

CHEM-E4235

Transport processes at electrodes and in membranes

Period I, 2020

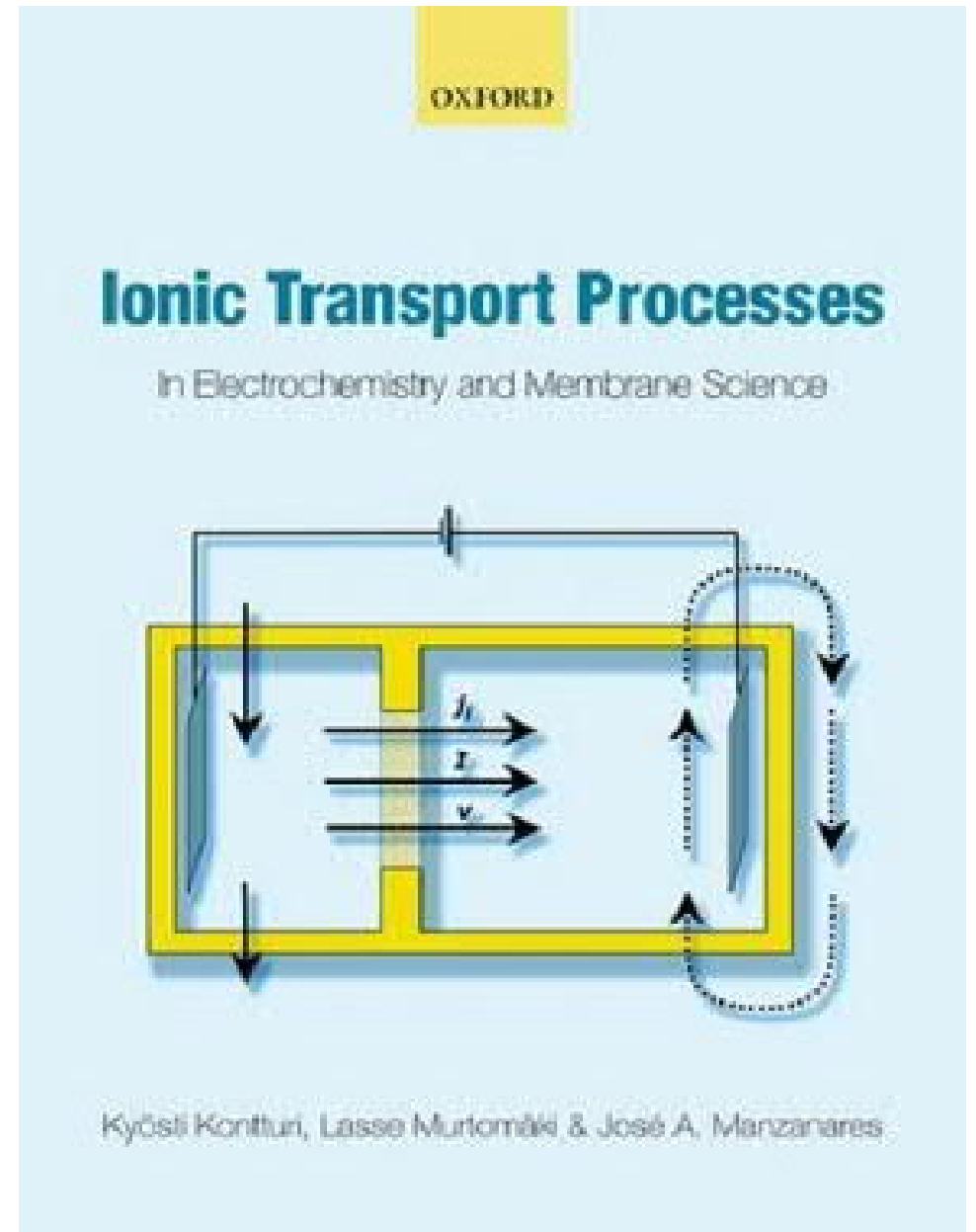
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What is needed?

