



Structural electroneutrality in Onsager–Stefan–Maxwell transport with charged species

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ABSTRACT

We present a method to embed local electroneutrality within Onsager–Stefan–Maxwell electrolytic-transport models, circumventing their formulation as differential systems with an algebraic constraint. Flux-explicit transport laws are developed for general multicomponent electrolytes, in which the ionic conductivity, component diffusivities, and transference numbers relate to Stefan–Maxwell coefficients through invertible matrix calculations. A construction we call a ‘salt–charge basis’ implements Guggenheim’s transformation of species electrochemical potentials into combinations describing a minimal set of neutral components, leaving a unique combination associated with electricity. Defining conjugate component concentrations and fluxes that preserve the structures of the Gibbs function and energy dissipation retains symmetric Onsager reciprocal relations. The framework reproduces Newman’s constitutive laws for binary electrolytes and the Pollard–Newman laws for molten salts; we also propose laws for salt solutions in two-solvent blends, such as lithium-ion-battery electrolytes. Finally, we simulate a potentiostatic Hull cell containing a non-ideal binary electrolyte with concentration-dependent properties.

1. Introduction

The growing impetus for improved electrochemical energy storage makes it vital to understand ion transport. Concentrated solution theory [1,2] is widely used to model mass and heat transport in electrolytic materials on the continuum scale. One of the most popular implementations is Doyle, Fuller and Newman’s landmark physics-based model of the dual-insertion lithium-ion battery, which incorporates a concentrated-solution model of a binary electrolyte, comprising a simple salt dissolved in an uncharged solvent [3,4].

Concentrated solution theory is grounded in both classical thermodynamics and linear irreversible thermodynamics, with a model structure that sharply distinguishes between equilibrium properties and transport properties. It derives from the Onsager–Stefan–Maxwell transport laws [1,5], written for n species in an isotropic, isothermal, isobaric common phase as

$$-\nabla \mu_i = \sum_{j=1}^n M_{ij} \tilde{N}_j, \quad (1.1)$$

where μ_i signifies the electrochemical potential of species $i \in \{1, \dots, n\}$ and \tilde{N}_i , its total molar flux. The transport coefficients make up an $n \times n$

matrix \mathbf{M} whose entries are

$$M_{ij} = \begin{cases} -\frac{RT}{c_T \mathcal{D}_{ij}} & \text{if } i \neq j \\ \frac{RT}{c_T} \sum_{k \neq i} \frac{c_k}{\mathcal{D}_{ik} c_j} & \text{if } i = j, \end{cases} \quad (1.2)$$

in which R represents the gas constant, T , the absolute temperature, and c_T , the total species molarity; c_i is the molarity of species i , and \mathcal{D}_{ij} , the Stefan–Maxwell diffusivity of species i through species j . It has been shown for solutions of uncharged constituents that Onsager’s reciprocal relations and the second law of thermodynamics require \mathbf{M} to be symmetric positive semidefinite [6]. Also, \mathbf{M} affords a single null eigenvector $\mathbf{c} = [c_1, c_2, \dots, c_n]^T$, a further structure which ensures that convection of material at the bulk velocity does not dissipate energy [7]. (In this work bold lower-case letters always indicate column matrices.) For fluids wholly made up of uncharged species, the Onsager–Stefan–Maxwell equations, when combined with an equation that establishes a convective velocity, have been shown to constitute a closed model, neither underdetermined nor overdetermined numerically [8].

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An important practicality emerges when considering transport in liquids such as electrolytic solutions, which conduct electricity via the motion of ions. When species that carry charge are mobile, their thermal motion screens local charge imbalances on a length scale comparable to the Debye length (typically of the order of 1 nm) [9]. Thus, if volume elements in a simulation have characteristic size much larger than the Debye length, the local excess charge density ρ_e within them can be assumed to vanish locally, that is,

$$\rho_e = F \sum_{j=1}^n z_j c_j = 0, \quad (1.3)$$

where F is Faraday's constant and z_i is the equivalent charge of species i . Local electroneutrality is foundational to concentrated solution theory and has been assumed nearly ubiquitously in its applications.

Adopting the local electroneutrality approximation simplifies transport models by allowing one charged-species concentration to be eliminated from the governing equations, both reducing the complexity of thermodynamic parametrization and streamlining calculations. Electroneutrality makes concentrated solution theory hard to reconcile with the Onsager–Stefan–Maxwell theory for nonelectrolytes, however, because the additional algebraic constraint imposed by Eq. (1.3) appears to induce an overdetermination within Eqs. (1.1). In particular, it is not clear whether the symmetry and rank of the transport matrix are preserved within electrolytic systems after electroneutrality restricts the available space of species compositions.

Newman and colleagues carefully circumvented the issues raised by electroneutrality when formulating models of binary electrolytes and salt melts [2,10,11]. These analyses emphasized the importance of separating terms into neutral and non-neutral contributions: individual ion concentrations were lumped into salt concentrations; species fluxes were expressed in terms of salt chemical potentials and current density; and terms associated with charge density and charge convection were explicitly neglected.

Possible applications of electroneutral Onsager–Stefan–Maxwell theory readily exceed the scope of the few cases that have been considered to date. For example, aqueous vanadium flow batteries – a transport system comprising at least eight distinct species – have recently been modeled [12,13], but it is not immediately clear how such a model could be extended to account for additional components in a consistent way. At the same time, the increased demand for battery simulations that account for electrolyte additives or contaminants, solution-phase reaction intermediates, or products of side reactions raises the need for a general, numerically robust model formulation.

This paper generalizes Newman's particular implementations of electroneutral concentrated solution theory for binary solutions and salt melts. We implement Guggenheim's thermodynamic programme [14] by creating a structure-preserving, invertible linear transformation that maps the free-energy changes incurred by individual charged species into changes involving uncharged combinations of species, assembling the species electrochemical potentials into a basis set of component chemical potentials and a single quantity that can be interpreted as an electric potential. The same transformation regroups charged-species fluxes into component fluxes and current density. As well as reconciling the electroneutrality approximation with the fundamental equations of linear irreversible thermodynamics in a structure-preserving way, the theory produces a general set of transference numbers and an ionic conductivity that match definitions given for binary electrolytes by Newman, as well as leading to a naturally symmetric set of component diffusivities.

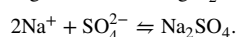
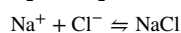
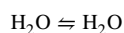
Our development enables the extension of Newman's flux-explicit transport laws for binary electrolytes to general multicomponent electrolytes containing any number of charged or uncharged species, while maintaining the crucial benefits of thermodynamic consistency, convection-invariance of diffusion, and symmetric reciprocal relations inherited from the Onsager–Stefan–Maxwell equations. A numerical simulation of a Hull cell that leverages a solver for Onsager–Stefan–Maxwell transport illustrates the practical utility of this structure-based approach to local electroneutrality within concentrated solution theory.

2. Construction of a salt–charge basis

The key mathematical concepts employed below are linear transformations and inner products, typically represented by matrix operations. These tools are used to develop a change of composition basis from one that lists charged-species molarities into one that lists neutral-salt molarities alongside charge density. Instead of beginning with species concentrations, however, the new composition basis is identified by following Guggenheim's process of grouping species electrochemical potentials into new quantities that represent electrically neutral combinations of species [14]. For any given electrolytic material, one can establish a minimal set of such combinations by positing a set of independent hypothetical chemical reactions that we call *simple association equilibria*, which leave uncharged species alone or bring charged species together to form neutral salts. We refer to products of the simple association equilibria as *components*, rather than species.

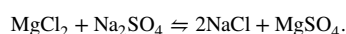
Every electrochemical system is globally electroneutral at equilibrium and every electrochemical reaction necessarily balances both charge and atoms between its reactants and products. Moreover, any physically realizable electrolytic solution must contain at least two countercharged species. It follows that the n species comprising any electrolyte combine to form at most $n - 1$ distinct uncharged components. Thus, association equilibria can be used to combine ions into a set of uncharged products of association reactions, whose energetics in solution is described unambiguously in terms of classical chemical potentials. This idea dates back to the work of Guggenheim almost a century ago [14]; the process we outline in this paper is merely intended to systematize Guggenheim's framework, and consequently, to enable an analysis of electrolyte thermodynamics with the tools of modern linear algebra. We will call the elementary structure that establishes the species charges and a minimal set of hypothetical reactions that neutralize them a *salt–charge basis*.

It is helpful to illustrate with an example before formalizing the process for defining a salt–charge basis. Consider a solution of Na^+ , Cl^- , Mg^{2+} and SO_4^{2-} in water (H_2O). Among these five species, one can write at most $5 - 1 = 4$ independent reactions to form electrically neutral entities. For instance, one could write a trivial equilibrium between the naturally uncharged water molecule and itself, and then write three equilibria that combine distinct countercharged pairs of ions to neutralize their charges:

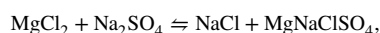


Along with the list of species charges $\{0, 1, -1, 2, -2\}$, these simple association equilibria define a salt–charge basis for this five-species aqueous solution, in this case involving the uncharged components H_2O , NaCl , MgCl_2 , and Na_2SO_4 .

The choice of reactions to form a salt–charge basis is not generally unique, but any neutral component not defined can always be recovered by writing additional reactions involving products formed by the selected simple association equilibria. In the example system, observe that one can create the fourth possible simple binary salt, MgSO_4 , via the recombination reaction



Through this equilibrium, any thermodynamic property of MgSO_4 within this system – such as its chemical potential, partial molar volume, or partial molar entropy – is determined by the properties of dissolved NaCl , Na_2SO_4 , and MgCl_2 . The energetics of any multi-ion salt with higher formula-unit stoichiometry also follows from the simple association equilibria. Consider



which forms a more complex salt, MgNaClSO_4 , from all four of the available ions.

The formal procedure for creating a salt-charge basis generalizes the preceding example. Given a set of species that comprise an electrolytic solution, start by placing them in an ordered list, wherein each species' position assigns its numerical index. Let n_c denote the number of charged species. List all $(n - n_c)$ uncharged species first, and charged species afterward. For consistency with prior approaches, ensure that the n th and $(n - 1)$ th species have opposite charges [15,16]. Then let $\mathbf{z} = [z_1, \dots, z_n]^T$ be a column matrix comprising the species equivalent charges in their assigned order. The ordering ensures that entries z_1, \dots, z_{n-n_c} of \mathbf{z} equal zero, entries z_{n-n_c+1}, \dots, z_n of \mathbf{z} are nonzero, and $z_n/z_{n-1} < 0$.

Next, write a set of $n - 1$ simple association equilibria involving the species, beginning with $n - n_c$ trivial reactions for the naturally uncharged species, and following with $n_c - 1$ linearly independent association reactions, within which countercharged pairs of charged species combine to form simple binary salts. (Here 'simple' means that the reactant stoichiometric coefficients are coprime positive integers.) Let column matrix $\mathbf{v}_i = [v_{i1}, v_{i2}, \dots, v_{in}]^T$ contain the stoichiometric coefficients v_{ij} of reactant species j in the i th simple association equilibrium. For uncharged species $k = 1, \dots, n - n_c$, stoichiometric column \mathbf{v}_k will be the k th column of the identity matrix, notated henceforth as \mathbf{i}_k . For $k = n - n_c + 1, \dots, n - 1$, \mathbf{v}_k has two positive-integer entries, corresponding to the stoichiometric coefficients of species in a formula unit of the simple binary salt they form. The restriction to simple salts ensures that the total number of ions in each formula unit is minimal.

Guggenheim's condition for association equilibria requires that the ion stoichiometry within a formula unit of salt always serves to neutralize its charge [17]. In terms of reactant stoichiometry in the i th simple association equilibrium, the condition is expressed as

$$\mathbf{v}_i^T \mathbf{z} = 0, \quad (2.1)$$

where superscript T indicates the matrix transpose. Note that this condition also holds for every trivial simple association equilibrium based on an uncharged reactant.

It is useful to view Eq. (2.1) as a statement about a matrix inner product, namely: the Guggenheim condition requires that each column of stoichiometric coefficients \mathbf{v}_i is orthogonal to the charges \mathbf{z} . Since the set of stoichiometric columns is also linearly independent by construction, the reactant stoichiometries from the $n - 1$ simple association equilibria establish an $(n - 1)$ -dimensional linear space orthogonal to the span of \mathbf{z} . Moreover, the n -tuple $\{\mathbf{v}_1, \dots, \mathbf{v}_{n-1}, \mathbf{z}\}$ is linearly independent, and consequently forms a basis for the entire n -dimensional composition space. This set of column matrices formally represents the chosen salt-charge basis.

3. Chemical potential in a salt-charge basis

Selecting a salt-charge basis enables one to construct a linear transformation that maps the n_c charged-species electrochemical potentials into $n_c - 1$ chemical potentials of neutral salts, leaving a unique additional combination of electrochemical potentials that can be used to describe charge. The transformation is represented generally by an $n \times n$ matrix \mathbf{Z} ,

$$\mathbf{Z} = \begin{bmatrix} \mathbf{v}_1^T \\ \vdots \\ \mathbf{v}_{n-1}^T \\ \mathbf{z}^T / \|\mathbf{z}\| \end{bmatrix}, \quad (3.1)$$

in which $\|\mathbf{v}\| = \sqrt{\mathbf{v}^T \mathbf{v}}$ for any column \mathbf{v} . Its rows are linearly independent, so \mathbf{Z} is invertible. Each of the first $n - 1$ rows is orthogonal to the last (n)th row, and each of the first $n - n_c$ rows, which correspond to uncharged species, is orthogonal to every other row. Bear in mind that

internal rows corresponding to salts, that is, rows $i = n - n_c + 1, \dots, n - 1$ of \mathbf{Z} , are not necessarily mutually orthogonal.

The transformation \mathbf{Z} combines species electrochemical potentials into component chemical potentials as follows. Let the column matrix $\boldsymbol{\mu} = [\mu_1, \dots, \mu_n]^T$ contain the species electrochemical potentials in order. Then multiplication by \mathbf{Z} maps $\boldsymbol{\mu}$ into new coordinates $\boldsymbol{\mu}_Z$ that stand over the chosen salt-charge basis. In the form of a matrix equation, $\boldsymbol{\mu}_Z$ is defined as

$$\boldsymbol{\mu}_Z = \mathbf{Z}\boldsymbol{\mu}. \quad (3.2)$$

The first $n - 1$ rows of $\boldsymbol{\mu}_Z$ so formed comprise the chemical potentials of a minimal number of neutral components, with the i th row representing the chemical potential of the product formed by the i th simple association equilibrium used to define the salt-charge basis. The last row quantifies all of the information in the set of species electrochemical potentials associated with reversible processes that do not conserve charge. It is convenient to subdivide $\boldsymbol{\mu}_Z$ as

$$\boldsymbol{\mu}_Z = \begin{bmatrix} \boldsymbol{\mu}_v \\ \mu_z \end{bmatrix}, \quad (3.3)$$

where the $(n - 1)$ -dimensional column $\boldsymbol{\mu}_v$ contains the $n - 1$ component chemical potentials. More explicitly, if \mathbf{v}_k has two nonzero entries, $\mu_{v,k} = (\boldsymbol{\mu}_v)_k = \mathbf{v}_k^T \boldsymbol{\mu}$ is a salt chemical potential formed by the same process used by Newman and Thomas-Alyea [1]; otherwise (if $\mathbf{v}_k = \mathbf{i}_k$), $\mu_{v,k}$ reproduces the chemical potential expected for a naturally uncharged species. As we shall see later, the remaining quantity, μ_z , leads naturally to a definition of solution voltage.

4. Concentration and flux in a salt-charge basis

The transformation to a salt-charge basis embodied by \mathbf{Z} can be exploited to form quantities which describe the amounts and motion of uncharged components. Natural definitions of component concentrations and component fluxes arise heuristically from an invariance argument.

We assert as a physical principle that the elementary laws from thermodynamics and irreversible thermodynamics should retain their structures when expressed in terms of components, rather than species. The essential thermodynamic relation among species is the Euler equation,

$$\tilde{G} = \sum_{i=1}^n \mu_i c_i, \quad (4.1)$$

which defines volumetric Gibbs free energy \tilde{G} in terms of species molarities. The essential relation from irreversible thermodynamics is the dissipation function, written at a point within an isothermal, isobaric single phase as

$$T\dot{s} = \sum_{i=1}^n \tilde{N}_i \cdot (-\nabla \mu_i), \quad (4.2)$$

which relates local energy loss $T\dot{s}$ to the species fluxes.

To identify a natural set of composition variables over a given salt-charge basis, require \tilde{G} to retain its structure whether written in terms of species or components. Then the matrix relationship

$$\tilde{G} = \boldsymbol{\mu}^T \mathbf{c} = \boldsymbol{\mu}_Z^T \mathbf{c}_Z \quad (4.3)$$

expresses \tilde{G} either in terms of the species concentrations \mathbf{c} or a column matrix \mathbf{c}_Z that lists component concentrations in the chosen salt-charge basis. Since \mathbf{Z} is nonsingular, it follows from the second equality in Eq. (4.3) and Eq. (3.2) that

$$\mathbf{c}_Z = \mathbf{Z}^{-T} \mathbf{c}, \quad (4.4)$$

where superscript $-T$ indicates the inverse transpose.

Introducing Faraday's law helps to show how the column matrix \mathbf{c}_Z parses electrical information. Faraday's law for charge combines with

Eq. (4.4) to show that excess charge density can be expressed in two equivalent ways,

$$\rho_e = F \mathbf{z}^T \mathbf{c} \quad \text{or} \quad \rho_e = F (\mathbf{Z} \mathbf{z})^T \mathbf{c}_Z, \quad (4.5)$$

in which the distributive property of the matrix transpose was used to rearrange the last equality. Since the first $n-1$ rows of \mathbf{Z} are orthogonal to \mathbf{z}^T , $\mathbf{Z} \mathbf{z} = \|\mathbf{z}\| \mathbf{i}_n$ by Eq. (3.1), and consequently Eq. (4.5) implies that

$$(\mathbf{c}_Z)_n = \frac{\rho_e}{F \|\mathbf{z}\|}, \quad (4.6)$$

i.e., the last entry of \mathbf{c}_Z quantifies excess charge density. Thus \mathbf{c}_Z naturally partitions into a column that represents an ordered set of $n-1$ neutral *component concentrations*, written as \mathbf{c}_v , followed by an entry expressing the excess charge in molar units,

$$\mathbf{c}_Z = \begin{bmatrix} \mathbf{c}_v \\ \frac{\rho_e}{F \|\mathbf{z}\|} \end{bmatrix}, \quad (4.7)$$

which is zero when the local electroneutrality approximation holds. Entry $c_{v,i} = (\mathbf{c}_v)_i$ of the component concentrations \mathbf{c}_v represents the molarity of the product formed by the i th simple association equilibrium.

