Chapter 6

Mass transfer

As an introduction to mass transfer, the self-diffusion[1] mechanism on a molecular level is discussed.

6.1 Molecular concept of diffusion processes

6.1.1 Diffusion in gases

A gaseous, diluted, binary mixture of substances (substance A, B), in which molecules behave very similarly, is considered. Figure 6.1 shows a one-dimensional example. On the left side the number of molecules A is higher than the number of molecules B. This relation is inverse on the right side. Temperature and pressure of the mixture are assumed constant and the velocity of the centre of mass, i.e. the velocity that describes the movement of all particles on a macroscopic level, is zero.

On a molecular level, each molecule moves with a velocity $\vec{w}$, which varies in absolute value and direction from one to another. This velocity is also called thermal velocity. The mean velocity at which the molecules A and B move is defined as $\bar{w}$. Hence the average frequency at which molecules pass the plane $x = x_0$ is proportional to $c \cdot \bar{w}$, where c is the number of molecules per Volume [$1/\mathrm{m^3}$]. Before molecules pass the x_0 plane they travel a mean free path length l. The mean free path length is the average path length that a particle or molecule travels without interacting with other particles or molecules. The right-hand particle flow of molecules A across x_0 from their initial position $x_0 - l$ is proportional to the number of molecules A, given as $\frac{c_A}{c_{tot}}$ at position $x_0 - l$. The left-hand particle flow from $x_0 + l$ to x_0 is proportional to the amount content of molecules A $\frac{c_A}{c_{tot}}$ at position $x_0 + l$. There is a higher chance of molecules A to flow across the plane x_0 from left to right than the other way around, as the number of molecules A is higher on the left-hand side (assuming the particle distribution from fig 6.1). Hence the expected value of random molecule movement determines this kind of mass transfer.

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[1]This process is called self-diffusion, because the driving potential is the concentration difference
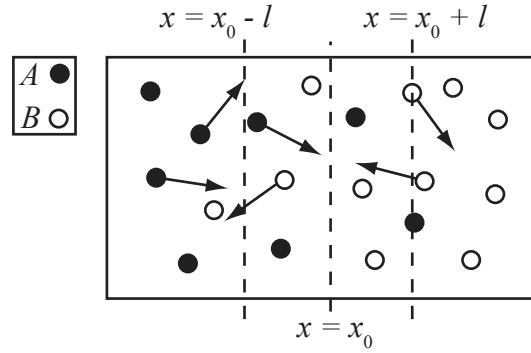
Figure 6.1: Diffusion regarded on molecular level

The mass of the molecules of A, m_A, is related to the molar concentration c_A by $\frac{M_A}{N_A}$, where N_A is the Avogadro constant and M_A the molecular mass of A. Hence the mass flow in x-direction is:

$$j''_A\big|_{x=x_0} \approx \eta(c_{\text{tot}}\overline{w})\left(\frac{M_A}{N_A}\right)\left(\frac{c_A}{c_{\text{tot}}}\bigg|_{x_0-l} - \frac{c_A}{c_{\text{tot}}}\bigg|_{x_0+l}\right) \tag{6.1}$$

Where η is a proportional constant. Because the concentration doesn't change much in the range of twice the free path length $2l$, the difference can be approximated by a first order taylor series expansion about x_0.

$$j''_A\big|_{x=x_0} = \eta(c_{\text{tot}}\overline{w})\left(\frac{M_A}{N_A}\right)\left(-2l\frac{\text{d}\left(c_A/c_{\text{tot}}\right)}{\text{d}x}\bigg|_{x_0}\right) = -2\eta(\overline{w}l)\rho\frac{\text{d}\xi_A}{\text{d}x}\bigg|_{x_0} \tag{6.2}$$

With $\xi_A = m_A/m_{\text{tot}}$ as mass concentration. While in the transformation c_A, as it is used in the unit of $[1/\text{m}^3]$, was substituted by:

$$c_A = \frac{m_{\text{ges}}}{V} \cdot \frac{\xi_A N_A}{M_A}$$

Hence the mass flow of component A is proportional to the gradient of the mass concentration of A. The constants that scale the gradient can be summarized in the diffusion coefficient D_{AB}. The indexation of this coefficient defines which component diffuses in which (e.g. D_{AB} stands for a diffusion from A to B).

$$D_{\text{AB}} = 2\eta\left(\overline{w}l\right) \tag{6.3}$$

This yields the following equation for the mass flow, which is also known as Fick's law:

$$j''_A = -\rho D_{\text{AB}}\frac{\text{d}\xi}{\text{d}x} \tag{6.4}$$

Eventually the indication of this mass transfer as "self-diffusion" shall be explained. As equation (6.3) shows, the only driving potential is the gradient of mass- and molar concentration. The stochastic process of molecular movement is responsible for an even distribution of the components after all and hence for mass transfer. See Lienhard (2008).

6.1.2 Diffusion in liquids

The kinetic gas theory is not valid anymore, if diffusion occurs in liquids instead of gases, because every molecule has strong interactions with its surrounding molecules. For this case Einstein (1905) developed the theory of diffusion of small suspended spheres A, which is briefly explained here: A liquid layer in which suspended particles are randomly spread is assumed, as shown in figure 6.2. The number of particles
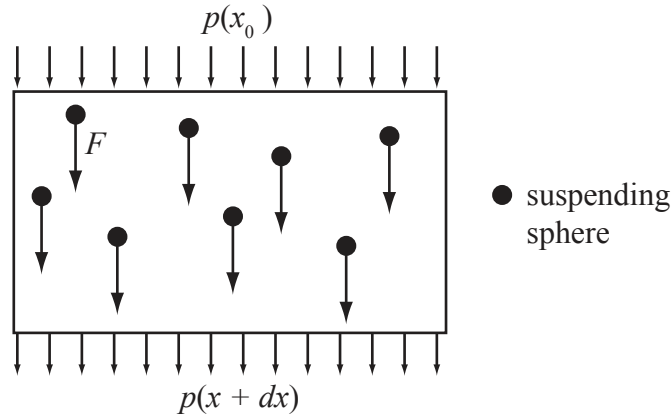

