Non-Equilibrium Thermodynamics: Foundations and Applications.

Lecture 5: Multicomponent heat and mass diffusion

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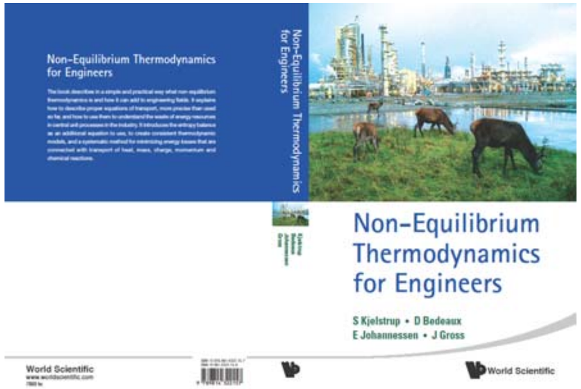
Non-Equilibrium Thermodynamics: Foundations and Applications

	Tuesday, Sept. 7	Wednesday, Sept. 8	Thursday, Sept.9	Friday, Sept.10
9:00-10:30	Why non-equilibrium thermodynamics?	Transport of heat and mass	Transport of heat and charge	Entropy production minimization theory
11:00-12:30	Entropy production for a homogeneous phase	Multi-component heat and mass diffusion	Transport of mass and charge	Entropy production minimization. Examples.
16:00-17:00	Flux equations and Onsager relations	Power from regular and thermal osmosis	Modeling the polymer electrolyte fuel cell	

Lecture 5. Multicomponent heat and mass diffusion

Chapter 5



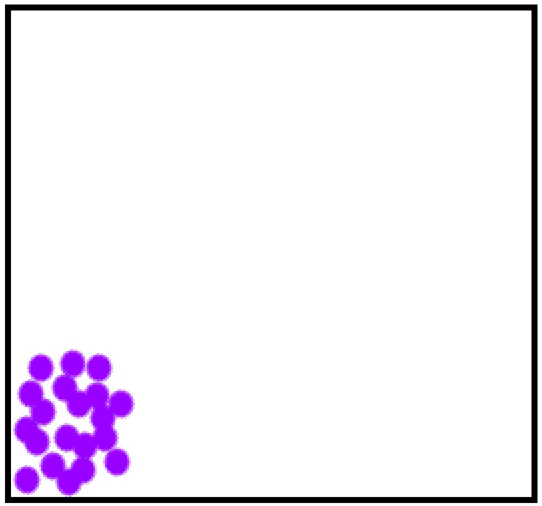
Chapter 12

Exercise

Your working procedure

1. The entropy production.
   Relating to experiments or models.
2. The fluxes and the coefficients
3. Equivalent sets of descriptions
4. Can the system perform work
   (separation)?

Diffusion of one-component?

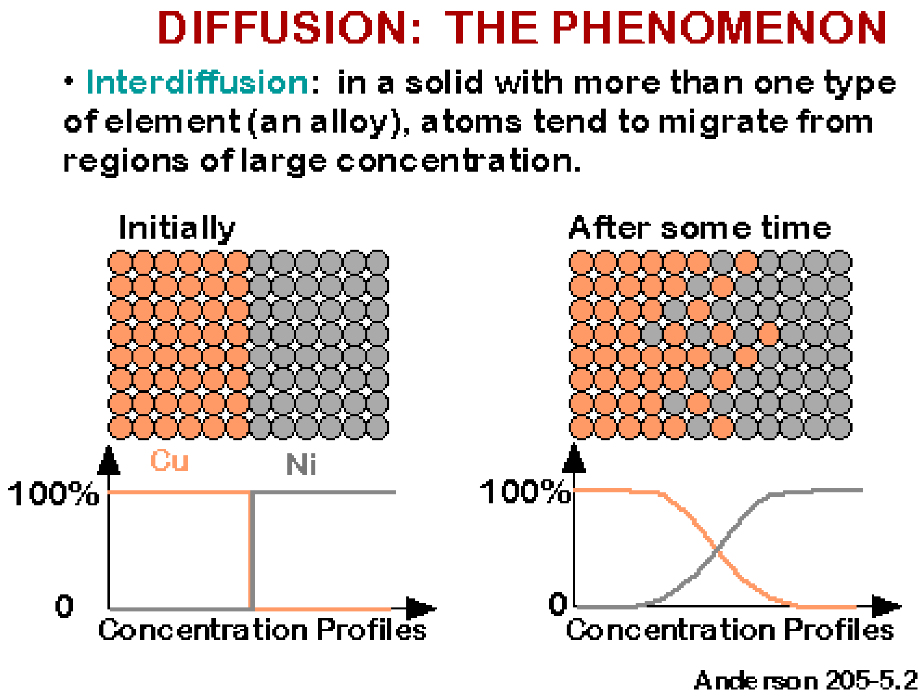


Chemical potential:

