1. The Stoichiometric Number for Complex reaction mechanisms

1.1 Background for a Systematic Determination of the Stoichiometric Number

For simple two and three step reaction mechanisms it is seldom a problem to determine how many times a specific elementary step has to occur in order for the net reaction to occur ones. Most catalytic reaction mechanisms though consists of a much larger number of elementary steps which often form a web of interdependent catalytic cycles. This makes it difficult to determine the stoichiometric number defined as the number of times the individual elementary reaction has to occur for the net reaction to occur once. There is therefore a need for a systematic approach on how to determine the stoichiometric number for the individual elementary reaction in a given reaction mechanism. The following is a short description of such a systematic approach adopted from S. Wedel [1].

1.2 Reaction Mechanism

A reaction mechanism consist of a number of elementary reactions. Each balanced elementary reaction equation defines the stoichiometric coefficients \( \nu_{ij} \) for component \( j \) in reaction \( i \). The internationally accepted IUPAC (International Union for Pure and Applied Chemistry) rules demand, that the stoichiometric coefficients be positive for products and negative for reactants. Furthermore products are defined as the components on the right side of the reaction arrows and reactants as components at the left side of the reaction arrows.

Components that do not participate in the specific reaction as either reactants or products have the stoichiometric coefficient \( \nu_{ij} = 0 \).

The suggested reaction mechanism has to give a complete description of the reactions in which the catalyst and any intermediate component is expected to participate during the catalytic transformation of reactant to product. To facilitate the description of the reaction mechanism the following nomenclature is introduced:

\[
\begin{align*}
\text{Total of number of elementary reactions in the suggested reaction mechanism:} & \quad R \\
\text{Total number of components in the suggested reaction mechanism:} & \quad S \\
\end{align*}
\]

The \( S \) components are formally denoted \( A_j \), where \( j \) is an index between 1 and \( S \) that denotes the individual component.

Using this notation the reaction mechanism can formally be written as:

\[
\begin{align*}
|v_{1,1}|A_1 + |v_{1,2}|A_2 + \ldots + |v_{1,r_1}|A_{1,r_1} + |v_{1,r_1+1}|A_{r_1+1} + \ldots + |v_{1,S}|A_S \\
\vdots \\
|v_{R,1}|A_1 + |v_{R,2}|A_2 + \ldots + |v_{R,s}|A_{s} + |v_{R,s+1}|A_{s+1} + \ldots + |v_{R,S}|A_S
\end{align*}
\]

where

- \( R \) is the total number of balanced reaction equation in the reaction mechanism.
- \( S \) is the total number of components.
- \( r_i \) is the total number of reactants in reaction \( i \).

Included in the components are also the active sites on the catalyst since they are necessary in order to describe the reaction path and the function of the catalyst.
The S components can be divided into two main groups:

- $S_N$: Components that enters into the net reactions. That is components not fixed to the catalyst or in any other way only appears as intermediates in the suggested reaction mechanism.

- $S_C$: Components that contain a catalyst site or in any other way appears as an intermediate that does not enter into the net reactions.

This of course yields

\[ S = S_N + S_C \]  

(1.2)

1.3 The stoichiometric coefficient matrix - Formalism for suggested reaction mechanism.

An often used formal way of stating a reaction equation is:

\[ \sum_{j=1}^{S} v_{ij} A_j = 0 \quad i = 1,2,...,R \]  

(1.3)

Which in matrix form becomes:

\[ \mathbf{v}_{R \times S} \mathbf{A}_{S \times 1} = \mathbf{0}_{R \times 1} \]  

(1.4)

Where $\mathbf{v}$ denotes the stoichiometric coefficient matrix for the suggested reaction mechanism.

The stoichiometric coefficient matrix contain all the stoichiometric coefficients for the S components in the R suggested elementary reactions for the mechanism:

\[ \mathbf{v} = \begin{pmatrix} v_{1,1} & \cdots & v_{1,S} \\ \vdots & \ddots & \vdots \\ v_{R,1} & \cdots & v_{R,S} \end{pmatrix} \]  

(1.5)
1.4 Determination of the stoichiometric number for the elementary reactions

The set of elementary reactions given by equation (1.4), the suggested reaction mechanism, might contain more than one reaction path for the same net reaction and the mechanism may also contain reaction paths describing more than one simultaneous net reaction. The suggested set of elementary reactions might also be incomplete so that it does not lead to the net reaction it should describe. It is therefore necessary to make a systematic analysis of (1.4).

It should be noted that the elements in the component vector \( \mathbf{A} \) can be arranged in such a way that the \( S_N \) net reaction components is placed first in the vector while the \( S_C \) intermediate components are placed last:

\[
\mathbf{A} = \begin{pmatrix} \mathbf{A}_N \\ \mathbf{A}_C \end{pmatrix} = \begin{pmatrix} \mathbf{A}_1 \\ \vdots \\ \mathbf{A}_{S_N} \\ \mathbf{A}_{S_N + 1} \\ \vdots \\ \mathbf{A}_{S_N + S_C} \end{pmatrix} \tag{1.6}
\]

in this way the stochiometric coefficient matrix is split into a first submatrix \( \mathbf{v}_N \) containing the stochiometric coefficients for the net reaction components followed by a second submatrix \( \mathbf{v}_C \) containing the stochiometric coefficients for the intermediate components.

\[
\mathbf{v} = \begin{pmatrix} v_{11} & \cdots & v_{1S_N} & v_{1S_N+1} & \cdots & v_{1S_N+S_C} \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ v_{R1} & \cdots & v_{RS_N} & v_{RS_N+1} & \cdots & v_{RS_N+S_C} \end{pmatrix} \tag{1.7}
\]

Or in a more compact form

\[
\mathbf{v}_{R \times S} = \begin{pmatrix} \mathbf{v}_{R \times S_N} & \mathbf{v}_{R \times S_C} \end{pmatrix} \tag{1.8}
\]

Valid reaction mechanisms can now be determined by demanding that the net reaction contain no intermediate components.
Independent net reactions, \( \ell \), in systems of elementary reactions as (1.4) can be found by multiplying each elementary reaction \( i \) with the stoichiometric number for that elementary reaction, \( \sigma_{i,i} \), and add the resulting reaction equations:

\[
\text{Net reaction } \ell = \sigma_{1,1} \cdot \text{reaction 1} + \sigma_{2,1} \cdot \text{reaction 2} + \ldots + \sigma_{R,1} \cdot \text{reaction } R \quad (1.9)
\]

This operation leads to \( R \) stoichiometric numbers, \( \sigma_{i,\ell} \), for each independent net reaction \( \ell \). Ordered in matrix form this leads to the stoichiometric number matrix:

\[
\mathbf{a} = \begin{pmatrix}
\sigma_{1,1} & \ldots & \sigma_{1,L} \\
\vdots & \ddots & \vdots \\
\sigma_{R,1} & \ldots & \sigma_{R,L}
\end{pmatrix}
\quad (1.10)
\]

where \( L \) is the total number of independent net reactions. Combined with the elementary reactions (1.4) and the net reactions (1.9) this yields:

\[
\text{Net reactions } = \mathbf{a}^T \mathbf{v} = \mathbf{A}_S \mathbf{x}_1 = \mathbf{v}^T \mathbf{y} = \mathbf{A}_S \mathbf{x}_1 = \mathbf{0}
\quad (1.11)
\]

Where \( \mathbf{v} \) is the stoichiometric coefficients for the net reactions.

It follows from (1.11) that each row in the stoichiometric number matrix, \( \mathbf{a} \), yields one net reaction that can be described by the reaction formalism (1.4).

On the precondition that the component vector \( \mathbf{A} \) is not a null vector, a condition which will be fulfilled if there is a suggested reaction mechanism, the stoichiometric number for the individual reaction \( i \) in the net reaction \( \ell \), \( \sigma_{i,\ell} \), according to (1.11) can be determined by

\[
\mathbf{v}_{N \times L} \cdot \mathbf{A}_{S \times 1} = \mathbf{A}_{N \times S} \cdot \mathbf{A}_{S \times 1} = \mathbf{v}_{N \times L} \cdot \mathbf{A}_{S \times 1} = \mathbf{0}
\quad (1.12)
\]

Where the net reaction stoichiometric coefficient matrix, \( \mathbf{v}_{N \times L} \), is split into a first submatrix containing the stoichiometric coefficients for non-intermediate components and a second submatrix containing the stoichiometric coefficients for the intermediate components.
If the net reactions are not to contain any intermediate components then all elements in $\mathbf{w}_{\text{in}}$ must be 0. This leads to the following equation:

$$\mathbf{0}_{L \times S_c} = \left( \begin{array}{c} \mathbf{a}_{R \times L} \\ \mathbf{v}_{C} \end{array} \right)^T \mathbf{y}_{R \times S_c}$$  \hspace{1cm} (1.13)

If (1.13) has only the null solution the suggested reaction mechanism (1.4) is incomplete and further elementary reactions have to be found. To determine if $\mathbf{a}$ has other solutions than the null solution (1.13) can be restated:

$$\left( \begin{array}{c} \mathbf{v}_{C} \\ \mathbf{y}_{R \times S_c} \end{array} \right)^T \mathbf{a}_{R \times L} = \mathbf{0}_{L \times S_c}$$  \hspace{1cm} (1.14)

If (1.13) has other solutions than the null solution then the stochiometric numbers, $\sigma_{ij}$, can be found by solving the set of linear equations given by

$$\mathbf{v}_{N_{L \times S}} = \left( \begin{array}{c} \mathbf{a}_{R \times L} \\ \mathbf{v}_{R \times S} \end{array} \right)^T \mathbf{v}_{R \times S_c}$$  \hspace{1cm} (1.15)

To determine $\mathbf{a}$ (1.15) can be rewritten in the form:

$$\left( \begin{array}{c} \mathbf{v}_{C} \\ \mathbf{y}_{R \times S} \end{array} \right)^T \mathbf{a}_{R \times L} = \left( \begin{array}{c} \mathbf{v}_{N_{L \times S}} \\ \mathbf{v}_{N_{L \times S}} \end{array} \right)^T$$  \hspace{1cm} (1.16)
Example E 1.1 Determination of the Stoichiometric Numbers in a Catalytic Cycle:

The formation of SO₃ from SO₂ and O₂ using the K₂S₂O₇-V₂O₅-catalyst.

Industrially concentrated sulphuric acid is produced by diluting oleum that has been formed by absorption of sulphur trioxide in concentrated sulphuric acid. Sulphur trioxide is formed by catalytic oxidation of sulphur dioxide with oxygen over a catalyst. The catalyst consists of a melt which main constituents are vanadium in the pentavalent and tetravalent oxidation states, potassium pyrosulphate and potassium sulphate, all absorbed in porous silica particles.

The net reaction for the oxidation process is:

$$2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$$

In a paper from 1989 Balzhinimaev et al [2] suggested the following set of elementary reactions to describe the reaction mechanism behind the formation of SO₃ from SO₂ and O₂:

$$\begin{align*}
\text{SO}_2 + \text{V}^\text{V} - \text{O}_2 - \text{V}^\text{V} & \rightleftharpoons \text{V}^\text{V} - \text{O} - \text{V}^\text{V} + \text{SO}_3 \\
\text{SO}_2 + \text{V}^\text{V} - \text{O} - \text{V}^\text{V} & \rightleftharpoons \text{V}^\text{V} - \text{SO}_3 - \text{V}^\text{V} \\
\text{V}^\text{V} - \text{SO}_3 - \text{V}^\text{V} + \text{O}_2 & \rightleftharpoons \text{V}^\text{V} - \text{O}_2 - \text{V}^\text{V} + \text{SO}_3 \\
\text{V}^\text{V} - \text{SO}_3 - \text{V}^\text{V} & \rightleftharpoons [\text{V}^\text{IV}]_2 + \text{SO}_3 \\
\text{V}^\text{V} - \text{O} - \text{V}^\text{V} + \text{S}_2\text{O}_7^{2-} & \rightleftharpoons \text{V}^\text{V} - \text{SO}_4 - \text{V}^\text{V} + \text{SO}_4^{2-} \\
\text{V}^\text{V} - \text{O} - \text{V}^\text{V} + \text{S}_2\text{O}_7^{2-} & \rightleftharpoons \text{V}^\text{V} - \text{S}_2\text{O}_7^{2-} - \text{O} - \text{V}^\text{V}
\end{align*}$$

It has to be stressed that the shown vanadium intermediates are simplified notations for far more complex vanadium compounds for which the true composition is still partly unknown.

The question is, if the suggested elementary steps do describe a catalytic cycle for the formation of sulphurtrioxide?

To answer this question we must determine the stoichiometric number $\sigma_i$ for each elementary step. This is done by solving equation (1.14). If this equation has other solutions than the null solution the suggested elementary steps can form the basis for a reaction mechanism. If the stoichiometric numbers are determined from equation (1.16) the catalytic cycle can be stated.

First all components and reaction equations are numbered. Then each reaction can be allocated a stoichiometric number. For the net reaktion we get:

$$\begin{align*}
\ell &= 1 \\
j &= 1, 2, 3 \\
v_{s_{i,j}} &= -2, -1, 2
\end{align*}$$
and for the elementary steps:

1: \[
\begin{align*}
\text{SO}_2 + \text{O}^\text{v} - \text{O}_2^{-} - \text{V}^\text{v} & \leftrightarrow \text{V}^\text{v} - \text{O}_2 - \text{V}^\text{v} + \text{SO}_3 \\
1 & 1 \\
4 & 5 \\
5 & 3 \\
\end{align*}
\]

\[
v_{1j} = \begin{bmatrix}
-1 \\
-1 \\
1 \\
1 \\
\end{bmatrix}
\]

2: \[
\begin{align*}
\text{SO}_2 + \text{V}^\text{v} - \text{O}^\text{v} - \text{O}_2^{-} & \leftrightarrow \text{V}^\text{v} - \text{SO}_3 - \text{V}^\text{v} \\
1 & 1 \\
5 & 6 \\
\end{align*}
\]

\[
v_{2j} = \begin{bmatrix}
-1 \\
-1 \\
1 \\
\end{bmatrix}
\]

3: \[
\begin{align*}
\text{V}^\text{v} - \text{SO}_3 - \text{V}^\text{v} + \text{O}_2 & \leftrightarrow \text{V}^\text{v} - \text{O}_2 - \text{V}^\text{v} + \text{SO}_3 \\
6 & 2 \\
4 & 3 \\
\end{align*}
\]

\[
v_{3j} = \begin{bmatrix}
-1 \\
-1 \\
1 \\
1 \\
\end{bmatrix}
\]

4: \[
\begin{align*}
\text{V}^\text{v} - \text{SO}_3 - \text{V}^\text{v} & \leftrightarrow [\text{V}^\text{IV}_{2}]^+ + \text{SO}_3 \\
6 & 7 \\
3 & \\
\end{align*}
\]

\[
v_{4j} = \begin{bmatrix}
-1 \\
1 \\
1 \\
\end{bmatrix}
\]

5: \[
\begin{align*}
\text{V}^\text{v} - \text{O}^\text{v} - \text{V}^\text{v} + \text{S}_2\text{O}_7^{2-} & \leftrightarrow \text{V}^\text{v} - \text{SO}_4 - \text{V}^\text{v} + \text{SO}_4^{2-} \\
5 & 8 \\
9 & 10 \\
\end{align*}
\]

\[
v_{5j} = \begin{bmatrix}
-1 \\
-1 \\
1 \\
1 \\
\end{bmatrix}
\]

6: \[
\begin{align*}
\text{V}^\text{v} - \text{O}^\text{v} - \text{V}^\text{v} + \text{S}_2\text{O}_7^{2-} & \leftrightarrow \text{V}^\text{v} - \text{S}_2\text{O}_7^{2-} - \text{O} - \text{V}^\text{v} \\
5 & 8 \\
11 & \\
\end{align*}
\]

\[
v_{6j} = \begin{bmatrix}
-1 \\
-1 \\
1 \\
\end{bmatrix}
\]

From these tabulations the stoichiometric coefficient matrix for the elementary reactions $v_{ij}$ can be written:

\[
v_{ij} = \begin{bmatrix}
-1 & 0 & 1 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
-1 & 0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & -1 & 1 & 1 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & -1 & 0 & 0 & -1 & 1 & 1 & 0 \\
0 & 0 & 0 & 0 & -1 & 0 & 0 & -1 & 0 & 0 & 1 \\
\end{bmatrix}
\]

and the stoichiometric coefficient matrix for the net reaction $v_{ik}$ stated as:

\[
v_{ik} = \begin{bmatrix}
-2 & -1 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\end{bmatrix}
\]
From this we can determine if equation (1.14) has other solutions than the null solution:

\[
\begin{pmatrix}
-1 & 0 & 1 & 0 & 0 & 0 \\
1 & -1 & 0 & 0 & -1 & -1 \\
0 & 1 & -1 & -1 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & -1 & -1 \\
0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 \\
\end{pmatrix}
\begin{pmatrix}
\sigma_1 \\
\sigma_2 \\
\sigma_3 \\
\sigma_4 \\
\sigma_5 \\
\sigma_6 \\
\end{pmatrix}
= \begin{pmatrix}
0 \\
0 \\
0 \\
0 \\
0 \\
0 \\
0 \\
\end{pmatrix}
\]

By restating the linear equations in total matrix form:

\[
\begin{pmatrix}
-1 & 0 & 1 & 0 & 0 & 0 \\
1 & -1 & 0 & 0 & -1 & -1 \\
0 & 1 & -1 & -1 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & -1 & -1 \\
0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 \\
\end{pmatrix}
\begin{pmatrix}
\sigma_1 \\
\sigma_2 \\
\sigma_3 \\
\sigma_4 \\
\sigma_5 \\
\sigma_6 \\
\end{pmatrix}
= \begin{pmatrix}
0 \\
0 \\
0 \\
0 \\
0 \\
0 \\
0 \\
\end{pmatrix}
\]

and then reduce this total matrix using Gauss-elimination [3, s.344-352]:

\[
\begin{pmatrix}
-1 & 0 & 1 & 0 & 0 & 0 \\
0 & 1 & -1 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 \\
\end{pmatrix}
\begin{pmatrix}
\sigma_1 \\
\sigma_2 \\
\sigma_3 \\
\sigma_4 \\
\sigma_5 \\
\sigma_6 \\
\end{pmatrix}
= \begin{pmatrix}
0 \\
0 \\
0 \\
0 \\
0 \\
\end{pmatrix}
\]

it is seen that the range of the coefficient matrix is 5 while the number of unknown \(\sigma\)’s are 6. Therefore other solutions than the null solution exists for (1.14) [3, s.361-364]. We now need only to determine the stoichiometric number for each elementary reaction. To this purpose the linear equations (1.16) are setup.
By inserting the already reduced stoichiometric coefficient matrix $\mathbf{v}_c^{\text{c}}$ in (1.16) we get:

$$
\begin{pmatrix}
-1 & -1 & 0 & 0 & 0 & 0 \\
0 & 0 & -1 & 0 & 0 & 0 \\
1 & 0 & 1 & 1 & 0 & 0 \\
-1 & 0 & 1 & 0 & 0 & 0 \\
0 & 1 & -1 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
\end{pmatrix}
\begin{pmatrix}
\sigma_1 \\
\sigma_2 \\
\sigma_3 \\
\sigma_4 \\
\sigma_5 \\
\sigma_6 \\
\end{pmatrix}
= 
\begin{pmatrix}
-2 \\
-1 \\
2 \\
0 \\
0 \\
0 \\
0 \\
0 \\
0 \\
\end{pmatrix}
$$

which in more compact form can be written:

$$
\begin{pmatrix}
-1 & -1 & 0 & 0 & 0 & 0 & -2 \\
0 & 0 & -1 & 0 & 0 & 0 & -1 \\
1 & 0 & 1 & 1 & 0 & 0 & 2 \\
-1 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 1 & -1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\end{pmatrix}
\begin{pmatrix}
\sigma_1 \\
\sigma_2 \\
\sigma_3 \\
\sigma_4 \\
\sigma_5 \\
\sigma_6 \\
\end{pmatrix}
= 
\begin{pmatrix}
-2 \\
-1 \\
2 \\
0 \\
0 \\
0 \\
0 \\
0 \\
0 \\
\end{pmatrix}
$$

This set of linear equations is again solved by Gauss-elimination.
leading to the stoichiometric numbers:

$$\begin{pmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 1 \\
0 & -1 & 0 & 0 & 0 & 0 & -1 \\
0 & 0 & -1 & 0 & 0 & 0 & -1 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}$$

As seen reactions 1 to 3 describes the catalytic cycle while reactions 4 through 6 does not take part in the catalytic cycle. From the solution to the graphical depiction of the reaction pathway shown in figure E 1.1 can be drawn. As seen reaction 4 through 6 do not participate in the catalytic cycle but they do influence the reaction rate as some of the catalytic material is stored in an inactive form in the three side reactions.

Figure E 1.1 Catalytic cycle for the oxidation of SO₂ to SO₃ using a vanadium catalyst according to Balzhinimaev et al [2].
2. Internal Heat and Mass Transport Limitations

Until now, we have assumed that there has been no resistance to mass or heat transfer in the catalyst pellets. This has meant that the rate of reaction measured in the laboratory reactor was the kinetic rate of reaction and that sizing and reactor design depended on the kinetic rate of reaction alone. Unfortunately, both internal and external heat and mass transport limitations might influence the rate of conversion in an industrial reactor. In the laboratory, transport limitations can be avoided by choosing appropriate experimental conditions but in full scale production diffusive transport often limits the production rate. It is therefore necessary to take a closer look at how to deal with internal and external mass and heat transport for solid catalyzed reactions.

In order to do this, experimental criteria for checking the influence of internal mass and energy transport will be setup and a stringent mathematical model for internal mass and energy transport will be derived for selected catalyst shapes.

2.1 Experimental Criteria for Neglecting Internal Mass Transport Limitations

2.1.1 A Closer Look at Catalyst Pellets

Numerous criteria for when internal heat and mass transport limitations are of no or little importance have been put forward. In the following, some of the experimental criteria will be presented. As these criteria depend on the internal structure of the catalyst a more detailed description of catalyst pellets follows.

Most catalyst pellets consist of a cheap, porous inert carrier material like \( \text{Al}_2\text{O}_3 \), \( \text{SiO}_2 \) or \( \text{MgO} \) on which a catalytically active material like \( \text{V}_2\text{O}_5 \), Pt, Ni or Fe has been deposited. The structure of such pellets are seen in figure 2.1.

![Electron microscopic picture of porous catalyst pellet, Rh on Al\(_2\)O\(_3\) [4].](image)

![Mass transport in and out of a catalyst pore.](image)

Figure 2.1 a. Electron microscopic picture of porous catalyst pellet, Rh on Al\(_2\)O\(_3\) [4]. b. Mass transport in and out of a catalyst pore.

It is obvious that the catalyst particles closest to the pellet centre will not experience the same reactant concentration as the particles closer to the pellet’s exterior. In server cases, no reactants will actually reach the pellet centre and catalyst particles close to the centre will remain inactive due to lack of reactant. In the same way, the reaction might develop a high amount of heat or be very endothermic. The temperature and reactant concentration may therefore differ inside the
catalyst pellet as seen in figure 2.2. In the laboratory, mass and heat transport limitations might lead to a difference between the observed rate of reaction and the true kinetic rate of reaction:

$$-r_{A,\text{obs}} 
eq -r_{A,\text{kin}}$$ (2.1)

As we need to know the reaction rate in order to upscale from laboratory to full scale and the laboratory pellets are usually not the same size as the industrial catalyst pellets it is important to know the kinetic rate of reaction and not only the observed rate of reaction.

One could of cause think that using the same catalyst pellet shape and size in laboratory and full scale would lead to the same observed rate of reaction in full scale and laboratory. Unfortunately, the concentration outside the catalyst pellet will seldom be the same in laboratory and full scale set-up and carrying out laboratory experiments with all possible combinations of concentrations would be time consuming. Therefore practical experimental tests have been developed in order check if the measured rate of reaction is the true kinetic rate of reaction or it is influenced by internal mass and heat transport limitations.

