Masterarbeit

Brennkammer-Berechnungsmodell für Schwarzlaugenkessel

Ausgeführt zum Zwecke der Erlangung des akademischen Grades eines Diplomingenieurs der technischen Wissenschaften

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Abstract

This paper describes at the beginning and in a nutshell the underlying Kraft-process followed by a description of the problem. The main part concentrates on the description of a program for combustion chambers to determine the reacting mass quantities, the combustion temperature with heat fluxes and upward and downward mass flow directions. The model is 1-dimensional and refers specifically to the black liquor boiler, but the modular design is particularly noteworthy, allowing a variety of different combustion chambers to be calculated. In principle, it consists of a set of chemical reactions and any number of layers with a fuel or air supply. With regard to the black liquor boiler, a model is described that deals with the simplifications and assumptions of this boiler. In the middle part of the paper the theoretical calculation is presented, which contains the mathematical basis and the simplifications and assumptions which are included in it. After the mathematical basis, the code is discussed step by step and analysed in more detail. The basic structure of the program and a flow chart showing the exact procedure are shown. Also the calculation of the temperature of each single cell as well as the exchange of the substance quantities among each other are presented. One of the last chapters describes the verification of the program with several comparisons of existing examples or the comparison with other calculation programs. The summary and future prospects of this model complete the work.

Acknowledgments

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Nomenclature

Greek symbols

α	degree of absorption	
δ	Kronecker-delta	
ϵ	degree of emissivity	
λ	thermal conductivity	$\mathrm{W\,m^{-1}\,K^{-1}}$
ν	stoichiometric coefficient	
ρ	degree of reflection	
σ	Stefan Boltzmann constant	$\mathrm{W\,m^{-2}\,K^{-4}}$
τ_{ij}	Degree of transmission between surface i and j	
ε_i	run number of chemical equation i	
ε_{max}	highest possible run number of a chemical equation	
ε_{min}	lowest possible run number of a chemical equation	

Roman symbols

$\dot{q}_i$	net heat flux density to wall i	$\mathrm{W\,m^{-2}}$
$\dot{Q}_{aus\;oberer\;Stoffstrom}$	outgoing heat flux of the upward mass flow	W
$\dot{Q}_{aus\;unterer\;Stoffstrom}$	outgoing heat flux of the downward mass flow	W
$\dot{Q}_{Brennstoff}$	heat flux of the ingoing fuel	W
$\dot{Q}_{ein\;oberer\;Stoffstrom}$	ingoing heat flux of the upward mass flow	W
$\dot{Q}_{ein\;unterer\;Stoffstrom}$	ingoing heat flux of the downward mass flow	W
$\dot{q}_{i,conv}$	convective heat flux to wall i	$\mathrm{W\,m^{-2}}$
$\dot{Q}_{Konvektion}$	convective heat flux	W
$\dot{Q}_{Luft}$	heat flux of the ingoing air	W
$\dot{Q}_{Strahlung}$	radiation heat flux	W
A	coefficient for the kelley-polynomial	
A_i	Area of the wall i in the camber	$\mathrm{m^2}$
A_{Arr}	pre exponential factor of the Arrhenius equation	
B	coefficient for the kelley-polynomial	
b_{strom}	vector that describes the species in the upward flow	
C	coefficient for the kelley-polynomial	
c_p	specific isobaric heat capacity	$\mathrm{J\,mol^{-1}\,K^{-1}}$
c_X	concentration of Species X	
D	coefficient for the kelley-polynomial	
E_A	activasion energy	J

E_{bi}	blackbody emission	$\mathrm{W\,m^{-2}}$
F_{ij}	form factors	
H	enthalpy at a given temperature	$\mathrm{kJ\,mol^{-1}}$
H_f	standard enthalpy of formation at 298.15K	$\mathrm{kJ\,mol^{-1}}$
H_i	incoming heat flux density to wall i	$\mathrm{W\,m^{-2}}$
H_{tr}	enthalpy of transformation	$\mathrm{kJ\,mol^{-1}}$
K	equilibrium constant	
k	reaction rate constant of the Arrhenius equation	
N	Number of chemical equations	
n	associated species-vector of the stoichiometric matrix	
n_{ij}	amount of substance of species i in reaction j	
R	universal gas constant	J
R_β	rank of the element-species-matrix	
R_ν	rank of the stoichiometric matrix (linear independent equations, also called "key reactions")	
T	absolute temperature	K
T_g	absolute temperature of the gas inside the chamber	K
W_i	outgoing heat flux density to wall i	$\mathrm{W\,m^{-2}}$

