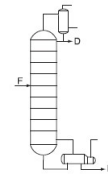
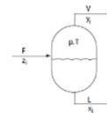


TKP4105 (Sep-tek.)
Ch. 11
VLE and Flash slides
Sigurd Skogestad

Chapter 11. Vapor-Liquid
Separation Processes

- **Introduction (Diffusion is slow!)**
- **Flash and VLE (Skogestad lectures 1+2+3)**
 - Simple separations
 - Oil/gas-separation offshore (series of simple flashes with decreasing pressure)
- **Distillation (lectures 4+5+6+7)**
 - The most important separation process for liquids
 - About 7% of industrial usage of energy is for distillation!
 - Oil refining, synfuels
 - Petro- og fine chemicals
 - Air separation
- **Lectures 8-12: "Gas"-liquid separation processes (Ch. 10)
Absorption and stripping**
 - Example: CO₂-removal using amine solutions



Diffusion is slow!

Ficks law (Mass transfer by diffusion):

$$J_{Az} = -D_{AB} \frac{dc_A}{dz} \quad \left[\frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \right]$$

To get mass flow \dot{m}_A [kg/s] multiply by $S[\text{m}^2] \cdot M_A \left[\frac{\text{molA}}{\text{kgA}} \right]$

Use $c_A = x_A c_{tot}$ and $c_{tot} M_A = \rho$ (assuming $M_A = M_{tot}$):

$$\dot{m}_{Az} = -D_{AB} \cdot \rho \frac{dx_A}{dz} S \quad \left[\frac{\text{kg}}{\text{s}} \right]$$

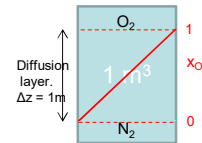
Typical data gas (1 bar): $D_{AB} \rho = 10^{-5} \frac{\text{m}^2}{\text{s}} \cdot 1 \frac{\text{kg}}{\text{m}^3} = 10^{-5} \frac{\text{kg}}{\text{s} \cdot \text{m}}$

Typical data liquid: $D_{AB} \rho = 10^{-9} \frac{\text{m}^2}{\text{s}} \cdot 10^3 \frac{\text{kg}}{\text{m}^3} = 10^{-6} \frac{\text{kg}}{\text{s} \cdot \text{m}}$

Example gas. Concentration difference: $\Delta x_A = 1$ (max).

Diffusion layer: $\Delta z = 1 \text{ m}$. Surface area: $S = 1 \text{ m}^2$. $\Rightarrow m_A = 10^{-5} \text{ kg/s}$

Process applications: Want $m_A \approx 1 \text{ kg/s}$. Need $S/\Delta z$ a factor 10^5 larger!!



IN PRACTISE: Mass transfer between phases (including distillation):

- USE INTENSIVE MIXING to get small Δz (small boundary layer)
- + use large surface area S between phases

Class quiz (1)

1. How much CO₂ gas [liter] in 1 liter coke?
2. What is the equilibrium pressure for coke?

- Data: Temperature=25C
- CO₂ concentration in coke is about 5 g/l (about 0.5 wt%).
- VLE: Water-CO₂ at 25 C has Henry's constant (Hco₂) = 1670 bar.
Vapor pressure of water at 25C is about 0.03 bar.
- Mole weight water = 18 g/mol
- Mole weight CO₂ = 44 g/mol

• Solution:

- **Question 1.** 1 liter coke contains $n = 5 \text{ g} / 44 \text{ g/mol} = 0.114 \text{ mol CO}_2$

• Question 2.

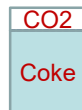
- x_{CO_2} = mole fraction CO₂ in liquid
- From data (0.5 wt% CO₂): $x_{\text{CO}_2} = 0.5 \text{ g} / (44 \text{ g/mol}) / [95 \text{ g} / 18 \text{ g/mol} + 5 \text{ g} / 44 \text{ g/mol}] = 0.0021$
- **Assume vapor-liquid equilibrium:**
- Partial pressure of CO₂ from Henry's law:
- Partial pressure of H₂O from Raoult's law:
- Total pressure,
 - google: Typical filling pressure for CO₂ is about 8 bar (but equilibrium is not reached)

Class quiz (2)

3. Is the pressure really 3.53 bar inside a coke bottle?

4. Why not?

Answer: because of slow diffusion



3. How can we increase the pressure?

Experiment Diet Coke

- Skru av korken... det er litt overtrykk....kommer ut litt gass (CO₂), men neppe 2.8 liter. ...
- Hvorfor kommer ikke resten ut?.....
- Hvordan få ut mer?...
- Riste
- eller bedre: Menthos
- Let us try!

