3.1 Separation and entropy
Separation process and entropy /1

- Separation processes involve de-mixing of species or phases, in thermodynamic sense resulting in a decrease of the total entropy of these
- $\sum$ Entropy of components or phases < Entropy of mix
- One way of accomplishing a separation is to create more phases; Gibbs’ phase rule gives for the degrees of freedom, $f$, for a system of $p$ phases and $n$ components: $f = n + 2 - p$. $f\uparrow$ gives $\Delta S\uparrow$; $f\downarrow$ gives $\Delta S\downarrow$.
- A new phase can be created by 1) adding a new component (absorption/desorption, extraction), or 2) by adding or removing energy (e.g. heat) (distillation, crystallisation)
- Creating an "un-equilibrium" gives rise to a separation (or a chemical reaction) if $\Delta G = \Delta H - T \cdot \Delta S < 0$, or $\Delta S > \Delta H / T$

Separation process and entropy /2

Steady-state mass balance, 1st Law, 2nd Law:

$m_{\text{mix}} = m_A + m_B$
$m_{\text{mix}} \cdot h_{\text{mix}} + Q_{\text{in}} = m_A \cdot h_A + m_B \cdot h_B + Q_{\text{out}}$

$\frac{Q_{\text{out}}}{T_{\text{out}}} + m_A \cdot s_A + m_B \cdot s_B \geq \frac{Q_{\text{in}}}{T_{\text{in}}} + m_{\text{mix}} \cdot s_{\text{mix}}$

$\Rightarrow \frac{Q_{\text{out}}}{T_{\text{out}}} - \frac{Q_{\text{in}}}{T_{\text{in}}} \geq m_{\text{mix}} \cdot s_{\text{mix}} - m_A \cdot s_A - m_B \cdot s_B$

Distillation

Crystallisation
Separation process and entropy /3

- Clearly, some entropy must be produced to
  1) compensate for $\Delta S < 0$ resulting from the separation, and
  2) create some driving force $\Delta G < 0$, $\Delta S > \Delta H/T$.

- Proper engineering requires minimisation of this entropy production $\Delta S$ and the exergy losses $T^\circ \cdot \Delta S$, and balancing this against economical considerations.

- It was found that a uniform production of entropy is preferable: the equipartitioning principle (TK87, B97, SAKS04) – see also macroscopic organisation in natural processes!

- For example, for a heat exchanger this implies that the driving force $\Delta(1/T) = \text{constant}$.

- It can be extended to considering stable, non-equilibrium states $S > S_{\text{min}}$, with stability criterion $dS_{\text{gen}}/dt < 0$.

---

Separation process and entropy /4

- Example taken from TK87
3.2 Binary Distillation I
(the McCabe-Thiele procedure)

Assumed pre-knowledge: Continuous distillation
see course 424302 Massöverföring & separationsteknik, #12
or re-wrap course 424102 Principles of process engineering
(which summarises courses 424101, 424302 and 424300)
Continuous distillation (binary) /1

- Separating a mixture of 2 components A and B, with A more volatile
- Liquid for absorption section produced by condensing some top product
- Gas for stripping section produced by boiling some bottom product

Mass balance and equilibrium: absorption

mass balance: \( V \cdot y_i + L \cdot x_i = V \cdot y_{i+1} + L \cdot x_{i-1} \)

\[ y_i = Kx_i \]

slope \( L/V \)
Mass balance and equilibrium: desorption / stripping

\[ y_i = Kx_i \]

\[ \text{mass balance: } V \cdot y_i + L \cdot x_i = V \cdot y_{i+1} + L \cdot x_{i-1} \]
\[ \rightarrow \text{ working line } y_{i+1} - y_i = \left( \frac{L}{V} \right) (x_{i-1} - x_i) \]

Continuous distillation (binary) /2

- Roughly equimolar exchange:
  1 mol A liquid → gas
  ↔ 1 mol B gas → liquid

- As a result: Gas and liquid streams ~ constant in each section:
  - L and V in top section, L' and V' in bottom section

- Feed enters where it is similar to the mixture inside
Continuous distillation

- Some general considerations and assumptions:
  - The equimolar exchange \( A \leftrightarrow B \) requires balanced energy exchange as well: vaporisation heats of \( A \) and \( B \) should be roughly the same
  - **Pressure** and the **temperature ranges** must be chosen:
    - Below the critical pressures and temperatures of the components
    - The components must be thermally stable (for hydrocarbon fractions of crude oil: below 300 ~ 350°C)
    - The temperature at the top of the column should preferably be > 40°C, allowing for heat transfer with surrounding air or water
  - **Equilibrium data is needed**, + data for feed and products specifications

→ The necessary gas and liquid streams, the number of stages and heat consumption can be calculated

- A simple procedure based on local equilibrium and mass balances was suggested by McCabe and Thiele

### Equilibrium data

**Example:**

\( C_3 \) – \( iC_4 \)

- **Pressures < critical**
  - Pressures allowable for \( C_3 \) – \( iC_4 \): \( p < 37 \text{ bar} \)

- 37 bar boiling points
  - 85 - 140°C: stability OK

Raoults law:

\[
yp_{\text{total}} = xp^°
\]

\[
K = \frac{y}{x} = \frac{p^°}{p_{\text{total}}}
\]
**Equilibrium data**

**Example:**

\[ C_3 - iC_4 / 2 \]

Chose 40°C as the temperature at the condenser.

At \( T_{min} = 40°C \), the vapour pressure of the more volatile component which is \( C_3 \) = 14 bar \( \rightarrow p \geq 14 \) bar

Then \( T_{boil} \approx 81°C \) for \( iC_4 \)

---

**Binary distillation, McCabe-Thiele /1**

- The McCabe-Thiele \( x, y \) diagram procedure for continuous binary distillation is **limited** to cases where the vapour and liquid mass flows are \( \approx \) **constant** in both the top and bottom section of the column.

- This requires that the **vaporisation / condensation heats** for the two components are \( \approx \) **the same**, and that mixing heat effects are negligible.