Figure 6.2: Model for diffusion in liquids

per volume unit is defined as n_V. A force F acts on each particle, which is position but not time-dependent. To simplify the example it is assumed that the force acts in x-direction only. This yields the following equation for the partial pressure:

$$-\frac{\partial p_i}{\partial x} = n_V F \tag{6.5}$$

Because of the force acting on the particle, it moves, assuming Stokes' hypothesis (creeping flow, Re<1) with the velocity

$$u = \frac{F}{6\pi\eta r}, \tag{6.6}$$

With η as the viscosity of the liquid and r the radius of the particle. The particle flow through a plane derives from $u \cdot n_V$ and the mass flow:

$$\dot{m}'' = M_i \cdot u \cdot \frac{n_V}{N_A}.$$ (6.7)

With M_i as the molar mass of component i and N_A, the Avogadro constant. Inserting the force F (6.6) to the mass flow (6.7) yields:

$$\dot{m}'' = -\frac{M_i n_V}{6\pi\eta r n_V N_A} \frac{\partial p_i}{\partial x}$$ (6.8)

Hereafter it is assumed, that partial pressure of the gas dissolved in the liquid can be described using the ideal gas law ($pV = Nk_B T$), with N as the number of particles. This assumption is valid, if the individual dissolved gas molecules don't interact. With the Bolzman constant[2] k_B follows:

$$\dot{m}'' = -\frac{M_i}{6\pi\eta r N_A} \frac{k_B T}{V} \frac{\partial N_i}{\partial x}$$ (6.9)

If the mass flow on the other side is described by Fick's law and a concentration gradient, the diffusion coefficient D can be determined.

$$\dot{m}'' = -\rho D \frac{\partial \xi_i}{\partial x}$$ (6.10)

With $\xi_i = \rho_i/\rho$, the density can be eliminated on the right side. Substituting ρ_i by $N_i \cdot M_i/(N_A \cdot V)$ leads to

$$\dot{m}'' = -\frac{M_i}{6\pi\eta r N_A} \frac{k_B T}{V} \frac{\partial N_i}{\partial x} = -D \frac{M_i}{N_A V} \frac{\partial N_i}{\partial x}$$ (6.11)

which leads to the diffusion coefficient

$$D = \frac{k_B T}{6\pi\eta r}$$ (6.12)

Many empiric correlations are based on this equation.

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[2]The Bolzmann-constant is named after the austrian physicist Ludwig Boltzmann (1844-1906), know as one of the founders of statistical mechanics. This constant is not to be mistaken for the Stefan-Boltzmann-constant from heat radiation. $k_B = 1{,}3806504 \cdot 10^{-23}$ J/K

6.2 Fundamentals

In the previous introduction the diffusion process was described by the amount of substance and the mass concentration ξ. Hence the system describing variables are introduced again: The following relationship can be formed for the mole fraction ψ and the mass concentration ξ:

Table 6.1: Definition of variables in binary mixtures

(filling) mass	$m_1; m_2$	[kg]
molar mass of the gases	$M_1; M_2$	[kg/kmol]
partial density	$\rho_1 = \frac{m_1}{V}; \rho_2 = \frac{m_2}{V}$	[kg/m^3]
mixture density	$\rho = \frac{m_1 + m_2}{V}$	[kg/m^3]
molar quantity	$n_1 = \frac{m_1}{M_1}; n_2 = \frac{m_2}{M_2}$	[kmol]
molar concentration	$C_1 = \frac{n_1}{V}; C_2 = \frac{n_2}{V}$	[kmol/m^3]
molar concentration of the mixture	$C = \frac{n_1 + n_2}{V}$	[kmol/m^3]
mole fraction	$\psi_1 = \frac{n_1}{n_1 + n_2} = \frac{C_1}{C}; \psi_2 = \frac{n_2}{n_1 + n_2} = \frac{C_2}{C}$	[$-$]
mass concentration	$\xi_1 = \frac{\rho_1}{\rho} = \frac{m_1}{m_{\text{tot}}}; \xi_2 = \frac{\rho_2}{\rho} = \frac{m_2}{m_{\text{tot}}}$	[$-$]
partial pressure	$p_1 = \frac{R_{\text{m}}}{M_1}\rho_1 T = R_{\text{m}} C_1 T; p_2 = \frac{R_{\text{m}}}{M_2}\rho_1 T = R_{\text{m}} C_2 T$	[N/m^2]

$$\psi_1 = \frac{\frac{\rho_1}{M_1}\frac{1}{\rho}}{\left(\frac{\rho_1}{M_1} + \frac{\rho_2}{M_2}\right)\frac{1}{\rho}} = \frac{\frac{\xi_1}{M_1}}{\frac{\xi_1}{M_1} + \frac{\xi_2}{M_2}} \tag{6.13}$$

Furthermore the mean molar mass is defined as:

$$\overline{M} = \frac{m_1 + m_2}{n_1 + n_2} = \frac{\frac{1}{V}(m_1 + m_2)}{\frac{1}{V}(n_1 + n_2)} = \frac{\rho}{C} \tag{6.14}$$
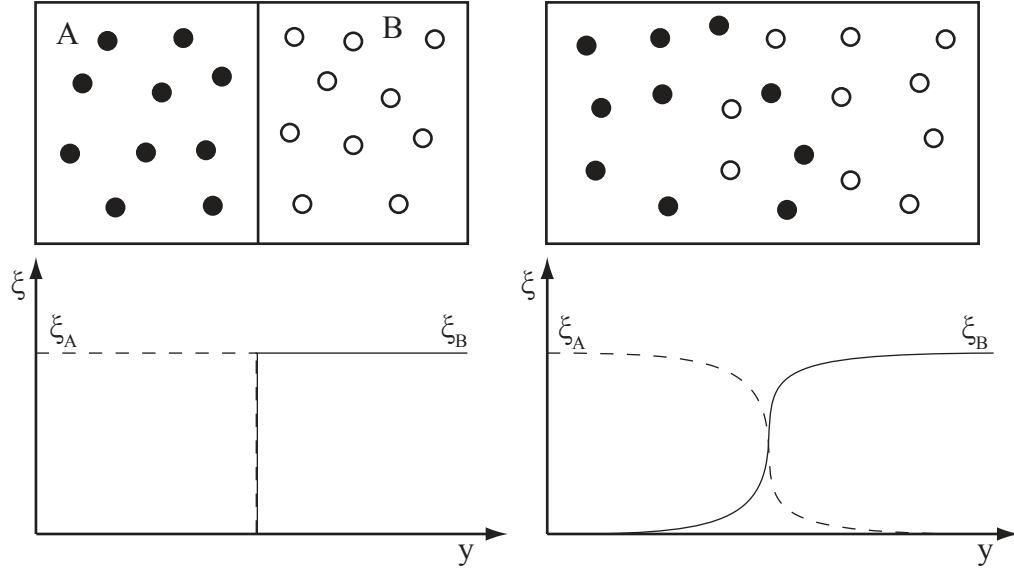
Figure 6.3: One-dimensional, equimolar diffusion in resting, binary mixtures

