Introduction to mass transfer in staged processes (including continuous contact)

- **mass exchange**: 
  - **mass transfer** – from within the phase to the interface
  - **overall mass transfer** – from within the phase to the other phase across the interface
- **diffusion**: relative motion of a component with respect to the mixture (within one phase)
- **permeation**: transport from one phase to the second across a membrane

**Purpose of mass exchange:**
- removal of unwanted components from a product
- removal of impurities from raw materials, waste water or polluted air

**Basic processes of mass exchange** (= separation processes)

- **extraction** – separation of a liquid mixture by adding another liquid - solvent so that two liquid phases are formed
- **distillation** – separation of a liquid mixture by partial vaporization (i.e. by adding heat); reverse process is partial condensation
- **rectification** – distillation in a staged or packed column with reflux
- **absorption** – separation of a gaseous mixture by dissolving some component(s) in a liquid; reverse process is **desorption**
- **adsorption** – separation of either gaseous or liquid mixture by binding some component(s) on a solid surface; reverse process is **desorption**
- **drying** – evaporation of liquids from a mixture with a solid
- **leaching** – separation of a solid mixture by adding a liquid solvent (analogous to extraction)
- **crystallization** – formation of crystals from a solution or a melt
- **membrane separations** – separation of homogeneous (single-phase) systems by using a membrane

**Types of mass exchangers**

- contact of phases
  - **continuous**: column with a film, column with a packing, spray column, bubbled column
  - **staged**: column with stages (= plates), cascade of stages
Amount of transferred component is proportional to:

- the interface area (enhanced by packing, foam or bubbles)
- rate of interface transport
- contact time of the phases

Basic equations form mass exchange

1) material balances: $\sum \text{inputs} + \underbrace{\text{source}}_{\text{normally zero}} = \sum \text{outputs} + \text{accumulation}

   $\text{accumulation} = 0$ at steady state

2) energy (enthalpy) balances

3) equilibrium condition – relation between composition in both phases

4) kinetic equation – rate of mass transfer

5) additional equations: $pV = nRT, \sum x_i = 1,$ etc.

Equilibrium stage

- streams leaving are at equilibrium and phases are separated

Balance equations for flow system (differential time period)
moles of component k
\[ \dot{n}_{x_i} x_{ki} + \dot{n}_{y_i} y_{ki} + \frac{dn_{kr}}{dr} = \dot{n}_{xe} x_{ke} + \dot{n}_{ye} y_{ke} + \frac{dn_{ks}}{dr}, \quad k = 1, \ldots, K \]

no chemical reaction: \[ \frac{dn_{kr}}{dr} = 0 \]
steady state: \[ \frac{dn_{ks}}{dr} = 0 \]

enthalpy:
\[ \dot{n}_{x_i} h_{xi} + \dot{n}_{y_i} h_{yi} + \frac{Q_{\text{heat flow}}}{\text{flow}} = \dot{n}_{xe} h_{xe} + \dot{n}_{ye} h_{ye} + \frac{dH_S}{dr} \]

equilibrium relations:
\[ p_{xe} = p_{ye} = p_e \quad \ldots \text{pressure} \]
\[ T_{xe} = T_{ye} = T_e \quad \ldots \text{temperature} \]
\[ y_{ke} = f(x_{1e}, \ldots, x_{ke}, p_e, T_e) = \psi_k x_{ke}, \quad k = 1, \ldots, K \]

In general, \( \psi_k \) is a function of \( x_{1e}, \ldots, x_{ke}, p_e, T_e \)

**Real (nonequilibrium) stage**

Kinetic equations should be used, but often this is avoided (too difficult) and replaced by an empirical relation called **efficiency**.

\[ \text{Efficiency} = \frac{\text{difference of input/output composition}}{\text{maximum such difference}} \]
\[ E_{xk} = E_{yk} = E_k = \frac{x_{ki} - x_{ke}}{x_{ki} - x_{ke}^*} = \frac{y_{ke} - y_{ki}}{y_{ke}^* - y_{ki}} \]

(transport of component k from phase x to phase y is assumed). Here \( y_{ke}^* = \psi_k x_{ke}^* \)

Remark: for counter-current cascade of stages or for a counter-current column a different efficiency is defined (Murphree eq., see later)

