Extraction

- separation of a liquid mixture by adding a liquid solvent forming a second phase enriched by some component(s)

Notation:

A … extracted component
B … added solvent
C … original solvent
F … feed
R … rafinate
S … solvent
E … extract

Two cases:

1) immiscible solvents B and C (only A is transported)
2) partially miscible solvents (A is transported, but B and C also a little)

Example: extraction of acetic acid from water solution by adding an ether; after extraction, ether is regenerated by distillation; this is cheaper than distilling water solution of acetic acid directly

Extractors

1) staged
   a. cascade of mixers and separators (settlers)
   b. column with plates (vibration is used to facilitate separation)
2) continuous
   a. packed or spray columns (slow)
   b. centrifuge (fast)

General extractor is described as a general equilibrium stage (see earlier chapter), only enthalpy balance is often neglected (no heat effects). For correction to non-equilibrium → efficiency

Special case – immiscible solvents

- only A crosses the interface
- F and R contain only A+C (phase x)
- S and E contain only A+B (phase y)

It is convenient to use relative mass fractions:

\[ X_A = \frac{m_A}{m_C} = \frac{x_A}{1 - x_A}; \quad x_A = \frac{X_A}{1 + X_A}; \quad m_A = x_A(m_A + m_C) \]
\[ Y_A = \frac{m_A}{m_B} = \frac{y_A}{1 - y_A}; \quad y_A = \frac{Y_A}{1 + Y_A}; \quad m_A = y_A (m_A + m_B) \]

\( m_B \) and \( m_C \) are constant.

**Single stage**

For mass balances we use finite time intervals → no flows only masses

- mass balance of A at steady state:
  \[ m_C X_{AF} + m_B Y_{AS} = m_C X_A + m_B Y_A \]
  or
  \[ m_C (X_{AF} - X_A) = m_B (Y_A - Y_{AS}) \]

- equilibrium relation for A:
  \[ y_A = \psi_A x_A \quad \text{or} \quad Y_A = \varphi_A X_A \]

By using the definition of relative fractions we obtain:

\[ Y_A = \frac{\psi_A}{1 - (\psi_A - 1)X_A} X_A \]

Remark: for low concentrations \( x_A = X_A \) and \( y_A = Y_A \) and thus \( \psi_A = \varphi_A = \text{const} \)

To find \( X_A, Y_A \) we solve the balance and equilibrium equations simultaneously either graphically or algebraically.

**Graphical solution:**

We rewrite the balance of A:

\[ Y_A = - \frac{m_C}{m_B} (X_A - X_{AF}) + Y_{AS} \]

which is an operational line with slope equal to \( -\frac{m_C}{m_B} \) passing through point \( [X_{AF}, Y_{AS}] \).
Algebraic solution:

By combining balance of A and equilibrium relation

\[ m_c X_{AF} + m_B Y_{AS} = X_A (m_c + \psi_A m_B) \quad / \quad \frac{1}{m_c} \]

\[ X_{AF} + \frac{m_B}{m_c} Y_{AS} = X_A \left( 1 + \frac{\psi_A m_B}{m_c} \right) \]

we introduce an extraction factor

\[ \zeta_x = \psi_A \frac{m_B}{m_c} \quad \text{and} \quad \zeta_y = \frac{m_c}{\psi_A m_B} = \frac{1}{\zeta_x} \]

Thus:

\[ X_A = (1 + \zeta_x)^{-1} \left( X_{AF} + Y_{AS} \frac{m_B}{m_c} \right) \]

In general, solution of this equation is by iterations, because \( \zeta_x \) may depend \( X_A \) on through \( \psi_A = \psi_A(X_A) \).

That is, we estimate \( X_A^{(0)} \), then calculate \( X_A^{(1)} \) from the equation, and then use \( X_A^{(1)} \) to calculate \( X_A^{(2)} \), etc. until \( |X_A^{(n+1)} - X_A^{(n)}| < \varepsilon \) where \( \varepsilon \) is small.

