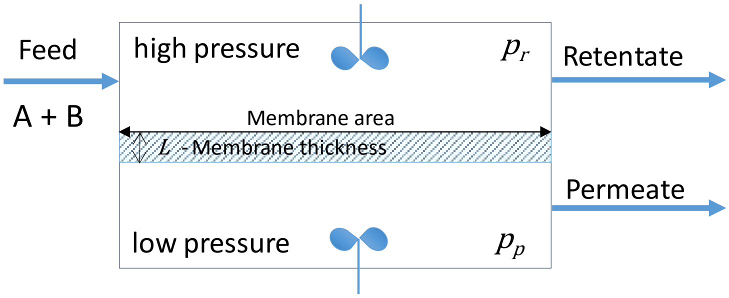
Problem 1: Membrane gas separation

A gas mixture consisting of components A and B is to be separated by a membrane of the thickness L = 0,002 cm and permeability for component A P_A = $400\cdot10^{-10}$ cm^3(STP).cm/(s.cm^2.cm Hg). The gas mixture has a flow rate of $2\cdot10^3$ cm^3(STP)/s. The retentate side pressure is p_r =80 cm Hg and the permeate side pressure is p_p = 20 cm Hg. The fraction of the feed permeating the membrane is θ = 0,3, the volume fraction of component A in the feed is y_{Af} = 0,413 and the volume fraction of component A in the retentate is y_{Ar} = 0,3. Consider complete mixing model illustrated bellow.



a) Explain the underlying assumptions of a complete mixing model. 2p

- Assumption of complete mixing on both sides of the membranes means no concentration gradient along the membrane – we do not need differential balance
- It is further assumed that there is no mass transfer resistance in the gas phases which means no concentration gradient from the bulk liquid towards the membrane surface. The only mass transfer resistance is the membrane

b) Formulate the overall material balance equation and the balance equation for component A. Calculate the volume fraction of component A in the permeate y_{Ap}. 7p

- Volumetric flow is given so we use it as basis
  Overall balance: 1

$$V_f = V_r + V_p$$

Balance for component A: 2

$$V_f y_{Af} = V_r y_{Ar} + V_p y_{Ap}$$

It is further given that: 1

$$\theta = \frac{V_p}{V_f} = 0{,}3$$

so 1

$$V_p = 0{,}3 \cdot 2\cdot10^3 = 600\ \mathrm{cm^3/s}$$

and 1

$$V_r = V_f - V_p = 1400\ \mathrm{cm^3/s}$$

Then 1

$$\boldsymbol{y_{Ap}} = \left(V_f y_{Af} - V_r y_{Ar}\right)/V_p = (2000\cdot 0{,}413 - 1400\cdot 0{,}3)/600 = \mathbf{0{,}667}$$

c) The general relation for the overall flux of component A across the membrane (N_A = cm^3(STP)/(s.cm^2)) considering mass transfer resistance in the gas phases on both sides of the membrane can be formulated as:

$$N_A = K\left(p_r y_{Ar} - p_p y_{Ap}\right)$$

where K is the overall mass transfer coefficient:

$$K = \frac{1}{\left(\frac{1}{k_{gr}} + \frac{L}{P_A} + \frac{1}{k_{gp}}\right)}$$

Apply the principle of resistances in series and show how the relation for overall mass transfer coefficient is derived. Draw a sketch of partial pressure/concentration profiles and explain the assumptions made. Explain what membrane permeability is. 9p

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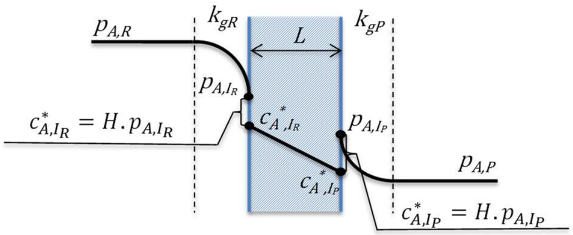