- University calculus
- Basic understanding of (electro)chemistry
- Fundamental chemical thermodynamics
- Problem solving readiness



Tentative plan of lectures

1. Lecture, text book Chapter 1:

- Substantial derivative and reference speed
- Balance equation
- Dissipation function

2. Lecture, text book p. 38-49:

- Phenomenological transport equations and dissipation function
- Electrokinetic phenomena (not in the text book)
- Ionic phenomenological equation

3. Lecture, text book p. 50-70:

- Nernst-Planck equation
- Friction coefficient formalism (Stefan-Maxwell)

4. Lecture, text book p. 78 -88:

- Transport at electrodes, using Nernst-Planck equation

5. Lecture, text book p. 79-98:

- Some solution of transport problems at steady-state
- Spherical symmetry, ultramicroelectrodes

6. Lecture, text book p. 98-110:

- Hydrodynamic methods

7. Lecture, text book p. 110-122:

- Transient methods

8. Lecture, Introduction to Comsol Multiphysics

9. Lecture, text book p. 126-152:

- Transport across a neutral porous membrane

10. Lecture, text book p. 152-173:

- Donnan equilibrium in ion exchange membranes
- Transport equations in ion exchange membranes

11. Lecture, text book p. 173-204:

- Transport across an ion exchange membrane
- Membrane potentials and selectivity

12. Lecture, text book p. 205-220:

- Porous ion exchange membrane

In addition to the textbook, lecture slides where issues are presented in a condensed form.

Three approaches to transport:

- Irreversible thermodynamics and dissipation function (Lars Onsager)
- Friction coefficient formalism (Stefan-Maxwell)
- Nernst-Planck equation (most useful)

Transport processes via Thermodynamics of Irreversible Processes

- An approach developed by Lars Onsager ca. 1930, Nobel Prize in chemistry in 1968
- Later developers, e.g. Rolf Haase, Thermodynamik der irreversiblen Prozesse, 1963; Ilya Prigogine, Nobel Prize in Chemistry in 1977 (dissipative structures)
- Based on the 2nd law of Thermodynamics, i.e. entropy production
- Dissipation function \sim the rate of entropy production > 0

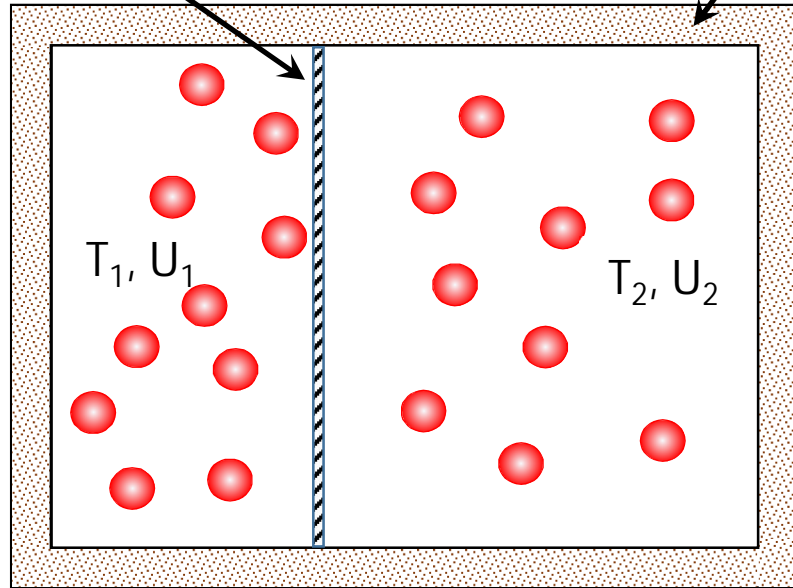
What is entropy?

- Classical interpretation: energy that is changed into a form where the system is no more capable of doing work (see next page)
- Statistical interpretation: measure of disorder, $S = k_B \ln(W)$ (Boltzmann)
- Transport processes: dissipation function = force \cdot flux (see later)
- Information theory: average information (expectation value) of a received signal (Shannon entropy). Consequence: white noise is the richest in information content.

