
2.1 Heat transfer by stationary heat conduction

2.1.1 Problem statement and Fourier’s law

Heat transfer has been defined in section 1.1 as energy transferred from one system to another one due to temperature differences. A simple scenario has been discussed in terms of the thermal equilibration of two systems of different initial temperature. There, the transferred heat has been obtained from the temperature gradients at the systems boundaries after the solution of the appropriate energy balance equation (governing transport mechanism: heat conduction at the boundaries), compare section 1.2.1 and 1.3.5.

For heat transfer by stationary heat conduction we extend the scenario of section 1.3.5 by separating the two systems via a solid material, see Figure 2.1.1-1.

One planar body of area $A$ at low temperature is separated by a planar sheat from a second planar body at high temperature. The sheat thickness is $s_1$ and the area also $A$.

Due to the different (stationary) temperatures a heat flux from the system at higher temperature to that at lower temperature is established. The only transport mechanism of heat again is heat conduction, now under stationary conditions (no flow velocity, no conversion). The heat flux then is given by the temperature gradients at the boundaries (section 1.3 and 1.3.5).

Fig. 2.1.1-1: Heat transfer by stationary heat conduction in planar geometries.
We obtain the temperature gradients at the boundaries by solving the appropriate balance equation. From table 1.3.4-1 we take (one dimensional formulation considering the planar geometry):

$$\frac{\partial (\rho \cdot c_v \cdot \nabla T)}{\partial t} = - \frac{\partial}{\partial x} \left( \varphi \cdot \rho \cdot \nabla - \lambda \cdot \frac{\partial T}{\partial x} \right) + s$$

(2.1.1-1)

Considering stationary conditions, no conversion, no flow velocity this reduces after integration to (compare section 1.3 and 1.3.5):

$$- \lambda \cdot \frac{dT}{dx} = \text{const.} = J_Q \text{diff}$$

(2.1.1-2)

and

$$J_Q \text{diff} = - \lambda \cdot A \cdot \frac{dT}{dx}$$

(2.1.1-3)

Equation (2.1.1-3) is Fourier’s law of stationary (one-dimensional) heat conduction. **The heat flux is the product of heat conductivity \( \lambda \), area \( A \) and temperature gradient \( dT/dx \).** The heat flux vector is anti-parallel to the temperature gradient (also vector). This is noted by the negative sign in equation (2.1.1-2). Heat, therefore, always is transported in the direction of lower temperatures.

The heat conductivity \( \lambda \) [W/(m\(^2\cdot\)K)] according to Fourier’s law (equation (2.1.1-3)) is the heat flux [W] by heat conduction per unit of negative temperature gradient \( dT/dx \) [K/m] and unit area \( A \) [m\(^2\)]. **The heat conductivity \( \lambda \) is a material property.**

(in English language use: \( \lambda \) also thermal conductivity. Not to be confused with \( a = \frac{\lambda}{\rho \cdot c_p} \).)
2.1.2 Mechanisms of heat conduction in gases, liquids and solids

Gases. We consider a gas with a temperature gradient in one direction, see figure 2.1.2-1. The gas molecules move by thermal motion from an isotherm with a certain temperature to an other isotherm with higher (lower) temperature. Hopping between the isotherms the gas molecules carry their internal energy and transfer the energy by collisions to other molecules. Thereby, „hotter“ regions are cooled and „cooler“ regions are heated. If the temperature gradient is kept at constant, a heat flux is established from high temperature to low temperature.

Gaseous molecules accumulate their internal energy in form of kinetic energy (translation), rotational energy and oscillation energy (the latter forms only in multi-atom molecules, e.g. H₂O, N₂, CO₂,…). Rotational energy and oscillation energy are quantized.

Heat conductivity of gases. According to the simple model of heat conduction, the heat conductivity \( \lambda \) of ideal gases can be described with the kinetic theory of gases:

\[
\lambda = \frac{1}{3} \rho \cdot \overline{v} \cdot \Lambda \cdot c_v = \eta \cdot c_v \quad (2.1.2-1)
\]

In equation (2.1.2-1) \( \Lambda \) is the mean free path of the molecules and \( \overline{v} \) the mean molecular velocity of the molecules.

\[
\Lambda = \frac{1}{\sqrt{2} \cdot \pi \cdot d^2 \cdot N_A} \cdot \frac{RT}{p} \quad \overline{v} = \sqrt{\frac{8RT}{\pi \cdot M}} \quad (2.1.2-2)
\]

Then:

\[
\lambda = \frac{2}{3} \cdot \frac{1}{\pi \cdot d^2 N_A} \cdot \sqrt{\frac{MRT}{\pi}} \cdot c_v \quad (2.1.2-3)
\]
According to equation (2.1.2-3) the heat conductivity increases with increasing temperature (for atoms $T^{0.5}$) and with increasing molar mass. According to the kinetic theory of gases, there is no pressure dependence of the heat conductivity for ideal gases.

Table 2.1.2-1 contains the heat conductivities of some gases. From the table a slight pressure dependence of the heat conductivity can be seen (in contrast to the simple kinetic gas theory).

<table>
<thead>
<tr>
<th>temperature $T/°C$</th>
<th>-173</th>
<th>-73</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>substance</td>
<td>heat conductivity $\lambda$/Wm$^{-1}$K$^{-1}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>hydrogen</td>
<td>0,06802</td>
<td>0,12626</td>
<td>0,17694</td>
</tr>
<tr>
<td>methane</td>
<td>0,01063</td>
<td>0,02185</td>
<td>0,03428</td>
</tr>
<tr>
<td>propane</td>
<td></td>
<td>0,01800</td>
<td></td>
</tr>
<tr>
<td>carbon dioxide</td>
<td></td>
<td>0,00950</td>
<td>0,01666</td>
</tr>
<tr>
<td>oxygen</td>
<td>0,00904</td>
<td>0,01833</td>
<td>0,02658</td>
</tr>
<tr>
<td>air</td>
<td></td>
<td>0,02640</td>
<td></td>
</tr>
<tr>
<td>air</td>
<td></td>
<td>0,03150 (10 MPa)</td>
<td></td>
</tr>
<tr>
<td>water vapor</td>
<td></td>
<td>0,01940 (0,0023 MPa)</td>
<td></td>
</tr>
</tbody>
</table>

*Table 2.1.2-1: Heat conductivity of some gases.*
Heat conductivity of liquids. The mechanism of heat conduction in liquids is similar to that of heat conduction in gases, however, the interactions of molecules play an important role (hydrogen bridge bonds, van der Waals interactions, ionic interactions, other long range and short range interactions).

Table 2.1.2-2 gives an overview over the heat conductivities of some liquids. The heat conductivity of most liquids is one order of magnitude higher than the heat conductivity of gases.

Water and other inorganic fluids (ammonia) exhibit a much higher heat conductivity than organic fluids; molten salts show even higher heat conductivities.

The heat conductivity of liquids increases generally with increasing temperature.

<table>
<thead>
<tr>
<th>Stoff</th>
<th>Temperatur T°C</th>
<th>Wärmeleitfähigkeit λ/Wm⁻¹K⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wasser</td>
<td>20</td>
<td>0,59</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0,65</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0,67</td>
</tr>
<tr>
<td>Thermalöl S</td>
<td>100</td>
<td>0,126</td>
</tr>
<tr>
<td>HTS-Schmelze</td>
<td>500</td>
<td>0,5</td>
</tr>
<tr>
<td>Ammoniak</td>
<td>25</td>
<td>0,480 (1MPa)</td>
</tr>
<tr>
<td>Butan</td>
<td>25</td>
<td>0,098 (0,25 MPa)</td>
</tr>
<tr>
<td>Heptan</td>
<td>25</td>
<td>0,124</td>
</tr>
<tr>
<td>Oktan</td>
<td>25</td>
<td>0,131</td>
</tr>
<tr>
<td>Dodekan</td>
<td>25</td>
<td>0,143</td>
</tr>
<tr>
<td>Benzol</td>
<td>25</td>
<td>0,144</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0,15</td>
</tr>
<tr>
<td>Tetrachlorkohlenstoff</td>
<td>20</td>
<td>0,1</td>
</tr>
<tr>
<td>Äther</td>
<td>30</td>
<td>0,13</td>
</tr>
<tr>
<td>Ethylalkohol</td>
<td>20</td>
<td>0,16</td>
</tr>
<tr>
<td>Glyzerin</td>
<td>20</td>
<td>0,29</td>
</tr>
</tbody>
</table>

*Table 2.1.2-2: Heat conductivity of some liquids.*
Simple model for heat conduction in solids. In solids molecules (lattice building blocks) cannot move freely. They are fixed at their lattice places, see figure 2.1.2-2.