![Catalyst Pellet](image)

Figure 2.2. Expected temperature change, $\Delta T$, and concentration profile, $C_A$, in a spherical catalyst pellet

### 2.1.2 A First Experimental Test for Internal Mass and Heat Transport Limitations

A simple initial laboratory test that can be performed with most catalyst pellets is to measure the rate of reaction as a function of catalyst pellet size. The procedure is as follows:

a. Measure the rate of reaction at a specific set of experimental conditions using catalyst pellets of diameter $d_{p1}$. This determines the observed rate of reaction for the pellet diameter $d_{p1}$:

$$-r_{A,\text{obs}}(d_{p1})$$

b. Repeat experiment a. with a catalyst pellet diameter $d_{p2}$ smaller than $d_{p1}$. This determines the observed rate of reaction for pellet diameter $d_{p2}$:

$$-r_{A,\text{obs}}(d_{p2})$$

If $-r_{A,\text{obs}}(d_{p2})$ is equal to $-r_{A,\text{obs}}(d_{p1})$ the observed rate of reaction is equal to the kinetic rate of reaction $-r_{A,\text{kin}}$.

If $-r_{A,\text{obs}}(d_{p1})$ is less than $-r_{A,\text{obs}}(d_{p2})$ the pellet diameter should be reduced and b. repeated until the rate of reaction does not increase with decreasing pellet diameter.
2.1.3 The Koros-Nowak Criteria for Neglecting Internal Mass and Heat Transport Limitations

One could raise the objection that using the simple test mentioned in section 2.1.2 does not guarantee that an internal temperature raise does not compensate for a lower reactant concentration as shown in figure 2.3.

This effect can be avoided using the Koros-Nowak criteria [5]. Koros and Nowak use the rule of thumb that

1. The kinetic reaction rate is proportional to the concentration of active sites: \( -r_{A,kin} \propto [\ast] \)
2. That reactions influenced by internal mass transfer limitations are proportional to the square root of the concentration of active sites: \( -r_{A,kin} \propto [\ast]^{1/2} \)
3. That reaction rates determined by external transport limitations are independent of the concentration of active sites: \( -r_{A,kin} \propto [\ast]^0 \)

Koros and Nowak therefore suggests the following procedure in order to test if internal or external mass transport limit the observed reaction rate:

a. Measure the rate of reaction at a specific set of experimental conditions using catalyst pellets of a diameter \( d_{p1} \), for which the criteria of section 1.1.2 shows no mass transport limitations. This determines the observed rate of reaction for the pellet diameter \( d_{p1} \):

\[ -r_{A,obs1} \]

b. Grind the catalyst pellet into a fine powder. Mix the catalyst powder with a known amount of inert powder, preferably the carrier material used for the catalyst pellet. Press this mixture into a new catalyst pellet of diameter \( d_{p2} \). Determine the dilution factor \( f_d \) from

\[
 f_d = \frac{w_{cat,powder}}{w_{cat,powder} + w_{inert,powder}} \tag{2.2}
\]

Where \( f_d \) is the catalyst dilution factor

- \( w_{cat,powder} \) is the weight of catalyst powder mixed in pellet [kg]
- \( w_{inert,powder} \) is the weight of inert powder mixed in pellet [kg]

Repeat experiment a. and determine the new observed rate of reaction for the diluted catalyst pellet

\[ -r_{A,obs2} \]

if the new measured rate of reaction is equal to the rate of reaction determined under a. times the dilution factor \( f_d \), no transport limitations exist:

\[
 \text{if } -r_{A,obs2} = f_d \cdot (-r_{A,obs1}) \text{ then } -r_{A,obs1} = -r_{A,kin} \tag{2.3}
\]

The Koros-Nowak method is more difficult to carry out than the criteria of section 2.1.2. It should therefore first be used after an expected mass transfer limitation free diameter has been found using criteria 2.1.2.
Though the Koros-Nowak criteria works well for solid catalysts deposited on inert carriers, it does not work for supported liquid phase catalysts.

### 2.1.4 Criteria for Neglecting Internal Mass Transport Limitations in Supported Liquid Phase Catalysts

A special case where the Koros-Nowak criteria does not apply is supported liquid phase catalysts (SLPC). An SLPC consists of a liquid phase catalyst absorbed in a porous solid carrier typically SiO$_2$ or Al$_2$O$_3$. This might at first seem like a very special case, but industrially important catalysts like the V$_2$O$_5$-K$_2$S$_2$O$_7$-SiO$_2$ catalyst for oxidation of SO$_2$ to SO$_3$ or the P$_2$O$_5$-clay catalyst for hydrogenation are in fact SLPCs. Industrially SLPCs are thus used to catalyse reactions where reactant gases are transported from the gas phase and absorbed in the liquid catalyst phase there to react and form products that desorbs into the gas phase leaving as gaseous products.

Liquid absorbed in a porous carrier will distribute itself so as to reach the lowest Gibbs free energy. For liquid-solid interactions with contact angles below 90°, the liquid will adhere to the surface of the solid so as to reach as low a liquid-gas interface as possible. For liquid-solid interactions with contact angles above 90°, the liquid will try to reject the surface and form spheres so as to get least possible contact with both gas and solid. Both cases are shown in figure 2.4. As liquids with contact angles above 90° tend to be ejected from the solid carrier, SLPCs tend to be made from liquids with contact angles below 90° and the liquid catalyst distribution tends to be as shown in figure 2.4a.

![Figure 2.4](image)

**Figure 2.4** Distribution of liquid catalyst for a. A liquid with contact angle below 90° and b. A liquid with contact angle above 90°.

Since the diffusivity in a liquid is in the order of $10^{-10}$ m$^2$/s while the diffusivity in a gas is around $10^{-6}$ m$^2$/s the mass transport by diffusion in the liquid phase is roughly $10^4$ of what is expected in the gas phase. Therefore mass transfer limitations can occur in the liquid phase even though no mass transfer occur in the gas phase. While the simple criteria suggested in section 2.1.2 and the Koros-Nowak criteria will insure that no mass transport limitations occur in the gas phase they cannot guarantee that mass transport limitations do not influence the reaction rate in the liquid phase. To check for mass transport limitations in the liquid phase, a different procedure therefore has been suggested by Livbjerg et al [6].
First the volume ratio of liquid absorbed in the carrier pores has to be known. This is defined as the liquid loading

\[
\alpha = \frac{\text{volume liquid}}{\text{volume of pores}}
\]  

(2.4)

Where \( \alpha \) is the liquid loading defined as catalyst containing liquid volume to pore volume.

Then the following procedure can be applied

a. Use a catalyst pellet of diameter \( d_{p1} \) for which the criteria of section 2.1.2 and the Koros-Nowak criteria show no mass transfer limitations. Then measure the rate of reaction at a specific set of experimental conditions using a liquid loading of \( \alpha_1 \). This determines the observed rate of reaction for this liquid loading:

\[-r_{A,\text{obs}_1}\]

b. Prepare a new catalyst with carrier diameter \( d_{p1} \) and a liquid loading \( \alpha_2 \) lower than \( \alpha_1 \). Repeat experiment a. and determine the new observed rate of reaction for the this catalyst pellet

\[-r_{A,\text{obs}_2}\]

if the new measured rate of reaction is equal to the ratios between the new and the old liquid loading times the rate of reaction determined under a, no transport limitations exist:

\[
\text{if } \frac{-r_{A,\text{obs}_2}}{-r_{A,\text{obs}_1}} = \frac{\alpha_2}{\alpha_1} \text{ then } -r_{A,\text{obs}_1} = -r_{A,\text{kin}} \]  

(2.5)

The Livbjerg criteria is of cause an extention of the Koros-Nowak criteria and need only to be carried out for SLPCs.

### 2.2 Models for Predicting the Influence of Internal Mass Transport Limitations

In the laboratory, it is possible to avoid mass and heat transport limitations by reducing the catalyst pellet diameter and for SLPC’s the liquid loading. For industrial size reactors, such an approach will often lead to large pressure drops in the reactor. This leads to poor economics since the pressure drop has to be overcome by larger pumps or compressors. In industrial use catalyst pellets therefore often have large diameters leading to observed reaction rates below the kinetic reaction rate as determined in the laboratory. From a design and operational point of view it is therefore attractive to be able to predict the rate of reaction observed during industrial conditions based on the kinetic rate of reaction measured in the laboratory. For this purpose, a catalyst pellet internal effectiveness factor is defined

\[
\eta = \frac{-r_{A,\text{obs}}}{-r_{A,\text{kin}}} 
\]  

(2.6)

Where \( \eta \) is the internal catalyst effectiveness factor.
Based on this definition, the observed reaction rate which should enter into the design equation for an industrial reactor can be calculated from

\[ -r_{A,\text{obs}} = \eta \cdot (-r_{A,\text{kin}}) \]  

(2.7)

as long as the effectiveness factor is known. In principle, the effectiveness factor could be found from experiments in the laboratory, but a cheaper and more efficient approach would be to set up a mathematical model which a priori could give a reliable estimate of the internal catalyst effectiveness factor. Such models should take into account the shape and structure of the catalyst pellet be relatively simple to use but still give sufficiently accurate results. For three simple but often seen catalyst pellet geometries: the slab, the cylinder and the spherical pellet, such models do exist.

### 2.2.1 A Mathematical Model for Mass Transport in a Catalyst Slab

An idealized catalyst slab is shown in figure 2.5. It has a thickness of 2L_p, a length b and height a. Both length and height are much larger than 2L_p. Therefore, the transport of reactants and products through the end surfaces can be ignored and only the transport through the surface areas A_1 and A_2 need to be considered. The reactant concentration profile through the slab will therefore be symmetrical around the slab centerline as shown in figure 2.5 b.

![Figure 2.5. a. Ideal catalyst slab. b. Cut through a catalyst slab.](image-url)
The molar flow per area through the catalyst slab is termed the molecular flux, \( N_A \). The flux is positive if the flow of \( A \) is in the direction of \( z \). At steady state, the amount of \( A \) entering the slab will equal the observed rate of reaction as no \( A \) is accumulated inside the catalyst slab:

\[
-2 \cdot A_1 \cdot N_A |_{z=L_p} = -r_{Aobs} \cdot \rho_p \cdot A_1 \cdot 2 \cdot L_p
\]  

(2.8)

where \( A_1 \) is the cross sectional area of the catalyst slab given by \( a \cdot b \) [m²]

\( a \) is the catalyst height as seen in figure 2.5 [m]

\( b \) is the catalyst length as seen in figure 2.5 [m]

\( L_p \) is half the catalyst thickness as seen in figure 2.5 [m]

\( N_A |_{z=L_p} \) is the flux of component \( A \) at the catalyst outer surface

\(-r_{Aobs}\) is the observed rate of reaction

\[ \text{mole/m}^2 \cdot \text{s} \]

\( \rho_p \) is the catalyst pellet density

\[ \text{gcat/m}^3 \]

The observed rate of reaction and therefore the internal effectiveness factor can be calculated if the molar flux at the pellet surface is known:

\[
\eta = \frac{-r_{Aobs}}{-r_{Akin}} = \frac{-r_{Aobs} \cdot \rho_p \cdot A_1 \cdot 2 \cdot L_p}{-r_{Akin} \cdot \rho_p \cdot A_1 \cdot 2 \cdot L_p} = \frac{-2 \cdot A_1 \cdot N_A |_{z=L_p}}{-r_{Akin} \cdot \rho_p \cdot L_p} = \frac{-N_A |_{z=L_p}}{-r_{Akin} \cdot \rho_p \cdot L_p}
\]  

(2.9)

The flux at the pellet surface can be found from a molar balance over the catalyst slab:

\[
\begin{align*}
\text{in} &+ \text{generated} = \text{out} + \text{accumulated} \\
(N_A \cdot A_1) |_z \cdot \Delta t - (-r_A) \cdot \rho_p \cdot A_1 \cdot \Delta z \cdot \Delta t &= (N_A \cdot A_1) |_{z+\Delta z} \cdot \Delta t + 0 \\
\downarrow \\
(N_A \cdot a \cdot b) |_z \cdot \Delta t - (-r_A) \cdot \rho_p \cdot a \cdot b \cdot \Delta z \cdot \Delta t &= (N_A \cdot a \cdot b) |_{z+\Delta z} \cdot \Delta t + 0 \\
\downarrow \\
\frac{N_A |_{z+\Delta z} - N_A |_z}{\Delta z} + (-r_A) \cdot \rho_p &= 0 \\
\Delta z &= 0 \\
\downarrow \\
\frac{dN_A}{dz} + (-r_A) \cdot \rho_p &= 0
\end{align*}
\]  

(2.10)
As the reaction rate is a function of concentration and not the flux, a Fick’s first law description of the flux is introduced:

\[ N_A = -D_{Ac} \frac{dC_A}{dz} \quad (2.11) \]

where \( D_{Ac} \) is the effective diffusivity inside the pellet \( \left[ \frac{m^2}{s} \right] \).

This leads to:

\[
\begin{align*}
\frac{dN_A}{dz} + (-r_A) \cdot \rho_p &= 0 \\
\frac{d}{dz} \left( -D_{Ac} \frac{dC_A}{dz} \right) + (-r_A) \cdot \rho_p &= 0 \\
-D_{Ac} \frac{d^2C_A}{dz^2} + (-r_A) \cdot \rho_p &= 0
\end{align*}
\]  \quad (2.12)

The boundary conditions for this second order differential equation is

\[
\begin{align*}
\zeta @: & \frac{dC_A}{dz} \bigg|_{z=0} = 0 \\
C_A &= C_{AS} \text{ at } z = L_p
\end{align*}
\]  \quad (2.13)

as seen from figure 2.5b.

In general, it is more useful to have equation (2.12) in dimensionless form. This is accomplished by the substitutions:

\[
\begin{align*}
\zeta &= \frac{z}{L_p} \\
\xi_A &= \frac{C_A}{C_{AS}}
\end{align*}
\]  \quad (2.14)
This substitution leads to:

\[
\frac{d\zeta}{dz} = \frac{1}{L_p} \\
\frac{d}{dz} = \frac{1}{L_p} \cdot \frac{d}{d\zeta} \\
\frac{dC_A}{d\xi_A} = C_{AS} \\
\frac{dC_A}{dz} = \frac{dC_A}{d\xi_A} \cdot \frac{d\xi_A}{d\zeta} = \frac{dC_A}{d\zeta} = \frac{C_{AS} \cdot \frac{d\xi_A}{d\zeta}}{L_p} \\
\frac{d^2C_A}{dz^2} = \frac{1}{L_p} \cdot \frac{d}{d\zeta} \left( \frac{C_{AS} \cdot \frac{d\xi_A}{d\zeta}}{L_p} \right) = \frac{C_{AS} \cdot \frac{d^2\xi_A}{d\zeta^2}}{L_p^2} \\
\frac{d^2\xi_A}{d\zeta^2} = \frac{1}{L_p} \cdot \frac{d}{d\zeta} \left( \frac{C_{AS} \cdot \frac{d\xi_A}{d\zeta}}{L_p} \right) = \frac{C_{AS} \cdot \frac{d^2\xi_A}{d\zeta^2}}{L_p^2}
\]

The dimensionless form of the differential equation then becomes:

\[
-D_{Ac} \cdot C_{AS} \cdot \frac{d^2\xi_A}{d\zeta^2} + (-r_{\lambda}) \cdot \rho_{\text{pellet}} = 0 \\
\frac{1}{L_p} \cdot \frac{d^2\xi_A}{d\zeta^2} - \frac{L_p^2}{D_{Ac} \cdot C_{AS}} \cdot (-r_{\lambda}) \cdot \rho_{\text{pellet}} = 0
\]

with the boundary conditions:

\[
\left. \frac{d\xi_A}{d\zeta} \right|_{\xi = 0} = 0 \\
\xi_A = 1 \text{ at } \zeta = 1
\]

Equation (2.16) does not in general have an analytical solution and therefore often has to be solved using a numerical method for solving ordinary differential equations (ODE). In most cases a differential equation like (2.16) needs to be solved for each reactant and product simultaneously leading to a set of coupled differential equations. This though is not a problem for most ODE-solvers.
2.2.2 A Mathematical Model for Mass Transport in a Catalyst Slab: Irreversible First Order Reactions

For first order irreversible reactions, an analytical solution to equation (2.16) does exist:

\[
\frac{d^2 \xi_A}{d\xi^2} - \frac{L_p^2}{D_{ae} \cdot C_{as}} \cdot k \cdot \rho_p \cdot C_A = 0
\]

(2.18)

\[
\frac{d^2 \xi_A}{d\xi^2} - \frac{L_p^2 \cdot k \cdot \rho_p \cdot \xi_A}{D_{ae}} = 0
\]

(2.20)

The dimensionless constant in front of \( \xi_A \) is the square of the Thiele modulus:

\[
\phi = L_p \cdot \sqrt{\frac{k \cdot \rho_p}{D_{ae}}}
\]

(2.19)

Inserting the Thiele modulus into equation (2.18) yields

\[
\frac{d^2 \xi_A}{d\xi^2} - \phi^2 \cdot \xi_A = 0
\]

(2.20)

Equation (2.20) can be solved using LaPlace transformation:

\[
\mathcal{L}\left\{ \frac{d^2 \xi_A}{d\xi^2} \right\} = s^2 \cdot \overline{\xi_A}(s) - s \cdot \xi_A(0) - \frac{d\xi_A}{d\xi} \bigg|_{\xi=0} = s^2 \cdot \overline{\xi_A}(s) - s \cdot \xi_A(0)
\]

\[
\mathcal{L}\{\phi^2 \cdot \xi_A\} = \phi^2 \cdot \overline{\xi_A}(s)
\]

\[
s^2 \cdot \overline{\xi_A}(s) - s \cdot \xi_A(0) - \phi^2 \cdot \overline{\xi_A}(s) = 0
\]

(2.21)

\[
\overline{\xi_A}(s) = \frac{s}{s^2 - \phi^2} \cdot \xi_A(0)
\]

\[
\xi_A(\zeta) = \xi_A(0) \cdot \cosh(\phi \cdot \zeta)
\]
From the boundary condition:

\[ \xi_A(1) = 1 \quad (2.17) \]

The unknown constant \( \xi_A(0) \) can be found:

\[ \begin{align*}
1 &= \xi_A(0) \cdot \cosh(\phi \cdot 1) \\
\xi_A(0) &= \frac{1}{\cosh(\phi)}
\end{align*} \quad (2.22) \]

The solution to the differential equation then is

\[ \xi(\zeta) = \frac{\cosh(\phi \cdot \zeta)}{\cosh(\phi)} \quad (2.23) \]

The flux at the catalyst surface therefore becomes

\[ \begin{align*}
N_A \bigg|_{z=L_p} &= -D_{ae} \cdot \frac{dC_A}{dz} \bigg|_{z=L_p} = -D_{ae} \cdot \frac{C_{AS}}{L_p} \cdot \frac{d\xi_A}{d\zeta} \bigg|_{\zeta=1} \\
&= -D_{ae} \cdot \frac{C_{AS}}{L_p} \cdot \phi \cdot \frac{\sinh(\phi \cdot 1)}{\cosh(\phi)} = -D_{ae} \cdot \frac{C_{AS}}{L_p} \cdot \phi \cdot \tanh(\phi)
\end{align*} \quad (2.24) \]

The effectiveness factor for a first order irreversible reaction can now be determined from (2.9) as

\[ \eta = -N_A \bigg|_{z=L_p} - \frac{D_{ae} \cdot \frac{C_{AS}}{L_p} \cdot \phi \cdot \tanh(\phi)}{-r_{A,\text{kin}} \cdot \rho_p \cdot L_p} = \frac{\tanh(\phi)}{\phi} \quad (2.25) \]
2.2.3 A Mathematical Model for Mass Transport in a Cylindrical Catalyst Pellet

An idealized cylindrical catalyst pellet is shown in figure 2.6. It has a diameter of $2L_p$ and a length $L$ which is much larger than $2L_p$. Therefore the transport of reactants and products through the end surfaces can be ignored and only the transport through the surface area $A_1$ needs to be considered. The reactant concentration profile through the cylinder will therefore be symmetrical around the centre axis of the cylinder as shown in figure 2.6 b.

![Diagram of a cylindrical catalyst pellet]

At steady state, the amount of A entering the cylinder will equal the observed rate of reaction as no A is accumulated inside the catalyst pellet:

\[ -A_1 \cdot N_A \mid_{z=L_p} = -r_{\text{obs}} \cdot \rho_p \cdot \pi \cdot L_p^2 \cdot L \]  

(2.26)

where

- $A_1$ is the surface area of the catalyst pellet given by $2 \cdot \pi \cdot L_p \cdot L$ [m$^2$]
- $L$ is the catalyst length as seen in figure 2.6 [m]
- $L_p$ is the catalyst pellet radius as seen in figure 2.6 [m]
The observed rate of reaction and therefore the internal effectiveness factor can thus be calculated if the molar flux at the pellet surface is known:

$$\eta = \frac{-r_{\text{Apps}}}{-r_{\text{Akin}}} = \frac{-r_{\text{Apps}} \cdot \rho_p \cdot \pi \cdot L_p^2 \cdot L}{-r_{\text{Akin}} \cdot \rho_p \cdot \pi \cdot L_p^2 \cdot L} = \frac{-2 \cdot \pi \cdot L_p \cdot \frac{N_A}{z-l_p} |_{z-l_p}}{-r_{\text{Akin}} \cdot \rho_p \cdot L_p} = \frac{-2 \cdot \pi \cdot L_p \cdot \frac{N_A}{z-l_p}}{-r_{\text{Akin}} \cdot \rho_p} \quad (2.27)$$

The flux at the pellet surface can be found from a molar balance over the catalyst pellet:

$$\left( N_A \cdot 2 \cdot \pi \cdot L \cdot z \right) |_{z=\Delta t} = -(-r_A) \cdot \rho_p \cdot 2 \cdot \pi \cdot z \cdot \Delta z \cdot L \cdot \Delta t = \left( N_A \cdot 2 \cdot \pi \cdot L \cdot z \right) |_{z=\Delta t} + 0$$

$$\downarrow$$

$$\frac{(N_A \cdot z)}{\Delta z} \bigg|_{z+\Delta z} - \frac{(N_A \cdot z)}{\Delta z} + (-r_A) \cdot \rho_p \cdot z = 0$$

$$\downarrow$$

$$\Delta z \rightarrow 0$$

$$\frac{d(z \cdot N_A)}{dz} + (-r_A) \cdot \rho_p \cdot z = 0$$

$$\downarrow$$

$$z \cdot \frac{dN_A}{dz} + N_A + (-r_A) \cdot \rho_p \cdot z = 0 \quad (2.28)$$

Introducing Fick’s first law:

$$N_A = -D_{\text{Ae}} \cdot \frac{dC_A}{dz} \quad (2.11)$$

leads to:

$$z \cdot \frac{dN_A}{dz} + N_A + (-r_A) \cdot \rho_p \cdot z = 0$$

$$\downarrow$$

$$z \cdot \frac{d}{dz} \left( -D_{\text{Ae}} \cdot \frac{dC_A}{dz} \right) = -D_{\text{Ae}} \cdot \frac{dC_A}{dz} + (-r_A) \cdot \rho_p \cdot z = 0$$

$$\downarrow$$

$$-D_{\text{Ae}} \cdot z \cdot \frac{d^2C_A}{dz^2} = -D_{\text{Ae}} \cdot \frac{dC_A}{dz} + (-r_A) \cdot \rho_p \cdot z = 0$$

$$\downarrow$$

$$\frac{d^2C_A}{dz^2} + \frac{1}{z} \cdot \frac{dC_A}{dz} - \frac{(-r_A) \cdot \rho_p}{D_{\text{Ae}}} = 0 \quad (2.29)$$

with the boundary conditions:
To make equation (2.29) more useful in general it is often put in dimensionless form. This is accomplished by the substitutions used in (2.14):

\[
\zeta = \frac{z}{L_p},
\]

\[
\xi_A = \frac{C_A}{C_{AS}}
\]

leading to the results of equation (2.15):

\[
\frac{dC_A}{dz} = \frac{C_{AS}}{L_p} \cdot \frac{d\xi_A}{d\zeta}
\]

\[
\frac{d^2C_A}{dz^2} = \frac{C_{AS}}{L_p^2} \cdot \frac{d^2\xi_A}{d\zeta^2}
\]

The dimensionless form of the differential equation then is:

\[
\frac{d^2C_A}{dz^2} + \frac{1}{z} \cdot \frac{dC_A}{dz} - \frac{(-r_A) \cdot \rho_p}{D_{ae}} = 0
\]

\[
\downarrow
\]

\[
\frac{C_{AS}}{L_p^2} \cdot \frac{d^2\xi_A}{d\zeta^2} + \frac{1}{z} \cdot \frac{C_{AS}}{L_p} \cdot \frac{d\xi_A}{d\zeta} - \frac{(-r_A) \cdot \rho_p}{D_{ae}} = 0
\]

\[
\downarrow
\]

\[
\frac{d^2\xi_A}{d\zeta^2} + \frac{1}{\zeta} \cdot \frac{d\xi_A}{d\zeta} - \frac{L_p^2 \cdot (-r_A) \cdot \rho_p}{C_{AS} \cdot D_{ae}} = 0
\]
with the boundary conditions:

\[
\begin{align*}
\xi_A(0) &= 0 \\
\frac{d\xi_A}{d\zeta} \bigg|_{\zeta=0} &= 0 \\
\xi_A(1) &= 1 \text{ at } \zeta = 1
\end{align*}
\] (2.17)

Equation (2.31) does not in general have an analytical solution and therefore often has to be solved using a numerical method for solving ordinary differential equations (ODE). In most cases, a differential equation like (2.31) needs to be solved for each reactant and product simultaneously leading to a set of coupled differential equations.