Example of classical interpretation: two ideal gases are mixed

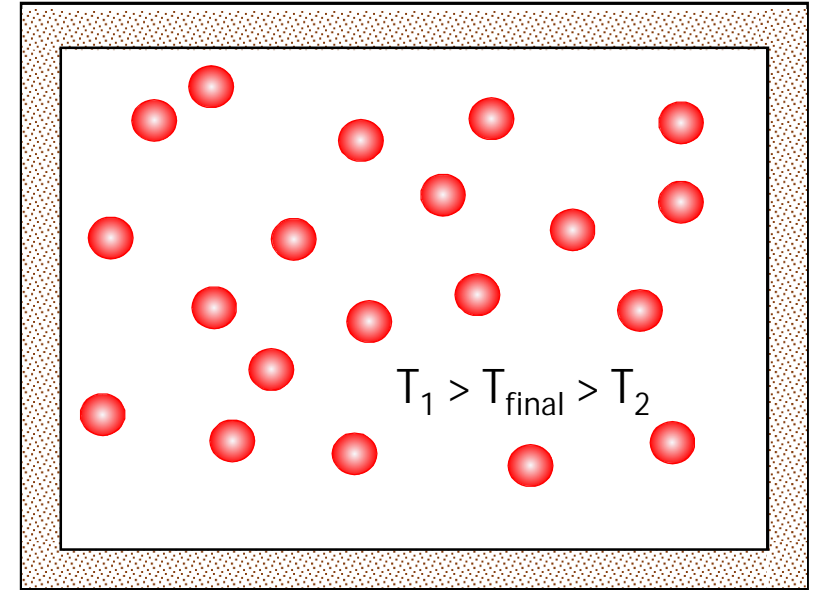
adiabatic diaphragm

adiabatic wall



$$U_{\text{TOT}} = U_1 + U_2 \quad T_1 > T_2$$

Remove diaphragm
Energy remains the same!



$$U_{\text{TOT}} = U_1 + U_2$$

$$dS = C_v \frac{dT}{T} \Rightarrow \Delta S = \frac{3}{2}R \left(\ln \frac{T_{\text{final}}}{T_2} - \ln \frac{T_{\text{final}}}{T_1} \right) = \frac{3}{2}R \ln \left(\frac{T_1}{T_2} \right)$$

The original system could have done work $nR(T_1 - T_{\text{final}}) = nR \frac{1}{2}(T_1 - T_2)$.

Preparative issues I: components and species

Any identifiable particles in the system (e.g. solution) – ions, molecules, electrons etc. – are called species while components are those species that can be varied independently in the system. For example, an aqueous solution of acetic acid contains species H^+ , OH^- , H_2O , CH_3COO^- (Ac^-) and CH_3COOH (HAc), but only two components, H_2O and HAc . Protons (or H_3O^+) and hydroxyl ions OH^- are bound together by the ionic product of water:

$$K^w = [\text{H}^+][\text{OH}^-] = 10^{-14} \text{ M} \quad \text{at } 25 \text{ }^\circ\text{C} \quad (1.1)$$

The dissociation (acid) constant of acetic acid couples H^+ , Ac^- and HAc :

$$K_a = \frac{[\text{H}^+][\text{Ac}^-]}{[\text{HAc}]} = 1.7378 \times 10^{-5} \text{ M} \quad \text{at } 25 \text{ }^\circ\text{C} \quad (1.2)$$

Additionally, electrolyte systems are bound by the very strong electroneutrality condition:

$$\sum_i z_i c_i = 0 \quad (1.3)$$

Generally, in a system containing N species, bound by m reactions and p other constrains, the number of components is M :

$$M = N - m - p \quad (1.4)$$

In the acetic acid case, $N = 5$, $m = 2$ and $p = 1$, hence $M = 2$. It must be realized that Gibbs-Duhem equation (see later) brings yet an extra constrain.