- For example \( \text{EtOH/H}_2\text{O}: \Delta_{vap} h(\text{EtOH}) \approx \Delta_{vap} h(\text{H}_2\text{O}) \approx 40 \text{ kJ/mol} \)
  \( \rightarrow \) elementary courses (e.g. \( \text{ÅA424302, Z12} \))

*Pic: WK92*
Binary distillation, McCabe-Thiele /2

- $q =$ fraction of feed that gives liquid on the feeding tray: $L' = L + q \cdot F$
- $F \cdot q = \Delta L$ and $F \cdot (1-q) = \Delta V$
- $q$ is related to the energy needed to convert the feed completely into vapour. With enthalpies $H$ for saturated liquid and saturated gas it is found that:

$$q = \frac{H_{G,\text{sat}} - H_F}{H_{G,\text{sat}} - H_{L,\text{sat}}}$$

---

Binary distillation, McCabe-Thiele /3

- The McCabe-Thiele $x,y$ diagram procedure is thus based on mass balances (giving straight operating lines) and chemical equilibrium data.
- If this method cannot be used, a graphical method based on enthalpy – composition ($h,x$ or $h,\xi$) diagrams as given by Ponchon – de Savarit can be used, based on local equilibrium, mass balances and energy balances.

→ elementary courses (e.g. ÅA424302, Z12)
Restrictions McCabe-Thiele method

- Molar heats of vaporisation should not differ more than ~10%
- Heats of dissolution or mixing are negligible
- Relative volatilities should be $1.3 < \alpha < 5$
- Reflux ratio’s ($\rightarrow L/V$) should be $R > 1.1 \cdot R_{\text{min}}$
- Number of trays $N \ll 50$ preferably
- Otherwise: operating lines are presumably not straight
  use a more exact method that includes an energy balance

Source: CR83
Mixing heat for binary mixtures

For this mixing process:
\[ h = \xi \cdot h_a + (1-\xi) \cdot h_b + q_{\text{mix}} \]

with mixing heat \( q_{\text{mix}} \) to keep temperature constant

Mixing heat data can be used to produce \( h, x \) or \( h, \xi \) diagrams

\[ \xi = \text{mass fraction for the most volatile compound} \]
\[ x = \text{molar fraction for the most volatile compound} \]

With molar masses \( M_a \) and \( M_b \):
\[ x = \frac{1}{1 + \frac{1 - \xi}{\xi} \frac{M_b}{M_a}} \]
\[ \xi = \frac{1}{1 + \frac{1 - x}{x} \frac{M_a}{M_b}} \]

Mixing heat, \( h, \xi \) diagram /1

↑ Mixing heat data for NH\(_3\)-H\(_2\)O and for EtOH-H\(_2\)O (liq)

Schematic \( h, x \) or \( h, \xi \) diagram → for three temperatures (\( t_1, t_2, t_3 \))
Mixing heat, $h, \xi$ diagram /2

- Determination of heat of mixing, $q_{\text{mix}}$, versus composition, $\xi$: a boiling liquid mixture (mass $m$, composition $\xi_f$, enthalpy $h_f$) is fed into a calorimeter; a small amount of heat $dq$ gives a small amount of vapour, $dm$ (composition $\xi_d$, enthalpy $h_d$)

- Mass balance, heat balance:

\[
m \xi_f = dm \xi_d + (m - dm)(\xi_f + d\xi_f)
\]

\[
m h_f + dq = dm h_d + (m - dm)(h_f + dh_f)
\]

gives (eliminate $m$) $q_{\text{mix}} = dq/dm = h_d - h_f - (\xi_d - \xi_f) \frac{dh_f}{d\xi_f}$

Mixing heat, $h, \xi$ diagram /3

- Construction of condensation line from boiling line, heat of vaporisation and heat of mixing
- For point $P$, which demixes into liquid $F$ and gas $D$, the relative amounts are $G/L = FP/PD$ (lever rule)

Schematic $h, \xi$ diagram:
- Condensation line $c$
- Boiling line $b$
- Isotherms $i$

Pics: B01
s,ξ diagram

- For 2nd Law analysis, exergy analysis or for tracking down irreversibilities in mixture applications (for example mixtures of refrigerants) s,ξ or s,x diagrams may be used.

- Note that during adiabatic mixing \( h_{\text{mix}} = h_a + h_b \), but \( s_{\text{mix}} = s_a + s_b + \Delta s_{\text{mix}} \)

\[ s, x \text{ and } \Delta s_{\text{mix}} \text{ for two ideal gases} \]

3.4 Flash vaporisation
Flash vaporisation, h,x diagram /1

- Consider a flash vaporisation process, in which a binary liquid at temperature $T_0$, pressure $p_0$ is brought to a lower pressure $p_1$ using a throttling valve. Temperature drops to $T_1$. Part of the liquid vaporises, giving a vapour that is more rich in the more volatile component.

- Mass balance: $F = G + L$
- Mass balance volatile component: $x_F \cdot F = y \cdot G + x \cdot L$
- Heat balance: $h_F \cdot F = h_G \cdot G + h_L \cdot L$, with heat of vaporisation $\Delta_{vap} h = h_G - h_L$ at $T_0$.

Flash vaporisation, h,x diagram /2

- Initially, at $p_0$ the feed point $A$ with $x = x_F$ is in the liquid region of the h,x diagram.
- After the pressure reduction to $p_1$, point $A$ lies in the 2-phase region, giving liquid (L) $C$ + gas (G) $B$.
- Amount ratio $G/L$ equals $= \frac{CA}{AB}$, or $\frac{G}{L} = \frac{x_F - x}{y - x_F} = \frac{h_F - h_L}{h_G - h_F}$.
Flash vaporisation, example /1

An enthalpy versus concentration diagram for the system ethanol water at 1 atm total pressure is given in Figure 2.11. A mixture containing 60 wt percent ethanol and 40 wt percent water is received with an enthalpy of 400 Btu/lb at high pressure (referred to the same bases as Figure 2-11), and is expanded adiabatically to a pressure of 1 atm. Find the product compositions and flow rates, and the flash temperature.