$$m = m^0 + RT \ln \frac{p}{p^0}$$

Knudsen effusion, self diffusion

One or two-component diffusion?



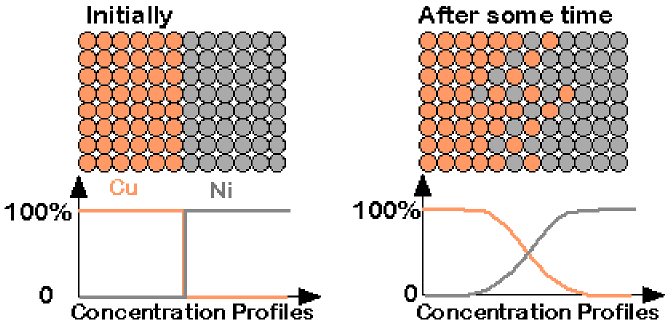
The driving forces are related by Gibbs-Duhem's equation:

$$N_1 d\mu_1 + N_2 d\mu_2 - SdT - Vdp = 0$$

At constant *T,p,* the mixture has only one independent driving force!

DIFFUSION: THE PHENOMENON

- Interdiffusion: in a solid with more than one type of element (an alloy), atoms tend to migrate from regions of large concentration.



Anderson 205-5.2

$$\sigma = J_1\left(-\frac{1}{T}\frac{d\mu_1}{dx}\right) + J_2\left(-\frac{1}{T}\frac{d\mu_2}{dx}\right)$$

$$= J_1\frac{1}{T}\left(1+\frac{N_1}{N_2}\right)\left(-\frac{d\mu_1}{dx}\right)$$

Driving force for component 1, wall frame of reference

volume frame of reference

$$J_V = J_1V_1 + J_2V_2 = 0;$$

$$J_2 = -\frac{V_1}{V_2}J_1$$

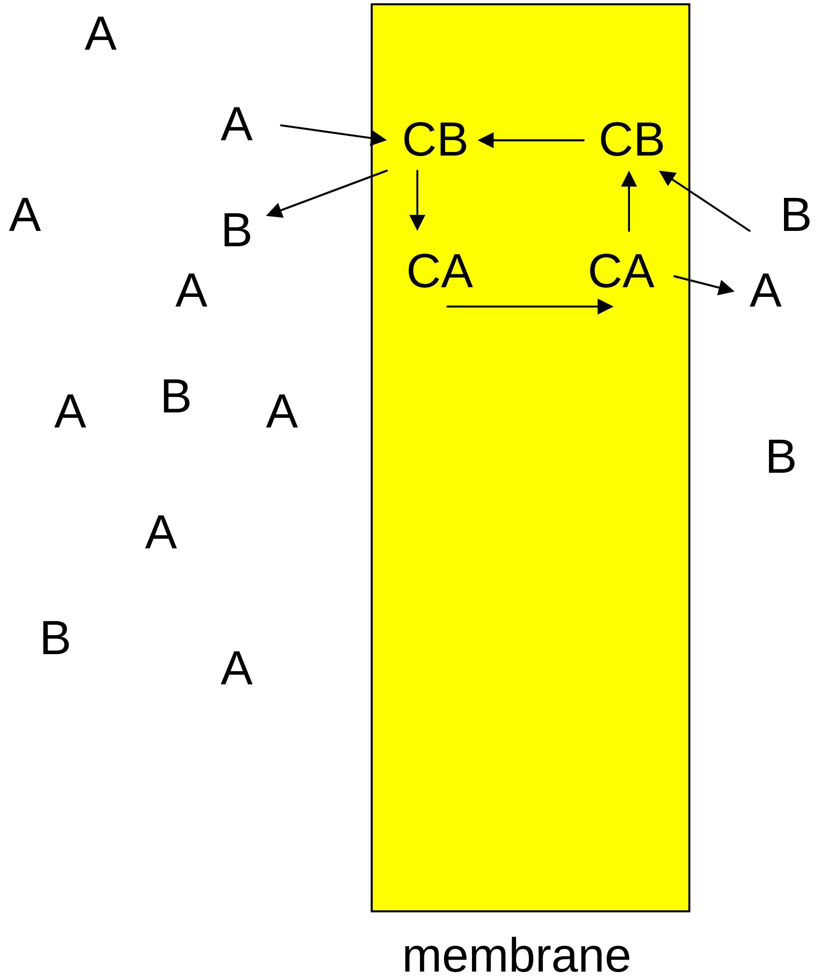
$$\sigma = J_1\left(-\frac{1}{T}\frac{d\mu_1}{dx}\right) - J_1\frac{V_1}{V_2}\left(-\frac{1}{T}\frac{d\mu_2}{dx}\right)$$