White Mentos + Diet Coke = Explosion

- **Mythbusters Status: True (Discovery Channel, 09 Aug. 2006)**
- <http://www.museumofhoaxes.com/hoax/weblog/comments/3600/P20/>
- Given the urban legend about kids eating pop rocks and soda, and then having their stomachs explode, I wouldn't have believed that mixing Mentos and soda could cause such a violent reaction. But after watching the [video posted on WLTX's website](#), I do. (You need Windows Media Player to view it, and I had to click the "Trouble Viewing" button to make it work.) To summarize what the video shows, three Mentos are dropped into a bottle of soda, causing a geyser of soda to shoot up about three or four feet high out of the bottle. WLTX provides this scientific explanation for the phenomenon:

Mentos contains a chemical known as ARABIC GUM (this is the ingredient that makes the mint "chewy"). This ingredient causes the surface tension of the water molecules to break even more easily, releasing more carbon dioxide gas at an astounding rate!The gas causes pressure to rapidly build inside the bottle which thrusts the soda upwards in a wonderful fountain-like BLAST!
- Posted By: Alex | Date: Fri Sep 23, 2005 | [Permalink](#) | Total Comments: 184
Category: [Food](#)
- Adresseavisen [Ida Alysén](#) Publisert: 24.07.2010 kl. 13:30
- Vi prøver å lage en Mentos-Cola light-fontene.
Et kjent og kjært triks prøvd av utallige hjemmevideotentusiaster på Youtube, for ikke å snakke om Mythbusters på Discovery Channel.
- Daniel Greiner Edvardsen, jan. 2011: Need to use WHITE Mentos
- Se også [vitenwahl.no](#) (bl.a. for bestilling av påfyllingsrør for Mentos)

Class quiz (3)

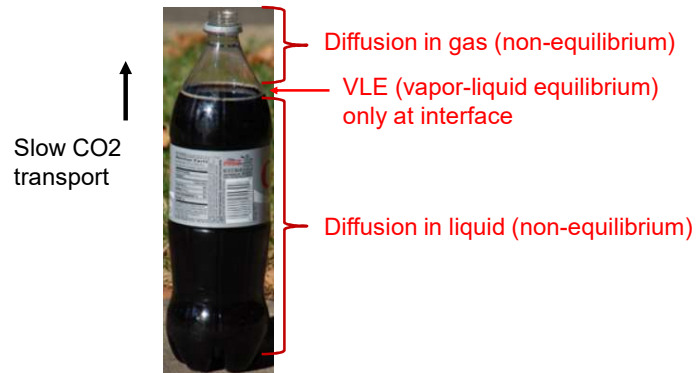
6. Why does pressure increase when we shake (or add Menthos)?

- Shaking gives mixing and better mass transfer (do not need to rely on diffusion) ... so approach equilibrium and CO₂ is released and pressure rises
- **Menthos** give large surface area + low surface tension -> helps formation of CO₂-bubbles. These bubbles provide "artificial mixing" for further release of CO₂

Class quiz (4)

7. Why does not pressure stay high after shaking?

- The CO₂ leaks out and equilibrium is not maintained because of slow diffusion



Diffusion is slow!

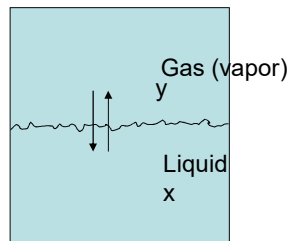
Lesson: Need to work hard to get equilibrium!

Shaking, mixing...
large contact area between phases



Equilibrium stage concept

- Assume well mixed (turbulence!) and large contact area so that there are no diffusion limitations for mass transfer
- Liquid and vapor phases* in equilibrium!