Assumptions

- Steady state ($N_A = N_{A,R} = N_{A,M} = N_{A,P}$) 1
- Equilibrium at the interfaces described by Henry's law 1

Then 1

$$N_A = k_{gR}\left(p_{A,R} - p_{A,I_R}\right)$$

$$N_A = \frac{D_A.H}{L}\left(p_{A,I_R} - p_{A,I_P}\right)$$

$$N_A = k_{gP}\left(p_{A,I_P} - p_{A,P}\right)$$

1

$$N_A\left(\frac{1}{k_{gR}} + \frac{L}{D_A.H} + \frac{1}{k_{gP}}\right) = \left(p_{A,R} - p_{A,I_R}\right) + \left(p_{A,I_R} - p_{A,I_P}\right) + \left(p_{A,I_P} - p_{A,P}\right) = \left(p_{A,R} - p_{A,P}\right)$$

$$N_A = \frac{1}{\left(\frac{1}{k_{gr}} + \frac{L}{P_A} + \frac{1}{k_{gp}}\right)}.\left(p_r y_{Ar} - p_p y_{Ap}\right)$$

here permeability of component A was introduced as: 1

$$P_A = D_A.H$$

Permeability is a measure of the rate of the transport of molecules through the membrane. 1

d) Simplify the expression for the flux of component A through the membrane assuming infinitely fast mass transfer in the gas phases on both sides of the membrane. Calculate the membrane area. 3p
Under the assumptions above the flux of A through the membrane is: 1

$$N_A = \frac{P_A}{L}.\left(p_r y_{Ar} - p_p y_{Ap}\right)$$

then the flow through the membrane is: **1**

$$V_p y_{Ap} = \frac{P_A}{L} \cdot (p_r y_{Ar} - p_p y_{Ap}) \cdot A_m$$

and the membrane area is: **1**

$$\boldsymbol{A_m} = \frac{V_p y_{Ap}\, L}{P_A (p_r y_{Ar} - p_p y_{Ap})} = \frac{600 \cdot 0{,}677 \cdot 0{,}002}{400 \cdot 10^{-10}(80 \cdot 0{,}3 - 20 \cdot 0{,}677)} = \mathbf{0{,}194 \cdot 10^7\ cm^2}$$

e) Formulate an analogous expression for the flux of component B through the membrane. Calculate the membrane selectivity. Explain what membrane selectivity is. **6p**

The flux of B through the membrane is: **1**

$$N_B = \frac{P_B}{L} \cdot (p_r y_{Br} - p_p y_{Bp})$$

The flow of B is then: **1**

$$V_p y_{Bp} = \frac{P_B}{L} \cdot (p_r y_{Br} - p_p y_{Bp}) \cdot A_m$$

Selectivity is defined as: $\alpha = P_A/P_B$ **1**

And can be calculated by combining the two relations:

$$\frac{V_p y_{Ap}}{V_p y_{Bp}} = \frac{\frac{P_A}{L}(p_r y_{Ar} - p_p y_{Ap}) \cdot A_m}{\frac{P_B}{L}(p_r y_{Br} - p_p y_{Bp}) \cdot A_m}$$

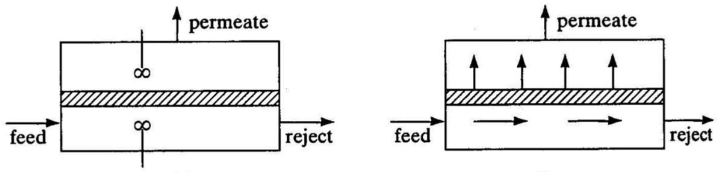
$$\boldsymbol{\alpha} = \frac{\boldsymbol{P_A}}{\boldsymbol{P_B}} = \frac{y_{Ap}(p_r y_{Br} - p_p y_{Bp})}{y_{Bp}(p_r y_{Ar} - p_p y_{Ap})} = \frac{0{,}677 \cdot (80 \cdot (1 - 0{,}3) - 20 \cdot (1 - 0{,}677))}{(1 - 0{,}677) \cdot (80 \cdot 0{,}3 - 20 \cdot 0{,}677)} = \mathbf{9{,}93}$$