We use the following notation: subscript 0 denotes for the solvent and species are denoted by subscripts 1, 2, 3,... If the species are ions from electrolytes (salts), the following applies: Let us consider, e.g. a mixture of NaCl and CaCl₂ and denote the concentration of Na⁺ with c₁, that of Ca²⁺ with c₂ and that of Cl⁻ with c₃. The concentration NaCl is c₁₃ and that of CaCl₂ c₂₃, hence, c₃ = c₁₃ + 2c₂₃. Yet another important quantity is the mean electrolyte concentration c_± and mean activity coefficient γ_±:

$$c_{\pm} = c \left(\nu_+^{\nu_+} \nu_-^{\nu_-} \right)^{1/\nu} \quad ; \quad \gamma_{\pm} = \left(\gamma_+^{\nu_+} \gamma_-^{\nu_-} \right)^{1/\nu} \quad ; \quad \nu = \nu_+ + \nu_- \quad (1.5)$$

ν₊ and ν₋ are the stoichiometric coefficients of the cation and anion, respectively. To continue with our example,

$$c_{\pm,13} = c_{13} \left(1^1 1^1 \right)^{1/2} = c_{13} \quad ; \quad c_{\pm,23} = c_{23} \left(1^1 2^2 \right)^{1/3} = c_{23} \sqrt[3]{4} \quad (1.6)$$

The electrolyte chemical potential is continuous when crossing a phase boundary (at equilibrium):

$$\begin{aligned} \mu_{\pm} &= \nu_+ \mu_+ + \nu_- \mu_- = \nu_+ \left(\mu_+^0 + RT \ln a_+ + z_+ F \phi \right) + \nu_- \left(\mu_-^0 + RT \ln a_- + z_- F \phi \right) \\ &= \nu_+ \mu_+^0 + \nu_- \mu_-^0 + RT \ln \left[(a_+)^{\nu_+} (a_-)^{\nu_-} \right] = \mu_{\pm}^0 + RT \ln (a_{\pm}^{\nu}) = \mu_{\pm}^0 + RT \ln (c_{\pm} \gamma_{\pm})^{\nu} \end{aligned} \quad (1.7)$$

where the electrochemical potential of a species is used (φ is the Galvani or inner potential of the phase):

$$\mu_i = \mu_i + z_i F \phi \quad (1.8)$$

Hence, if the standard chemical potentials are the same in the two phases, the mean activity a_± is continuous. Single ion activity coefficients cannot be measured but they can be estimated with a convention

$$\sum_i \frac{c_i}{z_i} \ln \gamma_i = 0 \quad (1.9)$$

Preparative issues II: Euler's homogeneous functions

A system is described in terms of a set of independent variables which are chosen in a pragmatic way, i.e. with variables which we are able to control. Thermodynamic variables U, H, F, G are state functions, and more importantly, Euler's homogeneous functions of the first order.

Euler's homogeneous function of the order n (derivation with only one variable for the sake of simplicity):

$$\begin{aligned} F(kx) &= k^n F(x) \Rightarrow \frac{\partial F(kx)}{\partial k} = nk^{n-1} F(x) \\ \frac{\partial F(kx)}{\partial k} &= \frac{\partial F(kx)}{\partial(kx)} \frac{\partial(kx)}{\partial k} = \frac{1}{k} \frac{\partial F(kx)}{\partial x} x = \frac{x}{k} k^n \frac{\partial F(x)}{\partial x} = k^{n-1} x \frac{\partial F(x)}{\partial x} \\ \Rightarrow nk^{n-1} F(x) &= k^{n-1} x \frac{\partial F(x)}{\partial x} \Rightarrow nF(x) = x \frac{\partial F(x)}{\partial x} \end{aligned} \tag{1.10}$$

Thus, for example: $U(S, V, n_1, \dots, n_k) = S \frac{\partial U}{\partial S} + V \frac{\partial U}{\partial V} + n_1 \frac{\partial U}{\partial n_1} + \dots + n_k \frac{\partial U}{\partial n_k}$

When it is written in textbooks, e.g.

$$dU = TdS - PdV + \sum_i \mu_i dn_i \Rightarrow U = ST - PV + \sum_i \mu_i n_i$$

this is not an integration (as frequently stated) but the property of the Euler's homogeneous function.