2.2.4 A Mathematical Model for Mass Transport in a Cylindrical Catalyst Pellet:

Irreversible First Order Reactions

For first order irreversible reactions an analytical solution to equation (2.31) does exist:

\[
\frac{d^2\xi_A}{d\zeta^2} + \frac{1}{\zeta} \frac{d\xi_A}{d\zeta} - \frac{L_p^2 \cdot \rho_p \cdot k \cdot C_A}{C_A^* D_{ae}} = 0
\] (2.32)

As for the slab, the dimensionless constant in front of $\xi_A$ is the square of the Thiele modulus:

\[
\phi = L_p \sqrt{\frac{k \cdot \rho_p}{D_{ae}}} \] (2.19)

Inserting the Thiele modulus into equation (2.32) yields

\[
\frac{d^2\xi_A}{d\zeta^2} + \frac{1}{\zeta} \frac{d\xi_A}{d\zeta} - \phi^2 \cdot \xi_A = 0
\] (2.33)

Rearranging equation (2.33) into (2.34)

\[
\zeta^2 \cdot \frac{d^2\xi_A}{d\zeta^2} + \zeta \cdot \frac{d\xi_A}{d\zeta} - \phi^2 \cdot \zeta^2 \cdot \xi_A = 0
\] (2.34)
it becomes obvious that this is a modified Bessel differential equation to which the general solution is [7]:

\[ \xi_A = \text{Constant}_1 \cdot I_0(\phi \cdot \zeta) + \text{Constant}_2 \cdot K_0(\phi \cdot \zeta) \tag{2.35} \]

where \( \text{Constant}_1 \) and \( \text{Constant}_2 \) are determined from the boundary conditions.

- \( I_0 \) is the modified Bessel function of the first kind of order 0
- \( K_0 \) is the modified Bessel function of the second kind of order 0

\( \text{Constant}_2 \) is readily determined from the boundary condition

\[ \left. \frac{d\xi_A}{d\zeta} \right|_{\zeta=0} = 0 \tag{2.17} \]

which indicates that \( \xi_A \) is finite at \( \zeta = 0 \). As \( K_0(\phi \cdot \zeta) \) goes toward infinity as \( \zeta \) goes toward zero, \( \text{Constant}_2 \) must be zero.

\( \text{Constant}_1 \) can now be found from the boundary condition

\[ \xi_A = 1 \text{ at } \zeta = 1 \tag{2.17} \]

leading to

\[ 1 = \text{Constant}_1 \cdot I_0(\phi \cdot 1) \]

\[ \Downarrow \]

\[ \text{Constant}_1 = \frac{1}{I_0(\phi)} \tag{2.36} \]

The solution to the differential equation is then

\[ \xi(\zeta) = \frac{I_0(\phi \cdot \zeta)}{I_0(\phi)} \tag{2.37} \]

The flux at the catalyst surface therefore becomes

\[ N_{A|z=L_p} = -D_{Ae} \left. \frac{dC_A}{dz} \right|_{z=L_p} = -D_{Ae} \cdot \frac{C_{AS}}{L_p} \cdot \left. \frac{d\xi_A}{d\zeta} \right|_{\zeta=1} \]

\[ = -D_{Ae} \cdot \frac{C_{AS}}{L_p} \cdot \frac{\phi \cdot I_1(\phi \cdot 1)}{I_0(\phi)} \]

\[ = -D_{Ae} \cdot \frac{C_{AS}}{L_p} \cdot \frac{\phi \cdot I_1(\phi)}{I_0(\phi)} \tag{2.38} \]
The effectiveness factor for a first order irreversible reaction can now be determined from (2.27) as

\[
\eta = \frac{-2 \cdot N_A \cdot \phi \cdot I_1(\phi)}{-r_{\text{kin}} \cdot \rho_p \cdot L_p} = \frac{-2 \cdot D_{\text{AD}} \cdot C_{\text{AS}} \cdot \phi \cdot I_1(\phi)}{k \cdot C_{\text{AS}} \cdot \rho_p \cdot L_p} = \frac{2 \cdot I_1(\phi)}{\phi \cdot I_0(\phi)}
\]

(2.39)

2.2.5 A Mathematical Model for Mass Transport in a Spherical Catalyst Pellet

An idealized spherical catalyst pellet is shown in figure 2.7. It has a diameter of 2L_p. The reactant concentration profile through the sphere is symmetrical around the centre of the sphere as shown in figure 2.7 b.

At steady state, the amount of A entering the sphere will equal the observed rate of reaction as no A is accumulated inside the catalyst pellet:

\[
- A_1 \cdot N_A \bigg|_{z=L_p} = -r_{\text{obs}} \cdot \rho_p \cdot \frac{4}{3} \cdot \pi \cdot L_p^3
\]

(2.40)

where A_1 is the surface area of the catalyst pellet given by \( 4 \cdot \pi \cdot L_p^2 \) [m^2]

L_p is the catalyst pellet radius as seen in figure 2.7 [m]
The observed rate of reaction and therefore the internal effectiveness factor can be calculated if the molar flux at the pellet surface is known:

\[
\eta = \frac{-r_{\text{obs}}}{-r_{\text{kin}}} = \frac{-r_{\text{obs}} \cdot \rho_p \cdot \frac{4}{3} \cdot \pi \cdot L_p^3}{-r_{\text{kin}} \cdot \rho_p \cdot \frac{4}{3} \cdot \pi \cdot L_p^3} = \frac{-4 \cdot \pi \cdot L_p^2 \cdot N_A|_{z=L_p}}{-4 \cdot \pi \cdot L_p^2 \cdot N_A|_{z=L_p}} = \frac{-3 \cdot N_A|_{z=L_p}}{-3 \cdot N_A|_{z=L_p}}
\]

(2.41)

The flux at the pellet surface can be found from a molar balance over the catalyst pellet:

\[
\begin{align*}
\frac{(N_A \cdot 4 \cdot \pi \cdot z^2)|_z \cdot \Delta t}{\Delta z} - (r_A) \cdot \rho_p \cdot 4 \cdot \pi \cdot z^2 \cdot \Delta z \cdot \Delta t &= (N_A \cdot 4 \cdot \pi \cdot z^2)|_{z+\Delta z} \cdot \Delta t + 0 \\
\frac{(N_A \cdot z^2)|_{z+\Delta z} - (N_A \cdot z^2)|_z}{\Delta z} + (r_A) \cdot \rho_p \cdot z^2 &= 0 \\
\frac{d(z^2 \cdot N_A)}{dz} + (r_A) \cdot \rho_p \cdot z^2 &= 0 \\
z^2 \cdot \frac{dN_A}{dz} + 2 \cdot z \cdot N_A + (r_A) \cdot \rho_p \cdot z^2 &= 0 \\
\frac{dN_A}{dz} + \frac{2}{z} \cdot N_A + (r_A) \cdot \rho_p &= 0
\end{align*}
\]

(2.42)

Introducing Fick’s first law:

\[
N_A = -D_{\text{Ae}} \cdot \frac{dC_A}{dz}
\]

(2.11)
leads to:

\[
\begin{align*}
\frac{dN_A}{dz} + \frac{2}{z} \cdot N_A + (-\tau_A) \cdot \rho_p &= 0 \\
\frac{d}{dz} \left( -D_{ae} \cdot \frac{dC_A}{dz} \right) - \frac{2}{z} \cdot D_{ae} \cdot \frac{dC_A}{dz} + (-\tau_A) \cdot \rho_p &= 0 \\
-D_{ae} \cdot \frac{d^2C_A}{dz^2} - \frac{2}{z} \cdot D_{ae} \cdot \frac{dC_A}{dz} + (-\tau_A) \cdot \rho_p &= 0 \\
\frac{d^2C_A}{dz^2} + \frac{2}{z} \cdot \frac{dC_A}{dz} - \frac{(-\tau_A) \cdot \rho_p}{D_{ae}} &= 0
\end{align*}
\]  

(2.43)

with the boundary conditions:

\[
\begin{align*}
\left. \frac{dC_A}{dz} \right|_{z=0} &= 0 \\
C_A &= C_{AS} \text{ at } z = L_p
\end{align*}
\]  

(2.44)

Equation (2.43) can be stated in dimensionless form. This is accomplished by the substitutions (2.14):

\[
\zeta = \frac{z}{L_p} \\
\xi_A = \frac{C_A}{C_{AS}}
\]  

(2.14)

leading to the results of equation (2.15):

\[
\begin{align*}
\frac{dC_A}{dz} &= \frac{C_{AS}}{L_p} \cdot \frac{d\xi_A}{d\zeta} \\
\frac{d^2C_A}{dz^2} &= \frac{C_{AS}}{L_p^2} \cdot \frac{d^2\xi_A}{d\zeta^2}
\end{align*}
\]  

(2.15)
The dimensionless form of the differential equation then becomes:

\[
\frac{d^2 C_A}{dz^2} + \frac{2}{z} \frac{dC_A}{dz} - \frac{(-r_A) \cdot \rho_p}{D_{Ae}} = 0
\]

\[
\frac{C_{AS} \cdot d^2 \xi_A}{L_p^2 \cdot d\zeta^2} + \frac{2}{z} \frac{C_{AS} \cdot d\xi_A}{L_p \cdot d\zeta} - \frac{(-r_A) \cdot \rho_p}{D_{Ae}} = 0
\]

(2.45)

\[
\frac{d^2 \xi_A}{d\zeta^2} + \frac{2}{\zeta} \frac{d\xi_A}{d\zeta} - \frac{L_p^2 \cdot (-r_A) \cdot \rho_p}{C_{AS} \cdot D_{Ae}} = 0
\]

with the boundary conditions:

\[
\begin{align*}
\xi_A & \bigg|_{\zeta = 0} = 0 \\
\zeta_A & = 1 \text{ at } \zeta = 1
\end{align*}
\]

(2.17)

Equation (2.45) does not in general have an analytical solution and therefore often has to be solved using a numerical method for solving ordinary differential equations (ODE). In most cases, a differential equation like (2.45) needs to be solved for each reactant and product simultaneously leading to a set of coupled differential equations.

### 2.2.6 A Mathematical Model for Mass Transport in a Spherical Catalyst Pellet:

**Irreversible First Order Reactions**

For first order irreversible reactions, an analytical solution to equation (2.45) does exist:

\[
\frac{d^2 \xi_A}{d\zeta^2} + \frac{1}{\zeta} \frac{d\xi_A}{d\zeta} - \frac{L_p^2 \cdot \rho_p \cdot k \cdot C_A}{C_{AS} \cdot D_{Ae}} = 0
\]

(2.46)
As for the slab the dimensionless constant in front of $\xi_A$ is the square of the Thiele modulus:

$$\phi = L_p \cdot \sqrt{\frac{k \cdot \rho_{\text{ pellet}}}{D_A \varepsilon}}$$  \hspace{1cm} (2.19)

Inserting the Thiele modulus into equation (2.46) yields

$$\frac{d^2 \xi_A}{d\zeta^2} + \frac{2}{\zeta} \cdot \frac{d\xi_A}{d\zeta} - \phi^2 \cdot \xi_A = 0$$  \hspace{1cm} (2.47)

Equation (2.47) can be solved using the substitution:

$$\gamma_A = \xi_A \cdot \zeta$$  \hspace{1cm} (2.48)

leading to the results of equation (2.49):

$$\frac{d\xi_A}{d\zeta} = \frac{1}{\zeta} \cdot \frac{d\gamma_A}{d\zeta} - \frac{\gamma_A}{\zeta^2}$$

$$\frac{d^2 \xi_A}{d\zeta^2} = \frac{1}{\zeta} \cdot \frac{d^2 \gamma_A}{d\zeta^2} - \frac{1}{\zeta^2} \cdot \frac{d\gamma_A}{d\zeta} - \frac{1}{\zeta^2} \cdot \frac{d\gamma_A}{d\zeta} + \frac{2}{\zeta} \cdot \frac{d\gamma_A}{d\zeta} = \frac{1}{\zeta} \cdot \frac{d^2 \gamma_A}{d\zeta^2} - \frac{2}{\zeta^2} \cdot \frac{d\gamma_A}{d\zeta} + \frac{2}{\zeta^3} \cdot \frac{d\gamma_A}{d\zeta}$$  \hspace{1cm} (2.49)

Substituting (2.49) into equation (2.47) yields

$$\frac{d^2 \gamma_A}{d\zeta^2} + \frac{2}{\zeta} \cdot \frac{d\gamma_A}{d\zeta} - \phi^2 \cdot \gamma_A = 0$$

$$\downarrow$$

$$\frac{1}{\zeta} \cdot \frac{d^2 \gamma_A}{d\zeta^2} - \frac{2}{\zeta^2} \cdot \frac{d\gamma_A}{d\zeta} + \frac{2}{\zeta} \cdot \gamma_A + 2 \cdot \left( \frac{1}{\zeta} \cdot \frac{d\gamma_A}{d\zeta} - \frac{\gamma_A}{\zeta^2} \right) - \phi^2 \cdot \frac{\gamma_A}{\zeta} = 0$$  \hspace{1cm} (2.50)

$$\downarrow$$

$$\frac{d^2 \gamma_A}{d\zeta^2} - \phi^2 \cdot \gamma_A = 0$$
This equation is in mathematical terms identical to equation (2.20) for a slab except that the boundary conditions now becomes

\[
\begin{align*}
\frac{\partial}{\partial \xi_A} \bigg|_{\xi=0} & = \left( \frac{1}{\xi} \frac{d\gamma_A}{d\xi} - \frac{\gamma_A}{\xi^2} \right) \bigg|_{\xi=0} = 0 \\
\frac{d\gamma_A}{d\xi} \bigg|_{\xi=0} & = \frac{d\xi_A}{d\xi} \bigg|_{\xi=0} + \gamma_A \bigg|_{\xi=0} = \xi_A(0) \\
\gamma_A & = 1 \text{ at } \zeta = 1
\end{align*}
\]  
(2.51)

Equation (2.51) can be solved using LaPlace transformation:

\[
\begin{align*}
\mathcal{L} \left\{ \frac{d^2\gamma_A}{d\xi^2} \right\} & = s^2 \cdot \overline{\gamma}_A(s) - s \cdot \gamma_A(0) - \frac{d\gamma_A}{d\xi} \bigg|_{\xi=0} = s^2 \cdot \overline{\gamma}_A(s) - \xi_A(0) \\
\mathcal{L} \left\{ \phi^2 \cdot \gamma_A \right\} & = \phi^2 \cdot \overline{\gamma}_A(s) \\
\int \left( s^2 \cdot \overline{\gamma}_A(s) - \xi_A(0) - \phi^2 \cdot \overline{\gamma}_A(s) \right) = 0 \\
\overline{\gamma}_A(s) & = \frac{1}{s^2 - \phi^2} \cdot \xi_A(0) \\
\gamma_A(\zeta) & = \frac{\xi_A(0)}{\phi} \cdot \sinh(\phi \cdot \zeta)
\end{align*}
\]  
(2.52)

From the boundary condition:

\[
\gamma_A(1) = 1 
\]  
(2.51)

the unknown constant \(\xi_A(0)\) can be found:

\[
1 = \frac{\xi_A(0)}{\phi} \cdot \sinh(\phi \cdot 1) \\
\xi_A(0) = \frac{\phi}{\sinh(\phi)}
\]  
(2.53)
The solution to the differential equation then is

$$\xi(\zeta) = \frac{Y_A(\zeta)}{\zeta} = \frac{\sinh(\phi \cdot \zeta)}{\zeta \cdot \sinh(\phi)}$$  \hspace{1cm} (2.54)

The flux at the catalyst surface therefore becomes

$$N_A\bigg|_{z=L_p} = -D_A \cdot \frac{dC_A}{dz} \bigg|_{z=L_p} = -D_A \cdot \frac{C_{AS}}{L_p} \cdot \frac{d\xi_A}{d\zeta} \bigg|_{\zeta=1}$$

$$= -D_A \cdot \frac{C_{AS}}{L_p} \left( \frac{\phi \cdot \cosh(\phi \cdot \zeta)}{\zeta \cdot \sinh(\phi)} - \frac{\sinh(\phi \cdot \zeta)}{\zeta^2 \cdot \sinh(\phi)} \right)$$  \hspace{1cm} (2.55)

The effectiveness factor for a first order irreversible reaction can now be determined from (2.41) as

$$\eta = \frac{-3 \cdot N_A|_{z=L_p}}{-r_{A_{kin}} \cdot \rho_p \cdot L_p} = \frac{3 \cdot D_A \cdot \frac{C_{AS}}{L_p} \left( \frac{\phi \cdot \cosh(\phi)}{\zeta \cdot \sinh(\phi)} - \frac{\sinh(\phi)}{\zeta^2 \cdot \sinh(\phi)} \right)}{k \cdot \rho_p \cdot C_{AS} \cdot L_p} = \frac{3}{\phi^2} \left( \phi \cdot \coth(\phi) - 1 \right)$$  \hspace{1cm} (2.56)

### 2.2.7 Conclusions on the Internal Catalyst Effectiveness Factor for Irreversible First Order Reactions

The internal catalyst effectiveness factor for first order irreversible reactions can for an ideal catalyst slab, an ideal cylindrical and spherical catalyst pellet be calculated from the equations (2.26), (2.38) and (2.56) respectively as given in table 2.1. Calculating the effectiveness factor from these equations leads to the curves shown in figure 2.8.
Figure 2.8 Effectiveness factor as a function of the Thiele modulus. Analytical solution for irreversible first order reactions.

As seen, the three different catalyst pellet shapes lead to three nearly identical though shifted asymptotes for \( \phi \) going towards infinity. The asymptotes are for the slab \( \phi^{-1} \), for the cylinder \( 2\phi^{-1} \) and for the sphere \( 3\phi^{-1} \). A general though approximated description would therefore be

\[
\eta = \frac{\text{tanh}(\phi_{Ai})}{\phi_{Ai}}
\]

\[
\phi_{Ai} = \frac{L_p}{i} \sqrt{\frac{k \rho_p}{D_{ Ae}}}
\]

Slab: \( i = 1 \)
Cylinder: \( i = 2 \)
Sphere: \( i = 3 \)

(2.57)

Where \( i \) is a shape factor given by (2.57)
\( \phi_{Ai} \) is the approximation Thiele modulus as defined by (2.57)
Figure 2.9  Error when using the approximate solution to the effectiveness factor for irreversible first order reactions as a function of the Thiele modulus.

For small and large values of \( \phi \) equation (2.57) leads to a correct result though in the intermediate range an error of up to 16\% can occur as shown in figure (2.9). This slight disadvantage is off-set by the fact that the approximate formulation (2.57) readily lends itself to generalisation for any given compact pellet shape as equation (2.58)

\[
\eta = \frac{\tanh(\phi_{AS})}{\phi_{AS}}
\]

\[
\phi_{AS} = \frac{V_p}{S_p} \sqrt{\frac{k \cdot \rho_p}{D_{ae}}}
\]

(2.58)

Where  
- \( S_p \) is the outer surface area of the catalyst pellet [m\(^2\)]
- \( V_p \) is the volume of the catalyst pellet [m\(^3\)]
- \( \phi_{AS} \) is the general shape approximation Thiele modulus as defined by (2.58)

It should be stressed that equation (2.58) is only valid for single first order irreversible reactions. For single reactions of a more complex nature, the approach given in section 2.2.8 could be used, and solving the more general ODE’s be out of the question.
Table 2.1 Internal effectiveness factor for first order irreversible reactions.

<table>
<thead>
<tr>
<th>Pellet shape</th>
<th>Analytical Solution</th>
<th>Approximate solution</th>
</tr>
</thead>
</table>
| Sphere        | \[ \eta = \frac{3}{\phi^2} \left( \phi \cdot \cosh(\phi) - 1 \right) \]  
\[ \phi = L_p \cdot \sqrt{\frac{k' \rho_p}{D_{ae}}} \]  
\[ \eta_{A3} = \frac{\tanh(\phi_{A3})}{\phi_{A3}} \]  
\[ \phi_{A3} = \frac{L_p}{3} \cdot \sqrt{\frac{k' \rho_p}{D_{ae}}} \]  | |
| Cylinder      | \[ \eta = \frac{2}{\phi} \frac{I_1(\phi)}{I_0(\phi)} \]  
\[ \phi = L_p \cdot \sqrt{\frac{k' \rho_p}{D_{ae}}} \]  
\[ \eta_{A2} = \frac{\tanh(\phi_{A2})}{\phi_{A2}} \]  
\[ \phi_{A2} = \frac{L_p}{2} \cdot \sqrt{\frac{k' \rho_p}{D_{ae}}} \]  | |
| Slab          | \[ \eta = \frac{\tanh(\phi)}{\phi} \]  
\[ \phi = L_p \cdot \sqrt{\frac{k' \rho_p}{D_{ae}}} \]  
\[ \eta_{A1} = \frac{\tanh(\phi_{A1})}{\phi_{A1}} \]  
\[ \phi_{A1} = L_p \cdot \sqrt{\frac{k' \rho_p}{D_{ae}}} \]  | |
| Arbitrary shape | \[ \eta = \frac{\tanh(\phi_{AS})}{\phi_{AS}} \]  
\[ \phi_{AS} = \frac{V_p}{S_p} \cdot \sqrt{\frac{k' \rho_p}{D_{ae}}} \]  | |
2.2.8 Internal Catalyst Effectiveness Factor from the Generalized Thiele Modulus

For a single reaction occurring in a catalyst pellet slab, solving the ODE (2.12) with boundary conditions (2.13) can be transformed into solving an integral analytically or numerically. This can sometimes be an advantage, should only a pocket calculator and no ODE-solver be available. Equation (2.12)

\[-D_{Ae} \cdot \frac{d^2C_A}{dz^2} + (-r_A) \cdot \rho_p = 0 \tag{2.12}\]

can be restated as:

\[-D_{Ae} \cdot \frac{d^2C_A}{dz^2} + (-r_A) \cdot \rho_p = 0 \]

\[\downarrow\]

\[d \left( \frac{D_{Ae} \cdot \frac{dC_A}{dz}}{dz} \right) = (-r_A) \cdot \rho_p \]

\[\downarrow\]

\[\int_{c_0}^{c_{A0}} \frac{d \left( \frac{D_{Ae} \cdot \frac{dC_A}{dz}}{dz} \right)}{dz} \, dC_A = \int_{c_{A0}}^{c_{A0}} (-r_A) \cdot \rho_p \, dC_A \tag{2.59}\]

\[\downarrow\]

\[\int_{0}^{L} \left[ \frac{D_{Ae} \cdot \frac{dC_A}{dz}}{dz} \right] \, \left( \frac{D_{Ae} \cdot \frac{dC_A}{dz}}{dz} \right) \, dz = \int_{c_{A0}}^{c_{A0}} D_{Ae} \cdot (-r_A) \cdot \rho_p \, dC_A \]
This integral on the left side of the equal sign can be solved using the following substitution:

\[
\begin{align*}
    y &= \left( D_{\text{Ae}} \cdot \frac{dC_A}{dz} \right) \\
    \int \frac{dy}{dz} \cdot y \, dz &= \int \frac{c_A}{c_{A0}} \cdot (-\tau_A) \cdot \rho_p \, dC_A \\
    \int \frac{dy}{dz} \cdot y \, dz - \int_{y(0)}^{y} y \, dy &= \int \frac{c_A}{c_{A0}} \cdot (-\tau_A) \cdot \rho_p \, dC_A \\
    \left[ y^2 - \frac{1}{2} \cdot y^2 \right]_{y(0)}^{y} &= \frac{1}{2} \cdot (y^2 - y(0)^2) = \int \frac{c_A}{c_{A0}} \cdot (-\tau_A) \cdot \rho_p \, dC_A \\
    \frac{1}{2} \cdot \left( \left( D_{\text{Ae}} \cdot \frac{dC_A}{dz} \right)^2 - \left( \frac{D_{\text{Ae}} \cdot dC_A}{dz} \right)_{z=0}^b \right) &= \int \frac{c_A}{c_{A0}} \cdot (-\tau_A) \cdot \rho_p \, dC_A
\end{align*}
\]

Using the first boundary condition from (2.13)

\[
\frac{dC_A}{dz} \Bigg|_{z=0} = 0 \tag{2.13}
\]

\[C_A = C_{A0} \text{ at } z = L_p\]

yields

\[
\left( D_{\text{Ae}} \cdot \frac{dC_A}{dz} \right) = \sqrt{2} \cdot \left( \int \frac{c_A}{c_{A0}} \cdot (-\tau_A) \cdot \rho_p \, dC_A \right)^{\frac{1}{2}} \tag{2.61}
\]

The concentration at the center of the pellet, \( C_{A0} \), is unknown, but can be determined iteratively from the integrated form of equation (2.61) using the second boundary condition from (2.13):

\[
L_p = \int_{C_{A0}}^{C_A} \frac{D_{\text{Ae}}}{\sqrt{2} \cdot \left( \int \frac{c_A}{c_{A0}} \cdot (-\tau_A) \cdot \rho_p \, dC_A \right)^{\frac{1}{2}}} \, dC_A \tag{2.62}
\]
Using $C_{A0}$ determined from (2.62), the flux at the pellet surface can be found from (2.61):

$$N_A\mid_{z=L_p} = \left( \frac{D_{Ae} \cdot \frac{dC_A}{dz}}{L_p} \right) = \sqrt{\frac{1}{2}} \cdot \left( \frac{c_{A0}^s \cdot \left( D_{Ae} \cdot (-r_A) \cdot \rho_p \cdot dC_A \right)}{c_{A0}^s \cdot \left( -r_{kin} \cdot \rho_p \cdot L_p \right)} \right)^{\frac{1}{2}}$$

(2.63)

and according to equation (2.9) the internal catalyst effectiveness factor for a slab for a single reaction becomes

$$\eta = \frac{-N_A\mid_{z=L_p}}{-r_{kin} \cdot \rho_p \cdot L_p} = \sqrt{\frac{1}{2}} \cdot \left( \frac{c_{A0}^s \cdot \left( D_{Ae} \cdot (-r_A) \cdot \rho_p \cdot dC_A \right)}{c_{A0}^s \cdot \left( -r_{kin} \cdot \rho_p \cdot L_p \right)} \right)^{\frac{1}{2}}$$

(2.64)

Solutions like (2.64) unfortunately are not available for cylindrical or spherical catalyst pellets. Instead the idea of an approximated description for the effectiveness factor of a form similar to (2.58) is sought

$$\eta = \frac{\tanh(\phi_{GS})}{\phi_{GS}}$$

(2.65)

where $\phi_{GS}$ is an as yet unknown general Thiele modulus.

