

BJ20A1800 Chemical Engineering Unit Operations II B

INSTRUCTIONS OF THE EXAMINATION

1. The examination consists of two successive parts, namely theory and calculations. The duration of the examination is 3 hours.
2. The examination starts with the theory part. Only writing tools (pens, erasers, rulers) are allowed. Three questions are presented, and short essay type answers (not exceeding one A4 page, if possible) are requested.
3. The examiner can decide, when to start the calculation part (max. 1.5 h for theory is recommended). The rest of the examination time is reserved for calculations. The examiner may totally leave the examination after 15 minutes from the start of the examination, but she/he is not allowed to receive the problems of the calculation part.
4. The problems of the calculation part will be given to the examiner, while she/he assigns the answers of the theory part. In the calculation part a scientific pocket calculator is allowed. No literature is allowed. The collection of mathematical formulas is delivered with the problems. Two calculation problems is to be solved in the examination. The problems are quite similar to the problems treated in exercises.
5. After the assignment of the answers of the theory part, the calculation part continues without any break. The examiner is not allowed to visit outside the examination classroom.
6. For passing the examination, at least 40 % of the maximum points of the examination is required. In addition, at least 25 % of the individual parts (theory, calculations) of the examination is required. (i.e low knowledge in either part can be compensated by good knowledge in the other one: for example 25 % in theory + 55 % in calculations makes 40 % total, and vice versa). The individual parts of the examination are equally weighted. The grade limits are as follows: 1: 40 %, 2: 50 %, 3: 60 %, 4: 70 %, 5: 80 %.

Marjatta Louhi-Kultanen, professor

LAPPEENRANTA UNIVERSITY OF TECHNOLOGY
Department of Chemical Technology
Laboratory of Separation Technology
BJ20A01800 Chemical Engineering Unit Operations II B
Marjatta Louhi-Kultanen, Harri Niemi

EXAMINATION 8.3.2010

THEORY

The examination consists of two successive parts, namely theory and calculations. The duration of the examination is 3 hours. In the theory part only writing tools (pens, erasers, rulers) are allowed. The problems of the calculation part will be given to the examiner, while she/he assigns the answers of the theory part. In the calculation part a scientific pocket calculator is allowed. The collection of mathematical formulas is delivered with the calculation problems.

QUESTIONS

1. Describe the fluxes and frictions when two liquid components A and B (molecular masses of A and B: $M_A = 10 M_B$) are diffusing through a membrane at isothermal conditions. Initially A liquid is on the left hand side related to the membrane (diffusion from left to right) and B on the right hand side (diffusion from right to left). (10 p)
2. Industrial batch crystallizers. (10 p)
3. Give a short description (max. two sentences and/or a picture) for
 - pervaporation
 - diafiltration
 - composite membrane
 - cross-flow filtration(4 x 2.5 p = 10 p)

EXAMINATION 8.3.2010

CALCULATIONS

These problems are delivered after the theory part, while the examiner assigns the answers of the theory part!

The examination consists of two successive parts, namely theory and calculations. The duration of the examination is 3 hours. In the theory part only writing tools (pens, erasers, rulers) are allowed. The problems of the calculation part will be given to the examiner, while she/he assigns the answers of the theory part. In the calculation part a scientific pocket calculator is allowed. The collection of mathematical formulas are delivered with the calculation problems.

PROBLEMS

1. Salt (NaCl) is removed from water by reverse osmosis using hollow fiber modules. The system of the membrane and solution has the following mass transfer parameters: membrane permeability coefficient $A = 3.04 \times 10^{-7}$ kmol/(m² s kPa), parameter of the solution-diffusion model $D_{AM}K_A/\delta_M = 8.03 \times 10^{-7}$ m/s, and mass transfer coefficient at the membrane surface $k = 22 \times 10^{-6}$ m/s. The feed concentration of salt is 0.6 mol/kg solution, feed pressure is 4.0 MPa, and temperature 298 K. The present process treats the feed solution 25 m³/h with total volumetric concentration ratio $VCR = 2$, i.e. the volumetric flow rate of the concentrate is half of the feed flow rate. The diameter of the fiber bundle in a single module is 30 cm. The length of the fibers is 88 cm, of which 8 cm is the sealing section, where no permeation takes place. The inner diameter of the fiber is 20 micrometers, and the outer diameter is 40 micrometers. The porosity of the fiber bundle is 0.4.

