Appendix. Mass transfer in multi-component mixtures

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Mass transfer and separation technology
Massöverföring och separationstechnik
(“MÖF-ST”)  

Multi-component mass transfer
using transparencies that accompany “Mass Transfer in Multicomponent mixtures”

Mass Transfer:

\[
J_i = -D \frac{dc_i}{dz}
\]

Diffusion with Drift:

\[
N_i = -D \frac{dc_i}{dz} + N_x
\]

Classic - in Gases:

\[
J_i = -D \frac{dc_i}{dz}
\]

Three Gases (1):

A

\[\begin{array}{c}
N_2 \\
H_2 \\
CO_2
\end{array}\]

Ideal gases, 100 kPa, 298 K

beginning:

\[
\begin{align*}
x_{N_2} &= 0.46 \\
x_{H_2} &= 0.54 \\
x_{CO_2} &= 0.52
\end{align*}
\]

Question: Does \( N_2 \) transfer
\[(a) \text{ from A to B?} \quad (b) \text{ from B to A?} \quad (c) \text{ not at all?} \quad (d) \text{ or does it do (a), (b) and (c)?} \]
### A.2 Driving forces

The potential difference is the work required to change the condition of the weight:

\[
\Delta w = mg \Delta z = 9.81 \text{ J} \quad ( = 9.81 \text{ Nm})
\]

or, per mole

\[
\Delta w_i = M_i g \Delta z
\]

The driving force is the negative potential gradient:

\[
F = -\frac{\Delta w_i}{\Delta z} = -M_i g
\]

The force is downwards.
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Multi-component mass transfer

Chemical Potential

chemical potential

μ = const(p, T) + RT \ln x

Momentum Balance

forces \sum F

momentum 'in'

\sum (mv)_{in}

momentum 'out'

\sum (mv)_{out}

change of momentum

\frac{d}{dt} \sum (mv) = \sum (mv)_{in} - \sum (mv)_{out} + \sum F

Forces on Hydrogen (1)

Driving Force (per Mole of i)

F_i = \frac{d\mu_i}{dz} = -RT \ln a_i - \frac{RT da_i}{a_i dz}

for a given T and p

\text{in ideal solutions}

Driving Force

\text{Driving Force for Each Other}

H_2 (1)

CO_2 (2)

species velocities

\text{moving through each other}

\text{partial pressure}

µ in an Ideal Solution

µ = \text{const}(p, T) + RT \ln x

\text{in an ideal gas}

µ = \text{const}(p, T) + \frac{p_i}{p}
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Multi-component mass transfer
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Maxwell-Stefan Equation

\[ F_i = \sum_k x_k (u_i - u_k) \]

- \( F_i \): driving force on \( i \)
- \( x_k \): mole fraction of \( j \)
- \( m \): species velocities

Film Theory, Thickness of Films

two thin, one dimensional 'films' next to the phase boundary

Approximation

\[ \frac{\Delta \mu_i}{RT} \approx \ln \left( \frac{a_{i\alpha}}{a_{i\beta}} \right) \]

in ideal solutions

'approximate' works out better in difference equations

Example (3.1 from book)

3.1 A species in a gas has a molar mass of \( M = 0.083 \) kg mol\(^{-1}\). The gas diffuses through a film with a thickness \( \Delta z = 10^{-4} \) m. The velocity of the gas changes from \( u_i = 1 \) cm s\(^{-1} \) to \( u_{i\alpha} = 2 \) cm s\(^{-1} \). There are driving forces and friction forces on the species.

