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)

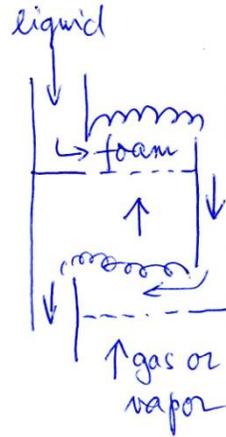**crystallization** – formation of crystals from a solution or a melt

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
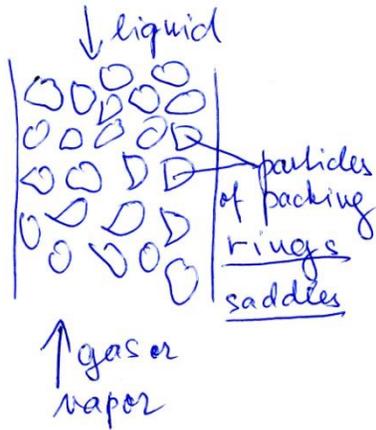
Scheme of packed column   Staged column

**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: $\sum inputs + \underbrace{source}_{\substack{normally \\ zero}} = \sum outputs + accumulation$

   $accumulation = 0$ 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
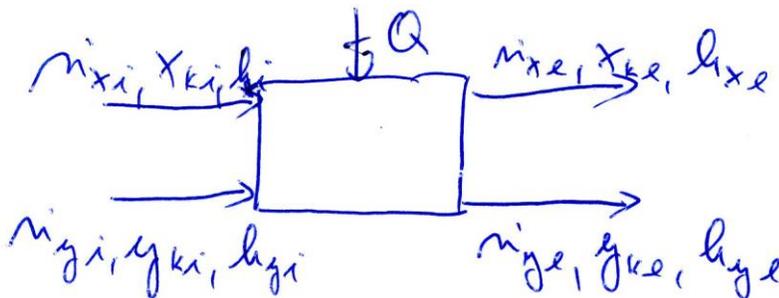
i	… inlet
e	… outlet
x	… "heavier" phase
y	… "lighter" phase
$\dot{n}$	… molar flow
x, y	… molar fractions
h	… molar enthalpy

Balance equations for flow system (differential time period)

- moles of component k

$$\dot{n}_{xi}x_{ki} + \dot{n}_{yi}y_{ki} + \frac{dn_{kr}}{d\tau} = \dot{n}_{xe}x_{ke} + \dot{n}_{ye}y_{ke} + \frac{dn_{kS}}{d\tau}, \qquad k = 1, \dots, K$$

no chemical reaction: $\dfrac{dn_{kr}}{d\tau} = 0$

steady state: $\qquad \dfrac{dn_{kS}}{d\tau} = 0$

enthalpy:

$$\dot{n}_{xi}h_{xi} + \dot{n}_{yi}h_{yi} + \underbrace{\dot{Q}}_{\substack{heat \\ flow}} = \dot{n}_{xe}h_{xe} + \dot{n}_{ye}h_{ye} + \frac{dH_S}{d\tau}$$

equilibrium relations:

$$p_{xe} = p_{ye} = p_e \qquad \dots \; pressure$$

$$T_{xe} = T_{ye} = T_e \qquad \dots \; temperature$$

$$y_{ke} = f(x_{1e}, \dots, x_{ke}, p_e, T_e) = \psi_k x_{ke}, \qquad k = 1, \dots, K$$

In general, ψ_k is a function of $x_{1e}, \dots, x_{ke}, p_e, T_e$

Real (nonequilibrium) stage

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

$$Efficiency = \frac{difference \; of \; input/output \; compostion}{maximum \; such \; difference}$$

$$E_{xk} = E_{yk} = E_k = \frac{x_{ki} - x_{ke}}{x_{ki} - x_{ke}^*} = \frac{y_{ke} - y_{ki}}{y_{ke}^* - y_{ki}}$$