Solids store thermal energy in form of oscillations of the atoms about their positions of rest in the lattice. In solids the transport of energy occurs via the oscillations of neighboring molecules. All molecules in the solid form a system of coupled oscillators (same mechanism as the transport of sound in solids).

The energy quanta released or accepted from this system of coupled oscillators are called phonons. Therefore, heat conduction in solids is accomplished by transport of phonons.

In addition, in metals and electrical conductors the transport of phonons is superimposed by the transport of electrons in the conductivity band. Therefore, heat conductivity in solids is caused by the transport of phonons and the thermal movement of conductivity electrons. The latter effect increases the heat conductivity.

The heat conductivity of metals is two to three orders of magnitudes higher than that of gases. Metals show a much higher thermal conductivity compared with other solids.

Heat conductivities of metals correspond to electrical conductivities (Fe < Al < Cu < Ag); Wiedemann-Franz-Lorenz law; contribution of conductivity electrons to heat conduction.

\[ \frac{\lambda}{\kappa \cdot T} = 2.45 \cdot 10^{-8} \left[ \frac{V}{K} \right]^2 \]  

(\( \kappa \): electrical conductivity in \( \text{Wm}^{-1} \)).
Table 2.1.2-3: Heat conductivities of some solids.

Table 2.1.2-3 gives some values for the heat conductivity of solids. Often the heat conductivity is non isotropic (graphite, wood).

Detailed information about heat conductivities of different materials and methods of calculation can be found in VDI-Wärmeatlas.

For metals and other electrical conductors the heat conductivity is a complicated function of temperature.

Difference between electrical conductors and semi-conductors and insolaters in the temperature dependency of the heat conduction.
2.1.3 Heat transfer by stationary heat conduction in planar and non-planar geometries, heat transfer coefficient

Heat transfer by stationary heat conduction through planar geometries. We consider the scenario from Figure 2.1.1-1. A planar plate with homogeneous material properties \( \lambda_1 \) separates two bodies at different temperatures, see figure 2.1.3-1. Lateral extension is large compared to thickness \( s_1 \) (reduction to a 1-dimensional problem). Boundary conditions at the left and right surface are kept at constant temperatures.

Using the balance equation (2.1.1-1) in integrated form (Fourier’s law) we obtain:

\[
J_Q = -\lambda_1(T) \cdot A \cdot \frac{dT}{dx} \tag{2.1.3-1}
\]

Assuming \( \lambda_1 \) being constant, separation of variables leads to:

\[
dT = -\frac{J_Q}{\lambda_1 \cdot A} \, dx \tag{2.1.3-2}
\]

Integration within boundaries 0 and \( x \) results in:

\[
T = T_2 - \frac{J_Q}{\lambda_1 \cdot A} \cdot x \tag{2.1.3-3}
\]

For this problem we obtain a linear decrease of temperature within the plate. Setting \( x = s_1 \) and \( T(s_1) = T_1 \) and resolving for \( J_Q \) gives:

\[
J_Q = \lambda_1 \cdot A \cdot \frac{T_2 - T_1}{s_1} \tag{2.1.3-4}
\]

- Heat flux \( \to 0 \), if \( \lambda \to 0 \),
- Heat flux \( \to 0 \), if \( s \to \infty \),
- Heat flux \( \to 0 \), if \( \Delta T \to 0 \).

For \( \lambda_1 \) varying with temperature, no linear temperature profile!
Generally, the heat transfer coefficient is "non-dimensionalized" with a characteristic length $L$ and the heat conductivity $\lambda$:

$$\alpha \cdot \frac{L}{\lambda} = Nu$$  \hspace{1cm} (2.1.3-9)

This number is called **Nusselt number**.

Introducing the heat transfer coefficient reduces the spatial dimension of a heat transfer problem (in the planar case from a 1-d problem in space to a 0-d problem)!

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For this problem a heat transfer coefficient $\alpha$ is defined according to

$$\alpha = \frac{\text{heat flux}}{\text{area} \cdot \text{driving temperature difference}}$$

or

$$\alpha = \frac{I_Q}{A \cdot \Delta T}$$ \hspace{1cm} (2.1.3-6)

With $\Delta T = T_2 - T_1$ and equation (2.1.3-4) we obtain for this case

$$\alpha = \frac{\lambda_1}{s_1}$$ \hspace{1cm} (2.1.3-7)

Generally, the heat transfer coefficient $\alpha$ is the heat conductivity $\lambda$ divided by a distance $s$ (normalized conductivity).

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With the help of the heat transfer coefficient $\alpha$ given in equation (2.1.3-7) any heat transfer problem can be now written as:

$$J_Q = \alpha \cdot A \cdot \Delta T$$ \hspace{1cm} (2.1.3-8)
Heat transfer by stationary heat conduction in spherical geometries. We replace the planar arrangement from Figure 2.1.1-1 by a spherical one, where a sphere at temperature $T_i$ is separated by a spherical shell from a system at temperature $T_a$. The system can be treated as one-dimensional problem (coordinate radius $r$). The temperatures at the inner and outer surface are constant in time and surface, see figure 2.1.3-2. The material has the heat conductivity $\lambda_1$.

Using the balance equation (2.1.1-1) in integrated form (Fourier’s law) we obtain for this case:

$$J_Q = -\lambda_1 \cdot A(r) \cdot \frac{dT}{dr} = -\lambda_1 \cdot 4\pi r^2 \cdot \frac{dT}{dr} \quad (2.1.3-10)$$

Again the total heat flux is constant. In this case the area increases with radius. Therefore, according to Fourier’s law we expect a decrease of the temperature gradient. Separation of variables in equation (2.1.3-10) gives:

$$dT = -\frac{J_Q}{4\pi \lambda_1} \cdot \frac{dr}{r^2} \quad (2.1.3-11)$$

Integration within the boundaries $R_i$ and $r$ gives:

$$T(r) = T_i - \frac{J_Q}{4\pi \lambda_1} \cdot \left(\frac{1}{R_1} - \frac{1}{r}\right) \quad (2.1.3-12)$$

The temperature in the spherical shell varies hyperbolically with the radius $r$ (at constant heat conductivity, compare planar problem: linear).
Setting \( r = R_a \) and \( T(R_a) = T_a \) in equation (2.1.3-12) and resolving for the heat flux \( J_Q \) we obtain:

\[
J_Q = \lambda_1 \cdot \frac{4\pi}{\left(\frac{1}{R_i} - \frac{1}{R_a}\right)} \cdot (T_i - T_a) = \lambda_1 \cdot 4\pi \cdot R_a \cdot R_i \cdot \frac{(T_i - T_a)}{(R_a - R_i)} \quad (2.1.3-13)
\]

With this we obtain the same form for the equation of heat flux by conduction as in the planar geometry. However, at otherwise constant conditions (\( \Delta T, s, \lambda_1 \)) the heat flux in spherical geometries is smaller compared to planar geometries.

For \( R_a \gg R_i \) in equation (2.1.3-13) \( l/R_a \) can be neglected against \( l/R_i \). Using this we obtain:

\[
J_q = \lambda_1 \cdot 4\pi \cdot R_1 \cdot (T_i - T_a) \quad (2.1.3-14)
\]

Even at high wall thicknesses (strong isolation) a minimum residual heat flux remains in spherical shell geometries according to equation (2.1.3-14).

- Heat flux \( \rightarrow 0 \), if \( \lambda \rightarrow 0 \).
- Heat flux \( \rightarrow 0 \), if \( \Delta T \rightarrow 0 \).
- Heat flux \( \rightarrow \) minimum heat flux, if \( s \rightarrow \infty \).

Fig. 2.1.3-2: Heat transfer by stationary heat conduction in non-planar geometries (spherical shells).
Heat transfer coefficient for heat transfer from a sphere to surroundings. We consider the problem analogous to heat transfer by heat conduction in a spherical geometry, figure 2.1.3-2, but extend the spherical shell to infinity. The surface temperature of the sphere is constant and the temperature far away from the surface is also kept at constant, see figure 2.1.3-3.

The shell material (which is now surrounding the sphere) has the heat conductivity $\lambda_j$. This scenario describes the heat transfer from a sphere into surroundings at rest (no macroscopic motion).