Friction force - no eddies:

\[ F_{\text{friction}} = \frac{a_i}{a_{i\alpha}} (a_i - a_{i\alpha}) \]

Convection - large scale eddies:

\[ F_{\text{convection}} = -\frac{u_i}{u_{i\alpha}} (a_i - a_{i\alpha}) \]

The driving force during transport through a film has a value of \( 10^{-5} \) N mol\(^{-1}\). The momentum balance for the species reads:

\[ F_{\text{friction}} + F_{\text{convection}} = \Delta \mu_i \frac{a_i}{a_{i\alpha}} \]

How does the change in momentum compare with the driving force?
Example (3.1 from book): answer

3.1. The residence time in the film is \( t = 1.5 \times 10^{-3} \text{ ms}^{-1} \) \( \approx 1.5 \times 10^{-3} \text{ s} \), resulting in a change in the moment:

\[
\Delta \tau = \frac{3(\pi^2)}{4} (1 \times 10^{-3}) (2 \times 10^5) \text{ kg m}^2 \text{ s}^{-1}
\]

\[
\approx 1.9 \times 10^{-3} \text{ N m} \text{ s}^{-1}
\]

This is negligible compared to the driving force.

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\[\text{Diffusion and Friction Coefficients}\]

\[\text{Diffusion Coefficients:}\]

\[D_{ij} = \frac{RT}{A_{ij}}\]

\[\zeta_{ij} = \frac{RT}{A_{ij}}\]

Each other's 'inverse'.

We use both.

\[D_{ij} = \frac{RT}{A_{ij}} = \frac{8.314 \times 300}{6 \times 10^{-3} \times 10^{-3} \times (0.4 \times 10^{-6})} = 10^7 \text{ m}^2 \text{ s}^{-1}\]

Maxwell-Stefan diffusivity of large molecules in dilute liquids (not gases)

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\[\text{One Equation Missing}\]

1. Components: 1 relative velocity
   - 1 independent equation

2. Components: 2 relative velocities
   - 2 independent equations

3. Components: \( n \) relative velocities
   - \( n \) independent equations

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\[\text{Bootstrap (1)}\]

\[F_i = \sum \zeta_{ij} (u_j - u_i)\]

'Floating' transport relations: have to be 'tied' to surroundings.
APPENDIX


Bootstraps (2)

no net volume flow plug does not move

membrane does not move (almost) no charge transfer

From Differential to Difference

binary: \[ \frac{RT \, da_i}{a_i} = x \frac{RT}{D_{ij}} (u_i - u_j) \]

infinite layer finite layer (approximate) \[ \Delta x_k \approx \frac{x}{a_k} \]

Average Velocity

\[ u_i = \text{average concentration} \]

(positive velocity)

species velocity at the average composition

species velocity (depends on position in film)

Differences with Fluxes

\[ - \frac{\Delta a_i}{a_i} \frac{1}{k_{ij}} \frac{x}{a_k} \]

\[ - \frac{\Delta a_i}{a_i} \frac{1}{k_{ij}} (\pi_i N - \pi_i N_j) \]

Multicomponent Equations

using velocities

using fluxes

for ideal solutions

in practical problems we use fluxes:

\[ N_i = \text{fluxes} \]

membrane does not move

plug does not move

\[ F = \text{flux form of MS-equation:} \]

\[ F \frac{dx}{dz} = \sum c_{ij} x_i (u_i - u_j) \]

\[ f = \sum c_{ij} (x_i N_j - x_j N_i) \]

\[ f = \left( \text{force on i per unit volume of mixture} \right) \]
A.4 Binary examples

Temperature Effects

MS-equation

\[
F_i = \sum_j x_{ij} (u_i - u_j) + (\text{thermal diffusion terms})
\]

driving force

\[
F_i = \frac{d\mu_i}{dx_i} = -\frac{RT}{x_i} \frac{dx_i}{dz}
\]

difference form:

\[
F_i = \frac{RT}{x_i} \frac{dx_i}{dz}
\]

at constant temperature

average film temperature changes are not very important

\[X = \frac{\text{mass transfer term}}{\text{vapour removed by convection}} \]

Vaporising Droplet

heat

benzene (1), volatile toluene (2)

\[y_1 = K x_{1u} \]

vapour removed by convection

bootstrap

\[
\frac{N_1}{N_2} = \frac{y_1}{N_2}
\]

...as you already knew...

\[\alpha \beta \]