Preparative issues III: Legendre transforms

$$dU = TdS - PdV + \sum_i \mu_i dn_i \quad ; \quad U = U(S, V, n_i) = TS - PV + \sum_i \mu_i n_i \quad (1.11)$$

If we want to change V to P as an independent variable, we form a new function, enthalpy, through Legendre transformation:

$$H = U - \frac{\partial U}{\partial V} V = U - (-P)V = U + PV$$
$$dH = dU + PdV + VdP = TdS + VdP + \sum_i \mu_i dn_i \quad ; \quad H = H(S, P, n_i) \quad (1.12)$$

Similarly, changing S to T leads to Helmholtz energy (in some textbooks symbol A):

$$F = U - \frac{\partial U}{\partial S} S = U - TS \Rightarrow dF = -SdT - PdV + \sum_i \mu_i dn_i \quad ; \quad F = F(T, V, n_i) \quad (1.13)$$

Changing S to T in enthalpy gives Gibbs free energy:

$$G = H - \frac{\partial H}{\partial S} S = H - TS \Rightarrow dG = -SdT + VdP + \sum_i \mu_i dn_i \quad ; \quad G = G(T, P, n_i) \quad ; \quad G = \sum_i \mu_i n_i \quad (1.14)$$

Legendre transform provides the means of creating new state functions from variables of our interest.

Preparative issues IV: Gibbs-Duhem equation

In chemistry, an extra term is included in the thermodynamic state functions to take into account the amount of species:

$$dU = TdS - PdV + \sum_i \mu_i dn_i \quad ; \quad U = U(S, V, n_1, n_2, \dots, n_k) \quad (1.15)$$

where μ_i is the chemical potential of the species i and n_i its amount (in moles). Since U is Euler's homogeneous function of the 1st order,

$$U = TS - PV + \sum_i \mu_i n_i \quad (1.16)$$

In terms of calculus, the total differential of U is

$$dU = TdS + SdT - PdV - VdP + \sum_i \mu_i dn_i + \sum_i n_i d\mu_i \quad (1.17)$$

Comparison of (1.10) with (1.12) leads to

$$SdT - VdP + \sum_i n_i d\mu_i = 0 \quad (1.18)$$

which is the Gibbs-Duhem equation. Usually chemical processes are carried out at constant T and P ($dT = dP = 0$), giving the more familiar form of

$$\sum_i n_i d\mu_i = 0 \quad \text{or} \quad \sum_i c_i d\mu_i = 0 \quad (1.19)$$

Gibbs-Duhem equation means that, e.g. in a binary system (solvent-solute) there is only one independent component the concentration of which can be varied.

We start the analysis from Gibbs equation (1.15) where we can see that the fundamental variables are S , V and n_i 's. Interpreting it as a differential it can be seen that

$$\frac{\partial S}{\partial U} = \frac{1}{T} \quad ; \quad \frac{\partial U}{\partial V} = -P \quad ; \quad \frac{\partial U}{\partial n_i} = \mu_i \quad (1.20)$$

The first of these equations can be considered as the definition of temperature. Temperature as such has no meaning for a single particle, it can be considered only when a macroscopic limit of the number of particles is reached; that is why it is not a fundamental variable. On the contrary, even a smallest collection of particles has, indeed, volume and entropy, although entropy is not that illustrative quantity (we have no entropy meter) in an every day life. Internal energy, U , includes all the modes of molecular motion as well as chemical energy stored in chemical bonds.

Dividing Gibbs equation by V it is obtained:

$$T \frac{\partial s}{\partial t} = \frac{\partial u}{\partial t} - \sum_i \mu_i \frac{\partial c_i}{\partial t} \quad (1.21)$$