\[
1 \text{ BTU} = 1055.06 \text{ J} \quad 100 \text{ BTU/lb} = 2.326 \text{ kJ/kg}
\]

\[
220^\circ F = 104^\circ C \quad 170^\circ F = 77^\circ C
\]

\[\text{K71- Fig 2.11} \quad \text{K71- Fig 2.12}\]

\[\text{Pics: K71}\]

Flash vaporisation, example /2

Equilibrium data for this system are shown in Figure 2.12. We know the point representing \( (h_x, z_x) \) on Figure 2-11, and we know that the straight-line connection \( (H_x, y_x) \) and \( (h_x, x_x) \) must pass through that point. Since we have an equilibrium flash, we know that the product composition, enthalpies, and temperature must lie on the saturation curves of Figures 2-11 and 2-12. By trial and error we seek a \( y \) and \( x \) pair from Figure 2-12 which will provide a straight line through the known point on Figure 2-11. The result is \( y_x = 0.76, x_x = 0.425, \) and \( T = 181.4^\circ F \). The product flow rates then come from an application of the lever rule to either Figure 2-11 or Figure 2-12:

\[
L = 0.76 - 0.60 \quad V = 0.60 - 0.425 \quad W = 0.91
\]

\[\text{Lever rule – see for example:}\]

http://www.doitpoms.ac.uk/tlplib/phase-diagrams/lever.php

\[\text{Pics: K71}\]
3.5 Binary Distillation II
(the Ponchon-Savarit method)

Ponchon-Savarit method /1

- Continuous distillation
- Feed \( F(\text{kg/s}), x_f \) (kg/kg)
- Top product \( D, x_d \)
- Bottom product \( W, x_w \)
- Upward vapour flows \( V \) (kg/s), downward liquid flows \( L \) (kg/s)
- Liquid mass fractions \( x \), vapour mass fractions \( y \)
- Reboiler heat input \( Q_B \) (kW), condenser heat output \( Q_C \) (kW)

Top section I, index \( n \) (downwards)
Bottom section II, index \( m \) (downwards)
Ponchon-Savarit method /2

- $H^L$ and $H^V$ are enthalpies of liquid and vapour streams (kJ/kg)
- Mass balances top section stages (total, and for the most volatile species of the two)

\[
V_n = L_{n-1} + D
\]
\[
V_n - L_{n-1} = D
\]
\[
V_n y_n = L_{n-1} x_{n-1} + D x_d
\]
\[
V_n y_n - L_{n-1} x_{n-1} = D x_d
\]

Ponchon-Savarit method /3

- Heat balances (top section)

\[
V_n H^V_n = L_{n-1} H^L_{n-1} + D H^L_d + Q_C
\]
\[
V_n H^V_n - L_{n-1} H^L_{n-1} = D H^L_d + Q_C
\]

- $H^L_d = H$ of liquid $D$ ($x = x_d$)

- Constant $H'_d = H^L_d + Q_C/D$:

\[
V_n H^V_n = L_{n-1} H^L_{n-1} + D H'_d
\]
\[
V_n H^V_n - L_{n-1} H^L_{n-1} = D H'_d
\]
Ponchon-Savarit method /4

- From the mass balances *)
  \[ \frac{L_{n-1}}{D} = \frac{x_d - y_n}{y_n - x_{n-1}} \]

- From mass balance *) and heat balances **)
  \[ \frac{L_{n-1}}{D} = \frac{H_d' - H_n^V}{H_n^V - H_{n-1}^L} \]

\[ \rightarrow \]

\[ \frac{H_d' - H_n^V}{H_n^V - H_{n-1}^L} = \frac{x_d - y_n}{y_n - x_{n-1}} \]

Functions \( y_n(x_{n-1}) \) are all lines that go through point (pole) \( N = (x_d', H_d') \) in the \((x,H)\) plot.

---

Ponchon-Savarit method /5

- The lines \( y_n(x_{n-1}) \) can be put in the \( h,x \) or \( h,\xi \) diagram (see next slide).
- Similarly, mass and heat balances for the bottom section:
  \[ V_m + W = L_{m-1} \]
  \[ -V_m + L_{m-1} = W \]
  \[ V_m y_m + W x_w = L_{m-1} x_{m-1} \]
  \[ -V_m y_m + L_{m-1} x_{m-1} = W x_w \]
  \[ V_m H_m^V + W H_w^L = L_{m-1} H_{m-1}^L + Q_B \]
  \[ -V_m H_m^V + L_{m-1} H_m^L = WH_w^L - Q_B \]
Ponchon-Savarit method /6

- \( H_{w}^{L} = H \) of liquid \( W \)
  \( (x = x_{w}) \)
- Constant
  \( H'_{w} = H_{w}^{L} - Q_{B}/W \)
- This then gives
  \[ -VH_{m}^{V} + L_{m-1}H_{m-1}^{L} = WH'_{w} \]

"leaving" system via bottom:
\( W \cdot H_{w}^{L} - Q_{B} \)

Functions \( y_{m}(x_{m-1}) \), all lines go through point (pole)
\( M = (x_{w}, H'_{w}) \) in \((x,H)\) plot

Ponchon-Savarit method /7

- A stream \( N \) can be visualised with composition \( x_{d} \), enthalpy \( H'_{d} \), mass \( V_{n} - L_{n-1} \)
- Similarly, \( M \) can be visualised as a stream with composition \( x_{w} \), enthalpy \( H'_{w} \), mass \( L_{m-1} - V_{m} \)
- Then also: \( F = M + N \), and \( F \cdot x_{F} = M \cdot x_{w} + N \cdot x_{d} \) Pic: CR83
### Ponchon-Savarit method /8

- The necessary number of theoretical stages can be determined graphically as shown →
- Feed point F is shown on the boiling line (here, q = 1)
- \( V_1 \) is vapour from first plate, \( L_1 \) is liquid from first plate to second plate, et c.