* the entire («bulk») phases

Vapor/liquid-equilibrium (VLE)

Partial pressure of component A: $p_A = y_A p$

Total pressure for mixture: $p = p_A + p_B + \dots$

Raoult's law (ideal liquid): $p_A = x_A p_A^{\text{sat}}(T)$

Nonideal liquid: $p_A = \gamma_A x_A p_A^{\text{sat}}(T)$

Henry's law (dilute solution): $p_A = x_A H_A(T)$

- **K-value.** $K_i = y_i/x_i$ K is generally a function of: T, p, x, y
Raoult's law: $K_A = p_A^{\text{sat}}(T)/p$
Henry's law: $K_A = H_A(T)/p$

- **Relative volatility, α (11.3B)**

$$\alpha = \frac{K_A}{K_B} = \frac{y_A/x_A}{y_B/x_B}$$

$$\text{Raoult's law: } \alpha = \frac{p_A^{\text{sat}}(T)}{p_B^{\text{sat}}(T)}$$

α can often be assumed constant (ideal mixture of similar components)!

VLE diagrams. Binary mixture

TABLE 11.1-1. Vapor-Pressure and Equilibrium-Mole-Fraction Data for Benzene-Toluene System

Temperature		Benzene		Toluene		Mole Fraction Benzene at 101.325 kPa	
K	°C	kPa	mm Hg	kPa	mm Hg	x_A	y_A
353.3	80.1	101.32	760			1.000	1.000
358.2	85	116.9	877	46.0	345	0.780	0.900
363.2	90	135.5	1016	54.0	405	0.581	0.777
368.2	95	155.7	1168	63.3	475	0.411	0.632
373.2	100	179.2	1344	74.3	557	0.258	0.456
378.2	105	204.2	1532	86.0	645	0.130	0.261
383.8	110.6	240.0	1800	101.32	760	0	0

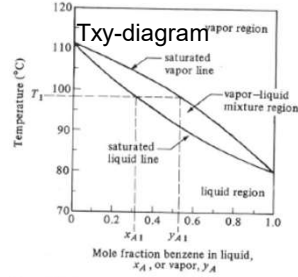
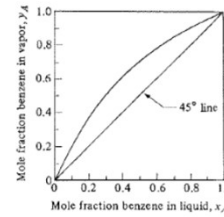


FIGURE 11.1-1. Boiling point diagram for benzene (A)-toluene (B) at 101.325 kPa (1 atm) total pressure.

FIGURE 11.1-2. Equilibrium diagram for system benzene (A)-toluene (B) at 101.32 kPa (1 atm).

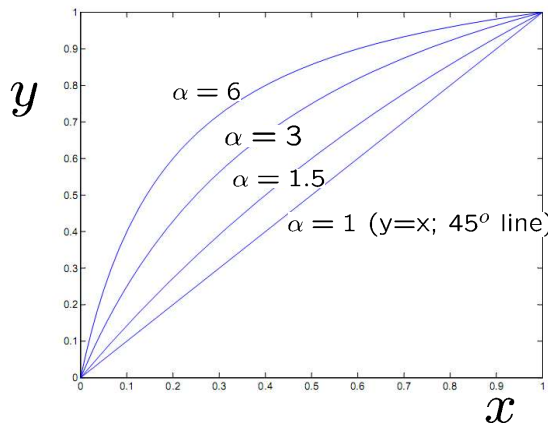
xy-diagram ("equilibrium line") (11.1B)



Constant relative volatility

• Binary mixture: $\alpha = \frac{y_A/x_A}{y_B/x_B} = \frac{y/x}{(1-y)/(1-x)} \Rightarrow y = \frac{\alpha x}{1+(\alpha-1)x}$

xy-diagram



Ideal mixture

Ideal mixture: Estimate of relative volatility (Sigurd's method)

$$\ln \alpha \approx \frac{\Delta H^{vap}}{RT_B} \cdot \frac{\Delta T_B}{T_B}$$

typical: $\approx 9-15$

ΔH^{vap} - avg. heat of vap. at T_B [kJ/mol]

ΔT_B - boiling point difference [K]

T_B - geometric avg. boiling point [K]

Ref: King, Separation process, 2nd Ed. 1980, p.680

Example. iso-pentane (L) – pentane (H)

$T_L = 301.0 \text{ K}, \Delta H_L^{vap} = 25 \text{ kJ/mol},$

$T_H = 309.2 \text{ K}, \Delta H_H^{vap} = 27 \text{ kJ/mol},$

$\Delta T_B = 8.2 \text{ K}, T_B = \sqrt{301 \cdot 309.2} = 305.1 \text{ K},$

$\ln \alpha = \frac{\sqrt{25 \cdot 27} \cdot 1000}{8.31 \cdot 305.1} \cdot \frac{8.2}{305.1} = 0.275; \alpha \approx 1.32$