How many modules are needed? The pressure inside the fibers (at the permeate side) is allowed to increase max. 50 % of the feed pressure (4.0 MPa). (15 p)

2. You should size a batch cooling crystallizer of a fine chemical whose solubility in water is shown in the table below. The production capacity is expected to be 500 kg crystalline product per batch. Based on the laboratory studies, the batch time of 5 hours is sufficient.

- Which initial concentration you would use?
- Which temperature range you would use?
- Which kind of cooling and seeding policy you would use?
- What is the required crystallizer volume in your system?

(15 p)

| $T, ^\circ\text{C}$ | $c^*, \text{g}/100 \text{ g H}_2\text{O}$ |
|---------------------|---|
| 0 | 12.4 |
| 20 | 18.4 |
| 40 | 24.9 |
| 60 | 31.2 |
| 100 | 40.2 |

Department of Chemical Technology
Laboratory of Separation Technology

BJ20A1800 Chemical Engineering Unit Operations IIB

Part 1. Membrane Separation

Osmotic pressure

Definition
$$\Pi = -\frac{R_g T}{V_1} \ln(\gamma_1 x_1) \quad (1)$$

van't Hoff
$$\Pi = c R_g T \quad (2)$$

Permeability and selectivity

Permeate flux
$$J_m = A(\Delta p - \Delta \Pi) \quad (3)$$

Observed rejection
$$R_m = 1 - \frac{c_p}{c_b} \quad (4)$$

True rejection
$$R = 1 - \frac{c_p}{c_w} \quad (5)$$

Mass transfer inside the membrane

Statistical-mechanical theory

$$\sum_{j=1}^N \frac{c_j}{c D_{ij}} (u_i - u_j) + \frac{u_i}{D_{iM}} = -\frac{l}{R_g T} (\nabla_T \mu_i - F_i) - \frac{\alpha_i B_0}{\eta_m D_{iM}} (\nabla p - cF) - \sum_{j=1}^N \frac{c_j}{c D_{ij}} D_{ij}^T \nabla \ln T \quad (6)$$

$$R = \frac{\sigma (e^{Pe} - 1)}{e^{Pe} - \sigma} \quad (7)$$

$$J_v = \left(\frac{L_p}{\Delta z} \right) [\Delta p - \sigma R_g T (c_w - c_p)] \quad (8)$$

$$Pe = \frac{(1 - \sigma) J_v}{P} \quad (9)$$

$$P = \frac{\omega R_g T}{\Delta z} \quad (10)$$

$$\frac{l}{R} = \frac{P}{\sigma} \frac{l}{J_v} + \frac{(1 + \sigma)}{2\sigma} + K_1 J_v + K_2 J_v^2 + \dots \quad (11)$$

The solution-diffusion model

$$J_i = -L_{ij} \nabla \mu_j \quad (12)$$

$$\nabla \mu_i = RT \nabla \ln a_{iM} + V_{iM} \nabla p \quad (13)$$

$$J_A = -D_{AM} \frac{\Delta c_{AM}}{\delta} \quad (14)$$

$$R_w = \frac{l}{1 + \frac{D_{AM} K_A RT c_{Bp}}{D_{BM} c_{BM} V_{BM} (p_w - p_p - \Pi_w + \Pi_p)}} \quad (15)$$

The finely porous model

$$R = 1 - \left[A_1 - (1 - A_1) e^{\left(-A_2 \frac{J_v}{D_{sw}} \right)} \right]^{-1} \quad (16)$$

$$J_v = \frac{\Delta p_m}{B_1 c_p + B_2 \eta} \quad (17)$$

Mass transfer at the membrane interface

$$J_v = \frac{\Delta X}{\eta R_{tot}} \quad (18)$$

The film theory

$$\frac{\partial c}{\partial t} + J_v \frac{\partial c}{\partial y} = D_{sw} \frac{\partial^2 c}{\partial y^2} \quad (19)$$