For this problem we obtain the heat transfer coefficient $\alpha$ according to equation (2.1.3-5):

$$\alpha = \frac{J_Q}{A_{bez} \Delta T_{bez}} \quad (2.1.3-15)$$

With $\Delta T_{bez} = (T_i - T_a)$ and $A_{bez} = 4\pi \cdot R_i^2$ and equation (2.1.3-14) we obtain

$$\alpha = \frac{J_Q}{A_{bez} \Delta T_{bez}} = \frac{\lambda_1 \cdot 4\pi \cdot R_i \cdot (T_i - T_a)}{4\pi \cdot R_i^2 \cdot (T_i - T_a)} = \frac{\lambda_1}{R_i} \quad (2.1.3-16)$$

For the Nusselt number for the problem of heat transfer from a sphere into a surrounding at rest we obtain finally:

$$Nu_K = \frac{\alpha \cdot D_K}{\lambda_1} = \frac{\lambda_1}{R_i} \cdot D_K \cdot \frac{\lambda_1}{\lambda_1} = 2 \quad (2.1.3-17)$$
2.1.4 Heat transfer by stationary heat conduction in layered materials, over all heat transfer coefficient

Stationary heat conduction in layered materials. We replace the planar sheet between two bodies at different temperatures in section 2.1.2 by a sheet consisting of layers of different materials. The over-all thickness is small compared with the lateral dimensions, so that the problem can be treated as a one-dimensional heat conduction problem. At the left and right wall constant temperatures are applied, see figure 2.1.4-1. The different layers have the heat conductivities \( \lambda_1 \), \( \lambda_2 \) and \( \lambda_2 \).

Applying Fourier’s law in integrated form we obtain:

\[
J_Q = \lambda_1 \cdot A \cdot \frac{T_1 - T_{1/2}}{s_1} \quad (2.1.4 - 1)
\]

and

\[
J_Q = \lambda_2 \cdot A \cdot \frac{T_{1/2} - T_{2/3}}{s_2} \quad (2.1.4 - 2)
\]

and

\[
J_Q = \lambda_3 \cdot A \cdot \frac{T_{2/3} - T_3}{s_3} \quad (2.1.4 - 3)
\]

Resolving for the temperature differences and adding results in:

\[
\frac{J_Q}{A} \left( \frac{s_1}{\lambda_1} + \frac{s_2}{\lambda_2} + \frac{s_3}{\lambda_3} \right) = T_1 - T_{1/2} + T_{1/2} - T_{2/3} + T_{2/3} - T_3 \\
\]

or

\[
J_Q = \frac{1}{\frac{1}{\lambda_1} + \frac{1}{\lambda_2} + \frac{1}{\lambda_3}} A \cdot (T_1 - T_3) \quad (2.1.4 - 4)
\]

\[
J_Q = \frac{s_1 + s_2 + s_3}{\lambda_1 + \lambda_2 + \lambda_3} A \cdot (T_1 - T_3) \quad (2.1.4 - 5)
\]
From equations (2.1.4-1) to (2.1.4-3) we find that the temperature differences in the single layers are inversely proportional to the heat conductivities per unit length (insolation problem).

\[
\frac{T_{1/2} - T_{2/3}}{T_1 - T_{1/2}} = \frac{\lambda_1}{s_1} \quad \frac{T_{2/3} - T_3}{T_{1/2} - T_{2/2}} = \frac{\lambda_2}{s_2} \quad \frac{T_{1} - T_{1/2}}{T_1 - T_{1/2}} = \frac{\lambda_3}{s_3}
\]  

\(2.1.4-6\)

**Over-all heat transfer coefficient.** For the heat transfer problem by stationary heat conduction through a system boundary of layered material we define an over-all heat transfer coefficient \(k_i\) analogously to the heat transfer coefficient in section 2.1.3 (one layer problem):

\[
\alpha = \frac{\text{heat flux}}{\text{area} \cdot \text{driving temperature difference}} \quad (2.1.4-7)
\]

\[
k_1 = \frac{J_Q}{A(T_1 - T_{1/2})} = \frac{\lambda_1}{s_1} \quad (2.1.4-8)
\]

\[
k_2 = \frac{J_Q}{A(T_{1/2} - T_{2/3})} = \frac{\lambda_2}{s_2} \quad (2.1.4-9)
\]

\[
k_3 = \frac{J_Q}{A(T_{3/2} - T_3)} = \frac{\lambda_3}{s_3} \quad (2.1.4-10)
\]

The heat transfer coefficients according to equations (2.1.4-8) to (2.1.4-10) are heat conductivities normalized to the thickness of the layers (specific conductivities). Then the reciprocal of the heat transfer coefficients are specific resistances (analogy to conduction of electricity).
Using equations (2.1.4-8) to (2.1.4-10) in equation (2.1.4-5) yields:

\[ J_Q = \frac{1}{k} A \cdot (T_1 - T_3) \quad (2.1.4-11) \]

or

\[ J_Q = \frac{1}{k} A \cdot (T_1 - T_3) = k \cdot A \cdot (T_1 - T_3) \quad (2.1.4-12) \]

With the overall heat transfer coefficient \( k \)

\[
\frac{1}{k} = \frac{1}{k_1} + \frac{1}{k_2} + \frac{1}{k_3} \quad R = R_1 + R_2 + R_3 \quad (2.1.4-13)
\]

For heat transfer by heat conduction through "heat conduction resistances" in series the single resistances add to the total resistance! (reciprocal specific conductivities, see figure 3.1.4-2).

For heat transfer by heat conduction through "heat conduction resistances" in parallel the single specific conductivities add to the total conductivity! (reciprocal specific resistances, see figure 3.1.4-3).
2.1.5 Examples of heat transfer by stationary heat conduction in engineering

Heat transfer by stationary heat conduction from surfaces to slabs with heat transfer into the ambient. We consider a cylindrical slab with the length \( L \), mounted perpendicular to a hot surface. The surface is kept at temperature \( T_0 \) and the ambient temperature is \( T_a \). The material has the heat conductivity \( \lambda \), see fig. 2.1.5-1 („thermal or cold bridge“).

Problem: Heat transfer from the wall into the slab via heat conduction through the slab and from the slab to the ambient. The wall is insulated perfectly, heat transfer occurs solely via the slab (problem to solve: temperature gradient at the connecting surface, temperature distribution in the slab, heat loss from the slab (thermal bridge, cold bridge)).

For the calculation of the temperature profile in the slab we consider the heat balance for a differential volume of the slab. Within the slab we have heat conduction, at the surface we have heat transfer to the ambient. (Simplification: temperature constant over the radius, 1-d problem, has to be justified!).

Heat balance:

Heat flux in = heat flux out \hspace{1cm} (2.1.5-1)

Heat flux into the balance volume:

\[
J_Q(x) = -\lambda \cdot A \cdot \left( \frac{dT}{dx} \right)_x \quad (2.1.5-2)
\]

Heat flux out of the balance volume:

\[
J_Q(x + \Delta x) = -\lambda \cdot A \cdot \left( \frac{dT}{dx} \right)_{x+\Delta x} \quad (2.1.5-3)
\]
Heat transfer to the ambient ($U$: circumference):
\[
J_{Q_{\text{ub}}} = \alpha_{\text{aus}} \cdot U \cdot \Delta x \cdot (T - T_a) \quad (2.1.5-4)
\]

Heat balance for stationary conditions:
\[
J_{Q_x} = J_{Q_{x+\Delta x}} + J_{Q_{\text{ub}}} \quad (2.1.5-5)
\]

Heat flux at $x+\Delta x$ is obtained by a Taylor series expansion of the heat flux at $x$ and linearisation:
\[
J_Q(x+\Delta x) \approx J_Q(x) + \frac{dJ_Q}{dx} \Delta x \\
= J_Q(x) - \lambda \cdot A \cdot \left( \frac{d^2 T}{dx^2} \right) \Delta x \quad (2.1.5-6)
\]

For the heat balance we obtain:
\[
0 = -\lambda \cdot A \cdot \left( \frac{d^2 T}{dx^2} \right) \Delta x + \alpha_{\text{aus}} \cdot U \cdot \Delta x \cdot (T - T_a) \quad (2.1.5-7)
\]

Transformation with $\theta = (T-T_a)/(T_0-T_a)$ and $\eta = x/L$ gives:
\[
\left( \frac{d^2 \theta}{d\eta^2} \right) = \frac{\alpha_{\text{aus}} \cdot U \cdot L^2}{\lambda \cdot A} \cdot \theta = m^2 \cdot \theta \quad (2.1.5-8)
\]

In equation (2.1.5-8) $m^2 = 4L(\alpha_{\text{aus}}/\lambda)(L/D)$. The ratio $(\alpha_{\text{aus}}R/\lambda)$ can be understood as ratio of the heat transfer resistance slab/wall to wall/ambient.