1 Introduction

1.1 Introductory remarks

1.1.1 The Kraft-process

The Kraft-process is a paper manufacturing process that separates pieces of wood into their components and then processes the resulting cellulose into paper. It is called Kraft-process because "Kraft" means strength and the pulp produced with this process was historically known for its superior strength. Until the beginning of the 20th century paper was produced in this way and the remaining substances separated from the cellulose, such as lignin and polyose, were disposed of as waste materials. With the idea of recovering the chemicals used to separate the individual components, a cycle was created, the so called Kraft-process, see figure 1.1. In principle this consists of 2 circuits which overlap each other. Firstly the actual sodium and sulphur cycle in which the wood boils, the black liquor is further processed and finally burnt and reduced. The second is the calcium cycle with the help of which sodium carbonate is regenerated to sodium hydroxide.

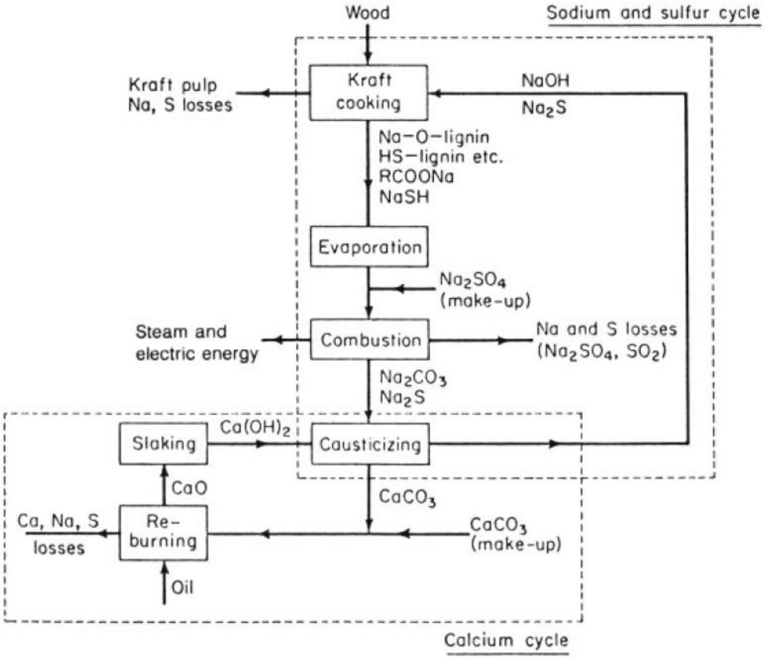


Figure 1.1: The Kraft-recovery cycle [4]

The first sub process is cooking. Wood chips and smaller plant residues are heated for several hours in a pressure boiler, at roughly $165 - 175°$ C, with a caustic solution consisting mainly of sodium hydroxide $NaOH$, sodium sulphate and sodium sulphite Na_2S. Under these conditions, the lignin stored in the plant cell wall split into smaller parts. Cellulose and polyose (hemicellulose) are also dissolved from the cell walls. The viscous "pulp" from the cellulose fibres is bleached in further processes and further processed into paper. The remainder consisting of lignin fragments, hemicellulose, sodium sulphate, sodium sulphite, sodium carbonate and other salts like chlorine Cl and potassium K. It is called weak black liquor because of its colour and the low percentage of solids (13-17%) like wood lignins, organic material and other inorganic compounds. Especially potassium and chlorine do a direct impact on the boiler operation and design as both influence the melting point of formed ashes and chlorine worsens corrosion. The raw pulp is then screened, cleaned to get rid of dirt and knots and to improve quality.

In order to increase the solid content and thus improve the combustion properties, the black liquor is heated, to evaporate the liquid mostly with so called multistage vacuum systems. Depending on the degree of evaporation, a black liquor with up to 85 % solid components remains (commonly refereed to as black liquor dry solids or BLDS). These multistage systems consist of 4 to 7 evaporators arranged in series to boil away the stored water, see 1.2). [9]

