

IV. Transport Phenomena

Lecture 22: Transport in Bulk Electrolytes

Notes by MIT Student (and MZB)

1 Nernst-Planck Equations

As introduced in the previous lecture, the flux of species i in a concentrated solution is

$$\vec{F}_i = M_i c_i \nabla \mu_i \quad (1)$$

according to linear irreversible thermodynamics, where the mobility is related to the (tracer) diffusivity by the Einstein relation,

$$M_i = \frac{D_i}{k_B T} \quad (2)$$

As in our theory of Faradaic reactions, the diffusional *electro*-chemical potential μ_i of an ionic species i is formally broken into chemical and electrostatic contributions,

$$\mu_i = k_B T \ln a_i + z_i e \phi \quad (3)$$

where ϕ is the mean electrostatic potential, and $a_i = \gamma_i c_i$ is the chemical activity, and γ_i the activity coefficient. The flux density (number per area per time) is then given by the *Nernst-Planck equation* (NP),

$$\vec{F}_i = -D_i^{chem} \nabla c_i + M_i z_i e \vec{E} \quad (4)$$

where $\vec{E} = -\nabla \phi$ is the electric field and

$$D^{chem} = D_i \left(1 + \frac{\partial \ln \gamma_i}{\partial \ln c_i} \right) \quad (5)$$

is the chemical diffusivity. In a dilute solution ($\gamma_i = 1$, $a_i = c_i$), the NP flux takes the simple form,

$$\vec{F}_i = -D_i (\nabla c_i + z_i c_i \nabla \phi) \quad (6)$$

where $\tilde{\phi} = e\phi/k_B T$ is the dimensionless potential, scaled to the thermal voltage. In the NP equation, the flux is decomposed into contributions, *chemical diffusion* due to concentrated gradients, and *electromigration*, or drift, in the electric field.

Conservation of mass implies,

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (\vec{u}c_i + \vec{F}_i) = \bar{R}_i \quad (7)$$

where \vec{u} is the fluid velocity, which transports ions by convection leading to a flux density $\vec{u}c_i$, and \bar{R}_i is the the bulk production rate of species i by reactions. The latter is usually neglected in electrolytes, but it can be important for aqueous solutions far from equilibrium, due to the water self-ionization reaction, $H^+ + OH^- \leftrightarrow H_2O$.

The same Nernst-Planck equations are also used to describe semiconductors, where electrons and holes play the role of ions, and the homogeneous reaction can result from exciton (electron-hole) annihilation or production (e.g. by absorption of sunlight in a solar cell).

2 Charge Transport in Electrolytes

The electrostatic charge density

$$\rho_e = \sum_i z_i e \phi \quad (8)$$

and the electrical current density (charge per area per time) in the electrolyte,

$$\vec{J} = \sum_i z_i e (\vec{u}c_i + \vec{F}_i) \quad (9)$$

involves sums over the ionic species, $i = 1, 2, \dots, N$. Charge conservation follows,

$$\frac{\partial \rho_e}{\partial t} + \nabla \cdot \vec{J} = \sum_i \bar{R}_i = 0 \quad (10)$$

where we assume that the bulk reactions do not produce any net charge (only local charge transfer between molecules).

The current has three contributions,

$$\vec{J} = \vec{J}_c + \vec{J}_d + \vec{J}_e \quad (11)$$

where

$$\vec{J}_c = \rho_e \vec{u} \quad (12)$$

is the *streaming current* due to convection of charge,

$$\vec{J}_d = - \sum_u (z_i e D_i^{chem}) \nabla c_i \quad (13)$$

is the *diffusion current*, driven by concentration gradients, and

$$\vec{J}_e = \sigma_e \vec{E} \quad (14)$$

is the *Ohmic current*, due to electromigration (Ohm's law) carried by the *ionic conductivity*,

$$\sigma_e = \sum_i (z_i e)^2 M_i c_i = \sum_i \frac{(z_i e)^2 D_i c_i}{k_B T} \quad (15)$$

3 Bulk Electroneutrality

As we shall see in subsequent lectures, electrolytes are *quasi-neutral* in “bulk” regions away from charged boundaries, in the sense that charge fluctuations are much smaller than the total number of charges in a given location,

$$|\rho_e| \ll \sum_i |z_i| e c_i \quad (16)$$

As a result, we can set the bulk charge density to zero when computing ion concentrations,

$$\rho_e = \sum_i z_i e c_i = 0 \quad (17)$$

and this condition implicitly defines the electrostatic potential. Equivalently, we can ensure that no charge is created,

$$-\frac{\partial \rho_e}{\partial t} = \nabla \cdot \vec{J} = 0 \quad (18)$$

A subtle consequence of quasi-electroneutrality is that the *bulk electric field generally does not satisfy Maxwell's equations*. In particular, in a linear dielectric medium, one should properly impose Poisson's equation, $-\varepsilon \nabla^2 \phi = \rho_e$ (where ε is the permittivity) with an electrostatic boundary condition, such as $\phi = V$ or $\hat{n} \cdot \varepsilon \nabla \phi = q_s$, where q_s is a surface charge. However, we do not have the flexibility to satisfy these equations in a neutral electrolyte, since ϕ is determined implicitly by $\rho_e = 0$. Electroneutrality would seem to imply Laplace's equation, $\nabla^2 \phi = 0$, but this follows from $\nabla \cdot \vec{J} = 0$ only in a

uniform, neutral electrolyte, $c_i = \text{constant}$. If concentration gradients exist, then $\nabla^2 \phi \neq 0$ in a neutral electrolyte. The resolution of this paradox is that there are always some *small charge fluctuations*, which produce electric fields that lead to ionic fluxes that continuously neutralize the solution, over very short length and time scales compared to macroscopic ionic transport.