Natural flux descriptors over a salt-charge basis can be created by a similar route, by demanding that the structure of the energy dissipation $T\dot{s}$ is preserved. Assemble the species fluxes into a column matrix $\tilde{\mathbf{n}} = [\tilde{n}_1, \dots, \tilde{n}_n]^T$.¹ Structure preservation of Eq. (4.2) requires that

$$T\dot{s} = \tilde{\mathbf{n}}^T \cdot (-\nabla \mu) = \tilde{\mathbf{n}}_Z^T \cdot (-\nabla \mu_Z), \quad (4.8)$$

where the column $\tilde{\mathbf{n}}_Z$ lists fluxes over the chosen salt-charge basis \mathbf{Z} . (The notation $\nabla \mathbf{v}$ indicates a column matrix whose i th entry is the vector ∇v_i , where v_i is the i th entry of \mathbf{v} .) The transformation from $\tilde{\mathbf{n}}$ into $\tilde{\mathbf{n}}_Z$ therefore must be

$$\tilde{\mathbf{n}}_Z = \mathbf{Z}^{-T} \tilde{\mathbf{n}}, \quad (4.9)$$

identical to the mapping that sends species concentrations into component concentrations.

Faraday's law – this time, for current – also provides detail about the new fluxes $\tilde{\mathbf{n}}_Z$. In matrix form, Faraday's law casts the current density \vec{i} in terms of species fluxes as

$$\vec{i} = F \mathbf{z}^T \tilde{\mathbf{n}} = F (\mathbf{Z} \mathbf{z})^T \tilde{\mathbf{n}}_Z. \quad (4.10)$$

Again, the fact that $\mathbf{Z} \mathbf{z} = \|\mathbf{z}\| \mathbf{i}_n$ comes into play, yielding

$$(\tilde{\mathbf{n}}_Z)_n = \frac{\vec{i}}{F \|\mathbf{z}\|}. \quad (4.11)$$

Thus the last entry of $\tilde{\mathbf{n}}_Z$ represents a renormalized current density. It is again natural to partition $\tilde{\mathbf{n}}_Z$ as

$$\tilde{\mathbf{n}}_Z = \begin{bmatrix} \tilde{\mathbf{n}}_v \\ \frac{\vec{i}}{F \|\mathbf{z}\|} \end{bmatrix}, \quad (4.12)$$

in which $\tilde{\mathbf{n}}_v$ is an $(n-1)$ -dimensional column matrix representing the set of *total component fluxes*.

Other fundamental thermodynamic laws also readily transform. For example, prior definitions imply that

$$\sum_{i=1}^n c_i \nabla \mu_i = \mathbf{c}^T \nabla \mu = \mathbf{c}_Z^T \nabla \mu_Z = \vec{0}, \quad (4.13)$$

so the change to a salt-charge basis retains a structurally identical isothermal, isobaric Gibbs–Duhem equation.

¹ The overarrow indicates that each entry in the column $\tilde{\mathbf{n}}$ is a vector quantity. Whenever the matrix multiplication makes sense, $\mathbf{A} \tilde{\mathbf{B}}$ forms a matrix $\tilde{\mathbf{C}}$ with vector entries $\tilde{C}_{ij} = \sum_k A_{ik} \tilde{B}_{kj}$, and $\tilde{\mathbf{A}} \cdot \tilde{\mathbf{B}}$ forms \mathbf{C} , with scalar entries $C_{ij} = \sum_k \tilde{A}_{ik} \cdot \tilde{B}_{kj}$.

One can also cast the total species concentration c_T in terms of the component concentrations. Letting $\mathbf{1}$ stand for a column matrix whose entries are all '1', one has that

$$c_T = \sum_{i=1}^n c_i = \mathbf{1}^T \mathbf{c} = \mathbf{v}_Z^T \mathbf{c}_Z, \quad (4.14)$$

in which the column matrix \mathbf{v}_Z , defined as

$$\mathbf{v}_Z = \mathbf{Z} \mathbf{1} = \begin{bmatrix} \mathbf{v} \\ \mathbf{z}^T \mathbf{1} \\ \|\mathbf{z}\| \end{bmatrix}, \quad (4.15)$$

summarizes information about net reactant stoichiometry in the simple association equilibria. The second equality here indicates that the stoichiometric column \mathbf{v}_Z also partitions into $(n-1)$ entries \mathbf{v} that describe components and a final entry associated with charge. When component $i < n$ derives from a naturally uncharged species, the corresponding entry of \mathbf{v} , that is, v_i , is 1; when component $i < n$ is a salt, v_i is the total number of ions in its formula unit.

Molar concentrations are convenient for stating the thermodynamic laws, but they make characterization efforts error-prone because molarity varies with temperature and pressure at fixed composition. It is useful to introduce two alternative composition descriptors, called the *species fractions* \mathbf{y} and *component fractions* \mathbf{y}_Z , and defined as

$$\mathbf{y} = \frac{1}{c_T} \mathbf{c} \quad \text{and} \quad \mathbf{y}_Z = \frac{1}{c_T} \mathbf{c}_Z, \quad (4.16)$$

respectively. These afford the fundamental properties that

$$\mathbf{1}^T \mathbf{y} = 1 \quad \text{and} \quad \mathbf{v}_Z^T \mathbf{y}_Z = 1, \quad (4.17)$$

and are independent of temperature or pressure.

5. Governing equations over a salt-charge basis

The move to a salt-charge basis preserves the structure of material balances. In the absence of homogeneous reactions, all the species continuity equations are summarized in matrix form as

$$\frac{\partial \mathbf{c}}{\partial t} = -\nabla \cdot \tilde{\mathbf{n}}. \quad (5.1)$$

(Given any column $\tilde{\mathbf{v}}$, the operation $\nabla \cdot \tilde{\mathbf{v}}$ forms a column matrix whose i th entry is the scalar $\nabla \cdot \tilde{v}_i$.) Multiplication from the left by \mathbf{Z}^{-T} and use of Eqs. (4.4) and (4.9) yields

$$\frac{\partial \mathbf{c}_Z}{\partial t} = -\nabla \cdot \tilde{\mathbf{n}}_Z, \quad (5.2)$$

confirming structure preservation. Bringing in the decompositions from Eqs. (4.7) and (4.12), one can alternatively express Eq. (5.2) as a set of $n-1$ component mole balances,

$$\frac{\partial \mathbf{c}_v}{\partial t} = -\nabla \cdot \tilde{\mathbf{n}}_v, \quad (5.3)$$

along with the single equation

$$\frac{\partial \rho_e}{\partial t} = -\nabla \cdot \vec{i}, \quad (5.4)$$

which establishes charge continuity. Note that any model governed by species material balances which also incorporates Faraday's law is compatible with Maxwellian electrodynamics, because Maxwell's equations imply a charge-continuity relationship identical to Eq. (5.4).

Because the transformations that form \mathbf{c}_Z and $\tilde{\mathbf{n}}_Z$ preserve the structure of the dissipation function, they also preserve the structure of the Onsager–Stefan–Maxwell constitutive laws. Eq. (1.1) takes the matrix form

$$-\nabla \mu = \mathbf{M} \tilde{\mathbf{n}}. \quad (5.5)$$

Eqs. (3.2) and (4.9) show that this transforms to

$$-\nabla \mu_Z = \mathbf{M}_Z \tilde{\mathbf{n}}_Z \quad (5.6)$$

over a salt-charge basis. The transport matrix \mathbf{M}_Z in the salt-charge representation of the Onsager–Stefan–Maxwell laws relates to the matrix \mathbf{M} from Eq. (1.2) through

$$\mathbf{M}_Z = \mathbf{Z}\mathbf{M}\mathbf{Z}^\top, \quad (5.7)$$

a congruence transformation. It follows from this congruence that \mathbf{M} is symmetric if and only if \mathbf{M}_Z is symmetric, so that the Onsager–Stefan–Maxwell transport coefficients retain symmetry when expressed over a salt-charge basis. Sylvester's law of inertia implies further that the signatures and ranks of \mathbf{M} and \mathbf{M}_Z equate. As mentioned before, the non-dissipative nature of convection implies that \mathbf{M} affords \mathbf{c} as its sole null eigenvector; in light of congruence relation (5.7) and Sylvester's law, this implies that \mathbf{c}_Z is the sole null eigenvector of \mathbf{M}_Z .

Thus, transformation to a salt-charge basis preserves the structure of the differential balance equations as well as all spectral properties of the Onsager–Stefan–Maxwell equations. Both \mathbf{M} and \mathbf{M}_Z are symmetric matrices, and each matrix is singular. Although the null spaces of \mathbf{M} and \mathbf{M}_Z generally differ, each matrix affords just one null eigenvector (\mathbf{c} and \mathbf{c}_Z , respectively). The nonzero eigenvalues of \mathbf{M} generally differ from those of \mathbf{M}_Z , but they are all positive for both matrices.

6. The salt-charge potential

It is prudent to introduce a thermodynamic potential with units of voltage to quantify electrical energy and power. To put electricity in a thermodynamic context, however, one must acknowledge an essential limitation on how electrochemical equilibria are parametrized.

When proposing the electrochemical potential concept, Guggenheim introduced constitutive laws

$$\mu_i = RT \ln a_i + F z_i \Phi, \quad (6.1)$$

in which a_i represents the chemical activity of species i and Φ is an electric potential in the solution phase [1,14,17]. Observing that the equilibrium compositions of practical macroscopic systems cannot be adjusted along paths that violate global electroneutrality, Guggenheim noted that the partitioning of electrochemical potentials into chemical and electrical parts is necessarily ambiguous. Therefore a model of electrolyte energetics must never depend on the chemical activity of a single charged species in isolation [17]. To cast this notion formally, define a non-neutral free-energy contribution μ_z , written in terms of Guggenheim's species activities and solution potential as

$$\mu_z = \frac{1}{\|\mathbf{z}\|} \sum_{i=1}^n z_i \mu_i = \frac{RT}{\|\mathbf{z}\|} \sum_{i=1}^n z_i \ln a_i + F \|\mathbf{z}\| \Phi. \quad (6.2)$$

Guggenheim's principle states that no macroscopic experiment can discern the term that involves the solution potential Φ in this expression from those involving the species activities a_i [14].

Rather than using the solution potential Φ , we instead employ a quantity we call the *salt-charge potential* Φ_z , defined as

$$\Phi_z = \frac{\mu_z}{F \|\mathbf{z}\|}. \quad (6.3)$$

Guggenheim's principle requires that no experiment can distinguish chemical and electrical contributions to Φ_z . Despite this ambiguity, one can still understand the salt-charge potential Φ_z as a type of electrical potential. Inserting decompositions (3.3) and (4.7), then introducing definition (6.3) recasts the Euler equation for \tilde{G} as

$$\tilde{G} = \boldsymbol{\mu}_v^\top \mathbf{c}_v + \Phi_z \rho_e. \quad (6.4)$$

Here, the $\Phi_z \rho_e$ term apparently quantifies excess coulomb energy, that is, the available energy associated with imbalanced charge. Similarly, inserting decompositions (3.3) and (4.12) restates the dissipation as

$$T\dot{s} = \tilde{\mathbf{n}}_v^\top \cdot (-\nabla \boldsymbol{\mu}_v) + \vec{i} \cdot (-\nabla \Phi_z). \quad (6.5)$$

The $-\vec{i} \cdot \nabla \Phi_z$ term is the local ohmic loss—the rate of energy dissipation associated with electrical current flow. Observe that local electroneutrality makes the coulomb term disappear from \tilde{G} , but leaves the ohmic term in $T\dot{s}$.

Although the species material balances summarized in Eq. (5.1) imply charge-continuity Eq. (5.4), and are therefore compatible with Maxwell's equations, equilibrium thermodynamics cannot provide insight into the Maxwellian electric field, because Guggenheim's principle mandates that it is impossible to determine experimentally whether or not $-\nabla \Phi_z$ is a purely electrical quantity.

Still, the energy density and dissipative power associated with salt-charge potential (and its gradient) have unambiguous meanings, because the coulomb term in \tilde{G} and ohmic term in $T\dot{s}$ do not vary with the choice of components. Whereas one can only speak of 'a' salt-charge basis since \mathbf{Z} is not always unique, one may refer to 'the' salt-charge potential, which is unique for a given \mathbf{z} .

7. Thermodynamic factors in a salt-charge basis

To implement a simulation of any transport system, one requires constitutive relationships that express how thermodynamic potentials depend on the concentrations of extensive properties. The particular mapping that sends composition gradients into electrochemical-potential gradients in isothermal, isobaric situations is expressed by a matrix of equilibrium properties commonly referred to as *thermodynamic factors*.

For an isothermal, isobaric, n -species mass-transport system, the thermodynamic factors depend parametrically on $\frac{1}{2}n(n-1)$ composition-dependent state functions—one state function for every pair of species [6,16,18]. In their discussion of Onsager reciprocal relations for multicomponent diffusion, Monroe and Newman introduced an $(n-1) \times (n-1)$ matrix of dimensionless Darken factors \mathbf{Q} [19], defined such that

$$\text{diag}(\mathbf{y}) \nabla \boldsymbol{\mu} = RT \begin{bmatrix} \mathbf{I}_{n-1} \\ -\mathbf{1}^\top \end{bmatrix} \mathbf{Q} [\mathbf{I}_{n-1} \quad \mathbf{o}]^\top \nabla \mathbf{y}, \quad (7.1)$$

where \mathbf{I}_{n-1} indicates the $(n-1) \times (n-1)$ identity matrix, \mathbf{o} represents a column of zeroes, and the linear operator $\text{diag}(\mathbf{v})$ forms column matrix \mathbf{v} into a diagonal square matrix whose i th diagonal entry is v_i .² Each entry Q_{ij} of \mathbf{Q} represents the thermodynamic derivative of the (log) activity of species i with respect to the particle fraction of species $j < n$, leaving temperature, pressure, and all particle fractions save those of species j and n fixed. (Experiments to measure Q_{ij} adopt a convention that when one varies y_j , one specifically adjusts y_n to maintain the constraint that $\mathbf{1}^\top \mathbf{y} = 1$.) In terms of species activities, Q_{ij} is defined as

$$Q_{ij} = y_i \left(\frac{\partial \ln a_i}{\partial y_j} \right)_{T,p,y_{k \neq j,n}} = \delta_{ij} + y_i \left(\frac{\partial \ln \lambda_i}{\partial y_j} \right)_{T,p,y_{k \neq j,n}}, \quad (7.2)$$

in which δ_{ij} represents the Kronecker delta. The expression on the right of Eq. (7.2) introduces the *activity coefficient* of species i , λ_i , defined such that $a_i = \lambda_i y_i$. Introducing λ_i emphasizes the expectation that $\mathbf{Q} = \mathbf{I}_{n-1}$ within solutions whose mixing free energies are thermodynamically ideal.

Although the simplicity of \mathbf{Q} in the ideal case is useful, Maxwell relations among these Darken factors in non-ideal situations are obscure. It is sometimes convenient to work instead with the $(n-1) \times (n-1)$ Hessian matrix \mathbf{K} ,

$$K_{ij} = \frac{\partial^2}{\partial y_i \partial y_j} \left(\frac{\tilde{G}}{RT c_T} \right)_{T,p,y_{k \neq i,j,n}}, \quad (7.3)$$

² Generally $\text{diag}(\mathbf{a})\mathbf{b} = \text{diag}(\mathbf{b})\mathbf{a}$; both products form a column \mathbf{c} with entries $c_i = a_i b_i$. Also $\mathbf{1}^\top \text{diag}(\mathbf{a}) = \mathbf{a}^\top$ and $\text{diag}(\mathbf{a})\mathbf{1} = \mathbf{a}$. The notation $\text{diag}(\mathbf{a})^{-1}$ indicates the diagonal matrix whose i th entry is $1/a_i$, such that $\text{diag}(\mathbf{a})^{-1} \mathbf{a} = \mathbf{1}$.

for which Maxwell relations imply that $\mathbf{K} = \mathbf{K}^T$ [6]. Thermodynamic stability demands that \mathbf{K} is positive semidefinite [16]. The Darken factors \mathbf{Q} depend on \mathbf{K} through

$$\mathbf{Q} = \mathbf{Y}^{-1} \mathbf{K}, \quad (7.4)$$

where the definition

$$\mathbf{Y}^{-1} = \begin{bmatrix} \mathbf{I}_{n-1} & \mathbf{o} \end{bmatrix} (\text{diag}(\mathbf{y}) - \mathbf{y}\mathbf{y}^T)^{-1} \begin{bmatrix} \mathbf{I}_{n-1} \\ \mathbf{o}^T \end{bmatrix} \quad (7.5)$$

puts in matrix form the $(n-1) \times (n-1)$ inverse composition matrix \mathbf{Y}^{-1} employed by Monroe and Newman [20]. Substituting Eqs. (7.4) and (7.5) into Eq. (7.1) and algebraically simplifying the result gives

$$\nabla \mu = RT (\mathbf{I} - \mathbf{1}\mathbf{y}^T) \begin{bmatrix} \mathbf{K} & \mathbf{o} \\ \mathbf{o}^T & 0 \end{bmatrix} \nabla \mathbf{y}, \quad (7.6)$$

which shows how the isothermal, isobaric composition dependence of $\nabla \mu$ is parametrized by the $\frac{1}{2}n(n-1)$ independent entries of \mathbf{K} . Observe that the block matrix here has a nullspace spanned by the null eigenvector \mathbf{i}_n , which reflects the fact that gradients ∇y_n have no independent effect on species electrochemical potentials.

Some of the benefits of the Darken matrix \mathbf{Q} can be brought into the analysis of equations expressed in terms of \mathbf{K} . The composition Hessian separates into two parts,

$$\mathbf{K} = \mathbf{Y} + \Delta \mathbf{K}, \quad (7.7)$$

such that \mathbf{Y} accounts for derivatives of ideal mixing free energy and $\Delta \mathbf{K}$ expresses the Hessian of excess free energy. The composition matrix \mathbf{Y} here is written explicitly as

$$\mathbf{Y} = \begin{bmatrix} \mathbf{I}_{n-1} & \mathbf{o} \end{bmatrix} \left(\text{diag}(\mathbf{y})^{-1} + \frac{\mathbf{1}\mathbf{1}^T}{\mathbf{i}_n^T \mathbf{y}} \right) \begin{bmatrix} \mathbf{I}_{n-1} \\ \mathbf{o}^T \end{bmatrix}. \quad (7.8)$$

Upon substitution into Eq. (7.6), algebraic simplification yields an equivalent alternative form,

$$\nabla \mu = RT \text{diag}(\mathbf{y})^{-1} \nabla \mathbf{y} + RT (\mathbf{I} - \mathbf{1}\mathbf{y}^T) \begin{bmatrix} \Delta \mathbf{K} & \mathbf{o} \\ \mathbf{o}^T & 0 \end{bmatrix} \nabla \mathbf{y}, \quad (7.9)$$

in which the $(n-1) \times (n-1)$ matrix $\Delta \mathbf{K}$ is symmetric, and vanishes when mixing is ideal.

