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- and 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!

Fick's law (Mass transfer by diffusion):

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

To get mass flow \( \dot{m}_A [\text{kg/s}] \) multiply by \( S [\text{m}^2] \cdot M_A [\text{mol/kg}] \):

\[ \dot{m}_A = -D_{AB} \cdot \rho \frac{dA}{dz} S \left[ \frac{\text{kg}}{\text{s}} \right] \]

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

Typical data liquid: \( D_{AB} = 10^{-9} \text{ m}^2/\text{s} \cdot \frac{1}{\text{m}^2} = 10^{-6} \text{ m}^2/\text{s} \)

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

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

Process applications: Want \( m_A \approx 1 \text{ kg/s} \). Need \( S/\Delta z \) a factor 10^6 larger!!

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

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

Class quiz (1)

1. How much CO2 gas [liter] in 1 liter 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 \( n=5g / 44g/mol = 0.114 \text{ mol CO2} \)

   • Question 2.

   • \( x_{wq} = \text{mole fraction CO2 in liquid} \)
   • From data (0.5 wt% CO2): \( x_{wq} = 0.5g/44g/mol / (95g/18g/mol + 5g/44g/mol) = 0.0021 \)
   • 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

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

**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!

![Diagram of gas (vapor) and liquid 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: \( p = p_A + p_B + \cdots \)

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

- Relative volatility, \( \alpha \) (11.3B)
  \[
  \alpha = \frac{K_A}{K_B} = \frac{y_A/x_A}{y_B/x_B}
  \]
  Raoult's law: \( \alpha = \frac{p_A^{\text{sat}}(T)}{p_B^{\text{sat}}(T)} \)

\( \alpha \) can often be assumed constant (ideal mixture of similar components)!
VLE diagrams. Binary mixture

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

Constant relative volatility

- Binary mixture: \( \alpha = \frac{y_A}{x_A} = \frac{y_b}{x_b} = \frac{y}{x} = \frac{(1-y)}{(1-x)} \) \( \Rightarrow y = \frac{\alpha x}{1+(\alpha-1)x} \)

xy-diagram

\( \alpha = 6 \)
\( \alpha = 3 \)
\( \alpha = 1.5 \)
\( \alpha = 1 \) (y=x; 45° line)
**Ideal mixture:**

**Estimate of relative volatility**  (Sigurd’s method)

\[
\ln \alpha \approx \frac{\Delta H_{vap}^L}{RT_B} \cdot \frac{\Delta T_B}{T_B}
\]

typical: \(\approx 9 - 15\)

- \(\Delta H_{vap}\) - avg. heat of vap. at \(T_B\) [kJ/mol]
- \(\Delta T_B\) - 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)

\[T_L = 301.0 \text{ K}, \quad \Delta H_{vap}^L = 25 \text{ kJ/mol},\]
\[T_H = 309.2 \text{ K}, \quad \Delta H_{vap}^H = 27 \text{ kJ/mol},\]
\[\Delta T_B = 8.2 \text{ K}, \quad T_B = \sqrt{301 \cdot 309.2} = 305.1 \text{ K},\]
\[\ln \alpha = \frac{\sqrt{25 \cdot 27 \cdot 1000}}{8.31 \cdot 305.1} \approx 0.275; \quad \alpha \approx 1.32\]

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**Binary mixture**

**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

xy-diagrams (here: \(A\) = “light” component = with lowest boiling point):
Ethanol-water at 1 atm: Minimum-boiling azeotrope at about $x_1 = 0.90$ (96 liquid volume-%)


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

Given pressure

Binary mixture

- **Ideal mixture**
- **Non-ideal**
- **Difficult separation**
  - (almost az.)
- **Easy sep.**
- **Azeotropes**
  - (non-ideal)
  - less common high-boiling az.
- **common low-boiling az.**

xy-diagrams:

- Equilibrium line $y = f(x)$
- Maximum Boiling Point
- Minimum Boiling Point
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 \( p = 1 \text{ atm} \): System is uniquely determined (cannot specify T)
2. Given \( x_{\text{ethanol}} = y_{\text{ethanol}} \) (azeotrope) and \( p = 1 \text{ atm} \): 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,...,\( N_c \))
  - \( K_i \) given function of \( p, T, x_i, y_i \)
  - \( N_c \) Component balances (In=Out, steady-state)
    - \( Fx_i = Ly_i + Vy_i \) (mol/s) (i=1,2,...,\( N_c \)) [mol/s]
  - 2 summation equations:
    - \( \sum x_i = x_1 + x_2 + x_3 + ... = 1 \)
    - \( \sum y_i = y_1 + y_2 + y_3 + ... = 1 \)
    - [Also have total material balance \( F = L + V \) but not independent from the others]
  - 1 energy balance (In=Out) *
    - \( H + Q = H_L + H_V \) (kJ)
  - In total: \( 2N_c + 3 \) independent equations