$$\frac{c_w - c_p}{c_b - c_p} = \exp\left(\frac{J_v}{k} \right) \quad (20)$$

Tubular modules

Mass transfer correlations for tubular flow
- turbulent flow

$$Sh = 0.04 Re^{0.75} Sc^{0.33} \quad (21)$$

or

$$Sh = 0.023 Re^{0.88} Sc^{0.25} \quad (22)$$

- laminar flow

$$Sh = \left(3.66^3 + 1.61^3 Re Sc \frac{d}{L} \right)^{0.33} \quad (23)$$

Plate and frame modules

Mass transfer correlation for plate and frame narrow channel

$$Sh = \left(3.66^3 + 1.61^3 Re Sc \frac{h}{W} \right)^{0.33} \quad (24)$$

Where dimensionless numbers are

$$Sh = kd/D \quad (25)$$

$$Re = \rho dv/\eta \quad (26)$$

$$Sc = \eta/(\rho D) \quad (27)$$

Hollow fiber modules

Mass transfer correlations

$$Sh = 0.61 Re^{0.5} Sc^{0.33} \quad (Re > 40) \quad (28)$$

$$Sh Sc^{-0.3} = 0.35 + 0.56 Re^{0.52} \quad (1 < Re < 10000) \quad (29)$$

Performance of a hollow fiber module

$$n_A \frac{\pi}{4} d_e^2 = S_v \frac{d_e}{4} = I - \varepsilon \quad (30)$$

$$\dot{V}_{pi} = \frac{\pi d_e}{H} A \left(p_b - p_{pw} - R_m b c_b \right) \frac{\tanh(HL)}{1 + H l_s \tanh(HL)} \quad (31)$$

$$H = \sqrt{\frac{128 \eta d_e A}{d_i^3}} \quad (32)$$

Spiral wound module

Mass transfer correlation for spiral wound module

$$Sh = 1.065 \left(\frac{h_i}{L_{SP,i}} \frac{\eta_{SP,i}}{2 - \eta_{SP,i}} \right)^{0.5} Re^{0.5} Sc^{0.33} \quad (33)$$

Performance of a spiral wound module

- pressure drop at the feed side is negligible

Permeate recovery (volumetric flow rate of the permeate/volumetric flow rate of the feed)

$$\phi = (1 - \Pi_3^+) \left\{ 1 - \exp \left[\frac{\beta_1}{\Pi_3^+} \left(\frac{\phi}{\phi_1} - 1 \right) \right] \right\} \quad (34)$$

$$\Pi_3^+ = \frac{\frac{A_M \rho b}{B_M} - 1}{\frac{A_M \rho b}{B_M}} \frac{\rho b c_{F0}}{p_{F0}} \frac{1}{1 - \frac{p_{PW}}{p_{F0}}} \quad (35)$$

$$\beta_1 = \varphi_1 \left(1 - \frac{p_{PW}}{p_{F0}} \right) \kappa \quad (36)$$

$$\varphi_1 = \frac{2 A_M p_{F0} \varepsilon_F L}{v_{F0} h_F} \quad (37)$$

$$\kappa = \frac{\tanh \sqrt{\frac{C_p \eta A_M \varepsilon_F^2 W^2}{4 \varepsilon_p^2 h_p^3}}}{\sqrt{\frac{C_p \eta A_M \varepsilon_F^2 W^2}{4 \varepsilon_p^2 h_p^3}}} \quad (38)$$

- Osmotic pressure of the feed solution is negligible ($\Pi_3^+ \rightarrow 0$)

- permeate recovery (volumetric flow rate of the permeate/volumetric flow rate of the feed)

$$\phi = 1 - \left(\cosh \sqrt{\beta_2} - \frac{\beta_1}{\sqrt{\beta_2}} \sinh \sqrt{\beta_2} \right) \quad (39)$$

$$\beta_2 = \frac{A_M L^2 C_F \eta}{4 h_F^3 \varepsilon_F} \kappa \quad (40)$$

Process design

Volumetric concentration ratio

$$VCR = \frac{\dot{V}_F}{\dot{V}_R} \quad (41)$$

$$c_R = c_F (VCR)^R \quad (42)$$

Batch process

$$-\frac{dV}{dt} = A J_v \quad (43)$$

$$-\frac{d(Vc)}{dt} = A J_v c_p = A J_v c_w (1 - R) \quad (44)$$

$$J_v = f(t); R = g(t) \quad (45)$$

Continuous processes

- feed and bleed
- multi stage recycle

with equal concentration ratios of each recycle stage

$$VCR_i = \sqrt[N]{VCR} \quad (46)$$

With equal permeate flow rates of each recycle stage

Cost estimation

Investment

$$C_I = C_A A \left(\frac{A}{A_{ref}} \right)^b \quad (47)$$

$$C_{a,I} = \frac{r(1+r)^a}{(1+r)^a - 1} C_I \quad (48)$$

Operating costs (annually)