$$= J_1\frac{1}{T}\left(-\frac{d\mu_1}{dx} + \frac{V_1}{V_2}\frac{d\mu_2}{dx}\right)$$

Example:

Coupled transports of A(1) and B(2)

- The large gradient in concentration of A drives A to the right
- If C moves only with A or B attached, B can be transported against its concentration gradient.



Membrane transport of two components

A common factor 1/*T* is absorbed in the transport coefficients

$$J_1 = -L_{11}\frac{\partial \mu_1}{\partial x} - L_{12}\frac{\partial \mu_2}{\partial x}$$

$$J_2 = -L_{21}\frac{\partial \mu_1}{\partial x} - L_{22}\frac{\partial \mu_2}{\partial x} \qquad J_3 = 0$$

Relation to Fick's law, component 1:

$$J_1 = -D_1\frac{\partial c_1}{\partial x} = -L_{\mu\mu}\frac{\partial \mu_1}{\partial x} = -\left(L_{\mu\mu}\frac{RT}{c_1}\frac{\partial \mu_1}{\partial c_1}\right)\frac{\partial c_1}{\partial x}$$

$$L_{12} = L_{21}$$

Onsager relations. When are the coupling coefficients significant?

Transport of A(1) and B(2):

Membrane frame of reference

$$J_1 = -L_{11}\frac{\partial \mu_1}{\partial x} - L_{12}\frac{\partial \mu_2}{\partial x}$$
$$J_2 = -L_{21}\frac{\partial \mu_1}{\partial x} - L_{22}\frac{\partial \mu_2}{\partial x}$$

Coupling reduces the stationary state diffusion coefficient

$$J_1 = -\left(L_{11} - \frac{L_{12}L_{21}}{L_{22}}\right)\frac{\partial \mu_1}{\partial x} + \frac{L_{12}}{L_{22}} J_2$$