- **Unknowns with given feed \( F, x_F, y_F \):**
  - \( 2N_c + 5 \) unknowns \( x_i, y_i, V, L, T, Q \)
- **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 $a$, see exercise) or graphical solution (any $V/F$, book 11.2)
   - Special cases:
     - 1A. Bubble point at given $p$ ($V/F=0$)  
       \[ pT-Flash \]
     - 1B. Dew point at given $p$ ($V/F=1$)  
       \[ pH-Flash \]

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 $p + H$ ($H=H_0=enthalpy$ of feed for adiabatic flash)
   - Tank, adiabatic flash
   - Generally, need energy balance to find $L$ and $V$:
     \[ \Delta H = H_L + H_V + Q \]  
   - Usually requires computer (Aspen, Hypros, Univim, ...)
   - Example: Stage in distillation column; $p$ flash = $p$/$V/F$-flash; if we know liquid fraction in feed streams $+ assume constant rotor flows$

5. Specify $p + S$
   - Compressor

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Flytskjema Statfjord A

Compressors: Calculated as $pS$-“flash”  
(given $p$ and constant entropy)
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
  I. Analytical solution / hand calculations (see below and exercise)
  II. Graphical solution (see below)
  III. 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

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### Binary mixture

1. p+V/F-flash

I. Analytical solution (const. $\alpha$)

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: $75 = 70x + 80 \times \frac{6x}{1+5x}$

\[ 350 x^2 + 175 x - 75 = 0 \]
\[ x = 0.2761 \]
\[ y = 0.6959 \]
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")
     - \( y = f_2(x) = -\frac{L}{V} x + \frac{F}{V} x F = -\frac{q}{1-q} x + \frac{1}{1-q} x F \)

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

**Dew and bubble point**

- Numerical example. See exercise, Problem 2

**Case 2A**

**Case 1B**

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

(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, \( K_i = p_{sat}(T)/p \)
- Combine mass balance and VLE:
  - \( Fx_i = Lx_i + VKx_i \)
  - Solve for \( x_i \):
    - \( x_i = Fx_i / (F+V+VK) \) or \( x_i = x_i / [1 + V/F(K_i-1)] \)
  - Need to find \( V/F \)...(iterative solution = «trial and error»)
    - Book 11.7C-3: Use \( x_F = 1 \).
    - Often better: Use \( \sum y_i - \sum x_i = 0 \) — Rachford-Rice equation to get convex function in \( V/F \):
      \[
      \sum_i \frac{x_F(K_i-1)}{1 + p(K_i-1)} = \frac{x_F(K_1-1)}{1 + p(K_1-1)} + \frac{x_F(K_2-1)}{1 + p(K_2-1)} + \cdots = 0
      \]

3. Example pT-flash: Numerical solution

**Problem.**
Feed: \( F = 1 \) mol/s, 40 mole% propane (1), 10% pentane (2), 50% hexane (3)
Flash at \( T = 356 \) 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 (\( K_i = p_{sat}/p \)): \( K_1 = 2.792, K_2 = 0.3931, K_3 = 0.1299 \)
- Find \( V/F \) from Rachford-Rice by iteration. Want: LHS = 0.
1. First try: \( V/F=0 \):
   \[
   \text{LHS} = \sum \frac{x_F(K_i-1)}{1 + p(K_i-1)} = 0.4 \cdot 1.792 + 0.1 \cdot (-0.601) + 0.5 \cdot (-0.870) = 0.2154
   \]
2. Second try: \( V/F = 0.1 \):
   \[
   \text{LHS} = \frac{0.4 \cdot 1.792}{1 + 0.1 \cdot 2.792} + \frac{0.1 \cdot (-0.601)}{1 + 0.1 \cdot 2.792} + \frac{0.5 \cdot (-0.870)}{1 + 0.1 \cdot 2.792} = 0.0697
   \]
3. Further "trial and error" gives finally \( V/F = 0.1436 \):
   \[
   \text{LHS} = \frac{0.4 \cdot 1.792}{1 + 0.1 \cdot 2.792} + \frac{0.1 \cdot (-0.601)}{1 + 0.1 \cdot 2.792} + \frac{0.5 \cdot (-0.870)}{1 + 0.1 \cdot 2.792} = 0
   \]
- With \( V/F = 0.1436 \) we then find:
  - Liquid composition: \( x_1 = \frac{x_F}{1 + 0.1436(K_i-1)} \): \( x_1 = 0.318, x_2 = 0.111, x_3 = 0.571 \)
  - Vapor composition: \( y_i = K_i x_i \): \( y_1 = 0.888, y_2 = 0.038, y_3 = 0.074 \)
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:
  - \( \text{Acc} = \text{In} - \text{Out} \)
  - Total: \( dL = 0 - dV \) [mol]
  - Component: \( (xL) = 0 - y dV \) [mol A]
- Get
  \[
  x dL + L dx = y dL
  \]
  \[
  dx/(y-x) = dL/L
  \]
  Integrate: Get Rayleigh equation: 
  \[
  \int_{L_0}^{L_1} \frac{dL}{L} = \ln \frac{L_1}{L_0} = \int_{x_0}^{x_1} \frac{dx}{y-z}
  \]

- 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.
- Question 2.