This ratio is called Biot number, $Bi$. Then $m^2 = 8 \ (L/D)^2 \ Bi$ (Bi must be small for treating the problem as 1-d problem).

Solution of the ordinary differential equation of second order (2.1.5-8):
\[
\theta = C \cdot e^{\mu \eta} \quad (2.1.5-9)
\]
Differentiating equation (2.1.5-9) twice by \( \eta \) gives:

\[
\frac{d^2 \theta}{d \eta^2} = \mu^2 \cdot C \cdot e^{\mu \eta} = \mu^2 \cdot \theta \quad (2.1.5-10)
\]

Equation (2.1.5-9) is a solution of (2.1.5-8) only if

\[ \mu^2 = m^2 \quad \text{or} \quad \mu_1 = +m \quad \mu_2 = -m \]

with \( m = \frac{L}{D} \cdot \sqrt{8 \cdot Bi} \quad (2.1.5-11) \)

General solutions: linear combination of particular solutions:

\[
\theta = A \cdot e^{m \eta} + B \cdot e^{-m \eta} \quad (2.1.5-12)
\]

Integrations constants \( A \) and \( B \) from boundary conditions.

**Boundary condition 1:** For \( \eta = 0 \quad T = T_0 \), therefore \( \theta = 1 \). This gives:

\[
1 = A + B \quad (2.1.5-13)
\]

**Boundary condition 2:** Finite long slab, heat transfer to the ambient at the front end side negligible. Then \( d\theta/d\eta = 0 \), for \( \eta = 1 \). This gives:

\[
0 = A \cdot m \cdot e^m - B \cdot m \cdot e^{-m} \quad B = A \frac{e^m}{e^{-m}} \quad (2.1.5-14)
\]

Considering equation (2.1.5-13) we have:

\[
A = \frac{e^{-m}}{e^m + e^{-m}} \quad B = \frac{e^m}{e^m + e^{-m}} \quad (2.1.5-15)
\]

The solution then is:

\[
\theta = \frac{\cosh[m \cdot (1 - \eta)]}{\cosh[m]} \quad 1.5 - 16
\]

**Fig. 2.1.5-2:** Equation (2.1.5-16) for \( m = 5 \).
Heat loss from the wall at $T_0$ via the „cold bridge“ to the ambient as heat transfer problem: The total heat flux from the wall via the slab to the ambient is supplied by heat conduction from the wall to the slab (see fig. 2.1.5-1). Therefore

$$J_Q = -\lambda \cdot A \cdot \left( \frac{dT}{dx} \right)_{x=0} = -\frac{\lambda \cdot A \cdot (T_0 - T_a)}{L} \left( \frac{d\theta}{d\eta} \right)_{\eta=0} \tag{2.1.5-17}$$

The heat supplied by heat conduction into the slab is transferred to the ambient. Therefore, $J_Q = J_{Q\text{übr}}$.

Solution for the temperature distribution for the stationary problem at $x \to 0$:

$$\theta = \frac{\cosh[m(1-\eta)]}{\cosh[m]} \quad \text{therefore} \quad \left( \frac{d\theta}{d\eta} \right)_{\eta=0} = -m \frac{\sinh(m)}{\cosh(m)} = -m \tanh(m) \approx -m \quad \text{for} \quad m \geq 5 \tag{2.1.5-18}$$

With this we obtain from equation (2.1.5-17):

$$J_Q = \frac{\lambda \cdot A \cdot m}{L} \cdot (T_0 - T_a) \tag{2.1.5-19}$$

On the other hand, the heat transfer problem can be formulated based on the fundamental heat transfer equation (2.1.3-14):

$$J_Q = \alpha \cdot A \cdot (T_0 - T_a) \tag{2.1.5-20}$$

Comparing equations (2.1.5-19) and (2.1.5-20) we obtain:

$$\alpha = \frac{\lambda \cdot m}{L} \quad \text{or} \quad \frac{\alpha \cdot L}{\lambda} = Nu_L = m = 2L \cdot \sqrt{\frac{\alpha_{\text{aussen}}}{\lambda \cdot D}} = \frac{L}{D} \cdot \sqrt{8 \cdot Bi} \tag{2.1.5-21}$$

We learn from this example that heat transfer from the slab to the ambient and heat conduction into the slab are coupled processes that affect each other!
**Exact temperature measurement.** We mount a temperature sensor (thermo couple) into the slab to measure the temperature $T_a$ in the ambient atmosphere. How close is the temperature at the front end to the ambient temperature $T_a$? In this case $T_a > T_0$.

\[
\theta = \frac{(T - T_a)}{T_0 - T_a} = \frac{\cosh[m(1-\eta)]}{\cosh[m]} \quad (2.1.5-22)
\]

For the front end of the slab ($\eta = 1$) we obtain:

\[
\frac{T_a - T_L}{T_a - T_0} = \frac{1}{\cosh[m]} \quad (2.1.5-23)
\]

For the measuring error to be smaller than 0.5% we have:

\[
\frac{T_a - T_L}{T_a - T_0} = \frac{1}{\cosh[m]} = \frac{2}{e^m + e^{-m}} \leq 0.005 \quad (2.1.5-24)
\]

Transformation gives:

\[
\frac{2}{0.005} \leq e^m + e^{-m} \quad (2.1.5-25)
\]

Finally:

\[
1 \geq \frac{\ln 400}{m} = \frac{6}{m} \quad m \geq 6 \quad (2.1.5-26)
\]

Example: $\alpha = 100 \text{ W/m}^2 \text{ K}$, $\lambda = 60 \text{ W/m} \text{ K}$, $U/A = 1/s$, $s = 1 \text{ mm}$.

**Fig. 2.1.5-3:** For the demonstration of the thermometry problem.

\[
\text{Then} \quad m = \sqrt{\frac{\alpha_{aussen} \cdot U}{\lambda \cdot A}} \cdot L = \sqrt{1600} \cdot L = 40 \cdot L
\]

$L \geq 0.15 \text{ m}$

For the prevailing conditions the slab has to have a length of minimum 15 cm!
Summary of section 2.1

- The different mechanisms of heat conduction have been qualitatively discussed.
- The basics of heat conduction in fluids and solids have been elaborated.
- The material property „heat conductivity“ has been discussed.

- The heat transfer coefficient has been introduced.
- The overall heat transfer coefficient has been introduced.

- Stationary heat conduction for different geometries and some problems from process engineering has been elucidated.
2.2 Heat transfer by non stationary heat conduction

2.2.1 Fourier’s law of non stationary heat conduction and thermal conductivity

Up to now only stationary heat conduction problems have been discussed. For these problems temperatures and heat fluxes are invariant against time. In process technology most problems are non stationary, so that non stationary heat conduction has to be discussed in the following.

Basics of heat transfer by non stationary heat conduction; Fourier’s law of non stationary heat conduction. Again we consider a cylindrical slab with homogeneous material properties \((\lambda, c_p, \rho)\) which is mounted at a wall. (Simplification: temperature constant over the radius (1-d problem! Justification !). The wall temperature is initially \(T_a\) and is increased at \(t = 0\) to \(T_0\). The temperature distribution and heat fluxes are now dependent on distance and time!

For determination of heat transfer we need the temperature gradient at the connecting surface. For that we need the temperature distribution in the slab. Again, for solving this task we consider the heat balance for a differential volume of the slab. Within the slab we have conduction and in this case in addition accumulation of heat, at the surface we have heat transfer to the ambient.

Heat balance:

\[
\text{accumulation of heat} = \text{heat flux in} - \text{heat flux out} \tag{2.2.1-1}
\]
Heat flux into the balance volume by heat conduction:
\[ J_Q(x,t) = -\lambda \cdot A \cdot \left( \frac{dT(x,t)}{dx} \right)_x \quad (2.2.1-2) \]

Heat flux out of the balance volume by heat conduction:
\[ J_Q(x+\Delta x,t) = -\lambda \cdot A \cdot \left( \frac{dT(x,t)}{dx} \right)_{x+\Delta x} \quad (2.2.1-3) \]

Heat transfer to the ambient \((U: \text{circumference})\):
\[ J_{Q_{\text{aussen}}}(x,t) = \alpha_{\text{aussen}} \cdot U \cdot \Delta x \cdot (T(x,t) - T_a) \quad (2.2.1-4) \]

Accumulation of heat:
\[ J_{Q_{\text{acc}}} = \rho \cdot c_p \cdot \Delta V \cdot \frac{dT(x,t)}{dt} \quad (2.2.1-5) \]

All fluxes are dependent on \(x\) and \(t\)!