Stripping - concentrated

drops on a tray

gas: trace of NH3 (1)

bulk of N2 (2)

transport relation

\[N_i = \frac{k_i \rho \Delta x_i}{x_i} = k_i \rho \Delta x_i \]

as you already knew...

\[\alpha \beta \]

Transfer Coefficients

\[k_{ij} = \frac{D_{ij}}{\Delta x} \]

10^5

10^4

10^3

10^2

gases

in pores

\[\text{speed} = 10^{-1} \text{ m s}^{-1}\]

liquids

in pores

\[\text{speed} = 10^{-4} \text{ m s}^{-1}\]

Temperature Effects

MS-equation

\[
F_i = \sum_j x_{ij} (u_i - u_j) + (\text{thermal diffusion terms})
\]

driving force

\[
F_i = \frac{d\mu_i}{dx_i} = -\frac{RT}{x_i} \frac{dx_i}{dz}
\]

difference form:

\[
F_i = \frac{RT}{x_i} \frac{dx_i}{dz}
\]

at constant temperature

average film temperature changes are not very important
Fluxes from Vaporising Droplet

\[-\Delta x_i = \frac{x_i N_i - x_j N_j}{k_{ij} c} \quad \Delta x_j = \frac{x_j N_j - x_i N_i}{k_{ij} c}\]

\[N_i = \frac{v}{k_{12} c} \quad N_j = \frac{v}{k_{21} c} \Delta x_i \quad N_j = \frac{v}{k_{12} c} \Delta x_j \]

example \( v = 2 \), \( x_i = x_j = 0.5 \)

\[N_i = -4 k_{12} c \Delta x_1 \quad N_j = -(2) k_{12} c \Delta x_2 \]

Stefan (drift) corrections

Fluxes in Gasification

\[\Delta x_i = \frac{x_i N_i - x_j N_j}{k_{ij} c} = \frac{(x_i + 2x_j)N_j}{k_{ij} c} \]

\[N_i = \frac{k_{12} c}{x_i + 2x_j} \Delta x_i = -10^{-2} \times 10^{-0.6} \]

\[N_i = 0.046 \text{ (exact: 0.047)} \text{ mol m}^{-2} \text{ s}^{-1} \]

\[N_j = -0.092 \text{ (exact: -0.094)} \text{ mol m}^{-2} \text{ s}^{-1} \]

almost the same

Carbon Gasification

\[O_2 + 2C \rightarrow 2CO \]

bootstrap: \( N_j = -2N_i \)

calculate \( N_i \) and \( N_j \)

Binary Distillation

Transport relation

\[-\Delta x_i = \frac{x_j N_i - x_i N_j}{k_{ij} c} \quad \Delta x_j = \frac{(x_j + x_i)N_i}{k_{ij} c} \]

\[N_i = -k_{12} c \Delta x_i \quad N_j = -k_{21} c \Delta x_2 \]

A.5 Ternary examples

Some Bootstraps

1. membrane stagnant \( u_z = 0 \)
2. bulk stagnant (absorption) \( N_z = 0 \)
3. trace stagnant (polarisation) \( \pi_i = 0 \)
4. equimolar exchange (distillation) \( N_i + N_j = 0 \)
5. interface determined (vapourisation) \( N_i = \frac{N_i}{N_j} = \frac{y_1}{y_2} \)
6. reaction stoichiometry \( N_i = \frac{N_i}{N_j} = \frac{v_1}{v_2} \)
Multi-component mass transfer

Ternary - per mole of i

\[
\frac{dx_1}{dz} = \zeta_{12}x_2(u_1-u_2) + \zeta_{13}x_3(u_1-u_3)
\]

forces per mole of ‘1’

\[
\frac{dx_2}{dz} = \zeta_{21}x_1(u_2-u_1) + \zeta_{23}x_3(u_2-u_3)
\]

forces per mole of ‘2’

More Components

binary

\[
\begin{align*}
\Delta x_1 &= \frac{x_N - x_N}{k_{1e}} \\
\Delta x_2 &= \frac{x_N - x_N}{k_{2e}}
\end{align*}
\]

quaternary

\[
\begin{align*}
\Delta x_1 &= \frac{x_N - x_N}{k_{1e}} \\
\Delta x_2 &= \frac{x_N - x_N}{k_{2e}}
\end{align*}
\]

