

S10.E. Entropy Production in Discontinuous Systems

Consider the case where two fluids are separated by a thin membrane of thickness h . For most purposes, the membrane can be treated as a mathematical plane with a per area entropy production σ_A related to the (per volume) entropy production σ by

$$\sigma_A = \int_0^h dh \sigma \quad (10.289a)$$

In the absence of chemical reactions, we have [see (10.178a) of §10.F.1]

$$\sigma_A = \int_0^h dh \left[\mathbf{J}_q \cdot \nabla_r \left(\frac{1}{T} \right) - \sum_{j=1}^N \tilde{\mathbf{J}}_j \cdot \nabla_r \left(\frac{\tilde{\mu}_j}{T} \right) \right] \quad (10.289b)$$

For the case of a quasi-1-D system, all fluxes and gradients are normal to the membrane, and have the same value everywhere on it. Assuming the membrane normal to be along the z -axis, (10.289b) simplifies to

$$\begin{aligned} \sigma_A &= \int_0^h dz \left[J_q \frac{d}{dz} \left(\frac{1}{T} \right) - \sum_{j=1}^N \tilde{J}_j \frac{d}{dz} \left(\frac{\tilde{\mu}_j}{T} \right) \right] \\ &\approx J_q \int_0^h dz \frac{d}{dz} \left(\frac{1}{T} \right) - \sum_{j=1}^N \tilde{J}_j \int_0^h dz \frac{d}{dz} \left(\frac{\tilde{\mu}_j}{T} \right) \end{aligned} \quad (10.289c)$$

where we have neglected the variations of the fluxes within the membrane. Note that this brings in the boundary condition:

$$\text{All fluxes are continuous across the membrane.} \quad (10.289d)$$

Setting

$$\int_0^h dz \frac{df}{dz} = f(h) - f(0) = \Delta f \quad (10.289e)$$

(10.289c) becomes

$$\begin{aligned} \sigma_A &= J_q \Delta \left(\frac{1}{T} \right) - \sum_{j=1}^N \tilde{J}_j \Delta \left(\frac{\tilde{\mu}_j}{T} \right) \\ &= -\frac{J_q}{T^2} \Delta T + \sum_{j=1}^N \frac{\tilde{J}_j \tilde{\mu}_j}{T^2} \Delta T - \sum_{j=1}^N \frac{\tilde{J}_j}{T} \Delta \tilde{\mu}_j \\ &= -\frac{1}{T} J_S \Delta T - \frac{1}{T} \sum_{j=1}^N \tilde{J}_j \Delta \tilde{\mu}_j \quad [(10.178) \text{ used. }] \end{aligned} \quad (10.289)$$

$$\rightarrow T \sigma_A = -J_S \Delta T - \sum_{j=1}^N \tilde{J}_j \Delta \tilde{\mu}_j \quad (10.290)$$

Since $\nabla_r T$ and $\nabla_r \tilde{\mu}_j$ are driving forces in transports in a continuous system, they are necessarily finite. The discontinuities in T or $\tilde{\mu}_j$ across the membrane render their derivatives singular, and hence unphysical, there. Obviously, one should overlook this as a price to pay for mathematical convenience. Technically, one must replace all references to $\nabla_r T$ and $\nabla_r \tilde{\mu}_j$ at the membrane with ΔT and $\Delta \tilde{\mu}_j$, respectively.

S10.E.I. Volume Flow Across a Membrane

Solution (water+solute) of different concentrations are separated in a container by a rigid membrane permeable, with different permeability, to both water & solute. Assuming quasi-1-D configuration and a uniform temperature throughout, the areal entropy production is [see (10.290)]

$$\begin{aligned} T \sigma_A &= - \sum_{j=s,w} \tilde{J}_j \Delta \tilde{\mu}_j \\ &= -\tilde{J}_s \Delta \tilde{\mu}_s - \tilde{J}_w \Delta \tilde{\mu}_w \\ &= -J_s \Delta \mu_s - J_w \Delta \mu_w \end{aligned} \quad (10.291)$$

The basic thermodynamics of the system were already discussed in §S2.C, with the simplifying assumption that the membrane is permeable only to water.