Binary mixture

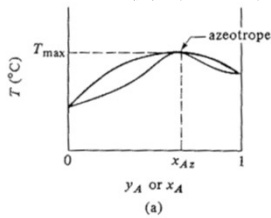
Given pressure

AZEOTROPES ($y_A = x_A$ at some composition)

Max-boiling: **Unusual.**

Example: Formic acid-water

Molecules "like" each other ($\gamma < 1$) and prefer to be in liquid



Min-boiling: **Common.**

Example: Ethanol-water

Molecules "dislike" each other ($\gamma > 1$) and vaporize more easily

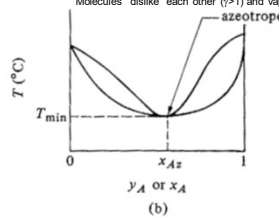
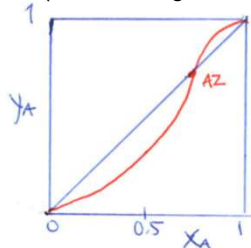
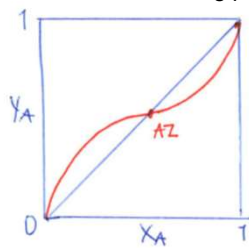


FIGURE 11.1-3. Equilibrium boiling-point diagrams: (a) maximum-boiling azeotrope, (b) minimum-boiling azeotrope.

xy-diagrams (here: A = «light» component = with lowest boiling point):



(a) Maximum-boiling

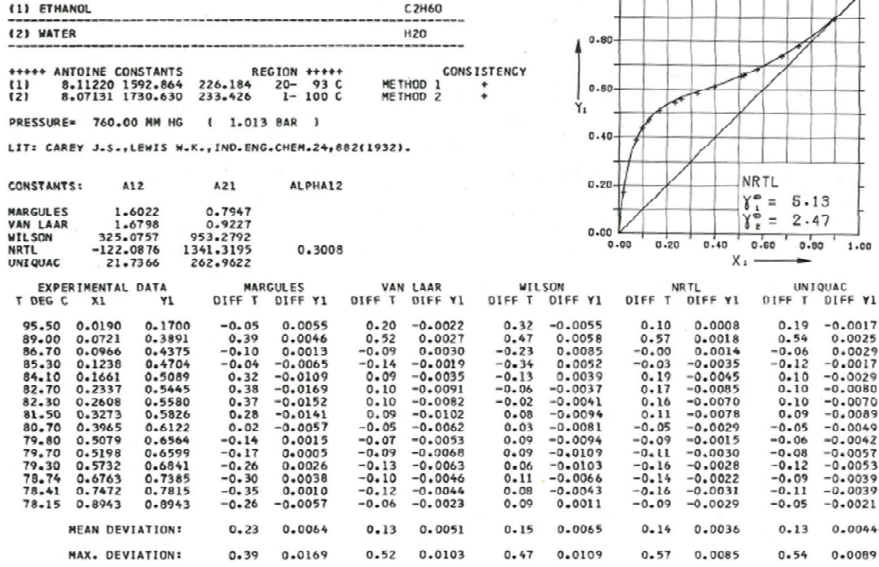


(b) Minimum-boiling

Binary mixture

Given pressure

Ethanol-water at 1 atm: Minimum-boiling azeotrope at about $x_1=0.90$ (96 liquid volume-%)