In order to define the general Thiele modulus, the limits for equation (2.65) should be examined. For a catalyst slab the limits for the effectiveness factor are

$$\eta \rightarrow 1 \quad \text{for} \quad \phi_{GS1} \rightarrow 0$$

$$\eta \rightarrow \frac{1}{\phi_{GS1}} \quad \text{for} \quad \phi_{GS1} \rightarrow \infty$$

(2.66)

As the general Thiele modulus, $\phi_{GS1}$, goes towards infinity, server diffusive mass transport limitation occurs and the concentration of reactant $A$ in the centre of the pellet reaches its lowest possible value, the equilibrium value of $A$ for the reaction in question, $C_{Aeq}$. Combining equation (2.64) with (2.66), therefore leads to

$$\eta \rightarrow \frac{\sqrt{\frac{1}{2}} \cdot \left( \frac{c_{A0}^s \cdot \left( D_{Ae} \cdot (-r_A) \cdot \rho_p \cdot dC_A \right)}{c_{A0}^s \cdot \left( -r_{kin} \cdot \rho_p \cdot L_p \right)} \right)^{\frac{1}{2}}}{\phi_{GS1}} \quad \text{for} \quad \phi_{GS1} \rightarrow \infty$$

(2.67)
From (2.67), the generalized Thiele modulus for a slab thus becomes

\[
\phi_{GS1} = \frac{-r_{\text{Akin}} \cdot \rho_p \cdot L_p}{\sqrt{2} \cdot \left( \frac{c_{\text{A}}}{c_{\text{A}0}} \cdot \left( \int c_{\text{A}} \cdot (-r_{\lambda}) \cdot \rho_p \, dC_A \right)^{1/2} \right)}
\]  

(2.68)

When the general Thiele modulus approaches zero, the effectiveness factor approaches 1 as it should according to equation (2.66) and the boundary conditions are thus fulfilled. In the intermediate range, equation (2.65) and (2.68) compared to equation (2.64) and (2.62) overshoot with up to 16% and with modern days pocket calculators (2.64) and (2.62) are as easy to use as the more approximate equation (2.65) and (2.68).

The approach of the generalized Thiele modulus though has the benefit that it according to Froment and Bischoff [8] lends it self to be generalized to cylindrical and spherical catalyst pellets as well:

\[
\eta = \frac{\tanh(\phi_{GSi})}{\phi_{GSi}}
\]

\[
\phi_{GSi} = \frac{-r_{\text{Akin}} \cdot \rho_p \cdot L_p}{\sqrt{2} \cdot \left( \frac{c_{\text{A}}}{c_{\text{A}0}} \cdot \left( \int c_{\text{A}} \cdot (-r_{\lambda}) \cdot \rho_p \, dC_A \right)^{1/2} \right)}
\]

(2.69)

Slab: \( i = 1 \)
Cylinder: \( i = 2 \)
Sphere: \( i = 3 \)

and to more general compact catalyst shapes:

\[
\eta = \frac{\tanh(\phi_{GS})}{\phi_{GS}}
\]

\[
\phi_{GS} = \frac{-r_{\text{Akin}} \cdot \rho_p \cdot V_p}{\sqrt{2} \cdot \left( \frac{c_{\text{A}}}{c_{\text{A}0}} \cdot \left( \int c_{\text{A}} \cdot (-r_{\lambda}) \cdot \rho_p \, dC_A \right)^{1/2} \right)}
\]

(2.70)

These findings are summarized in table 2.2.

The real benefit of equations (2.67) to (2.70) though is that they make it possible to set up a simple criteria for when to ignore mass transport limitations.
Table 2.2 Generalized internal effectiveness factor for single isothermal reactions.

<table>
<thead>
<tr>
<th>Pellet shape</th>
<th>Approximate solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphere</td>
<td>[ \eta = \frac{\tanh(\phi_{GS3})}{\phi_{GS3}} ] [ \phi_{GS3} = \frac{-r_{\text{Akin}} \rho_p \cdot L_p}{3} ] [ \sqrt{2} \cdot \left( \frac{c_{as}}{c_{ao}} \cdot (-r_\lambda) \cdot \rho_p \cdot dC_A \right)^{\frac{1}{2}} ]</td>
</tr>
<tr>
<td>Cylinder</td>
<td>[ \eta = \frac{\tanh(\phi_{GS2})}{\phi_{GS2}} ] [ \phi_{GS2} = \frac{-r_{\text{Akin}} \rho_p \cdot L_p}{2} ] [ \sqrt{2} \cdot \left( \frac{c_{as}}{c_{ao}} \cdot (-r_\lambda) \cdot \rho_p \cdot dC_A \right)^{\frac{1}{2}} ]</td>
</tr>
<tr>
<td>Slab</td>
<td>[ \eta = \frac{\tanh(\phi_{GS1})}{\phi_{GS1}} ] [ \phi_{GS1} = \frac{-r_{\text{Akin}} \rho_p \cdot L_p}{2} ] [ \sqrt{2} \cdot \left( \frac{c_{as}}{c_{ao}} \cdot (-r_\lambda) \cdot \rho_p \cdot dC_A \right)^{\frac{1}{2}} ]</td>
</tr>
<tr>
<td>Arbitrary shape</td>
<td>[ \eta = \frac{\tanh(\phi_{GS})}{\phi_{GS}} ] [ \phi_{GS} = \frac{-r_{\text{Akin}} \rho_p \cdot V_p}{S_p} ] [ \sqrt{2} \cdot \left( \frac{c_{as}}{c_{ao}} \cdot (-r_\lambda) \cdot \rho_p \cdot dC_A \right)^{\frac{1}{2}} ]</td>
</tr>
</tbody>
</table>
2.2.9 The Weisz-Prater Criteria for Ignoring Internal Mass Transport Limitations

The experimental approach for checking for internal mass transport limitations discussed in section 2.1 might not always be possible especially when dealing with experimental data from literature or other laboratories. To circumvent this problem, Weisz and Prater for first order irreversible reactions suggested the following procedure based upon equation (2.70)

\[
\begin{align*}
-\dot{r}_{\text{obs}} &= \eta \cdot (-\dot{r}_{\text{kin}}) \\
-\dot{r}_{\text{obs}} \cdot \rho_{\text{pellet}} &= \eta \cdot k \cdot \rho_p \cdot C_{\text{AS}} \\
-\dot{r}_{\text{obs}} \cdot \rho_{\text{pellet}} \left( \frac{V_p}{S_p} \right)^2 &= \eta \cdot \left( \frac{V_p}{S_p} \right)^2 \cdot \frac{k \cdot \rho_p \cdot C_{\text{AS}}}{D_{\text{ae}}} = \eta \cdot \phi_{\text{AS}}^2 \cdot C_{\text{AS}} \\
\phi_{\text{WP}} &= \frac{-\dot{r}_{\text{obs}} \cdot \rho_{\text{pellet}} \left( \frac{V_p}{S_p} \right)^2}{D_{\text{ae}} \cdot C_{\text{AS}}} = \eta \cdot \phi_{\text{AS}}^2
\end{align*}
\]

where \( \Phi_{\text{WP}} \) is the Weisz module as defined in equation (2.71).

As seen from equation (2.71), all observed (measured) values that normally should be available from literature or laboratory data are now gathered in the dimensionless Weisz module, \( \Phi_{\text{WP}} \). For severe mass transport limitations, equation (2.71) becomes

\[
\Phi_{\text{WP}} = \eta \cdot \phi_{\text{AS}}^2 - \frac{1}{\phi_{\text{AS}}} \Phi_{\text{AS}}^2 = \phi_{\text{AS}} >> 1 \quad \text{for} \quad \phi_{\text{AS}} \to \infty
\]

and a suitable criteria for no mass transfer limitations for first order irreversible reactions therefore is

\[
\Phi_{\text{WP}} << 1
\]
Equation (2.73) is the original Weisz-Prater criteria for when to ignore internal mass transport limitations \([5]\). Using the generalized Thiele modulus, the criteria can be extended to cover any single isothermal reaction

\[
-r_{\text{Aobs}} = \eta \cdot (-r_{\text{Akin}}) = \eta \cdot k \cdot \rho_p \cdot g(C_{A\text{s}})
\]

\[
\frac{-r_{\text{Aobs}} \cdot \rho_p \left( \frac{V_p}{S_p} \right)^2}{D_{A\text{e}} \cdot C_{A\text{s}}} = \eta \left( \frac{V_p}{S_p} \right)^2 \cdot \frac{k \cdot \rho_p \cdot g(C_{A\text{s}})}{D_{A\text{e}}} \cdot \frac{C_{A\text{s}}}{C_{A\text{s}}}
\]

\[
\Phi_{\text{WP}} = \eta \left( \frac{V_p}{S_p} \right)^2 \cdot \frac{k \cdot \rho_p \cdot g(C_{A\text{s}})}{D_{A\text{e}}} \cdot \frac{C_{A\text{s}}}{C_{A\text{s}}}
\]

\[
\Phi_{\text{WP}} = \eta \left( \frac{-r_{\text{Akin}} \cdot \rho_p}{S_p} \right) \cdot \frac{V_p}{S_p} \cdot \left( \frac{C_{A\text{s}}}{C_{A\text{a}}} \right)^{1/2} \cdot \frac{2 \cdot \int_{C_{A\text{a}}}^{C_{A\text{s}}} (-r_{\text{Akin}}) \cdot \rho_p \cdot dC_{A}}{-r_{\text{Akin}} \cdot \rho_p \cdot C_{A\text{s}} \cdot D_{A\text{e}}}
\]

\[
\Phi_{\text{WP}} = \eta \cdot \phi_{\text{GS}}^2 \frac{C_{A\text{s}}}{g(C_{A\text{s}}) \cdot C_{A\text{s}} \cdot D_{A\text{e}}}
\]

For sever mass transport limitations, equation (2.74) becomes

\[
\Phi_{\text{WP}} = \eta \cdot \phi_{\text{GS}}^2 \cdot \left( \frac{C_{A\text{s}}}{g(C_{A\text{s}}) \cdot C_{A\text{s}} \cdot D_{A\text{e}}} \right) + \frac{2 \cdot \int_{C_{A\text{a}}}^{C_{A\text{s}}} D_{A\text{e}} \cdot g(C_{A}) \cdot dC_{A}}{\phi_{\text{GS}}^2 \cdot \frac{C_{A\text{s}}}{g(C_{A\text{s}}) \cdot C_{A\text{s}} \cdot D_{A\text{e}}}} \quad \text{for} \quad \phi_{\text{GS}} \to \infty
\]

\[
\Phi_{\text{WP}} = \phi_{\text{GS}} \cdot \frac{C_{A\text{s}}}{g(C_{A\text{s}}) \cdot C_{A\text{s}} \cdot D_{A\text{e}}} \quad >> \quad \frac{2 \cdot \int_{C_{A\text{a}}}^{C_{A\text{s}}} D_{A\text{e}} \cdot g(C_{A}) \cdot dC_{A}}{g(C_{A\text{s}}) \cdot C_{A\text{s}} \cdot D_{A\text{e}}}
\]

and a suitable criteria for no mass transfer limitations for single isothermal reactions therefore is

\[
\Phi_{\text{WP}} \ll \frac{2 \cdot \int_{C_{A\text{a}}}^{C_{A\text{s}}} D_{A\text{e}} \cdot g(C_{A}) \cdot dC_{A}}{g(C_{A\text{s}}) \cdot C_{A\text{s}} \cdot D_{A\text{e}}}
\]
Equation (2.76) is the generalized Weisz-Prater criteria for neglecting internal mass transport limitations as suggested by Petersen and Bischoff [5].

2.3 Models for Predicting the Influence of Internal Heat Transport Limitations

Even though heat transport limitations occur more seldom than mass transport limitations, they do in some cases play an important role. If heat transport limitation does occur, it will for exothermic reactions lead to a temperature increase inside the pellet and thereby a faster reaction than predicted from the kinetic rate equation. If the reaction is endothermic, it leads to a temperature decrease. Therefore the reaction rate will be lower than predicted from the kinetic rate equation. In order to describe the influence of the heat transport in a catalyst pellet and thereby to predict the reaction rate more accurately, a heat balance can be setup for the catalyst pellet. As for the mass balances for the three simple catalyst pellet geometries: the slab, the cylindrical and the spherical pellet, heat balances will be derived and a simple criteria for when to ignore heat transport limitations will be stated.

2.3.1 A Mathematical Model for Heat Transport in a Catalyst Slab

An idealized catalyst slab is shown in figure 2.10. It has a thickness of $2L_p$, a length $b$ and height $a$. Both length and height are much larger than $2L_p$. Therefore the heat transport through the end surfaces can be ignored and only the transport through the surface areas $A_1$ and $A_2$ needs to be considered. The temperature profile through the slab will therefore be symmetrical around the slab centerline as shown in figure 2.10 b.

Figure 2.10 a. Ideal catalyst slab. b. Cut through a catalyst slab.

The heat flow per area through the catalyst slab is termed the heat flux, $J$. The flux is positive if the heat flow is in the direction of $z$. 
The temperature profile through the pellet can be found from a heat balance over the catalyst slab:

\[
\text{in} + \text{generated} = \text{out} + \text{accumulated}
\]

\[
(J \cdot A_j)_z \Delta t + \sum_{i=1}^{m} \left( r_i \cdot \rho_p \cdot (-\Delta H_i) \right) \cdot A_i \cdot \Delta z \cdot \Delta t = (J \cdot A_j)_{z+\Delta z} \Delta t + 0
\]

\[
(J \cdot a \cdot b)_z \Delta t + \sum_{i=1}^{m} \left( r_i \cdot \rho_p \cdot (-\Delta H_i) \right) \cdot a \cdot b \cdot \Delta z \cdot \Delta t = (J \cdot a \cdot b)_{z+\Delta z} \Delta t + 0
\]

\[
\frac{J|_{z+\Delta z} - J|_z}{\Delta z} - \sum_{i=1}^{m} \left( r_i \cdot \rho_p \cdot (-\Delta H_i) \right) = 0
\]

\[
\Delta z \to 0
\]

\[
\frac{dJ}{dz} - \sum_{i=1}^{m} \left( r_i \cdot \rho_p \cdot (-\Delta H_i) \right) = 0
\]

Where

- \( J \) is the heat flux \( \left[ \frac{W}{m^2 \cdot s} \right] \)
- \( m \) is the total number of independent reactions
- \( r_i \) is the reaction rate for the independent reaction \( i \) \( \left[ \frac{molek}{gcat \cdot s} \right] \)
- \( \Delta H_i \) is the heat of reaction for reaction \( i \) \( \left[ \frac{molek}{molek} \right] \)

To introduce the temperature, Fourier's law is used:

\[
J = -\lambda_e \cdot \frac{dT}{dz}
\]

(2.78)

where

- \( \lambda_e \) is the effective conductivity of the porous pellet \( \left[ \frac{W}{m \cdot K \cdot s} \right] \)
This leads to:

\[
\frac{dJ}{dz} - \sum_{i=1}^{m} \left( r_i \cdot \rho_p \cdot (-\Delta H_p) \right) = 0
\]

\[
\frac{d\left( -\lambda_e \cdot \frac{dT}{dz} \right)}{dz} - \sum_{i=1}^{m} \left( r_i \cdot \rho_p \cdot (-\Delta H_p) \right) = 0
\]  

(2.79)

\[
-\lambda_e \cdot \frac{d^2T}{dz^2} - \sum_{i=1}^{m} \left( r_i \cdot \rho_p \cdot (-\Delta H_p) \right) = 0
\]

The boundary conditions for this second order differential equation is:

\[
\frac{dT}{dz} \bigg|_{z=0} = 0 \quad \text{(2.80)}
\]

\[T = T_s \text{ at } z = L_p\]

as seen from figure 2.10b.

In order to use equation (2.79) together with the molar balance (2.16), it is stated in dimensionless form. This is accomplished by the substitutions:

\[
\zeta = \frac{z}{L_p}
\]

\[
\theta = \frac{T - T_s}{\Delta T_{\text{max}}}
\]  

(2.81)

where \( \Delta T_{\text{max}} \) is found as described in section 2.3.5
This substitution leads to:

\[
\begin{align*}
\frac{d\zeta}{dz} &= \frac{1}{L_p} \\
\frac{d}{dz} &= \frac{1}{L_p} \frac{d}{d\zeta} \\
\frac{dT}{d\theta} &= \Delta T_{\text{max}} \\
\frac{dT}{dz} &= \frac{dT}{d\theta} \cdot \frac{d\theta}{d\zeta} = \frac{\Delta T_{\text{max}}}{L_p} \cdot \frac{d\theta}{d\zeta} \\
\frac{d^2T}{dz^2} &= \frac{1}{L_p} \cdot \frac{d}{d\zeta} \left( \frac{\Delta T_{\text{max}}}{L_p} \cdot \frac{d\theta}{d\zeta} \right) = \frac{\Delta T_{\text{max}}}{L_p^2} \cdot \frac{d^2\theta}{d\zeta^2}
\end{align*}
\]  

(2.82)

The dimensionless form of the differential equation then becomes:

\[
\begin{align*}
-\lambda_e \cdot \Delta T_{\text{max}} \cdot \frac{d^2\theta}{d\zeta^2} - \sum_{i=1}^{m} \left( r_i \cdot \rho_p \cdot (-\Delta H_p) \right) &= 0 \\
\downarrow \\
\frac{d^2\theta}{d\zeta^2} + \frac{L_p^2}{\lambda_e \cdot \Delta T_{\text{max}}} \sum_{i=1}^{m} \left( r_i \cdot \rho_p \cdot (-\Delta H_p) \right) &= 0
\end{align*}
\]  

(2.83)

with the boundary conditions:

\[
\begin{align*}
\frac{d\theta}{d\zeta} \bigg|_{\zeta=0} &= 0 \\
\theta &= 1 \text{ at } \zeta = 1
\end{align*}
\]  

(2.84)

In general, equation (2.83) has to be solved numerically together with the molar balance for a catalyst slab (2.16) as a set of coupled ordinary differential equations (ODE). This is not a problem for most ODE solvers. For single reactions, a simpler approach can be used as shown in section 2.3.5.
2.3.2 A Mathematical Model for Heat Transport in a Cylindrical Catalyst Pellet

An idealized cylindrical catalyst pellet is shown in figure 2.11. It has a diameter of $2L_p$ and a length $L$ which is much larger than $2L_p$. Therefore the heat transport through the end surfaces can be ignored and only the transport through the surface area $A$ needs to be considered. The temperature profile through the cylinder will therefore be symmetrical around the centre axis of the cylinder as shown in figure 2.11b.