To begin, the independent variables are $T, P, \{n_j\}$ so that the natural thermodynamic potential is the Gibbs free energy.

μ_j is just the partial molar Gibbs energy for the j^{th} species [see §S2.C]. Since it depends only on intensive variables [see (2.220)]

$$\mu_j = \mu_j \left(T, P, \frac{n_s}{n_w} \right) = \mu_j(T, P, x_s) \quad x_j = \frac{n_j}{n_w + n_s} \quad j = s, w$$

$$\rightarrow d\mu_j = \left(\frac{\partial \mu_j}{\partial T} \right)_{P, x_s} dT + \left(\frac{\partial \mu_j}{\partial P} \right)_{T, x_s} dP + \left(\frac{\partial \mu_j}{\partial T} \right)_{T, P} dx_s \quad (10.292)$$

$$= \left(\frac{\partial \mu_j}{\partial P} \right)_{T, x_s} dP + \left(\frac{\partial \mu_j}{\partial T} \right)_{T, P} dx_s \quad [T = \text{const}] \quad (10.292a)$$

The **partial molar volume** of the j^{th} species is defined as

$$\bar{v}_j = \left(\frac{\partial V}{\partial n_j} \right)_{T, P, n_{i \neq j}} \quad (10.292b)$$

$$= \left(\frac{\partial \mu_j}{\partial P} \right)_{T, \{n_j\}} \quad [\text{Maxwell relation.}] \quad (10.292c)$$

The volume of a dilute solution is determined mainly by the volume of the water, with a correction due to the solute. Let $v_w = v_w(T, P)$ be the molar volume of water, then

$$\begin{aligned} V &\approx n_w v_w + n_s \left(\frac{\partial V}{\partial n_s} \right)_{T, P, n_w} \\ &= n_w v_w + n_s \bar{v}_s \end{aligned} \quad [(10.292b) \text{ used.}]$$

Since water is highly incompressible, $v_w \approx \bar{v}_w \approx \text{const}$ and we have

$$V \approx n_w \bar{v}_w + n_s \bar{v}_s \quad (10.292d)$$

For dilute solutions, each solute molecule can be taken as occupying some fixed volume v_m so that

$$\bar{v}_s = N_A v_m = \text{const} \quad N_A = \text{Avogadro's number}$$

(10.292d) thus agrees with (10.292b).

If we improve the ideal gas mixture expression (2.242) with a 1st order Taylor expansion term in P , we get, for low pressures,

$$\begin{aligned}\mu_j &\approx \mu_j^0(T) + \left(\frac{\partial \mu_j}{\partial P}\right)_{T, x_s} P + RT \ln \frac{P_j}{P} \\ &= \mu_j^0(T) + \bar{v}_j P + RT \ln x_j\end{aligned}\quad (10.292e)$$

where $P_j = x_j P$ is the **partial pressure**.

Let the difference between the values of any quantity X in the two solutions be denoted as

$$\Delta X = X^{II} - X^I \quad (10.292f)$$

Since both \bar{v}_w & \bar{v}_s are constants, (10.292f) gives

$$\Delta \mu_j = \bar{v}_j \Delta P + RT \ln \left(\frac{x_j^{II}}{x_j^I} \right) \quad (10.293a)$$

For water,

$$\Delta \mu_w \approx \bar{v}_w \Delta P + RT \ln \left(\frac{x_w^{II}}{x_w^I} \right) \quad (10.293)$$