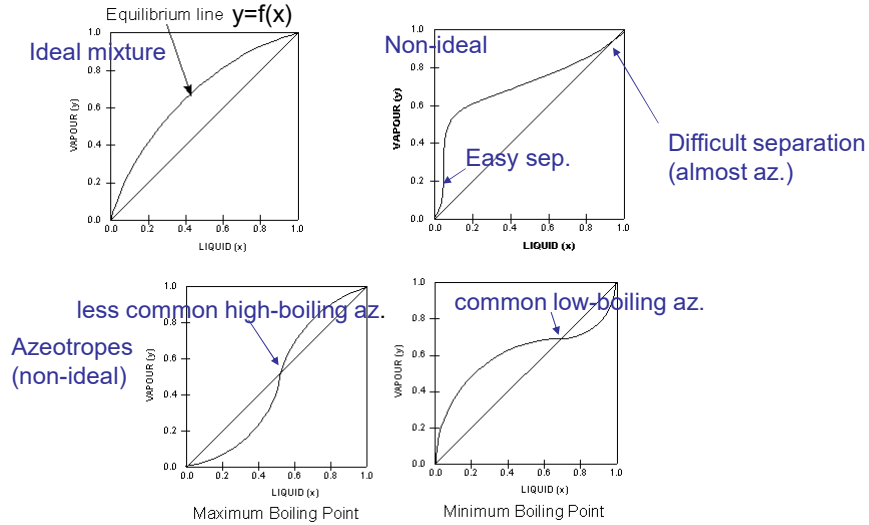


Binary mixture

Given pressure

SUMMARY. Vapor-liquid equilibrium (VLE) = "Equilibrium line"

xy-diagrams:



Gibbs' phase rule for a system in equilibrium

- F = degrees of freedom that can be specified among the variables
 - Temperature*
 - Pressure*
 - Composition (of a given phase)
- $F = 2 + C - P - R$
 - C = no. components
 - P = no. of coexisting phases in equilibrium
 - R = no. of independent chemical reactions in equilibrium

Example. Ethanol-water in vapor/liquid equilibrium.

$$F = 2 + 2 - 2 - 0 = 2$$

1. Given $x_{\text{ethanol}}=0.5$ and $p=1$ atm: System is uniquely determined (cannot specify T)
2. Given $x_{\text{ethanol}}=y_{\text{ethanol}}$ (azeotrope) and $p=1$ atm: System is uniquely determined (cannot specify T)

* Book (10.2.A) does not state clearly that the rule involves the variables p and T

"Proof": There are originally $2 + (C-1)$ degrees of freedom among the variables temperature, pressure and composition. However, each extra phase or chemical reaction introduces an equation (equilibrium constraint) that reduces the degrees of freedom

11.2 Single-stage equilibrium contact for vapor-liquid system

Flash

- **Flash: Products L and V in equilibrium**

1. Important process in itself
 - Separators for mixtures with large relative volatility (Example: Offshore oil and gas)
2. Building block for multistage processes

Comment: The book calls "flash" for "flash distillation" or "equilibrium distillation", but in the process industry the term "distillation" is used for multistage processes with reflux.

- Here: Assume steady state (continuous operation)

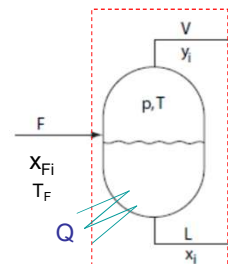
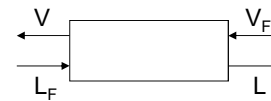
- Equations:

- N_c VLE equations:
 - $y_i = K_i x_i$ ($i=1,2,\dots,N_c$)
 - K_i : given function of p, T, x_i, y_i
- N_c Component balances (In=out, steady-state)
 - $Fx_{Fi} = Lx_i + Vy_i$ ($i=1,2,\dots,N_c$) [mol i/s]
- 2 summation equations:
 - $\sum x_i = x_1 + x_2 + x_3 + \dots = 1$
 - $\sum y_i = y_1 + y_2 + y_3 + \dots = 1$
 - (Also have total material balance $F = L + V$ but not independent from the others)
- 1 energy balance (In=out)*
 - $H_F + Q = H_L + H_V$ [J/s]
- In total: $2N_c + 3$ independent equations

- Unknowns with **given feed** (F, x_{Fi}, h_F):