Heat balance for non-stationary conditions:
\[ J_{Q_{\text{acc}}} = J_{Q_x} - J_{Q_{x+\Delta x}} - J_{Q_{\text{aussen}}} \quad (2.2.1-6) \]
Heat balance results in:

\[
\rho \cdot c_p \cdot \Delta V \frac{\partial T}{\partial t} = -\lambda \cdot A \cdot \left( \frac{\partial T}{\partial x} \right)_x + \lambda \cdot A \cdot \left( \frac{\partial T}{\partial x} \right)_{x+\Delta x} - \alpha_{aussen} \cdot U \cdot \Delta x (T - T_a) \quad (2.2.1-7)
\]

The Temperature gradient is expanded into a Taylor series. Linearization of the temperature gradient leads to:

\[
\left( \frac{\partial T}{\partial x} \right)_{x+\Delta x} = \left( \frac{\partial T}{\partial x} \right)_x + \frac{\partial}{\partial x} \left( \frac{\partial T}{\partial x} \right) \Delta x + \ldots \quad (2.2.1-8)
\]

Using this in the heat balance gives:

\[
\rho \cdot c_p \cdot \Delta V \frac{\partial T}{\partial t} = \lambda \cdot A \cdot \frac{\partial^2 T}{\partial x^2} \Delta x - \alpha_{aussen} \cdot U \cdot \Delta x (T - T_a) \quad (2.2.1-9)
\]

Transformation results in:

\[
\frac{\partial T}{\partial t} = \frac{\lambda}{c_p \rho} \cdot \frac{\partial^2 T}{\partial x^2} - \alpha_{aussen} \cdot \frac{U}{A} \cdot (T - T_a) \quad (2.2.1-10)
\]

For \( \alpha_{aussen} \rightarrow 0 \), no heat transfer to the ambient, we obtain Fourier’s law for non stationary heat conduction in one dimension:

\[
\frac{\partial T}{\partial t} = \frac{\lambda}{c_p \rho} \cdot \frac{\partial^2 T}{\partial x^2} = a \cdot \frac{\partial^2 T}{\partial x^2} \quad (2.2.1-11)
\]

The property \( a = \frac{\lambda}{\rho c_p} \) [m²/s] is called thermal conductivity (temperature conductivity). It is a material property. Some values are given in Table 2.2.1-1.

**Table 2.2.1-1: Thermal conductivities of some materials.**

<table>
<thead>
<tr>
<th>Stoff</th>
<th>Temperaturleitzahl ( a ) in ( 10^6 \text{ m}^2 \text{ s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Luft ((20^\circ \text{C}, 0,1 \text{ MPa}))</td>
<td>21,4</td>
</tr>
<tr>
<td>Wasser</td>
<td>0,143</td>
</tr>
<tr>
<td>Org. Flüssigkeiten</td>
<td>0,09- 0,1</td>
</tr>
<tr>
<td>Stein, Keramik</td>
<td>0,5- 1,5</td>
</tr>
<tr>
<td>Glas</td>
<td>0,6 – 0,8</td>
</tr>
<tr>
<td>Metalle</td>
<td>0,5 - 100</td>
</tr>
</tbody>
</table>
2.2.2 Examples of heat transfer by non stationary heat conduction in engineering

Solutions of Fourier’s differential equation for non-stationary heat conduction. Geometry: cylindrical slab with \( \frac{L}{D} \gg 1 \), then \( T_L = T_a \), for the time being no heat transfer to the ambient.

\[
\frac{\partial T}{\partial t} = a \cdot \frac{\partial^2 T}{\partial x^2} - \left[ \frac{\alpha_{\text{aussen}}}{c_p \rho} \cdot \frac{U}{A} (T - T_a) \right] \quad (2.2.2-1)
\]

Initial and boundary conditions:

\( t = 0, T = T_0 \) for \( x = 0 \), \( T = T_a \) for \( 0 < x \leq L \) \hspace{1cm} (2.2.2-2)

\( t > 0, T = T_0 \) for \( x = 0 \), \( T = T_a \) for \( x = L \) \hspace{1cm} (2.2.2-3)

Normalization of temperature \( \theta = \frac{T-T_a}{T_0-T_a} \)
gives:

\[
\frac{\partial \theta}{\partial t} = a \cdot \frac{\partial^2 \theta}{\partial x^2} \quad (2.2.2-4)
\]

Initial and boundary conditions:

\( t = 0, \theta = 1 \) for \( x = 0 \), \( \theta = 0 \) for \( 0 < x \leq L \) \hspace{1cm} (2.2.2-5)

\( t > 0, \theta = 1 \) for \( x = 0 \), \( \theta = 0 \) for \( x = L \) \hspace{1cm} (2.2.2-6)

Approach for solution: partial differential equation is transformed into an ordinary differential equation by use of a new variable which connects time and distance. For transformation the Fourier number is introduced:

\[
Fo = \frac{a \cdot t}{x^2} \quad (2.2.2-7)
\]

The Fourier number has the meaning of a normalized time: \( a/x^2 \): „Intrusion time“ for temperature. New variable:

\[
\phi = \frac{1}{2} \frac{1}{\sqrt{Fo}} = \frac{1}{2} \frac{x}{\sqrt{a \cdot t}} \quad (2.2.2-8)
\]
Transformation rules:

\[
\frac{\partial \theta}{\partial \alpha} = \frac{\partial \theta}{\partial \phi} \frac{\partial \phi}{\partial \alpha} = \left( -\frac{x}{2\sqrt{t}} \frac{1}{2} \frac{1}{t^{3/2}} \right) \frac{\partial \theta}{\partial \phi} = -\frac{1}{2} \frac{\phi}{t} \frac{d\theta}{d\phi} \tag{2.2.2-9}
\]

\[
\frac{\partial \theta}{\partial x} = \frac{\partial \theta}{\partial \phi} \frac{\partial \phi}{\partial x} = \frac{1}{2\sqrt{at}} \frac{\partial \theta}{\partial \phi} \tag{2.2.2-10}
\]

\[
\frac{\partial^2 \theta}{\partial \phi^2} = \frac{1}{4at} \frac{\partial^2 \theta}{\partial \phi^2} \tag{2.2.2-11}
\]

Considering the transformation rules we obtain from the heat conduction equation:

\[
-\frac{1}{2} \frac{\phi}{t} \frac{d\theta}{d\phi} = \frac{a}{4at} \frac{\partial^2 \theta}{\partial \phi^2} \tag{2.2.2-12}
\]

And after transformation:

\[
\frac{\partial^2 \theta}{\partial \phi^2} = -2\phi \frac{d\theta}{d\phi} \tag{2.2.2-13}
\]

Finally we obtain by further transformation a system of coupled ordinary differential equations of first order:

\[
\frac{dY}{d\phi} = -2\phi Y \quad \text{and} \quad \frac{d\theta}{d\phi} = Y \tag{2.2.2-14}
\]

Integration of the first equation after separation of variables considering the boundary condition \( Y = Y_0 \) for \( \phi = 0 \):

\[
\ln \frac{Y}{Y_0} = -\phi^2 \quad \text{or} \quad Y = Y_0 e^{-\phi^2} \tag{2.2.2-15}
\]

Integration of the second equation within the boundaries \( \phi = 0 \) and \( \phi \) and \( \theta \), respectively, yields:

\[
(\theta - 1) = \left( \frac{d\theta}{d\phi} \right)_{\phi=0}^{\phi} e^{-\phi^2} d\phi \tag{2.2.2-16}
\]
The integral in equation (2.2.2-16) is given by \( \pi^{1/2}/2 \cdot \text{erf}(\phi) \), where \( \text{erf}(\phi) \) is the error function.