Here, 7 theoretical stages needed.  Pic: CR83

### Ponchon-Savarit method /9

- The heat removed in the condenser per unit mass \( D \) is \( q_c = Q_c / D \).
- Lowering \( N \) → \( N' \) means that more stages are needed
- At \( N \) → \( N_m \) the number of stages → \( \infty \)

Here, 7 theoretical stages needed.  Pic: CR83
Ponchon-Savarit method /10

- Using $q_c = Q_c/D$ and

$$\frac{H'_d - H'_n}{H'_n - H'_{n-1}} = \frac{x_d - y_n}{y_n - y_{n-1}}$$

the minimum heat requirements can be found:

$$\frac{H'_{n-1} + q_c - H'_n}{H'_n - H'_{n-1}} = \frac{x_d - y_n}{y_n - x_{n-1}}$$

$$q_c = (H'_n - H'_{n-1}) \left( \frac{x_d - y_n}{y_n - x_{n-1}} \right) + H'_n - H'_d$$

$$(q_c)_{\text{min}} = (H'_f - H'_{f-1}) \left( \frac{x_d - y_f}{y_f - x_f} \right) + H'_f - H'_d$$

Increasing the reflux ratio requires more heat to be removed, → point N upwards, reducing the number of stages

Pic: CR83

---

Ponchon-Savarit method Example /1

It is required to separate 1 kg/s (3.6 tonnes/h) of a solution of ammonia in water, containing 30 per cent by mass of ammonia, to give a top product of 99.5 per cent purity and a weak solution containing 10 per cent by mass of ammonia.

Calculate the heat required in the boiler and the heat to be rejected in the condenser, assuming a reflux 8 per cent in excess of the minimum and a column pressure of 1000 kN/m². The plates may be assumed to have an ideal efficiency of 60 per cent.

Mass balances

$$D + W = 1.0$$

$$0.995D + 0.1W = (1.0 \times 0.3)$$

$$D = 0.22 \text{ kg/s}$$

$$W = 0.78 \text{ kg/s}$$

Source: CR83
Ponchon-Savarit method Example /2

\[ h, \xi \text{ diagram} \]
\[ \text{NH}_3-\text{H}_2\text{O} \]
\[ 1.013 \text{ MPa} = 10 \text{ atm} \]

*Source: CR83*

---

Ponchon-Savarit method Example /3

\[ N_m \text{ for minimum reflux is found by drawing a tie-line through F, representing the feed, to cut the line } x = 0.995 \text{ at } N_m. \]

\[ \gamma \]
\[ \text{The minimum reflux ratio, } R_m = \frac{\text{length } N_mA}{\text{length } AL} = \frac{(1952 - 1547)}{(1547 - 295)} = 0.323 \]

Since the actual reflux is 8 per cent above the minimum, then:

\[ \gamma \]
\[ NA = 1.08 \times N_mA = 1.08 \times 405 = 437 \]

Point N therefore has an ordinate of \((437 + 1547) = 1984\) and an abscissa of 0.995.

Point M is found by drawing NF to cut the line \(x = 0.10\), through W, at M.

The number of theoretical plates is found, as on the diagram, to be 5+.

The number of plates to be provided = \((5/0.6) = 8.33\), say 9.

The feed is introduced just below the third ideal plate from the top, or just below the fifth actual plate.

\[ \gamma \]
\[ \text{The heat input at the boiler per unit mass of bottom product is:} \]
\[ \frac{Q_b}{W} = 582 - (-209) = 791 \]

Heat input to boiler = \((791 \times 0.78) = 617 \text{ kW}\)

Condenser duty = \(\text{length } NL \times D\)

\[ = (1984 - 296) \times 0.22 = 372 \text{ kW} \]

*Source: CR83*
3.6 Ideal distillation column analysis

Analysis of ideal column /1

- Exergy analysis shows that the minimum work for separation of 1 mol of mixture equals
  \[ w_{\text{min}} = \Delta \text{ex} = T^\circ \cdot \Delta s \]
- For distillation with reboiler heat \( Q_{\text{in}} \) and condenser heat \( Q_{\text{out}} \), the exergy loss \(-\Delta \text{Ex}\) can be approximated as
  \[ -\Delta \text{Ex} = Q_{\text{in}} \cdot T^\circ \cdot \left( \frac{1}{T_{\text{top}}} - \frac{1}{T_{\text{bottom}}} \right) \]
  (if \( H_F \approx H_B + H_D \))

Thus, the separation is accomplished by degrading \( Q_{\text{in}} \) at \( T_{\text{in}} \) to \( Q_{\text{out}} (= Q_{\text{in}}) \) at \( T_{\text{out}} < T_{\text{in}} \)

Pic: SAKS04
Analysis of ideal column /2

- The **Clausius Clapeyron** expression for phase transitions based on the slope of the two-phase co-existence (boiling) curve in a \( p-T \) diagram,

\[
\frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta v_{ap}H}{(T\Delta V)}
\]
gives for ideal gases:

\[
\left( \frac{dp}{p} \right)_{sat} = \frac{\Delta v_{ap}H}{R} \cdot \frac{dT}{T^2} \Rightarrow \ln \frac{p_{sat,1}}{p_{sat,2}} = -\frac{\Delta v_{ap}H}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]

- Also, for an ideal mixture the relative volatility for two similar* components is

\[
\alpha_{12} = \frac{p_{sat,1}}{p_{sat,2}}
\]

* Chemically similar, boiling points not too far apart, \( \alpha \sim \mathcal{O}(1) \)

Analysis of ideal column /3

- This then gives, for the distillation temperature range \( (T_{top}, T_{bottom}) \):

\[
\ln \alpha_{12} = -\frac{\Delta v_{ap}H}{R} \left( \frac{1}{T_{bottom}} - \frac{1}{T_{top}} \right)
\]

- which if \( \alpha \sim 1 \), and using \( \ln(1+z) \approx z \) if \( z \ll 1 \), it simplifies to:

\[
\alpha_{12} - 1 = -\frac{\Delta v_{ap}H}{R} \left( \frac{1}{T_{bottom}} - \frac{1}{T_{top}} \right)
\]

This requires that
- heat \( Q_{in} \) is supplied using a Carnot heat pump
- heat \( Q_{out} \) is converted into work in a Carnot process,
- minimum reflux is used

Pic: SAKS04
Analysis of ideal column /4

- Assume a propane C3, propene C3 = distillation with $x_F = \frac{1}{2}$, $q = 1$, $B/F = D/F = \frac{1}{2}$ (mol/s)/(mol/s)

- **Note**: for this equimolar mix, $\Delta s_{mix}$ is at its maximum (if ideal)

- Then per mole of feed, $L/F = r \cdot D/F = \frac{1}{2} \cdot r$, $(r = \text{reflux ratio}^* = L/D)$ above the feed, $L/F = (\frac{1}{2} \cdot r + 1)$ below the feed, and $V/F = \frac{1}{2} \cdot (r + 1)$ in the whole column.