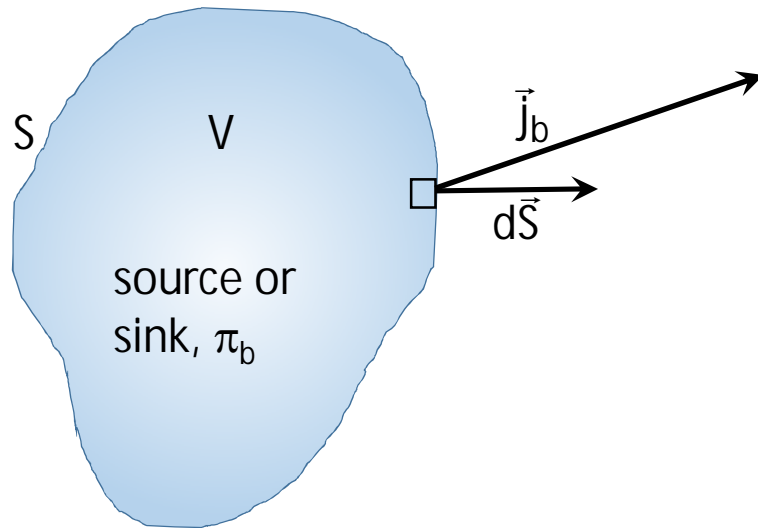
where $s = S/V$, $u = U/V$, $c_i = n_i/V$; $dV = 0$ in an incompressible fluid (e.g. aqueous solution). Now, on the left hand side we have **the dissipation function** in terms of intensive variables; Eq. (1.21) thus provides the starting point for its quest. Eq. (1.20) comes into the form of

$$\frac{\partial s}{\partial u} = \frac{1}{T} \quad ; \quad \frac{\partial u}{\partial c_i} = \mu_i \quad (1.22)$$

Balance equation

Let's consider an arbitrary volume V with its surface area S . The change of a general variable B within this volume is, in words
change = input – output

Hence, if the input to the volume is larger than output the change of B is positive, in terms of calculus, $\partial B/\partial t > 0$.



Change comes from the difference of the inflow of B into the volume and outflow from it, plus the possible production and consumption of B within V (e.g. due to a chemical reaction). The flux term is the surface integral over S :

$$-\oint_S \vec{j}_b \cdot d\vec{S}$$

where \vec{j}_b is the flux density of B across the surface and $d\vec{S}$ is a vector pointing out perpendicularly from the surface, representing an infinitesimal area dS ; minus sign comes because a positive scalar product means outflux. π_b is positive for the net production of B (source) and negative for its net consumption (sink).

The balance of B in V thus is

$$\frac{\partial B}{\partial t} = -\oint_S \vec{j}_b \cdot d\vec{S} + \iiint_V \pi_b dV \quad (1.23)$$

Next we apply Gauss' divergence theorem:

$$-\oint_S \vec{j}_b \cdot d\vec{S} = -\iiint_V \nabla \cdot \vec{j}_b dV \quad (1.24)$$

