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Continuum transport laws for locally non-neutral concentrated electrolytes

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ABSTRACT

Flux-explicit transport laws based on Newman's concentrated-solution theory are developed for application to phases with domains of imbalanced charge. General procedures are provided to create flux laws and a current–voltage relation that describe diffusion and migration in isothermal, isobaric, non-neutral multicomponent electrolytes. To retain thermodynamic consistency within the non-neutral concentrated-solution theory, driving forces for diffusion are based on the chemical potentials of neutral combinations of species, and an excess current density is used as a driving force for migration. Procedures are developed for identifying the solution conductivity and Hittorf transference numbers in non-neutral electrolytes comprising three or more species. Flux laws for non-neutral binary electrolytic solutions involving the thermodynamic diffusion coefficient, cation transference number, and ionic conductivity are presented. When local electroneutrality is assumed, the new transport equations reduce to the familiar flux laws for binary electrolytes.

1. Introduction

Flux-explicit transport laws describing diffusion, convection, and migration are useful because they can be substituted directly into material balances. They allow an electrolyte-transport model to be expressed as a system of second-order differential equations, improving the stability of solvers and reducing computation time. Recent work on electrolyte diffusion has focused on applying and extending Newman's application of Stefan–Maxwell theory to multicomponent electrochemical transport [1,2]. Relatively thorough reviews of contemporary developments in concentrated-solution transport theory are given by Datta and Vilekar [3] and Psaltis and Farrell [4].

This paper develops flux-explicit transport laws and a MacInnes current–voltage relation applicable to concentrated n-ary electrochemical phases, without assuming local electroneutrality. The approach formalizes Newman's derivation of transport laws for binary electrolytic solutions [5], and extends it to create flux-explicit transport laws for isobaric, isothermal, non-neutral concentrated multicomponent electrolytes. The current density is taken to drive migration, and chemical potential gradients of independent neutral combinations of species (neutral molecules or salt formula units) are taken to drive diffusion.

Thermodynamically consistent simulations of an electrochemical transport system can be performed by using $n-1$ flux laws in the form of Eq. (32) to handle the couplings among composition gradients, electric current, and flux, which suffice for the modeling of galvanostatic conditions. To introduce an electric potential, Eq. (22) can be added to set up a thermodynamic voltage relative to a reference electrode of a given kind; or Eq. (25) can be added to introduce a quasi-electrostatic potential referred to a specific ion, yielding the modified form of Ohm's law given in Eq. (26). The ionic conductivity defined in Eq. (24) and independent transference numbers from Eq. (33) together represent $n-1$ independent transport properties, leaving $1/2\cdot(n-1)\cdot(n-2)$ diffusion coefficients that can be specified independently without overdetermining the model. In systems comprising more than three species, one probably has to resort to the direct use of Stefan–Maxwell coefficients, basing all analysis on the **M** matrix defined by Eq. (4). But the procedure laid out here is nevertheless an efficient route to derive flux-explicit transport laws that compare easily with Nernst–Planck transport equations [6].

The example of a concentrated binary electrolyte provides a concrete application of the method, yielding flux laws (55)–(57); the electroneutrality assumption then retrieves Newman's theory, Eqs. (61)–(63). Commentary about thermodynamic rigor is provided throughout, and a closing section discusses additional constraints on the constitutive laws for chemical potentials and the solution's molar volume.

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2. Onsager–Stefan–Maxwell theory

Isothermal, isobaric, isotropic transport systems with n constituent species can be modeled accurately [7,8] by the extended Stefan–Maxwell equation

$$-c_i\vec{\nabla}\mu_i = \sum_{j\neq i}\frac{c_i c_j RT}{c_T \mathcal{D}_{ij}}(\vec{v}_i - \vec{v}_j) \quad \text{for } i \in \{1,\ldots,n\}, \tag{1}$$

where c_i is the concentration of species i, μ_i, its electrochemical potential, and $\vec{v}_i$, its particle-averaged velocity; the $\mathcal{D}_{ij}$ are Stefan–Maxwell coefficients, which parameterize the drag force exerted on each species i as it diffuses through every other species j; R is the ideal-gas constant and T, the absolute temperature; c_T abbreviates the total molar concentration, $c_T = \sum_i c_i$. To simplify notation it is convenient to introduce a matrix $\mathbf{K}$ of diffusional drag coefficients, with units of force per volume per velocity,

$$K_{ij} = \frac{c_i c_j RT}{c_T \mathcal{D}_{ij}}, \text{ so that } -c_i\vec{\nabla}\mu_i = \sum_{j\neq i} K_{ij}(\vec{v}_i - \vec{v}_j). \tag{2}$$

Since species velocities only appear as differences, the extended Stefan–Maxwell transport laws are invariant with respect to the choice of reference velocity for convection.

Following Onsager [9], transport Eq. (1) can be expressed equivalently using a basis set of velocities relative to the nth species. Add $(\vec{v}_n - \vec{v}_n)$ within the parentheses of each summand in Eq. (2), then regroup terms to get a sum over velocity differences relative to species n. The result of this rearrangement is represented by

$$c_i\vec{\nabla}\mu_i = \sum_j M_{ij}(\vec{v}_j - \vec{v}_n), \tag{3}$$

in which the $n \times n$ transport matrix $\mathbf{M}$ has entries

$$M_{ij} = \begin{cases} K_{ij} & \text{if } i \neq j, \\ -\sum_{k\neq i} K_{ik} & \text{if } i = j, \end{cases} \tag{4}$$

The entries M_{in} are not necessarily zero, but the difference $(\vec{v}_j - \vec{v}_n)$ does vanish if $j = n$. Consequently the corresponding summands in Eq. (3) do not affect the force density $-c_i\vec{\nabla}\mu_i$ that drives diffusion or migration of species i.