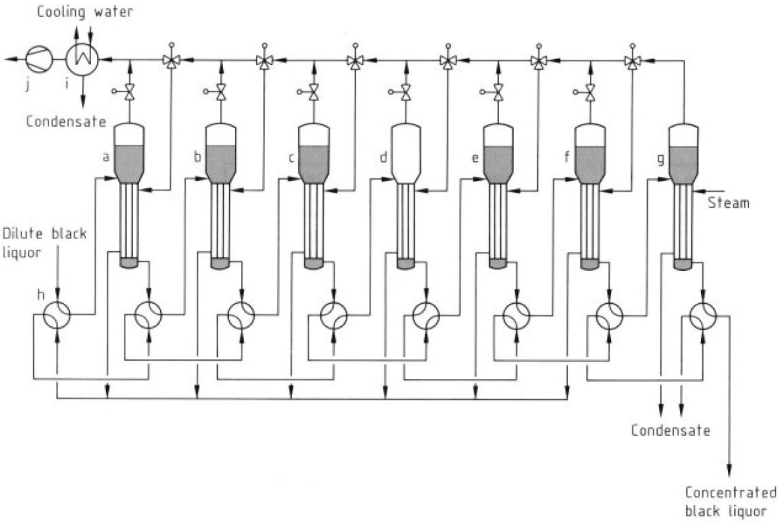


Figure 1.2: Process drawing of a multistage vacuum evaporation plant - **a)** to **g)** active evaporatores **d)** evaporator switched to washing, **h)** reversing valve, **i)** condensener, **j)** compressor [4]

In the next step, the black liquor is sprayed in the recovery boiler and the organic part is burned to produce heat. The inorganic material collects oneself on the char bed at the bottom and gets reduced.

Sodium sulphate is reduced to sodium sulphite by the carbon in the black liquor.

$$Na_2SO_4 + 2C = Na_2S + 2CO_2$$

The melt consists of sodium sulphite Na_2S and sodium carbonate Na_2CO_3 is then discharged to the dissolving tank and dissolved with so called weak wash to form green liquor. In the next step the clarified green liquor is fed to a slaker together with lime CaO to rapidly form calcium hydroxide $Ca(OH)_2$.

$$CaO + H_2O = Ca(OH)_2 + heat$$

In the so called causticizing process Na_2CO_3 is regenerated to sodium hydroxide $NaOH$ and calcium carbonate $CaCO_3$. The causticizing process itself is relatively slow and thus finished in a series of agitated tanks - the actual causticizers.

$$Na_2S + Na_2CO_3 + Ca(OH)_2 = Na_2S + 2NaOH + CaCO_3$$

The mix of Na_2S and $NaOH$ is also called white liquor and is used again for boiling the wood chips and the cycle is closed. The calcium carbonate $CaCO_3$ is separated from the white liquor and heated so that calcium oxide CaO and carbon dioxide CO_2 are produced again. The calcium oxide is then returned to the circulation.

$$CaCO_3 + heat = CaO + CO_2$$

2 Problem description

Due to the numerous chemical reactions of the black liquor at different temperatures and the simultaneous reduction to oxidation in the boiler, it is a relatively complex process compared to normal boilers where more conventional fuels such as coal or wood are burned. In order for reduction and oxidation to take place in the boiler, these must be separated from each other in an airtight manner by a melt. This means that sufficient melting products must be produced and sufficient carbon must reach the bottom of the boiler. It is therefore a complex interaction of several reactions and substances that have to be considered and finely tuned to each other in order to realize a smooth process flow with the desired starting products and temperatures. In principle, such a 3D simulation would be possible with today's computer programs, but it is not carried out for reasons of practicality. The high programming and time expenditure of such a simulation are not in a good relation with the results. An interim solution is required which, by means of simplifications and certain assumptions, can calculate useful reference values at short computing times, be it with regard to temperature, the resulting quantities of substances or other parameters.

3 Model

Models are used to better understand technical problems and to optimize processes based on simulation results. The typical life cycle of a modelling effort is illustrated in Figure 3.1. Starting from the real system that is subject to investigation, the problem is transferred to an abstract model structure. This step is most important because a first decision is made whether certain aspects are relevant or not. In a second phase, the model parameters are determined by comparison of the model prediction to real system behaviour. At the end of this process, a validated parametric model ready to predict the outcome of the real system in various operating states is available. In the third phase, the parametric model is used to simulate new processes based on the experience gained from the investigated system.[5]

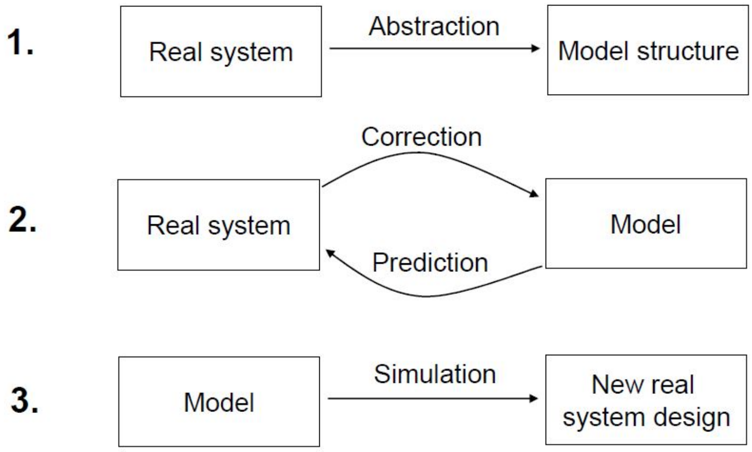


Figure 3.1: Stages in development and application of models [5]