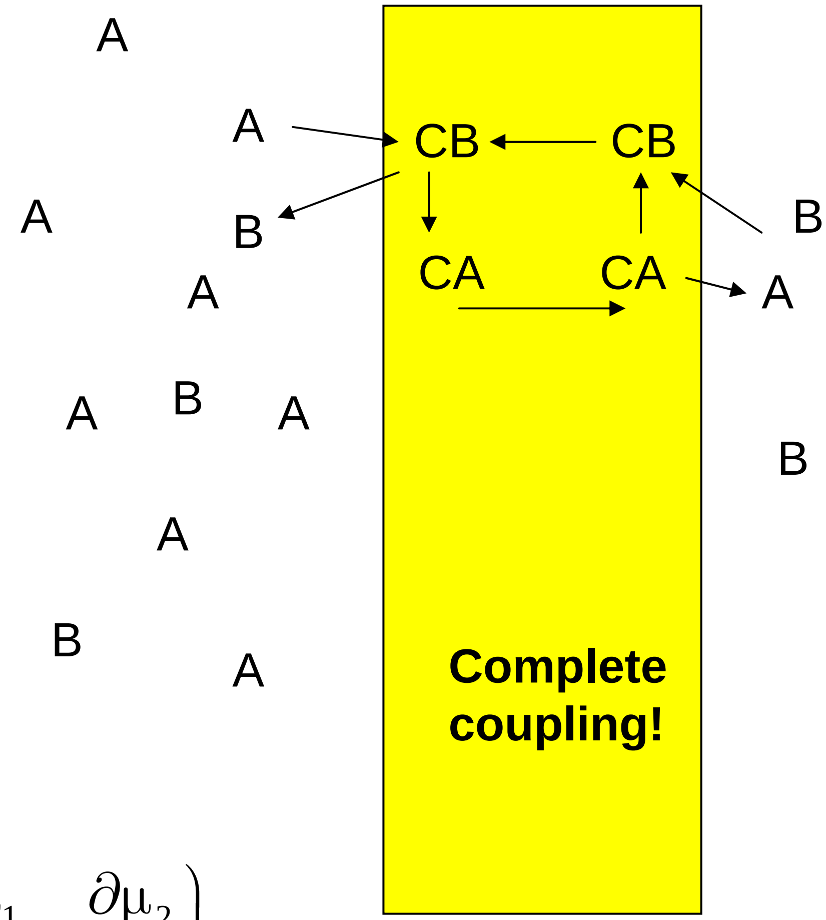
When

$$J_1 \equiv -J_2, \qquad L_{12} = L_{21} = -L_{22} = -L_{11}$$

$$J_1 = L_{21}\left(\frac{\partial \mu_1}{\partial x} - \frac{\partial \mu_2}{\partial x}\right)$$

Net work is created.

$$J_1 = -J_2, \quad \sigma = -J_1\left(\frac{\partial \mu_1}{\partial x} - \frac{\partial \mu_2}{\partial x}\right)$$



Separation work using a membrane

$$J_1 = -L_{11}\frac{\partial \mu_1}{\partial x} - L_{12}\frac{\partial \mu_2}{\partial x}$$
$$J_2 = -L_{21}\frac{\partial \mu_1}{\partial x} - L_{22}\frac{\partial \mu_2}{\partial x}$$

Defining the co-transfer coefficient

$$\tau_1 \equiv \left[\frac{J_1}{J_2}\right]_{d\mu_1=0} = \frac{L_{12}}{L_{22}}$$

The work done:

$$\Delta\mu_2 = \int_L \frac{\partial \mu_2}{\partial x}dx = -\int_L \left[\tau_1 \frac{\partial \mu_1}{\partial x} - \frac{1}{L_{22}} J_2\right] dx$$

The gradient in chemical potential of 1 Is used to move 2

We used the Onsager relation

Frictional loss

The Maxwell- Stefan description; invariant to the frame of reference

Example: 3 components

$$\sigma = J_A\left(-\frac{1}{T}\frac{\partial \mu_A}{\partial x}\right) + J_B\left(-\frac{1}{T}\frac{\partial \mu_B}{\partial x}\right) + J_C\left(-\frac{1}{T}\frac{\partial \mu_C}{\partial x}\right)$$

$$= v_A\left(-\frac{c_A}{T}\frac{\partial \mu_A}{\partial x}\right) + v_B\left(-\frac{c_B}{T}\frac{\partial \mu_B}{\partial x}\right) + v_C\left(-\frac{c_C}{T}\frac{\partial \mu_C}{\partial x}\right)$$

$$-\frac{c_A}{T}\frac{d\mu_A}{dx} = r_{AA}c_A(c_A v_A) + r_{AB}c_A(c_B v_B) + r_{AC}c_C(c_B v_B)$$

$$-\frac{c_B}{T}\frac{d\mu_B}{dx} = r_{BA}c_B(c_A v_A) + r_{BB}c_B(c_B v_B) + r_{BC}c_B(c_B v_B)$$

$$-\frac{c_C}{T}\frac{d\mu_C}{dx} = r_{CA}c_C(c_A v_A) + r_{CB}c_C(c_B v_B) + r_{CC}c_C(c_B v_B)$$

Gibbs-Duhem's $$c_A d\mu_A + c_B d\mu_B + c_C d\mu_C = 0$$

3 Onsager relations,
3 other interdependencies

Three dependent force relations

$$-\frac{c_A}{T}\frac{d\mu_A}{dx}=r_{AA}c_A(c_Av_A)+r_{AB}c_A(c_Bv_B)+r_{AC}c_C(c_Bv_B)$$
$$-\frac{c_B}{T}\frac{d\mu_B}{dx}=r_{BA}c_B(c_Av_A)+r_{BB}c_B(c_Bv_B)+r_{BC}c_B(c_Bv_B)$$
$$-\frac{c_C}{T}\frac{d\mu_C}{dx}=r_{CA}c_C(c_Av_A)+r_{CB}c_C(c_Bv_B)+r_{CC}c_C(c_Bv_B)$$