4 Supporting Electrolyte

In many situations, one wants to enable the diffusion of an active ionic species $i = 1$ without any significant electromigration. This can be achieved adding a large excess of other, inert ions, comprising *supporting electrolyte* ($c_1 \ll c_2, \dots, c_N$), whose concentration remains approximately constant during the passage of a small current carried by the active species. In that case, the large, nearly constant conductivity of the solution leads to small electric fields, which produce negligible electromigration of the active species, so that convection and diffusion dominate¹,

$$\frac{\partial c_1}{\partial t} + \vec{u} \cdot \nabla c_1 = D_1 \nabla^2 c_1 \quad (19)$$

(where we also assume incompressible flow $\nabla \cdot \vec{u} = 0$). This allows the diffusion equation to be solved as the theoretical basis for electroanalytical methods, such as cyclic voltammetry or chronoamperometry, in supported electrolytes². Supporting electrolyte is also used in situations, such as electroplating, where one wants to avoid ion concentration polarization and limited current in the electrolyte (next lecture).

5 Binary Electrolyte

Consider a bulk binary electrolyte with cations of charge z_+e and anions of charge $-z_-e$. Quasi-neutrality allows us to define the bulk salt concentration,

$$c = z_+c_+ = z_-c_- \quad (20)$$

On the homework, we consider the general case of a concentrated solution, so here we focus on the limit of a dilute solution ($D_i^{chem} = D_i = \text{constant}$, $a_i = c_i$), in which the NP conservation equations take the form,

$$\frac{\partial c_{\pm}}{\partial t} = D_i \left(\nabla^2 c_i \pm \nabla \cdot (c_{\pm} \nabla \tilde{\phi}) \right). \quad (21)$$

¹For a more detailed asymptotic analysis, due to Levich, see J. Newman's book.

²See Bard and Faulker.

Subtracting these equations, we obtain the condition of charge conservation,

$$\frac{\partial \rho_e}{\partial t} = z_+ \frac{\partial c_+}{\partial t} - z_- \frac{\partial c_-}{\partial t} = 0 \quad (22)$$

which implies

$$-\nabla \cdot (c \nabla \tilde{\phi}) = \left(\frac{D_+ - D_-}{z_+ D_+ + z_- D_-} \right) \nabla^2 c \quad (23)$$

Adding the NP equations, we obtain the condition of neutral salt conservation,

$$\frac{\partial c}{\partial t} = \frac{1}{2} \left(z_+ \frac{\partial c_+}{\partial t} + z_- \frac{\partial c_-}{\partial t} \right) \quad (24)$$

$$= \frac{1}{2} \left((D_+ + D_-) \nabla^2 c + (z_+ D_+ - z_- D_-) \nabla \cdot (c \nabla \tilde{\phi}) \right) \quad (25)$$

$$= D \nabla^2 c \quad (26)$$

where in the last step we use (23) and define the effective *ambipolar diffusivity* for neutral salt,

$$D = \frac{(z_+ + z_-) D_+ D_-}{z_+ D_+ + z_- D_-} \quad (27)$$

Curiously, the salt concentration appears to diffuse as a neutral species, even though each species experiences electromigration in opposite directions. This remarkable cancellation will be clarified by an example in the next lecture.

The ambipolar diffusivity can be expressed in more illuminating forms. It is the harmonic mean of the individual ion diffusivities, weighted by the charge of the opposite species,

$$\frac{1}{D} = \left(\frac{z_+}{z_+ + z_-} \right) \frac{1}{D_-} + \left(\frac{z_-}{z_+ + z_-} \right) \frac{1}{D_+} \quad (28)$$

which is *dominated by the ion with the smaller diffusivity and/or smaller charge*. The reason is that the faster-diffusing or more highly charged ion responds more quickly to the Coulomb force attracting it to the slower, less highly charged ion, which thus controls the effective diffusivity of the neutral solution. This fact can also be understood by writing the ambipolar diffusivity as the arithmetic mean of the ion diffusivities, weighted by the field mobility of the opposite species,

$$D = \frac{\mathcal{M}_+ D_- + \mathcal{M}_- D_+}{\mathcal{M}_+ + \mathcal{M}_-} \quad (29)$$

where $\mathcal{M}_i = z_i e M_i = z_i e D_i / k_B T$ is the drift velocity per electric field. (M_i is the velocity per electrostatic force, $z_i e E$.)

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