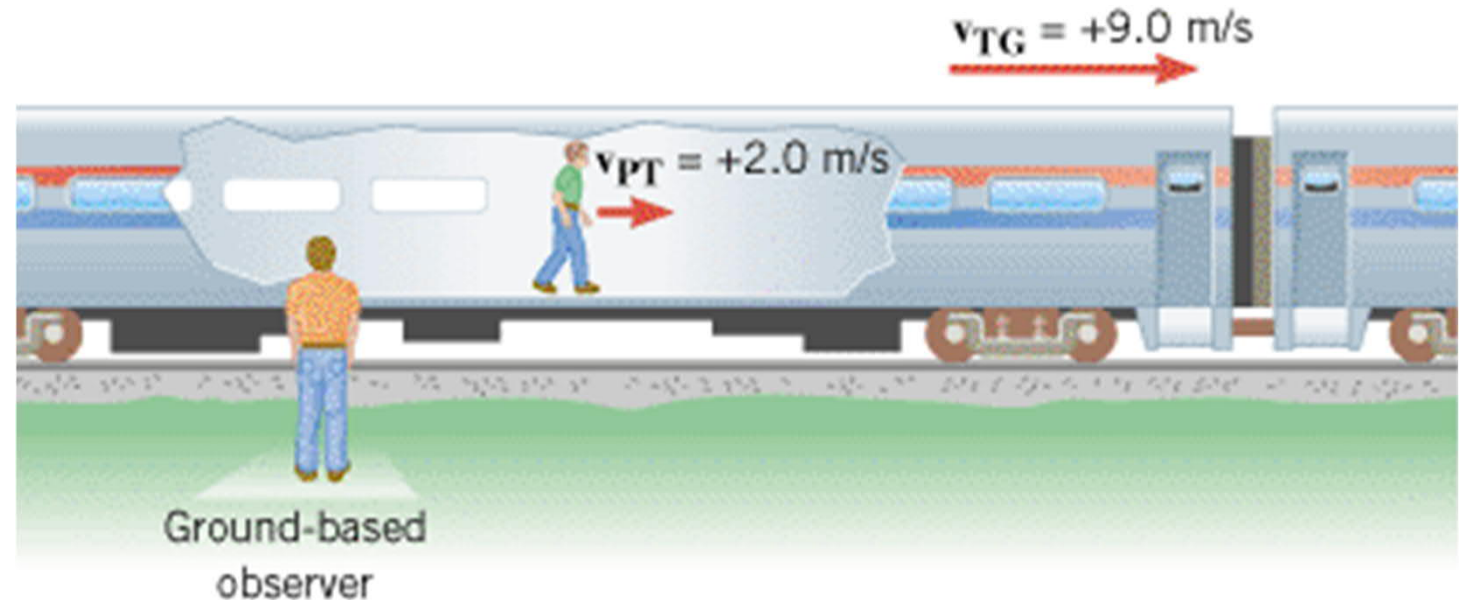
Hence, the balance equation becomes

$$\frac{\partial B}{\partial t} = \iiint_V \frac{\partial b}{\partial t} dV = -\iiint_V \nabla \cdot \vec{j}_b dV + \iiint_V \pi_b dV \quad (1.25)$$

where $b = B/V$. Since the volume V is completely arbitrary, we can 'divide' the above equation with V , giving the local form:

$$\frac{\partial b}{\partial t} + \nabla \cdot \vec{j}_b = \pi_b \quad (1.26)$$

The above balance equation can be considered to apply in the fixed laboratory coordinates. But what happens if the volume V moves along a fluid flow? The situation is analogous depicted aside, where the velocity of the person in train is 2 m/s with respect to the train, but 11 m/s with respect to the fixed coordinates. For this case the balance equation can be written in terms of the substantial derivative.



The easiest way to derive the substantial derivative of b is to consider it as quantity of three spatial coordinates and time, $b = b(x,y,z,t)$. The total differential of b thus is

$$Db = \left(\frac{\partial b}{\partial x}\right)dx + \left(\frac{\partial b}{\partial y}\right)dy + \left(\frac{\partial b}{\partial z}\right)dz + \left(\frac{\partial b}{\partial t}\right)dt$$

$$\frac{Db}{dt} = \left(\frac{\partial b}{\partial x}\right)\frac{dx}{dt} + \left(\frac{\partial b}{\partial y}\right)\frac{dy}{dt} + \left(\frac{\partial b}{\partial z}\right)\frac{dz}{dt} + \left(\frac{\partial b}{\partial t}\right) = \left(\frac{\partial b}{\partial x}\right)v_x + \left(\frac{\partial b}{\partial y}\right)v_y + \left(\frac{\partial b}{\partial z}\right)v_z + \left(\frac{\partial b}{\partial t}\right) \quad (1.27)$$

As the volume V is moving with the speed $\vec{v} = v_x\vec{i} + v_y\vec{j} + v_z\vec{k}$, the above equation can be written in a compact form of

$$\frac{Db}{Dt} = \nabla b \cdot \vec{v} + \frac{\partial b}{\partial t} = \nabla \cdot (b\vec{v}) - b\nabla \cdot \vec{v} - \nabla \cdot \vec{j}_b + \pi_b = \nabla \cdot (b\vec{v} - \vec{j}_b) + \pi_b \quad (1.28)$$

Noticing that $\vec{j}_b = \vec{j}_b^m + b\vec{v}$, Eq. (1.28) reduces to ($\nabla \cdot \vec{v} = 0$ for an incompressible fluid, e.g. water, see p. 13 in the textbook)

$$\frac{Db}{Dt} + \nabla \cdot \vec{j}_b^m = \pi_b \quad (1.29)$$

In the equations above, it is customary to use capital D to emphasize the substantial derivative; \vec{j}_b^m is the flux density in the mass-average (barycentric) frame of velocity (see Table 1.1, p. 12 in the textbook). The analogy between Eqs. (1.26) and (1.29) is obvious. If b is interpreted as the electric charge density, $\rho_e = F \sum_i z_i c_i$, eq. (1.26) becomes

$$\frac{\partial \rho_e}{\partial t} + \nabla \cdot \vec{I} = 0 \quad ; \quad \vec{I} = \vec{j}_e = F \sum_i z_i \vec{j}_i \quad (1.30)$$

$\pi_e = 0$ in electroneutral systems, and electric current density \vec{I} is independent of the frame of velocity (home exercise).