Although it is necessary to distinguish diffusion or migration from convection, the invariance of thermodynamic driving forces with respect to the reference velocity complicates the manipulation of transport equations. Reference-velocity invariance and the isothermal, isobaric Gibbs–Duhem equation

$$\sum_i c_i\vec{\nabla}\mu_i = \vec{0} \tag{5}$$

imply that the $n \times n$ transport matrix $\mathbf{M}$ must be singular, with rank $n-1$. Onsager first stated these facts [9], as well as positing a symmetric reciprocal relation among the entries of $\mathbf{M}$ based on an examination of the expression for local entropy generation [10]. Onsager's symmetry hypothesis has been verified experimentally by Miller [11] and validated theoretically in detail for Stefan–Maxwell diffusion of neutral components by Monroe and Newman [12].

A primary thesis of Onsager's analysis is that on the basis of Eq. (5), only $n-1$ Stefan–Maxwell equations are needed to describe an n-species transport system, because one driving force depends linearly on the others. Fundamental properties of the $\mathbf{M}$ matrix are

$$\sum_j M_{ij} = 0, \quad \sum_i M_{ij} = 0, \quad \textit{and} \quad M_{ij} = M_{ji}. \tag{6}$$

In accord with the second law of thermodynamics, the $\mathbf{M}$ matrix must also be non-positive definite and afford a single null eigenvalue. Be aware that the non-positive-definite nature of $\mathbf{M}$ does not in principle restrict all the Stefan–Maxwell coefficients to be positive.

Onsager's reciprocal relation for $\mathbf{M}$ implies the symmetry of $\mathbf{K}$ through Eq. (4), and consequently, through Eq. (2), that the Stefan–Maxwell coefficients satisfy $\mathcal{D}_{ij} = \mathcal{D}_{ji}$. When developing transport equations for an n-ary transport system, it is convenient to use the symmetry of $\mathbf{M}$ at the outset to reduce the number of independent transport properties involved in the analysis to a set of $1/2 \cdot n \cdot (n-1)$ independent Stefan–Maxwell coefficients. Although claims have recently been made to the contrary [13], these considerations guarantee the thermodynamic consistency of Newman's electrolyte-transport theory.

Helfand (also transliterated from Russian as Gelfand or Gel'fand) pointed out that the singularity of $\mathbf{M}$ prevents rearrangement of the Stefan–Maxwell equations into flux-explicit forms, and solved the inversion problem as follows [14]. Since any one of the Stefan–Maxwell relations is linearly dependent on the others, one can discard the equation that involves the chemical potential gradient of species $i = n$; furthermore, since the nth summand vanishes on the right of Eq. (3), all of the M_{in} can be discarded as well without a loss of information. After this adjustment of the transport matrix, one can immediately write a set of $n-1$ independent transport laws,

$$c_i\vec{\nabla}\mu_i = \sum_{j\neq n} M_{ij}^{nn}(\vec{v}_j - \vec{v}_n) \quad \text{for } i \in \{1,\ldots,n-1\}. \tag{7}$$

Here $\mathbf{M}^{nn}$ is the $(n-1)\times(n-1)$ matrix formed by removing all entries of $\mathbf{M}$ whose indices refer to species n, so that i and j in M_{ij}^{nn} range over all $i \neq n$ and all $j \neq n$. (Note: in this discussion, the superscript mn on a transport matrix will generally indicate that the 'row' index i ranges over all species except the mth, and the 'column' index j ranges over all species except the nth.) As well as being symmetric, the truncated transport matrix $\mathbf{M}^{nn}$ is negative definite and therefore nonsingular, so Eq. (7) can in principle be inverted into a velocity-explicit form. Observe that the commonly used positive-definite transport matrix $\mathbf{L}^{nn} = -(\mathbf{M}^{nn})^{-1}$ that appears in the inverted form of Eq. (7) is also symmetric [11,15].

3. Application to electrochemical systems

In systems with electrically charged constituents, let z_i represent the equivalent charge of species i. Any system will be called 'electrochemical' if $z_i \neq 0$ for some i.

When first defining the concept of electrochemical potential, Guggenheim pointed out a fundamental difficulty that arises when applying chemical potentials to the description of species in electrochemical transport systems [16,17]. Gauss's law suggests that equilibrium states with homogeneous imbalanced charge cannot be created in the laboratory. Therefore, in constitutive laws, the partitioning of electrochemical potentials between terms associated with species activity and terms associated with electrostatic potential must necessarily be arbitrary. To ensure that component activities are experimentally accessible and independent of the electrical state, continuum-scale physical equations should always be phrased such that electrochemical potentials appear in groups associated with electrically neutral combinations of species.

To adopt Guggenheim's principle in electrochemical transport systems, add the requirement that the species n used earlier to establish a reference velocity is charged, so that $z_n \neq 0$. Define the notation

$$\mu_i^n = \mu_i - \frac{z_i}{z_n}\mu_n \tag{8}$$