The nonideal term in Eq. (7.9) translates readily into a salt-charge basis. Use the congruence relationship

$$\Delta \mathbf{K}_Z = \mathbf{Z} \begin{bmatrix} \Delta \mathbf{K} & \mathbf{o} \\ \mathbf{o}^T & 0 \end{bmatrix} \mathbf{Z}^T \quad (7.10)$$

to define a transformed excess Hessian $\Delta \mathbf{K}_Z$. All n^2 entries of this symmetric matrix are generally nonzero. The nullspace of $\Delta \mathbf{K}_Z$ has a minimum dimension of 1, however, because $\mathbf{Z}^{-T} \mathbf{i}_n$ is always a null eigenvector. Multiplying Eq. (7.9) through by \mathbf{Z} and inserting $\Delta \mathbf{K}_Z$, one finds the expression

$$\nabla \mu_Z = RT \mathbf{Z} \text{diag}(\mathbf{y})^{-1} \nabla \mathbf{y} + RT (\mathbf{I} - \mathbf{v}_Z \mathbf{y}_Z^T) \Delta \mathbf{K}_Z \nabla \mathbf{y}_Z \quad (7.11)$$

after using Eqs. (3.2), (4.4), and (4.17) to simplify. The assertion that species potentials within an electrolyte at constant temperature and pressure depend on all the independent species fractions necessitates that the differential component potentials have this structure.

It is noteworthy that the ideal part of the component chemical-potential gradients – the first term on the right of Eq. (7.11) – involves entries of the salt-charge transformation \mathbf{Z} as prefactors. Thus the ideal mixing free energy of a dissolved salt scales linearly with its ion stoichiometry, in addition to the ideal logarithmic dependence on its mole fraction. Note also that multiplication from the left by $\mathbf{c}_Z^T = \mathbf{c}_T \mathbf{y}_Z^T$ verifies that the Gibbs–Duhem equation is satisfied by constitutive laws (7.11) for any choice of the symmetric excess Hessian matrix $\Delta \mathbf{K}_Z$.

Although Eq. (7.11) is formally correct, the parameters within $\Delta \mathbf{K}_Z$ are not all measurable. In particular, as discussed after Eq. (6.2), adherence to Guggenheim's principle demands that the coefficients of

∇y_Z on the right side of the equation for $\nabla \mu_Z$ should remain ambiguous because they cannot be disentangled with equilibrium experiments. Therefore it is appropriate to discard this component of the expansion in Eq. (7.11).

The notation is simplified by defining an $n \times (n-1)$ matrix \mathbf{N} , whose columns represent the reactant stoichiometries in all of the simple association equilibria:

$$\mathbf{N} = [\mathbf{v}_1 \quad \dots \quad \mathbf{v}_{n-1}], \quad \text{so} \quad \mathbf{Z} = \begin{bmatrix} \mathbf{N}^T \\ \frac{\mathbf{z}^T}{\|\mathbf{z}\|} \end{bmatrix}. \quad (7.12)$$

Further observing that $\mathbf{v} = \mathbf{N}^T \mathbf{1}$, the general expression

$$\nabla \mu_v = RT \mathbf{N}^T \text{diag}(\mathbf{y})^{-1} \nabla \mathbf{y} + RT ([\mathbf{I}_{n-1} \quad \mathbf{o}] - \mathbf{v} \mathbf{y}_Z^T) \Delta \mathbf{K}_Z \nabla \mathbf{y}_Z \quad (7.13)$$

expresses the portion of the expansion that remains after striking the last row of matrix Eq. (7.11) to accommodate Guggenheim's principle. In the next section, this form of the component chemical-potential gradients will facilitate analyzing constraints on properties under the electroneutrality approximation.

8. Structural implications of electroneutrality

Imposing local electroneutrality on the Onsager–Stefan–Maxwell transport model impacts both the variables involved and the parameters that quantify material properties. The approximation separately impacts the thermodynamic and dynamical aspects of the general theory.

8.1. Electroneutral composition

The simplest consequence of electroneutrality is that it limits the available composition space, because one charged-species concentration becomes linearly dependent on the others. It is useful to establish some relationships that demonstrate the effect of this constraint.

When excess charge density vanishes everywhere, the n -dimensional column of species concentrations \mathbf{c} becomes limited to a set of locally electroneutral species concentrations, which we notate as \mathbf{c}^0 . Necessarily, any solution compositions in the space that \mathbf{c}^0 occupies must be instantiable by assembling uncharged components in the appropriate proportions and then dissociating them into their constituent species. This idea can be put in mathematical terms by leveraging a salt-charge basis. Over such a basis \mathbf{c}^0 is determined by the mapping

$$\mathbf{c}^0 = \mathbf{Z}^T \begin{bmatrix} \mathbf{c}_v \\ 0 \end{bmatrix} = \mathbf{N} \mathbf{c}_v, \quad (8.1)$$

which results from Eqs. (4.4) and (4.7) when $\rho_e = 0$. Thus the first $(n-1)$ columns of \mathbf{Z}^T (that is, the columns of \mathbf{N}) serve as a basis for the subspace occupied by \mathbf{c}^0 , and the $(n-1)$ -dimensional column of electroneutral component concentrations \mathbf{c}_v expresses the coordinates of a given \mathbf{c}^0 over this basis. Electroneutrality constrains the total concentration's domain in a similar way. The electroneutral total concentration, c_T^0 , depends on \mathbf{c}_v as

$$c_T^0 = \mathbf{1}^T \mathbf{c}^0 = \mathbf{v}_Z^T \begin{bmatrix} \mathbf{c}_v \\ 0 \end{bmatrix} = \mathbf{v}^T \mathbf{c}_v, \quad (8.2)$$

simplified with the definition of \mathbf{v} from Eq. (4.15).

Some additional physical principles outside thermodynamics restrict the range of neutral compositions. Since negative species molarities are meaningless, every entry of \mathbf{c}^0 must be non-negative. Because mass transport cannot occur in the absence of species, c_T^0 is strictly positive. These inequalities place bounds on the entries of the component-composition column \mathbf{c}_v .

The restrictions on \mathbf{c}^0 and c_T^0 also imply that every entry of the electroneutral species fractions, y^0 , defined as

$$y^0 = \frac{1}{c_T^0} \mathbf{c}^0 = \mathbf{Z}^T \begin{bmatrix} \mathbf{y}_v \\ 0 \end{bmatrix} = \mathbf{N} \mathbf{y}_v, \quad (8.3)$$

must be strictly non-negative. Under electroneutrality this object retains the property that $\mathbf{1}^\top \mathbf{y}^0 = 1$, established by Eq. (4.17). Furthermore, the condition

$$\mathbf{v}^\top \mathbf{y}_v = 1 \quad (\text{electroneutral}) \quad (8.4)$$

constrains component fractions under electroneutrality.

Note that requiring \mathbf{c}^0 or \mathbf{y}^0 to have non-negative entries does not ensure that every component concentration within \mathbf{c}_v (or \mathbf{y}_v) is non-negative. Over a salt-charge basis, negative component concentrations can occur when the choice of products in the simple association equilibria is not unique. Consider the solution of Na^+ , Cl^- , Mg^{2+} and SO_4^{2-} in H_2O from Section 2 by way of example. The electroneutral composition space for this solution reaches extremes corresponding to four distinct binary electrolytes: aqueous NaCl with a trace amount of MgSO_4 ; aqueous MgCl_2 with trace Na_2SO_4 ; aqueous Na_2SO_4 with trace MgCl_2 ; and aqueous MgSO_4 with trace NaCl . Suppose the neutral salts for a salt-charge basis are chosen to be NaCl , MgCl_2 , and Na_2SO_4 , as in Section 2. In the laboratory, these salts cannot be mixed with water to produce, say, 1 M aqueous MgSO_4 . To formulate 1 M MgSO_4 with the given precursor salts, one would have to add Na_2SO_4 to supply the sulfate, add MgCl_2 to introduce magnesium, and then utilize a separation process (e.g., precipitation, heterogeneous extraction, etc.) to remove NaCl . Thus, aqueous 1 M MgSO_4 is represented by a \mathbf{c}_v column with entries for 1 M Na_2SO_4 , 1 M MgCl_2 , and -2 M NaCl . Although the NaCl molarity is negative, that of every ion remains non-negative. Since MgSO_4 can be formed by recombination reaction 2, its chemical potential depends unambiguously on those of Na_2SO_4 , MgCl_2 , and NaCl . The negative concentration just indicates that NaCl is a product of a recombination reaction involving the salt-charge basis' components, rather than a reactant.

8.2. Component activity coefficients

Electroneutrality has ramifications for Guggenheim's constitutive framework. Definition (6.1) can be rewritten in terms of species activity coefficients λ_i^0 as

$$\begin{aligned} \mu_i^0 &= \mu_i^\ominus + RT \ln (\lambda_i^0 y_i^0) + z_i F \Phi, \quad \text{or} \\ \boldsymbol{\mu}^0 &= \boldsymbol{\mu}^\ominus + RT \ln (\mathbf{y}^0) + RT \ln (\boldsymbol{\lambda}^0) + F \Phi \mathbf{z}, \end{aligned} \quad (8.5)$$

where the composition-independent parameters μ_i^\ominus that make up the n -dimensional column $\boldsymbol{\mu}^\ominus$ quantify species electrochemical potentials in a secondary reference state, and $\ln(\mathbf{v})$ represents a column matrix wherein each entry is the natural logarithm of the corresponding entry of \mathbf{v} . Thermodynamic consistency mandates that every activity coefficient comprising $\boldsymbol{\lambda}^0$ is positive. Since $(\mathbf{c}^0)^\top \mathbf{z} = 0$ by design, these constitutive laws meet the requirement that

$$\tilde{G} = (\mathbf{c}^0)^\top \boldsymbol{\mu}^0 = \mathbf{c}_v^\top \boldsymbol{\mu}_v^0 \quad (8.6)$$

as a consequence of Eqs. (3.2) and (8.1).

Constitutive laws for component chemical potentials in accord with Guggenheim's formulation are identified by using the second equality in Eq. (8.6), which implies

$$(\mathbf{c}^0)^\top \mathbf{Z}^{-1} (\mathbf{Z} \boldsymbol{\mu}^0 - \boldsymbol{\mu}_Z^0) = 0. \quad (8.7)$$

Insertion of Eqs. (7.12) and (8.5) into Eq. (8.7), followed by partitioning of $\boldsymbol{\mu}_Z^0$ with Eq. (3.3), application of the relation $\mathbf{Z}\mathbf{z} = \|\mathbf{z}\| \mathbf{i}_n$, and substitution of Φ in favor of Φ_Z with Eqs. (6.2) and (6.3), reveals that Guggenheim's laws are consistent with component chemical potentials constituted by equations of the form

$$\mu_{v,k}^0 = \mu_{v,k}^\ominus + RT \sum_{m=1}^n v_{km} \ln y_m^0 + RT v_k \ln \lambda_{v,k}^0, \quad (8.8)$$

wherein $\mu_{v,k}^\ominus(T, p)$ is the chemical potential of component k in the reference state and v_k is the k th entry of the column \mathbf{v} that quantifies

total component stoichiometry. The parameter $\lambda_{v,k}^0$ is called the *mean molar activity coefficient* of component k .

All of the component chemical-potential constitutive laws can therefore be summarized by a matrix equation,

$$\boldsymbol{\mu}_v^0 = \boldsymbol{\mu}_v^\ominus + \boldsymbol{\mu}_v^{0,\text{ideal}} + RT \text{diag}(\mathbf{v}) \ln \boldsymbol{\lambda}_v^0, \quad (8.9)$$

in which the term

$$\boldsymbol{\mu}_v^{0,\text{ideal}} = RT \mathbf{N}^\top \ln \mathbf{y}^0 \quad (8.10)$$

accounts for the part of a component's chemical potential that is attributable to ideal mixing of its constituent species, and the reference chemical potentials and mean molar activity coefficients of each component make up the $(n-1)$ -dimensional columns $\boldsymbol{\mu}_v^\ominus$ and $\boldsymbol{\lambda}_v^0$, respectively: the expression

$$\boldsymbol{\mu}_v^\ominus = \mathbf{N}^\top \boldsymbol{\mu}^\ominus, \quad \text{or} \quad \mu_{v,k}^\ominus = \sum_{m=1}^n v_{km} \mu_m^\ominus, \quad (8.11)$$

where $k \in \{1, \dots, n-1\}$, shows how reactant stoichiometries in the simple association equilibria relate the reference potentials of components and species, and

$$\ln \boldsymbol{\lambda}_v^0 = \text{diag}(\mathbf{v})^{-1} \mathbf{N}^\top \ln \boldsymbol{\lambda}^0, \quad \text{or} \quad \ln \lambda_{v,k}^0 = \sum_{m=1}^n \frac{v_{km}}{v_k} \ln \lambda_m^0, \quad (8.12)$$

puts the mean molar component activity coefficients in terms of species activity coefficients. Note that the versions of Eqs. (8.11) and (8.12) written in terms of summations identify with the definitions stated by both Guggenheim [17] and Newman [1].

8.3. Electroneutral thermodynamic factors

Applying electroneutrality to Eqs. (4.13) and (6.4) reveals equilibrium energetics to be independent of Φ_Z . The electroneutral Euler and Gibbs–Duhem equations,

$$\tilde{G} = (\boldsymbol{\mu}_v^0)^\top \mathbf{c}_v \quad (8.13)$$

and

$$\mathbf{c}_v^\top \nabla \boldsymbol{\mu}_v^0 = \vec{0}, \quad (8.14)$$

respectively, imply that isothermal, isobaric component chemical potentials have the functionality $\boldsymbol{\mu}_v^0 = \boldsymbol{\mu}_v^0(\mathbf{c}_v)$, or, equivalently, $\boldsymbol{\mu}_v^0(\mathbf{y}_v)$.³ The mean molar activity coefficients in electroneutral constitutive laws (8.9) thus depend only on \mathbf{y}_v at constant temperature and pressure.

These facts come together with the discussion of Darken factors from Section 7 to establish Maxwell relations and component thermodynamic factors for the electroneutral Onsager–Stefan–Maxwell diffusion driving forces. Let

$$A_{v,i,j}^0 = v_i \left(\frac{\partial \ln \lambda_{v,i}^0}{\partial y_{v,j}} \right)_{T,p,y_{v,k \neq j,n-1}} \quad (8.15)$$

represent the partial derivative of the mean molar activity coefficient of component i with respect to the fraction of component j , leaving all of the $n-1$ component fractions save the j th and $(n-1)$ th fixed. In light of Gibbs–Duhem equation (8.14), the component chemical-potential gradients can be expanded as

$$\nabla \boldsymbol{\mu}_v^0 = \nabla \boldsymbol{\mu}_v^{0,\text{ideal}} + RT \left(\mathbf{I}_{n-1} - \mathbf{v} \mathbf{y}_v^\top \right) \begin{bmatrix} \mathbf{A}_v^0 & \mathbf{0} \\ \mathbf{0}^\top & 0 \end{bmatrix} \nabla \mathbf{y}_v, \quad (8.16)$$

³ The implication $\boldsymbol{\mu}_v^0(\mathbf{c}_v) \implies \boldsymbol{\mu}_v^0(\mathbf{y}_v)$ relies on the fact that total concentration depends only on the species particle fractions at fixed temperature and pressure. This is justified by Euler equation (4.1) because the molar Gibbs energy $\bar{G} = \tilde{G}/c_T$ must produce the molar volume $1/c_T$ through the derivative $(\partial \bar{G} / \partial p)_{T,y_i} = 1/c_T$.

in which Λ_v^0 is an $(n-2) \times (n-2)$ matrix of electroneutral component Darken factors, and

$$\begin{aligned}\nabla \mu_v^{0,\text{ideal}} &= RT \mathbf{N}^\top \text{diag}(\mathbf{y}^0)^{-1} \nabla \mathbf{y}^0 \\ &= RT \mathbf{N}^\top \text{diag}(\mathbf{N} \mathbf{y}_v)^{-1} \mathbf{N} \nabla \mathbf{y}_v\end{aligned}\quad (8.17)$$

expresses the gradient of the ideal contribution to every component chemical potential.

Eq. (8.16) contains $(n-2)^2$ excess component Darken factors $\Lambda_{v,ij}^0$, but these are not all independent because of Maxwell relations, whose structure can be understood by revisiting the electroneutral form of Eq. (7.13). After insertion of Eq. (8.17) and simplification with Eq. (8.3), Eq. (7.13) becomes

$$\nabla \mu_v^0 = \nabla \mu_v^{0,\text{ideal}} + RT (\mathbf{I}_{n-1} - \mathbf{v} \mathbf{y}_v^\top) \Delta \mathbf{K}_v^0 \nabla \mathbf{y}_v, \quad (8.18)$$

in which the $(n-1)$ by $(n-1)$ matrix $\Delta \mathbf{K}_v^0$ is formed by striking the n th row and n th column of $\Delta \mathbf{K}_Z^0$,

$$\Delta \mathbf{K}_v^0 = \begin{bmatrix} \mathbf{I}_{n-1} & \mathbf{0} \end{bmatrix} \Delta \mathbf{K}_Z^0 \begin{bmatrix} \mathbf{I}_{n-1} \\ \mathbf{0}^\top \end{bmatrix}, \quad (8.19)$$

and is consequently symmetric. Equating the right sides of Eqs. (8.16) and (8.18) shows that

$$(\mathbf{I}_{n-1} - \mathbf{v} \mathbf{y}_v^\top) \begin{bmatrix} \Lambda_v^0 & \mathbf{0} \\ \mathbf{0}^\top & 0 \end{bmatrix} = (\mathbf{I}_{n-1} - \mathbf{v} \mathbf{y}_v^\top) \Delta \mathbf{K}_v^0, \quad (8.20)$$

which relates the thermodynamic factors that make up Λ_v^0 to the truncated excess Hessian $\Delta \mathbf{K}_v^0$. Compatibility of the species and component perspectives thus demands that the last column of $\Delta \mathbf{K}_v^0$ lies in the nullspace of $(\mathbf{I}_{n-1} - \mathbf{v} \mathbf{y}_v^\top)$, that is, it must be proportional to \mathbf{v} . (Guggenheim's principle demands that the constant of proportionality cannot be determined, however.) The last row of $\Delta \mathbf{K}_v^0$ is therefore proportional to \mathbf{v}^\top , as required by the Hessian's symmetry. Multiplication through by \mathbf{y}_v^\top additionally verifies that the last row of Eq. (8.20) is linearly dependent, since Gibbs–Duhem relations constrain both sides of the equality in the same way.

In short, the last row of Eq. (8.20) is redundant, and the last column, trivial. Discarding these, isolating the truncated Hessian that remains by exploiting a Sherman–Morrison formula, and further rearranging demonstrate that for all $i \neq j$, the Maxwell relations

$$v_i \left(\frac{\partial \ln \lambda_{v,i}^0}{\partial y_{v,j}} \right)_{T,p,y_{v,k \neq j,n-1}} = v_j \left(\frac{\partial \ln \lambda_{v,j}^0}{\partial y_{v,i}} \right)_{T,p,y_{v,k \neq i,n-1}} \quad (8.21)$$

hold; the matrix Λ_v^0 is symmetric. This substantiates the claim that $\frac{1}{2}(n-1)(n-2)$ properties, which quantify isothermal, isobaric gradients of $n-1$ component chemical potentials, parametrize the mixing free energy of any n -ary electroneutral electrolyte.