(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:

$$\underbrace{p_k}_{\substack{partial \\ pressure}} = \underbrace{y_k p}_{\substack{Dalton's \\ law}} = \underbrace{p_k^0 x_k}_{\substack{Raoult's \\ law}} \quad \text{(holds for ideal mixtures)}$$

$$x, y \dots \text{molar fractions !}$$

$$\text{thus } y_k = \frac{p_k^0}{p} x_k = \psi_k x_k$$

p ... overall pressure

p_k^0 ... vapor pressure of pure component k (from Antoine equation $p_k^0 = \exp\left(A - \frac{B}{C+T}\right)$)
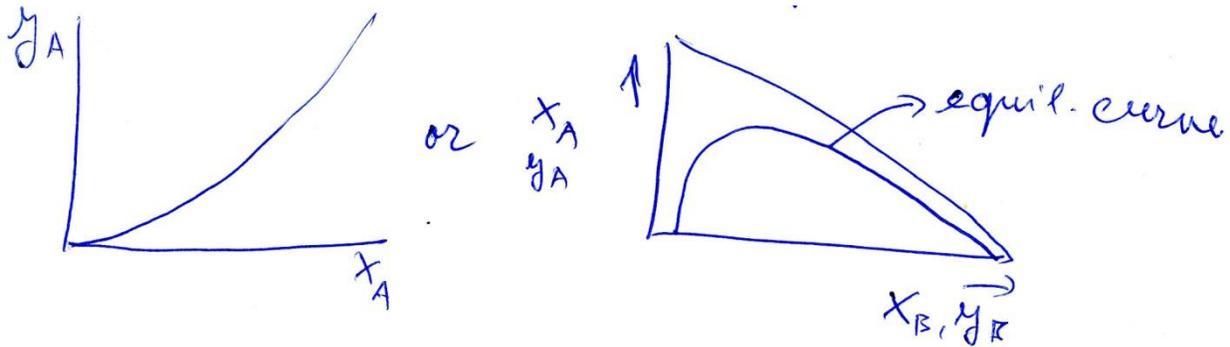
absorption: $y_k = \frac{H_k}{p} x_k$ Henry's law, H_k is found in tables (empirical)

extraction: non-ideal behavior

$a_{kx} = a_{ky}$ activities in both phases

$$\gamma_{kx} x_k = \gamma_{ky} y_k \;\rightarrow\; y_k = \frac{\gamma_{kx}}{\gamma_{ky}} x_k = \psi_k x_k$$

Activity coefficients γ_{kx}, γ_{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:

$$J_{k,conv} = c_k v$$

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**:

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

z ... spatial coordinate of diffusion [m]

D_k ... diffusivity of k [m² s⁻¹]

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:**

$$\underbrace{\frac{\partial c_k}{\partial \tau}}_{accumulation} = \underbrace{-\frac{\partial\left(J_{k,conv} + J_{k,diff}\right)}{\partial z}}_{input-output} \rightarrow \frac{\partial c_k}{\partial \tau} + \frac{\partial(c_k v)}{\partial z} = D_k \frac{\partial^2 c_i}{\partial z^2}$$

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

assumptions:

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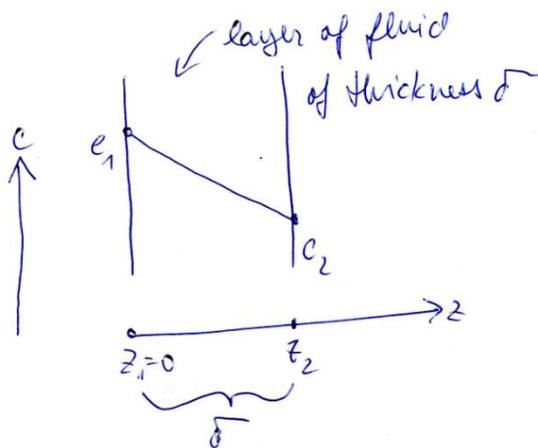- no accumulation (steady state): $\frac{\partial c_k}{\partial \tau} = 0$

Continuity equation the reduces to

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

Thus

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

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

$$\dot{n}_k = \left(J_{k,conv} + J_{k,diff}\right)A; \quad A \ldots \text{surface}$$

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 ($\rightarrow$ 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**:
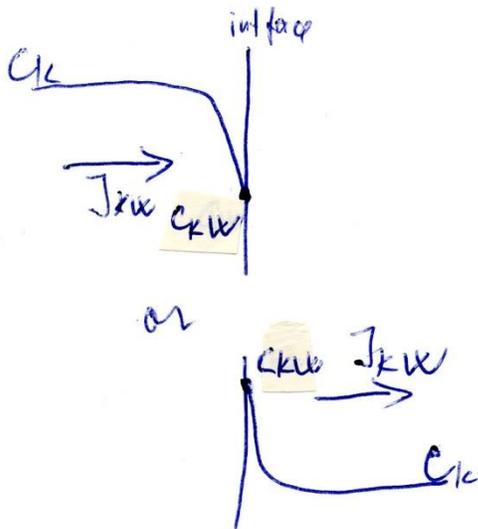
$$J_{k,w} = \underbrace{k_c(c_k - c_{kw})}_{\substack{flow\ toward \\ interface}} = \underbrace{k_c(c_{kw} - c_k)}_{\substack{flow\ form \\ interface}}$$