**Examples of equilibrium relations**

**distillation:**
\[ \frac{p_k}{\text{partial pressure}} = \frac{y_{ke}}{\text{Dalton's law}} = \frac{p_k^0 x_k}{\text{Raoult's law}} \quad \text{(holds for ideal mixtures)} \]
\[ x, y \ldots \text{molar fractions !} \]
thus \( y_k = \frac{p_k^0}{p} x_k = \psi_k x_k \)

\( p \) … overall pressure

\( p_k^0 \) … vapor pressure of pure component \( k \) (from Antoine equation \( p_k^0 = \exp\left(A - \frac{B}{C + T}\right)\))

**absorption:** \( y_k = \frac{H_k}{p} x_k \) Henry’s law, \( H_k \) is found in tables (empirical)

**extraction:** non-ideal behavior

\[ a_{kx} = a_{ky} \] activities in both phases

\[ y_{kx} x_k = y_{ky} y_k \rightarrow y_k = \frac{y_{kx}}{y_{ky}} x_k = \psi_k x_k \]

Activity coefficients \( y_{kx}, y_{ky} \) depend on composition and so equilibrium relation is nonlinear often in form of a graph

**Mass transfer** occurs whenever there is a concentration difference or gradient. In theory, equilibrium is attained only after an infinite period during which mass transfer occurs. In practice, however, an effective equilibrium is achieved after a finite time → in equilibrium stages sufficient time must be allowed (→ contact time of the phases). In devices with continuous contact of phases (i.e. packed beds, spray towers, etc.). The equilibrium does not have time to get established, therefore we need **rate equations** to describe:

a) **mass transport** (transport within one phase)
b) **mass transfer** (transport to the interface)
c) **overall mass transfer** (transport from one phase to the interface and from the interface to the second phase)

**Remark:** Even in an equilibrium stage we need rate equations if we want to calculate contact time → size of the stage

a) **Mass transport within one phase**

There are two main mechanisms of such transport, **diffusion** and **convection**. In convection, a component \( k \) in a mixture is carried by the hydrodynamic flow of the phase. Convection molar flux of \( k \) is proportional to the velocity in the direction of the flow:

\[ J_{k,\text{conv}} = c_k v \]

\( c_k \) … molar concentration of \( k \) [mol m\(^{-3}\)]
In diffusion, the diffusion flux of component $k$ is proportional to the concentration gradient (= concentration change per distance). This equation is call Fick’s law:

$$J_{k,\text{diff}} = -D_k \frac{\partial c_i}{\partial z}$$

$z$ ... spatial coordinate of diffusion [m]

$D_k$ ... diffusivity of $k$ [m$^2$ s$^{-1}$]

Diffusion occurs even at zero velocity and is directed from higher to lower concentration

**Equation of continuity**

Transport in a one-dimensional flow system is described by local balance of $k$:

$$\frac{\partial c_k}{\partial \tau} = \frac{\partial (J_{k,\text{conv}} + J_{k,\text{diff}})}{\partial z} \rightarrow \frac{\partial c_k}{\partial \tau} + \frac{\partial (c_k v)}{\partial z} = D_k \frac{\partial^2 c_i}{\partial z^2}$$

Application of the continuity equation to the steady-state diffusion in a planar layer of fluid

assumptions:

- no convection: $J_{k,\text{conv}} = c_k v = 0$
- no accumulation (steady state): $\frac{\partial c_k}{\partial \tau} = 0$

Continuity equation the reduces to

$$\frac{d(J_{k,\text{diff}})}{dz} = 0 \text{ or } J_{k,\text{diff}} = \text{const}$$

Thus

$$J_{k,\text{diff}} = -D_k \frac{\Delta c_i}{\Delta z} = -D_k \frac{c_2 - c_1}{z_2 - z_1} = D_k \frac{c_1 - c_2}{\delta}$$

As shown in the Figure, the concentration profile is linear.
**Remarks:**

i) Notice that diffusive flux is in the direction from higher to lower concentration (i.e. against the gradient)

ii) Molar flow by diffusion + convection is

\[ n_K = (J_{k, \text{conv}} + J_{k, \text{diff}}) A; \quad A \ldots \text{surface} \]