- membranes

$$C_{mbr} = \frac{C_m A}{a_m} \quad (49)$$

- power consumption

$$C_{pwr} = C_e P_T t_a \quad (50)$$

$$P_T = \sum_{i=0}^n P_i \quad (51)$$

$$P_i = \frac{\dot{V} \Delta p}{\eta} \quad (52)$$

- cleaning

$$C_{cn} = C_c A n_c t_d \quad (53)$$

- maintenance

$$C_{mn} \approx 0.03 C_I \quad (54)$$

- labour

to be estimated by the required annual man-hours and the price per man-hour

Part 2. Industrial Crystallization

Solubility

van't Hoff equation:

$$\text{Ideal solution:} \quad \ln x = \frac{\Delta H_f}{R} \left(\frac{1}{T_{fus}} - \frac{1}{T} \right) \quad (1)$$

$$\text{Non-ideal solution:} \quad \ln x = \ln \frac{1}{\gamma} + \frac{\Delta H_f}{R} \left(\frac{1}{T_{fus}} - \frac{1}{T} \right) \quad (2)$$

Nucleation rate

$$B = A \exp \left[- \frac{16\pi\gamma^3 v^2}{3k^3 T^3 (\ln S)^2} \right] \quad (3)$$

$$B = \frac{4\alpha_v}{k_v G^3 t_{ind}^4} \quad (4)$$

Crystal growth rate

Surface nucleation based birth and spread (B+S) mechanism:

$$G_{B+S} = A_{B+S} (S-1)^{5/6} \exp[-B_{B+S}/(S-1)] \quad (5)$$

Screw dislocation mechanism described by Burton, Cabrera and Frank (BCF):

$$G_{BCF} = A_{BCF} \left[(S-1)^2 / B_{BCF} \right] \tanh[-B_{BCF}/(S-1)] \quad (6)$$

MSMPR theory (Mixed Suspension Mixed Product Removal)

Population density

$$n = \frac{m_i}{\alpha \rho_c \bar{L}_i^3 V \Delta L_i} \quad (7)$$

MSMPR crystallization

$$n = n_0 \exp\left(-\frac{L}{G\tau}\right) \quad \text{or} \quad \ln \frac{n}{n_0} = -\frac{L}{G\tau} \quad (8)$$

Total number of crystals, i.e. the zeroth moment of the distribution

$$N_T = \int_0^\infty n_0 \exp\left(-\frac{L}{G\tau}\right) dL = n_0 G\tau \left[\frac{\text{particles}}{m^3_{\text{suspension}}} \right] \quad (9)$$

Cumulative length of crystals, i.e. the first moment

$$L_T = \int_0^\infty L n_0 \exp\left(-\frac{L}{G\tau}\right) dL = n_0 (G\tau)^2 \left[\frac{\text{particles}}{m^3_{\text{suspension}}} \right] \quad (10)$$

Total crystal surface, i.e. the second moment

$$A_T = \beta \int_0^{\infty} L^2 n_0 \exp\left(-\frac{L}{G\tau}\right) dL = 2\beta n_0 (G\tau)^3 \left[\frac{m^2_{crystalsurface}}{m^3_{suspension}} \right] \quad (11)$$

where β is the surface shape factor. The suspension density, i.e. total mass of crystals per unit volume (the third moment of size distribution multiplied by crystal density):

$$M_T = \alpha \rho_c \int_0^{\infty} L^3 n_0 \exp\left(-\frac{L}{G\tau}\right) dL = 6\alpha \rho_c n_0 (G\tau)^4 \left[\frac{kg_{crystals}}{m^3_{suspension}} \right] \quad (12)$$

where α is the volume shape factor and ρ_c the crystal density.