For a real stage we have to combine mass balance, equilibrium relation and efficiency. We denote equilibrium composition by stars:

\[ Y_A^* = \varphi_A X_A^* \]

And efficiency is:

\[ E_A = \frac{Y_A - Y_{AS}}{Y_A^* - Y_{AS}} = \frac{X_{AF} - X_A}{X_{AF}^* - X_A^*} \]
Graphical solution

Algebraic solution

1) solution for equilibrium case:
\[ X_A^* = (1 + \zeta_x)^{-1} \left( X_{AF} + Y_{AS} \frac{m_B}{m_C} \right) \]

2) from efficiency we have:
\[ X_A = X_{AF} - E_X(X_{AF} - X_A^*) \]

Repeated extraction (or cross-flow extraction)

- mass balance of A in the entire cascade:
\[ m_C X_{AF} + \sum m_{B,n} Y_{AS} = m_C X_A + \sum m_{B,n} \langle Y_A \rangle \]

or
\[ m_C (X_{AF} - X_A) = \sum m_{B,n} (\langle Y_A \rangle - Y_{AS}) = m_A \]

where \( m_A \) is the mass of A being transferred from phase x to phase y. This equation serves for determining \( m_A \) or \( \langle Y_A \rangle \)
- mass balance of A in the stage \( n \)

\[
m_C X_{A,n-1} + m_{B,n} Y_{AS} = m_C X_{A,n} + m_{B,n} Y_{A,n}; \quad n = 1 \ldots N
\]

or

\[
Y_{A,n} = -\frac{m_C}{m_{B,n}} (X_{A,n} - X_{A,n-1}) + Y_{AS}
\]

which are operational lines with slopes \(-\frac{m_C}{m_{B,n}}\) passing through points \([X_{A,n-1}, Y_{AS}]; \quad n = 1 \ldots N\)

Equilibrium condition (in equilibrium stages):

\[
Y_{A,n} = \varphi_A X_{A,n}; \quad n = 1 \ldots N
\]

Solution of mass balance and equilibrium conditions leads to all \( N \) unknown pairs \( X_{A,n}, Y_{A,n} \).

Graphical solution

- intersection of operational lines and equilibrium curve
- either repeat \( N \) times (if \( N \) is given) or do until a given is reached

Algebraic solution

- the use of combined balance and equilibrium equations with extraction factor \( \zeta_{x,n} \)
- in analogy to one extractor:

\[
X_{A,n} = \left(1 + \zeta_{x,n}\right)^{-1} \left(X_{A,n-1} + Y_{AS} \frac{m_{B,n}}{m_C}\right)
\]

where

\[
\zeta_{x,n} = \zeta_{A,n} \frac{m_{B,n}}{m_C}
\]

- simulation (or control) calculation
- design calculation
  - $X_{A,n}$ is given. $N$ is calculated either for $n = 1, 2, \ldots$ until $X_{A,N}$ is reached or for $n = N, N - 1, \ldots$ until $X_{A,0}$ is reached (more convenient if $\varphi_{A,n}$ depends on $X_{A,n}$).

For a **real cascade** efficiency must be used in addition to mass balance and equilibrium condition.

- for equilibrium we use asterisks:
  \[ Y_{A,n}^* = \varphi_{A,n}X_{A,n}^* \]
- the efficiency is
  \[ E_A = \frac{Y_{A,n} - Y_{AS}}{Y_{A,n}^* - Y_{AS}} = \frac{X_{A,n-1} - X_{A,n}}{X_{A,n-1}^* - X_{A,n}^*} \]

**Graphical solution** (analogous to one stage):

**Algebraic solution**

1) solution for the equilibrium stage $n$:

   \[ X_{A,n}^* = (1 + \xi_{x,n})^{-1} \left( X_{A,n-1} + Y_{AS} \frac{m_B,n}{m_C} \right) \]

2) the use of efficiency:

   \[ X_{A,n} = X_{A,n-1} - E_{A,n}(X_{A,n-1} - X_{A,n}^*) \]

We can introduce **overall efficiency**:

\[ E_C = \frac{N}{N_{\text{real}}} = \frac{\text{number of equilibrium stages}}{\text{number of real stages}} \]

and use it to calculate $N_{\text{real}}$.