- $2N_c + 5$ unknowns: x_i, y_i, V, L, p, T, Q

- **Need 2 more specifications (e.g., p and T)**

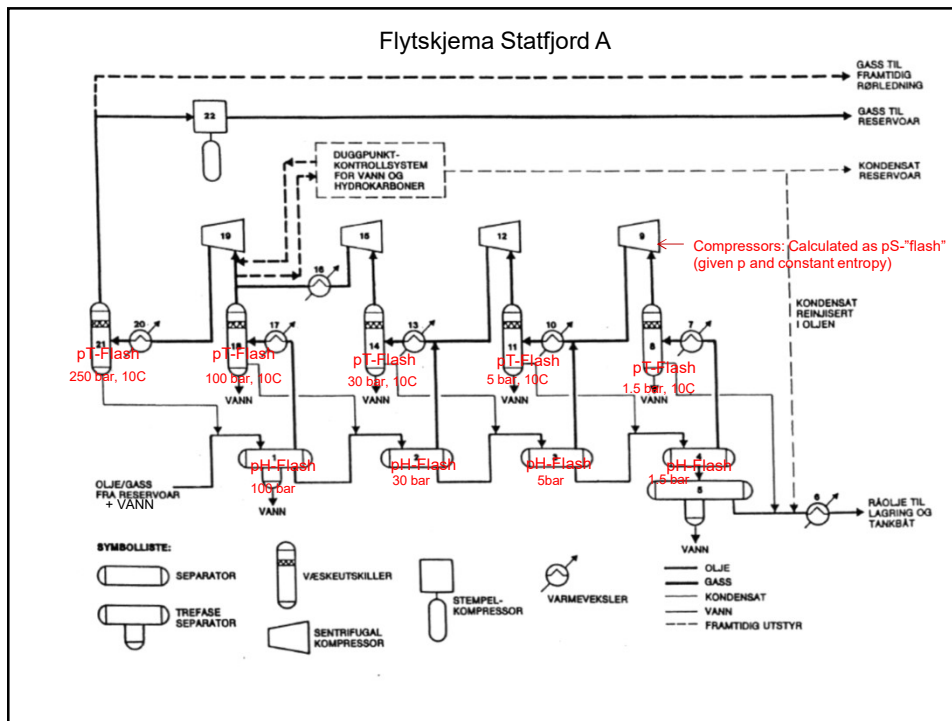


* Energy balance: Normally not used in this course. Often replaced by "constant molar flows" assumption (gives $V = V_F, L = L_F$ for adiabatic flash, $Q=0$)

Example of flashes (given feed)

Need 2 more specifications:

- 1. Specify $p + V/F$
 - Analytical solution (constant α , see exercise) or graphical solution (any VLE, book 11.2)
 - Special cases:
 - 1A. Bubble point at given p ($V/F=0$). Book 11.7C-1
 - 1B. Dew point at given p ($V/F=1$) Book 11.7C-2
- 2. Specify $T + V/F$
 - Special case: 2A. Bubble point at given T ($V/F=0$), see exercise
 - Special case: 2B. Dew point at given T ($V/F=1$)
- 3. Specify $p + T$ (pT-flash)
 - Iterative solution, book 11.7 (Rachford-Rice)
- 4. Specify $p + H$ ($H=H_F$ =enthalpy of feed for adiabatic flash)
 - Tank, adiabatic flash
 - Generally, need energy balance to find L and V :
 - $H \cong H_L + H_V = H_F + Q$ [J/s]
 - Usually requires computer (Aspen, Hysys, Unisim...)
 - Comment. Stage in distillation column: pH-flash = p V/F-flash if we know liquid fraction in feed streams + assume constant molar flows.
- 5. Specify $p + S$
 - Compressor



Flash calculations

- First formulate equations
 - VLE
 - Component balance (In feed = Out V + Out L)
 - Energy balance (not always needed)
- In general three approaches to solve equations
 - Analytical solution / hand calculations (see below and exercise)
 - Graphical solution (see below)
 - Numerical solution (most general!)
 - Manual iteration by hand ("trial and error", see below)
 - Programming (e.g. using Matlab)
 - Commercial process simulation software like Hysys/Unisim, Aspen, etc.
- For more details flash, see my book
 - S. Skogestad, Chemical and Energy Process Engineering, CRC Press, 2009, Ch. 7.4
 - See: <http://www.nt.ntnu.no/users/skoge/septek/lectures>

Binary mixture

Given pressure

1. p+V/F-flash

I. Analytical solution (const. α)

1. VLE at given p: Assume constant relative volatility

$$y = \frac{\alpha x}{1 + (\alpha - 1)x}$$

2. Component mass balance

$$F x_F = L x + V y$$

Combine to get 2nd-order equation in x

$$F x_F = L x + V \frac{\alpha x}{1 + (\alpha - 1)x}$$

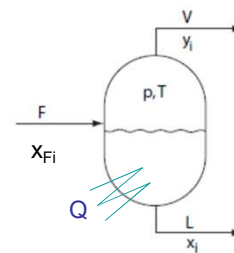
Example: $F=150$, $x_F=0.50$, $\alpha = 6$ (propane-butane), $V=80$

Analytical solution: $75 = 70x + 80 \cdot 6x / (1 + 5x)$

$$350 x^2 + 175 x - 75 = 0$$

$$x = 0.2761$$

$$y = 0.6959$$



Analytical solution: Not in book
But relevant for exam!
See also Exercise.