The remaining task is the determination of the wall gradient in equation (2.2.2-16) \((d\theta/d\phi)_0\). The error function \( \text{erf}(\phi) \) converges assymptoticly at large \( \phi \) versus 1. Therefore \( \pi^{1/2}/2 \cdot \text{erf}(\phi) \) converges against 0,8862, compare figure 2.2.2-2. From equation (2.2.2-16) we then obtain for large \( \phi \) (where \( \theta = (T-T_a)/(T_0-T_a)=0 \)):

\[
-1 = \left( \frac{d\theta}{d\phi} \right)_0 \frac{\sqrt{\pi}}{2} \quad \text{for} \quad \phi \geq 2.5 \quad (2.2.2-17)
\]

Or:

\[
\left( \frac{d\theta}{d\phi} \right)_0 = -\frac{2}{\sqrt{\pi}} \quad (2.2.2-18)
\]

The general solution of the non-stationary heat conduction equation for the cylindrical slab with the above initial and boundary conditions then is:

\[
\theta = 1 - \int_0^\phi \exp(-\phi^2) d\phi = \text{erfc}(\phi) \quad (2.2.2-19)
\]
Solutions of Fourier's differential equation for non-stationary heat conduction. Geometry: cylindrical slab with \(L/D >> 1\), then \(T_L = T_a\), now with heat transfer to the ambient!

\[
\frac{\partial T}{\partial t} = a \cdot \frac{\partial^2 T}{\partial x^2} - \frac{\alpha_{\text{aussen}}}{c_p \rho} \cdot \frac{U}{A} \cdot (T - T_a) \tag{2.2.2-20}
\]

Initial and boundary conditions identical to the case without heat transfer to the ambient. Normalization of temperature as before with \(\theta = (T-T_a)/(T_0-T_a)\) gives:

\[
\frac{\partial \theta}{\partial t} = a \cdot \frac{\partial^2 \theta}{\partial x^2} - n \cdot \theta \tag{2.2.2-21}
\]

with \(n=(\alpha_{\text{aussen}}/c_p \rho)(4/D)\). Initial and boundary conditions:

\(t = 0, \theta = 1\) for \(x = 0, \theta = 0\) for \(0 < x \leq L\) \((2.2.2-22)\)

\(t > 0, \theta = 1\) for \(x = 0, \theta = 0\) for \(x = L\) \((2.2.2-23)\)

If the solution for \(n = 0\) is

\[
\theta = \frac{T-T_a}{T_0-T_a} = \text{erfc} \left( \frac{1}{2} \cdot \frac{x}{\sqrt{a \cdot t}} \right) \tag{2.2.2-19}
\]

then the solution for \(n \neq 0\) is (Dankwerts, Crank):

\[
\Theta = \frac{T-T_a}{T_0-T_a} = n \cdot \int_0^t \theta \cdot \exp(-n \cdot t) \, dt + \theta \cdot \exp(-n \cdot t) \tag{2.2.2-24}
\]

\[
\Theta = \frac{1}{2} \cdot \exp \left( -x \cdot \sqrt{\frac{n}{a}} \right) \cdot \text{erfc} \left( \frac{1}{2} \cdot \frac{x}{\sqrt{a \cdot t}} - \sqrt{n \cdot t} \right) + \frac{1}{2} \cdot \exp \left( x \cdot \sqrt{\frac{n}{a}} \right) \cdot \text{erfc} \left( \frac{1}{2} \cdot \frac{x}{\sqrt{a \cdot t}} + \sqrt{n \cdot t} \right) \tag{2.2.2-25}
\]

Fig. 2.2.2-4: Non-stationary heat conduction in a cylindrical slab with heat transfer to the ambient.
Heat transfer via the „cold bridge“ from the wall to the ambient for non stationary conditions as heat transfer problem: The total heat flux from the slab to the ambient is supplied by heat conduction from the wall to the slab (see fig. 2.2.2-5). From equation (2.2.2-19) we obtain (for the case without heat transfer to the ambient):

\[
J_Q = -\lambda \cdot A \cdot \left(\frac{dT}{dx}\right)_{x=0} = -\lambda \cdot A \cdot \frac{(T_0 - T_a)}{2\sqrt{at}} \cdot \left(\frac{d\theta}{d\phi}\right)_{\phi=0} = \lambda \cdot A \cdot \frac{(T_0 - T_a)}{2\sqrt{at}} \cdot \frac{2}{\sqrt{\pi}} = \lambda \cdot A \cdot \frac{2}{\sqrt{\pi}} \cdot \frac{(T_0 - T_a)}{\sqrt{a\pi t}} \quad (2.2.2-26)
\]

On the other hand, the heat transfer problem can be formulated with the help of the fundamental heat transfer equation:

\[
J_Q = \alpha \cdot A \cdot (T_0 - T_a) \quad (2.2.2-27)
\]

Comparing equation (2.2.2-26) and (2.2.2-27) we obtain

\[
\alpha = \lambda \cdot \sqrt{\frac{1}{\pi \cdot a \cdot t}} = \sqrt{\frac{\rho \cdot c_p \cdot \lambda}{\pi \cdot t}} \quad (2.2.2-28)
\]

In this case the heat transfer coefficient for the heat loss via the „cold bridge“ is time dependent!

**Fig. 2.2.2-5**: Non-stationary heat conduction in a cylindrical slab ($a = 2 \cdot 10^{-5} \text{ m}^2 \text{ s}^{-1}$, $n = 10^{-3} \text{ s}^{-1}$).
Averaging the heat transfer coefficient for the non stationary problem over time gives:

\[ \alpha_m = \frac{1}{t} \cdot \int_0^t \alpha(t) dt = 2 \cdot \sqrt{\frac{\rho \cdot c_p \cdot \lambda}{\pi \cdot t}} \]  \hspace{1cm} (2.2.2-29)

The averaged heat transfer coefficient is exactly the double of the instantaneous heat transfer coefficient at time \( t \).

For the case including heat transfer to the ambient (coupled inner and outer heat transfer) we obtain:

\[ J_Q = -\lambda \cdot A \cdot \left( \frac{dT}{dx} \right)_{x=0} = -\lambda \cdot A \cdot (T_0 - T_a) \cdot \left[ \sqrt{\frac{n}{a}} \cdot \text{erfc} (\sqrt{n \cdot t}) + \frac{1}{\sqrt{\pi \cdot a \cdot t}} \cdot \exp(-n \cdot t) \right] \]  \hspace{1cm} (2.2.2-30)

The heat transfer coefficient then is given by:

\[ \alpha = \lambda \cdot \left[ \sqrt{\frac{n}{a}} \cdot \text{erfc} (\sqrt{n \cdot t}) + \frac{1}{\sqrt{\pi \cdot a \cdot t}} \cdot \exp(-n \cdot t) \right] \]  \hspace{1cm} (2.2.2-31)

For \( t \to 0 \) error function \( \to 0 \) and \( \exp(-nt) \to 1 \), so that

\[ \alpha = \lambda \cdot \sqrt{\frac{1}{\pi \cdot a \cdot t}} = \sqrt{\frac{\rho \cdot c_p \cdot \lambda}{\pi \cdot t}} \]  \hspace{1cm} (2.2.2-32)

For \( t \to \) large error function \( \to 1 \) and \( \exp(-nt) \to 0 \), so that

\[ \alpha = \lambda \cdot \frac{n}{a} = \lambda \frac{4 \cdot \alpha_{\text{außen}}}{\lambda \cdot D} \]  \hspace{1cm} or

\[ \frac{\alpha \cdot L}{\lambda} = Nu_L = 2L \frac{\alpha_{\text{außen}}}{\lambda \cdot D} = \frac{L}{D} \cdot \sqrt{8 \cdot Bi} \]  \hspace{1cm} (2.2.2-33)

Fig. 2.2.2-6: Non-stationary heat conduction in a cylindrical slab \((a = 2 \cdot 10^{-5} \text{ m}^2 \text{ s}^{-1}, n = 10^{-3} \text{ s}^{-1})\); heat transfer coefficients.
Summary section 2.2

- Fundamentals of non-stationary heat conduction have been deduced.

- A method for the solution of the partial differential equation for non-stationary heat conduction has been discussed.

- Definition of the heat transfer coefficient has been extended to non-stationary heat conduction problems.
2.3 Mass transfer by stationary diffusion

2.3.1 Problem statement, Fick´s law of stationary diffusion and diffusion coefficient

Mass transfer has been defined in section 1.1 as mass (of a chemical species) transferred form one system to another one due to differences in mass densities. A simple scenario may be the diffusion of a chemicals species $A$ in a solution through a membrane which is permeable only for that species. There, the transferred mass through the membrane is obtained from the mass density gradients at the systems boundaries after the solution of the appropriate mass balance equation (governing transport mechanism: mass diffusion at the boundaries), compare section 1.2.1 and 1.3.5.

For mass transfer by stationary diffusion we use a scenario similar to that of heat transfer in section 2.1.1. Two systems containing solutions of the component $A$ with molar densities $c_{A2}$ and $c_{A1}$ where $c_{A2} > c_{A1}$, are separated by a membrane of thickness $s_1$ permeable only for component $A$, see figure 2.3.1-1.