Now,

$$\ln x_w = \ln \frac{n_w}{n_w + n_s} = \ln \frac{1}{1 + \frac{n_s}{n_w}} \approx -\frac{n_s}{n_w} \quad [\text{for dilute solution}]$$

$$= -\frac{c_s}{c_w} \quad c_j = \frac{n_j}{V} = \text{concentration} \quad (10.293a)$$

$$= -c_s \bar{v}_w = -c_s V_w \quad (10.293b)$$

(10.293) then gives

$$\begin{aligned}\Delta \mu_w &\approx \bar{v}_w \Delta P - RT \bar{v}_w (c_s^{II} - c_s^I) \\ &= \bar{v}_w (\Delta P - RT \Delta c_s) \\ &= \bar{v}_w (\Delta P - \Delta \pi)\end{aligned}\quad (10.294)$$

where $\Delta \pi$ is the **osmotic pressure difference** and we have made use of the **van't Hoff's law** [see (2.226) of §S2.C]

$$\Delta \pi \approx \frac{\Delta n_s}{V} RT = \Delta c_s RT \quad (10.294a)$$

For the solute,

$$\Delta \mu_s = \bar{v}_s \Delta P + RT \ln \left(\frac{x_s^{II}}{x_s^I} \right) \quad (10.295)$$

Since

$$x_s = \frac{n_s}{n_w + n_s} = \frac{n_s/n_w}{1 + n_s/n_w}$$

the power series for $\ln x_s$ takes the form

$$-\ln \frac{y+1}{y} \approx -2 \left[\frac{1}{2y+1} + \frac{1}{3(2y+1)^3} + \dots \right] \quad \text{for } (2y+1)^2 > 1$$

where $y = n_s/n_w$. Unfortunately, the series converges poorly for $y \rightarrow 0$.

We therefore tackle the problem from another angle. Using

$$\bar{x}_s = \frac{1}{2} (x_s^{II} + x_s^I) \quad \Delta x_s = x_s^{II} - x_s^I$$

$$\rightarrow \quad x_s^{II} = \bar{x}_s + \frac{1}{2} \Delta x_s \quad x_s^I = \bar{x}_s - \frac{1}{2} \Delta x_s$$

we have

$$\begin{aligned} \ln\left(\frac{x_s^{II}}{x_s^I}\right) &= \ln\left(\frac{\bar{x}_s + \frac{1}{2} \Delta x_s}{\bar{x}_s - \frac{1}{2} \Delta x_s}\right) = \ln\left(\frac{1 + \frac{\Delta x_s}{2\bar{x}_s}}{1 - \frac{\Delta x_s}{2\bar{x}_s}}\right) \\ &\approx \frac{\Delta x_s}{\bar{x}_s} = \frac{\Delta c_s}{\bar{c}_s} \end{aligned}$$

(10.295) thus becomes

$$\begin{aligned} \Delta\mu_s &\approx \bar{v}_s \Delta P + R T \frac{\Delta c_s}{\bar{c}_s} \\ &= \bar{v}_s \Delta P + \frac{\Delta\pi}{\bar{c}_s} \end{aligned} \quad (10.297)$$

Putting (10.294) & (10.297) into the areal entropy production (10.291) gives

$$\begin{aligned} T \sigma_A &= -J_s \left(\bar{v}_s \Delta P + \frac{\Delta\pi}{\bar{c}_s} \right) - J_w \bar{v}_w (\Delta P - \Delta\pi) \\ &= -\left(J_s \bar{v}_s + J_w \bar{v}_w \right) \Delta P - \left(\frac{J_s}{\bar{c}_s} - J_w \bar{v}_w \right) \Delta\pi \\ &= -J_V \Delta P - J_D \Delta\pi \end{aligned} \quad (10.298)$$

where

$$\begin{aligned} J_V &= J_s \bar{v}_s + J_w \bar{v}_w \\ &= \text{volume flux (total flux of fluid volume) across membrane.} \end{aligned} \quad (10.298a)$$

$$J_D = \frac{J_s}{\bar{c}_s} - J_w \bar{v}_w \quad (10.298b)$$

= volume exchange (or diffusion) flux cross membrane.