Because in an electroneutral system $\rho_e = 0$ it follows that also $\nabla \cdot \vec{\Gamma} = 0$.

For the concentration of species i , c_i , the balance equation is

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \vec{j}_i = \pi_i \quad (1.31)$$

The source/sink term π_i comes from chemical reactions. In the absence of reactions and at steady-state

$$\nabla \cdot \vec{j}_i = 0 \quad (1.32)$$

Furthermore,

$$\vec{j}_i = c_i \vec{v}_i = c_i (\vec{v}_i - \vec{v}_0) + c_i \vec{v}_0 = \vec{j}_i^H + c_i \vec{v}_0 \quad (1.33)$$

where \vec{v}_0 is the velocity of the solvent (water). This reference frame is called Hittorf's reference (Table 1.1). In practice, barycentric, Fick's and Hittorf's reference frame are the same except in very concentrated solutions (cf. molarity and molality).

Balance equation for entropy density is

$$\frac{\partial s}{\partial t} + \nabla \cdot \vec{j}_s = \frac{\theta}{T}, \quad (1.34)$$

where θ is the dissipation function. For internal energy ($\vec{\Gamma}^m = \vec{\Gamma}$ in an electroneutral system, see p. 20-21 and Table 1.2)

$$\frac{\partial u}{\partial t} + \nabla \cdot \vec{j}_u = \vec{\Gamma} \cdot \vec{E} \quad (1.35)$$

Now we are ready to write down the dissipation function due to electrodiffusion. From Eq. (1.21), (1.34) and (1.35):

$$\theta_{ed} = T \frac{\partial s}{\partial t} + T \nabla \cdot \vec{J}_s = \frac{\partial u}{\partial t} - \sum_i \mu_i \frac{\partial c_i}{\partial t} + T \nabla \cdot \vec{J}_s = \vec{T} \cdot \vec{E} - \nabla \cdot \vec{J}_u - \sum_i \mu_i \frac{\partial c_i}{\partial t} + T \nabla \cdot \vec{J}_s \quad (1.36)$$

The entropy flux density is given in the textbook, Eq. (1.65); it is based on the relation $s = \frac{1}{T} \left(u + p - \sum_i \mu_i c_i \right)$.

$$\vec{J}_s = \frac{1}{T} \left(\vec{J}_u + p\vec{v} - \sum_i \mu_i \vec{J}_i \right) \quad (1.37)$$

The $\partial c_i / \partial t$ term on the right hand side of (1.36) is given by the textbook equation (1.67). Inserting it in (1.36) gives

$$\theta_{ed} = \vec{T} \cdot \vec{E} - \cancel{\nabla \cdot \vec{J}_u} + \nabla \cdot \left(\cancel{\sum_i \mu_i \vec{J}_i} - p\vec{v} \right) - \sum_i \vec{J}_i^m \cdot \nabla \mu_i + \nabla \cdot \left(\cancel{\vec{J}_u} + p\vec{v} - \cancel{\sum_i \mu_i \vec{J}_i} \right) = \vec{T} \cdot \vec{E} - \sum_i \vec{J}_i^m \cdot \nabla \mu_i \quad (1.38)$$

Using the electrochemical potential of species i , it can shown (home exercise) that the dissipation function can be written as

$$\theta_{ed} = - \sum_i \vec{J}_i^m \cdot \nabla \mu_i \quad \text{Dissipation function} = \text{flux} \times \text{force} \quad (1.39)$$

Since we concentrate on the transport processes we bypass the contributions of chemical reactions and viscous forces to the dissipation function. Interested reader can refer to the textbook, Chapter 1.