If the gaseous components and the mixture are assumend to behave like ideal gases

$$p = R_{\mathrm{m}}cT = R_{\mathrm{m}}(c_1 + c_2)T = p_1 + p_2 \tag{6.15}$$

is valid. Hence total pressure is the sum of partial pressures (Dalton's law, 1805). Because pressure is directly proportional to the amount of substance this yields:

$$\psi_1 = \frac{p_1}{p} \text{ and } \psi_2 = \frac{p_2}{p} \tag{6.16}$$

Example: One-dimensional, equimolar diffusion in resting binary gas mixtures
The system shown in figure 6.3 is closed, hence the amount of substance of each component and consequently the overall amount of substance is constant. As a result, mixture concentration C and pressure are also constant. The particle flow, which is responsible for the mixing of the components, depends on the negative concentration gradient.

$$\text{Flow} = \text{diffusion coefficient} \cdot \text{neg. mass concentration gradient} \tag{6.17}$$

This yields

$$\dot{n}_1'' = D_{12} \cdot \left(-\frac{dC_1}{dy}\right) \tag{6.18}$$

and

$$\dot{n}_2'' = D_{21} \cdot \left(-\frac{dC_2}{dy}\right) \tag{6.19}$$

for the substance flow. The initial precondition, that the molar concentrations of the components and the overall molar concentration are constant within the regarded system

$$C_1 + C_2 = C = \text{const} \qquad (6.20)$$

leads to the equality of both concentration gradients

$$\frac{dC_1}{dy} + \frac{dC_2}{dy} = 0 \qquad (6.21)$$

With the additional precondition of constant amount of substance

$$n = n_1 + n_2 = \text{const} \qquad (6.22)$$

the sum of substance flows has to be zero

$$\dot{n}_1'' + \dot{n}_2'' = 0 \rightarrow \dot{n}_1'' = -\dot{n}_2'' \qquad (6.23)$$

Equations (6.18) and (6.19) yield

$$\frac{\dot{n}_1''}{D_{12}} + \frac{\dot{n}_2''}{D_{21}} = -\left(\frac{dC_1}{dy} + \frac{dC_2}{dy}\right) \qquad (6.24)$$

(6.21) and (6.22) yield the equality of diffusion coefficients in a binary mixture

$$D_{12} = D_{21} \qquad (6.25)$$

This is only valid for a binary mixture.

6.3 Mass transfer in flows

In this section mass transfer through diffusion based on a concentration gradient, as previously introduced, is extended to the three-dimensional case.

If the fluid is a mixture of n different components, as in the previous example, and not a single pure substance, the convective mass transfer can be overlaid by mass transfer by diffusion caused by a concentration, pressure or temperature gradient.

If a differential volume, as shown in figure 6.4, is regarded, then the mean flow velocity $\vec{w}$, which is averaged over all components, can differ from the mean value of the flow velocities w_{xi}, w_{yi}, w_{zi} of each component i, due to diffusion processes.[3]

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[3]Of course other phenomenon can cause a deviation of velocities, e.g. solid particles in an accelerated flow, due to inertial forces. These effects are not part of this consideration.
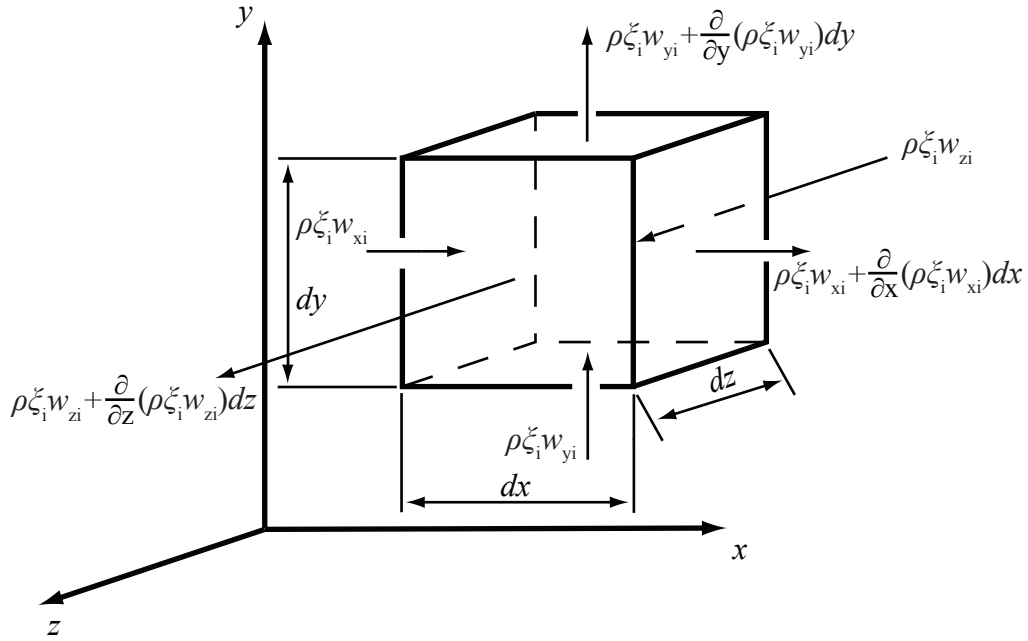
Figure 6.4: Substance balance at the control volume

There are different definitions of the mean velocity. In this case the mean velocity is defined as the mass centre velocity:

$$\vec{w} = \begin{pmatrix} w_{\mathrm{x}} \\ w_{\mathrm{y}} \\ w_{\mathrm{z}} \end{pmatrix} = \frac{1}{\rho} \sum_{i=1}^{n} \rho \xi_i \begin{pmatrix} w_{\mathrm{x}i} \\ w_{\mathrm{y}i} \\ w_{\mathrm{z}i} \end{pmatrix} \tag{6.26}$$

with the fluid density ρ in kg/m^3 and ξ_i as mass fraction of component i within the mixture.