1. p+V/F-flash

II. Graphical solution (any VLE)

- Book 11.2, example 11.2-1

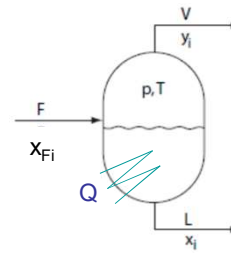
1. Equilibrium curve (given p)

- $y = f_1(x)$

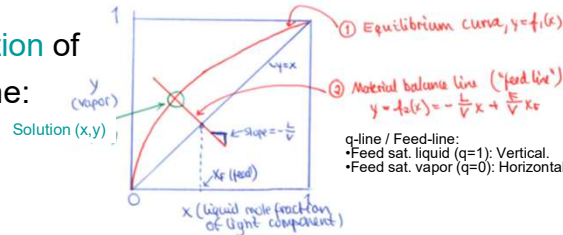
2. Component mass balance ("feed line", "q-line")

- $y = f_2(x) = -\frac{L}{V}x + \frac{F}{V}x_F = -\frac{q}{1-q}x + \frac{1}{1-q}x_F$

$q = L/F =$ liquid fraction
 $1-q = V/F =$ vapor fraction



- Solution at intersection of VLE-curve & feed line:



Dew and bubble point

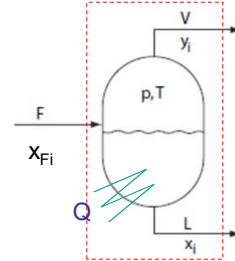
- Numerical example. See exercise, Problem 2

Case 2A (d) What is the saturation pressure (bubble point pressure) and vapor composition for a liquid mixture at 100C (373.2K) with 50 mol-% benzene and 50 mol-% toluene.

Case 1B (e) Explain what a dew point is. Consider a gas mixture at 911 mmHg (1.21 bar) with 50 mol-% benzene and 50 mol-% toluene. What is the dew point temperature and what is the composition of the first liquid drop?

3. pT-Flash

- Solve numerically
- Usually best to find V/F first
- Write VLE as: $y_i = K_i x_i$
 - K_i is mainly a function of p and T , so can often be assumed constant for pT-flash
 - For example, ideal mixture, $K_i = p_i^{\text{sat}}(T)/p$
- Combine mass balance and VLE:
 - $F x_{Fi} = L x_i + V K_i x_i$
 - Solve for x_i :
 - $x_i = F x_{Fi} / (F - V + V K_i)$ or $x_i = x_{Fi} / [1 + V/F(K_i - 1)]$
 - Need to find V/F... (iterative solution = «trial and error»)
 - Book 11.7C-3: Use $\sum x_i = 1$.
 - Often better: Use $\sum y_i - \sum x_i = 0 \rightarrow$ Rachford-Rice equation to get convex function in V/F::



$$\sum_i \frac{x_{Fi}(K_i - 1)}{1 + \frac{V}{F}(K_i - 1)} = \frac{x_{F1}(K_1 - 1)}{1 + \frac{V}{F}(K_1 - 1)} + \frac{x_{F2}(K_2 - 1)}{1 + \frac{V}{F}(K_2 - 1)} + \dots = 0$$

3. Example pT-flash: Numerical solution

Problem.

Feed: $F = 1$ mol/s. 40 mole-% propane (1), 10 % pentane (2), 50% hexane (3).

Flash at $T = 350$ K and $p = 10$ bar.

VLE data: Vapor pressures at 350K: 27.92 bar (1), 3.391 bar (2), 1.299 bar (3).

Solution:

K-values ($K_i = p_i^{\text{sat}}/p$): $K_1 = 2.792$, $K_2 = 0.3391$, $K_3 = 0.1299$.

Find V/F from Rachford-Rice by iteration. Want: LHS = 0.