**Special case:**

a) $m_{B,n} = \text{const} = m_B$

b) $\varphi_{A,n} = \text{const} = \varphi_A \rightarrow \text{linear equilibrium line}$

then also $\xi_{x,n} = \text{const} = \xi_x = \varphi_A \frac{m_B}{m_C}$
Combined mass balance and equilibrium equation reads:

\[ X_{A,n} = (1 + \zeta_x)^{-1} \left( X_{A,n-1} + Y_{AS} \frac{m_B}{m_C} \right) \]

let us assume for simplicity that the solvent B is pure \( \rightarrow Y_{AS} = 0 \). Then

\[ \frac{X_{A,n}}{X_{A,n-1}} = (1 + \zeta_x)^{-1} \quad \text{or} \quad \frac{X_{A,n-1}}{X_{A,n}} = 1 + \zeta_x \]

For all stages together:

\[ \frac{X_{A,0} X_{A,1} \ldots X_{A,N-1}}{X_{A,1} X_{A,2} \ldots X_{A,N}} = (1 + \zeta_x)^N \]

A more general form with \( Y_{AS} > 0 \) is:

\[ \frac{X_{A,0} - Y_{AS}/\varphi_A}{X_{A,N} - Y_{AS}/\varphi_A} = (1 + \zeta_x)^N \]

**Remark:** A similar formula with efficiency for real stages can be derived.

**Counter-current cascade** (for flow systems)

Mass balance for A in the entire cascade

\[ \dot{m}_C X_{AF} + \dot{m}_B Y_{AS} = \dot{m}_C X_{A,N} + \dot{m}_B Y_{A,1} \]

or

\[ \dot{m}_C (X_{AF} - X_{A,N}) = \dot{m}_B (Y_{A,1} - Y_{AS}) = \dot{m}_A \]

where \( \dot{m}_A \) is flow of A from phase x to phase y.

**Mass balance of A in stage n:**

\[ \dot{m}_B (Y_{A,n} - Y_{A,n+1}) = \dot{m}_C (X_{A,n-1} - X_{A,n}); \quad n = 1 \ldots N \]

or
\[
\frac{(Y_{A,n} - Y_{A,n+1})}{(X_{A,n-1} - X_{A,n})} = \frac{m_c}{m_B}
\]

**operational line** with slope \(\frac{m_c}{m_B}\) passing through the points \([X_{A,n-1}, Y_{A,n}]\); \(n = 1 \ldots N\)

**Equilibrium condition:**

\[Y_{A,n} = \varphi_{A,n} X_{A,n}; \ n = 1 \ldots N\]

**Graphical solution**

- slope is constant, all points \([X_{A,n-1}, Y_{A,n}]\) lie on one line
- stages are found as rectangular steps

**Minimal consumption of the solvent (B)**

- two cases
  - no tangent
  - tangent
Minimal consumption can be calculated from:

$$\frac{\dot{m}_C}{\dot{m}_{B,\text{min}}} = \frac{(Y_{A,max} - Y_{AS})}{(X_{AF} - X_{A,N})} \rightarrow \dot{m}_{B,\text{min}} = \frac{\dot{m}_C}{\theta} \frac{(X_{AF} - X_{A,N})}{(Y_{A,max} - Y_{AS})}$$

Remark: if $\dot{m}_B = \dot{m}_{B,\text{min}}$ then $N \to \infty$; in practice $\dot{m}_B = \gamma \dot{m}_{B,\text{min}}$ where $\gamma = 1.2 - 1.5$

**Algebraic solution**

The mass balance in stage $n$ can be rewritten as

$$\dot{m}_c X_{A,n-1} + \dot{m}_B Y_{A,n} = \dot{m}_c X_{A,n} + \dot{m}_B Y_{A,n+1} = \Delta \dot{m}_A$$

where $\Delta \dot{m}_A$ is constant for all stages and can be determined from balance of all stages.