For the balance of molar flows the volume cell $dV = dx\,dy\,dz$ is regarded again. The mass of substance i within the volume is $\xi_i \rho dV$, and its temporal alteration is $\partial(\xi_i \rho)/\partial t$. The temporal alteration of mass can be defined by the mass flows though the six surfaces of the volume cell dV:

$$
\begin{aligned}
\frac{\partial(\xi_i\rho)}{\partial t}dV = & \quad \rho\xi_i w_{\mathrm{x}i}dydz - \left[\rho\xi_i w_{\mathrm{x}i} + \frac{\partial}{\partial x}(\rho\xi_i w_{\mathrm{x}i})dx\right]dydz \\
+ & \quad \rho\xi_i w_{\mathrm{y}i}dxdz - \left[\rho\xi_i w_{\mathrm{y}i} + \frac{\partial}{\partial y}(\rho\xi_i w_{\mathrm{y}i})dy\right]dxdz \\
+ & \quad \rho\xi_i w_{\mathrm{z}i}dxdy - \left[\rho\xi_i w_{\mathrm{z}i} + \frac{\partial}{\partial z}(\rho\xi_i w_{\mathrm{z}i})dz\right]dxdy \\
= & \quad -dV\left[\frac{\partial}{\partial x}(\rho\xi_i w_{\mathrm{x}i}) + \frac{\partial}{\partial y}(\rho\xi_i w_{\mathrm{y}i}) + \frac{\partial}{\partial z}(\rho\xi_i w_{\mathrm{z}i})\right]
\end{aligned}
\tag{6.27}
$$

To describe mass flow by diffusion, terms like diffusion velocity and **diffusion stream density** are used. Here, the diffusion velocity is defined as the difference between the mean particle velocity $\vec{w_i} = (w_{\mathrm{x}i}, w_{\mathrm{y}i}, w_{\mathrm{z}i})$ and the mass centre velocity $\vec{w} = (w_{\mathrm{x}}, w_{\mathrm{y}}, w_{\mathrm{z}})$. The diffusion stream density $\vec{j_i}$ is to be understood as the related mass flow of component i (kg/m^{2}s):

$$
\vec{j_i''} = \rho\xi_i(\vec{w_i} - \vec{w})
\tag{6.28}
$$

The sum of all diffusion stream densities has to dissolve according to equation (6.26) and definition (6.28)

$$
\sum_{i=1}^{n} \vec{j_i''} = \sum_{i=1}^{n} \rho\xi_i(\vec{w_i} - \vec{w}) = 0
\tag{6.29}
$$

As early as 1885, Fick empirically found the law for the diffusion stream density $\vec{j_i}$ (Fick (1855)), that is named after him, which states, that the diffusion stream density is proportional to the concentration gradient:

$$
j_{\mathrm{x}i}'' = -\rho D \frac{\partial\xi_i}{\partial x}
\tag{6.30}
$$

Putting the definition of diffusion stream velocity (6.28) into equation (6.27) yields

$$
\frac{\partial(\xi_i\rho)}{\partial t} = -\left[\frac{\partial}{\partial x}(\xi_i\rho w_{\mathrm{x}} + j_{\mathrm{x}i}'') + \frac{\partial}{\partial y}(\xi_i\rho w_{\mathrm{y}} + j_{\mathrm{y}i}'') + \frac{\partial}{\partial z}(\xi_i\rho w_{\mathrm{z}} + j_{\mathrm{z}i}'')\right]
\tag{6.31}
$$

This equation can be partially differentiated and rewritten assuming constant density and using the continuity equation. This yields the following conservation equation for component i (the index i is left out hereafter):

$$
\rho\frac{\partial\xi}{\partial t} + \rho u\frac{\partial\xi}{\partial x} + \rho v\frac{\partial\xi}{\partial y} + \rho w\frac{\partial\xi}{\partial z} + \frac{\partial j''}{\partial x} + \frac{\partial j''}{\partial y} + \frac{\partial j''}{\partial z} = 0
\tag{6.32}
$$

Using Fick's law (6.30) yields

$$\rho\frac{\partial(\xi)}{\partial t} + \rho u\frac{\partial\xi}{\partial x} + \rho v\frac{\partial\xi}{\partial y} + \rho w\frac{\partial\xi}{\partial z} - \frac{\partial}{\partial x}\left(\rho D\frac{\partial\xi}{\partial x}\right) - \frac{\partial}{\partial y}\left(\rho D\frac{\partial\xi}{\partial y}\right) - \frac{\partial}{\partial z}\left(\rho D\frac{\partial\xi}{\partial z}\right) = 0$$
(6.33)

In the stationary case assuming constant properties and introducing the Schmidt-number $\mathrm{Sc} = \frac{\eta}{\rho D}$ yields the simplified form

$$\rho u\frac{\partial\xi}{\partial x} + \rho v\frac{\partial\xi}{\partial y} + \rho w\frac{\partial\xi}{\partial z} = \frac{\eta}{\mathrm{Sc}}\left(\frac{\partial^2\xi}{\partial x^2} + \frac{\partial^2\xi}{\partial y^2} + \frac{\partial^2\xi}{\partial z^2}\right)$$
(6.34)

which can be rendered dimensionless analogous to the energy equation in the convection section, introducing reference values. If these values are defined as follows:

$$\mathrm{x}^* \equiv \frac{\mathrm{x}}{L};\ \mathrm{y}^* \equiv \frac{\mathrm{y}}{L};\ \mathrm{z}^* \equiv \frac{\mathrm{z}}{L};\ u^* \equiv \frac{u}{u_\infty};\ v^* \equiv \frac{v}{u_\infty};\ w^* \equiv \frac{w}{u_\infty};\ \xi^* \equiv \frac{\xi - \xi_\mathrm{W}}{\xi_\infty - \xi_\mathrm{W}}$$
(6.35)

this leads to the dimensionless conservation equation

$$u^*\frac{\partial\xi^*}{\partial x^*} + v^*\frac{\partial\xi^*}{\partial y^*} + w^*\frac{\partial\xi^*}{\partial z^*} = \frac{1}{\mathrm{Re}\,\mathrm{Sc}}\left(\frac{\partial^2\xi^*}{\partial x^{*2}} + \frac{\partial^2\xi^*}{\partial y^{*2}} + \frac{\partial^2\xi^*}{\partial z^{*2}}\right)$$
(6.36)

which leads to the fact, that the related concentration field has to be dependent on the dimensionless location variables and the characteristic numbers Re and Sc:

$$\xi^* = f\left(\mathrm{x}^*,\mathrm{y}^*,\mathrm{z}^*,\mathrm{Re},\mathrm{Sc}\right)$$
(6.37)