1. First try: $V/F = 0$.

$$\text{LHS} = \sum_i \frac{x_{Fi}(K_i - 1)}{1 + \frac{V}{F}(K_i - 1)} = 0.4 \cdot 1.792 + 0.1 \cdot (-0.661) + 0.5 \cdot (-0.870) = 0.2158$$

2. Second try: $V/F = 0.1$

$$\text{LHS} = \frac{0.4 \cdot 1.792}{1 + 0.1 \cdot 1.792} + \frac{0.1 \cdot (-0.661)}{1 + 0.1 \cdot (-0.661)} + \frac{0.5 \cdot (-0.870)}{1 + 0.1 \cdot (-0.870)} = 0.0607$$

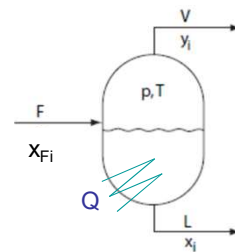
3. Further "trial and error" gives finally $V/F = 0.1436$:

$$\text{LHS} = \frac{0.4 \cdot 1.792}{1 + 0.1436 \cdot 1.792} + \frac{0.1 \cdot (-0.661)}{1 + 0.1436 \cdot (-0.661)} + \frac{0.5 \cdot (-0.870)}{1 + 0.1436 \cdot (-0.870)} = 0$$

With $V/F = 0.1436$ we then find:

$$\text{Liquid composition: } x_i = \frac{x_{Fi}}{1 + \frac{V}{F}(K_i - 1)} : \quad x_1 = 0.318, x_2 = 0.111, x_3 = 0.571$$

$$\text{Vapor composition: } y_i = K_i x_i : \quad y_1 = 0.888, y_2 = 0.038, y_3 = 0.074$$



Example from:
S. Skogestad,
Prosessteknikk, 3. utgave,
Tapir, 2009, page 57

Single-stage **batch** distillation = Differential flash (**Dynamic!**)

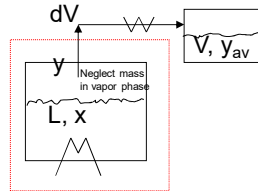
- Ch. 11.3D (see also exercise)

- L = amount of liquid in still [mol]
- V = amount of vapor product [mol]

- Over short time dt: Evaporate amount dV

- Balance over still for short time dt:

- Total: $dL = 0 - dV$ [mol]
- Component: $d(xL) = 0 - y dV$ [mol A]



- Get

$$\begin{aligned} x dL + L dx &= y dL \\ L dx &= (y-x) dL \\ dx/(y-x) &= dL/L \end{aligned}$$

Integrate: Get Rayleigh equation: $\int_{L_0}^{L_1} \frac{dL}{L} = \ln \frac{L_1}{L_0} = \int_{x_0}^{x_1} \frac{dx}{y-x}$ ($y=f(x)$ from VLE)

- Comments:

1. Multistage batch distillation with reflux is common in industry – see lab. exercise
2. Single-stage batch distillation is more “efficient” than (continuous steady-state) flash. For example, need to vaporize less (smaller V/F) for a given separation. See Exercise.

- Steam distillation (usually for separating organic components):

- Add water (nonsoluble) to feed mixture
- Water makes separate liquid phase
- Get low temperature (similar to vacuum distillation) because water reduces partial pressure

- Solution:

- **Question 1.** 1 liter coke contains $n=5g / 44g/mol = 0.114$ mol CO₂
- Assuming ideal gas this corresponds to (at 298K and 1 bar): $V = nRT/p = 0.114 \cdot 8.31 \cdot 298 / 1 \cdot e5 = 0.028$ m³ = **2.8 liter**
- **Question 2.**
- x_{CO_2} = mole fraction CO₂ in liquid
- From data (0.5 wt% CO₂): $x_{CO_2} = 0.5g/44g/mol / (95g/18g/mol + 5g/44g/mol) = 0.0021$
- Partial pressure of CO₂ from Henry's law: $p_{CO_2} = x_{CO_2} \cdot p_{CO_2}^* = 0.0021 \cdot 1670 \text{ bar} = 3.5 \text{ bar}$
- Partial pressure of H₂O from Raoult's law: $p_{H_2O} = x_{H_2O} \cdot p_{sat}(H_2O) = 0.998 \cdot 0.03 \text{ bar} = 0.03 \text{ bar}$
- Total pressure, $p = p_{CO_2} + p_{H_2O} = 3.5 \text{ bar} + 0.03 \text{ bar} = \mathbf{3.53 \text{ bar}}$
- google: Typical filling pressure for CO₂ is about 8 bar (but equilibrium is not reached)