- Then the heat input at the reboiler is equal to $Q_{in}/F = V/F \cdot \Delta_{vap}H = \frac{1}{2} \cdot (r+1) \cdot \Delta_{vap}H \approx Q_{out}/F^*$

- Using "r" to distinguish it from gas constant R.

Analysis of ideal column /5

- The **minimum work** required to separate the mixture can be found by considering a heat pump between $T_{out}$ and $T_{in}$ – see Figure – and exergy analysis gives (per mole feed): $W_{sep} = -R \cdot T^o \cdot \sum x_i \cdot \ln x_i = R \cdot T^o \cdot \ln 2$ for an equimolar mixture

- This can be used to define the minimum reflux ratio $r_{min}$:
  
  $$
  W_{sep}^* = -R \cdot T^o \cdot \sum_i x_i \cdot \ln x_i = W_{min}^* = \frac{Q_{in}^*}{F} \cdot T^o \left( \frac{1}{T_{top}} - \frac{1}{T_{bottom}} \right)
  $$

  $$
  \Rightarrow \frac{Q_{in}^*}{F} = \frac{1}{2} \cdot (r_{min} + 1) \cdot \Delta_{vap}H \Rightarrow \ r_{min} = \frac{2 \ln 2}{\ln \alpha_{12}} - 1 \quad (\alpha < 4 !)
  $$

  Pic: SAKS04

100% efficient! (reversible)
3.7 Real distillation column analysis I: efficiency

Analysis of real column /1

- What will be the **efficiency** of a real column for this case?
- Heat transfer requires temperature differences!
- $Q_{in}$ is supplied at 377K, $Q_{out}$ goes out at 298K
- The minimum heat input for the separation is
  
  $Q_{min} / F = \frac{1}{2} \cdot (r_{min} + 1) \cdot \Delta_{vap} H$ with $r_{min} = 9.64$ ($\alpha_{12} \approx 1.14$), per mole feed
- Deviations from ideal thermodynamics $\rightarrow r_{real} = 15.9$ ($\alpha_{12} \approx 1.09$)
  
  $Q_{real} / F = \frac{1}{2} \cdot (r_{real} + 1) \cdot \Delta_{vap} H$

$r_{real} / r_{min} = 1.65$  

Pic: SAKS04
Analysis of real column /2

- Bottom section $\Delta T = 46$ K, top section $\Delta T = 22$ K
- The total thermodynamic efficiency of the column is calculated as:

\[
\eta_{\text{overall}} = \frac{Q^{\text{min}} \Delta \left(\frac{1}{T}\right)_{\text{column}}}{Q_{\text{in}} \left[\Delta \left(\frac{1}{T}\right)_{\text{bottom}} + \Delta \left(\frac{1}{T}\right)_{\text{column}} + \Delta \left(\frac{1}{T}\right)_{\text{top}}\right] T_0}
\]

which gives $\eta_{\text{overall}} = 0.093 = 9.3\%$

- The main sources of the inefficiency are the driving forces $\Delta (1/T)$ in reboiler and condenser
- The ratio $Q_{\text{in}}^{\text{min}}/Q_{\text{in}}^{\text{real}} = 0.63$ reflects exergy losses inside the column

Analysis of real column /3

- The amount of exergy (work) lost in the column + the exergy used for the separation = the difference between the exergies of the reboiler heat and the condenser heat
- For the minimum work (exergy) needed it was shown that

\[
W_{\text{in}}^{\text{min}} = Q_{\text{in}}^{\text{min}} T_0 \left(\frac{1}{T_t} - \frac{1}{T_b}\right)
\]

so that the work (exergy) lost in the column is equal to

\[
W_{\text{lost}} = Q_{\text{in}}^{\text{real}} T_0 \left(\frac{1}{T_t} - \frac{1}{T_b}\right) - Q_{\text{in}}^{\text{min}} T_0 \left(\frac{1}{T_t} - \frac{1}{T_b}\right)
\]

→ see Table on next slide
Analysis of real column /4

- Efficiency of the distillation column: summary

<table>
<thead>
<tr>
<th></th>
<th>Exergy in</th>
<th>Exergy out</th>
<th>Exergy lost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reboiler</td>
<td>$Q_{\text{real}}^\text{in} \left(1 - \frac{T_0}{T_R}\right)$</td>
<td>$Q_{\text{real}}^\text{in} \left(1 - \frac{T_0}{T_b}\right)$</td>
<td>$Q_{\text{real}}^\text{in} T_0 \left(\frac{1}{T_b} - \frac{1}{T_R}\right)$</td>
</tr>
<tr>
<td>Column</td>
<td>$Q_{\text{real}}^\text{in} \left(1 - \frac{T_0}{T_b}\right)$</td>
<td>$Q_{\text{real}}^\text{in} \left(1 - \frac{T_0}{T_T}\right)$</td>
<td>$(Q_{\text{real}}^\text{in} - Q_{\text{min}}^\text{in}) T_0 \left(\frac{1}{T_T} - \frac{1}{T_b}\right)$</td>
</tr>
<tr>
<td>Condenser</td>
<td>$Q_{\text{real}}^\text{in} \left(1 - \frac{T_0}{T_T}\right)$</td>
<td>$Q_{\text{real}}^\text{in} \left(1 - \frac{T_0}{T_0}\right)$</td>
<td>$Q_{\text{real}}^\text{in} T_0 \left(\frac{1}{T_0} - \frac{1}{T_T}\right)$</td>
</tr>
</tbody>
</table>