The analogy to heat transfer is apparent again. In section 4, convection:

$$T^* = f\left(\mathrm{x}^*,\mathrm{y}^*,\mathrm{z}^*,\mathrm{Re},\mathrm{Pr}\right)$$
(6.38)

was valid for the dimensionless temperature field.

6.3.1 Examples for transient diffusion

Regarding a one-dimensional transient problem, equation (6.33) can be simplified to

$$\rho\frac{\partial\xi}{\partial t} + \rho u\frac{\partial\xi}{\partial x} = \frac{\partial}{\partial x}\left(\rho D\frac{\partial\xi}{\partial x}\right)$$
(6.39)

If in addition, convection is neglected, this yields the following differential equation, which is known as "Fick's second law".

$$\rho \frac{\partial \xi}{\partial t} = \frac{\partial}{\partial x}\left(\rho D \frac{\partial \xi}{\partial x}\right) \tag{6.40}$$

This equation has a similar structure as equation (3.69) from chapter 3.5.2 and therefore can be solved in an analogue way.
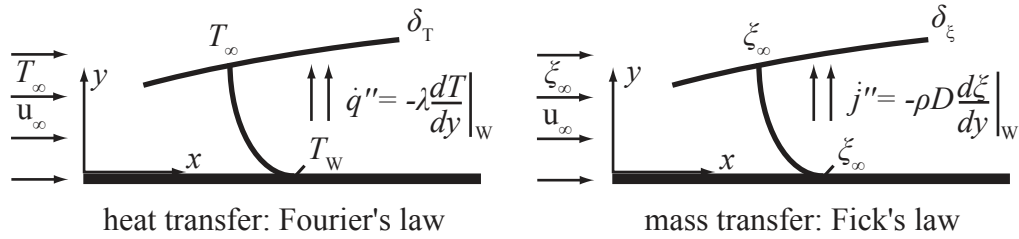
6.4 Transition laws in mass transfer

Figure 6.5: Analogy between heat and mass transfer

Similar to the heat transfer coefficient α introduced in heat transfer, which linked heat flux $\dot{q}''$ and the temperature difference between the wall temperature T_{W} and the surrounding T_∞

$$\dot{q}'' \equiv \alpha(T_{\mathrm{W}} - T_\infty) \tag{6.41}$$

in mass transfer a material transfer coefficient g can be defined:

$$j_{\mathrm{A}}'' \equiv g\left(\xi_{\mathrm{W}} - \xi_\infty\right) \tag{6.42}$$

To find a characteristic number for this transition coefficient it's useful to visualise the definition of the heat transfer coefficient once more. There, heat flux was determined drawing a balance using the local temperature gradient right next to the wall. Making $T^* = \frac{T}{T_\infty - T_{\mathrm{W}}}$ and $y^* = \frac{y}{L}$ [2] dimensionless yielded

$$\dot{q}_{\mathrm{W}}'' = -\lambda \left.\frac{\partial T}{\partial y}\right|_{y=0} = -\lambda \frac{T_\infty - T_{\mathrm{W}}}{L} \left.\frac{\partial T^*}{\partial y^*}\right|_{y^*=0} \tag{6.43}$$

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[2]L resembles a characteristic length in the regarded problem

Comparing equation (6.41) and (6.43) the dimensionless Nusselt number was introduced

$$\frac{\alpha L}{\lambda} \equiv \mathrm{Nu} = \left.\frac{\partial T^*}{\partial y^*}\right|_{y^*=0} = f(\mathrm{Re},\mathrm{Pr}) \tag{6.44}$$

although for this number, for different cases, correlations of the following form exist:

$$\mathrm{Nu} = C\,\mathrm{Re}^{\mathrm{m}}\,\mathrm{Pr}^{\mathrm{n}} \tag{6.45}$$

The same approach is used for the material transfer coefficient. For the diffusive material stream density, Fick's law is applied with reference values:

$$j_{\mathrm{A}}'' = -\rho D \left.\frac{\partial \xi}{\partial y}\right|_{y=0} = -\rho D \frac{\xi_\infty - \xi_{\mathrm{W}}}{L} \left.\frac{\partial \xi^*}{\partial y^*}\right|_{y^*=0} \tag{6.46}$$

Comparing this equation to the material transfer coefficient already introduced in equation (6.42) yields the characteristic material transfer number, the Sherwood number Sh:

$$\frac{gL}{\rho D} \equiv \mathrm{Sh} = \left.\frac{\partial \xi^*}{dy^*}\right|_{y^*=0} = f\,(\mathrm{Re},\mathrm{Sc}) \tag{6.47}$$

Sherwood numbers can also be rewritten using characteristic numbers for material transfer

$$\mathrm{Sh} = C\,\mathrm{Re}^{\mathrm{m}}\,\mathrm{Sc}^{\mathrm{n}} \tag{6.48}$$

Because the type of the mass conservation equation and the energy equation match, in case of similar boundary conditions, the constant C and the exponents m and n of both characteristic number relationships have to be equal.

