and the substrate are in a solution containing an electroactive species. A biasing potential is applied to the electrode, which is scanned at a constant height above the substrate. The Faradaic current response of the electrode is related to the substrate kinetics through transport modeling of the redox species. Chemical focusing utilizes a homogeneous reaction to limit the diffusive spreading of the electrochemically generated product. In our example, the heterogeneous redox reactions occurring at the electrode and conducting portions of the substrate are

$$Fe^{2+} \rightleftarrows Fe^{3+} + e^- \quad (39)$$

The bulk solution contains Fe^{2+} at a known concentration and the electrode reaction produces Fe^{3+}. Thiocyanate (SCN^-) is added to the solution to effect focusing via the homogeneous reaction

$$Fe^{3+} + SCN^- \rightleftarrows [Fe(SCN)]^{2+} \quad (40)$$

Because the reaction in eq 40 is not solute particle number preserving, Oldham and Feldberg's principle of unchanging total concentration cannot be applied.[1] Furthermore, the diffusivities of the four ionic species vary by as much as a factor of 2,[11] so that the assumption of equal diffusivities is not necessarily justified. For typical scan speeds (1−10 μm/s) and electrode sizes (1−10 μm), consideration of eqs 11 and 12 shows that the problem can be treated as quasi-steady with negligible advection. Also, with the addition of excess supporting electrolyte, migration effects can be neglected, as discussed in the Background section of the main body of the text. Hence, the principle of unchanging diffusivity weighted total atomic concentration can be used, as indicated in Table 1. We use Table 2 to organize

General Principles of Unchanging Total Concentration

J. Phys. Chem. B, Vol. 109, No. 35, 2005 **16817**

TABLE 2: Example 1 Coefficients, ν_{ij}

	species, index i			
element, index j	Fe^{2+}, 1	Fe^{3+}, 2	$(SCN)^-$, 3	$[Fe(SCN)]^{2+}$, 4
Fe, 1	1	1	0	1
S, 2	0	0	1	1
C, 3	0	0	1	1
N, 4	0	0	1	1

TABLE 3: Example 2 Coefficients, ν_{ij}

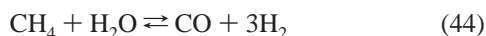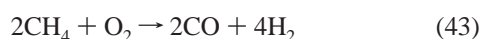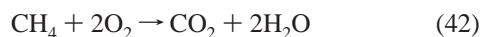|	species, index i					
element, index j	CH_4, 1	H_2, 2	CO_2, 3	O_2,4	CO, 5	H_2O, 6
C, 1	1	0	1	0	1	0
H, 2	4	2	0	0	0	2
O, 3	0	0	2	2	1	1

the coefficients needed for eq 28, and the substitution of the coefficients, ν_{ij}, from Table 2 into eq 28 gives

$$D_1c_1 + D_2c_2 + 3D_3c_3 + 4D_4c_4 =$$
$$D_1c_1{}^\infty + D_2c_2{}^\infty + 3D_3c_3{}^\infty + 4D_4c_4{}^\infty \quad (41)$$

Note that the numerical coefficients in eq 41 are simply obtained by adding the numbers in each column of Table 2. Instead of solving four linked transport equations, we can solve only three, after using eq 41 to eliminate one unknown from the problem formulation.

As noted in the main body, groupings such as (SCN) in this example can be treated as atoms. An alternative choice would lead to different coefficients; for instance, in eq 41, treating (SCN) as a single atom would result in the replacement of occurrences of 3 and 4 with 1 and 2, respectively.

Example 2. As an example from outside of electroanalysis, we consider endothermic steam reforming and exothermic catalytic oxidation for the conversion of methane (CH_4) to hydrogen (H_2), in which the following heterogeneous reactions occur:[13]

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad (42)$$

$$2CH_4 + O_2 \rightarrow 2CO + 4H_2 \quad (43)$$

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \quad (44)$$

The reaction in eq 42 can also occur in the bulk as a homogeneous reaction. We consider the limit of isothermal transient operation of a closed reactor.