= Previous table, rated by normalising with $Q_{\text{real}}^\text{in} \left(1 - \frac{T_0}{T_R}\right)$

Pic: SAKS04

Analysis of real column /5

- Efficiency of the distillation column: summary

<table>
<thead>
<tr>
<th></th>
<th>Exergy in</th>
<th>Exergy out</th>
<th>Exergy lost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reboiler</td>
<td>$Q_{\text{real}}^\text{in} \left(1 - \frac{T_0}{T_R}\right)$</td>
<td>$Q_{\text{real}}^\text{in} \left(1 - \frac{T_0}{T_R}\right)$</td>
<td>$Q_{\text{real}}^\text{in} T_0 \left(\frac{1}{T_b} - \frac{1}{T_R}\right)$</td>
</tr>
<tr>
<td>Column</td>
<td>$Q_{\text{real}}^\text{in} \left(1 - \frac{T_0}{T_b}\right)$</td>
<td>$Q_{\text{real}}^\text{in} \left(1 - \frac{T_0}{T_T}\right)$</td>
<td>$(Q_{\text{real}}^\text{in} - Q_{\text{min}}^\text{in}) T_0 \left(\frac{1}{T_T} - \frac{1}{T_b}\right)$</td>
</tr>
<tr>
<td>Condenser</td>
<td>$Q_{\text{real}}^\text{in} \left(1 - \frac{T_0}{T_T}\right)$</td>
<td>$Q_{\text{real}}^\text{in} \left(1 - \frac{T_0}{T_0}\right)$</td>
<td>$Q_{\text{real}}^\text{in} T_0 \left(\frac{1}{T_0} - \frac{1}{T_T}\right)$</td>
</tr>
</tbody>
</table>

= Previous table, rated by normalising with $Q_{\text{real}}^\text{in} \left(1 - \frac{T_0}{T_R}\right)$

Pic: SAKS04
Binary distillation efficiency: overview

Maximum efficiency:

\[ E_{\text{max}} = \frac{W_{\text{min}}}{Q_{\text{min}}} \]

\[ = -RT \left( x \ln x + (1 - x) \ln(1 - x) \right) \]

\[ \frac{\Delta H_{\text{vap}} \left( \frac{1}{x - 1 + x} \right)}{\Delta H_{\text{vap}}} \]

where \( x \) = mole fraction of the more volatile component

Reboiler heat duty:

\[ Q_{\text{REB}} = \Delta H_{\text{vap}} D (r + 1) \]

where \( r \) = reflux ratio, \( D \) = distillate product flow

For \( Q_{\text{REB}} \approx Q_{\text{COND}} \):

\[ W_{\text{heat, dist}} = E_{\text{XREB}} - E_{\text{XCOND}} \]

\[ = Q_{\text{REB}} T_a \left( \frac{1}{T_{\text{COND}}} - \frac{1}{T_{\text{REB}}} \right) \]

Reboiler duty exergy:

\[ E_{\text{XREB}} = Q_{\text{REB}} \left( 1 - \frac{T_a}{T_{\text{Bottoms}} + \Delta T} \right) \]

3.8 Real distillation column analysis II: exergy analysis
Exergy analysis /1

- An analysis can also be made based on exergy flows:
  \[ \text{Ex}_F + \text{Ex}_{Q1} = \text{Ex}_B + \text{Ex}_{Q2} + \text{Ex}_D + \text{Ex}_{\text{lost}} \]

- **Note** that still no enthalpy of mixing is considered, and ideal mixing entropy \(-R \cdot \sum x \cdot \ln x\).

- Flowsheeting programs (should) give values for H’s, S’s, and Q’s, making it easy to calculate exergy streams.

- No chemistry → physical exergy is sufficient!

Exergy analysis /2

- Exergy balance for the equimolar C\(_3\)/C\(_3\) = distillation

  * **reversible case:**
    \[ \frac{1}{2} \left( (h_{C_3} + h_{C_3}) - T_0(s_{C_3} + s_{C_3}) \right) - \frac{1}{2} \left( (h_{C_3} + h_{C_3}) - T_0(s_{C_3} + s_{C_3}) \right) \bigg|_0 - RT_0 \ln 2 + Q_{\text{in}}^\text{min} \left( 1 - \frac{T_0}{T_b} \right) = \frac{1}{2} (h_{C_3} - T_0 s_{C_3}) - \frac{1}{2} (h_{C_3} - T_0 s_{C_3}) \bigg|_0 + Q_{\text{in}}^\text{min} \left( 1 - \frac{T_0}{T_1} \right) \]

  * **real case**
    \[ \frac{1}{2} \left( (h_{C_3} + h_{C_3}) - T_0(s_{C_3} + s_{C_3}) \right) - \frac{1}{2} \left( (h_{C_3} + h_{C_3}) - T_0(s_{C_3} + s_{C_3}) \right) \bigg|_0 - RT_0 \ln 2 + Q_{\text{real}}^\text{in} \left( 1 - \frac{T_0}{T_R} \right) = \frac{1}{2} (h_{C_3} - T_0 s_{C_3}) - \frac{1}{2} (h_{C_3} - T_0 s_{C_3}) \bigg|_0 + \text{Ex}_{\text{lost}} \]
Exergy analysis /3

- Exergy streams for ideal and real case: summary

<table>
<thead>
<tr>
<th>Reversible</th>
<th>Real</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_x_F$</td>
<td>$1/2((h_{C1} - h_{C1}) - T_0(s_{C1} - s_{C1}))$</td>
</tr>
<tr>
<td></td>
<td>$-1/2((h_{C2} - h_{C2}) - T_0(s_{C1} - s_{C1}))$</td>
</tr>
<tr>
<td>$E_x_Q1$</td>
<td>$Q_{min}^{in} \left(1 - \frac{T_0}{T_b}\right)$</td>
</tr>
<tr>
<td>$E_x_B$</td>
<td>$1/2(h_{C1} - T_0s_{C1}) - 1/2(h_{C1} - T_0s_{C1})$</td>
</tr>
<tr>
<td>$E_x_Q2$</td>
<td>$Q_{min}^{in} \left(1 - \frac{T_0}{T_l}\right)$</td>
</tr>
<tr>
<td>$E_x_D$</td>
<td>$1/2(h_{C2} - T_0s_{C2}) - 1/2(h_{C2} - T_0s_{C2})$</td>
</tr>
</tbody>
</table>