Table 6.2: 1-D balance, no convection, constant material properties

heat transfer	mass transfer	momentum transfer
$\frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial x^2}$	$\rho \frac{\partial \xi_i}{\partial t} = D\rho \frac{\partial^2 \xi_i}{\partial x^2}$	$\frac{\partial u}{\partial t} = \nu \frac{\partial^2 u}{\partial x^2}$

6.4.1 Analogy between heat and mass transfer

A comparison of the characteristic numbers between heat and mass transfer shows that:

$$\frac{\mathrm{Sh}}{\mathrm{Nu}} = \left(\frac{\mathrm{Sc}}{\mathrm{Pr}}\right)^n \tag{6.49}$$

and hence

$$\frac{g}{\alpha/c_p} = \left(\frac{\text{Sc}}{\text{Pr}}\right)^{n-1} \tag{6.50}$$

For gases the Prantl and Schmidt number are almost identical. In this case a simple connection between the mass and heat transfer coefficient can be derived as an approximation, also known as Lewis' law:

$$\frac{g}{\alpha/c_p} = 1 \quad \text{Lewis' law (for gases)} \tag{6.51}$$

6.4.2 Solving the one-dimensional transient heat conduction and diffusion problem respectively
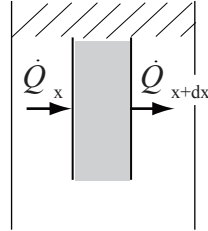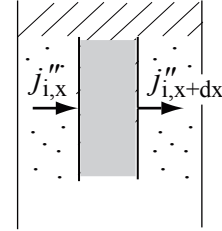

Figure 6.6: Transient heat conduction

Figure 6.7: Transient diffusion

The energy conservation equation used to determine the temperature profile of transient heat conduction in a half-infinite plate (left-hand side) and the mass transfer equation for component i regarding mere diffusion to determine the concentration field (right-hand side) are almost identical. Hence hereafter these two problems are described and solved concurrent to demonstrate the similarity of the solutions.

$$\frac{\partial T}{\partial t} = \frac{\lambda}{\rho c_p}\frac{\partial^2 T}{\partial x^2} \qquad\qquad \rho\frac{\partial \xi_i}{\partial t} = \rho D\frac{\partial^2 \xi_i}{\partial x^2}$$

Transforming both equations yields

$$\frac{\partial T}{\partial t} = \frac{\lambda}{\rho c_p}\frac{\partial^2 T}{\partial x^2} \qquad\qquad \frac{\partial \xi_i}{\partial t} = D\frac{\partial^2 \xi_i}{\partial x^2}$$

with the following boundary conditions

$$T(t = 0,x) = T_\text{o} \qquad\qquad \xi_i(t = 0,x) = \xi_{i,\text{o}}$$

$$T(t > 0,x = 0) = T_\text{u} \qquad\qquad \xi_i(t > 0,x = 0) = \xi_{i,\text{u}}$$

$$T(t > 0,x \to \infty) = T_\text{o} \qquad\qquad \xi_i(t > 0,x \to \infty) = \xi_{i,\text{o}}$$

Introducing an overtemperature and a dimensionless concentration, as well as a coefficient a

$$\theta^* = \frac{T - T_\text{o}}{T_\text{u} - T_\text{o}}, \quad a = \frac{\lambda}{\rho c_p} \qquad\qquad \theta^* = \frac{\xi_i - \xi_{i,\text{o}}}{\xi_{i,\text{u}} - \xi_{i,\text{o}}}, \quad a = D$$

eventually yields the same second order differential equation

$$\frac{\partial \theta^*}{\partial t} = a \frac{\partial^2 \theta^*}{\partial x^2} \tag{6.52}$$

using the transformed boundary conditions

$$\theta^*(t > 0, x \to \infty) = 0$$

$$\theta^*(t > 0, x = 0) = 1$$

$$\theta^*(t = 0, x) = 0$$

and the substitution

$$\eta \equiv \frac{x}{\sqrt{4at}} \tag{6.53}$$

the equation can be transformed into an ordinary differential euqation

$$\frac{\partial^2 \theta^*}{\partial \eta^2} = 2\eta \frac{\partial \theta^*}{\partial \eta} \tag{6.54}$$

its solution

$$\theta^* = 1 - erf(\eta)$$

or

$$\theta^* = 1 - erf\left(\frac{x}{\sqrt{4at}}\right)$$

respectively is valid for the temperature- as well as for the concentration field. A retransformation leads to the normal form with dimensions

$$\frac{T - T_{\mathrm{o}}}{T_{\mathrm{u}} - T_{\mathrm{o}}} = 1 - erf\left(\frac{x}{\sqrt{4\frac{\lambda}{\rho c_p}t}}\right) \qquad\qquad \frac{\xi_i - \xi_{i,\mathrm{o}}}{\xi_{i,\mathrm{u}} - \xi_{i,\mathrm{o}}} = 1 - erf\left(\frac{x}{\sqrt{4Dt}}\right)$$

Figure 6.8 and 6.9 qualitatively show the profiles. The heat flux at the wall can be derived from the temperature gradient

$$\dot{q}''|_{\mathrm{x}=0} = -\lambda \left.\frac{dT}{dx}\right|_{x=0} = \frac{\lambda}{\sqrt{\pi at}}(T_{\mathrm{u}} - T_{\mathrm{o}}) = \sqrt{\frac{\lambda c_p \rho}{\pi t}}(T_{\mathrm{u}} - T_{\mathrm{o}}) \tag{6.55}$$

The following equation is valid for the diffusion stream of component i at the surface

$$j_i''|_{\mathrm{x}=0} = \frac{\rho D}{\sqrt{\pi Dt}}(\xi_{i,\mathrm{u}} - \xi_{i,\mathrm{o}}) \tag{6.56}$$
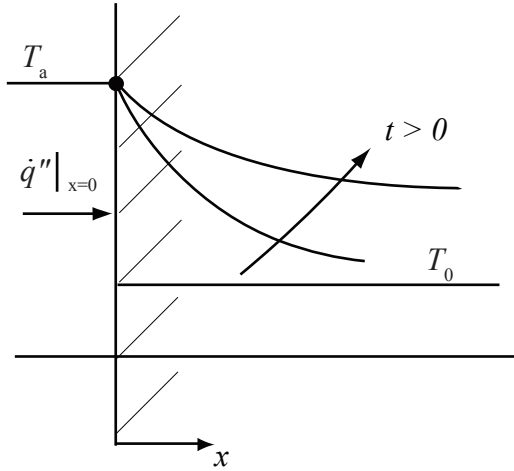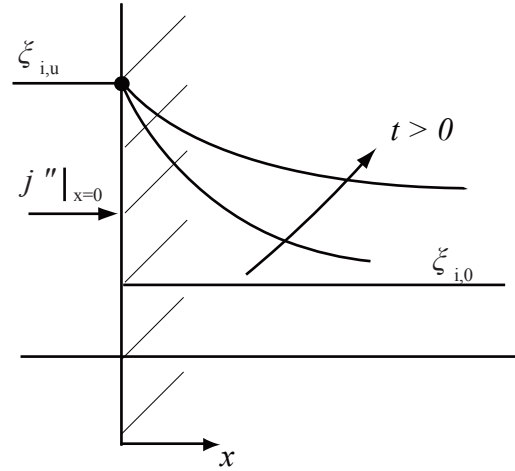
Figure 6.8: Temperature field