Volume flow rate of feed or product stream in continuous process, Q

$$Q = \frac{P}{M_T} \quad (13)$$

where P is the production capacity, [kg crystals/s]. The median size L_M

$$\frac{\int_0^{L_M} L^3 n_0 \exp(-L/G\tau) dL}{\int_0^{\infty} L^3 n_0 \exp(-L/G\tau) dL} = 0.5 \quad (14)$$

yields

$$L_M = 3.67 G\tau \quad (15)$$

Dominating crystal size, mode, L_D

$$L_D = 3 G\tau \quad (16)$$

Nucleation rate is defined from equation, as $B=B_0$, when $L=0$

$$B_0 = \frac{dN_0}{dt} = \frac{dN_0}{dL} \frac{dL}{dt} = n_0 G \quad (17)$$

Substituting Eq. (24) and $n_0=B_0/G$ into Eq. (21) gives to suspension density an expression where the crystal size is expressed by the median:

$$M_T = \frac{\alpha \rho_c B L_M^4}{30G} \quad (18)$$

and substituting Eq. (25) including modal crystal size gives

$$M_T = \frac{2\alpha \rho_c B L_D^4}{27G} \quad (19)$$

When nucleation rate is expressed by $B_0 = k_N G^j M_T^j$ and $j=1$, from Eqs (24) and (25) is obtained:

$$G = \left[\frac{30}{\alpha \rho_c k_N L_M^4} \right]^{\frac{1}{j-1}} \quad (20)$$

$$G = \left[\frac{27}{2\alpha\rho_c k_N L_D^4} \right]^{i-1} \quad (21)$$

The dependence of nucleation rate on different variables:

$$B = k'_N M_T^j N^b \Delta C^n \quad (22)$$

where secondary nucleation usually $1 < n < 2,5$

$$B = k'_N G^i M_T^j N^k \quad (23)$$

Generally the influence of mixing is usually expressed by the mixing power/unit mass term, ($[\varepsilon]=W/kg$), which gives

$$B = k'_N G^i M_T^j \varepsilon^l \quad (24)$$

Crystal growth rate on crystal size can be expressed by ASL model (Abegg-Stephan-Larson)

$$G = G_0 \left(1 + \frac{L}{G_0 \tau} \right)^b \quad (25)$$

Population density:

$$n = n_0 \left(1 + \frac{L}{G_0 \tau} \right)^{-b} \exp \left[\frac{1 - (1 + L/G_0 \tau)^{1-b}}{1-b} \right] \quad (26)$$

Clear-liquor Advance Operation

The overflow liquid is continuously removed from the tank. This overflow is not actually clear but contains small crystals that did not settle in the overflow section. The removal rate R :

$$R = \frac{\dot{V}_p + \dot{V}_c}{\dot{V}_p} \quad (27)$$

Since the mixing intensity is constant, nucleation rate is

$$B = k'_N G^i M_T^j \quad (28)$$

Dominating crystal size is

$$\frac{L_{d2}}{L_{d1}} = \left(\frac{\dot{V}_p + \dot{V}_c}{\dot{V}_p} \right)^{(i-1)/(i+3)} = R^{(i-1)/(i+3)} \quad (29)$$

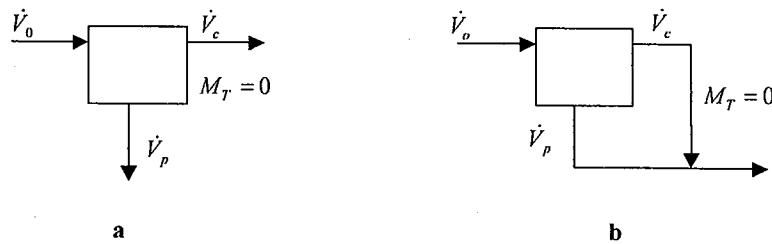


Figure 2. Clear-liquor Advance Operation

Fines Destruction with Solute Recycle

If the nucleus size to be dissolved is small compared to dominating size, the dissolving time t_{dis} is

$$t_{dis} = \frac{L_n^2 c_c}{8cD_{AB} \ln[c/(c-c^*)]} \tag{30}$$

The ratio of volume flow rates flowing to fines destruction and that of product stream, R , is determined

$$R = \frac{\tau_p}{\tau_F} = \frac{\dot{V}_p + \dot{V}_0}{\dot{V}_p} \tag{31}$$

Population density of fines destruction with solute recycle for MSMPR crystallization is

$$n = n_0 \exp\left(-\frac{RL_F}{G\tau}\right) \exp\left(-\frac{L-L_F}{G\tau}\right) \tag{32}$$

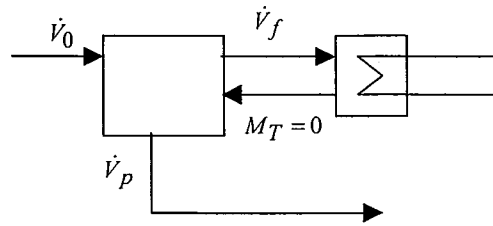


Figure 3. Fines Destruction.