Henceforth, we will write the electroneutral gradients of component chemical potentials in the more compact form

$$\nabla \mu_v^0 = RT \mathbf{X}_v^0 \nabla \mathbf{y}_v, \quad (8.22)$$

in which the $(n-1) \times (n-1)$ matrix of *electroneutral thermodynamic factors* \mathbf{X}_v^0 is defined as

$$\mathbf{X}_v^0 = \mathbf{N}^\top \text{diag}(\mathbf{N} \mathbf{y}_v)^{-1} \mathbf{N} + (\mathbf{I}_{n-1} - \mathbf{v} \mathbf{y}_v^\top) \begin{bmatrix} \Lambda_v^0 & \mathbf{0} \\ \mathbf{0}^\top & 0 \end{bmatrix}, \quad (8.23)$$

wherein $\Lambda_v^0 = (\Lambda_v^0)^\top$, and Eq. (8.15) establishes how independent entries in Λ_v^0 can be measured experimentally.

8.4. Electroneutrality and dynamics

Application of the electroneutrality approximation to the dynamical governing equations is simpler than electroneutral thermodynamics. When excess charge density vanishes uniformly, there is no change to the $(n-1)$ -dimensional component material balance, Eq. (5.3), that

was produced by moving to a salt–charge basis. Charge continuity, embodied by Eq. (5.4), does simplify slightly, to

$$\nabla \cdot \vec{i} = 0, \quad (\text{electroneutral}) \quad (8.24)$$

which expresses Kirchhoff's law of the node.

Entries in the Onsager drag matrix from Eq. (1.2) change their structure under electroneutrality. The transport matrix \mathbf{M}^0 that relates species fluxes to species driving forces in the electroneutral case has entries given by

$$M_{ij}^0 = \begin{cases} -\frac{RT}{c_T^0 \mathcal{D}_{ij}} & \text{if } i \neq j \\ \frac{RT}{c_T^0} \sum_{k \neq i} \frac{c_k^0}{\mathcal{D}_{ik} c_j^0} & \text{if } i = j, \end{cases} \quad (8.25)$$

where the neutral composition descriptors c^0 and c_T^0 are given in terms of the component concentrations c_v by Eqs. (8.1) and (8.2), respectively. Although the n species concentrations here depend only on $n-1$ component concentrations from a salt–charge basis, the effect is relatively minor because the constraint does not affect the rank of the matrix \mathbf{M}^0 .

When the whole set of Onsager–Stefan–Maxwell equations is put over a salt–charge basis, the transport coefficients that appear after applying electroneutrality follow from congruence relation (5.7):

$$\mathbf{M}_Z^0 = \mathbf{Z} \mathbf{M}^0 \mathbf{Z}^\top = \begin{bmatrix} \mathbf{M}_v & \mathbf{m}_z \\ \mathbf{m}_z^\top & M_{zz} \end{bmatrix}. \quad (8.26)$$

The second equality here defines sub-blocks that will be useful for expressing other macroscopic transport properties in terms of the electroneutral Onsager drag coefficients over a salt–charge basis, \mathbf{M}_Z^0 . Sub-block \mathbf{M}_v is an $(n-1) \times (n-1)$ square matrix, \mathbf{m}_z , an $(n-1)$ -dimensional column matrix, and M_{zz} , a scalar.

Recall from Section 5 that the change to a salt–charge basis implies that \mathbf{c}_Z is the sole null eigenvector of \mathbf{M}_Z^0 . After electroneutrality is adopted, the column \mathbf{c}_Z^0 , defined as

$$\mathbf{c}_Z^0 = \begin{bmatrix} \mathbf{c}_v \\ 0 \end{bmatrix}, \quad (8.27)$$

is a null eigenvector of \mathbf{M}_Z^0 . This in turn implies that

$$\mathbf{M}_v \mathbf{c}_v = \mathbf{0}, \quad (8.28)$$

which is to say, the column of component concentrations is a null eigenvector of the symmetric sub-block \mathbf{M}_v , and also that

$$\mathbf{m}_z^\top \mathbf{c}_v = 0, \quad (8.29)$$

so that the column \mathbf{m}_z is orthogonal to the component concentrations.

Once the transport matrix from Eq. (8.26) has been incorporated, the Onsager–Stefan–Maxwell equations over a salt–charge basis from Eq. (5.6) become

$$-\begin{bmatrix} \nabla \mu_v^0 \\ F \|\mathbf{z}\| \nabla \phi^0 \end{bmatrix} = \begin{bmatrix} \mathbf{M}_v & \mathbf{m}_z \\ \mathbf{m}_z^\top & M_{zz} \end{bmatrix} \begin{bmatrix} \bar{\mathbf{n}}_v \\ \vec{i} \\ F \|\mathbf{z}\| \end{bmatrix} \quad (8.30)$$

under local electroneutrality. The transport matrix here is symmetric positive semidefinite and affords the single null eigenvector \mathbf{c}_Z^0 , preserving the spectral structure of the species flux laws. Bear in mind that the component chemical potential gradients $\nabla \mu_v^0$ are parametrized by a set of thermodynamic factors \mathbf{X}_v^0 dependent on \mathbf{y}_v and a matrix of material parameters through Eqs. (8.23), in turn constrained by the symmetry of the excess property matrix Λ_v^0 . Henceforth we call Eq. (8.30), with $\nabla \mu_v^0$ parametrized by Eqs. (8.22) and (8.23), the *electroneutral Onsager–Stefan–Maxwell equations*.

9. Mass continuity and excess fluxes

Compatibility of the material balances with the familiar mass continuity equation is ensured by identifying the mass-average (barycentric) velocity as a combination of the species fluxes. Developing excess fluxes relative to the mass-average velocity allows an understanding of the non-dissipative phenomenon of convection, which is distinct from the dissipative diffusion process.

To incorporate mass into the governing framework, let \bar{m}_i represent the molar mass of species i , and assemble the set of these masses into an n -dimensional column $\bar{\mathbf{m}}$. The mass density ρ of a multi-species solution is generally given by

$$\rho = \sum_{i=1}^n \bar{m}_i c_i = \bar{\mathbf{m}}^T \mathbf{c}. \quad (9.1)$$

Further let ψ_i represent a weighting factor with units of inverse molarity (or, equivalently, molar volume),

$$\psi_i = \frac{\bar{m}_i}{\rho}, \quad \text{or} \quad \boldsymbol{\psi} = \frac{\bar{\mathbf{m}}}{\rho}, \quad (9.2)$$

where the second relationship summarizes the definition for all i by introducing an n -dimensional column matrix $\boldsymbol{\psi}$ with entries ψ_i . Note that Eq. (9.1) implies a general constraint among the weighting factors,

$$\boldsymbol{\psi}^T \mathbf{c} = 1, \quad (9.3)$$

that is, the species mass fractions $\psi_i c_i$ sum to unity. The mass-average velocity $\bar{\mathbf{v}}$ is generally defined as

$$\bar{\mathbf{v}} = \sum_{i=1}^n \psi_i \bar{\mathbf{N}}_i = \boldsymbol{\psi}^T \bar{\mathbf{n}}. \quad (9.4)$$

With Eqs. (9.1), (9.3), and (9.4) in hand, one can multiply Eq. (5.1) through from the left by the constant row matrix $\rho \boldsymbol{\psi}^T (= \bar{\mathbf{m}}^T)$ to get

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \bar{\mathbf{v}}), \quad (9.5)$$

showing consistency of the material balances with the common understanding of mass continuity.

Defining a bulk velocity such as $\bar{\mathbf{v}}$ distinguishes convective mass transport from diffusion as follows. Let the excess molar flux of species i relative to the mass-average velocity, $\bar{\mathbf{J}}_i$, be defined as

$$\bar{\mathbf{J}}_i = \bar{\mathbf{N}}_i - c_i \bar{\mathbf{v}}, \quad \text{or} \quad \bar{\mathbf{J}} = \bar{\mathbf{n}} - \bar{\mathbf{v}} \mathbf{c}, \quad (9.6)$$

where the latter equation introduces the n -dimensional column $\bar{\mathbf{J}}$ whose entries are each of the $\bar{\mathbf{J}}_i$ in sequence. Insertion of definition (9.6) into Eq. (5.5) gives

$$-\nabla \mu = \mathbf{M} (\bar{\mathbf{J}} + \bar{\mathbf{v}} \mathbf{c}) = \mathbf{M} \bar{\mathbf{J}}, \quad (9.7)$$

which is to say, because \mathbf{c} is a null eigenvector of \mathbf{M} , the physical content of the Onsager–Stefan–Maxwell equations is independent of convection.

Importantly, the very presence of a bulk velocity constrains excess fluxes. In light of Eqs. (9.3) and (9.4), multiplying Eq. (9.6) through by $\boldsymbol{\psi}^T$ reveals that

$$\boldsymbol{\psi}^T \bar{\mathbf{J}} = \bar{\mathbf{0}}, \quad (9.8)$$

establishing a kinematic relation among the set of excess molar species fluxes relative to the barycentric velocity.

Electroneutrality affects density and the kinematic relation in different ways. Application of electroneutrality to Eq. (9.1) and insertion of Eq. (8.1) show that density is a function of $n - 1$ component concentrations,

$$\rho^0 = \bar{\mathbf{m}}^T \mathbf{c}^0 = \bar{\mathbf{m}}_v^T \mathbf{c}_v, \quad (9.9)$$

in which $\bar{\mathbf{m}}_v = \mathbf{N}^T \bar{\mathbf{m}}$ is an $(n - 1)$ -dimensional column comprising the component molar masses. Excess species fluxes then transform into the salt–charge basis as

$$\bar{\mathbf{J}}_Z = \mathbf{Z}^{-T} \bar{\mathbf{J}} = \begin{bmatrix} \bar{\mathbf{J}}_v \\ \bar{\mathbf{i}} - \rho_e \bar{\mathbf{v}} \\ F \|\mathbf{z}\| \end{bmatrix}, \quad (9.10)$$

because $\rho_e = F \mathbf{z}^T \mathbf{c}$. Imposing local electroneutrality on $\bar{\mathbf{J}}_Z$ here shows that the current density, embodied by the last entry of $\bar{\mathbf{J}}_Z^0$, becomes independent of convection. This entry does not vanish entirely, however, and consequently electroneutrality does not reduce the dimensionality of the space of excess fluxes in the same way that it reduces the domain of ρ^0 .

Defining $\boldsymbol{\psi}_Z = \mathbf{Z} \boldsymbol{\psi}$, one can change basis to write kinematic relation (9.8) as

$$\boldsymbol{\psi}_Z^T \bar{\mathbf{J}}_Z = \bar{\mathbf{0}}, \quad (9.11)$$

showing that the column of excess component fluxes is orthogonal to $\boldsymbol{\psi}_Z^T$. Electroneutral species fluxes $\bar{\mathbf{J}}_Z^0$ depend on the component excess fluxes over a salt–charge basis, $\bar{\mathbf{J}}_v$, as

$$\bar{\mathbf{J}}_Z^0 = \mathbf{Z}^T \bar{\mathbf{J}}_v^0 = \mathbf{N} \bar{\mathbf{J}}_v + \frac{\bar{\mathbf{i}}}{F \|\mathbf{z}\|} \cdot \frac{\mathbf{z}}{\|\mathbf{z}\|}, \quad (9.12)$$

a form that notably includes the current density, as well as the excess component fluxes.

10. Flux-explicit transport laws

Typical constitutive laws for electrolytic transport, including the standard concentrated solution theory and the Nernst–Planck equations, are written in flux-explicit forms. Laws giving component flux and current density in terms of the gradients of composition and voltage can be derived from force-explicit Onsager–Stefan–Maxwell equations by exploiting the inversion formulas reported previously by the authors [18]. Generally, flux-explicit laws for diffusion must be expressed using excess species fluxes in order to exclude the effects of convection; transport-law inversion therefore necessitates the selection of a representative bulk velocity.

Section 9 set out the preliminary definitions needed to develop flux-explicit transport laws relative to the mass-average velocity by the inversion method of Van-Brunt et al. [18]. This method begins with a statement of the electroneutral Onsager–Stefan–Maxwell equations (8.30) in terms of excess fluxes. Through Eq. (9.10), they become

$$-\begin{bmatrix} \nabla \mu_v^0 \\ F \|\mathbf{z}\| \nabla \phi_z^0 \end{bmatrix} = \begin{bmatrix} \mathbf{M}_v & \mathbf{m}_z \\ \mathbf{m}_z^T & M_{zz} \end{bmatrix} \begin{bmatrix} \bar{\mathbf{J}}_v \\ \bar{\mathbf{i}} \\ F \|\mathbf{z}\| \end{bmatrix} \quad (10.1)$$

in terms of $\bar{\mathbf{J}}_v$. To implement the inversion, we first observe that within the flux-explicit form of these laws, the electroneutral excess component fluxes $\bar{\mathbf{J}}_v$ and current density $\bar{\mathbf{i}}$ must be constrained such that $\boldsymbol{\psi}_Z^0 \bar{\mathbf{J}}_Z^0 = \mathbf{0}$, wherein the kinematic relation over the salt–charge basis, $\boldsymbol{\psi}_Z^0$, is defined such that $\boldsymbol{\psi}_Z^0 = \mathbf{Z} \boldsymbol{\psi}^0$. (Here $\boldsymbol{\psi}^0$ expresses the basic kinematic relation that constrains excess species fluxes relative to the barycentric velocity under local electroneutrality, identified by replacing ρ with ρ^0 in Eq. (9.2).) Therefore, the flux-explicit transport laws must involve a coefficient matrix \mathbf{L}_Z^0 with null eigenvector $\boldsymbol{\psi}_Z^0$. This matrix is formed uniquely from \mathbf{M}_Z^0 through the limit process

$$\mathbf{L}_Z^0 = \lim_{\gamma \rightarrow 0} \left(\mathbf{M}_Z^0 + \frac{\boldsymbol{\psi}_Z^0 \boldsymbol{\psi}_Z^{0T}}{\gamma} \right)^{-1}, \quad (10.2)$$

or, equivalently, from the algebraic equation

$$\mathbf{L}_Z^0 = \left(\mathbf{M}_Z^0 + \gamma \boldsymbol{\psi}_Z^0 \boldsymbol{\psi}_Z^{0T} \right)^{-1} - \frac{\mathbf{c}_Z^0 (\mathbf{c}_Z^0)^T}{\gamma}, \quad (10.3)$$

whose result is identical for any nonzero value of the augmentation parameter γ [18]. After partitioning \mathbf{L}_Z^0 into the block form

$$\mathbf{L}_Z^0 = \begin{bmatrix} \mathbf{L}_v & \mathbf{I}_z \\ \mathbf{I}_z^\top & L_{zz} \end{bmatrix}, \quad (10.4)$$

one finds

$$\begin{bmatrix} \bar{\mathbf{j}}_v \\ \bar{i} \\ F \|\mathbf{z}\| \end{bmatrix} = - \begin{bmatrix} \mathbf{L}_v & \mathbf{I}_z \\ \mathbf{I}_z^\top & L_{zz} \end{bmatrix} \begin{bmatrix} \nabla \mu_v^0 \\ F \|\mathbf{z}\| \nabla \Phi_z^0 \end{bmatrix}, \quad (10.5)$$

the desired flux-explicit form of the electroneutral Onsager transport laws with respect to a salt-charge basis.

11. Distinguishing ionic conductivity, migration, and molecular diffusion

One can leverage the flux-explicit electroneutral Onsager transport laws to generalize the process by which concentrated solution theory distinguishes the various dissipative phenomena that drive electrochemical mass transport [1]. First and foremost, the last row of Eq. (10.5) establishes the MacInnes equation—a current-voltage relation that can be viewed as a modified form of Ohm's law accounting for concentration overpotential [21]. Identifying the *ionic conductivity* κ^0 as

$$\kappa^0 = F^2 \|\mathbf{z}\|^2 L_{zz}, \quad (11.1)$$

and further letting an $(n-1)$ -entry column ξ represent a set of what we will call *component migration coefficients*, defined by

$$\xi = \frac{1}{L_{zz}} \mathbf{I}_z, \quad (11.2)$$

the MacInnes equation can be written as

$$\bar{i} = -\kappa^0 \nabla \Phi_z^0 - \frac{\kappa^0 \xi^\top \nabla \mu_v^0}{F \|\mathbf{z}\|} \quad (11.3)$$

in terms of the salt-charge potential and the component chemical potentials with respect to the chosen salt-charge basis. The first term on the right describes charge flow by ionic conduction, i.e., current driven by electric-potential gradients, in the absence of composition gradients.

Migration is defined as the excess mass flux driven by electric current flow in the absence of composition gradients. To isolate this effect, one writes the species flux laws in a partially inverted form, with current density replacing the electric-potential gradient. Newman does this by eliminating one of the species fluxes with Faraday's law (4.10) before performing a pseudoinversion of the electroneutral Onsager-Stefan-Maxwell equations [1]. Equivalently, one can rearrange the Onsager flux laws from Eq. (10.5), by using the MacInnes equation – the last row of Eq. (10.5) – to replace $\nabla \Phi_z^0$ with $\bar{i}/F \|\mathbf{z}\|$ in the laws for $\bar{\mathbf{j}}_v$ expressed by the remaining rows. Let the symmetric matrix

$$\bar{\mathbf{L}}_v = \frac{RT}{c_T^0} \left(\mathbf{L}_v - \frac{\kappa^0 \xi \xi^\top}{F^2 \|\mathbf{z}\|^2} \right) \quad (11.4)$$

define the set of *Onsager component diffusivities* relative to the mass-average velocity, $\bar{\mathbf{L}}_v$. The excess component fluxes become

$$\bar{\mathbf{j}}_v = - \frac{c_T^0 \bar{\mathbf{L}}_v}{RT} \nabla \mu_v^0 + \xi \frac{\bar{i}}{F \|\mathbf{z}\|}, \quad (11.5)$$

in which $\bar{\mathbf{L}}_v$ has the standard units of area per time. Here, the first term on the right describes the component flux associated with diffusion, and the second, migration.

Note that in the absence of current density, Eq. (11.5) reduces to a generalized form of Fick's law that expresses component excess fluxes solely in terms of the symmetric component-diffusivity matrix $\bar{\mathbf{L}}_v$. Miller deployed transport laws with this structure to describe solutions containing multiple dissolved salts in some of his experimental tests of

the Onsager reciprocal relations [22], which confirmed the symmetry of $\bar{\mathbf{L}}_v$.

When quantifying migration coefficients, one should bear in mind that their values must be constrained to ensure that ψ_v^0 is a null eigenvector of \mathbf{L}_Z^0 . By partitioning ψ_Z^0 into two parts ψ_v and ψ_z such that

$$\psi_Z^0 = \begin{bmatrix} \mathbf{N}^\top \psi^0 \\ \mathbf{z}^\top \psi^0 \\ \|\mathbf{z}\| \end{bmatrix} = \begin{bmatrix} \psi_v \\ \psi_z \end{bmatrix}, \quad (11.6)$$

one can write

$$\psi_v^\top \xi = -\psi_z \quad (11.7)$$

to phrase this constraint entirely in terms of species equivalent charges and species molar masses.