Figure 6.9: Concentration field

6.5 Evaporation at a liquid surface

The mechanism of a vaporous mass flow emerging from the surface of a liquid A into a gas mixture consisting of components A and B is called evaporation. This kind of mass transfer is driven by diffusion, i.e. diffusive resistances are determining. In contrast vaporisation is a process where the vapour component merges into a pure vapour-phase, hence diffusion resistances are irrelevant.

Hereafter, an evaporating mass flow is regarded, assuming, that component B from the gas mixture does not overflow into the liquid phase, hence the liquid surface is semipermeable. This process is described as single-sided diffusion in literature (see Mersmann (1986)).

Figure 6.10 shows this system. Here it is assumed, that the concentration of component A is permanently constant at position L, in simple terms $\xi(L) = 0$ is valid. Furthermore the phase boundary permanently stays at x = 0, due to a constant mass flow that cancels out the evaporation. In this steady state

$$\frac{\partial \xi_A}{\partial t} = \frac{\partial \xi_B}{\partial t} = 0 \tag{6.57}$$

is valid. A balance at the phase boundary for the mass flow of component B leads to $\dot{m}_B''(x = 0) = 0$, because component B does not dissolve in the liquid. Because in the area $0 < x < L$ no cross flow occurs, $\dot{m}_B''(0 < x < L) = 0$ is valid. For the evaporating component A, mass flow can be introduced as in section 6.3 using the effective velocity of the particles w_A, the desity and the mass fraction ξ of component A.

$$\dot{m}_A'' = w_A \rho \xi_A \tag{6.58}$$

As the effective particle velocity is a superposition of the mass centre velocity w and the diffusion stream $j_A^{''}$ (see equation (6.28)), the mass flow of A is

$$\dot{m}_A^{''} = w\rho\xi_A + j_A^{''} \tag{6.59}$$

A similar relationship can be derived for component B. Because the surface is impermeable for component B, as stated earlier, the mass flow is zero.

$$\dot{m}_B^{''} = w_B\rho\xi_B = w\rho\xi_B + j_B^{''} = 0 \tag{6.60}$$

The total mass flow is the sum of part mass flows

$$\dot{m}^{''} = \dot{m}_A^{''} + \dot{m}_B^{''} = w\rho\xi_A + j_A^{''} + w\rho\xi_B + j_B^{''} \tag{6.61}$$

With the requirement that the sum of diffusion flows equals zero from equation (6.29), and $\xi_A + \xi_B = 1$ yields

$$\dot{m}^{''} = \dot{m}_A^{''} + \dot{m}_B^{''} = w\rho \tag{6.62}$$
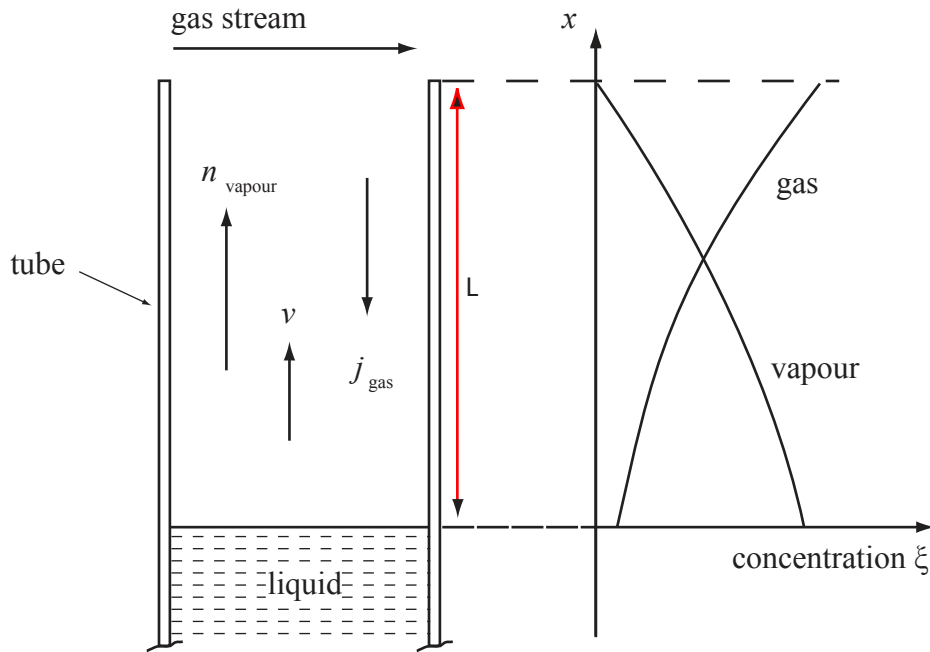

Figure 6.10: Stefan-stream

Applying this to equations (6.62) and (6.59), the total mass flow, as well as the mass flow of component A is:

$$\dot{m}'' = \dot{m}''_A = \underbrace{\frac{1}{1 - \xi_A}}_{F} j''_A \tag{6.63}$$

Apparently the net mass flow is larger than the diffusion flow by a factor F, the **Stefan-factor**. This factor takes into account that the surface is only permeable for the evaporating component ("semipermeable wall") and as a result the diffusive mass flow of component B driven by the concentration gradient towards the wall has to be compensated by a convective mass flow.