2

Membrane selectivity is the ratio of component permeabilities and so a measure of the difference in the rates of component mass transfer through the membrane. If selectivity is equal 1 the permeabilities are comparable and the membrane is not selective. **1**

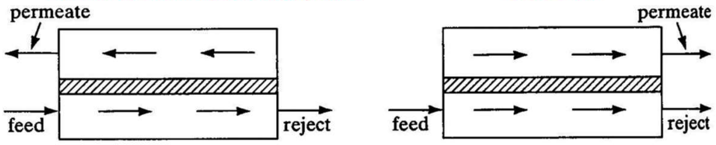
f) Name and explain with a sketch other alternative types of flow patterns in membrane modules and discuss briefly the implications it will have for model equations if the assumption of complete mixing is not valid. Sketch evt. the concentration profiles. **3p**

Hydrodynamics in membrane modules



a) Both sides of membrane ideally mixed

b) Cross flow



c) Countercurrent

d) Cocurrent

3

We will have to formulate the balance equations for a differential small element of the length Δz and work with differential equations. evt + p

Problem 2 - Distillation

(a) Overall mass balances.

F = D + B
xF F = xD D + xB B
gives 0.3*100 = 0.85*D + 0.02*(100-D).
D = (30 – 2)/0.83 = 33.73, B=66.26
Internal flows
L/D = 0.8 gives L=LT=25.29.
So VT = VB = D+LT = 59.02, LB=LT+q*F = 25.29+100=125.29.
Assumption: Constant molar flows and saturated feed corresponds to q=1.

(b) x = 0.71/18 / (0.71/18 + 0.29/90) = 0.92

(c) The operating lines is a mass balance relationship that gives the relationship between y and x between stages.
The McCabe Thiele method is a graphical method to solve the equations for the mass balance (operating line) and equilibrium on all stages in the column.

(d) Let y and x represent the vapor and liquid composition at a given cross section in the upper part of the column, and make a "control volume" to the top end of the column. The component balance (In=out) gives
VT y = LT x + D xD
Upper operating line: y = (LT/VT) x + (D/VT)xD (*)
Note that setting x=xD in (*) gives y = (LT+D)*xD/VT = VT*xD/VT = xD so (*) goes through the point (x,y)=(xD,xD).
With numbers the upper operating line becomes
y = 0.4285 x + 0.4858

(e) Stepping from each end gives; Ntop=2.9, Nbtm = 2.8 (including reboiler)

(f) The operating lines are the same but we don't switch at the feed. We start from the bottom and step upwards the column with Nbtm=6 (including reboiler). This gives a pinch around where the bottom operating crosses the equilibrium line (x about 0.35). We then switch to the upper operating line and need Ntop=1.6 to get to the top product.

(g) With leak Lw.
(i) Without leak we would have yT=xD because of total condenser.
(ii) Flowsheet (not shown)
(iii) Need to set up material balances.

Material balance for water around the condenser:
VT*yT + Lw*xw = (VT+Lw)*xD
With numbers:
(1) Condenser water: VT*0.86 + Lw = (VT+Lw)*0.89
(2) Condenser total: VT + Lw = L + D = 1.8*D
(3) Overall water: 30 + Lw = D*0.89 + (100+Lw-D)*0.02

This gives 3 equations with 3 unknowns (VT, Lw, D).

(iv) Solution.

From (1) we we get: VT = ((1-0.89)/(0.89-0.86))*Lw = 3.667*Lw
Put into (2) gives: D = (4.667/1.8)*Lw = 2.593*Lw
Put into (3) gives: Lw = 28/(2.593*0.87+0.02-1) = 21.95 (so leak is more than 20% of feed)

Furthermore:
$VT = 3.667*Lw = 80.47$
$D = 2.593*Lw = 56.92$
$L = LT = VT+Lw-D = 45.50$ (Check: so $L/D= 45.50/56.92 = 0.799$. OK!)