Within concentrated solution theory, transport laws are generally written for species fluxes, rather than component fluxes [1]. By leveraging Eq. (9.12), the species fluxes can be separated into terms associated with diffusion and migration using the properties defined above. Inserting Eqs. (11.5) yields

$$\bar{\mathbf{j}}^0 = - \frac{\mathbf{N} \bar{\mathbf{L}}_v c_T^0}{RT} \nabla \mu_v^0 + \left(\mathbf{N} \xi + \frac{\mathbf{z}}{\|\mathbf{z}\|} \right) \frac{\bar{i}}{F \|\mathbf{z}\|}. \quad (11.8)$$

As well as distinguishing diffusion from migration at the species level, this expression helps to elucidate the spectral structure of the diffusivity matrix $\bar{\mathbf{L}}_v$. Multiplying through from the left by $(\psi^0)^\top$, applying the electroneutral form of Eq. (9.8), introducing ψ_v and ψ_z with Eq. (11.6), and applying Eq. (11.7) show that

$$- \frac{c_T^0 \psi_v^\top \bar{\mathbf{L}}_v}{RT} \nabla \mu_v^0 = \bar{0} \quad (11.9)$$

for any $\nabla \mu_v^0$. Thus, because $\bar{\mathbf{L}}_v$ is symmetric, it must afford ψ_v as a null eigenvector: $\bar{\mathbf{L}}_v \psi_v = \mathbf{o}$.⁴

A property count is helpful here. Symmetry of the $(n-1) \times (n-1)$ matrix $\bar{\mathbf{L}}_v$ reduces its number of independent entries by $\frac{1}{2}(n-1)(n-2)$; the fact that it affords ψ_v as a null eigenvector adds $(n-1)$ additional constraints. Thus $\frac{1}{2}(n-1)(n-2)$ of the entries in $\bar{\mathbf{L}}_v$ are independently specifiable. The $(n-1)$ -dimensional column ξ is constrained through species molar masses and equivalent charges by Eq. (11.7), leaving $(n-2)$ independent migration coefficients. Finally, Eq. (11.1) defines a single ionic conductivity. Summing up, the symmetric, positive-semidefinite flux-explicit Onsager matrix with respect to the salt-charge basis breaks down as

$$\mathbf{L}_Z^0 = \frac{c_T^0}{RT} \begin{bmatrix} \bar{\mathbf{L}}_v & \mathbf{o} \\ \mathbf{o}^\top & 0 \end{bmatrix} + \frac{\kappa^0}{F^2 \|\mathbf{z}\|^2} \begin{bmatrix} \xi \xi^\top & \xi \\ \xi^\top & 1 \end{bmatrix}, \quad (11.10)$$

in which $\bar{\mathbf{L}}_v = \bar{\mathbf{L}}_v^\top$, $\bar{\mathbf{L}}_v \psi_v = \mathbf{o}$, and $\psi_v^\top \xi + \psi_z = 0$, with ψ_v and ψ_z defined in terms of stoichiometry in the simple association equilibria, species molar masses, species charges, and the electroneutral density ρ^0 through Eqs. (9.2) and (11.6). Consequently, \mathbf{L}_Z^0 depends on $\frac{1}{2}n(n-1)$ independent transport coefficients. This equals the number of Stefan-Maxwell diffusivities that underpin the original transport matrix \mathbf{M}^0 in Eq. (8.25).

Recently molecular-dynamics techniques have been deployed to measure the naive Onsager diffusion matrix \mathbf{L}^0 , which sits relative to

⁴ If $\nabla \mu_v^0$ is restricted to a space that satisfies the Gibbs–Duhem relation from Eq. (8.14), Eq. (11.9) permits that $\bar{\mathbf{L}}_v \psi_v = k c_v$ for some k . We choose $k = 0$ for consistency with the model formed by treating component transport in the absence of current as transport within a non-electrolytic system containing $n-1$ uncharged species, whose flux-explicit form matches Eq. (11.5) with $\xi = \mathbf{o}$.

the mass-average velocity and appears in the inverted form of Eq. (9.7) [23,24],⁵

$$\tilde{\mathbf{j}}^0 = -\mathbf{L}^0 \nabla \mu^0. \quad (11.11)$$

The transport properties that make up \mathbf{L}^0 relate to \mathbf{M}^0 directly through

$$\mathbf{M}^0 = \lim_{\gamma \rightarrow 0} \left[\mathbf{L}^0 + \frac{\mathbf{c}^0 (\mathbf{c}^0)^\top}{\gamma} \right]^{-1}, \quad (11.12)$$

where we have used the limit form of the inversion described by Van-Brunt et al. [18]. Through Eq. (11.10), the congruence transformation

$$\mathbf{L}_Z^0 = \mathbf{Z}^{-\top} \mathbf{L}^0 \mathbf{Z}^{-1} \quad (11.13)$$

shows how the component diffusivities, migration coefficients, and ionic conductivity over a salt-charge basis contribute to the naive Onsager matrix \mathbf{L}^0 .

12. Alternative convective velocities

Up to now we have adopted a convention of defining \mathbf{L}_Z^0 and $\tilde{\mathbf{j}}^0$ relative to the mass-average velocity, but it is straightforward to change the kinematic constraint that defines the convective reference velocity in Eq. (9.4) to any other ψ' satisfying Eq. (9.3). (For example, letting $\psi' = \mathbf{1}/c_T$ defines the mole-average velocity.) The conversion of the set of excess molar fluxes relative to the mass-average velocity, composed of $\tilde{\mathbf{j}}_i$, to excess fluxes relative to another velocity, composed of $\tilde{\mathbf{j}}_i^{\psi'}$, is accomplished by the projection operation

$$\tilde{\mathbf{j}}^{\psi'} = (\mathbf{I} - \mathbf{c}\psi'^\top) \tilde{\mathbf{j}}. \quad (12.1)$$

Observe that a similar projection can be used to move from excess fluxes that satisfy kinematic relation ψ' back to fluxes in excess of convection at the mass-average reference velocity:

$$\tilde{\mathbf{j}} = (\mathbf{I} - \mathbf{c}\psi'^\top) \tilde{\mathbf{j}}^{\psi'}. \quad (12.2)$$

Transformation (12.1) can be expressed in terms of excess fluxes over a salt-charge basis as

$$\tilde{\mathbf{j}}_Z^{\psi'} = [\mathbf{I} - \mathbf{c}_Z(\psi'_Z)^\top] \tilde{\mathbf{j}}_Z, \quad (12.3)$$

where $\psi'_Z = \mathbf{Z}\psi'$.

Under electroneutrality, the kinematic relation ψ_Z is replaced by ψ_Z^0 . Given any other kinematic relation ψ' defined under the electroneutrality approximation, one can exploit Eq. (10.2) or (10.3), with ψ'_Z in place of ψ_Z^0 , to identify the flux-explicit electroneutral transport relations relative to ψ' , as

$$\tilde{\mathbf{j}}_Z^{0,\psi'} = -\mathbf{L}_Z^{0,\psi'} \nabla \mu^0, \quad (12.4)$$

in which

$$\mathbf{L}_Z^{0,\psi'} = [\mathbf{I} - \mathbf{c}_Z^0(\psi'_Z)^\top] \mathbf{L}_Z^0 [\mathbf{I} - \psi'_Z(\mathbf{c}_Z^0)^\top] \quad (12.5)$$

establishes a congruence between $\mathbf{L}_Z^{0,\psi'}$ and \mathbf{L}_Z^0 . One can also compute $\mathbf{L}_Z^{0,\psi'}$ directly from \mathbf{M}_Z^0 , using

$$\mathbf{L}_Z^{0,\psi'} = \lim_{\gamma \rightarrow 0} \left(\mathbf{M}_Z^0 + \frac{\psi'_Z \psi'_Z{}^\top}{\gamma} \right)^{-1}, \quad (12.6)$$

which is analogous to Eq. (10.2). In the new reference frame for the excess fluxes established by ψ' , diffusivities and migration coefficients can be identified by partitioning $\mathbf{L}_Z^{0,\psi'}$ as

$$\mathbf{L}_Z^{0,\psi'} = \frac{c_T^0}{RT} \begin{bmatrix} \bar{\mathbf{L}}_v^{\psi'} & \mathbf{0} \\ \mathbf{0}^\top & 0 \end{bmatrix} + \frac{\kappa^0}{F^2 \|\mathbf{z}\|^2} \begin{bmatrix} \xi^{\psi'} (\xi^{\psi'})^\top & \xi^{\psi'} \\ (\xi^{\psi'})^\top & 1 \end{bmatrix}, \quad (12.7)$$

⁵ A molecular dynamics simulation can be described with Eq. (11.11) if the simulated control volume conserves charge and has characteristic dimensions much larger than the Debye length.

similar to how \mathbf{L}_Z^0 is partitioned in Eq. (11.10). Note that the second matrix on the right of Eq. (12.7) is proportional to the outer product of $[\xi^{\psi'}, 1]^\top$ with itself, and is consequently positive semidefinite in general.

One can write excess component fluxes relative to the alternative convective velocity defined by ψ' , and with respect to the salt-charge basis, as

$$\tilde{\mathbf{j}}_v^{\psi'} = -\frac{c_T^0 \bar{\mathbf{L}}_v^{\psi'}}{RT} \nabla \mu_v^0 + \xi^{\psi'} \frac{\tilde{i}}{F \|\mathbf{z}\|}, \quad (12.8)$$

which derives from Eq. (11.5). Here, the component diffusivities relative to the average velocity determined by ψ' are defined as

$$\bar{\mathbf{L}}_v^{\psi'} = [\mathbf{I}_{n-1} - \mathbf{c}_v(\psi'_v)^\top] \bar{\mathbf{L}}_v [\mathbf{I}_{n-1} - \psi'_v(\mathbf{c}_v)^\top], \quad (12.9)$$

and

$$\xi^{\psi'} = [\mathbf{I}_{n-1} - \mathbf{c}_v(\psi'_v)^\top] \xi - \psi'_z \mathbf{c}_v \quad (12.10)$$

defines migration coefficients in the new frame. Similar to the projection in Eq. (12.2), one can create transformations that change the reference frame from velocity $\psi'^\top \bar{\mathbf{n}}$ back to the mass-average velocity by replacing ψ'_v with ψ_v and ψ'_z with ψ_z in Eqs. (12.9) and (12.10), as well as swapping $\bar{\mathbf{L}}_v^{\psi'}$ with $\bar{\mathbf{L}}_v$ and $\xi^{\psi'}$ with ξ .

In Newman's implementations of concentrated solution theory [1], one of the species velocities – say, that of species m – is used as the convective reference. Thus the coefficients that Newman identifies in the flux-explicit equations follow from taking $\psi'_Z = \mathbf{Z} \mathbf{i}_m / c_m^0$ in Eq. (12.5). This produces species flux laws in the form

$$\tilde{\mathbf{j}}^{0,\psi'} = -\frac{c_T^0 \mathbf{N} \bar{\mathbf{L}}_v^{\psi'}}{RT} \nabla \mu_v^0 + \left(\mathbf{N} \xi^{\psi'} + \frac{\mathbf{z}}{\|\mathbf{z}\|} \right) \frac{\tilde{i}}{F \|\mathbf{z}\|}. \quad (12.11)$$

Newman's development also produces a slightly different MacInnes equation,

$$\tilde{i} = -\kappa^0 \nabla \Phi_z^0 - \frac{\kappa^0}{F \|\mathbf{z}\|} (\xi^{\psi'})^\top \nabla \mu_v^0, \quad (12.12)$$

wherein the migration coefficients are constrained by kinematic relation ψ' , but κ^0 remains unaffected because its value is independent of the choice of convective velocity.

Note that the embedding of an arbitrary reference velocity in flux-explicit transport matrices (e.g., \mathbf{L}^0) makes properties derived from them somewhat ambiguous. When tabulating transport parameters, it may be preferable to work with the electroneutral transport matrix \mathbf{M}_Z^0 , which conveys frame-invariant information. The computation of \mathbf{M}_v can be accomplished readily given a flux-explicit form; in fact, one can use the procedure of Van-Brunt et al. [18] and a block inversion identity to show for any ψ' that

$$\mathbf{M}_v = \frac{RT}{c_T^0} \lim_{\gamma \rightarrow 0} \left(\bar{\mathbf{L}}_v^{\psi'} + \frac{\mathbf{c}_v \mathbf{c}_v^\top}{\gamma} \right)^{-1}, \quad (12.13)$$

and also that

$$\mathbf{m}_z = \mathbf{M}_v \xi^{\psi'} \quad \text{and} \quad M_{zz} = \frac{F^2 \|\mathbf{z}\|^2}{\kappa^0} + (\xi^{\psi'})^\top \mathbf{M}_v \xi^{\psi'}, \quad (12.14)$$

elucidating the structure of \mathbf{M}_Z^0 through Eq. (8.26). Despite its computation from a transport matrix $\mathbf{L}_Z^{0,\psi'}$, it should be emphasized that \mathbf{M}_Z^0 enjoys uniqueness and is independent of the convective velocity. Notably, the submatrix \mathbf{M}_v depends only on the Onsager component diffusivities, and the only matrix inversion that needs to be performed is the one in Eq. (12.13). The entries of \mathbf{m}_z are zero in the absence of migration, and M_{zz} matches the ionic resistivity plus a quadratic correction that also vanishes when migration does.

13. Transference numbers

Eqs. (11.3) and (11.8) provide a pair of constitutive equations similar, but not identical, to the familiar equations from concentrated solution theory and Nernst–Planck dilute-solution theory. To achieve complete agreement, one must consider how migration coefficients relate to the transference numbers more familiar from electrochemistry [1,21,25]. Let the transference number of species i relative to the mass-average velocity be t_i . These can be formed into an n -dimensional column matrix \mathbf{t} , related to the migration coefficients as

$$\mathbf{t} = \frac{\text{diag}(\mathbf{z})}{\|\mathbf{z}\|} \left(\mathbf{N}\xi + \frac{\mathbf{z}}{\|\mathbf{z}\|} \right). \quad (13.1)$$

Multiplication of this result through by $\mathbf{1}^\top$ shows that $\mathbf{1}^\top \mathbf{t} = 1$, that is, transference numbers sum to unity. Note that if migration is neglected entirely ($\xi = \mathbf{0}$), the right side of Eq. (13.1) remains non-zero; each transference number becomes a partition of unity weighted by the corresponding squared species charge. The migration coefficients we introduced here deviate from this standard.

Sometimes it is desirable to change the reference velocity relative to which transference is expressed. Incorporating the alternative migration coefficient from Eq. (12.10) into Eq. (13.1) shows that

$$\mathbf{t}^{\psi'} = \frac{\text{diag}(\mathbf{z})}{\|\mathbf{z}\|} \left(\mathbf{N}\xi^{\psi'} + \frac{\mathbf{z}}{\|\mathbf{z}\|} \right) \quad (13.2)$$

yields the set of species transference numbers relative to the reference velocity associated with the kinematic relation represented by ψ' . These also afford the property that $\mathbf{1}^\top \mathbf{t}^{\psi'} = 1$.

Because $\text{diag}(\mathbf{z})$ appears on the right of Eq. (13.1), t_i vanishes for all i such that $z_i = 0$. Thus, transference numbers as traditionally defined only have meaning for charged species. Importantly, specifying a set of independent transference numbers does not generally suffice to specify the Onsager transport matrix. Newman addresses this point by using transference numbers for uncharged species expressed as ratios t_i/z_i , noting that the ratio is finite for any species i with $z_i = 0$ [1]. Indeed, one can see with Eq. (13.1) that t_i/z_i can be written under the assumption that $t_i \propto z_i$ as

$$\frac{t_i}{z_i} = \frac{1}{\|\mathbf{z}\|} \left(\mathbf{N}\xi + \frac{\mathbf{z}}{\|\mathbf{z}\|} \right)_i, \quad (13.3)$$

in which the right side is generally nonzero for any i .

Rather than taxing ourselves by ignoring apparent divisions by zero when transference numbers are involved, we propose that it is simpler to think of transport fundamentally in terms of migration coefficients, because they are defined unambiguously in terms of Onsager coefficients for species with and without charge. The nontrivial transference numbers that make up \mathbf{t} are subsidiary quantities that afford a useful physical interpretation, but the set as a whole does not have as much essential physical content. The distinction between \mathbf{t} and ξ becomes particularly important for electrolytes containing multiple uncharged species, such as the cosolvent blends commonly used in lithium-ion-battery electrolytes [26,27], fuel-cell membranes susceptible to gas crossover [28], or electrolytes for lithium–air batteries [29]. Within these systems, applied currents can drive migration of one neutral species relative to another—a dissipative phenomenon distinct from diffusion and charge conduction that cannot be accounted for by traditional transference numbers.

14. Component diffusion coefficients

The entries of the Onsager component-diffusivity matrices $\bar{\mathbf{L}}_\nu$ and $\bar{\mathbf{L}}_\nu^{\psi'}$ have the expected units, and each entry is paired with a particular chemical-potential gradient. Nevertheless, the dependences of these transport matrices on the convective velocity obfuscates their connection to the energy dissipation. Newman addresses this issue by identifying combinations of the Stefan–Maxwell coefficients between species that quantify the frame-invariant part of the dissipation

arising from component interdiffusion [1,30]. The process Newman uses to identify thermodynamic component diffusivities within binary solutions can be generalized to solutions comprising more than two components as follows.

Instead of using entries of Onsager's diffusivity matrix $\bar{\mathbf{L}}_\nu$, a frame-invariant set of thermodynamic component diffusivities is defined by revisiting the Stefan–Maxwell form. Physically, one expects that in situations where electroneutrality is maintained ($\rho_e = 0$) and the current density vanishes uniformly ($\vec{i} = \vec{0}$), the mass-transport model describing an n -species electrolytic phase should be no different than the model describing a corresponding $(n - 1)$ -species nonelectrolytic phase in which every uncharged species is taken to be a component of the original n -ary electrolyte. This equivalence suggests that \mathbf{M}_ν possesses the structure

$$\frac{c_\nu^0}{RT} (\mathbf{M}_\nu)_{ij} = \begin{cases} -\frac{v_i v_j}{\mathfrak{D}_{ij}} & \text{if } i \neq j \\ \sum_{k \neq i}^{n-1} \frac{v_i v_k c_{\nu,k}}{\mathfrak{D}_{ik} c_{\nu,j}} & \text{if } i = j, \end{cases} \quad (14.1)$$

which defines an alternative set of binary diffusion coefficients \mathfrak{D}_{ij} that describe drag interactions between components i and j as they move relative to each other. It should be borne in mind that the indices in \mathfrak{D}_{ij} refer to components in a given salt-charge basis.

In Eq. (14.1), the diffusivities that parametrize current-free, electroneutral component–component interactions are defined analogously to how species–species interactions are defined in Eq. (1.2), with a minor stoichiometric correction to account for the fact that component i within a salt-charge basis is actually made up of v_i species through the simple association equilibria. We shall distinguish component diffusion coefficients from Stefan–Maxwell coefficients by writing them in Fraktur font, rather than a script font.