Classified Product Removal

Population densities:

$$n = k_2 \exp\left(-\frac{L}{G_2\tau}\right) \quad \text{for } L < L_c \tag{33}$$

$$n' = k_2' \exp\left(-\frac{zL}{G_2\tau}\right) \quad \text{for } L > L_c \tag{34}$$

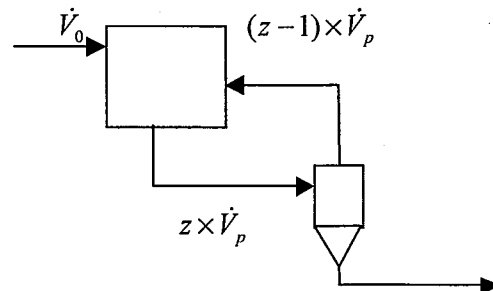


Figure 4. Classified Product Removal

Classified Product Removal With Fines Destruction

$$n = n_0 \exp\left(-\frac{RL}{G\tau}\right) \text{ for } L < L_F \quad (35)$$

$$n = n_0 \exp\left[-(R-1)\frac{L_F}{G\tau}\right] \exp\left(-\frac{L}{G\tau}\right) \text{ for } L_F < L < L_c \quad (36)$$

$$n = n_0 \exp\left[(z-1)\frac{L_c}{G\tau} - (R-1)\frac{L_F}{G\tau}\right] \exp\left(-\frac{zL}{G\tau}\right) \text{ for } L > L_c \quad (37)$$

Batch crystallization

Optimal cooling profile:

$$T = T_0 - (T_0 - T_f)(t/\tau)^n, \quad (38)$$

where T , T_0 ja T_f are the actual temperature at time t , the initial and final temperature, and τ the residence time, respectively. Mayrhofer ja Nyvlt derived optimal temperature profile with and without seeding:

$$\frac{T_0 - T}{T_0 - T_f} = \left[1 - K\left(1 - \frac{t}{\tau}\right)\right] \left(\frac{t}{\tau}\right)^3 \quad (39)$$

where K is the parametry, $K=(1+4N_s/B\tau)$, varying from 0 (no nucleation) to 1 (no seeding), N_s the number of seed crystals per unit solvent volume and B the nucleation rate.

Programmed cooling for seeded crystallization (Mullin & Nyvlt)

$$T = T_0 - XY(t/\tau) \left(1 + Y\frac{t}{\tau} + \frac{1}{3}Y^2\left(\frac{t}{\tau}\right)^2\right) \quad (40)$$

where

$$X = \frac{3w_s}{dc^*/dT} \quad (41)$$

$$Y = \frac{L_p - L_s}{L_s} \quad (42)$$

$$\frac{dc^*}{dT} \approx \frac{c_0 - c_f}{T_0 - T_f} \quad (43)$$

where w_s is the mass fraction of seed crystals (kg crystals/kg solvent), L_p the crystal size of the product and L_s the crystal size of seed crystals, c_0 and c_f are the initial and final concentrations (kg/kg solvent).

Programmed cooling for unseeded crystallization (Mullin & Nyvlt)

$$T = T_0 - \frac{w_s + w_y}{dc^*/dT} \left(\frac{t}{\tau}\right)^4 \quad (44)$$

where w_y is the mass fraction of crystals and solvent.

Natural cooling curve can be expressed by the function as follows

$$T = T_c + (T_0 - T_c)\exp(-K_f t) \quad (45)$$

where T_c is the coolant temperature

$$K_i = \frac{1}{\tau} \ln \frac{T_0 - T_c}{T_f - T_c} \quad (46)$$

The product crystal size for seeded crystallization

$$L_P = \left(\frac{w_S + w_Y}{w_S} \right)^{\frac{1}{3}} L_S \quad (47)$$

Part 3. Multicomponent mass transfer

Below are a few notes on the conventions used in this book. You may want to look back at this list occasionally while you are reading the book; do not expect to understand every detail on first reading.

- (1) In the drawings and sketches, the **positive direction is from left to right**. Velocities and fluxes in that direction are also positive.
- (2) A force is directed down a potential gradient. Examples are:

$$F_1 = - \frac{d\mu_1}{dz} \tag{48}$$

or

$$F_1 = F_{z_i} \frac{\Delta\phi}{\Delta z} \tag{49}$$

This convention holds both for differential and for difference equations.