By using equilibrium condition $Y_{A,n} = \varphi_{A,n} X_{A,n}$ we get:

$$X_{A,n-1} = \frac{\varphi_{A,n} \dot{m}_B}{\dot{m}_c} + \frac{\Delta \dot{m}_A}{\dot{m}_c}$$

This formula can be used repeatedly to calculate $N$ if is $X_{A,N}$ given or $X_{A,n}$ if $N$ is given.

For **real stages** a new efficiency must be defined → **Murphree efficiency**

$$E_{X,n} = \frac{X_{A,n-1} - Y_{A,n}}{X_{A,n-1} - X_{A,n}^*}$$

where $X_{A,n}^* = \frac{Y_{A,n}}{\varphi_{A,n}}$ (i.e. $Y_{A,n}$ is for real stage, not $Y_{A,n}^*$ for equilibrium stage).

$$E_{Y,n} = \frac{Y_{A,n} - Y_{A,n+1}}{Y_{A,n}^* - Y_{A,n+1}}$$
where $Y_{A,n}^* = \varphi_{A,n} X_{A,n}$ (i.e. $X_{A,n}$ is for real stage, not $X_{A,n}^*$ for equilibrium stage).

The two efficiencies $E_{X,n}$ and $E_{Y,n}$ are not equal.

**Graphical representation**

[Graphical representation of cascade and special case]

**Graphical solution of the cascade**

**Special case**

- $\varphi_{A,n} = \text{const} = \varphi_A \rightarrow$ linear equilibrium
  
  then $\zeta_X = \frac{\varphi_A \dot{m}_B}{\dot{m}_C} = \text{const}$

we introduce **effectiveness factors**

$$
\eta_X = \frac{X_{AF} - X_{AN}}{X_{AF} - \frac{Y_{AS}}{\varphi_A}}; \quad \eta_Y = \frac{Y_{A1} - Y_{AS}}{\varphi_A X_{AF} - Y_{AS}}
$$

**Graphical representation**
For $\eta_X = 1$ or $\eta_Y = 1$ the cascade would have $N \to \infty$.

It can be shown that

$$\frac{1 - \eta_X}{1 - \eta_Y} = \left(\frac{1}{\zeta_X}\right)^N = \zeta_Y^N$$

and $\eta_X = \frac{\eta_Y}{\zeta_Y}$; $\eta_Y = \frac{\eta_X}{\zeta_X}$

then

$$N = \ln \left( \frac{1 - \eta_Z/\zeta_Z}{1 - \eta_Z} \right) \ln \zeta_Z \quad \text{where } Z \text{ is either } X \text{ or } Y$$

for $\zeta_Z = 1$:

$$N = \frac{\eta_Z}{1 - \eta_Z}$$

**General case – partially miscible solvents**

In addition to A, also B and C cross the interface. Therefore, all three mass balances must be used now $\to$ relative mass fractions are not useful $\to$ ordinary mass fractions should be used together with masses of the streams, not just.

**Equilibrium:**

- formally $y_k = \psi_k x_k; k = A, B, C$
- $\psi_k$ depends on composition and temperature
- graphical representation in a triangle diagram is more convenient

$$x_C = 1 - x_A - x_B; \quad y_C = 1 - y_A - y_B$$
data for the equilibrium curve are typically given in tables.

Mass balance of A, B, C is graphically represented in the triangle diagram by the **lever rule**.

Extractor is thought of as a combination of a **mixer** and **settler**.