Exergy analysis /4

- The main difference between ideal and real performances are $E_x(Q_1)$ and $E_x(Q_2)$; note that $E_x(Q_2) = 0$ in the real case.
- The difference between the two cases as given on the previous two slides is

$$E_{xlost} = +Q_{real}^{in} T_0 \left(1 - \frac{T_0}{T_R}\right) - Q_{min}^{in} T_0 \left(1 - \frac{1}{T_b}\right)$$

or, normalised per unit input exergy:

$$\frac{E_{xlost}}{Q_{real}^{in} T_0 \left(1 - \frac{T_0}{T_R}\right)} = \frac{1}{Q_{real}^{in} T_0 \left(1 - \frac{1}{T_b}\right)} - 1$$

(gives again value 0.907 $\rightarrow$ efficiency 0.093)
Exergy analysis

The analysis showed that the main losses were at the reboiler and the condenser, due to heat transfer over large temperature differences $\Delta T$.

Instead of trying to reduce these $\Delta T$'s, waste heat from another process unit may be available.

→ Heat integration, which at the same time saves steam (for example)

Example: H$_2$O/EtOH distillation

A 5%/95% (w/w) EtOH/H$_2$O mix is to be distilled into a 90% EtOH top product and pure water bottom product.

Feed (18 kg/s) and bottom product (17 kg/s) exchange heat: feed is heated 20 → 70°C; bottom product cools 100 → 48.3°C; the heat exchanged is 3690 kJ/kg top product (1 kg/s).

The reflux cooling heat $q_r = 2640$ kJ/kg top product; the heat reboiler $q_b = 5620$ kJ/kg top product

Temperatures $q_r = 79°C$; $q_b = 104°C$

$m \cdot c_p$ (top) = 1·2.6 kJ/K, $m \cdot \Delta_{vap} H$ (top) = 980 kJ
$m \cdot c_p$ (bottom) = 17·4.2 kJ/K

Source: B01, H84
Example: H₂O/EtOH distillation /2

- The **minimum work** needed for making a 90% EtOH mix from a 5% EtOH mix: see the mass balance in moles.

- The mole fractions for water are 0.9798 for the feed, 0.2212 for the distillate and 1.00 for the bottom product; this then gives with the molar amounts as indicated:

\[
\Delta E = RT_0 \left( 5,555 \ln \frac{0.9798}{0.2212} + 944,44 \ln 0.9798 + 19,56 \ln \frac{0.0202}{0.7788} \right)
\]

\[
= 186 \text{ kJ/kg}
\]

for the minimum work per kg top product.

![Diagram of mass balance](image)

See section 1.6 of Exergy analysis

Source: B01, H84

---

Example: H₂O/EtOH distillation /3

- Assuming surroundings temperature T° = 293K an exergy analysis can be made (exergy flows per kg top product):

- **Reflux cooler**

\[
2640 \left(1 - \frac{293}{352}\right) = 442 \text{ kJ}
\]

- **Boiling top product**

\[
980 \left(1 - \frac{293}{352}\right) = 164 \text{ kJ}
\]

980 kJ/kg for 10% H₂O + 90% EtOH

- **Top product heat-up**

\[
1.26 \left(79 - 20\right) - 293 \ln \frac{352}{293} = 13 \text{ kJ}
\]

- **Bottom product**

\[
17.42 \left(100 - 20\right) - 293 \ln \frac{373}{293} = 661 \text{ kJ}
\]

- **Bottom product after heat exchange**

\[
17.42 \left(48,3 - 20\right) - 293 \ln \frac{321,3}{293} = 92 \text{ kJ}
\]

Source: B01, H84
Example: $\text{H}_2\text{O}/\text{EtOH}$ distillation

- Assume that the bottom heat $q_b$ is delivered by an ideal (Carnot) heat pump: $5620 \cdot (1-293/377) = 1252 \text{ kJ/kg top product exergy}$
  (Note the difference 5620 \rightleftharpoons 1252!)

- This goes to the cold bottom product (7%), top product (14%), reflux cooler (35%) and separation work (4%), total 60%.

- Thus, $1252 - 896 = 356 \text{ kJ}$ is lost as irreversibilities.

- For the heat exchanger, the losses per kg top product are

  $$293 \left(18.4, \ln \frac{343}{293} - 17.4, 2\ln \frac{373}{321,3}\right) = 286 \text{ kJ}$$

  which means that 70 kJ/kg top product is lost in the column itself; which is \~ 40% of the minimum separation work (186 kJ/kg top product.)  

Source: B01, H84

3.9 Distillation + heat pump and other improvements
One option: feed stream splitting

- Also known as hybrid distillation
- A **membrane** is used to split the feed into two streams, fed into the column at different locations
- Part of the separation is done (less irreversible) by the membrane → lower reflux ratio and/or less stages

A few other options

- Some GENERAL considerations for improving distillation column efficiency:
  - Process control
  - Feed pre-heat
  - Reduce pressure drop by optimising the trays (or packing)
  - Separate to lower purity and combine with another separation process
  - Use intermediate reboilers and condensers, bringing operating lines closer to the equilibrium line (but this may require more stages or trays)
Double columns

- Paraffin /olefin separations are very energy intensive.
- One example is propane / propylene, or $C_3$ (atm. b.p. - 42.1°C) / $C_3^\equiv$ (atm. b.p. - 47.7°C). For a single-column tray column distillation process 150-200 trays would be needed, giving a very high (> 100 m) column, with reflux condensing using air or water.
- A double-column process is preferred, with smaller (shorter) columns, using hot and cold water for condensing (column 2) and reboiling (column 1). Note that reboiler for column 2 = condenser for column 1.