![Diagram of a cylindrical catalyst pellet](image)

Figure 2.11. a. Ideal cylindrical catalyst pellet. b. Cut through a cylindrical catalyst pellet.
The temperature profile through the pellet can be found from a heat balance over the cylindrical catalyst pellet:

\[
\begin{align*}
(J \cdot A_1)_z \cdot \Delta t + \sum_{i=1}^{m} \left( r_i \cdot \rho_p \cdot (-\Delta H)_i \right) \cdot A_1 \cdot \Delta z \cdot \Delta t &= (J \cdot A_1)_{z+\Delta z} \cdot \Delta t + 0 \\
\downarrow \\
(J \cdot 2 \cdot \pi \cdot L \cdot z)_z \cdot \Delta t + \sum_{i=1}^{m} \left( r_i \cdot \rho_p \cdot (-\Delta H)_i \right) \cdot 2 \cdot \pi \cdot z \cdot \Delta z \cdot L \cdot \Delta t &= (J \cdot 2 \cdot \pi \cdot L \cdot z)_{z+\Delta z} \cdot \Delta t + 0 \\
\downarrow \\
\frac{(J \cdot z)_{z+\Delta z} - (J \cdot z)_z}{\Delta z} - \sum_{i=1}^{m} \left( r_i \cdot \rho_p \cdot (-\Delta H)_i \right) \cdot z &= 0 \\
\downarrow \\
\frac{d(z \cdot J)}{dz} - \sum_{i=1}^{m} \left( r_i \cdot \rho_p \cdot (-\Delta H)_i \right) \cdot z &= 0 \\
\downarrow \\
z \cdot \frac{dJ}{dz} + J - \sum_{i=1}^{m} \left( r_i \cdot \rho_p \cdot (-\Delta H)_i \right) \cdot z &= 0
\end{align*}
\]  

(2.85)

Inserting Fourier’s law:

\[
J = -\lambda_e \cdot \frac{dT}{dz}
\]  

(2.78)

leads to:

\[
\begin{align*}
z \cdot \frac{dJ}{dz} + J - \sum_{i=1}^{m} \left( r_i \cdot \rho_p \cdot (-\Delta H)_i \right) \cdot (-r_\alpha) \cdot z &= 0 \\
\downarrow \\
z \cdot \frac{d \left( -\lambda_e \cdot \frac{dT}{dz} \right)}{dz} - \lambda_e \cdot \frac{dT}{dz} - \sum_{i=1}^{m} \left( r_i \cdot \rho_p \cdot (-\Delta H)_i \right) \cdot z &= 0 \\
\downarrow \\
-\lambda_e \cdot z \cdot \frac{d^2T}{dz^2} - \lambda_e \cdot \frac{dT}{dz} - \sum_{i=1}^{m} \left( r_i \cdot \rho_p \cdot (-\Delta H)_i \right) \cdot z &= 0 \\
\downarrow \\
\frac{d^2T}{dz^2} + \frac{1}{z} \cdot \frac{dT}{dz} + \frac{\sum_{i=1}^{m} \left( r_i \cdot \rho_p \cdot (-\Delta H)_i \right)}{\lambda_e} &= 0
\end{align*}
\]  

(2.86)
with the boundary conditions:

\[ @: \]
\[
\frac{dT}{dz}\bigg|_{z=0} = 0 \\
T = T_s \text{ at } z = L_p
\] (2.87)

In order to use equation (2.86) together with the molar balance (2.31), it is stated in dimensionless form. This is accomplished by the substitutions of (2.81):

\[
\zeta = \frac{z}{L_p} \\
\theta = \frac{T - T_s}{\Delta T_{\text{max}}}
\] (2.81)

where \( \Delta T_{\text{max}} \) is found as described in section 2.3.5.

which with the reformulations of (2.82):

\[
\frac{dT}{dz} = \frac{\Delta T_{\text{max}}}{L_p} \cdot \frac{d\theta}{d\zeta} \\
\frac{d^2T}{dz^2} = \frac{\Delta T_{\text{max}}}{L_p^2} \cdot \frac{d^2\theta}{d\zeta^2}
\] (2.82)

leads to the dimensionless form of the differential equation:

\[
\frac{d^2\theta}{d\zeta^2} + \frac{1}{\zeta} \frac{d\theta}{d\zeta} + \frac{\sum_{i=1}^{m} \left( \tau_i \cdot \rho_p \cdot (-\Delta H_p) \right)}{\lambda_e} = 0
\]

\[
\frac{\Delta T_{\text{max}}}{L_p^2} \cdot \frac{\Delta T_{\text{max}}}{L_p} \cdot \frac{d^2\theta}{d\zeta^2} + \frac{1}{\zeta} \frac{\Delta T_{\text{max}}}{L_p} \cdot \frac{d\theta}{d\zeta} + \frac{\sum_{i=1}^{m} \left( \tau_i \cdot \rho_p \cdot (-\Delta H_p) \right)}{\lambda_e} = 0
\] (2.88)

\[
\frac{d^2\theta}{d\zeta^2} + \frac{1}{\zeta} \frac{d\theta}{d\zeta} + \frac{L_p^2 \cdot \sum_{i=1}^{m} \left( \tau_i \cdot \rho_p \cdot (-\Delta H_p) \right)}{\lambda_e \cdot \Delta T_{\text{max}}} = 0
\]
with the boundary conditions:

\[
\begin{aligned}
\theta & = 1 \text{ at } \zeta = 1 \\
\frac{d\theta}{d\zeta} \bigg|_{\zeta = 0} & = 0
\end{aligned}
\]

(2.84)

In general, equation (2.88) has to be solved numerically together with the molar balance for a cylindrical catalyst pellet (2.31) as a set of coupled ordinary differential equations (ODE). For single reactions a simpler approach can be used as shown in section 2.3.5.

1.3.3 A Mathematical Model for Heat Transport in a Spherical Catalyst Pellet

An idealized cylindrical catalyst pellet is shown in figure 2.12. It has a diameter of \(2L_p\). The temperature profile through the sphere will be symmetrical around the centre of the pellet as shown in figure 2.12b.

Figure 2.12. a. Spherical catalyst pellet. b. Cut through a spherical catalyst pellet.
The temperature profile through the pellet can be found from a heat balance over the spherical catalyst pellet:

\[
\begin{align*}
(J \cdot A_i)|_z \cdot \Delta t + \sum_{i=1}^{m} (r_i \cdot \rho_p \cdot (-\Delta H_i)) \cdot A_i \cdot \Delta z \cdot \Delta t &= (J \cdot A_i)|_{z + \Delta z} \cdot \Delta t + 0 \\
\sum_{i=1}^{m} (r_i \cdot \rho_p \cdot (-\Delta H_i)) \cdot \frac{4}{3} \cdot \pi \cdot z^2 \cdot \Delta z \cdot \Delta t &= \left( \frac{4}{3} \cdot \pi \cdot z^2 \right) |_{z + \Delta z} \cdot \Delta t + 0 \\
\frac{(J \cdot z^2)|_z - (J \cdot z^2)|_{z + \Delta z}}{\Delta z} - \sum_{i=1}^{m} (r_i \cdot \rho_p \cdot (-\Delta H_i)) \cdot z^2 &= 0 \\
\Delta z \to 0 \\
\frac{d(z^2 \cdot J)}{dz} - \sum_{i=1}^{m} (r_i \cdot \rho_p \cdot (-\Delta H_i)) \cdot z^2 &= 0 \\
z^2 \cdot \frac{dj}{dz} + 2 \cdot z \cdot J - \sum_{i=1}^{m} (r_i \cdot \rho_p \cdot (-\Delta H_i)) \cdot z^2 &= 0
\end{align*}
\]  

(2.89)

Inserting Fourier's law:

\[
J = -\lambda_e \cdot \frac{dT}{dz}
\]  

(2.78)

leads to:

\[
\begin{align*}
z^2 \cdot \frac{dj}{dz} + 2 \cdot z \cdot J - \sum_{i=1}^{m} (r_i \cdot \rho_p \cdot (-\Delta H_i)) \cdot (-r_A) \cdot z^2 &= 0 \\
\frac{d}{dz} \left( -\lambda_e \cdot \frac{dT}{dz} \right) - 2 \cdot z \cdot \lambda_e \cdot \frac{dT}{dz} - \sum_{i=1}^{m} (r_i \cdot \rho_p \cdot (-\Delta H_i)) \cdot z^2 &= 0 \\
-\lambda_e \cdot z^2 \cdot \frac{d^2T}{dz^2} - 2 \cdot z \cdot \lambda_e \cdot \frac{dT}{dz} - \sum_{i=1}^{m} (r_i \cdot \rho_p \cdot (-\Delta H_i)) \cdot z^2 &= 0 \\
\frac{d^2T}{dz^2} + \frac{2}{z} \cdot \frac{dT}{dz} + \sum_{i=1}^{m} \frac{(r_i \cdot \rho_p \cdot (-\Delta H_i))}{\lambda_e} &= 0
\end{align*}
\]  

(2.90)
with the boundary conditions:

\[
\begin{align*}
\frac{dT}{dz}_{z=0} &= 0 \\
T &= T_s \text{ at } z = L_p
\end{align*}
\tag{2.91}
\]

In order to use equation (2.90) together with the molar balance (2.45) it is stated in dimensionless form. This is accomplished by the substitutions of (2.81):

\[
\zeta = \frac{z}{L_p} \\
\theta = \frac{T - T_s}{\Delta T_{\text{max}}}
\tag{2.81}
\]

where \( \Delta T_{\text{max}} \) is found as described in section 2.3.5.

which with reformulations of (2.82):

\[
\begin{align*}
\frac{dT}{dz} &= \frac{\Delta T_{\text{max}}}{L_p} \frac{d\theta}{d\zeta} \\
\frac{d^2T}{dz^2} &= \frac{\Delta T_{\text{max}}}{L_p^2} \frac{d^2\theta}{d\zeta^2}
\end{align*}
\tag{2.82}
\]

leads to the dimensionless form of the differential equation:

\[
\begin{align*}
\frac{d^2T}{dz^2} + \frac{2}{z} \frac{dT}{dz} + \frac{\sum_{i=1} L_{p,i} \rho_{p,i} \cdot (-\Delta H_p)}{\lambda_e} &= 0 \\
\frac{\Delta T_{\text{max}}}{L_p^2} \frac{d^2\theta}{d\zeta^2} + \frac{2}{z} \frac{\Delta T_{\text{max}}}{L_p} \frac{d\theta}{d\zeta} + \frac{\sum_{i=1} L_{p,i} \rho_{p,i} \cdot (-\Delta H_p)}{\lambda_e} &= 0 \\
\frac{d^2\theta}{d\zeta^2} + \frac{2}{\zeta} \frac{d\theta}{d\zeta} + \frac{L_p^2 \sum_{i=1} L_{p,i} \rho_{p,i} \cdot (-\Delta H_p)}{\lambda_e \cdot \Delta T_{\text{max}}} &= 0
\end{align*}
\tag{2.92}
\]
with the boundary conditions:
\[
\begin{align*}
\text{at:} & \\
\frac{d\theta}{d\zeta} & = 0 \\
\theta & = 1 \text{ at } \zeta = 1
\end{align*}
\]

In general, equation (2.92) has to be solved numerically together with the molar balance for a spherical catalyst pellet (2.45) as a set of coupled ordinary differential equations (ODE). This though is not a problem for most ODE solvers. Though for single reactions a simpler approach can be used, as shown in section 2.3.4.

2.3.4 Single Reactions: A Simplified Mathematical Model for the Temperature Profile in Catalyst Pellets

For a single reaction occurring in a catalyst particle, the heat balance and the molar balance are particular simple. For a catalyst slab, the molar and the heat balances are (2.12) and (2.79):

\[
\begin{align*}
\frac{dN_A}{dz} + (-r_A) \cdot \rho_p = 0 \\
\frac{dJ}{dz} + (-r_A) \cdot \rho_p \cdot (-\Delta H_A) = 0
\end{align*}
\]

With the boundary conditions (2.13) and (2.80):
\[
\begin{align*}
\text{at:} & \\
\frac{dC_A}{dz} & = 0 \rightarrow N_A|_{z=0} = 0 \\
\frac{dT}{dz} & = 0 \rightarrow J|_{z=0} = 0 \\
C_A & = C_{AS} \text{ at } z = L_p \\
T & = T_S \text{ at } z = L_p
\end{align*}
\]

As the temperature change inside a catalyst pellet in most cases will be relatively small, the heat of reaction can normally be considered independent of temperature inside the pellet. Equation (2.93) can thus be restated as:

\[
\begin{align*}
\frac{dN_A}{dz} &= (-r_A) \cdot \rho_p \\
\frac{d\left(\frac{J}{(-\Delta H_A)}\right)}{dz} &= (-r_A) \cdot \rho_p
\end{align*}
\]
Taking the difference between the molar balance and the heat balance yields

\[
\frac{dN_A}{dz} - \frac{d}{dz} \left( \frac{J}{(-\Delta H_A)} \right) = 0
\]

\[
\downarrow
\]

\[
\frac{d}{dz} \left( N_A - \frac{J}{(-\Delta H_A)} \right) = 0
\]

\[
\downarrow
\]

\[
\int dN_A - \int_0^z \frac{J}{(-\Delta H_A)} dz = \int_0^z dz
\]

\[
\downarrow
\]

\[
N_A - N_A \bigg|_{z=0} - \frac{J}{(-\Delta H_A)} \bigg|_{z=0} = 0
\]

\[
\downarrow
\]

\[
N_A - \frac{J}{(-\Delta H_A)} = 0
\]

Introducing Fick’s first law (2.11) and Fourier’s law (2.78) leads to

\[
N_A - \frac{J}{(-\Delta H_A)} = 0
\]

\[
\downarrow
\]

\[
-D_{ae} \frac{dC_A}{dz} + \frac{\lambda_e}{(-\Delta H_A)} \frac{dT}{dz} = 0
\]

\[
\downarrow
\]

\[
\int_{C_A}^{C_A} - D_{ae} \cdot dC_A + \int_{T_e}^{T} \frac{\lambda_e}{(-\Delta H_A)} \cdot dT = \int_0^z dz
\]

\[
\downarrow
\]

\[
-D_{ae} \cdot (C_{AS} - C_A) + \frac{\lambda_e}{(-\Delta H_A)} \cdot (T_S - T) = 0
\]

\[
\downarrow
\]

\[
T = \frac{D_{ae} \cdot (-\Delta H_A)}{\lambda_e} \cdot (C_{AS} - C_A) + T_S
\]
For a single reaction, the maximum possible temperature change inside a pellet can therefore be estimated from (2.97)

\[
\Delta T_{\text{max}} = \frac{D_{\text{eq}} \cdot (\Delta H_{\text{A}}) \cdot C_{\text{AS}}}{\lambda_s}
\]  

(2.98)

For a cylindrical catalyst pellet, the molar and heat balances (2.28) and (2.85) with boundary conditions (2.13) and (2.80) lead to

\[
\frac{d(z \cdot N_A)}{dz} + (r_\lambda) \cdot \rho_p \cdot z = 0
\]

\[
\frac{d(z \cdot J)}{dz} + (r_\lambda) \cdot \rho_p \cdot (-\Delta H_{\text{A}}) \cdot z = 0
\]

\[
\frac{d(z \cdot N_A)}{dz} - \frac{d\left( \frac{z \cdot J}{(-\Delta H_{\text{A}})} \right)}{dz} = 0
\]

\[
\frac{d\left( z \cdot N_A - \frac{z \cdot J}{(-\Delta H_{\text{A}})} \right)}{dz} = 0
\]

\[
\int_0^{z} d(z \cdot N_A) = \frac{1}{(-\Delta H_{\text{A}})} \int_0^{z} d(z \cdot J) = \int_0^{z} dz
\]

\[
z \cdot N_A - \frac{z \cdot J}{(-\Delta H_{\text{A}})} = 0
\]

\[
N_A - \frac{J}{(-\Delta H_{\text{A}})} = 0
\]

which is equivalent to equation (2.96) for a catalyst slab. As Fick’s first law and Fourier’s law remain the same, equation (2.97) and (2.98) are also valid for a cylindrical catalyst pellet.
Using the molar and heat balances (2.41) and (2.89) with boundary conditions (2.13) and (2.80) for a spherical pellet leads to

\[
\begin{align*}
\frac{d(z^2 \cdot N_A)}{dz} + (-r_A) \cdot \rho_p \cdot z^2 &= 0 \\
\frac{d(z^2 \cdot J)}{dz} + (-r_A) \cdot \rho_p \cdot (-\Delta H_A) \cdot z^2 &= 0 \\
\frac{d(z^2 \cdot N_A)}{dz} - \frac{d\left(\frac{z^2 \cdot J}{(-\Delta H_A)}\right)}{dz} &= 0 \\
\frac{d\left(z^2 \cdot N_A - \frac{z^2 \cdot J}{(-\Delta H_A)}\right)}{dz} &= 0 \\
\int_0^{z^2 N_A} d(z^2 \cdot N_A) - \frac{1}{(-\Delta H_A)} \int_0^{z^2 J} d(z^2 \cdot J) &= \int_0^z dz \\
z^2 \cdot N_A - \frac{z^2 \cdot J}{(-\Delta H_A)} &= 0 \\
N_A - \frac{J}{(-\Delta H_A)} &= 0
\end{align*}
\] (2.100)

which is equivalent to equation (2.96) for a catalyst slab. Therefore equation (2.97) and (2.98) are also valid for spherical catalyst pellets.

A simple criteria for if heat transport limitations can be ignored for single reactions could thus be

\[
\Delta T_{\text{max}} = \frac{D_{ae} \cdot (-\Delta H_A) \cdot C_{AS}}{\lambda_e} < 2 \ [K]
\] (2.101)

where the upper boundary of 2 K is chosen since the true external temperature \(T_S\) seldom will be known with greater accuracy and few reactions will be very sensitive to so small a temperature change.
If the temperature change inside the pellet needs to be taken into account, this can be done by combining the respective molar balances and substituting equation (2.97) for the temperature in the respective molar balances or for arbitrary shapes using the generalized Thiele modulus with (2.97) substituted for the temperature.

2.3.5 Maximum Possible Temperature Change in Catalyst Pellet for Multiple Reactions

For multiple reactions occurring in a catalyst pellet, the maximum possible temperature change can by extension of equation (2.98) be estimated from

\[ \Delta T_{\text{max}} = \frac{D_{e} \cdot (-\Delta H_{\text{max}})}{\lambda_{e}} \]  

(2.102)

where \( \Delta H_{\text{max}} \) is the maximum possible heat of reaction based on the sum of the individual reactions and reactants present (J m\(^{-3}\)), and criteria (2.101) can be used to check if the temperature change needs to be taken into account. Should this though be the case the respective coupled differential equations describing the molar and energy balances have to be solved in their full form. Equation (2.97) cannot be used for multiple reactions.
2.4 Summary on Calculations for Internal Heat and Mass Transport Limitations

The purpose of this summary is to give a short guideline on how to deal with internal mass and heat transport limitations in catalyst pellets. The calculations are described in the order they should be performed rather than in the order in which they were derived. The flow chart in figure 2.13 should guide the reader through the procedures.

2.4.1 Calculating the Internal Effectiveness Factor for Single Reactions

First, use equation (1.101) to determine if the temperature change caused by the reaction can be ignored:

\[
\Delta T_{\text{max}} = \frac{D_{\text{e}} \cdot (\Delta H) \cdot C_{\text{AS}}}{\lambda_e} < 2 \, [K]
\]  

(2.101)

If so, the catalyst pellet can be considered to be isothermal.
If the catalyst pellet is isothermal, use the generalized Weisz-Prater criteria (2.76) to check if mass transport limitations are important:

\[
\Phi_{WP} \ll \frac{2 \cdot \int_{C_{A0}}^{C_{Af}} D_{Ae} \cdot g(C_A) dC_A}{\frac{C_{A0}}{g(C_{AS}) \cdot C_{AS} \cdot D_{Ae}}} \quad (2.76)
\]

If (2.76) is fulfilled, mass transport limitations are unimportant and the effectiveness factor \( \eta \) is equal to 1.

If mass transport limitations cannot be ignored but the catalyst pellet can be considered isothermal, for first order irreversible reactions, use the appropriate formulas in table (2.1) to calculate the effectiveness factor. If the reaction is not an irreversible first order reaction, use either the approximate method of the generalized Thiele modulus as given in table 2.2 or use an ODE-solver to solve the appropriate molar balance with \( T = T_s \) as shown in table 2.3 and calculate the effectiveness factor from the first derivative of the concentration from the appropriate formula in table 2.3.

If the reaction is not isothermal, use formula (2.97)

\[
T = \frac{D_{Ae} \cdot (-\Delta H_A)}{\lambda_e} \cdot (C_{AS} - C_A) + T_s \quad (2.97)
\]

to express the temperature as a function of concentration. Then use either the approximate method of the generalized Thiele modulus as given in table 2.2 or use an ODE-solver to solve the appropriate molar balance in table 2.3 and calculate the effectiveness factor from the first derivative of the concentration from the appropriate formula in table 2.3.
Table 2.3 Molar balances for calculation of the internal effectiveness factor for single reactions.

<table>
<thead>
<tr>
<th>Pellet shape</th>
<th>Molar balance</th>
<th>Effectiveness factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphere</td>
<td>[ \frac{d^2C_A}{dz^2} + \frac{2}{z} \frac{dC_A}{dz} - \frac{(-\tau_A) \cdot \rho_p}{D_{Ae}} = 0 ]</td>
<td>[ \eta = \frac{3 \cdot D_{Ae} \frac{dC_A}{dz}</td>
</tr>
<tr>
<td>Cylinder</td>
<td>[ \frac{d^2C_A}{dz^2} + \frac{1}{z} \frac{dC_A}{dz} - \frac{(-\tau_A) \cdot \rho_p}{D_{Ae}} = 0 ]</td>
<td>[ \eta = \frac{2 \cdot D_{Ae} \frac{dC_A}{dz}</td>
</tr>
<tr>
<td>Slab</td>
<td>[ \frac{d^2C_A}{dz^2} - \frac{(-\tau_A) \cdot \rho_p}{D_{Ae}} = 0 ]</td>
<td>[ \eta = \frac{D_{Ae} \frac{dC_A}{dz}</td>
</tr>
</tbody>
</table>

For the **Sphere**:
- Initial condition: \( \frac{dC_A}{dz} |_{z=0} = 0 \)
- Boundary condition: \( C_A = C_{AS} \) at \( z = L_p \)

For the **Cylinder**:
- Initial condition: \( \frac{dC_A}{dz} |_{z=0} = 0 \)
- Boundary condition: \( C_A = C_{AS} \) at \( z = L_p \)

For the **Slab**:
- Initial condition: \( \frac{dC_A}{dz} |_{z=0} = 0 \)
- Boundary condition: \( C_A = C_{AS} \) at \( z = L_p \)
2.4.2 Calculating the Internal Effectiveness Factor for Multiple Reactions

First use equation (2.102) to determine if the temperature change caused by the reaction can be ignored:

\[
\Delta T_{\text{max}} = \frac{D_A \cdot (-\Delta H_{\text{max}})}{\lambda_e} < 2 \text{ [K]}
\] (2.102)

If so, the catalyst pellet can be considered to be isothermal, the temperature can be set equal to the catalyst outer surface temperature \(T_s\) and the energy balance ignored. If the temperature change is important, the differential energy balance has to be solved together with the \(n\) appropriate differential molar balances in table 2.4 in order to get correct concentration profiles for each component through the catalyst pellet.

Based on the concentration and temperature profiles, the effectiveness factor for the individual reactions can be calculated from

\[
\eta_i = \frac{r_{\text{obs}}}{r_{\text{kin}}} = \frac{\int_{V_p} r_{i,\text{kin}}(C_j(V),T(V)) \, dV_p}{\int_{V_p} r_{i,\text{obs}} \, dV_p}
\] (2.103)

The volume integral (2.103) degenerates for the idealized catalyst slab into

\[
\eta_i = \frac{\int_{V_p} r_{i,\text{kin}}(C_j(V),T(V)) \, dV_p}{r_{i,\text{kin}}(C_{j_0},T_g) \cdot V_p} = \frac{2 \cdot \int_0^{L_p} \int_0^L \int_0^L r_{i,\text{kin}}(C_j(x,y,z),T(x,y,z)) \, dz \, dy \, dx}{r_{i,\text{kin}}(C_{j_0},T_g) \cdot a \cdot b \cdot L_p}
\] (2.104)

For an idealized cylindrical catalyst pellet, (2.103) becomes

\[
\eta_i = \frac{\int_{V_p} r_{i,\text{kin}}(C_j(V),T(V)) \, dV_p}{r_{i,\text{kin}}(C_{j_0},T_g) \cdot V_p} = \frac{2 \cdot \int_0^{L_p} \int_0^L \int_0^L r_{i,\text{kin}}(C_j(\theta_a,y,z),T(\theta_a,y,z)) \cdot z \, dz \, dy \, d\theta_a}{r_{i,\text{kin}}(C_{j_0},T_g) \cdot \pi \cdot L_p \cdot L_p^2}
\] (2.105)
Which for a spherical pellet (2.103) is simplified to

$$
\eta_l = \frac{\int_{V_p} r_{kin}(C_f(V), T(V)) \, dV_p}{r_{kin}(C_{gs}, T_g) \cdot V_p} = \frac{2 \pi \int_0^{L_p} \int_0^{2\pi} r_{kin}(C_f(\theta, \phi, z), T(\theta, \phi, z)) \cdot z^2 \cdot \sin \phi \, dz \, d\phi \, d\theta}{r_{kin}(C_{gs}, T_g) \cdot \frac{4}{3} \pi \cdot L_p^3} \\
= \frac{3 \int_0^{L_p} r_{kin}(C_f(z), T(z)) \cdot z^2 \, dz}{r_{kin}(C_{gs}, T_g) \cdot L_p^3}
$$

(2.106)
Table 2.4 Molar and energy balances for calculation of the internal effectiveness factor for multiple reactions.