Due to the different (stationary) molar densities a molar flux from the system at higher molar density to that at lower molar density is established. The only transport mechanism of mass is diffusion under stationary conditions (no flow velocity, no conversion). The molar flux then is given by the molar density gradients at the boundaries (section 1.3 and 1.3.5).
We obtain the molar density gradients at the boundaries by solving the appropriate balance equation. From table 1.3.4-1 we take (one dimensional formulation considering the planar geometry):

\[
\frac{\partial (\rho \cdot w_A)}{\partial t} = - \frac{\partial}{\partial x} \left( w_A \cdot \rho \cdot \mathbf{v} - D_A \cdot \frac{\partial c_A}{\partial x} \right) + s_A
\]

(2.3.1-1)

Considering stationary conditions, no conversion, no flow velocity this reduces after integration to (compare section 1.3 and 1.3.5):

\[
-D_A \cdot \frac{dc_A}{dx} = \text{const.} = j_{nA} \text{ diff} \quad \text{(2.3.1-2)}
\]

and

\[
J_{nA} \text{ diff} = -D_A \cdot A \cdot \frac{dc_A}{dx} \quad \text{(2.3.1-3)}
\]

Equation (2.3.1-3) is Fick’s law of stationary (one-dimensional) diffusion. The molar flux of A is the product of Diffusion coefficient \( D \), area \( A \) and molar density gradient \( dc_A/dx \). The molar flux vector is anti-parallel to the molar density gradient (also vector). This is noted by the negative sign in equation (2.3.1-2). Mass, therefore, always is transported in the direction of lower molar densities.

The diffusion coefficient \( D \) [m²/s] according to Fick’s law (equation (2.3.1-3) is the molar flux of species A [mol/s] by diffusion per unit of negative molar density gradient \( dc_A/dx \) [mol/m⁴] and unit area \( A \) [m²]. The diffusion coefficient \( D \) is a material property.

Equations (2.3.1-2) and (2.3.1-3) are similar to the equations for heat transfer by stationary heat conduction. Therefore, further discussion in section 2.5 !
2.3.2 Mechanisms of diffusion

Simple model for diffusion in a fluid (gas, liquid). Fluid particles (molecules in a gas) move driven by thermal molecular motion with a temperature dependent velocity. During this motion the molecules strike each other. Every strike leads to a change of the direction of the motion, so that the molecules in the average at constant pressure and constant temperature move homogeneously in all directions.

If in a closed system a concentration gradient for the single molecules exists, compare figure 2.3.2-1, on the time average more molecules from the region of higher concentration will move into the region of lower concentration. By this a diffusion flux is established into the direction of lower concentrations.

According to that simple model, the diffusion coefficient should be dependent on the mean molecular velocity and the mean free path of the molecules and from that on temperature and pressure.

**Diffusion coefficients of gases.** According to the above simple model for the diffusion of gases the diffusion coefficient of ideal gases can be calculated with the help of the kinetic gas theory:

\[
D_{AA} = \frac{1}{3} \cdot \bar{V} \cdot \Lambda \quad (2.3.2-1)
\]

In equation (2.3.2-1) \( \Lambda \) is the mean free path of the molecules and \( \bar{V} \) the mean molecular velocity (compare heat conductivity).

\[
\Lambda = \frac{1}{\sqrt{2 \cdot \pi \cdot d^2 \cdot N_A}} \frac{RT}{p} \quad (2.3.2-2)
\]
\[
\bar{v} = \sqrt{\frac{8RT}{\pi \cdot M}} \quad (2.3.2-3)
\]

\[
D_{AA} = \frac{2}{3} \cdot \frac{1}{\sqrt{M \cdot d^2 \cdot N_A \cdot p}} \cdot \left(\frac{RT}{\pi}\right)^{3/2} \quad (2.3.2-4)
\]

According to equation (2.3.2-4), kinetic gas theory, the diffusion coefficients increase with decreasing molar mass of the molecules. Increasing temperatures lead to a strong increase of the diffusion coefficients \((T^{1.5})\). According to the kinetic gas theory we have a pressure dependence according to \(p^{-1}\).

<table>
<thead>
<tr>
<th>Temperature T/°C</th>
<th>0</th>
<th>15</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂-N₂O</td>
<td>9,6 \times 10^{-6}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂-CO</td>
<td>1,39 \times 10^{-5}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂-N₂</td>
<td>1,44 \times 10^{-5}</td>
<td>1,58 \times 10^{-5}</td>
<td></td>
</tr>
<tr>
<td>Ar-O₂</td>
<td></td>
<td></td>
<td>1,65 \times 10^{-5}</td>
</tr>
<tr>
<td>H₂-SF₆</td>
<td>4,2 \times 10^{-5}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂-CH₄</td>
<td>7,26 \times 10^{-5}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Table 2.3.2-1: Binary diffusion coefficients for some gas mixtures.*
**Diffusion coefficients of liquids.** The diffusion coefficients of most liquids are about five orders of magnitude lower than those of gases.

The mechanism of diffusion in liquids is similar to the mechanism of diffusion in gases. However, the interactions of the molecules in the fluid (van der Waals interactions, hydrogen bridge bonds, long distance interactions) play an important role. Thereby, the diffusion coefficients of most species in liquids are dependent on concentration, compare table 2.3.2-2.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Temperature T/°C</th>
<th>X_A</th>
<th>D_{AB}/m^2s^{-1}*10^9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanole-Water</td>
<td>25</td>
<td>0.050</td>
<td>1.130</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.275</td>
<td>0.410</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.50</td>
<td>0.900</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.70</td>
<td>1.400</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.950</td>
<td>2.200</td>
</tr>
<tr>
<td>Water-n-Butanole</td>
<td>30</td>
<td>0.131</td>
<td>1.240</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.222</td>
<td>0.920</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.358</td>
<td>0.560</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.454</td>
<td>0.437</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.524</td>
<td>0.267</td>
</tr>
</tbody>
</table>

*Table 2.3.2-2: Diffusion coefficients of some liquid mixtures.*

**Diffusion coefficients of solids.** The mechanism of diffusion in solids is much more complicated (diffusion of empty places in the lattice, etc.).
2.4 Mass transfer by non stationary diffusion

2.4.1 Fick’s law for non stationary diffusion

Analogously to non-stationary heat conduction we can derive the differential equation for non-stationary diffusion with the help of a mass balance for the scenario given in figure 2.4.1-1. We focus again on a planar diffusion problem (e.g. solution of a solid in water), which can be treated 1-dimensionally. In the fluid initially a constant concentration \( c_{A0} \) prevails, compare figure 2.4.1-1. At time \( t = 0 \) the concentration is suddenly increased to \( c_{AS} \) (immersion of the solid into water). An equation of the evolution of the concentration \( c_A \) with time is obtained from a mass balance for species \( A \) in a differential balance volume:

\[
\text{Accumulation of moles of } A = \text{inflow of moles of } A - \text{outflow of moles of } A \quad (2.4.1-1)
\]

In the same way as for non-stationary heat conduction we obtain finally

\[
\frac{\partial c_A}{\partial t} = D_A \cdot \frac{\partial^2 c_A}{\partial x^2} \quad (2.4.1-2)
\]

Equation (2.4.1-2) is Fick’s law for non-stationary diffusion and is (formal) identical to the equation for non-stationary heat conduction!