(h) Upper operating line with leak.

Material balance for water over top part of column:

$$VT*y + Lw = LT*x + D*xD$$

or $y = (LT/VT)*x + (D*xD - Lw)/VT$

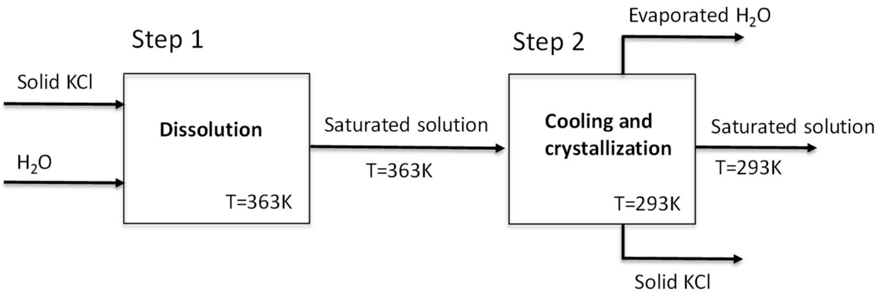
This line goes through (and starts from) the point (xD, yT) = (0.89, 0.86) because this point is on the material balance line at the top end of the column. This can be confirmed by putting in numbers.

$y = 0.565*x + 0.357$

We could use this upper operating line to compute the number of stages using McCabe-Thiele also in this case, but this is not asked for.

Problem 3: Re-crystallization of KCl in a batch equilibrium crystallizer

A batch of 1000 kg KCl is first dissolved in water to make a saturated solution at 363K. The solution is then cooled to 293K and KCl is re-crystallized. The process of the batch equilibrium crystallization is illustrated in the sketch bellow:



The solubility data for KCl are given in the table below:

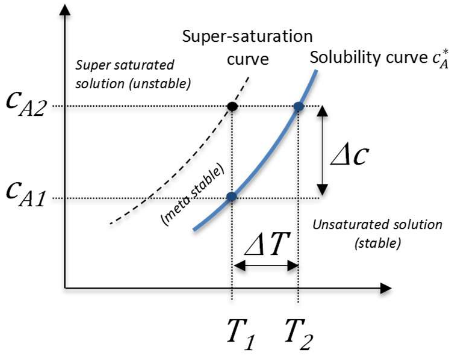
Temperature [K]	KCl solubility [wt %]
363	35,0
293	25,4

a) Explain and illustrate in the temperature – concentration diagram what is the driving force for crystallization. When does spontaneous crystallization occur and when has the crystallization process to be initiated? 4p

Saturated solution can separate into 2 phases

- Liquid
- Solid (crystal)

The concentration difference is the driving force. 1 Supersaturation is necessary for spontaneous crystallization. 1 In the meta-stable region the crystallization has to be initiated. 1



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b) Calculate the amount of water needed to prepare the saturated solution in step 1. From the table at T= 363 K: 2p

$$w_{KCL,feed} = 0{,}35$$
$$w_{H2O,feed} = 0{,}65$$

then

$$m_{feed} = \frac{m_{KCl,feed}}{w_{KCl,feed}} = \frac{1000}{0{,}35} = 2857\ \text{kg} \qquad 1$$

$$m_{H2O,feed} = m_{feed} w_{H2O,feed} = 2857 \cdot 0{,}65 = 1857\ \text{kg} \qquad 1$$

c) Formulate all the necessary mass balance equations and calculate the obtained weight of KCl crystals if no water evaporates on cooling in step 2. **4p**