<table>
<thead>
<tr>
<th>Pellet shape</th>
<th>Molar and energy balances</th>
<th>Substitutions</th>
</tr>
</thead>
</table>
| Sphere       | \[
\frac{d^2 \xi_j}{d\zeta^2} + \frac{2}{\zeta} \frac{d\xi_j}{d\zeta} - \frac{L_p^2 \cdot (-r_j) \cdot \rho_p}{C_{js} \cdot D_{js}} \cdot \frac{d\xi_j}{d\zeta} = 0
\]
|              | \[
\frac{d^2 \theta}{d\zeta^2} + \frac{2}{\zeta} \frac{d\theta}{d\zeta} + \frac{L_p^2 \cdot \sum_{i=1}^{m} (r_i \cdot \rho_p \cdot (-\Delta H_i))}{\lambda_e \cdot \Delta T_{\text{max}}} = 0 \]
|              | \[
\left. \frac{d\xi_j}{d\zeta} \right|_{\zeta=0} = 0 \quad \left. \frac{d\theta}{d\zeta} \right|_{\zeta=0} = 0
\]
|              | \[
\xi_j = 1 \text{ and } \theta = 1 \text{ at } \zeta = 1
\]
| Cylinder     | \[
\frac{d^2 \xi_j}{d\zeta^2} + \frac{1}{\zeta} \frac{d\xi_j}{d\zeta} - \frac{L_p^2 \cdot (-r_j) \cdot \rho_p}{C_{js} \cdot D_{js}} \cdot \frac{d\xi_j}{d\zeta} = 0
\]
|              | \[
\frac{d^2 \theta}{d\zeta^2} + \frac{1}{\zeta} \frac{d\theta}{d\zeta} + \frac{L_p^2 \cdot \sum_{i=1}^{m} (r_i \cdot \rho_p \cdot (-\Delta H_i))}{\lambda_e \cdot \Delta T_{\text{max}}} = 0 \]
|              | \[
\left. \frac{d\xi_j}{d\zeta} \right|_{\zeta=0} = 0 \quad \left. \frac{d\theta}{d\zeta} \right|_{\zeta=0} = 0
\]
|              | \[
\xi_j = 1 \text{ and } \theta = 1 \text{ at } \zeta = 1
\]
| Slab         | \[
\frac{d^2 \xi_j}{d\zeta^2} - \frac{L_p^2 \cdot (-r_j) \cdot \rho_p}{C_{js} \cdot D_{js}} = 0
\]
|              | \[
\frac{d^2 \theta}{d\zeta^2} + \frac{L_p^2 \cdot \sum_{i=1}^{m} (r_i \cdot \rho_p \cdot (-\Delta H_i))}{\lambda_e \cdot \Delta T_{\text{max}}} = 0 \]
|              | \[
\left. \frac{d\xi_j}{d\zeta} \right|_{\zeta=0} = 0 \quad \left. \frac{d\theta}{d\zeta} \right|_{\zeta=0} = 0
\]
|              | \[
\xi_j = 1 \text{ and } \theta = 1 \text{ at } \zeta = 1
\]

Numerous criteria have been setup for when external heat and mass transport limitations are of no or little importants. In the following the criterias first formulated by Mears [9, 10] will be derived and expanded to a broader field of reaction kinetics and pellet shapes than originally claimed by Mears.

3.1 Mears’ Criterion for Neglecting External Mass Transport Limitations

3.1.1 Mears’ Mass Transport Criterion for Spherical Pellets

D.E. Mears derived [9] a simple criteria for mass transport limitations in connection with solid catalyzed reactions. The derivation which will be given here is based on a simple perturbation method. The basic assumption is that the true kinetics for the reaction can be stated as

\[ -r_A = k(T) \cdot f(C_A, C_i) \]  

(3.1)

where \( k \) is a rate constant depending on temperature only

- \( C_A \) is the concentration of the rate limiting component \( A \) \([\text{mole/m}^3]\)

- \( C_i \) is the concentration of the non-rate limiting components \( i \) \([\text{mole/m}^3]\)

- \( r_A \) is the rate of formation for the rate limiting reactant \( A \) \([\text{mole/gcat\cdot s}]\)

The rate limiting component, \( A \), for the reaction is either the stoichiometric limiting component or if all components are present in stoichiometric amounts the component with the lowest diffusivity.

As external mass transport limitations cannot be completely avoided the question is: Does it actually influence the observed reaction rate?

Figure 3.1 Spherical catalyst pellet of radius \( L_p \). The surface concentration and temperature is \( C_{AS} \) and \( T_s \) respectively, the bulk concentration and bulk temperature \( C_{Abulk} \) and \( T_{bulk} \).
At steady state the amount of A transported from the pellet must equal the amount of A formed inside the pellet. For the spherical pellet illustrated in figure 3.1 this leads to

\[ -r_{A,obs} \rho_p \frac{4}{3} \pi L_p^3 = k_s (C_{A,\text{bulk}} - C_{A,S}) \cdot 4 \pi L_p^2 \]

(3.2)

where

- \( C_{A,\text{bulk}} \) is the concentration of the rate limiting component A in the bulk stream \([\text{mole/m}^3]\)
- \( C_{A,S} \) is the concentration of the rate limiting component A at the pellet surface \([\text{mole/m}^3]\)
- \( k_s \) is the mass transfer coefficient \([\text{m/s}]\)
- \( L_p \) is the pellet radius [m]
- \( r_{A,obs} \) is the observed rate of reaction for the catalyst pellet \([\text{mole/g cat \cdot s}]\)
- \( \rho_p \) is the catalyst pellet density \([\text{g/m}^3]\)

The difference between the bulk concentration and the actual surface concentration thus becomes

\[ C_{A,\text{bulk}} - C_{A,S} = \frac{-r_{A,obs} \rho_p L_p}{3 k_s} \]

(3.3)

Ideally the concentration at the catalyst surface should be the same as the bulk concentration and the observed rate of reaction equal to the kinetic rate of reaction based on the bulk concentration. In order to judge how important the surface concentration’s deviation from the bulk concentration is it is not so much the numerical difference between the two concentrations as how this difference influence the reaction rate that matters. In order to judge this Mears suggested calculating the perturbation, or deviation, for the rate of reaction using a first order truncation of a Taylor polynomial discription of the reaction rate. Using the Taylor polynomial developed at the surface concentration \( C_{A,S} \) leads to

\[ -r_A(C_A) = -r_A(C_{A,S}) + \frac{\partial (-r_A)}{\partial C_A} \bigg|_{C_{A,S}} (C_A - C_{A,S}) + \frac{1}{2!} \frac{\partial^2 (-r_A)}{\partial C_A^2} \bigg|_{C_{A,S}} (C_A - C_{A,S})^2 + .... \]

(3.4)

which for small deviations of \( C_{\text{bulk}} \) from \( C_{A,S} \) can be approximated by

\[ -r_A(C_A) \approx -r_A(C_{A,S}) + \frac{\partial (-r_A)}{\partial C_A} \bigg|_{C_{A,S}} (C_A - C_{A,S}) \]

(3.5)
This equation can be restated to yield

\[
-r_A(C_A) = -r_A(C_{AS}) + \frac{\partial (-r_A)}{\partial C_A} \cdot (C_A - C_{AS}) = -r_A(C_{AS}) \left( 1 + \frac{\partial (-r_A)}{\partial C_A} \cdot \frac{C_A - C_{AS}}{-r_A(C_{AS})} \right)
\]

\[
= -r_A(C_{AS}) \left( 1 + k \cdot \frac{\partial f(C_A)}{\partial C_A} \cdot \frac{C_A - C_{AS}}{k \cdot f(C_{AS})} \right) = -r_A(C_{AS}) \left( 1 + \frac{\partial f(C_A)}{\partial C_A} \cdot \frac{C_A - C_{AS}}{f(C_{AS})} \right)
\]

(3.6)

If one follows D.E. Mears and accepts a deviation in the rate of reaction caused by external mass transport limitations of maximum 5% this leads to

\[
\frac{-r_A(C_A)}{-r_A(C_{AS})} = 1 + \left| \frac{\partial f(C_A)}{\partial C_A} \cdot \frac{C_A - C_{AS}}{f(C_{AS})} \right| < 1.05
\]

(3.7)

or

\[
\left| \frac{\partial f(C_A)}{\partial C_A} \cdot \frac{C_A - C_{AS}}{f(C_{AS})} \right| < 0.05
\]

(3.8)

Combining (3.8) with the mass balance (3.3) yields a general version of Mears criterium for neglecting mass transport limitations for spherical catalyst pellets

\[
\left| \frac{\partial f(C_A)}{\partial C_A} \cdot \frac{-r_{A,obs} \cdot P \cdot L^2}{k_e} \right| < 0.05
\]

(3.9)
3.1.2 Mears’ Mass Transport Criterion for long cylindrical Pellets

D.E. Mears criterion for mass transport limitation in connection with solid catalyzed reactions can easily be expanded to cover other catalyst pellet shapes. While the Taylor expansion (3.5) and the perturbation equation (3.8) remains the same the mass balance (3.2) is influenced by the catalyst pellet geometry. For a very long cylindrical catalyst pellet as shown in figure 3.2 where the end surfaces of the cylinder can be neglected the mass balance becomes

\[
-t_{A,obs}\cdot \rho_p \cdot 2\cdot \pi \cdot L_p^2 \cdot L = k_g \cdot (C_{Abulk} - C_{AS}) \cdot 2 \cdot \pi \cdot L_p \cdot L
\]

\[
C_{Abulk} - C_{AS} = \frac{-t_{A,obs}\cdot \rho_p \cdot L_p}{2k_g}
\]  

(3.10)

where

\(L_p\) is the pellet radius as shown in figure 3.2 [m]
\(L\) is the pellet length as shown in figure 3.2 [m]

Inserting (3.10) into the perturbation equation (3.8) leads to a Mears’ criterion for neglecting external mass transfer limitations for cylindrical pellets

\[
\left| \frac{\partial f(C_A)}{\partial C_A} \right|_{C_{AS}} - t_{A,obs}\cdot \rho_p \cdot \frac{L_p}{2k_g} \]  

\[
< 0.05
\]

(3.11)
3.1.3 Mears’ Mass Transport Criterion for Catalyst Slabs

To extend D.E. Mears' criteria for mass transport limitations in connection with solid catalyzed reactions to include catalyst slabs as shown in Figure 3.3, the mass balance (3.2) has to be changed while the Taylor expansion (3.5) and the perturbation equation (3.8) remain the same. For a very thin slab where the end surfaces of the slab can be neglected, the mass balance becomes:

\[-r_{A,obs} \cdot \rho \cdot 2 \cdot L_p \cdot \dot{a} \cdot \dot{b} = k_g \cdot (C_{bulk} - C_{AS}) \cdot 2 \cdot \dot{a} \cdot \dot{b}\]

\[C_{bulk} - C_{AS} = \frac{-r_{A,obs} \cdot \rho \cdot \dot{L}_p}{k_g}\]  

(3.12)

where

- \(a\) is the pellet height as shown in Figure 3.3 [m]
- \(b\) is the pellet width as shown in Figure 3.3 [m]
- \(L_p\) is the half pellet thickness as shown in Figure 3.3 [m]

Inserting (3.12) into the perturbation equation (3.8) leads to a Mears’ Criterion for neglecting external mass transfer limitations for a catalyst slab:

\[\left| \frac{\partial f(C_A)}{\partial C_A} \right|_{C_{AS}, -r_{A,obs} \cdot \rho \cdot \dot{L}_p/k_g} < 0.05\]  

(3.13)
3.1.4 Mears’ Mass Transport Criterium for Arbitrary Catalyst Shapes

The examples of 3.1.1 to 3.1.3 directly lends themself to a general Mears’ criterium for any catalyst shape. Again only the mass balance is influenced by the pellet geometry while the perturbation equation (3.8) remain the same. For an arbitrary pellet shape the mass balance becomes

\[
- r_{A,obs} \cdot \rho_p \cdot V_p = k_g \cdot (C_{Abulk} - C_{AS}) \cdot S_p
\]

\[
\downarrow
\]

\[
C_{Abulk} - C_{AS} = \frac{- r_{A,obs} \cdot \rho_p \cdot V_p}{k_g \cdot S_p}
\]

(3.14)

where

- \( V_p \) is the pellet volume [m³]
- \( S_p \) is the outer pellet surface area [m²]

Inserting (3.14) into the perturbation equation (3.8) leads to a Mears’ Criterium for neglecting external mass transfer limitations for an arbitrary pellet shape

\[
\left| \frac{\partial f(C_A)}{\partial C_A} \right|_{C_{AS}} = \frac{- r_{A,obs} \cdot \rho_p \cdot V_p}{k_g \cdot S_p} < 0.05
\]

(3.15)
3.2 Mears’ Criterium for Neglecting External Heat Transport Limitations

3.2.1 Mears’ Heat Transport Criterion for Spherical Pellets
As for the mass transport limitations D.E. Mears derived [9] a simple criteria for heat transport limitations in connection with solid catalyzed reactions. The derivation which will be given here is also in this case based on a simple perturbation method. As external heat transport limitation cannot be completely avoided again the question is: Does it actually influence the observed reaction rate?

At steady state the amount of heat transported from the pellet must equal the amount of heat released inside the pellet. For the spherical pellet illustrated on figure 3.1 this leads to

\[
-\tau_{A,obs} \rho_p \cdot \frac{4}{3} \cdot \pi \cdot L_p^3 (-\Delta H_A) = h \cdot (T_{bulk} - T_S) \cdot 4 \cdot \pi \cdot L_p^2
\]  

(3.16)

where
- \( h \) is the heat transfer coefficient \[ \text{m}^2 \cdot \text{K} \cdot \text{s} \]
- \( T_{bulk} \) is the temperature in the bulk stream [K]
- \( T_S \) is the temperature at the pellet surface [K]
- \( \Delta H_A \) is heat of reaction based on conversion of the rate limiting component A \[ \text{J} \text{mole}^{-1} \]
- \( \rho_p \) is the catalyst pellet density \[ \text{g} \text{m}^{-3} \]

The difference between the bulk temperature and the actual surface temperature thus becomes

\[
T_{bulk} - T_S = \frac{(-\tau_{A,obs}) \rho_p L_p (-\Delta H_A)}{3 \cdot h}
\]  

(3.17)

Ideally the temperature at the catalyst surface should be the same as the temperature in the bulk stream and the observed rate of reaction equal to the kinetic rate of reaction based on the bulk temperature. In order to judge how important the surface temperature’s deviation from the bulk stream temperature is it is not so much the numerical difference between the two temperatures as how this difference influence the reaction rate that matters. In order to judge this Mears suggested calculating the perturbation, or deviation, in the rate of reaction using a first order truncation of a Taylor polynomial description of the reaction rate. Using the Taylor polynomial developed at the surface temperature \( T_S \) leads to

\[
-\tau_A(T) = -\tau_A(T_S) + \frac{\partial (-\tau_A)}{\partial T} \mid_{T_S} \cdot (T - T_S) + \frac{1}{2!} \frac{\partial^2 (-\tau_A)}{\partial T^2} \mid_{T_S} \cdot (T - T_S)^2 + \ldots
\]  

(3.18)
which for small deviations of $T_{\text{bulk}}$ from $T_s$ can be approximated by

$$-r_A(T) = -r_A(T_s) + \frac{\partial(-r_A)}{\partial T} \bigg|_{T_s} \cdot (T - T_s)$$  \hspace{2cm} (3.19)

This equation can then be restated to yield

$$-r_A(T) = -r_A(T_s) + \frac{\partial(-r_A)}{\partial T} \bigg|_{T_s} \cdot (T - T_s) = -r_A(T_s) \left( 1 + \frac{\partial(-r_A)}{\partial T} \bigg|_{T_s} \cdot \frac{(T - T_s)}{-r_A(T_s)} \right)$$  \hspace{2cm} (3.20)

If one follows D.E. Mears and accepts a deviation in the rate of reaction caused by external heat transport limitations of maximum 5% this leads to

$$\frac{-r_A(T)}{-r_A(T_s)} = 1 + \frac{\partial(-r_A(T))}{\partial T} \bigg|_{T_s} \cdot \frac{(T - T_s)}{-r_A(T_s)} < 1.05$$ \hspace{2cm} (3.21)

or

$$\left| \frac{\partial(-r_A(T))}{\partial T} \bigg|_{T_s} \cdot \frac{C_{\text{ca}}}{-r_A(T_s)} \cdot (T - T_s) \right| < 0.05$$ \hspace{2cm} (3.22)

Combining (3.22) with the heat balance (3.17) yields a general version of Mears criterion for neglecting heat transport limitations for spherical catalyst pellets

$$\left| \frac{\partial(-r_A(T))}{\partial T} \bigg|_{T_s} \cdot \frac{r_{A,obs} \cdot \rho_f \cdot \frac{L_p}{3} \cdot (-\Delta H_A)}{-r_A(T_s)} \right| < 0.05$$ \hspace{2cm} (3.23)
Even though most catalytic reactions follow a Langmuir-Hinshelwood or Eley-Rideal like mechanism leading to a rate expressions of the form

\[ -r_A = \frac{k(T) \cdot f(C_i)}{1 + K_1(T) \cdot g_1(C_i) + K_2(T) \cdot g_2(C_i) + \ldots} \]  
 \hspace{1cm} (3.24)

for small changes in temperature only the temperature dependency of the rate constant matter as the adsorption and desorption constants are less temperature sensitive than the rate constant. Therefore the rate expression to a good approximation can be written as in equations (3.1)

\[ -r_A = k(T) \cdot f(C_i) \cdot C_A \]  
 \hspace{1cm} (3.1)

If the rate constant follows an Arrhenius like expression equation (3.23) can be simplified further as

\[
-\frac{\partial -r_A(T)}{\partial T}\bigg|_{T_s} = \frac{\partial k(T)}{\partial T}\bigg|_{T_s} \cdot f(C_i) = \frac{\partial A \cdot \exp\left(-\frac{E}{R \cdot T}\right)}{\partial T}\bigg|_{T_s} = \frac{A \cdot \exp\left(-\frac{E}{R \cdot T_s}\right)}{k(T_s)} \cdot \frac{E}{R \cdot T_s^2} = \frac{E}{R \cdot T_s^2} \]  
 \hspace{1cm} (3.25)

leading to

\[
\frac{-r_{A,obs} \cdot \rho_p \cdot L_p \cdot (-\Delta H_A)}{\frac{3}{h} R \cdot T_s^2} < 0.05 \]  
 \hspace{1cm} (3.26)

Which in restated form is the original Mears’ criterium for neglecting external heat transport limitations for spherical catalyst pellets

\[
\left| \frac{-r_{A,obs} \cdot \rho_p \cdot L_p \cdot (-\Delta H_A)}{h \cdot T_s} \right| < 0.15 \cdot \frac{R \cdot T_s}{E} \]  
 \hspace{1cm} (3.27)
3.2.2 Mears’ Heat Transport Criterium for Cylindrical Pellets

Just as for mass transfer D.E. Mears’ criterium for heat transport limitation in connection with solid catalyzed reactions can easily be expanded to cover other catalyst pellet shapes. While the Taylor expansion (3.18) and the perturbation equation (3.22) remains the same the heat balance (3.16) is influenced by the catalyst pellet geometry. For a very long cylindrical catalyst pellet as shown in figure 3.2 where the end surfaces of the cylinder can be neglected the heat balance becomes

\[-r_{A,obs} \cdot \rho_p \cdot 2 \cdot \pi \cdot L_p^2 \cdot L \cdot (-\Delta H_A) = h \cdot (T_{bulk} - T_S) \cdot 2 \cdot \pi \cdot L_p \cdot L \]

\[T_{bulk} - T_S = \frac{-r_{A,obs} \cdot \rho_p \cdot L_p}{h} \cdot \frac{(-\Delta H_A)}{2} \]

(3.28)

Inserted in equation (3.22) this leads to the following criterium for neglecting heat transport limitations:

\[\left| \frac{\partial r_A(T)}{\partial T} \right| \bigg|_{T_S} - \frac{r_{A,obs} \cdot \rho_p \cdot L_p}{h} \cdot \frac{(-\Delta H_A)}{2} < 0.05 \]

(3.29)

In the simplified version (3.29) becomes

\[\left| -\frac{r_{A,obs} \cdot \rho_p \cdot L_p \cdot (-\Delta H_A)}{h \cdot T_S} \right| < 0.10 \cdot \frac{R \cdot T_S}{E} \]

(3.30)

3.2.3 Mears’ Heat Transport Criterium for Catalyst Slabs

To extend D.E. Mears’ criterium for heat transport limitations in connection with solid catalyzed reactions to include catalyst slabs as seen in figure 3.3 the heat balance (3.16) has to be changed while the Taylor expansion (3.18) and the perturbation equation (3.22) remains the same. For a very thin slab where the end surfaces of the slab can be neglected the heat balance becomes

\[-r_{A,obs} \cdot \rho_p \cdot 2 \cdot L_p \cdot a \cdot b \cdot (-\Delta H_A) = h \cdot (T_{bulk} - T_S) \cdot 2 \cdot a \cdot b \]

\[T_{bulk} - T_S = \frac{-r_{A,obs} \cdot \rho_p \cdot L_p}{h} \cdot \frac{(-\Delta H_A)}{h} \]

(3.31)
Inserting (3.31) into the perturbation equation (3.22) leads to a Mears’ criterium for neglecting external heat transfer limitations for a catalyst slab

\[
\left| \frac{\partial -r_A(T)}{\partial T} \right| \frac{-r_{A,obs} \cdot \rho_p \cdot L_p \cdot (-\Delta H_A)}{h} < 0.05 \quad (3.32)
\]

which in the simplified form yields

\[
\left| \frac{-r_{A,obs} \cdot \rho_p \cdot L_p \cdot (-\Delta H_A)}{h \cdot T_S} \right| < 0.05 \cdot \frac{R \cdot T_S}{E} \quad (3.33)
\]

### 3.2.4 Mears’ Heat Transport Criterium for Arbitrary Catalyst Shapes

The examples of 3.2.1 to 3.2.3 directly lends themselves to a general Mears’ criterium for any catalyst shape. Again only the heat balance is influenced by the pellet geometry while the perturbation equation (3.22) remain the same. For an arbitrary pellet shape as shown in figure 3.4 the heat balance becomes

\[
-r_{A,obs} \cdot \rho_p \cdot V_p \cdot (-\Delta H_A) = h \cdot (T_{bulk} - T_S) \cdot S_p
\]

\[
\downarrow
\]

\[
T_{bulk} - T_S = \frac{-r_{A,obs} \cdot \rho_p \cdot V_p}{S_p} \cdot (-\Delta H_A)
\]

(3.34)

Inserting (3.34) into the perturbation equation (3.22) leads to a Mears’ Criterium for neglecting external heat transfer limitations for an arbitrary pellet shape

\[
\left| \frac{\partial -r_A(T)}{\partial T} \right| \frac{-r_{A,obs} \cdot \rho_p \cdot V_p \cdot (-\Delta H_A)}{h \cdot S_p} < 0.05 \quad (3.35)
\]

which in the simplified form becomes

\[
\left| \frac{-r_{A,obs} \cdot \rho_p \cdot V_p \cdot (-\Delta H_A)}{h \cdot T_S} \right| < 0.05 \cdot \frac{R \cdot T_S}{E} \quad (3.36)
\]
### Table 3.1 Expanded Mears’ criteria for neglecting external heat and mass transport limitations.

<table>
<thead>
<tr>
<th>Pellet shape</th>
<th>Mass Transport Limitations</th>
<th>Heat Transport Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphere</td>
<td>$\frac{\partial f(C_A)}{f(C_{AS})} \frac{r_{A,obs} \cdot \rho_p \cdot L_p}{k_g} &lt; 0.05$</td>
<td>$\frac{-r_{A,obs} \cdot \rho_p \cdot L_p \cdot (-\Delta H_A)}{h \cdot T_s} &lt; 0.15 \cdot \frac{R \cdot T_s}{E}$</td>
</tr>
<tr>
<td>Cylinder</td>
<td>$\frac{\partial f(C_A)}{f(C_{AS})} \frac{r_{A,obs} \cdot \rho_p \cdot L_p}{2k_g} &lt; 0.05$</td>
<td>$\frac{-r_{A,obs} \cdot \rho_p \cdot L_p \cdot (-\Delta H_A)}{h \cdot T_s} &lt; 0.10 \cdot \frac{R \cdot T_s}{E}$</td>
</tr>
<tr>
<td>Slab</td>
<td>$\frac{\partial f(C_A)}{f(C_{AS})} \frac{r_{A,obs} \cdot \rho_p \cdot L_p}{k_g} &lt; 0.05$</td>
<td>$\frac{-r_{A,obs} \cdot \rho_p \cdot L_p \cdot (-\Delta H_A)}{h \cdot T_s} &lt; 0.05 \cdot \frac{R \cdot T_s}{E}$</td>
</tr>
<tr>
<td>Arbitrary shape</td>
<td>$\frac{\partial f(C_A)}{f(C_{AS})} \frac{r_{A,obs} \cdot \rho_p \cdot V_p}{k_g} &lt; 0.05$</td>
<td>$\frac{-r_{A,obs} \cdot \rho_p \cdot V_p \cdot (-\Delta H_A)}{h \cdot T_s} &lt; 0.05 \cdot \frac{R \cdot T_s}{E}$</td>
</tr>
</tbody>
</table>
4. Introduction to Dimensional Analysis

4.1 Justification of The Dimensional Analysis Approach

In physics as in engineering science problems of such a complex nature often arise that it can be difficult to derive a stringent mathematical model for them based on the basic principles of physics. Instead one can combine knowledge from a simpler problem with experimental data for the complex problem and then set up an empirical black-box model that describes the experimental data.