Note that

$$[J_V] = [J_D] = \left[\frac{1}{\text{area} \cdot \text{time}} \text{volume} \right] = [\text{velocity}]$$

Thus, we can write

$$J_D = \mathbf{v}_s - \mathbf{v}_w = \text{velocity of solute relative to water} \quad (10.298c)$$

where

$$\mathbf{v}_s = \frac{J_s}{\bar{c}_s} \quad \mathbf{v}_w = J_w \bar{v}_w \quad (10.298d)$$

The generalized Ohm's law associated with (10.298) is

$$\begin{pmatrix} J_V \\ J_D \end{pmatrix} = - \begin{pmatrix} L_{PP} & L_{PD} \\ L_{DP} & L_{DD} \end{pmatrix} \begin{pmatrix} \Delta P \\ \Delta\pi \end{pmatrix} \quad (10.299)$$

with the Onsager's relation

$$L_{PD} = L_{DP} \quad (10.299a)$$

If the concentrations are the same on both sides of the membrane,

$$\Delta c_s = 0 \rightarrow \Delta\pi = 0 \text{ [(10.294a) used.]}$$

(10.299) becomes

$$\begin{aligned} (J_V)_{\Delta\pi=0} &= -L_{PP} \Delta P && \text{(Hydraulic flux)} && L_{PP} = \text{hydraulic conductance.} \\ (J_D)_{\Delta\pi=0} &= -L_{DP} \Delta P && \text{(Ultrafiltration)} \end{aligned}$$

If the pressures are the same on both sides of the membrane,

$$\Delta P = 0$$

(10.299) becomes

$$\begin{aligned} (J_V)_{\Delta P=0} &= -L_{PD} \Delta \pi && \text{(Osmotic flux)} \\ (J_D)_{\Delta P=0} &= -L_{DD} \Delta \pi && \text{(diffusion flux)} && L_{DD} = \text{diffusional mobility.} \end{aligned}$$

(10.298a & b) give

$$\begin{aligned} J_V + J_D &= J_s \bar{v}_s + \frac{J_s}{\bar{c}_s} \\ &= -L_{PP} \Delta P - L_{PD} \Delta \pi - L_{DP} \Delta P - L_{DD} \Delta \pi && \text{[(10.299) used.]} \\ &= -(L_{PP} + L_{DP}) \Delta P - (L_{PD} + L_{DD}) \Delta \pi && \text{(10.301)} \end{aligned}$$

$$\rightarrow J_s = -\frac{\bar{c}_s}{1 + \bar{c}_s \bar{v}_s} \left[(L_{PP} + L_{DP}) \Delta P + (L_{PD} + L_{DD}) \Delta \pi \right] \quad \text{(10.301a)}$$

A membrane that blocks the passage of the solute completely is called **semipermeable**. Setting $J_s = 0$ for arbitrary ΔP & $\Delta \pi$ in (10.301a) gives the conditions for a semipermeable membrane as

$$L_{PP} = -L_{DP} \quad L_{PD} = -L_{DD} \quad \text{(10.301b)}$$

The **reflection coefficient** is defined as

$$\sigma = -\frac{L_{DP}}{L_{PP}} \quad \text{(10.301c)}$$

so that

$$\sigma = 1 \quad \text{for semipermeable membranes}$$

SI0.E.2. Ion Transport Across a Membrane

Let the solute in the foregoing discussion be a salt that dissociates into cations & anions. Furthermore, we apply an electric potential difference $\Delta\phi = \phi^I - \phi^II$ across the membrane. The areal entropy production (10.291) is thus modified to

$$T \sigma_A = -J_c \Delta \mu_c^e - J_a \Delta \mu_a^e - J_w \Delta \mu_w \quad \text{(10.302)}$$

where the subscripts a & c denote anion & cation, respectively. As usual,

$$\mu_j^e = \mu_j + z_j F \phi \quad j = a, c$$

where z_j is the ionic charge of the j^{th} type ion.