The overall mass balance is:

$$m_{feed} = m_{sol} + m_{KCl} + m_{H2O}$$

The mass balances for KCl and H_2O are:

$$m_{feed} w_{KCl,feed} = m_{sol} w_{KCl,sol} + m_{KCl} \qquad 1$$

$$m_{feed} w_{H2O,feed} = m_{sol} w_{H2O,sol} + m_{H2O} \qquad 1$$

From the table at T = 393 K:

$$w_{KCL,sol} = 0{,}254$$

$$w_{H2O,sol} = 0{,}746$$

then for

$$m_{H2O} = 0$$

$$m_{sol} = \frac{m_{feed} w_{H2O,feed}}{w_{H2O,sol}} = \frac{1857}{0{,}746} = 2489\ \text{kg} \qquad 1$$

$$\boldsymbol{m_{KCl}} = m_{feed} - m_{sol} = 2857 - 2489 = \mathbf{368\ kg} \qquad 1$$

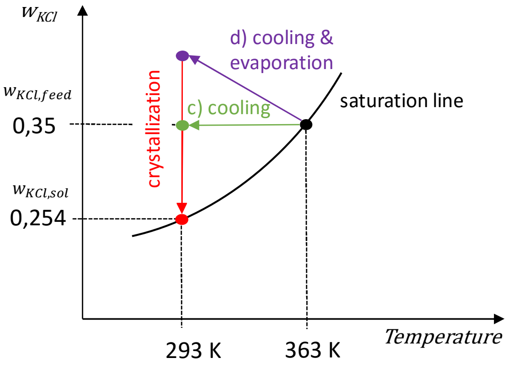
d) Assume that 5% of the original water evaporates on cooling in step 2 and then calculate the weight of KCl crystals formed in step 2. **3p**

$$m_{H2O} = 0{,}05 \cdot m_{H2O,feed} = 0{,}05 \cdot 1857 = 92{,}85\ \text{kg} \qquad 1$$

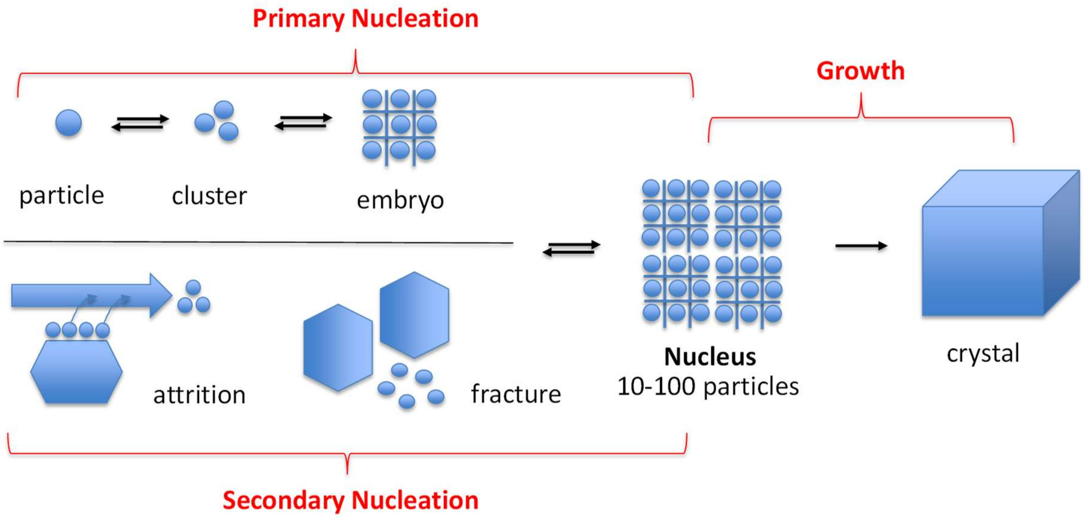
$$m_{sol} = \frac{m_{feed} w_{H2O,feed} - m_{H2O}}{w_{H2O,sol}} = \frac{1857 - 92{,}85}{0{,}746} = 2364\ \text{kg} \qquad 1$$

$$\boldsymbol{m_{KCl}} = m_{feed} - m_{sol} - m_{H2O} = 2857 - 2364 - 92{,}85 = \mathbf{400\ kg} \qquad 1$$

e) Explain and discuss your results in temperature – concentration diagram. **2p**



f) Describe qualitatively the process of crystal formation 3p



1

Crystals are created in 2 steps (both require super-saturation):