Expressing the mass flow j''_A according to (6.42) by the mass transfer coefficient and concentration difference yields:

$$\dot{m}''_A = g \frac{\xi_{A,W} - \xi_{A,\infty}}{1 - \xi_{A,W}} \tag{6.64}$$

Or in dimensionless form:

$$\frac{\dot{m}''_A}{\rho u_\infty} = \frac{Sh}{Re \cdot Sc} \underbrace{\frac{\xi_{A,W} - \xi_{A,\infty}}{1 - \xi_{A,W}}}_{B} \tag{6.65}$$

B is the driving potential for mass transfer.

6.5.1 Determining the mass transfer coefficient

With the previous solution of the evaporation problem at an open surface (6.64), the mass flow could only be determined, if the concentration gradient at the surface was known. Now the mass flow should be determined using the concentrations at the surface $\xi(x = 0)$ and at $\xi(x = L)$.

To begin with, the diffusion stream from equation (6.63) can be expressed by Fick's law.

$$\dot{m}'' = \dot{m}''_A = -\frac{1}{1 - \xi_A} \rho D \frac{\partial \xi_A}{\partial x} \tag{6.66}$$

Because the mass flow is constant at every position x, the equation above can be analysed at $x = 0$ (at the surface).

$$\dot{m}''\big|_O = \dot{m}''_A\big|_O = -\frac{1}{1 - \xi_{A,O}} \rho D \left(\frac{\partial \xi_A}{\partial x} \right)_O \tag{6.67}$$

Putting this mass flow into equation (6.59), regarding equation 6.62 yields:

$$\dot{m}_A'' = -\rho D \frac{\partial \xi_A}{\partial x} - \frac{\xi_A}{1 - \xi_{A,O}} \rho D \left(\frac{\partial \xi_A}{\partial x} \right)_O \tag{6.68}$$

Differentiating this equation after x leads to

$$\frac{\partial \dot{m}_A''}{\partial x} = -\rho D \left[\frac{\partial^2 \xi_A}{\partial x^2} + \frac{1}{1 - \xi_{A,O}} \left(\frac{\partial \xi_A}{\partial x} \right)_O \frac{\partial \xi_A}{\partial x} \right] = 0, \tag{6.69}$$

Whereat the derivation equals zero due to the constant mass flow. To solve this differential equation, the boundary conditions shall be defined. Because of the second order differential equation it is necessary to define two boundary conditions. For $x = 0$ (at the phase boundary), the mass fraction can be described, e.g. by Raoult's law. Hence the mass fraction, ξ_O is assumed to be known. Furthermore the mass fraction in the free-flow at the position $x = L$ with $\xi(L) = 0$ is known. The differential equation above (6.69) can be rewritten in a dimensionless form by using suitable reference values. Defining $\phi = x/L$ and $\theta = \xi_A/\xi_{A,O}$ yields the boundary conditions:

$$\text{BC1: for } \phi = \frac{0}{L} = 0 \; , \; \theta = \frac{\xi_{A,O}}{\xi_{A,O}} = 1 \text{ applies} \tag{6.70}$$

$$\text{BC2: for } \phi = \frac{L}{L} = 1 \; , \; \theta = \frac{0}{\xi_{A,O}} = 0 \text{ applies} \tag{6.71}$$

With this transformation and by introducing the constant

$$\Psi = -\frac{\xi_{A,O}}{1 - \xi_{A,O}} \left(\frac{\partial \theta_A}{\partial \phi} \right)_O \tag{6.72}$$

The following differential equation

$$\frac{\partial^2 \theta}{\partial \phi^2} - \Psi \frac{\partial \theta}{\partial \phi} = 0 \tag{6.73}$$

can be solved analytically. Introducing these dimensionless variables in equation (6.67) yields the mass flow

$$\dot{m}'' = \dot{m}_A'' = \frac{\rho D}{L} \Psi \tag{6.74}$$

In order to solve this differential equation, $\frac{\partial \theta}{\partial \phi}$ is substituted by K, which simplifies (6.73) to

$$\frac{\partial K}{\partial \phi} = \Psi K \tag{6.75}$$

This equation is solved by separation of variables.

$$K = e^{\Psi\phi + c_1} \tag{6.76}$$

Resubstituting K and integrating a second time yields

$$\theta = \frac{1}{\Psi} e^{\Psi\phi + c_1} + c_2 \tag{6.77}$$

Using both boundary conditions and transforming the equation yields:

$$\theta = \frac{e^{\Psi\phi} - e^{\Psi}}{1 - e^{\Psi}} \tag{6.78}$$

By Differentiating this equation after ϕ and evaluating the derivation at $\phi = 0$ (at the wall), this gradient can be put into equation (6.72). This leads to the following relationship

$$e^{\Psi} = \frac{1}{1 - \xi_{A,O}} \quad \text{oder: } \Psi = \ln\left(\frac{1}{1 - \xi_{A,O}}\right) \tag{6.79}$$

Which yields the mass flow from equation (6.74) with units

$$\dot{m}'' = \dot{m}_A'' = \frac{\rho D}{L} \ln\left(\frac{1}{1 - \xi_{A,O}}\right) \tag{6.80}$$

As expected the mass flow proceeds in positive x-direction, because the concentration decreases is x-direction. Furthermore the concentration profile can be indicated:

$$\ln\left(\frac{1 - \xi_A}{1 - \xi_{A,O}}\right) = \frac{x}{L} \ln\left(\frac{1}{1 - \xi_{A,O}}\right) \tag{6.81}$$

It should be pointed out, that the concentration profile is logarithmic and not linear. This profile derives from convection, which in turn is caused by diffusion. With the definition of a mass transfer coefficient g^*, that already takes the Stefan-stream into account, in case of evaporation at an open surface, can be determined as

$$g^* = \rho \frac{D}{L} \frac{1}{\frac{\xi_{A,O}}{\ln(\frac{1}{1 - \xi_{A,O}})}} \tag{6.82}$$

The analogy to heat transfer should here be pointed out once more. In case of mere heat conduction, i.e. no convection, the Nusselt number is one. In the case that has just been regarded there was also no forced stream from outside, so in case of mere diffusion, the Sherwood number also equals one. With equation (6.47) this leads to a mass transfer coefficient of $g = \frac{\rho D}{L}$. Comparing this to (6.82) shows that a second term was added. This term is know as "high flux correction", because it considers

the diffusion driven convection that appears. This is the factor by which the mass transfer increases compared to mere diffusion.