Intrinsic properties of the Onsager matrix \mathbf{M}_Z demand that the coefficients defined by Eq. (14.1) are symmetric in their indices, $\mathfrak{D}_{ij} = \mathfrak{D}_{ji}$, and that \mathfrak{D}_{ii} is undefined for all i . Hence Eq. (14.1) defines $\frac{1}{2}(n-1)(n-2)$ independent diffusion coefficients—one for each pair of components. The matrix \mathbf{M}_ν must be positive semidefinite, a property guaranteed if each \mathfrak{D}_{ij} is positive, and by construction it affords \mathbf{c}_ν as a null eigenvector. Furthermore, a block inversion identity shows that Eqs. (12.6) and (12.7) imply

$$\bar{\mathbf{L}}_\nu^{\psi'} = \lim_{\gamma \rightarrow 0} \left(\frac{c_\nu^0}{RT} \mathbf{M}_\nu + \frac{\psi'_\nu \psi'^\top_\nu}{\gamma} \right)^{-1}, \quad (14.2)$$

an inverted form of Eq. (12.13). Thus $\bar{\mathbf{L}}_\nu^{\psi'}$, the portion of the electroneutral Onsager component-diffusivity matrix that describes situations in which current density vanishes uniformly, relates directly to \mathbf{M}_ν .

When casting $\bar{\mathbf{L}}_\nu$ in terms of component diffusivities \mathfrak{D}_{ij} with definition (14.1) and inversion formula (14.2), it is necessary to assume that every entry of \mathbf{c}_ν is nonzero almost everywhere. This must be borne in mind when considering systems where products of the simple association equilibria are not unique. The situation described in Section 2, where two binary salts without a common ion are dissolved into an uncharged solvent, provides an example. That system can pass locally through compositions where a particular component concentration vanishes, but all of the ions retain non-negative concentrations, as described in the discussion at the end of Section 8.1. Such a state nominally induces singular behavior in one of the diagonal entries defined in Eq. (14.1). Observe, however, that the component diffusivities \mathfrak{D}_{ij} are defined solely in terms of the off-diagonal entries of \mathbf{M}_ν . Therefore, although one must take care when applying inversion formula (14.2), the diffusion coefficients \mathfrak{D}_{ij} remain well posed across the physically available range of \mathbf{c}_ν .

15. Reference electrodes

Introducing the concept of a reference electrode allows the salt-charge potential to be related unambiguously to an experimentally measurable voltage, despite the degree of freedom in Φ_z^0 demanded by Guggenheim's principle. A heterogeneous half-reaction suitable for use within a reference electrode is generally written as



in which $X_i^{z_i}$ is the chemical symbol of species i , Y_j is the symbol of uncharged entity j that forms in an immediately adjacent phase, e^- denotes electrons, the integer s_i is the stoichiometric coefficient of species i in the half-reaction, integer s'_j is the stoichiometric coefficient of Y_j , and the positive integer n_{e^-} is the number of electrons involved. Since half-reactions balance charge, the set $\{s_i\}_{i=1}^n$ must generally satisfy

$$\sum_{i=1}^n s_i z_i = \mathbf{s}^T \mathbf{z} = n_{e^-} z_{e^-}, \quad (15.2)$$

where z_{e^-} is the equivalent charge of electrons. (If a half-reaction is written as a reduction, then s_i or s'_i is negative when species i is a reactant and positive when it is a product.) Note that the matrix form in the middle of this expression indicates that by definition, the column \mathbf{s} representing half-reaction stoichiometry is not orthogonal to the column \mathbf{z} of species charges.

The electrode potential Φ^\ominus associated with reference-electrode reaction (15.1) is defined such that [1,17]

$$n_{e^-} F z_{e^-} \nabla \Phi^\ominus = \sum_{i=1}^n s_i \nabla \mu_i. \quad (15.3)$$

After defining $\mathbf{s}_Z = \mathbf{Z}^{-T} \mathbf{s} = [s_v, s_z]^T$ and assuming an electroneutral state, this is written equivalently as

$$n_{e^-} F z_{e^-} \nabla \Phi^\ominus = \mathbf{s}_Z^T \nabla \boldsymbol{\mu}_Z^0 = \mathbf{s}_v^T \nabla \boldsymbol{\mu}_v^0 + s_z F \|\mathbf{z}\| \nabla \Phi_z^0, \quad (15.4)$$

and since

$$n_{e^-} z_{e^-} = \mathbf{s}^T \mathbf{z} = \mathbf{s}_Z^T \mathbf{Z} \mathbf{z} = s_z \|\mathbf{z}\|, \quad (15.5)$$

it follows that

$$\nabla \Phi^\ominus = \frac{\mathbf{s}_v^T \nabla \boldsymbol{\mu}_v^0}{n_{e^-} F z_{e^-}} + \nabla \Phi_z^0, \quad (15.6)$$

a relation that allows the voltage of a given reference electrode to be inferred after one has computed the component and salt-charge potentials. Note that at uniform temperature, pressure, and composition,

$$(\nabla \Phi^\ominus)_{T,p,y_v} = (\nabla \Phi_z^0)_{T,p,y_v} \quad (15.7)$$

for any reference-electrode half-reaction, showing the intrinsic utility of the salt-charge potential.

16. Examples

16.1. The binary electrolyte

The model of a binary electrolytic solution – a liquid comprising a single simple salt dissolved in a single uncharged solvent – is the simplest and most common implementation of concentrated solution theory. Newman's identification of transport laws for this system begins by adopting Onsager–Stefan–Maxwell equations (1.1) with the transport coefficients defined in Eq. (1.2). He uses these in combination with the electroneutrality approximation (1.3), Guggenheim condition (2.1) for the salt, and Faraday's law (4.10) to derive species flux laws in the form of Eq. (12.11) and a MacInnes equation in the form of Eq. (12.12), casting both in terms of properties relative to the solvent velocity. The

development involves apparently ad hoc manipulation of the transport equations to obtain compact forms of the flux-explicit laws.

We now demonstrate how Newman's process can be formalized with a salt-charge basis under electroneutrality. Let 0, +, and – distinguish the solvent, cation, and anion species, respectively, and subscripts 0, e denote the solvent and salt components. Set the stoichiometric coefficients for the reactants in the simple association equilibrium forming the salt as

$$v_+ = -\frac{v z_-}{z_+ - z_-}, \quad v_- = \frac{v z_+}{z_+ - z_-}, \quad (16.1)$$

and note that $v = v_+ + v_-$. This framing demonstrates the Guggenheim condition $z_+ v_+ + z_- v_- = 0$ more directly, and will produce results more obviously consistent with Newman [31]. The products of the simple association equilibria for this system are unique, so the salt-charge basis is unique up to ordering of the ions. We let the salt-charge transformation \mathbf{Z} take the form

$$\mathbf{Z} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -\frac{v z_-}{z_+ - z_-} & \frac{v z_+}{z_+ - z_-} \\ 0 & \frac{z_+}{\|\mathbf{z}\|} & \frac{z_-}{\|\mathbf{z}\|} \end{bmatrix}, \quad (16.2)$$

in which $\|\mathbf{z}\| = \sqrt{z_+^2 + z_-^2}$ because $z_0 = 0$. Given this, one can write the set of species concentrations in the neutral state, \mathbf{c}^0 , as a parametric function of the component concentrations c_0 and c_e through Eq. (8.1),

$$\begin{bmatrix} c_0^0 \\ c_+^0 \\ c_-^0 \end{bmatrix} = \mathbf{Z}^T \begin{bmatrix} c_0 \\ c_e \\ 0 \end{bmatrix} = \begin{bmatrix} c_0 \\ -\frac{z_- v}{z_+ - z_-} \cdot c_e \\ \frac{z_+ v}{z_+ - z_-} \cdot c_e \end{bmatrix}. \quad (16.3)$$

The electroneutral component chemical potentials can be written using Eqs. (8.22) and (8.23), which together with the relation $y_0 = 1 - y_e$ show that

$$\begin{aligned} \nabla \begin{bmatrix} \mu_0^0 \\ \mu_+^0 \\ \mu_-^0 \end{bmatrix} &= RT \begin{bmatrix} X_{00}^0 & X_{0e}^0 \\ X_{e0}^0 & X_{ee}^0 \end{bmatrix} \nabla \begin{bmatrix} y_0 \\ y_e \end{bmatrix} \\ &= \frac{RT (1 + A_{00} y_e y_0)}{y_e y_0} \begin{bmatrix} -y_e \\ y_0 \end{bmatrix} \nabla y_e, \end{aligned} \quad (16.4)$$

a constitutive equation parametrized by the single mean molar activity coefficient derivative function $A_{00}(y_e)$.

Using the salt-charge transformation from Eq. (16.2) in Eq. (8.26) shows that

$$\mathbf{M}_v = \frac{v RT (z_+ \mathcal{D}_{0+} - z_- \mathcal{D}_{0-})}{c_T (z_+ - z_-) \mathcal{D}_{0+} \mathcal{D}_{0-}} \begin{bmatrix} \frac{c_e}{c_0} & -1 \\ -1 & \frac{c_0}{c_e} \end{bmatrix}, \quad (16.5)$$

$$\mathbf{m}_z = \frac{RT (z_+ \mathcal{D}_{0-} + z_- \mathcal{D}_{0+})}{c_T \|\mathbf{z}\|^2 \mathcal{D}_{0+} \mathcal{D}_{0-}} \begin{bmatrix} -1 \\ \frac{c_0}{c_e} \end{bmatrix}, \quad \text{and} \quad (16.6)$$

$$M_{zz} = -\frac{RT \|\mathbf{z}\|^2}{c_T z_+ z_-} \left[\frac{1}{\mathcal{D}_{+-}} + \frac{(z_+ - z_-)(z_+^2 \mathcal{D}_{0-} + z_-^2 \mathcal{D}_{0+}) c_0}{\|\mathbf{z}\|^4 \mathcal{D}_{0+} \mathcal{D}_{0-} v c_e} \right]. \quad (16.7)$$

Since the \mathbf{M}_Z^0 matrix is invariant with respect to the choice of convective velocity, these expressions can be used in Eq. (8.30) or (10.1), or even alternative versions of Eq. (10.1) in which the set of excess component fluxes relative to the mass-average velocity, $\tilde{\mathbf{J}}_Z^0$, is replaced with a set relative to some other velocity, $\tilde{\mathbf{J}}_Z^{0,\psi'}$.

Concentrated solution theory uses flux-explicit forms of the transport laws. Following Newman, we refer the excess fluxes to the solvent velocity (i.e., \tilde{N}_0/c_0) by taking

$$\boldsymbol{\psi}'_Z = \frac{\mathbf{Z}}{c_0^0} \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} = \frac{1}{c_0} \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \quad (16.8)$$

in Eq. (12.3). This changes the dynamical variables to a column matrix of electroneutral excess species fluxes

$$\bar{\mathbf{J}}_Z^{0,0} = \begin{bmatrix} 0 \\ \bar{J}_e^{0,0} \\ \bar{i} \\ F \|\mathbf{z}\| \end{bmatrix} \quad (16.9)$$

whose first entry is trivial, and whose second describes the excess salt flux relative to the solvent velocity.

Since matrix \mathbf{M}_Z^0 is built up of the sub-blocks defined by Eqs. (16.5) through (16.7), the transport matrix $\mathbf{L}_Z^{0,0}$ for the flux-explicit constitutive formulation relative to the solvent velocity can be computed directly with Eq. (12.6), using ψ'_Z from Eq. (16.8). The ionic conductivity is identified as the entry in the last row and column of $\mathbf{L}_Z^{0,0}$ through Eq. (12.7), yielding

$$\kappa^0 = -\frac{c_T F^2 z_+ z_-}{RT} \left[\frac{1}{\mathcal{D}_{+-}} + \frac{c_0 (z_+ - z_-)}{v c_e (z_+ \mathcal{D}_{0+} - z_- \mathcal{D}_{0-})} \right]^{-1}, \quad (16.10)$$

whence the last column (or last row) of $\mathbf{L}_Z^{0,0}$ reveals that

$$\xi^0 = \begin{bmatrix} \xi_0^0 \\ \xi_e^0 \end{bmatrix} = \begin{bmatrix} 0 \\ -\frac{(z_+ - z_-)(z_- \mathcal{D}_{0+} + z_+ \mathcal{D}_{0-})}{\|\mathbf{z}\| v (z_+ \mathcal{D}_{0+} - z_- \mathcal{D}_{0-})} \end{bmatrix} \quad (16.11)$$

are the component migration coefficients relative to the solvent velocity. Migration coefficients can be used to compute transference numbers with Eq. (13.2), yielding

$$\mathbf{t}^0 = \begin{bmatrix} t_0^0 \\ t_+^0 \\ t_-^0 \end{bmatrix} = \begin{bmatrix} 0 \\ \frac{z_+ \mathcal{D}_{0+}}{z_+ \mathcal{D}_{0+} - z_- \mathcal{D}_{0-}} \\ -\frac{z_- \mathcal{D}_{0-}}{z_+ \mathcal{D}_{0+} - z_- \mathcal{D}_{0-}} \end{bmatrix}. \quad (16.12)$$

The transference number t_0^0 vanishes necessarily because the solvent species is uncharged, conveniently matching the solvent component's null migration coefficient. Thus, for binary electrolytes, no information is lost by using transference numbers.

A third flux-explicit transport property, \mathcal{D} , is related to the Stefan–Maxwell coefficients by comparing the computed expression (16.5) with Eq. (14.1). This shows that

$$\mathcal{D} = \frac{(z_+ - z_-) \mathcal{D}_{0+} \mathcal{D}_{0-}}{z_+ \mathcal{D}_{0+} - z_- \mathcal{D}_{0-}} \quad (16.13)$$

defines the thermodynamic diffusivity of salt in solvent. Given \mathbf{M}_v from Eq. (16.5) and that $\psi'_v = [1/c_0 \ 0]^T$, Onsager component diffusivities relative to the solvent velocity, $\bar{\mathbf{L}}_v^0$, are given by Eq. (14.2), producing the matrix

$$\bar{\mathbf{L}}_v^0 = \begin{bmatrix} 0 & 0 \\ 0 & \frac{c_e (z_+ - z_-) \mathcal{D}_{0+} \mathcal{D}_{0-}}{v c_0 (z_+ \mathcal{D}_{0+} - z_- \mathcal{D}_{0-})} \end{bmatrix}. \quad (16.14)$$

Thus $\bar{\mathbf{L}}_v^0$ is seen to be proportional to \mathcal{D} , through a composition dependent prefactor.

Eqs. (16.10), (16.11), and (16.13) establish three macroscopic transport properties that parametrize Eqs. (12.11) and (12.12) in terms of Stefan–Maxwell diffusivities. Notably, Eqs. (16.10), (16.12), and (16.13) respectively match the definition of ionic conductivity in Newman's equation 12.23, cation transference number relative to the solvent velocity in Newman's 12.11, and thermodynamic diffusivity in Newman's 12.10 [1].

Identifying flux-explicit species laws and a MacInnes equation involving a single thermodynamic factor, with properties κ^0 , t_+^0 , and \mathcal{D} defined in terms of Stefan–Maxwell coefficients, completes Newman's development of concentrated solution theory. The structural properties laid out above make possible an opposite process, however, in

which one writes flux laws a priori with the structure that kinematic and thermodynamic consistency necessitates. Once such laws have been formulated, they can be analyzed to find how the Onsager–Stefan–Maxwell matrix \mathbf{M}_Z^0 depends on the posited set of flux-explicit properties. This route more naturally reflects how properties are typically measured, by fitting data to formulas derived from flux-explicit laws. It also develops the relationships needed to incorporate standard properties into numerical solvers that exploit the spectral structure of force-explicit transport formulations [8,18].

For the binary electrolyte, \mathbf{i}_0 (the first column of the identity matrix) sits in the nullspace of the symmetric Onsager component-diffusivity matrix relative to the solvent velocity, $\bar{\mathbf{L}}_v^0$, which therefore has one nonzero entry (in the second row and second column),

$$\bar{\mathbf{L}}_v^0 = \begin{bmatrix} 0 & 0 \\ 0 & \mathcal{L} \end{bmatrix} = \begin{bmatrix} 0 & 0 \\ 0 & \frac{c_e \mathcal{D}}{v c_0} \end{bmatrix}, \quad (16.15)$$

in which the single Onsager diffusivity of salt relative to the solvent velocity, \mathcal{L} , is expressed in terms of a thermodynamic diffusivity \mathcal{D} by applying inversion formula (14.2) to definition (14.1). Similarly, \mathbf{i}_0 is orthogonal to ξ^0 , which therefore also must have just one nonzero entry, that is,

$$\xi^0 = \begin{bmatrix} 0 \\ \xi \end{bmatrix} \quad (16.16)$$

where ξ stands for the salt migration coefficient relative to the solvent velocity. This property relates to the cation transference number relative to solvent as

$$\xi = -\frac{(z_+ - z_-) [(1 - t_+^0) z_+^2 - z_-^2 t_+^0]}{v z_+ z_- \|\mathbf{z}\|} \quad (16.17)$$

through Eq. (13.2).

The known structures of $\bar{\mathbf{L}}_v^0$ and ξ^0 allow species flux laws relative to the solvent velocity to be written directly in the form of Eq. (12.11). Bringing in Eqs. (16.1), (16.12), and (16.15), one finds

$$\bar{J}_0^0 = 0, \quad (16.18)$$

$$\bar{J}_+^0 = -\frac{\mathcal{D} c_T^0}{RT} \frac{v_+ c_e}{v c_0} \nabla \mu_e^0 + \frac{t_+^0 \bar{i}}{F z_+}, \quad (16.19)$$

$$\bar{J}_-^0 = -\frac{\mathcal{D} c_T^0}{RT} \frac{v_- c_e}{v c_0} \nabla \mu_e^0 + \frac{(1 - t_+^0) \bar{i}}{F z_-}. \quad (16.20)$$

Note that Eqs. (16.19) and (16.20) match Newman's equations 12.8 and 12.9, respectively [1].

Finally, posit an ionic conductivity κ^0 to write an electroneutral MacInnes equation in the form of (12.12), as

$$\frac{\bar{i}}{\kappa^0} = -\nabla \Phi^0 - \frac{(z_+ - z_-)}{v F z_+ z_-} \left(\frac{z_+^2}{z_+^2 + z_-^2} - t_+^0 \right) \nabla \mu_e^0, \quad (16.21)$$

which depends on the salt-charge potential. Introducing a reference-electrode potential with Eq. (15.6) gives

$$\begin{aligned} \frac{\bar{i}}{\kappa^0} = & -\nabla \Phi^\ominus + \frac{s_0 \nabla \mu_0^0}{n_e^- F z_{e^-}} \\ & + \frac{z_+ - z_-}{n_e^- F z_{e^-} v} \left[t_+^0 \frac{s_-}{z_+} - (1 - t_+^0) \frac{s_+}{z_-} \right] \nabla \mu_e^0, \end{aligned} \quad (16.22)$$

in harmony with Newman's equation 12.27 [1].