- **Nucleation** - when nuclei is formed (statistical theory explains the probabilities) 1
- **Growth** – when the nuclei grows 1

The processes are metastable equilibria

- because of the larger solubility of the very small crystals compared to medium and large ones, the small crystals (bellow a critical size) will dissolve and the large ones will grow

Formation of nucleus is a breaking moment:

probability of growth = probability of decay

g) The following equation describes the rate of crystal growth. 2p

$$G = \frac{\Delta L}{\Delta \tau} = K \Delta c_A$$

Which assumptions have to apply for the equation to be valid?

McCabe law of growth

- Growth Rate independent of size 1
- Constant super-saturation 1
- In the diffusion-integration model the order of integration reaction is assumed equal 1

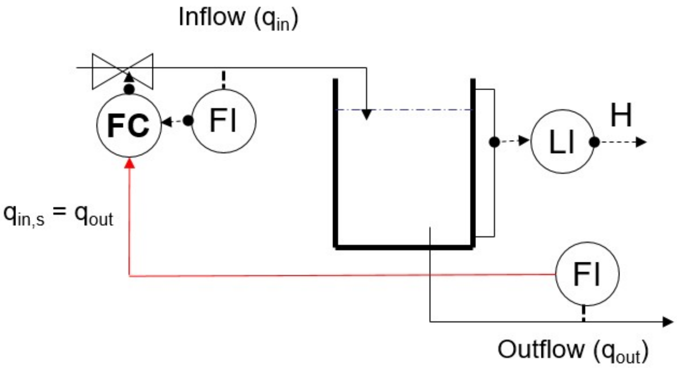
Problem 4 – Level control

(a) Assume constant liquid density.

Steady-state mass balance: qin = qout [m3/3]
Dynamic mass balance: dV/dt = qin – qout [m3/s]
If we assume that the tank has constant area A [m2] then V=A*H, and dV/dt = A*dH/dt

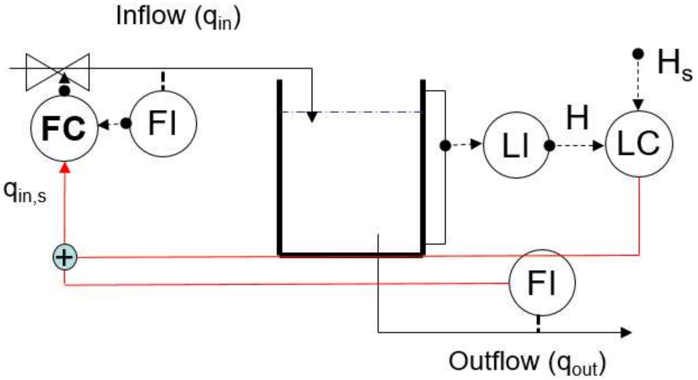
(b) MV: qin, DV: qout, CV: H

(c) Feedforward : Measure disturbance (qout) and change MV (qin).
Assume we want tight control of the level, then we want qin=quout because this makes dH/dt=0. To make qin=qout we may use a flow controller for qin with setpoint equal to qout. See Figure for feedforward



(d) Feedback: measure CV (H) and change MV (qin).

P-controller: u = Kc*(Hs-H) where u (=qin) is the output of the feedback controller
Comment (not asked for): We may also for the feedback use a flow controller, for example, to counteract disturbances in pin and linearize the valve. We may also combine feedback with feedforward control. See figure for combined feedback and feedforward:



More comments: 1) Actually, feedforward control cannot used alone for levels because otherwise the level will after some time drift away (integrating process). 2) This feedforward controller assumes that the objective is to have tight control of the level. In many cases the level should vary ("smooth" control") to avoid that the flow disturbance (here qout) propagates directly to the MV (here to qin).