To predict reaction yield and selectivity to hydrogen, one must solve the transient problem involving all six species: CH, O_2, CO_2, H_2O, H_2, and CO. The principle of unchanging total atomic concentration can be applied provided the following assumptions are reasonable: the reactor chamber is large enough for the continuum assumption to be valid, the chamber walls exhibit no normal motion, multispecies mass transport effects (Stefan–Maxwell diffusion) can be neglected,[12] and all species' diffusivities in the bulk gas are the same. In this example of a closed reactor, there are no far-field boundaries, but the $c_i{}^\infty$ come from the initial conditions.

We use Table 3 to organize the coefficients used in eq 28 for example 2. Substitution of the coefficients, ν_{ij}, from Table 3 into eq 28 gives

$$5c_1 + 2c_2 + 3c_3 + 2c_4 + 2c_5 + 3c_6 = 5c_1{}^\infty + 2c_2{}^\infty +$$
$$3c_3{}^\infty + 2c_4{}^\infty + 2c_5{}^\infty + 3c_6{}^\infty \quad (45)$$

Instead of solving six linked transient transport equations, we solve five, after using eq 45 to eliminate one unknown from the problem formulation.

Appendix C: Example of the Principle of Unchanging Diffusivity Weighted Species Concentration

Consider the indirect electrochemical detection of species A_O using the redox mediator B_R/B_O. The homogeneous redox reaction

$$A_O + B_R \rightleftharpoons A_R + B_O \quad (46)$$
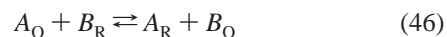
and the heterogeneous electrode reaction

$$B_O + e^- \rightleftharpoons B_R \quad (47)$$

are both "solute particle number preserving". It is likely that A_O and A_R will have similar diffusivities, as will B_O and B_R; however, the diffusivities of A and B could be sufficiently different that treating them as equal would be absurd. Assuming, as in example 1, the appropriateness of a quasi-steady, advection-free model due to the satisfaction of eqs 11 and 12 and justifying the neglect of migration effects due to the presence of excess supporting electrolyte, the principle of diffusivity weighted total species concentration, eq 36, can be applied, as indicated in Table 1. The result, which can be used to eliminate one of the four species, is

$$D_{A_R}c_{A_R} + D_{A_O}c_{A_O} + D_{B_R}c_{B_R} + D_{B_O}c_{B_O} =$$
$$D_{A_R}c_{A_R}{}^\infty + D_{A_O}c_{A_O}{}^\infty + D_{B_R}c_{B_R}{}^\infty + D_{B_O}c_{B_O}{}^\infty \quad (48)$$

Symbol List

c = molar concentration
c^∞ = unperturbed molar concentration
D = diffusion coefficient
F = Faraday's constant
$\vec{J}_i$ = molar flux vector of the ith species
$\tilde{J}_j$ = normal component of flux vector of the jth element
L_{diff} = diffusion length
M = total number of elements in the model
N = total number of species in the model
N_1 = number of species of interest in the system ($N_1 \leq N$)
N_2 = number of species of interest and those which are linked to them by reaction ($N_1 \leq N_2 \leq N$)
N_3 = number of ionic species in the system
R = universal gas constant
S_i = volumetric rate of generation of ith species due to homogeneous reaction
t = time
T = absolute temperature
$\vec{u}$ = velocity vector
u_n = normal component of velocity
z = valence number
α = diffusivity weighted atomic concentration deviation
β = chemical element
$\partial\Omega_\infty$ = far-field (unperturbed) boundary
$\partial\Omega_s$ = no-penetration (zero normal mass flux) boundary
ϵ = electric permittivity
ϕ = electric potential
λ_D = Debye length
$\tilde{\mu}$ = electrochemical potential
$\tilde{\mu}_{i0}$ = electrochemical potential at reference state

ν_{ij} = number of moles of atoms of the jth element in 1 mol of the ith species

Ω = problem domain

ρ_f = fixed charge density

σ = diffusivity weighted species concentration deviation

τ = transference number

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