- overall mass balance: \( m_F + m_S = m_M = m_R + m_E \)
- component k: \( m_F x_{kF} + m_S y_{kS} = m_M z_{kM} = m_R x_k + m_E y_k \)

Combination yields: \( m_F (x_{kF} - y_{kS}) = m_M (z_{kM} - y_{kS}) \)

or

\[
\frac{m_F}{m_M} = \frac{y_{kS} - z_{kM}}{x_{kF} - y_{kS}} = \frac{SM}{SF} \quad \text{lever rule for mixer}
\]

in analogy the **lever rule for the settler** is

\[
\frac{m_R}{m_M} = \frac{ME}{RE}
\]

Other variants of the lever rule (less convenient for calculations)
Repeated extraction (cross-flow)

mass balance of stage $n$ (assume constant mass of solvent)

- overall: $m_{R,n-1} + m_S = m_{M,n} = m_{R,n} + m_E,n$
- components: $m_{R,n-1}x_{k,n-1} + m_Sy_{k,n} = m_{M,n}z_{k,n} = m_{R,n}x_{k,n} + m_{E,n}y_{k,n}$

This implies lever rules for points

- mixer \( (R_{n-1}, M_n, S); \ n = 1 \ldots N \)
- settler \( (R_n, M_n, E_n); \ n = 1 \ldots N \)

Equilibrium in stage $n$: \( y_{k,n} = \psi_{k,n}x_{k,n}; \ n = 1 \ldots N \) or via graph

Graphical solution

a) lever ruler for stage 1:
   - mixer: \( \frac{m_F}{m_S} = \frac{MS}{FM} \rightarrow \text{determine } M_1 \)
   - then tie line and lever rule for settler: \( \frac{m_{R_1}}{m_{E_1}} = \frac{M_1E_1}{R_1E_1} \rightarrow \text{determine } m_{R_1} \)

b) for stage 2
- mixer: \( \frac{m_{R_1}}{m_{R_1} + m_S} = \frac{S M_2}{S R_1} \) → determine \( M_2 \)
- settler: \( \frac{m_{R_2}}{m_{R_2} + m_S} = \frac{M_2 E_2}{R_2 E_2} \) → determine \( m_2 \)

c) etc.

Counter current cascade of extractors (or counter-current staged column)

Mass balance of all stages – summing form:
- overall: \( \dot{m}_F + \dot{m}_S = \dot{m}_M = \dot{m}_{R_n} + \dot{m}_{E_1} \)
- components: \( \dot{m}_F x_{kF} + \dot{m}_S y_{ks} = \dot{m}_M z_{kM} = \dot{m}_{R_n} x_{k,n} + \dot{m}_{E_1} y_{k,1} \)

These equations imply lever rules connecting points (F, M, S) and (R\(_n\), M, E\(_1\))

Mass balance of stages 1 to \( n \) – difference form:
- overall: \( \dot{m}_F - \dot{m}_{E_1} = \dot{m}_{R_n} - \dot{m}_{E_{n+1}} = \dot{m}_P = \text{const} \)
- components: \( \dot{m}_F x_{kF} - \dot{m}_{E_1} y_{k,1} = \dot{m}_{R_n} x_{k,n} - \dot{m}_{E_{n+1}} y_{k,n+1} = \dot{m}_P z_{kP} = \text{const} \)

Here the point P with composition \( z_{kP} \) is hypothetical but useful; lever rule applies on the lines connecting (F, E\(_1\), P) and (R\(_n\), E\(_{n+1}\), P) for \( n = 1 \ldots N \) in particular (R\(_N\), E\(_{N+1}\)=S, P)

Equilibrium in stage \( n \)
- formally: \( y_{k,n} = \psi_{k,n} x_{k,n}; \ n = 1 \ldots N \)
- in graph: equilibrium curve + tie lines

Graphical solution

1) Summing form of mass balances serves to find the point M and then the point E\(_1\) provided that the compositions of F, S and R\(_n\) are given.

\[
\text{Lever rule: } \frac{\dot{m}_F}{\dot{m}_F + \dot{m}_S} = \frac{S M}{S F} \rightarrow \text{determine M, then connect R}_n \text{ and M to find E}_1
\]

2) Difference form of mass balances serves first to find the point P (=pole) as intersection of line (F, E\(_i\)) and (R\(_n\), S). The tie line from E\(_i\) determines R\(_1\) and connection of P with R\(_i\) determines E\(_2\) (see the difference form of balances). This is repeated until R\(_N\) is reached. In the figure below six step were needed to reach R\(_N \rightarrow N = 6\).