Given κ^0 , as well as $\bar{\mathbf{L}}_v^0$ and ξ^0 matrices in the forms from Eqs. (16.15) and (16.16), one can use relationships (12.13) and (12.14) to construct the \mathbf{M}_Z^0 matrix that would be needed to implement the electroneutral Onsager–Stefan–Maxwell equations. Performing the calculation, one finds

$$\mathbf{M}_v = \frac{v RT}{c_T^0 \mathcal{D}} \begin{bmatrix} \frac{c_e}{c_0} & -1 \\ -1 & \frac{c_0}{c_e} \end{bmatrix}, \quad (16.23)$$

$$\mathbf{m}_z = \frac{v RT \xi}{c_T^0 \mathcal{D}} \begin{bmatrix} 1 \\ -\frac{c_0}{c_e} \end{bmatrix}, \quad (16.24)$$

and

$$M_{zz} = \frac{F^2 \|z\|^2}{\kappa^0} + \frac{\nu RT c_0 \xi^2}{c_T^0 c_e \mathcal{D}}. \quad (16.25)$$

One can also elucidate the Stefan–Maxwell coefficients that describe species interdiffusion, by inverting the congruence transformation in Eq. (8.26): $M^0 = Z^{-1} M_Z^0 Z^{-T}$. Off-diagonal entries of M^0 relate to \mathcal{D}_{ij} values through Eq. (1.2). Once t_+^0 has been introduced in favor of ξ via Eq. (16.17), one finds

$$\begin{aligned} \frac{1}{\mathcal{D}_{0+}} &= -\frac{(1-t_+^0)(z_+ - z_-)}{z_- \mathcal{D}}, \\ \frac{1}{\mathcal{D}_{0-}} &= \frac{t_+^0(z_+ - z_-)}{z_+ \mathcal{D}}, \\ \frac{1}{\mathcal{D}_{+-}} &= -\frac{F^2 z_+ z_- c_T^0}{RT \kappa^0} + \frac{t_+^0(1-t_+^0)(z_+ - z_-)^2 c_0}{\nu \mathcal{D} z_+ z_- c_e}, \end{aligned} \quad (16.26)$$

consistent with Newman's equations 14.1–14.3.

16.2. The molten salt

Pollard and Newman applied concentrated solution theory to the other possible liquid electrolyte comprising three species: a molten solution of two simple salts that share a common ion [30]. From transport laws based on the Onsager–Stefan–Maxwell equations, they ultimately developed flux-explicit laws in the form of Eq. (12.11) and a MacInnes equation like Eq. (12.12).

Here we apply the salt–charge framework to obtain transport laws consistent with Pollard and Newman's results. The flux laws we formulate will not precisely identify with the Pollard–Newman equations, however. Whereas they used the common ion's velocity as the reference for convection, we instead use the velocity of one of the salts. This alternative convention creates component flux laws that involve a single chemical-potential gradient directly, rather than requiring additional use of the Gibbs–Duhem equation to eliminate a linearly dependent thermodynamic driving force.

Let the charges of the three species comprising the binary molten salt be $z = [z_1, z_2, z_3]^T$. We assume that the third species is counter-charged to the first two, so that $\text{sgn}(z_1) = \text{sgn}(z_2)$ and $\text{sgn}(z_1) = -\text{sgn}(z_3)$. Again, the choice of products of the simple association equilibria is unique; we label the simple salts formed from these three species with indices corresponding to the similarly charged ion that distinguishes them: e_1 and e_2 . The stoichiometric coefficients of the ions within these salts are written in terms of the species charges and total formula-unit stoichiometries ν_{e_1} and ν_{e_2} as

$$\nu_1^{e_1} = -\frac{\nu_{e_1} z_3}{z_1 - z_3}, \quad \nu_3^{e_1} = \frac{\nu_{e_1} z_1}{z_1 - z_3}, \quad (16.27)$$

$$\nu_2^{e_2} = -\frac{\nu_{e_2} z_3}{z_2 - z_3}, \quad \nu_3^{e_2} = \frac{\nu_{e_2} z_2}{z_2 - z_3}, \quad (16.28)$$

so that $\nu_{e_1} = \nu_1^{e_1} + \nu_3^{e_1}$ and $\nu_{e_2} = \nu_2^{e_2} + \nu_3^{e_2}$. The matrix Z that represents the salt–charge basis is unique up to ordering of the similarly charged ions. We choose to write it as

$$Z = \begin{bmatrix} \nu_1^{e_1} & 0 & \nu_3^{e_1} \\ 0 & \nu_2^{e_2} & \nu_3^{e_2} \\ \frac{z_1}{\|z\|} & \frac{z_2}{\|z\|} & \frac{z_3}{\|z\|} \end{bmatrix}, \quad (16.29)$$

where $\|z\| = \sqrt{z_1^2 + z_2^2 + z_3^2}$, bearing in mind that the reactant stoichiometric coefficients from the simple association equilibria satisfy Eqs. (16.27) and (16.28).

With the salt–charge transformation from Eq. (16.29), the electroneutral species concentrations c^0 are cast as parametric functions of

the component concentrations c_{e_1} and c_{e_2} through Eq. (8.1), as

$$\begin{bmatrix} c_1^0 \\ c_2^0 \\ c_3^0 \end{bmatrix} = Z^T \begin{bmatrix} c_{e_1} \\ c_{e_2} \\ 0 \end{bmatrix} = \begin{bmatrix} -\frac{\nu_{e_1} z_3}{z_1 - z_3} c_{e_1} \\ -\frac{\nu_{e_2} z_3}{z_2 - z_3} c_{e_2} \\ \nu_1^{e_1} c_{e_1} + \nu_2^{e_2} c_{e_2} \end{bmatrix}. \quad (16.30)$$

The electroneutral component chemical potentials can then be written using Eqs. (8.22) and (8.23). Together with the relation $\nu_{e_2} y_{e_2} = 1 - \nu_{e_1} y_{e_1}$, these show that

$$\begin{aligned} \bar{\nabla} \begin{bmatrix} \mu_{e_1}^0 \\ \mu_{e_2}^0 \end{bmatrix} &= RT \begin{bmatrix} X_{e_1 e_1}^0 & X_{e_1 e_2}^0 \\ X_{e_2 e_1}^0 & X_{e_2 e_2}^0 \end{bmatrix} \bar{\nabla} \begin{bmatrix} y_{e_1} \\ y_{e_2} \end{bmatrix} \\ &= RT \left[\frac{z_3 (z_1 \nu_{e_1} y_{e_1} + z_2 \nu_{e_2} y_{e_2})}{z_1 (z_3 - z_2) \nu_{e_1} y_{e_1} + z_2 (z_3 - z_1) \nu_{e_2} y_{e_2}} \right. \\ &\quad \left. + \frac{\nu_{e_1} y_{e_1} \nu_{e_2} y_{e_2} \Lambda_{e_1 e_1}^0}{\nu_{e_1}^2} \right] \begin{bmatrix} -\frac{1}{y_{e_1}} \\ \frac{1}{y_{e_2}} \end{bmatrix} \nu_{e_2} \nabla y_{e_2}, \end{aligned} \quad (16.31)$$

in which a single function $\Lambda_{e_1 e_1}(y_{e_2})$ parametrizes the composition gradient of either salt's mean molar activity coefficient within the solution. Observe that the ideal contribution to mixing free energy – the first term in the square brackets – depends in a rather subtle way on the salt fractions y_{e_1} and y_{e_2} .

Rather than repeating in its entirety the development illustrated for the binary electrolyte, we leverage the structural knowledge provided by our framework to abbreviate the process. Because the solution comprises three species, there are three flux-explicit transport properties \mathcal{D} , ξ and κ^0 . Using the structure posited in Eq. (14.1), we may write

$$M_v = \frac{RT \nu_{e_1} \nu_{e_2}}{c_T^0 \mathcal{D}} \begin{bmatrix} \frac{c_{e_2}}{c_{e_1}} & -1 \\ -1 & \frac{c_{e_1}}{c_{e_2}} \end{bmatrix}. \quad (16.32)$$

In order to eliminate the chemical-potential gradient of salt 1 from the flux-explicit laws, it is convenient to choose ψ' such that $\psi'_Z = i_{e_1}/c_{e_1}$, that is, to let the convective velocity be that of the first salt (i.e., \tilde{N}_{e_1}/c_{e_1}). There is a single non-trivial migration coefficient ξ relative to this reference velocity:

$$\xi^{e_1} = \begin{bmatrix} 0 \\ \xi \end{bmatrix}. \quad (16.33)$$

Using Eqs. (12.14) then shows that

$$m_z = \frac{RT \nu_{e_1} \nu_{e_2} \xi}{c_T^0 \mathcal{D}} \begin{bmatrix} -1 \\ \frac{c_{e_1}}{c_{e_2}} \end{bmatrix} \quad \text{and} \quad (16.34)$$

$$M_{zz} = \frac{F^2 \|z\|^2}{\kappa^0} + \frac{RT \nu_{e_1} \nu_{e_2} \xi^2}{c_T^0 \mathcal{D}} \frac{c_{e_1}}{c_{e_2}}. \quad (16.35)$$

Next, taking the transport matrix (1.2), performing the congruence transformation (5.7), and comparing the result to Eqs. (16.32), (16.34), and (16.35) allows identification of the three macroscopic transport properties in terms of Stefan–Maxwell coefficients. These are

$$\mathcal{D} = \frac{c_3^0 (z_1 - z_3)(z_2 - z_3)}{\left(\frac{c_3^0 z_2^2}{\mathcal{D}_{12}} + \frac{c_2^0 z_2^2}{\mathcal{D}_{13}} + \frac{c_1^0 z_1^2}{\mathcal{D}_{23}} \right)}, \quad (16.36)$$

$$\begin{aligned} \xi \cdot \frac{\nu_{e_1} \nu_{e_2} c_1^0 c_3^0 z_3^2}{\mathcal{D} \nu_1^{e_1}} &= \frac{z_3^2 c_3^0 (c_1^0 z_2 - c_2^0 z_1)}{\mathcal{D}_{12} \|z\|^2} - \frac{z_2 c_1^0 c_2^0 (z_1^2 + z_3^2) + (c_2^0)^2 z_1 z_2^2}{\mathcal{D}_{13} \|z\|^2} \\ &\quad + \frac{(c_1^0)^2 z_1^2 z_2 + c_1^0 c_2^0 z_1 (z_2^2 + z_3^2)}{\mathcal{D}_{23} \|z\|^2}, \end{aligned} \quad (16.37)$$

$$\kappa^0 = \frac{F^2 c_T^0 \left(\frac{z_1^2 c_1^0}{\mathcal{D}_{23}} + \frac{z_2^2 c_2^0}{\mathcal{D}_{13}} + \frac{z_3^2 c_3^0}{\mathcal{D}_{12}} \right)}{RT \left(\frac{c_1^0}{\mathcal{D}_{12} \mathcal{D}_{13}} + \frac{c_2^0}{\mathcal{D}_{12} \mathcal{D}_{23}} + \frac{c_3^0}{\mathcal{D}_{13} \mathcal{D}_{23}} \right)}. \quad (16.38)$$

Here the conductivity is identical to Pollard and Newman's equation 33 [30]. The diffusivity defined in Eq. (16.36) relates to the diffusion coefficient Pollard and Newman identified in their equation 9 [30], which we will label \mathcal{D} , as

$$\mathcal{D} = \mathcal{D} \frac{c_1^0 v_{e1} v_{e2}}{c_3^0 v_{e1} v_{e2}}. \quad (16.39)$$

Although the prefactor that relates our \mathcal{D} to Pollard and Newman's \mathcal{D} is composition-dependent, the factor only involves the particle fraction of the common ion, which is always of order unity.

It is equally straightforward to invert this process. Similar to the binary-electrolyte analysis, entries of \mathbf{M}^0 may be related to the original Stefan–Maxwell diffusivities \mathcal{D}_{ij} by inverting the congruence transformation in Eq. (8.26) and examining the off-diagonal elements in light of Eq. (8.25). This comparison shows that the diffusivities relate to the macroscopic properties as

$$\begin{aligned} \frac{1}{\mathcal{D}_{12}} &= \frac{[c_1^0(z_1^2 + z_3^2) + c_2^0 z_1 z_2] [c_2^0(z_2^2 + z_3^2) + c_1^0 z_1 z_2] v_{e1} v_{e2}}{\mathcal{D} c_1^0 c_2^0 v_{e1}^2 v_{e2}^2 \|z\|^4} \\ &\quad - \frac{\xi v_{e1} v_{e2} [c_1^0 z_1 (z_1^2 - z_2^2 + z_3^2) - c_2^0 z_2 (-z_1^2 + z_2^2 + z_3^2)]}{\mathcal{D} \|z\|^3 c_2^0 v_{e1}^2} \\ &\quad - \left(\frac{F^2 c_1^0}{RT \kappa^0} + \frac{v_{e1} v_{e2} \xi^2 c_{e1}}{\mathcal{D} c_{e2}} \right) \frac{z_1 z_2}{\|z\|^2}, \\ \frac{1}{\mathcal{D}_{13}} &= - \frac{z_3 (c_1^0 z_2 - c_2^0 z_1) [c_2^0(z_2^2 + z_3^2) + c_1^0 z_1 z_2] v_{e1} v_{e2}}{\mathcal{D} c_1^0 c_2^0 v_{e1}^2 v_{e2}^2 \|z\|^4} \\ &\quad + \frac{\xi z_3 v_{e1} v_{e2} [c_2^0 (-z_1^2 + z_2^2 + z_3^2) + 2c_1^0 z_1 z_2]}{\mathcal{D} c_2^0 v_{e1}^2 \|z\|^3} \\ &\quad - \left(\frac{F^2 c_1^0}{RT \kappa^0} + \frac{v_{e1} v_{e2} \xi^2 c_{e1}}{\mathcal{D} c_{e2}} \right) \frac{z_1 z_3}{\|z\|^2}, \\ \frac{1}{\mathcal{D}_{23}} &= - \frac{z_3 (c_2^0 z_1 - c_1^0 z_2) [c_2^0(z_2^2 + z_3^2) + c_1^0 z_1 z_2] v_{e1} v_{e2}}{\mathcal{D} c_1^0 c_2^0 v_{e1}^2 v_{e2}^2 \|z\|^4} \\ &\quad + \frac{\xi z_3 v_{e1} v_{e2} [c_1^0 (z_1^2 - z_2^2 + z_3^2) + 2c_2^0 z_1 z_2]}{\mathcal{D} c_2^0 v_{e1}^2 \|z\|^3} \\ &\quad - \left(\frac{F^2 c_1^0}{RT \kappa^0} + \frac{v_{e1} v_{e2} \xi^2 c_{e1}}{\mathcal{D} c_{e2}} \right) \frac{z_2 z_3}{\|z\|^2}. \end{aligned} \quad (16.40)$$

Pollard and Newman do not write down these relationships, presumably because of their algebraic complexity. Stating explicit forms for the Stefan–Maxwell coefficients in terms of flux-explicit properties becomes increasingly cumbersome as the number of species (and the number of charged species) in a system increases.

With our choice of convective velocity, the matrix $\bar{\mathbf{L}}_v^{e1}$ also affords a single non-trivial entry,

$$\bar{\mathbf{L}}_v^{e1} = \begin{bmatrix} 0 & 0 \\ 0 & \frac{\mathcal{D}}{v_{e1} v_{e2} c_{e1}} \end{bmatrix}. \quad (16.41)$$

After deriving transference numbers t_1^{e1} , t_2^{e1} , and t_3^{e1} relative to salt 1 with Eq. (13.2), the laws governing the species excess fluxes are found to be

$$\bar{J}_1^{e1} = \frac{t_1^{e1} \bar{i}}{F z_1}, \quad (16.42)$$

$$\bar{J}_2^{e1} = - \frac{c_1^0 \mathcal{D}}{RT} \frac{v_{e1} c_{e2}}{v_{e1} v_{e2} c_{e1}} \nabla \mu_{e2}^0 + \frac{t_2^{e1} \bar{i}}{F z_2}, \quad (16.43)$$

$$\bar{J}_3^{e1} = - \frac{c_1^0 \mathcal{D}}{RT} \frac{v_{e2} c_{e2}}{v_{e1} v_{e2} c_{e1}} \nabla \mu_{e2}^0 + \frac{t_3^{e1} \bar{i}}{F z_3}. \quad (16.44)$$

Interestingly, the excess flux of ion 1 relative to the velocity of salt 1 does not vanish; it can be driven by migration, but not by diffusion. Eq. (13.2) shows that all three transference numbers here are

parametric functions of the single migration coefficient ξ , through

$$\begin{bmatrix} t_1^{e1} \\ t_2^{e1} \\ t_3^{e1} \end{bmatrix} = \frac{\text{diag}(\mathbf{z}) \mathbf{Z}^T}{\|\mathbf{z}\|} \begin{bmatrix} 0 \\ \xi \\ 1 \end{bmatrix}. \quad (16.45)$$

Thus, as well as satisfying the relation $t_1^{e1} + t_2^{e1} + t_3^{e1} = 1$ that follows from the last row of this matrix equation, the species transference numbers relative to salt 1 are also constrained such that $(z_2^2 + z_3^2) t_1^{e1} + z_1^2 (t_2^{e1} + t_3^{e1}) = 0$, which follows from the first row.

The reference velocity under ξ^{e1} can be changed to that of the common ion by moving through the mass-average velocity with transference (12.10). Then one can derive the associated transference numbers, denoted t_i^3 , with Eq. (13.2) to find Pollard and Newman's expression

$$t_2^3 = \frac{\frac{z_2}{\mathcal{D}_{13}} - \frac{z_3}{\mathcal{D}_{12}}}{\left(\frac{z_2}{\mathcal{D}_{13}} - \frac{z_3}{\mathcal{D}_{12}} \right) + \frac{z_1 c_1^0}{z_2 c_2^0} \left(\frac{z_1}{\mathcal{D}_{23}} - \frac{z_3}{\mathcal{D}_{12}} \right)}, \quad (16.46)$$

which appears in their equation 10 [30]. With a migration coefficient relative to salt 1 and the reference-electrode potential from Eq. (15.6), one finds a concise MacInnes equation,

$$\frac{\bar{i}}{\kappa^0} = -\nabla \Phi^\ominus + \frac{s_{e1} \nabla \mu_{e1}^0}{n_{e-} F z_{e-}} + \left(\frac{s_{e2}}{n_{e-} F z_{e-}} - \frac{\kappa^0 \xi}{F \|\mathbf{z}\|} \right) \nabla \mu_{e2}^0, \quad (16.47)$$

in agreement with Pollard and Newman's equation 32 [30].

16.3. The cosolvent electrolyte

For a final illustration of our method of developing flux laws for concentrated multicomponent electrolytes, we consider a four-species liquid solution comprising two uncharged species, which we call a *cosolvent*, and a single salt. Electrolytic solutions of this type are used in lithium-ion batteries, which typically rely on blends of linear and cyclic carbonates to dissolve simple lithium salts [26]. We let subscripts + and – describe the cation and anion, respectively, a subscript e, the salt they associate to form, and let subscripts 0 and o stand for the two solvents. As was the case in the binary-electrolyte example, the stoichiometric coefficients for the salt satisfy Eq. (16.1), where v is the total salt stoichiometry.

A salt–charge basis for the cosolvent electrolyte is embodied by the transformation matrix

$$\mathbf{Z} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -\frac{v z_-}{z_+ - z_-} & \frac{v z_+}{z_+ - z_-} \\ 0 & 0 & \frac{z_+}{\|\mathbf{z}\|} & \frac{z_-}{\|\mathbf{z}\|} \end{bmatrix}. \quad (16.48)$$

The species concentrations in the neutral state can then be written as

$$\begin{bmatrix} c_0^0 \\ c_o^0 \\ c_+^0 \\ c_-^0 \end{bmatrix} = \mathbf{Z} \begin{bmatrix} c_0 \\ c_o \\ c_e \\ 0 \end{bmatrix} = \begin{bmatrix} c_0 \\ c_o \\ -\frac{v z_-}{z_+ - z_-} \cdot c_e \\ \frac{v z_+}{z_+ - z_-} \cdot c_e \end{bmatrix}, \quad (16.49)$$

revealing them to be parametric functions of the three component concentrations c_0 , c_o , and c_e .