6 relations among coefficients

$$0=r_{AA}c_Ac_A+r_{BA}c_Ac_B+r_{CA}c_Cc_A$$
$$0=r_{AB}c_Ac_B+r_{BB}c_Bc_B+r_{CB}c_Cc_B$$
$$0=r_{AC}c_Ac_C+r_{BC}c_Bc_C+r_{CC}c_Cc_C$$
$$r_{AB}=r_{BA},\quad r_{AC}=r_{CA},\quad r_{CB}=r_{BC}$$

Set of 2x2 force-flux reations

$$-\frac{c_A}{T}\frac{d\mu_A}{dx}=r_{AB}c_Ac_A(v_A-v_B)+r_{AC}c_Ac_C(v_A-v_C)$$
$$-\frac{c_B}{T}\frac{d\mu_B}{dx}=r_{BA}c_Bc_A(v_B-v_A)+r_{BC}c_Bc_C(v_B-v_C)$$

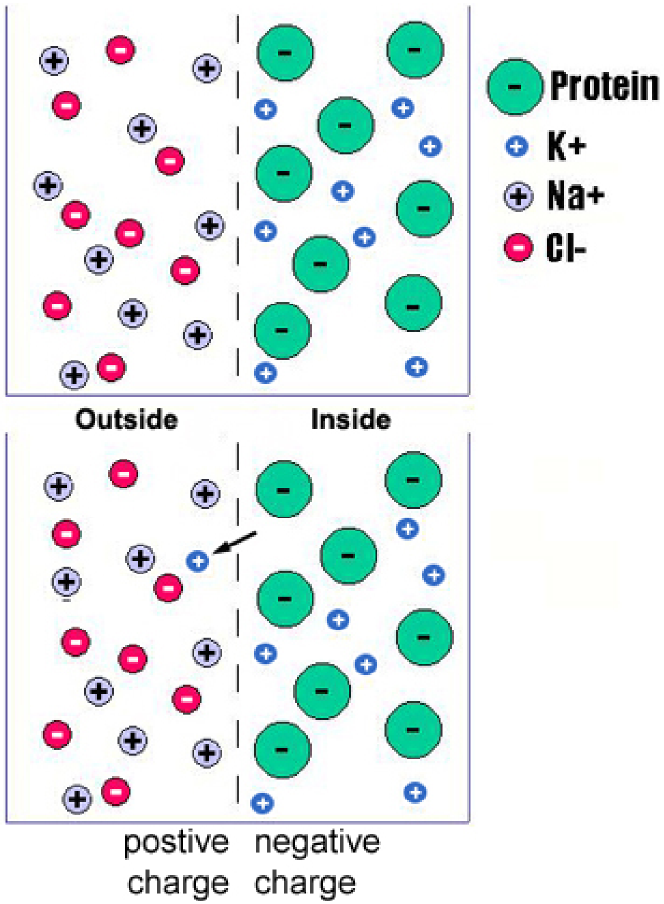
$$-\frac{c_C}{T}\frac{d\mu_C}{dx}=r_{CA}c_Cc_A(v_C-v_A)+r_{CB}c_Cc_B(v_C-v_B)$$

Maxwell-Stefan equations for any frame of reference

$$-\frac{1}{RT}\frac{d\mu_A}{dx}=-\frac{dx_A}{dx}\left[1+\frac{d\ln\gamma_A}{d\ln x_A}\right]=\frac{x_B}{D_{AB}}(v_A-v_B)+\frac{x_C}{D_{AC}}(v_A-v_C)\qquad D_{ij}=-\frac{R}{cr_{ij}}$$
$$-\frac{1}{RT}\frac{d\mu_B}{dx}=-\frac{dx_B}{dx}\left[1+\frac{d\ln\gamma_B}{d\ln x_B}\right]=\frac{x_A}{D_{AB}}(v_B-v_A)+\frac{x_C}{D_{BC}}(v_B-v_C)$$

(Relatively) constant

Separation by a selective membrane



What are convenient transport equations for components:
PCl,
NaCl,
KCl,
water
Fluxes
A: NaCl.
B: KCl.
C: Water
PCl is at rest, like the membrane.