Distillation column + heat pump

- Improved efficiency can be obtained by using a heat pump: the condenser is removed and the reflux is obtained after heat exchange in the reboiler and with the feed, and throttling.
- Drawback: complexity $\rightarrow$ costs...
Distillation column + heat pump /2

- Returning to the EtOH/water distillation (see the end of the previous section): the top product is compressed so that its temperature rises from 79 to 104°C (which implies $p_2 = 2$ bar).
- It can then give off heat to the water in the bottom of the column at 100°C. See points 1, 2, 3, 4 in the $h, \xi$ diagram below.
- The $h, \xi$ diagram gives masses $\delta:\phi:1 = (\ast-4):(\ast-1):(1-4) = 3.7:2.7:1$

Source: B01, H84

Distillation column + heat pump /3

- For the compressor work $w_c = \delta \cdot (h_2-h_1)$, and for the bottom heat exchanger $\Delta q_b = \delta \cdot (h_3-h_2)$ which is then found to be 3580 kJ per kg top product. This is 64% of the conventional process value as in the previous section.
- Note compressor losses; and that stream 3 may be used to preheat the top product before the compressor.

Source: B01, H84
Two-feed distillation

Two-feed, or two-enthalpy feed can

- Allow for lowering the number of stages, \( N \) (same \( L/D, x_D, x_B \))
- Improve the separation, better \( X_D, X_B \) (same \( L/D, N \))
- Allow for lowering reflux ratio \( r = L/D \) (same \( N, x_D, x_B \))
- 50% energy savings possible, but modifications are needed

Source: D04, WP93

Adiabatic versus diabatic distillation

- In conventional distillation, heat is only added/removed at reboiler/condensor; no heat is added/removed on the trays: **adiabatic operation**
- In **diabatic operation**, heat can be added/removed by heat exchange, in principle on each tray
- Heat is removed from each tray above feed, added to each tray below feed. Reboiler much smaller or not needed.
- More complicated (↔ process control), but more efficient: lower entropy production (decreases with increasing heat exchange area)

Source: KBJG10, J10
HIDiC Heat integrated distillation column

- Rectification ("top") section is operated at a higher pressure (= pressure of conventional column) than the stripping ("bottom") section
- Heat is transferred from rectification to stripping section

**Comparison for C₃ / C₃² splitter**

<table>
<thead>
<tr>
<th>Column Height (m)</th>
<th>Conventional</th>
<th>Heat pump (10 bar)</th>
<th>HIDiC (18 bar)</th>
<th>HIDiC (18/13 bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column Diameter (m)</td>
<td>1.5</td>
<td>1.4</td>
<td>2.15</td>
<td>2.15</td>
</tr>
<tr>
<td>Internal Heat Transfer Area (m²)</td>
<td>-</td>
<td>-</td>
<td>399</td>
<td>779</td>
</tr>
<tr>
<td>Number of Tubes</td>
<td>-</td>
<td>-</td>
<td>3</td>
<td>14</td>
</tr>
<tr>
<td>Tube Diameter (m)</td>
<td>-</td>
<td>-</td>
<td>0.7</td>
<td>0.35</td>
</tr>
<tr>
<td>Tube (Triangle) Pitch (m)</td>
<td>-</td>
<td>-</td>
<td>0.8</td>
<td>0.45</td>
</tr>
<tr>
<td>Column Weight (kg)</td>
<td>150000</td>
<td>140000</td>
<td>113000</td>
<td>107000</td>
</tr>
<tr>
<td>Bed Volume (m³)</td>
<td>205</td>
<td>119</td>
<td>224</td>
<td>217</td>
</tr>
</tbody>
</table>

**Final remarks**

Distillation accounts for ~3% of world energy consumption
- Heat integration can give significant energy efficiency improvements (but increased costs, more process control)
- Fully diabatic operation of a distillation column won’t be practically, not all temperature levels will be available
- Most important are the heat exchanger at the lowest and highest trays, these can be integrated using for example a heat pump.
- Maybe integration with other columns is possible
- Further improvement can be obtained by varying column cross sectional area:
  - in a diabatic column rectifier section the vapour flow decreases upwards, in the stripper section it is the opposite

Source: KBJG10, J10
Sources 3


Z87 F. Zuiderweg "Physical separation methods” (in Dutch: Fysische Scheidingsmethoden) TU Delft (1987) (vol. 1)

Z12: Zevenhoven, R. "Massöverföring & separationsteknik” / "Mass transfer & separation technology” course material 424302 (in English !) Åbo Akademi Univ. (2012) Chapter 12

Appendix: h,ξ & x,y diagram

NH₃ – H₂O
6.8 atm

100 PSIA = 6.8 atm
1 BTU/lb mole = 2.326 J/mol

Source: http://www.chemeng.ohio-state.edu/~koelling/523/Appendix_d17.pdf

### n-C₆ - n-C₈

<table>
<thead>
<tr>
<th>T °C</th>
<th>x</th>
<th>HL kJ/mol</th>
<th>y</th>
<th>HG kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>68.7</td>
<td>1</td>
<td>12.99</td>
<td>1</td>
<td>41.87</td>
</tr>
<tr>
<td>69.35</td>
<td>0.9772</td>
<td>13.22</td>
<td>0.9983</td>
<td>42.03</td>
</tr>
<tr>
<td>70</td>
<td>0.9541</td>
<td>13.43</td>
<td>0.9923</td>
<td>42.13</td>
</tr>
<tr>
<td>75</td>
<td>0.8617</td>
<td>15.19</td>
<td>0.9630</td>
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</tr>
<tr>
<td>80</td>
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<td>0.5749</td>
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<td>35.05</td>
<td>0.4925</td>
<td>59.14</td>
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<td>0.0000</td>
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<td>0.3426</td>
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<tr>
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<td>0</td>
<td>41.33</td>
<td>0</td>
<td>68.36</td>
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