(10.302) can therefore be written as

$$T \sigma_A = -J_c \Delta \mu_c - J_a \Delta \mu_a - J_w \Delta \mu_w - (J_c z_c + J_a z_a) F \Delta \phi \quad \text{(10.303)}$$

If the salt dissociates as [see Ex.10.8]



then

$$J_a = \nu_a J_s \quad J_c = \nu_c J_s \quad \text{(10.303b)}$$

$$\Delta \mu_s = \nu_a \Delta \mu_a + \nu_c \Delta \mu_c \quad \text{[see (6) of Ex.10.8.]} \quad \text{(10.303c)}$$

where the subscript s denotes salt.

Hence,

$$J_s \Delta \mu_s = J_a \Delta \mu_a + J_c \Delta \mu_c \quad (10.303d)$$

The electric flux across the membrane is

$$I = z_a F J_a + z_c F J_c \quad (10.303e)$$

Putting (10.303d-e) into (10.303) gives

$$T \sigma_A = -J_s \Delta \mu_s - J_w \Delta \mu_w - I \Delta \phi \quad (10.304)$$

If we keep the temperature and salt concentration uniform everywhere,

$$\Delta T = \Delta \pi = 0 \quad \rightarrow \quad \Delta \mu_j = \bar{v}_j \Delta P \quad j = s, w \quad (10.304a)$$

where (10.294) & (10.297) were used.

(10.304) thus becomes

$$\begin{aligned} T \sigma_A &= -J_s \bar{v}_s \Delta P - J_w \bar{v}_w \Delta P - I \Delta \phi \\ &= -J_V \Delta P - I \Delta \phi \quad [(10.298a) \text{ used. }] \end{aligned} \quad (10.305)$$

with the associated generalized Ohm's law

$$\begin{pmatrix} J_V \\ I \end{pmatrix} = - \begin{pmatrix} L_{PP} & L_{PE} \\ L_{EP} & L_{EE} \end{pmatrix} \begin{pmatrix} \Delta P \\ \Delta \phi \end{pmatrix} \quad (10.306-7)$$

and Onsager's relation

$$L_{PE} = L_{EP}$$

If we impose $\Delta \phi$ across a membrane with equal pressures on both sides, (10.306-7) become

$$J_V = -L_{PE} \Delta \phi \quad I = -L_{EE} \Delta \phi$$

This J_V is called **electro-osmosis**. As time goes on, J_V must decrease to zero since there are only a finite amount of matter present. Thus, a steady state is reached with

$$\begin{aligned} J_V &= 0 \\ \rightarrow \quad 0 &= L_{PP} \Delta P + L_{PE} \Delta \phi \end{aligned} \quad (10.308a)$$

The **electro-osmotic pressure (EOP)** is defined as

$$\begin{aligned} \text{EOP} &\equiv \left(\frac{\Delta P}{\Delta \phi} \right)_{J_V=0} \\ &= - \frac{L_{PE}}{L_{PP}} \quad [(10.308a) \text{ used. }] \end{aligned} \quad (10.308)$$

= osmotic pressure induced by unit potential difference
across membrane with no volume flow.

Conversely, we can impose ΔP across the same membrane with equal electric potentials on both sides. Setting $\Delta \phi = 0$ in (10.206-7) gives

$$J_V = -L_{PP} \Delta P \quad I = -L_{EP} \Delta P \quad (10.309a)$$

The **streaming current density (SC)** is defined as

$$\begin{aligned} \text{SC} &\equiv \left(\frac{I}{J_V} \right)_{\Delta \phi=0} \\ &= \frac{L_{EP}}{L_{PP}} \quad [(10.309a) \text{ used. }] \end{aligned} \quad (10.309) \quad (10.309b)$$

= electric current caused by unit volume flow
across membrane with no potential difference.

Since

$$-\frac{EOP}{SC} = \frac{L_{PE}}{L_{EP}}$$

its measured values (as compared to 1) can be used to check the validity of the Onsager relations.

See Reichl's Table 10.5 for data using a clay plug as membrane.