**b) Mass transfer to the interface**

When gas is flowing along an interface with liquid (as in absorption), there is always a component of the flow toward the interface (due to eddies and lateral motion in turbulent flow). This convection carries the component k toward the interface but becomes weak close to the interface (→ laminar sublayer), where diffusive transport dominates. So the convection and diffusion interact in a complex way and the continuity equation is difficult to use. Instead, an empirical **mass transfer rate equation** is used for the molar flux at the interface:

\[
J_{k, \text{w}} = k_c (c_k - c_{k, \text{w}}) = k_c (c_{k, \text{w}} - c_k)
\]

- \(k_c\) … mass transfer coefficient [m s\(^{-1}\)]
- \((c_k - c_{k, \text{w}})\) or \((c_{k, \text{w}} - c_k)\) … driving force
- \(c_k\) … average concentration in the bulk
- \(c_{k, \text{w}}\) … concentration at the interface

**Molar flow** is molar flux \(\times\) surface:

\[ \dot{n}_{k, \text{w}} = J_{k, \text{w}} A \]

Driving force may be expressed via another concentration, for example via relative molar fraction or (absolute) molar fraction

\[ J_{k, \text{w}} = k_x (X_k - X_{k, \text{w}}) = k_x (x_k - x_{k, \text{w}}) \]

Then \(k_c, k_x, k_x\) can be converted to one another using the definitions of the concentration quantities. For example:

\[ c_k = x_k c \quad \rightarrow \quad k_x = k_c c \]

(here \(c\) is **total molar concentration** or **molar density**)

\[ X_k = \frac{x_k}{1 - x_k} \quad \rightarrow \quad k_x = k_x (1 - x_k) \]
How to determine $k_c$:

A method of scaling called **dimensional analysis** provides a set of dimensionless numbers that characterize various processes. The most important for mass transfer are:

- **Sh** = $\frac{k_{c,l}}{D_k}$  
  Sherwood number ($l$ is a characteristic length)
  
  Sh is a ratio of mass transfer rate and diffusion transport rate

- **Re** = $\frac{v_l}{\nu}$  
  Reynolds number (ration of inertial and viscous forces)

- **Sc** = $\frac{v}{D_k}$  
  Schmidt number (ration of viscous momentum flow and diffusive flow)

From experiments in certain arrangement (flow through packed bed, flow in a pipe, etc.) a relation between Sh and other numbers can be established **empirically**.

For example: $\text{Sh} = \text{Sh(Re, Sc)}$

typically: $\text{Sh} = A \text{Re}^a \text{Sc}^b$ for large Re (turbulent flow)

Once Sh is evaluated:

$$k_c = \frac{\text{Sh}D_k}{l}$$

**c) overall mass transfer (from bulk of one phase to the interface and from the interface to the bulk of another fluid)**

We consider a two-phase system and assume no accumulation on the interface → flux is the same on both sides of the interface

Thus:

$$k_y(y_k - y_{kw}) = k_x(x_k - x_{kw}) = J_{kw}$$

or  

$$k_y(Y_k - Y_{kw}) = k_x(X_k - X_{kw}) = J_{kw}$$
The equilibrium relation holds only at the interface:

\[ y_{kw} = \psi_k x_{kw} \]
\[ y_{kw} = \varphi_k x_{kw} \]

By combining these equations we obtain:

\[ J_{kw} = \left( \frac{1}{k_y} + \frac{\psi'_k}{k_x} \right)^{-1} (y_k - \psi'_k x_k) = K_y (y_k - y^*_k) = \left( \frac{1}{\psi_k k_y} + \frac{1}{k_x} \right)^{-1} \left( \frac{y_k}{\psi_k} - x_k \right) = K_x (x^*_k - x_k) \]

where

i) \( K_y \) and \( K_x \) are overall mass transfer coefficients

ii) \( \frac{1}{k_y} \) and \( \frac{1}{k_x} \) are resistances against mass transfer (they can be modified by multiplying or dividing by \( \psi_k \)). These resistances sum up to an overall resistance which is a reciprocal value of \( K_y \) or \( K_x \)

iii) \( (y_k - y^*_k) \) or \( (x_k - x^*_k) \) are driving forces of the overall mass transfer

iv) \( y^*_k = \psi_k x_k \) and \( x^*_k = \frac{y_k}{\psi_k} \) are effective molar fractions at equilibrium with bulk molar fractions in the other phase

**Graph of driving forces**

Remark: Instead of \( x \) and \( y \), we can use \( X \) and \( Y \), the format of rate equation is unchanged.