k_c ... mass transfer coefficient $[\text{m s}^{-1}]$

$(c_k - c_{kw})$ or $(c_{kw} - c_k)$ ... driving force

c_k ... average concentration in the bulk

c_{kw} ... concentration at the interface

Molar flow is molar flux × surface:

$$\dot{n}_{kw} = J_{kw}A$$

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

$$J_{kw} = k_X(X_k - X_{kw}) = k_x(x_k - x_{kw})$$

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

$$c_k = x_k c \ \rightarrow \ k_x = k_c c$$

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

$$X_k = \frac{x_k}{1 - x_k} \rightarrow k_X = k_x(1 - x_k)$$

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:

$\text{Sh} = \dfrac{k_c l}{D_k}$ Sherwood number (l is a characteristic length)

          Sh is a ratio of mass transfer rate and diffusion transport rate)

$\text{Re} = \dfrac{vl}{v}$ Reynolds number (ration of inertial and viscous forces)

$\text{Sc} = \dfrac{v}{D_k}$ 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**.
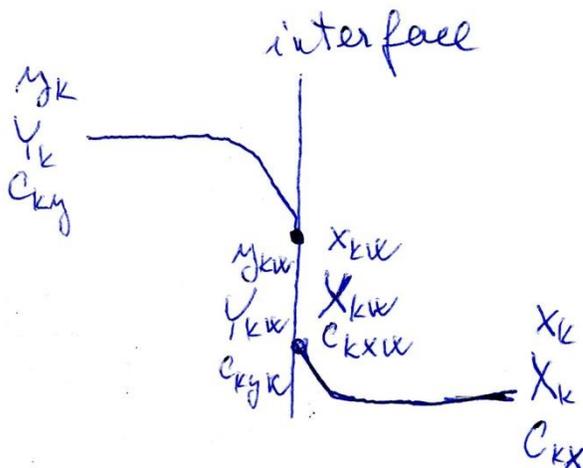
For example: $\text{Sh} = \text{Sh}(\text{Re}, \text{Sc})$

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:

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

$$\text{or} \ \ k_Y(Y_k - Y_{kw}) = k_X(X_k - X_{kw}) = J_{kw}$$

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 diving by Ψ_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
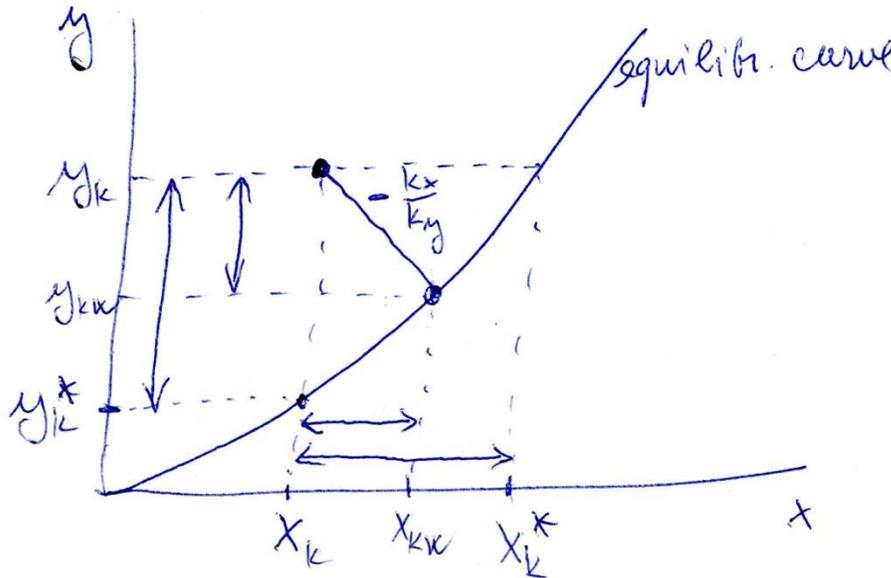
Remark: Instead of x and y, we can use X and Y, the format of rate equation is unchanged.