The solutions of this equation then are identical to the solutions of the equation for non-stationary heat conduction (if initial and boundary conditions are identical).
2.5 Similarity of heat and mass transfer

As can be seen from equations (2.1.1.-2), (2.2.2-1), (2.3.1-2) and (2.4.1-2) heat transport by (stationary and non stationary) conduction and mass transport by (stationary and non stationary) diffusion are closely related with vast analogies:

\[
\begin{align*}
J_Q &= -\lambda(T) \cdot A \cdot \frac{dT}{dx} \quad \text{stationary heat conduction /diffusion} \\
J_{nA} &= -D_A(T) \cdot A \cdot \frac{dc_A}{dx} \\
\end{align*}
\]

\[
\begin{align*}
\frac{\partial T}{\partial t} &= a \cdot \frac{\partial^2 T}{\partial x^2} \quad \text{non – stationary heat conduction /diffusion} \\
\frac{\partial c_A}{\partial t} &= D_A \cdot \frac{\partial^2 c_A}{\partial x^2} \\
\end{align*}
\]

Also, the transport coefficients (heat conductivity, diffusion coefficients) are closely related, e.g. from kinetic theory of gases we obtain for ideal gases:

\[
\eta = \frac{1}{3} \rho \cdot \bar{v} \cdot \Lambda \quad \text{viscosity} \quad \lambda = \frac{1}{3} \rho \cdot \bar{v} \cdot \Lambda \cdot c_v \quad \text{heat conductivity} \quad D_{AA} = \frac{1}{3} \bar{v} \cdot \Lambda \quad \text{diffusion coefficient}
\]

This gives then:

\[
\text{Pr} = \frac{\eta}{\rho \cdot a} = 1 \quad \text{Sc} = \frac{\eta}{\rho \cdot D} = 1 \quad (2.5 - 1)
\]

Due to this similarity, heat transfer problems and mass transfer problems can be often treated similarly / in the same way!

\[
\begin{align*}
J_{q_{\alpha b}} &= \alpha \cdot A \cdot (\Delta T) \quad (2.5 - 2) \\
\text{Nu}_L &= \frac{\alpha \cdot L}{\lambda} \\
J_{n_{k\alpha b}} &= \beta \cdot A \cdot (\Delta c_k) \quad (2.5 - 3) \\
\text{Sh}_L &= \frac{\beta \cdot L}{D}
\end{align*}
\]

general heat transfer equation !

general mass transfer equation !
2.6 Examples for stationary diffusion problems from process engineering

**Diffusion into a porous catalyst with simultaneous chemical reaction.** In a pellet of a catalyst we have round pores of the length $L$, into which from the surface of the pellet a chemical component diffuses and reacts at the inner surface of the pore. The pores can be treated for simplicity as cylinders. At the outer surface the concentration is $c_0$, compare figure 2.6-1. The diffusion coefficient of the species is $D_A$.

*Question:* concentration profile in the pore of the catalyst, molar flux into the catalyst.

We perform a mass balance for the species $A$ over a differential balance volume. Within the pore we have diffusion of the species $A$ and the species $A$ reacts at the wall of the pore into products according to a chemical reaction of first order. (Simplification: concentration only dependent on $x$, 1-dimensional problem.) Mass balance:

inflow of moles of $A =$ outflow of moles of $A + \text{change due to chemical reaction}$ \hspace{1cm} (2.6-1)

Diffusion flux of $A$ into the volume:

$$J_n(x) = -D_A \cdot A \cdot \left( \frac{dc}{dx} \right)_x \hspace{1cm} (2.6-2)$$

Diffusion flux of $A$ out of the volume:

$$J_n(x + \Delta x) = -D_A \cdot A \cdot \left( \frac{dc}{dx} \right)_{x+\Delta x} \hspace{1cm} (2.6-3)$$

Reaction of $A$ in the volume by heterogeneous chemical reaction ($U$: pore circumference):

$$J_{nReaktion} = k \cdot c \cdot U \cdot \Delta x \hspace{1cm} (2.6-4)$$

**Fig. 2.6-1:** Stationary diffusion into a round pore of a catalyst.
Mass balance for stationary conditions:

\[ J_{nx} = J_{nx+\Delta x} + J_{n\text{Reaktion}} \quad (2.6-5) \]

The molar flux at the position \( x+\Delta x \) is replaced by a Taylor series of the molar flux at the position \( x \):

\[ J_n(x + \Delta x) \approx J_n(x) + \frac{dJ_n}{dx} \Delta x \]

\[ = J_n(x) - D_A \cdot A \cdot \left( \frac{d^2c}{dx^2} \right) \Delta x \quad (2.6-6) \]

With this we have for the mass balance:

\[ 0 = -D_A \cdot A \cdot \left( \frac{d^2c}{dx^2} \right) \Delta x + k \cdot c \cdot U \cdot \Delta x \quad (2.6-7) \]

Transformation using \( \theta = c/c_0 \) and \( \eta = x/L \) gives:

\[ \left( \frac{d^2\theta}{d\eta^2} \right) = \frac{k \cdot U \cdot L^2}{D_A \cdot A} \cdot \theta = m^2 \cdot \theta \quad (2.6-8) \]

In equation (2.6-8) \( m^2 = \frac{k \cdot U \cdot L^2}{D_A \cdot A} = L^2 \frac{2k}{D_A \cdot R} = \phi^2 \). \( \phi \) is called the **Thiele-Modulus**. The Thiele modulus can be interpreted as ratio of reaction rate to diffusion rate.

Solution of the ordinary differential equation of second order for \( \theta \): \( e^{\lambda} \)-Ansatz:

\[ \theta = C \cdot e^{\lambda \eta} \quad (2.6-9) \]

Differentiating with respect to \( \eta \) gives:

\[ \frac{d^2\theta}{d\eta^2} = \lambda^2 \cdot C \cdot e^{\lambda \eta} = \lambda^2 \cdot \theta \quad (2.6-10) \]

Equation (2.6-9) is therefore only a solution of equation (2.6-8) if:

\[ \lambda^2 = m^2 \quad \text{or} \quad \lambda_1 = +m \quad \lambda_2 = -m \]

with \( m = L \cdot \sqrt{\frac{2k}{D_A \cdot R}} = \phi \) \quad (2.6-11)
General solution: linear combination of the particular solutions:
\[ \theta = A \cdot e^{m \eta} + B \cdot e^{-m \eta} \quad (2.6-12) \]

The integration constants \( A \) and \( B \) are calculated from the boundary conditions.

**Boundary condition 1:** For \( \eta = 0 \) is \( c = c_0 \), therefore \( \theta = 1 \). This gives:
\[ 1 = A + B \quad (2.6-13) \]

**Boundary condition 2:** The end of the pore is not permeable for material. Then \( d\theta/d\eta = 0 \), for \( \eta = 1 \). Then it follows:
\[ 0 = A \cdot m \cdot e^m - B \cdot m \cdot e^{-m} \quad B = A \frac{e^m}{e^{-m}} \quad (2.6-14) \]

With equation (2.6-13) we obtain:
\[ A = \frac{e^{-m}}{e^m + e^{-m}} \quad B = \frac{e^m}{e^m + e^{-m}} \quad (2.6-15) \]

The solution then is:
\[ \theta = \frac{\cosh[m(1-\eta)]}{\cosh[m]} \quad (2.6-16) \]

With increasing Thiele modulus, that is with increasing reaction rate compared to the diffusion rate, the concentration decreases steeper and the concentration gradient at the outer surface increases.
Diffusion into the pores as mass transfer problem: The mass of the component $A$ which is consumed by chemical reaction within the pore of the catalyst has to be transported through the pore entrance by diffusion. Therefore

$$J_{n,ges} = -D_A \cdot A \cdot \left( \frac{dc}{dx} \right)_{x=0} = -\frac{D_A \cdot A \cdot c_0}{L} \left( \frac{d\theta}{d\eta} \right)_{\eta=0} \quad (2.6-17)$$

Concentration profile for the stationary problem:

$$\theta = \frac{\cosh[m(1-\eta)]}{\cosh[m]}, \quad \left( \frac{d\theta}{d\eta} \right)_{\eta=0} = -m \cdot \tanh(m) \approx -m \quad \text{for } m \geq 5 \quad (2.6-18)$$

This gives:

$$J_{n,ges} = \frac{D_A \cdot A \cdot m}{L} \cdot c_0 \quad (2.6-19)$$

On the other hand, every mass transfer problem – in this case the mass transfer from the outer surface of the catalyst into the inner of the pore – can be written as (compare equation 2.5-3):

$$J_{n,ges} = \beta \cdot A \cdot (c_0 - c_\infty) \quad (2.6-20)$$

Comparing equation (2.6-19) and (2.6-20) we obtain (with $c_{oo} = 0$ for $m > 5$):

$$\beta = \frac{D_A \cdot m}{L} \quad \text{or} \quad Sh_L = \frac{\beta \cdot L}{D_A} = m = L \cdot \sqrt{\frac{2k}{D_A \cdot R}} = \phi \quad (2.6-21)$$

The mass transfer through the pore entrance of the catalyst and the chemical reaction at the inner surface are coupled! The faster the chemical reaction (the larger the Thiele modulus) the larger is the mass transfer coefficient! (compare stationary heat conduction in a slab?)
Summary sections 2.3 to 2.6

• The mechanisms of diffusion in gases, liquid and solids have been discussed.

• Basics of diffusion in fluids have been elaborated.
• The property „diffusion coefficient“ has been discussed.

• Stationary diffusion has been treated.

• Non-stationary diffusion has been introduced.

• Similarity between heat transport and mass transport has been identified.

• Simple problems for diffusion from process engineering have been discussed.