Condenser (2)

transport (MS) relations:

\[
\begin{align*}
\text{NH}_3 &: \quad -0.2 = \frac{0.4N_1 - 0.3N_2}{(1\times10^{-2})30} = \frac{0.3N_1 - 0.4N_2}{(3\times10^{-2})30} \\
\text{H}_2O &: \quad 0.4 = \frac{0.4N_1 - 0.3N_3}{(1\times10^{-2})30} = \frac{0.3N_1 - 0.3N_2}{(3\times10^{-2})30}
\end{align*}
\]

bootstrap \[ N_e = 0 \]

three linear equations, three unknowns

\[
\begin{align*}
N_1 &= 0.015 \\
N_2 &= 0.045 \text{ mol m}^{-2} \text{s}^{-1}
\end{align*}
\]

exact solutions: \[ N_1 = 0.013, N_2 = 0.049 \text{ mol m}^{-2} \text{s}^{-1} \]

Condenser (3)

\[
\begin{align*}
\text{H}_2O \text{ moves down its gradient} \\
\text{NH}_3 \text{ dragged against its gradient} \\
\text{H}_2 \text{ does not move at all}
\end{align*}
\]

Mix: NH_3 + H_2O + H_2

NH_3 (1) and H_2O (2) condense on a tube

H_2 (3) does not condense

\[
\begin{align*}
k_{12} &= 1 \times 10^{-3} \text{ m}^2 \text{s}^{-1} \\
k_{13} &= k_{23} = 3 \times 10^{-3} \text{ m}^2 \text{s}^{-1}
\end{align*}
\]

find the velocities in the gas film

\[
\begin{align*}
\text{liquid} &\quad \text{vapour} \\
0.0 &\quad 0.6 \\
0.2 &\quad 0.4 \\
\end{align*}
\]
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**Ternary Distillation (1)**

1. ethanol
2. water
3. a trace of butanol

large friction between 1) and 2)

\[ k_{12} = 8 \times 10^{-2} \text{ m}^2 \text{s}^{-1} \]
\[ k_{13} = 20 \times 10^{-2} \text{ m}^2 \text{s}^{-1} \]

bootstrap: equimolar exchange

\[ \alpha x_1 + \beta x_2 + \gamma x_3 = 0 \]

in which direction does 2) move?

---

**Ammonia reaction**

\[ N_2 + 3H_2 \rightleftharpoons 2NH_3 \]

transport relations:

\[ \Delta x_i = \frac{2}{k_{12}} N_i - \frac{x_i}{k_{13}} \]
\[ \Delta x_i = \frac{x_i - x_j}{k_{12}} + \frac{x_j - x_k}{k_{13}} \]
\[ \Delta x_i = \frac{x_i - x_j}{k_{12}} + \frac{x_j - x_k}{k_{13}} \]

bootstrap:

\[ N_1 - \frac{N_2}{3} - N_3 = -2 \]

---

**Butanol - which direction?**

\[ y_{21} = 0.022 \]
\[ y_{20} = 0.018 \]
\[ y_{21} = -3.75 \times 10^{-2} \]
\[ y_{20} = -1.58 \times 10^{-2} \]
\[ y_{21} = 0.018 \]
\[ y_{20} = -0.81 \times 10^{-2} \]

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**Effective Binary in Reactive System**

simplifying transport equation of \( N_2 \) in ammonia formation:

eliminate \( N_2 \) and \( N_3 \) with \( N_1 = 3N_2, N_3 = -2N_2 \)

\[ \Delta x_i = -k_{12} \alpha \Delta x_1 \]

with

\[ \frac{1}{k_{12}} x_2 - 3x_3 + 2x_1 \]

similarly for \( H_2 \) and \( NH_3 \)

---

If all fluxes \( N_i \) are related via the same reaction stoichiometry

\[ \text{pseudo - binary} \]