- (3) When computing a difference, we begin with the value at the most positive position (the right hand value) and subtract the other:

$$\Delta x_2 = x_{2\beta} - x_{2\alpha} \tag{50}$$

- (4) Examples may consider compositions in many positions; these are denoted by Greek subscripts. If the problem considers different phases, these are distinguished by accents (Figure 1.1).

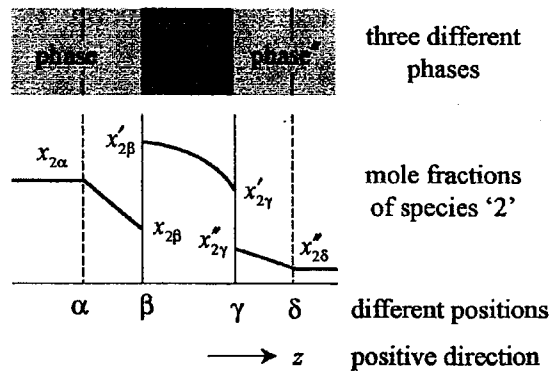


Fig. 1. Three different phases

(4) Two different forms of equations, binary mixtures

$$-\frac{\Delta a_1}{a_1} = \frac{1}{k_{1,2}} \bar{x}_2 (\bar{u}_1 - \bar{u}_2) \cdot \frac{\bar{c}x}{c} \quad (51)$$

$$\rightarrow \boxed{-x \frac{\Delta a_1}{a_1} = \frac{1}{k_{1,2}c} (\bar{x}_2 N_1 - \bar{x}_1 N_2)} \quad (52)$$

(5) Difference equation in velocity and flux forms

$$-\frac{\Delta a_i}{a_i} = \sum_{j \neq i} x_j \frac{\bar{u}_i - \bar{u}_j}{k_{i,j}} \quad (53)$$

$$-x_i \frac{\Delta a_i}{a_i} = \sum_{j \neq i} \frac{(\bar{x}_j N_i - \bar{x}_i N_j)}{k_{i,j}c} \quad (54)$$

for ideal solutions use driving force $-\Delta x_i$

(6) from binary to ternary and quaternary equations

$$-\Delta x_1 = \frac{\bar{x}_2 N_1 - \bar{x}_1 N_2}{k_{1,2}c} + \frac{\bar{x}_3 N_1 - \bar{x}_1 N_3}{k_{2,3}c} + \dots \quad (55)$$

$$-\Delta x_2 = \frac{\bar{x}_1 N_2 - \bar{x}_2 N_1}{k_{1,2}c} + \frac{\bar{x}_3 N_2 - \bar{x}_2 N_3}{k_{2,3}c} + \dots \quad (56)$$

(7) There is a number of different bootstrap relations.

- 1) membrane stagnant $u_M = 0$
- 2) bulk stagnant (absorption) $N_2 = 0$
- 3) trace stagnant (polarisation) $u_1 = 0$
- 4) equimolar exchange (distillation) $N_1 + N_2 = 0$
- 5) interface determined (vaporisation) $\frac{N_1}{N_2} = \frac{y_1}{y_2}$
- 6) reaction stoichiometry $\frac{N_1}{v_1} = \frac{N_2}{v_2}$

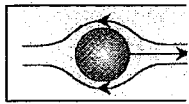
Empirical diffusion coefficient correlation of gases at ambient conditions:

$$\mathfrak{D}_{1,2} = 3.16 \times 10^{-8} \frac{T^{1.75}}{p(v_1^{1/3} + v_2^{1/3})^2} \times \left(\frac{1}{M_1} + \frac{1}{M_2}\right)^{1/2}$$

where

| | | | | | |
|--|----------------|----------------|-----------------|-----------------|------------------|
| $\frac{v_1}{10^{-6} \text{ m}^3 \text{ mol}^{-1}}$ | H ₂ | N ₂ | CO ₂ | NH ₃ | H ₂ O |
| | 7.07 | 17.9 | 26.9 | 14.9 | 12.7 |

Diffusivity of a dilute spherical species in a liquid:



this 'constant' varies with the ratio of the species.

$$\mathfrak{D}_{1,2} = \frac{RT}{2\pi A \eta_2 d_1^2 / d_2} \approx 10^{-9} \text{ m}^2 \text{ s}^{-1}$$