The nonideal parts of the electroneutral component chemical potentials are parametrized by a symmetric 2×2 block matrix

$$\mathbf{A} = \begin{bmatrix} A_{00} & A_{0o} \\ A_{o0} & A_{oo} \end{bmatrix}, \quad (16.50)$$

whose three independent entries are functions of only two of the three component fractions y_0 , y_o , and y_e . Following Eq. (8.16), the gradients of the electroneutral component chemical potentials are expanded as

$$\nabla \begin{bmatrix} \mu_0^0 \\ \mu_o^0 \\ \mu_e^0 \end{bmatrix} = RT \nabla \ln y_v + RT (\mathbf{I}_3 - v \mathbf{y}_v^T) \begin{bmatrix} \mathbf{A} & \mathbf{0} \\ \mathbf{0}^T & \mathbf{0} \end{bmatrix} \nabla y_v, \quad (16.51)$$

where in this case $\mathbf{v} = [1, 1, \nu]^T$ and $\mathbf{y}_v = [y_0, y_o, y_e]^T$.

To derive flux explicit laws, we again use the ansatz (14.1) to write

$$\frac{c_0^0 \mathbf{M}_v}{RT} = \begin{bmatrix} \frac{c_0}{c_0 \mathcal{D}_{00}} + \frac{\nu c_e}{c_0 \mathcal{D}_{0e}} & -\frac{1}{\mathcal{D}_{00}} & -\frac{\nu}{\mathcal{D}_{0e}} \\ -\frac{1}{\mathcal{D}_{00}} & \frac{c_0}{c_0 \mathcal{D}_{00}} + \frac{\nu c_e}{c_0 \mathcal{D}_{0e}} & -\frac{\nu}{\mathcal{D}_{0e}} \\ -\frac{\nu}{\mathcal{D}_{0e}} & -\frac{\nu}{\mathcal{D}_{0e}} & \frac{\nu c_0}{c_e \mathcal{D}_{0e}} + \frac{\nu c_o}{c_e \mathcal{D}_{oe}} \end{bmatrix}. \quad (16.52)$$

These entries straightforwardly relate to the Stefan–Maxwell coefficients through

$$\mathcal{D}_{00} = \mathcal{D}_{00}, \quad (16.53)$$

$$\mathcal{D}_{0e} = \frac{(z_+ - z_-)\mathcal{D}_{0+}\mathcal{D}_{0-}}{\mathcal{D}_{0+}z_+ - \mathcal{D}_{0-}z_-}, \quad (16.54)$$

$$\mathcal{D}_{oe} = \frac{(z_+ - z_-)\mathcal{D}_{0+}\mathcal{D}_{0-}}{\mathcal{D}_{0+}z_+ - \mathcal{D}_{0-}z_-}. \quad (16.55)$$

Observe that the second two definitions take forms similar to Eq. (16.13), despite the addition of a solvent.

Taking the reference velocity to be that of the first solvent, i.e., $\psi' = \mathbf{i}_0/c_0$, the diffusivity matrix and migration coefficients assume the forms

$$\bar{\mathbf{L}}_v^0 = \begin{bmatrix} 0 & 0 & 0 \\ 0 & \mathcal{L}_o & \mathcal{L}_x \\ 0 & \mathcal{L}_x & \mathcal{L}_e \end{bmatrix}, \quad \xi^0 = \begin{bmatrix} 0 \\ \xi_o \\ \xi_e \end{bmatrix}. \quad (16.56)$$

The terms appearing in the diffusion matrix are understood as follows. \mathcal{L}_o denotes the Onsager diffusivity of the second solvent relative to the velocity of the first, \mathcal{L}_x the cross-diffusivity between the second solvent and the salt in a frame moving with the first solvent, and \mathcal{L}_e the diffusivity of the salt relative to the first solvent's velocity. Each of these parameters is independent, and the 2×2 sub-block of Onsager diffusivities is positive definite. The set of migration coefficients depends on two independent parameters ξ_o and ξ_e . A distinction from the previous cases is that a neutral species – the second solvent – may carry current. Thus transference numbers as typically understood do not suffice to write complete flux-explicit transport laws for this system.

By relation (14.2), the Onsager diffusivities that make up $\bar{\mathbf{L}}_v^0$ can be understood in terms of component diffusivities, as

$$\mathcal{L}_o = \frac{c_0 \mathcal{D}_{00}(\mathcal{D}_{0e}c_0 + \mathcal{D}_{0e}c_o)}{c_0(\mathcal{D}_{0e}c_0 + \mathcal{D}_{00}\nu c_e + \mathcal{D}_{0e}c_o)} \quad (16.57)$$

$$\mathcal{L}_e = \frac{c_e \mathcal{D}_{0e}(\mathcal{D}_{0e}c_0 + \mathcal{D}_{00}\nu c_e)}{c_0(\mathcal{D}_{0e}c_0 + \mathcal{D}_{00}\nu c_e + \mathcal{D}_{0e}c_o)} \quad (16.58)$$

$$\mathcal{L}_x = \frac{\mathcal{D}_{00}\mathcal{D}_{0e}c_o c_e}{c_0(\mathcal{D}_{0e}c_0 + \nu \mathcal{D}_{00}c_e + \mathcal{D}_{0e}c_o)}. \quad (16.59)$$

Each of these expressions agrees within a prefactor with the thermodynamic oxygen diffusivity, the thermodynamic electrolyte diffusivity, and the cross diffusivity proposed to describe lithium/air-battery electrolytes by Monroe [29].

The benefits of relying on two migration coefficients and directly writing flux laws in the salt–charge basis are made clearest by this example. Eq. (12.8) reads for the two-solvent case as

$$\bar{\mathbf{J}}_0^0 = \bar{\mathbf{0}}, \quad (16.60)$$

$$\bar{\mathbf{J}}_o^0 = -\mathcal{L}_o \frac{c_0^0 \nabla \mu_o}{RT} - \mathcal{L}_x \frac{c_0^0 \nabla \mu_e}{RT} + \xi_o \frac{\bar{\mathbf{i}}}{F \|\mathbf{z}\|} \quad (16.61)$$

$$\bar{\mathbf{J}}_e^0 = -\mathcal{L}_x \frac{c_0^0 \nabla \mu_o}{RT} - \mathcal{L}_e \frac{c_0^0 \nabla \mu_e}{RT} + \xi_e \frac{\bar{\mathbf{i}}}{F \|\mathbf{z}\|}. \quad (16.62)$$

Eqs. (16.60)–(16.62) are equivalent to equations 14–16 in the paper by Monroe [29]. These laws combine with the MacInnes equation for a reference electrode, written through Eqs. (12.12) and (15.6) as

$$\bar{\mathbf{i}} = -\kappa^0 \nabla \Phi^\ominus + \frac{\kappa^0 \mathbf{s}_v^T \nabla \mu_v^0}{n_e - F z_e} - \frac{\kappa^0 \xi^0 \nabla \mu_v^0}{F \|\mathbf{z}\|}, \quad (16.63)$$

to offer a complete description of isothermal, isobaric mass transport in the cosolvent electrolyte.

One could proceed as in the previous examples to elucidate how the migration coefficients, diffusivities, and conductivity relate to the Stefan–Maxwell coefficients. This would show, for example, that the migration coefficient ξ_k is expected to be proportional to component concentration $c_{v,k}$, as observed by Monroe [29]. We refrain from completing this exercise here because of the meteoric rise in complexity of the intermediate equations. On account of the matrix inversion involved when moving between force- and flux-explicit forms, writing out entries within both the thermodynamic-factor and transport-property matrices becomes increasingly untenable as the number of species increases. Nevertheless, this process was implemented and found to produce relationships among parameters consistent with those reported in detail elsewhere [29].

Matrix forms that connect flux- and force-explicit representations of transport laws are compact and generally useful. The operations described in prior sections are readily implemented with symbolic-manipulation software for systems containing large numbers of species. Perhaps most important is that the structures of the coefficient matrices within the electroneutral transport laws are very general. As shown in these examples, structural knowledge can be leveraged to create consistent sets of thermodynamic and transport constitutive laws a priori in either the Stefan–Maxwell or Fick representation, for electrolytes involving any number of components.

17. Numerical implementation: Hull cell

Recently, the authors presented finite-element methods to simulate Onsager–Stefan–Maxwell transport of multiple uncharged species [8, 18]. The efficacy of these approaches generally relies on the spectral structure of the coefficient matrix \mathbf{M} . A significant advantage of the electroneutral Onsager–Stefan–Maxwell equations developed here is that they can be solved easily within this numerical scheme. Indeed, it was discussed in Sections 5 and 8.4 how Sylvester's law of inertia guarantees that the spectral structure of electrolyte-transport laws remains essentially intact, in that the electroneutral transport matrix over the salt–charge basis, \mathbf{M}_Z^0 , is symmetric positive semidefinite with one null eigenvalue corresponding to the column \mathbf{c}_Z^0 .

In the prior papers [8,18], the numerical challenge posed by singular transport matrices was resolved with a matrix augmentation. In the present context, for a given reference velocity in the component space defined by ψ'_Z , we solve the augmented electroneutral Onsager–Stefan–Maxwell equations as

$$-\bar{\nabla} \mu_Z = \mathbf{M}_Z^{0,\psi'}(\gamma) \bar{\mathbf{n}}_Z, \quad (17.1)$$

where $\mathbf{M}_Z^{0,\psi'}(\gamma) = \mathbf{M}_Z^0 + \gamma \psi'_Z \psi'^T_Z$ proves to be a symmetric positive definite matrix whenever $\gamma \neq 0$ (see Ref. [8]). These equations are coupled to the component balances (5.3) and electroneutral charge balance (8.24).

We demonstrate how the framework created above can facilitate numerical analysis by solving for the steady-state current distribution in a symmetric electrode Hull cell containing a nonideal binary electrolytic solution, from which cations are plated and stripped under potentiostatic conditions, assuming that the electrode reactions have very low overpotential (fast kinetics). To show how thermodynamic consistency and system nonideality can be brought into simulations in a meaningful way, we take the electrolyte to be lithium hexafluorophosphate (LiPF_6) in ethyl–methyl carbonate (EMC) – a formulation used in lithium-ion batteries – whose properties were measured as functions of composition by Wang et al. [32,33]. This electrolyte has total stoichiometry $\nu = 2$ and the species charges are $\mathbf{z} = [z_0, z_+, z_-]^T = [0, 1, -1]^T$; the transformation matrix to the salt–charge basis is

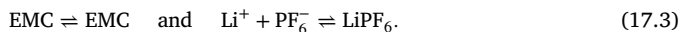
$$\mathbf{Z} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 1 \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{bmatrix}, \quad (17.2)$$

Table 1

Phenomenological property data necessary to specify the transport matrix \mathbf{M} and thermodynamic factor \mathbf{A} for solutions of lithium hexafluorophosphate in ethyl–methyl carbonate at room temperature, derived from data reported by Wang et al. [32,33].

Properties		
Term	Function	Units
κ	$(48.93y_e^{3/2} - 284.8y_e^{5/2} + 817.8y_e^4)^2$	S m^{-1}
D	$(4.998 - 29.96y_e + 53.78y_e^2) \times 10^{-10}$	$\text{m}^2 \text{ s}^{-1}$
χ	$1 - 18.38y_e^{1/2} + 155.3y_e - 450.6y_e^{3/2} + 1506y_e^{5/2}$	–
t_+^0	$0.4107 - 1.487y_e + 2.547y_e^2$	–
ρ	$1007.1 + 10^5 \times (0.0180y_e - 0.1946y_e^2 + 1.960y_e^3 - 7.008y_e^4 + 8.004y_e^5)$	g L^{-1}

in which the first two rows reflect the simple association equilibria



Wang's correlations for the composition dependences of ionic conductivity κ , Fickian diffusivity D , and Darken factor χ are expressed in terms of the salt fraction y_e and solvent fraction $y_0 = 1 - y_e$ in Table 1. Note that D and χ determine the properties Λ_{00} and \mathcal{D} defined in Section 16.1 through

$$\mathcal{D} = \frac{D}{\chi}, \quad (17.4)$$

$$\Lambda_{00} = \frac{\chi - 1}{y_e y_0}. \quad (17.5)$$

The migration coefficient ξ is determined by the cation transference number relative to the solvent velocity t_+^0 through Eq. (16.17), which reduces to

$$\xi = \frac{1 - 2t_+^0}{\sqrt{2}} \quad (17.6)$$

for this electrolyte system. Finally, it should be noted that the composition dependence of ρ appearing in Table 1 was not reported by Wang et al., but instead derives from a least-squares fit of the densitometric data reported in the supplementary information of those papers as a function of mass fraction [32,33]. For this system, $\rho(y_e)$ acts as the volumetric equation of state. When using density to compute properties relevant to concentration from ρ , the molar mass of EMC was taken to be $\bar{m}_0 = 104.105 \text{ g mol}^{-1}$, and that of LiPF_6 , $\bar{m}_e = 151.905 \text{ g mol}^{-1}$. After inferring the component diffusivity and migration coefficients by inserting the correlations from Table 1 into Eqs. (17.4) and (17.6), Eqs. (16.23)–(16.25) were used locally to assemble the matrix \mathbf{M}_Z . Simulations were performed assuming an equilibrium electrolyte composition of $\langle y_e \rangle = 0.15$ (ca. 1.9 mol L^{-1}).

To model potentiostatic electrodes with fast heterogeneous reaction kinetics, the voltages at the positive electrode (p) and negative electrode (n) were respectively assumed to be $V^p = 10 \text{ mV}$ and $V^n = 0$. At each electrode surface, we applied the Robin boundary condition

$$-(\vec{i} \cdot \vec{n})|_k = \frac{Fz_+i_0}{RT} (V^k - \Phi_Z^0|_k); \quad (17.7)$$

here \vec{n} is an outward unit normal vector, anodic overpotentials are positive, and $k \in \{p, n\}$. In simulations the exchange-current density i_0 was chosen to be very large (1 A cm^{-2}) so as to ensure that the solution-phase electrode potentials Φ_Z^0 matched V^a or V^c to an appropriate degree of precision (4 digits). To relate the electrode currents to interfacial fluxes, the flux of lithium ions was taken to be

$$(\vec{N}_{\text{Li}^+} \cdot \vec{n})|_k = \frac{1}{Fz_+} (\vec{i} \cdot \vec{n})|_k \quad (17.8)$$

at electrode surface $k \in \{p, n\}$; all other boundary conditions were set as homogenous Neumann conditions.

The stripping and plating of lithium at the boundary as expressed in (17.8) implies a transfer of mass across the solution. It would therefore be inconsistent to take the reference velocity as the mass-average

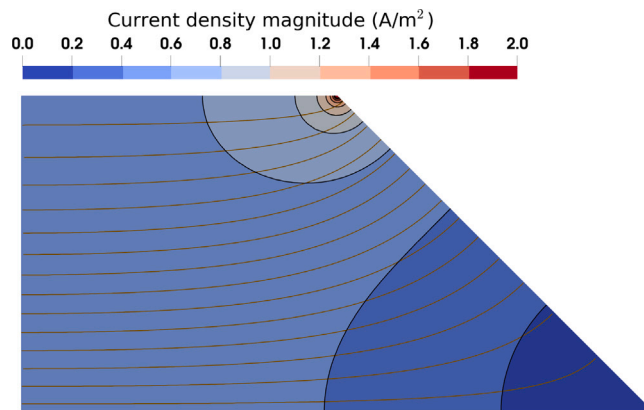


Fig. 1. Steady-state current density $|\vec{j}|$ within a Hull cell with reversible electrode reactions subjected to a constant voltage drop. Streamlines denote trajectories of current flow from the positive electrode (left) to the negative electrode (right). The top and left edges of the cell are 5 cm long, and the bottom edge is 10 cm long.

velocity and then assume this to be zero. Unfortunately, it is also not possible to solve for the distribution of mass-average velocity in two dimensions, because closure of problems in systems with more than one spatial dimension requires consideration of momentum continuity [34]. Instead we follow Newman and choose the reference velocity to be that of the solvent, and thence assume the solvent velocity to equal zero uniformly. Practically, this amounts to a formal neglect of the Faradaic convection phenomenon.

A steady-state simulation of the potentiostatic Hull cell was performed with Firedrake software [35], using the MUMPS direct linear solver [36,37] via PETSc [38,39]. The mesh of the geometry was constructed using the Gmsh software [40]. Each linear system had 183,831 degrees of freedom. The finite elements were chosen as CG_2 for component mole fractions/voltage and DG_1 for fluxes/current. The computed current distribution is plotted in Fig. 1. Observe that the current concentrates at the upper corner because of the obtuse angle with an insulating surface, and is dispersed at the lower corner, where the angle is acute, as might be expected from electrostatic analysis of the wedge geometry in cylindrical coordinates [1].

This example illustrates the potential of the structurally electroneutral Onsager–Stefan–Maxwell framework to model concentrated electrolytes with full composition dependence of all independent thermodynamic and transport properties, on complex geometries. Similarly we might consider modeling molten salts, or cosolvent electrolytes, or transient dynamics of any of these. Subject to availability of the necessary property data, the scope of applications can be extended much further.

Conclusion

We have detailed how local electroneutrality affects Onsager–Stefan–Maxwell mass transport within electrolytic solutions. Choosing a salt–charge basis according to the process we outline in Section 2 allows one to establish constitutive equations for component chemical-potential gradients in terms of a symmetric thermodynamic-factor matrix. Crucially, the use of a salt–charge basis also obviates the need to impose local electroneutrality as an algebraic constraint on the electrolytic mass-transport problem, allowing it to be woven into the parameter space of the differential governing system. This leads to the electroneutral Onsager–Stefan–Maxwell equations (8.30), which phrase $n - 1$ component chemical potential gradients and the salt–charge potential gradient explicitly in terms of $n - 1$ uncharged component fluxes and current density. Salt–charge potential relates in a straightforward way to the electric potential measured by a reference electrode of a given kind.

A process was established to invert the electroneutral Onsager–Stefan–Maxwell laws into the flux-explicit form familiar from concentrated solution theory, allowing the identification of standard transport properties such as ionic conductivity, component diffusivities, and species transference numbers. We introduced migration coefficients, a useful alternative that remedies the issue that transference numbers as commonly understood cannot describe all the electro-osmotic interactions in systems containing multiple uncharged species. Several examples were given to substantiate how the salt–charge basis concept enables the direct formulation of flux-explicit constitutive laws for mass and charge transport in locally electroneutral concentrated electrolytic solutions.

Establishing a salt–charge basis allows one to formulate the transport equations for locally electroneutral electrolytic solutions in a way that retains the spectral structure afforded by the Onsager–Stefan–Maxwell laws for nonelectrolytes. The utility of this perspective was underlined by using a code designed for nonelectrolytes to simulate electroneutral transport within a nonideal binary electrolytic solution with composition-dependent properties in a Hull cell.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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