Such empirical black-box models have to be dimensional consistent. In order to ensure this a dimensional analysis has to be carried out. Furthermore a dimensional analysis can be used to get a first guess on the mathematical structure of the empirical black-box model and the minimum number of experimental variables that need to be varied during the experiments that will form the basis for the model. Dimensional analysis therefore has an important role in engineering science [11].

The basis for dimensional analysis is simple. Any equation that expresses a relation between a set of physical entities \( Q \) has to be dimensional consistent so each term in the equation has to have the same dimension. If one for instance wants to express the physical entity \( Q_1 \) as a function of the physical entities \( Q_2 \) to \( Q_n \) this leads to

\[
Q_1 = F(Q_2, Q_3, ..., Q_n) = F(Q) \tag{4.1}
\]

Where \( Q \) is a vector which elements are the physical entities \( Q_i \).

Therefore the function \( F \) must have the same unit as \( Q_1 \). The function \( F \) is the empirical black-box model that has to be found from experimental data. Before the experiments have actually been carried out \( F \) is therefore unknown but if the Taylor expansion of \( F \) is used [12, s.37] one gets:

\[
\begin{align*}
Q_1(Q, h) &= F(Q) + \frac{1}{1!} \cdot dF(Q, h) + \frac{1}{2!} \cdot d^2F(Q, h) + \cdots + \frac{1}{k!} \cdot d^kF(Q, h) + O(||h||^k) \\
&= F(Q) + \frac{1}{1!} \cdot \sum_{i=2} \left( \frac{\partial F}{\partial Q_i} \right) (Q_i - Q_i) \\
&\quad + \frac{1}{2!} \cdot \sum_{i=2} \left( \sum_{j=2} \left( \frac{\partial^2 F}{\partial Q_i \partial Q_j} \right) (Q_i - Q_i)(Q_j - Q_j) \right) + \cdots \\
&\quad + \frac{1}{k!} \cdot \sum_{i=2} \left( \sum_{j=2} \left( \cdots \sum_{k=2} \left( \frac{\partial^k F}{\partial Q_i \partial Q_j \cdots \partial Q_k} \right) (Q_i - Q_i)(Q_j - Q_j) \cdots (Q_k - Q_k) \right) \right) \\
&\quad + O(||h||^k)
\end{align*} \tag{4.2}
\]

Where \( h \) is the deviation from a known set of experimental conditions \( Q_0 \), where the value of \( Q_1 \) is known.

\( k \) is the degree of the Taylor polynomial approximation.

\( O(||h||^k) \) is the Taylor approximation error.

The Taylor approximation can of course not be used to describe how \( Q_1 \) depend on the other physical properties \( Q_i \) before the function \( F \) is known but the Taylor approximation shows that all continuous functions \( F \) can be described within a
specified accuracy $O(||h||^k)$ by a polynomial of the order $k$ (4.3):

\[ Q_j = C_0 + \sum_{i_2}^m C_{i_1,i_2} \cdot Q_{i_1} + \sum_{i_2,i_3}^m C_{i_1,i_2,i_3} \cdot Q_{i_1,i_2} + \ldots + \sum_{i_k}^m \sum_{i_{k-1}}^m C_{i_1,i_{k-1},i_k} \cdot Q_{i_1,i_{k-1},i_k} + \ldots \cdot Q_{i_h} \]  

(4.3)

Where $C_{i_j}$ is a constant

or just an infinite power law expansion of the form

\[ Q_j = \sum_{j=1}^m A_j \cdot Q_{i_1}^{\alpha_{i_1,j}} \cdot Q_{i_2}^{\alpha_{i_2,j}} \cdot \ldots \cdot Q_{i_h}^{\alpha_{i_h,j}} \]  

(4.4)

Where $A_j$ are dimensionless constants that has to be found from experimental data

\[ \alpha_{i,j} \] is the power to which the physical entity $Q_i$ enters into term $j$ in function $F$.

The precondition for this assumption to be correct is that the relation between the physical entities can be described by a continuous differentiable function within the investigated experimental domain. This condition will normally be fulfilled for functions that describe physical phenomena.

Equation (4.4) can be written in dimensionless form

\[ 1 = \sum_{j=1}^m A_j \cdot \Pi_1^{\beta_{i_1,j}} \cdot \Pi_2^{\beta_{i_2,j}} \cdot \ldots \cdot \Pi_h^{\beta_{i_h,j}} \]  

(4.5)

Where $\Pi_i$ is a dimensionless product or number defined by $\Pi_i = Q_1^{\gamma_{i,1}} \cdot Q_2^{\gamma_{i,2}} \cdot Q_3^{\gamma_{i,3}} \cdot \ldots \cdot Q_n^{\gamma_{i,n}}$

$\beta_{i,j}$ is a constant that has to be found from experiments.

Examples of dimensionless products $\Pi_i$ are the Reynold number, the Prandtl number and the Nussel number.

The restatement of (4.4) to (4.5) logically leads to the general dimensionless relation between physical entities

\[ 0 = \varphi(\Pi_1, \Pi_2, \Pi_3, \ldots, \Pi_L) \]  

(4.6)

The main purpose with the dimensional analysis now becomes to determine the total number of dimensionless products necessary to describe a given problem and which physical entities $Q_i$ that enters in to each dimensionless product.
4.2 Basic Dimensions and the Minimum Number of Dimensionless Products

Which dimensions that enters into a dimensional analysis depends on the physical entities that enters into the problem to be analysed. It is however important to choose the correct set of dimensions to describe a given problem. In physics dimensions are divided into fundamental dimensions and derived units. For example the SI unit for force is Newton [N]. This though is not the fundamental SI-dimension but a unit derived from the dimensions for mass [kg], length [m] and time [s]. All units in the SI-system can in principle be expressed by the three fundamental dimensions for mass [M], length [L] and time [T]. These three dimensions alone could form the basis for a dimensional analysis of any physical problem imaginable at present. Such a restricted use of units though would lead to unsuitable dimensionless numbers as for instance electric capacitance would have the dimension of length [L]. To avoid such unfortunate incidences it is generally accepted that in addition to the three fundamental dimensions the units for electrical charge [q] and temperature [Θ] may be used [11]. The units on which to base a dimensional analysis therefore are:

- Mass [M]
- Lenght [L]
- Time [T]
- Electric charge [q]
- Temperature [Θ]

This does not imply that other units like the units for heat [H] or power [E] cannot be used but if these units are to enter into a dimensional analysis power would as an example replace time and heat would replace mass as power incorporates the unit for time and heat through the Einstein Relation the unit for mass.

The minimum number of dimensionless products L necessary to describe a given problem can be found from the number of physical entities Qi that is expected to form part of the mathematical description of the problem and the number of basic units connected with these entities. Buckingham's Π-theorem [13] states that the number of dimensional products can be found from

\[ L = n - r \]  \hspace{1cm} (4.7)

Where
- \( L \) is the number of dimensionless products \( \Pi_i \)
- \( n \) is the number of physical entities describing the problem \( Q_i \)
- \( r \) is the number of basic units \( R_k \) in use

The next step is to develop a systematic approach on how to describe a physical problem and do the dimensional analysis.
4.3 Approach for Setting-up an Empirical Black-Box Model for a Physical Problem

A flow diagram showing an approach to setting-up an empirical black-box model is shown in figure 4.1. The first step is, if possible, to derive a stringent physical model for a simplified case of the more general problem at hand. This simplified case then forms basis for further model development. The next step is to decide which physical entities \( Q_i \) that can be expected to influence the physical process. Which physical entities should be included in the model is partly a subjective decision. The choice though has to include the physical entities included in the stringent model for the simplified case, and prior experience from similar problems and common physical sense should be used. This step is very important as the success or failure to obtain a model from the dimensional analysis depend on it and it sets the boundaries for the final model’s validity. Based on the number of physical entities \( n \) and the number of basic units the minimum number of dimensionless products \( L \) is determined. In the third step the dimensional analysis is carried out. This is described in detail in paragraph 3.4. Based on the dimensional analysis step four can be carried out. In step four experimental work based on the dimensional analysis is carried out and the unknown model parameters in the dimensionless function \( \varphi \) is determined from a statistical fit of the model. Finally it is important to check if the empirical black-box model yields a satisfactory fit to the experimental data. If this is not the case one should return to step two to decide if further physical entities might influence the problem.
4.4 Dimensional Analysis for a Simple Physical Problem

The easiest way to do a dimensional analysis for a simple physical problem is based on equation (4.4). If the basic units for the individual physical entities are defined as

\[ Q_i = R_1^{d_{i1}} \cdot R_2^{d_{i2}} \cdots R_n^{d_{in}} \]  

(4.8)

Where \( d_{ij} \) is the power to which the basic unit \( R_j \) is raised in order to describe the parameter \( Q_i \)’s total dimension the dimensional relations based on equation (4.4) is

\[ [R_1^{d_{11}} \cdot R_2^{d_{12}} \cdots R_n^{d_{1n}}] = [R_1^{d_{21}} \cdot R_2^{d_{22}} \cdots R_n^{d_{2n}}] \cdots [R_1^{d_{m1}} \cdot R_2^{d_{m2}} \cdots R_n^{d_{mn}}] \]

(4.9)

Which means that the following set of equations have to be satisfied for equation (4.4) to be dimensional homogeneous

\[
\begin{align*}
    d_{1,1} &= d_{1,2} \cdot \alpha_2 + d_{1,3} \cdot \alpha_3 + \cdots + d_{1,r} \cdot \alpha_r \\
    d_{2,1} &= d_{2,2} \cdot \alpha_2 + d_{2,3} \cdot \alpha_3 + \cdots + d_{2,r} \cdot \alpha_r \\
    \vdots &
\end{align*}
\]

(4.10)

This linear set of equations has \( n - r \) solutions which is equivalent to the \( L \) dimensionless products. This means that based on a dimensional analysis alone one cannot in general expect to be able to determine into which power \( \beta_j \) the individual dimensionless products are to be raised. This has to be determined from experiments. One does on the other hand get the relation between the individual values of \( \alpha_i \) and thereby a set of dimensionless products on which the empirical black-box model can be based. This is illustrated in example E 4.1.
Example E 4.1 An Empirical Black-Box Model for The Mass Transfer Coefficient for a Sphere.

**Step 1**: Setting up a Stringent Model for Mass Transfer to a Sphere.

Around a spherical body submerged in a flowing gas or liquid a thin stagnant film may form. This is illustrated in figure E4.1. The thickness of this film can for catalyst pellets influence the rate of reaction as the concentration for a component A in the bulk flow, \( C_{A_{\text{bulk}}} \), can be different from the concentration of A at the outer surface of the catalyst pellet, \( C_{A_{S}} \).

![Figure E4.1](image)

Figure E4.1  Spherical catalyst pellet surrounded by a stagnant film. The film thickness \( \delta \) and the pellet radius \( L_p \) have the unit of [m]. The velocity \( v \) has the unit of [m/s].

The mass flux through the film can be described by Fick’s 1. law:

\[
N_A = -D_A \frac{dC_A}{dz}
\]

Where \( N_A \) is the mass flux \( \frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \),

\( D_A \) is the diffusivity for A \( \frac{\text{m}^2}{\text{s}} \),

\( z \) is the distance from the pellet center [m],

\( C_A \) is the concentration of A \( \frac{\text{mol}}{\text{m}^3} \).

This differential equation has the boundary conditions

\( @: z = L_p + \delta: C_A = C_{A_{\text{bulk}}}, \)

\( z = L_p: C_A = C_{A_{S}} \).
At steady-state the mass transport through the film will be independent of the distance from the pellet center:

\[ 4 \cdot \pi \cdot L_p^2 \cdot N_{A_{\text{film}}} = 4 \cdot \pi \cdot z^2 \cdot N_{A_{z}} = -4 \cdot \pi \cdot z^2 \cdot D_A \cdot \frac{dC_A}{dz} \]

\[ L_p^2 \cdot N_{A_{\text{film}}} = -z^2 \cdot D_A \cdot \frac{dC_A}{dz} \]

This differential equation can be solved by separation of the variables:

\[ \int_{L_p}^{L_p} \left( \frac{L_p}{z} \right)^2 \frac{dC_A}{C_{\text{AS}}} = - \int_{L_p}^{L_p} \frac{dC_A}{C_{\text{AS}}} \]

Where \( k_g \) is the mass transfer coefficient with dimension \([m/s]\).

The above equation defines the mass transfer coefficient \( k_g \) in relation to the film thickness \( \delta \), the diffusivity \( D_A \) and the pellet radius \( L_p \). Of these physical entities the film thickness \( \delta \) cannot be determined directly. Therefore a mathematical model that describes either the film thickness or the mass transfer coefficient from directly measurable entities is necessary. As the stringent mathematical model does not lead to this an empirical black-box model based on dimensional analysis might be sought instead. Before one embarks on the dimensional analysis it is worthwhile to see if a simplification of the physical model can yield some further information. The expression for the mass transfer coefficient is:

\[ k_g = \frac{D_A}{L_p^2 \left( \frac{1}{L_p} - \frac{1}{L_p + \delta} \right)} \]

If the fluid velocity \( v \) passed the pellet is zero the film thickness \( \delta \) will approach infinity leading to the following expression for the mass transfer coefficient \( k_g \):

\[ k_g = \frac{D_A}{L_p^2 \left( \frac{1}{L_p} - \frac{1}{L_p + \delta} \right)} - \frac{D_A}{L_p} \text{ for } \delta \to \infty \]

This then gives a boundary value for the mass transfer coefficient.
Step 2: Physical Entities That is Expected to Influence the Value of the Mass Transfer Coefficient

The following entities are expected to have influence on the value of the mass transfer coefficient:

<table>
<thead>
<tr>
<th>Physical Entity</th>
<th>Unit</th>
<th>Physical Entity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pellet radius</td>
<td>m</td>
<td>Density</td>
<td>kg/m³</td>
</tr>
<tr>
<td>Mass transfer coefficient</td>
<td>m/s</td>
<td>Diffusivity</td>
<td>m²/s</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Viscosity</td>
<td>kg/m³</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Velocity</td>
<td>m/s</td>
</tr>
</tbody>
</table>

Note that the shape of the pellet enters indirectly as the black-box model is assumed only to be valid for a sphere.

The number of dimensionless products \( \Pi \) that can describe the mass transfer coefficient is now found from Buckingham's \( \Pi \)-theorem (3.7):

\[
L = n - r = 6 - 3 = 3
\]

The dimensional analysis can then begin.

Step 3: Dimensional Analysis

It is now assumed that the mass transfer coefficient can be written as a function of the form (4.4) leading to:

\[
k_g = \sum_{j=1}^{6} A_j L_p^{a_{1j}} \rho_{fl}^{a_{2j}} D_A^{a_{3j}} \mu_{fl}^{a_{4j}} u^{a_{5j}}
\]

Based on this the dimension equation (4.9) becomes:

\[
[m \cdot s^{-1}] = [m]^{a_1} \cdot [m^{-2} \cdot \text{kg} \cdot \text{s}^{-1}]^{a_2} \cdot [m \cdot \text{s}^{-1}]^{a_3} \cdot [m^{-1} \cdot \text{kg} \cdot \text{s}^{-1}]^{a_4} \cdot [m \cdot \text{s}^{-1}]^{a_5} \cdot [m \cdot \text{s}^{-1}]^{a_6}
\]

Which leads to the following set of equations, equivalent to equation (4.10):

\[
1 = a_1 + 3a_2 + 2a_3 + a_4 + a_5 + a_6
\]

\[
1 = a_3 + a_4 + a_6
\]

\[
0 = a_3 + a_5
\]

This leads to three equations with five unknowns. If one rather arbitrarily chooses to express \( \alpha_1, \alpha_4 \) and \( \alpha_6 \) as functions of \( \alpha_2 \) and \( \alpha_3 \), one gets:

\[
\alpha_3 = -\alpha_5
\]
\[
\alpha_4 = -\alpha_2 - \alpha_5
\]
\[
\alpha_6 = 1 + \alpha_2
\]

The relation between the physical entities therefore takes the form:

\[
k_g = \sum_{j=1}^{6} A_j L_p^{a_{1j}} \rho_{fl}^{a_{2j}} D_A^{a_{3j}} \mu_{fl}^{a_{4j}} u^{a_{5j}}
\]
Traditionally the mass transfer coefficient is expressed in the dimensionless Sherwood number $Sh$

$$Sh = \frac{k_g \cdot 2 \cdot L_p}{D_A}$$

giving the following dimensionless form of the relation for the mass transfer coefficient:

$$Sh = \sum_{j=1}^{\infty} A_j \cdot L_p \cdot \rho_f \cdot \mu_f \cdot B_j \left( \frac{2 \cdot L_p \cdot \rho_f \cdot \mu_f}{\mu_f} \right)^{a_{j2} + 1} \left( \frac{\mu_f}{D_A \cdot \rho_f} \right)^{a_{j1} + 1}$$

$$= \sum_{j=1}^{\infty} B_j \cdot Re^{a_{j2} + 1} \cdot Sc^{a_{j1} + a_{j2} + 1}$$

Where $Re$ is the Reynold number and $Sc$ the Schmidt number, defined by the equation above.

Dimensional analysis therefore yields that the relation between the mass transfer coefficient and the other physical entities must be a function of the form:

$$Sh = \varphi (Re, Sc)$$

The exact expression can only be found from experiments where the Reynold number and the Schmidt number is varied. This can for example be done by varying the velocity $v$ and diffusivity $D_A$.

**Step 4:** Experimental determination of the relation between $Sh$, $Re$ og $Sc$.

Before any experiments are carried out one should include any information that can be derived from the simplified situation investigated in step 1.

In step 1 it was found that

$$k_g = \frac{D_A}{L_p}$$

in a stagnant fluid. This gives the Sherwood number for a stagnant film:

$$Sh = \frac{k_g \cdot 2 \cdot L_p}{D_A} = 2$$

This boundary condition has to be incorporated in the function $\varphi(Re, Sc)$.

Experimental data have lead to the following expressions for $Sh$ as a function of $Re$ and $Sc$ for a single spherical pellet [14, page 670-671]:

For $Re < 1$:

$$Sh = (4 + 1.21 \cdot Re^{2/3} \cdot Sc^{2/3})^{1/2}$$

For $20 < Re < 2000$

$$Sh = 2 + k_{sh} \cdot Re^{1/2} \cdot Sc^{1/3}$$

$$k_{sh} = 0.63 \text{ for } Sc \in [0.1; 10]$$

$$k_{sh} = 0.76 \text{ for } Sc \in [100; 10000]$$

As seen both equations include the boundary condition $Sh = 2$ for $Re = 0$ which is equivalent to zero fluid velocity. The more general empirical model in this case therefore incorporates the the stringent model for the simplified case. This should of cause always be the case but unfortunately is not always so.
4.5 Systematic Dimensional Analysis of Physical Problems

From equation (4.10) in paragraph 4.4 it is obvious that dimensional analysis from a mathematical point of view is reduced to the from linear algebra well known problem of solving $r$ linear equations with $n$ unknowns.

First an entity unit matrix $D_{r \times n}$ is setup. This contain as elements the powers into which the basic units are raised in the individual physical entity's total dimension:

$$D_{r \times n} = \begin{pmatrix}
  d_{1,1} & \ldots & d_{1,n} \\
  \vdots & & \vdots \\
  d_{r,1} & \ldots & d_{r,n}
\end{pmatrix} \quad (4.11)$$

In this way each row represent a basic unit and each column a physical entity. If equation (4.10) is restated in the form

$$0 = d_{1,1} \cdot \alpha_1 + d_{1,2} \cdot \alpha_2 + d_{1,3} \cdot \alpha_3 + \ldots + d_{1,n} \cdot \alpha_n$$
$$0 = d_{2,1} \cdot \alpha_1 + d_{2,2} \cdot \alpha_2 + d_{2,3} \cdot \alpha_3 + \ldots + d_{2,n} \cdot \alpha_n$$
$$\vdots$$
$$0 = d_{r,1} \cdot \alpha_1 + d_{r,2} \cdot \alpha_2 + d_{r,3} \cdot \alpha_3 + \ldots + d_{r,n} \cdot \alpha_n \quad (4.12)$$

the equation (4.12) can be written in matrix form as

$$D_{r \times n} \cdot \alpha_{n \times 1} = 0_{r \times 1} \quad (4.13)$$

Where $\alpha_{n \times 1}$ is a column vector containing the unknown exponents $\alpha_i$ for the physical entities $Q_i$:

$$\alpha_{n \times 1} = \begin{pmatrix}
  \alpha_1 \\
  \alpha_2 \\
  \vdots \\
  \alpha_n
\end{pmatrix} \quad (4.14)$$

In order to be able to set-up a dimensional consistent physical equation of the form (4.4) the number of equations has to be less than the number of unknowns $n$. Therefore the number of unknowns in equation (4.13) will allways be larger than the number of equations. There will then allways be one or more infinite set $L = n - r$ of consistent solutions to equation (4.12). These sets of solutions are the dimensionless products describing the physical problem.
Equation (4.13) can be solved by row reduction on the entity unit matrix $D_{nn}$ in echelon form. This can be done manually using Gauss-Elimination [3, s.344-364] or automatically using a pocket calculator or PC-math-software. The solution will be a solution to (4.13) of the form

$$\mathbf{a}_{nx1} = c_1 \cdot \begin{bmatrix} b_{1,1} \\ b_{2,1} \\ \vdots \\ b_{n,1} \end{bmatrix} + \cdots + c_i \cdot \begin{bmatrix} b_{1,i} \\ b_{2,i} \\ \vdots \\ b_{n,i} \end{bmatrix} + \cdots + c_L \cdot \begin{bmatrix} b_{1,L} \\ b_{2,L} \\ \vdots \\ b_{n,L} \end{bmatrix}$$

(4.15)

Where $c_i$ are arbitrary constants imaging the $L$ infinite sets of solution to (4.13) and $\mathbf{b}_{nxf}$ consist of column vectors containing a set of linearly independent solutions to (4.13). Each column vector $\mathbf{b}_{nxf}$ contains one set of exponents for physical entities in the dimensionless product $\Pi_j$ defined by $\Pi_j = Q_1^{b_{1,j}} Q_2^{b_{2,j}} Q_3^{b_{3,j}} \cdots Q_n^{b_{n,j}}$. One way of stating the function describing the physical problem defined by (4.5) or (4.6) would be:

$$1 = \sum_{j=1}^{n} \mathbf{A}_j \cdot \Pi_1^{\beta_{1,j}} \Pi_2^{\beta_{2,j}} \Pi_3^{\beta_{3,j}} \cdots \Pi_L^{\beta_{L,j}}$$

(4.16)

Where $\Pi_j$ is a dimensionless product defined by $\Pi_j = Q_1^{b_{1,j}} Q_2^{b_{2,j}} Q_3^{b_{3,j}} \cdots Q_n^{b_{n,j}}$.

These $L$ dimensionless products describes only one of many possible combinations of dimensionless products and not necessarily the set best suited for experimental determination of the empirical exponents $\beta_{ij}$. Furthermore some dimensionless products are used traditionally to describe specific conditions. For example the Reynold number is used to describe flow conditions, the Sherwood number to describe mass transfer and the Schmidt number to describe the relation between diffusive flow and convective flow. If one wish to substitute one or more of the dimensionless products arbitrarily determined by the row reduction with one or more of the traditional dimensionless products this can be done as long as the exponents $\gamma_{ij}$ for this product is a solution to (4.13). This is equivalent to changing one of the column vectors $\mathbf{b}_{nxf}$ in (4.15) and it is therefore necessary to ensure that this new column vector together with the remaining column vectors still describe all sets of solutions to (4.15). In analytical mathematics and geometry this is termed a change of basis in the $L$-dimensional sub-space of the $n$-dimensional space. This transformation of basis is done by first forming an exponent matrix of the transposed column vectors $\mathbf{b}_{nxf}$ as shown in (4.17):

$$\mathbf{B}_{nxn} = \begin{bmatrix} b_{1,1} \\ \vdots \\ b_{n,1} \\ b_{1,2} \\ \vdots \\ b_{n,2} \\ \vdots \\ b_{1,L} \\ \vdots \\ b_{n,L} \end{bmatrix} = \begin{bmatrix} b_{1,1} & \cdots & \cdots & b_{1,a} \\ \vdots & \ddots & \vdots & \vdots \\ \vdots & \cdots & \ddots & \vdots \\ b_{1,1} & \cdots & \cdots & b_{1,a} \end{bmatrix}$$

(4.17)

Then a row vector of the entity exponents in the traditional dimensionless product $\Pi_{1t} = Q_1^{\gamma_{11,t}} Q_2^{\gamma_{12,t}} Q_3^{\gamma_{13,t}} \cdots Q_n^{\gamma_{1n,t}}$ is formed.
A combined matrix of \( \frac{\mathbf{y}}{l_{1}x_{n}} \) og \( \mathbf{B}_{L_{1}x_{n}} \) can now be setup

\[
\mathbf{yB}_{L_{1}x_{n}} = \begin{pmatrix}
\mathbf{y}_{l_{1},1} & \cdots & \mathbf{y}_{l_{1},a} \\
\mathbf{b}_{l_{1},1} & \cdots & \mathbf{b}_{l_{1},a} \\
\mathbf{b}_{l_{1},1} & \cdots & \mathbf{b}_{l_{1},a} \\
\vdots & \ddots & \vdots \\
\mathbf{b}_{l_{1},1} & \cdots & \mathbf{b}_{l_{1},a}
\end{pmatrix}
\]

The rank of \( \mathbf{yB}_{L_{1}x_{n}} \) can now be reduced by one if the traditional dimensionless product is a solution to (4.13).