Each solution is electroneutral

$$-\frac{dx_A}{dx} = \frac{x_B}{D_{AB}}(v_A - v_B) + \frac{x_C}{D_{AC}}(v_A - v_C)$$

$$-\frac{dx_B}{dx} = \frac{x_A}{D_{AB}}(v_B - v_A) + \frac{x_C}{D_{BC}}(v_B - v_C)$$

A temperature gradient can also help separation

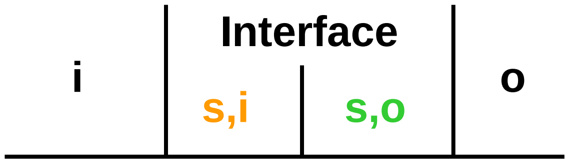
$$J_q' = L_{qq}\frac{\partial}{\partial x}\left(\frac{1}{T}\right) - L_{q1}\frac{\partial \mu_{1,T}}{\partial x} - L_{q2}\frac{\partial \mu_{2,T}}{\partial x}$$

$$J_1 = L_{1q}\frac{\partial}{\partial x}\left(\frac{1}{T}\right) - L_{11}\frac{\partial \mu_{1,T}}{\partial x} - L_{12}\frac{\partial \mu_{2,T}}{\partial x}$$

$$J_2 = L_{2q}\frac{\partial}{\partial x}\left(\frac{1}{T}\right) - L_{21}\frac{\partial \mu_{1,T}}{\partial x} - L_{22}\frac{\partial \mu_{2,T}}{\partial x}$$

→ **Generalised Maxwell-Stefan equations**

Cf. Lecture 4 and 6: Heat and mass transport couple at the interface



$$\sigma^{\mathrm{s}} = J_q'^{\mathrm{i}} \Delta_{\mathrm{i,s}} \frac{1}{T} + J_q'^{\mathrm{o}} \Delta_{\mathrm{s,o}} \frac{1}{T} + J_m^{\mathrm{i}} \left(-\frac{1}{T^{\mathrm{s}}} \Delta_{\mathrm{i,s}} \mu_{m,T} \left(T^{\mathrm{s}}\right) \right) + J_m^{\mathrm{o}} \left(-\frac{1}{T^{\mathrm{s}}} \Delta_{\mathrm{s,o}} \mu_{m,T} \left(T^{\mathrm{s}}\right) \right)$$

Linear flux-forces relations for the I and o -sides of the membrane interface

$$\Delta_{\mathrm{i,s}} \frac{1}{T} = r_{qq}^{\mathrm{s,i}} J_q'^{\mathrm{i}} + r_{qm}^{\mathrm{s,i}} J_m^{\mathrm{i}}$$

$$-\frac{1}{T^{\mathrm{s}}} \Delta_{\mathrm{i,s}} \mu_{m,T} \left(T^{\mathrm{s}}\right) = r_{mq}^{\mathrm{s,i}} J_q'^{\mathrm{i}} + r_{mm}^{\mathrm{s,i}} J_m^{\mathrm{i}}$$

$$\Delta_{\mathrm{s,o}} \frac{1}{T} = r_{qq}^{\mathrm{s,o}} J_q'^{\mathrm{o}} + r_{qm}^{\mathrm{s,o}} J_m^{\mathrm{o}}$$

$$-\frac{1}{T^{\mathrm{s}}} \Delta_{\mathrm{s,o}} \mu_{m,T} \left(T^{\mathrm{s}}\right) = r_{mq}^{\mathrm{s,o}} J_q'^{\mathrm{o}} + r_{mm}^{\mathrm{s,o}} J_m^{\mathrm{o}}$$

Coupling at interfaces is essential when the enthalpy of the phase transition is large

Summary

- Multicomponent heat and mass diffusion can be described in several equivalent ways
- One way translates into another via the entropy production
- The origin of work is the coupling coefficent, the co-transfer coefficient for diffusion, or the heat of transfer for thermal diffusion
- The coupling coefficient can be of the same order of magnitude as the other transport coefficients in membrane transport