If only the first row in (4.19), symbolised by \( \mathbf{y}_{l_{1},1} \), is used for the row reduction and the elements in this row is retained a new set of independent vectors are formed.

\[
\mathbf{yB} = \begin{pmatrix}
\mathbf{y}_{l_{1},1} & \cdots & \mathbf{y}_{l_{1},a} \\
\mathbf{b'}_{l_{1},1} & \cdots & \mathbf{b'}_{l_{1},a} \\
\mathbf{b'}_{l_{1},1} & \cdots & \mathbf{b'}_{l_{1},a} \\
\vdots & \ddots & \vdots \\
\mathbf{b'}_{l_{1},1} & \cdots & \mathbf{b'}_{l_{1},a} \\
0 & \cdots & 0
\end{pmatrix}
\]

\[
\begin{pmatrix}
\mathbf{y}_{l_{1}x_{n}} \\
\mathbf{b'}_{\mathbf{x_{n}}} \mathbf{T} \\
\mathbf{b'}_{\mathbf{x_{n}} \mathbf{a}} \mathbf{T} \\
0 \mathbf{T}
\end{pmatrix}
\]

\[
(4.20)
\]
These then are the set of exponents for the new set of dimensionless products. This approach can be used recursively by including a new traditional dimensionless product $\Pi_l = Q_1^{\gamma_{1,l}}, Q_2^{\gamma_{2,l}}, Q_3^{\gamma_{3,l}}, \ldots, Q_n^{\gamma_{n,l}}$ and form a new matrix of the form (4.21)

$$
\begin{pmatrix}
\gamma_{1,1} & \cdots & \gamma_{1,n} \\
\gamma_{2,1} & \cdots & \gamma_{2,n} \\
\vdots & \ddots & \vdots \\
\gamma_{l-1,1} & \cdots & \gamma_{l-1,n} \\
0 & \cdots & 0
\end{pmatrix}
$$

leading to a new set of exponents for the new set of dimensionless products. This can of course be done until all elements below the dotted line is zero and the physical problem stated as a function of traditional dimensionless products alone or no more substitutions are to be found in which case a new and perhaps important dimensionless product has to be included in the empirical black-box model.

This systematic procedure is illustrated in example E 4.2.
Example E 4.2 Systematic Dimensional Analysis for an Empirical Model Describing the Mass Transfer Coefficient $k_g$ for a sphere.

The physical entities that are expected to influence the value of the mass transfer coefficient, see example 4.1, still are

<table>
<thead>
<tr>
<th>Physical Entity</th>
<th>Unit</th>
<th>Physical Entity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pellet radius $L_p$</td>
<td>m</td>
<td>Density $\rho_f$</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>Mass transfer coefficient $k_g$</td>
<td>m/s</td>
<td>Diffusivity $D_A$</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Viscosity $\mu_f$</td>
<td>kg/(m·s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Velocity $u$</td>
<td>m/s</td>
</tr>
</tbody>
</table>

From these the entity unit matrix is formed:

$$
\begin{bmatrix}
  k_g & L_p & \rho_f & D_A & \mu_f & u \\
\end{bmatrix}
= 
\begin{bmatrix}
  1 & 1 & -3 & 2 & -1 & 1 \\
 0 & 0 & 1 & 0 & 1 & 0 \\
-1 & 0 & 0 & -1 & -1 & -1 \\
\end{bmatrix}
$$

Inserted in equation (4.13) this yields

$$
\begin{bmatrix}
  1 & 1 & -3 & 2 & -1 & 1 \\
 0 & 0 & 1 & 0 & 1 & 0 \\
-1 & 0 & 0 & -1 & -1 & -1 \\
\end{bmatrix}
\begin{bmatrix}
  \alpha_1 \\
  \alpha_2 \\
  \alpha_3 \\
  \alpha_4 \\
  \alpha_5 \\
  \alpha_6 \\
\end{bmatrix}
= 
\begin{bmatrix}
  0 \\
  0 \\
\end{bmatrix}
$$

Which in echelon form becomes

$$
\begin{bmatrix}
  1 & 1 & -3 & 2 & -1 & 1 | 0 \\
 0 & 0 & 1 & 0 & 1 & 0 | 0 \\
-1 & 0 & 0 & -1 & -1 & -1 | 0 \\
\end{bmatrix}
$$

Using Gauss elimination this leads to

$$
\begin{bmatrix}
  1 & 0 & 0 & 1 & 1 & 1 | 0 \\
 0 & 1 & 0 & 1 & 0 | 0 \\
0 & 0 & 1 & 0 & 1 | 0 \\
\end{bmatrix}
$$
As seen the rank of the matrix is 3. As there are 6 unknown exponents there will be 6-3 infinite set of solutions to equation (4.13). The mass transfer coefficient problem can therefore be described by three dimensionless products. One set of exponents in three dimensionless products $Q_i$ can now be determined by back-substitution in the equation:

$$
\begin{pmatrix}
1 & 0 & 0 & 1 & 1 & 1 \\
0 & 1 & 0 & 1 & 1 & 0 \\
0 & 0 & 1 & 0 & 1 & 0 \\
\end{pmatrix}
\begin{pmatrix}
\alpha_1 \\
\alpha_2 \\
\alpha_3 \\
\alpha_4 \\
\alpha_5 \\
\alpha_6 \\
\end{pmatrix}
=
\begin{pmatrix}
0 \\
0 \\
0 \\
\end{pmatrix}
$$

If one should wish for instance to let the exponents $\alpha_4$, $\alpha_5$ and $\alpha_6$, form a basis for the back-substitution they are set equal to

$$
\begin{align*}
\alpha_4 &= C_1 \\
\alpha_5 &= C_2 \\
\alpha_6 &= C_3 \\
\end{align*}
$$

and the set of equations are made quadratic by arbitrarily setting the parameters $C_1$, $C_2$ and $C_3$ equal to 1. This leads to the set of equations:

$$
\begin{pmatrix}
1 & 0 & 0 & 1 & 1 & 1 \\
0 & 1 & 0 & 1 & 1 & 0 \\
0 & 0 & 1 & 0 & 1 & 0 \\
\end{pmatrix}
\begin{pmatrix}
\alpha_1 \\
\alpha_2 \\
\alpha_3 \\
\alpha_4 \\
\alpha_5 \\
\alpha_6 \\
\end{pmatrix}
=
\begin{pmatrix}
0 \\
0 \\
0 \\
\end{pmatrix}
$$

The back-substitution is now done by calculating the inverse to the coefficient matrix

$$
\begin{pmatrix}
1 & 0 & 0 & 1 & 1 & 1 \\
0 & 1 & 0 & 1 & 1 & 0 \\
0 & 0 & 1 & 0 & 1 & 0 \\
\end{pmatrix}
^{-1}
= 
\begin{pmatrix}
1 & 0 & 0 & -1 & -1 & -1 \\
0 & 1 & 0 & -1 & -1 & 0 \\
0 & 0 & 1 & 0 & -1 & 0 \\
\end{pmatrix}
$$

The last $L-r$ columns in this case the last three columns contain the column vectors $\mathbf{b}$, each of which contain the set of exponents for one dimensional product $\Pi_i$. In this specific case equation (4.15) thus becomes:

$$
\begin{pmatrix}
\alpha_1 \\
\alpha_2 \\
\alpha_3 \\
\alpha_4 \\
\alpha_5 \\
\alpha_6 \\
\end{pmatrix}
= 
\mathbf{c}_1 \cdot
\begin{pmatrix}
-1 \\
-1 \\
0 \\
1 \\
0 \\
0 \\
\end{pmatrix}
+ 
\mathbf{c}_2 \cdot
\begin{pmatrix}
-1 \\
-1 \\
1 \\
0 \\
1 \\
0 \\
\end{pmatrix}
+ 
\mathbf{c}_3 \cdot
\begin{pmatrix}
-1 \\
0 \\
0 \\
1 \\
0 \\
1 \\
\end{pmatrix}
$$
and the dimensionless products

\[ \Pi_1 = \frac{D_A}{k_L \cdot L_p} \]
\[ \Pi_2 = \frac{\mu_n}{k_g \cdot L_p \cdot \rho_n} \]
\[ \Pi_3 = \frac{u}{k_g} \]

By a coincidence \( \Pi_1 \) ignoring the constant 2 is the reciprocal of the Sherwood Number \( Sh \). The remaining two dimensional products cannot easily be identified with any traditional dimensionless product. In \( \Pi_3 \), the velocity \( u \) normally associated with Reynolds number appears together with the mass transfer coefficient \( k_g \). It is also apparent that the mass transfer coefficient appears in all three dimensionless products. This is not very helpful as it is the mass transfer coefficient that is calculated from the model. As the mass transfer coefficient forms part of the Sherwood number but not part of the Reynold number these two dimensionless products are linearly independent. A good guess would therefore be to try to express the dimensionless products by the Sherwood number and the Reynold number and treat the last dimensionless product as an as yet unknown product. This is done by first setting up an exponent vector of the transposed column vectors \( \mathbf{b} \) as done in equation (4.17)

\[ \mathbf{B}_{3 \times 6} = \begin{pmatrix} b_1^T \\ b_2^T \\ b_3^T \end{pmatrix} = \begin{pmatrix} -1 & -1 & 0 & 1 & 0 & 0 \\ -1 & -1 & -1 & 0 & 1 & 0 \\ -1 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \]

Then a combined matrix of the dimensionless products \( \gamma \) and \( \mathbf{B} \) are formed together with the exponential matrix:

\[ \gamma \mathbf{B}_{3 \times 6} = \begin{pmatrix} \gamma_{\Pi_1}^{1 \times 6} \\ \gamma_{\Pi_2}^{1 \times 6} \\ \gamma_{\Pi_3}^{1 \times 6} \\ b_1^{6 \times 1} \\ b_2^{6 \times 1} \\ b_3^{6 \times 1} \end{pmatrix} = \begin{pmatrix} 1 & 1 & 0 & -1 & 0 & 0 \\ 0 & 1 & 1 & 0 & -1 & 1 \\ -1 & 1 & 0 & 0 & 0 & 1 \\ 1 & 1 & 0 & 0 & 0 & 1 \\ 1 & -1 & -1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \]

By row reduction on the last three rows in the \( \gamma \mathbf{B}_{3 \times 6} \) matrix using the first two rows the following row reduced matrix is formed

\[ \gamma \mathbf{B}_{3 \times 6} = \begin{pmatrix} \gamma_{\Pi_1}^{1 \times 6} \\ \gamma_{\Pi_2}^{1 \times 6} \\ b_1^{6 \times 1} \\ b_2^{6 \times 1} \\ b_3^{6 \times 1} \end{pmatrix} = \begin{pmatrix} 1 & 1 & 0 & -1 & 0 & 0 \\ 0 & 1 & 1 & 0 & -1 & 1 \\ 0 & 0 & -1 & -1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \]
The new set of dimensionless products describing the physical problem is:

\[
\Pi_1 = \frac{k_s \cdot 2 \cdot L_p}{D_A} = \text{Sh}
\]
\[
\Pi_2 = \frac{2 \cdot L_p \cdot \rho_n \cdot u}{\mu_n} = \text{Re}
\]
\[
\Pi_3 = \frac{\mu_n}{\rho_n \cdot D_A} = \text{Sc}
\]

Not surprising considering example E4.1 it is seen that the unknown dimensionless product turned out to be the Schmidt number Sc. That \(2 \cdot L_p\) is used in the Reynold number and the Sherwood number is partly due to convention partly to the fact that it is the pellet diameter not the radius that can be measured directly. As the factor 2 is a dimensionless constant it cannot be found from dimensional analysis but will form part of the experimental constants \(A_i\) in equation (4.5). Using the matrix method might seem very circumvential compared to the metod used in paragraph 4.4. It does though lent it self to be automated using PC-software or a pocket calculator thereby avoiding calculus errors.
5. Symbols

**A**
In section 1: The component vector, contains substance formulas or names of the individual reactants, products and intermediates.

**A**
In section 3: The preexponential factor in the Arrhenius expression for the reaction rate constant. Units vary according to the rate expression.

**A_j**
In section 2: Apparent surface area of catalyst [m²]

**A_C**
In section 1: The intermediate component vector, contains substance formulas or names of the individual intermediates.

**A_N**
In section 1: The net reaction component vector, contains substance formulas or names of the individual reactants and products.

**A_j**
In section 1: Name or substance formula for component j

**A_j**
In section 4: A dimensionless constant that has to be found from experimental data

**a**
In sections The catalyst pellet height for a slab [m]
2 and 3:

**b**
In sections The catalyst pellet length for a slab [m]
2 and 3:

**b**
In section 4: A matrix consisting of the transposed column vectors in column vectors

**b**
In section 4: A matrix consisting of column vectors containing a set of linearly independent solutions to (4.13).

**C_A**
In sections 3 and 4: The concentration of the rate limiting component A \( \text{[mole/m}^3] \)

**C_A_{bulk}**
In section 3: The concentration of the rate limiting component A in the bulk stream \( \text{[mole/m}^3] \)

**C_A_{S}**
In sections 2 and 3: The concentration of the rate limiting component A at the pellet surface \( \text{[mole/m}^3] \)

**C_i**
In section 3: The concentration of the non-rate limiting components i \( \text{[mole/m}^3] \)

**C_{ij}**
In section 4: A dimensional constant. Units vary according to expression

**c_i**
In section 4: Arbitrary constants imaging the L infinite sets of solution to (4.13)

**Constant_i**
In section 2: Arbitrary constants determined from the boundary conditions

**D_A**
In section 4: The diffusivity for A \( \text{[m}^2/\text{s]} \)

**D_Ae**
In section 3: The effective diffusivity inside the pellet \( \text{[m}^2/\text{s]} \)

**D**
In section 4: The an entity unit matrix. This contain as elements the \( d_{ij} \) powers into which the basic units are raised in the individual physical entity’s total dimension

**d_{ij}**
In section 4: The power to which the basic unit \( R_j \) is raised in order to describe the parameter \( Q_j \)’s total dimension

**d_p**
In section 2: Catalyst pellet diameter [m]

**E**
In section 3: The energy of activation for a reaction \( \text{[J/mole]} \)

**F(Q)**
In section 4: A function describing the physical entity \( Q \), based on the physical entities in \( Q \)

**f(C_i,C_A)**
In section 3: The rate expression divided by the rate constant \( k \), units vary according to the rate expression
Symbols

f_d
In section 2: Catalyst dilution factor

h
In section 4: The deviation from a known set of experimental conditions Q_i, where the value of Q_i is known.

h
In section 3: The heat transfer coefficient \( \frac{J}{m^2 \cdot K \cdot s} \)

I_0
In section 2: The modified Bessel function of the first kind of order 0

i
In section 1: Component i

i
In section 2: A shape factor given by (2.57)

J
In section 2: The heat flux \( \frac{J}{m^2 \cdot s} \)

j
In section 1: Reaction number j

K_i
In section 3: Adsorption or desorption coefficients units vary according to the adsorption or desorption expression.

K_0
In section 2: The modified Bessel function of the second kind of order 0

k
In sections 2 and 3: A rate constant depending on temperature only, units vary according to rate expression

k
In section 4: The degree of the Taylor polynomial approximation.

k_g
In sections 3 and 4: The mass transfer coefficient \( \frac{m}{s} \)

k_{sh}
In section 4: Dimensionless experimentally determined constant in the Sherwood number.

L
In section 1: The total number of independent reactions

L
In sections 2 and 3: The length of a cylindrical catalyst pellet [m]

L
In section 4: The number of dimensionless products \( \Pi_i \)

L_p
In sections 2, 3 and 4: A characteristic length for the catalyst pellet. For a spherical pellet and a cylindrical pellet it is the pellet radius, for a slab half the slab thickness [m]

l
In section 1: An individual independent reaction

m
In section 2: The total number of independent reactions

N_A
In sections 2 and 4: The mass flux \( \frac{mol}{m^2 \cdot s} \)

N_{A \cdot \ell_p}
In section 2: The flux of component A at the catalyst outer surface \( \frac{mol}{m^2 \cdot s} \)

n
In section 4: The number physical entities describing the entity Q_i

O( \| \mathbf{b} \|^k )
In section 4: The Taylor approximation error.

Q
In section 4: A vector which elements are the physical entities Q_i

Q_i
In section 4: A dimensional physical entity, i.e. length [m] or mass [kg]

R
In section 1: The total number of balanced reaction equation in a reaction mechanism.

R
In section 3: The universal gas constant \( \frac{J}{mol \cdot K} \)

R_k
In section 4: A basic unit, e.g. meters, seconds, kg

R_e
In section 4: Reynolds number as defined in example E4.1

r
In section 4: The number of basic units R_k in use.

r_{A_i}
In section 3: The rate of formation for the rate limiting reactant A \( \frac{mol}{g \cdot cat \cdot s} \)
$r_{A,\text{kin}}$ In section 2: The kinetic rate of formation for the rate limiting reactant $A$, [mole g cat $^{-1}$ s $^{-1}$]

$r_{A,\text{obs}}$ In sections 2 and 3: The observed rate of reaction for the catalyst pellet, [mole g cat $^{-1}$ s $^{-1}$]

$r_i$ In section 1: Total number of reactants in reaction $i$.

$r_i$ In section 2: The reaction rate for the independent reaction $i$, [mole g cat $^{-1}$ s $^{-1}$]

$S$ In section 1: The total number of components.

$S_C$ In section 1: Components that contain a catalyst site or in any other way appears as an intermediate that does not enter into the net reactions.

$S_N$ In section 1: Components that enter into the net reactions.

$S_P$ In sections 2 and 3: The external catalyst pellet surface [m$^2$]

$S_C$ In section 4: Schmidts number as defined in example E4.1

$S_h$ In section 4: Sherwoods number as defined in example E4.1

$T_{\text{bulk}}$ In section 3: Temperature in the bulk phase of the fluid media [K]

$T_s$ In section 3: Temperature at the external surface of a catalyst pellet [K]

$u$ In section 4: The superficial fluid velocity, [m s $^{-1}$]

$V_p$ In sections 2 and 3: The apparent catalyst pellet volume [m$^3$]

$w_{\text{cat.,powder}}$ In section 2: Weight of catalyst powder mixed in pellet [kg]

$w_{\text{inert.powder}}$ In section 2: Weight of inert powder mixed in pellet [kg]

$z$ In section 4: The distance from the pellet center [m]

$\alpha$ In section 2: The liquid loading defined as catalyst containing liquid volume to pore volume.

$\alpha_{ij}$ In section 4: A column vector containing the unknown exponents $\alpha_i$ for the physical entities $Q_i$.

$\beta_{ij}$ In section 4: The power to which the dimensionless number $\Pi_i$ enters in to term $j$ in a dimensionless formula describing a physical property. $\beta_{ij}$ is a constant that has to be found from experiments.

$\gamma_A$ In section 2: A dimensionless variable defined by equation (2.48).

$\gamma_{ij}$ In section 4: The power to which the physical entity $Q_i$ enters into the dimensionless number $\Pi_i$, $\gamma_{ij} = \alpha_{ij} - 1$.

$\mathbf{y_R}$ In section 4: A matrix defined by equation (4.19).

$\delta$ In section 4: The thickness of the stagnant film layer around a catalyst pellet [m]

$\Delta H_A$ In section 3: The heat of reaction based on conversion of the rate limiting component $A$, [J mole $^{-1}$]

$\Delta H_i$ In section 2: The heat of reaction for reaction $i$, [J mole $^{-1}$]

$\Delta H_{\text{max}}$ In section 2: The maximum possible heat of reaction based on the sum of the individual reactions and reactants present, [J m$^{-3}$]

$\Delta T_{\text{max}}$ In section 2: The maximum possible temperature change inside a catalyst pellet [K].
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Section</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta$</td>
<td>2</td>
<td>The internal catalyst effectiveness factor</td>
</tr>
<tr>
<td>$\varphi$</td>
<td>2</td>
<td>The Thiele modulus</td>
</tr>
<tr>
<td>$\varphi_A$</td>
<td>2</td>
<td>A function of the dimensionless numbers $\Pi_i$ describing a physical entity.</td>
</tr>
<tr>
<td>$\varphi_{AS}$</td>
<td>2</td>
<td>The approximation Thiele modulus as defined by (2.57)</td>
</tr>
<tr>
<td>$\varphi_{GSP}$</td>
<td>2</td>
<td>The general shape approximation Thiele modulus as defined by (2.58)</td>
</tr>
<tr>
<td>$\Phi_{WP}$</td>
<td>2</td>
<td>The general Thiele modulus as defined by equation (2.69) or (2.70).</td>
</tr>
<tr>
<td>$\lambda_c$</td>
<td>2</td>
<td>The effective conductivity of the porous pellet $\left[ \frac{J}{m \cdot K \cdot s} \right]$</td>
</tr>
<tr>
<td>$\nu$</td>
<td>1</td>
<td>A matrix containing the stochiometric coefficients for a set of reactions</td>
</tr>
<tr>
<td>$\nu^C$</td>
<td>1</td>
<td>A matrix containing the stochiometric coefficients for the intermediate components for a set of reactions</td>
</tr>
<tr>
<td>$\nu^N$</td>
<td>1</td>
<td>A matrix containing the stochiometric coefficients for the non-intermediate components for a set of reactions</td>
</tr>
<tr>
<td>$\nu_N$</td>
<td>1</td>
<td>A matrix containing the stochiometric coefficients for a set of net reactions</td>
</tr>
<tr>
<td>$\nu^C_N$</td>
<td>1</td>
<td>A matrix containing the stochiometric coefficients for the intermediate components for a set of net reactions</td>
</tr>
<tr>
<td>$\nu^N_N$</td>
<td>1</td>
<td>A matrix containing the stochiometric coefficients for the non-intermediate components for a set of net reactions</td>
</tr>
<tr>
<td>$\mu_f$</td>
<td>4</td>
<td>The fluid viscosity $\left[ \frac{kg}{m \cdot s} \right]$</td>
</tr>
<tr>
<td>$\nu_{ij}$</td>
<td>1</td>
<td>The stochiometric coefficient of component j in reaction i</td>
</tr>
<tr>
<td>$\Pi_t$</td>
<td>4</td>
<td>A dimensionless product or number defined by $\Pi_t = Q_1^{Y_1} \cdot Q_2^{Y_2} \cdot Q_3^{Y_3} \cdot \ldots \cdot Q_n^{Y_n}$</td>
</tr>
<tr>
<td>$\rho_C$</td>
<td>2 or 3</td>
<td>The catalyst pellet density $\left[ \frac{g}{m^3} \right]$</td>
</tr>
<tr>
<td>$\rho_f$</td>
<td>4</td>
<td>The fluid density $\left[ \frac{g}{m^3} \right]$</td>
</tr>
<tr>
<td>$\theta$</td>
<td>1</td>
<td>A matrix containing the stochiometric numbers for the individual reactions in one or more reaction mechanisms.</td>
</tr>
<tr>
<td>$\xi_A$</td>
<td>2</td>
<td>The dimensionless temperature as defined by equation (2.81).</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>2</td>
<td>Dimensionless concentration of A inside pellet as defined by equation 2.14.</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>Dimensionless distance inside pellet as defined by equation 2.14.</td>
</tr>
</tbody>
</table>
6. Literature