To describe reality, simplified mathematical models are created that describe the desired process in sufficient detail with mathematical equations. This "basic model" can later be extended to more complex models in order to describe reality piece by piece. A more elaborate model therefore also means a higher computation and time expenditure. So an optimum is to find so that mathematical description describes reality with as little effort as possible. As in manufacturing technology, the phrase "As fine as necessary and as coarse as possible" applies.

3.1 Important aspects of the model

As in every model, there are also some important aspects/phenomena in this model that must be depicted more precisely or not neglected. They're special for the black liquor kettle:

1. The simultaneous oxidation and reduction that takes place in the boiler
2. The composition of the black liquor and the products resulting from the chemical reactions, whereby intermediate products occurring for a short time also play an important role.
3. Heat release in the various zones of the black liquor boiler
4. Material flows flowing up and down, both substances in the black liquor and products of chemical reactions

3.2 Layers of the black liquor boiler

For the 1-dimensional black liquor boiler model, the lower part of the furnace was divided into several layers. It is advisable to introduce a cell if the composition changes, for example in the case of air intakes or a change in the state of the fuel e.g. degassing or combustion. As can be seen in figure 3.2, the black liquor is sprayed through the spray nozzles and falls onto the bottom of the furnace. This means that two material streams exist in parallel. On the one hand the black liquor falling to the ground and on the other hand the ascending gases. With direct entry, the water contained in the fuel begins to evaporate at the high temperatures and drying takes place. For this zone a layer was introduced, layer 5 in 3.4. After drying, the volatile components begin to evaporate from the fuel. This is therefore referred to as degassing. After these processes, the second air supply leads to the actual oxidation of the fuel and heat is released. Therefore another layer was introduced. Combustion takes place sub-stoichiometrically, i.e. there is not enough oxygen for sufficient combustion. The burned and unburned components fall to the ground and a char bed is formed via which the first air supply is supplied. In the char bed itself, the reduction of sodium sulphate to sodium sulphite begins in the absence of air and with the unburned carbon. In order to keep the char bed mass constant and to transfer the sodium sulphite to the next process in the power process chain, a certain part of the melt is removed. In the last step, the ascending gas passes through the third air stage, where the carbon monoxide and other pollutants are post-combusted.

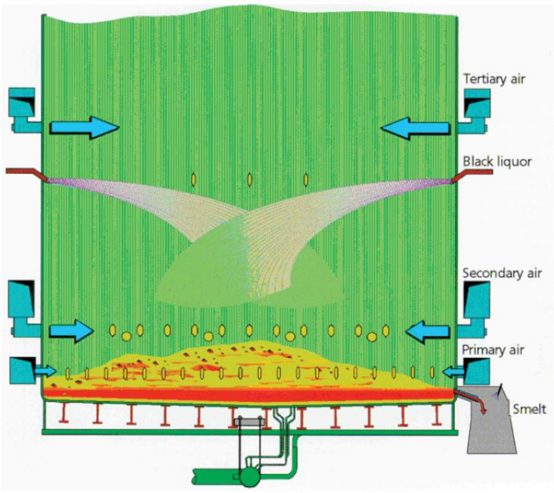


Figure 3.2: Recovery boiler lower furnace [7]

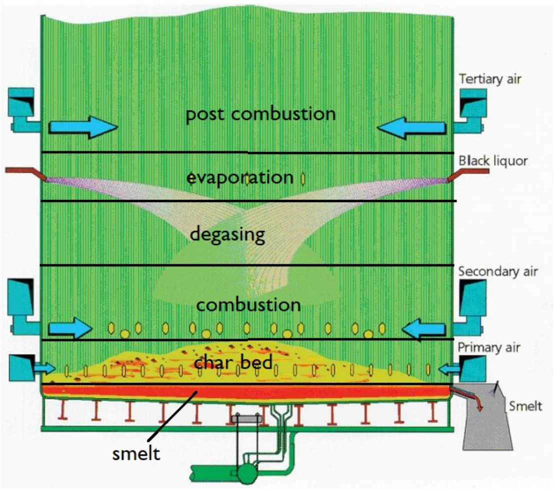


Figure 3.3: Layering of the lower furnace [7]

The model in 3.4 was extended by more fuel- and air supplies to allow more possibilities for modelling and adaptation.

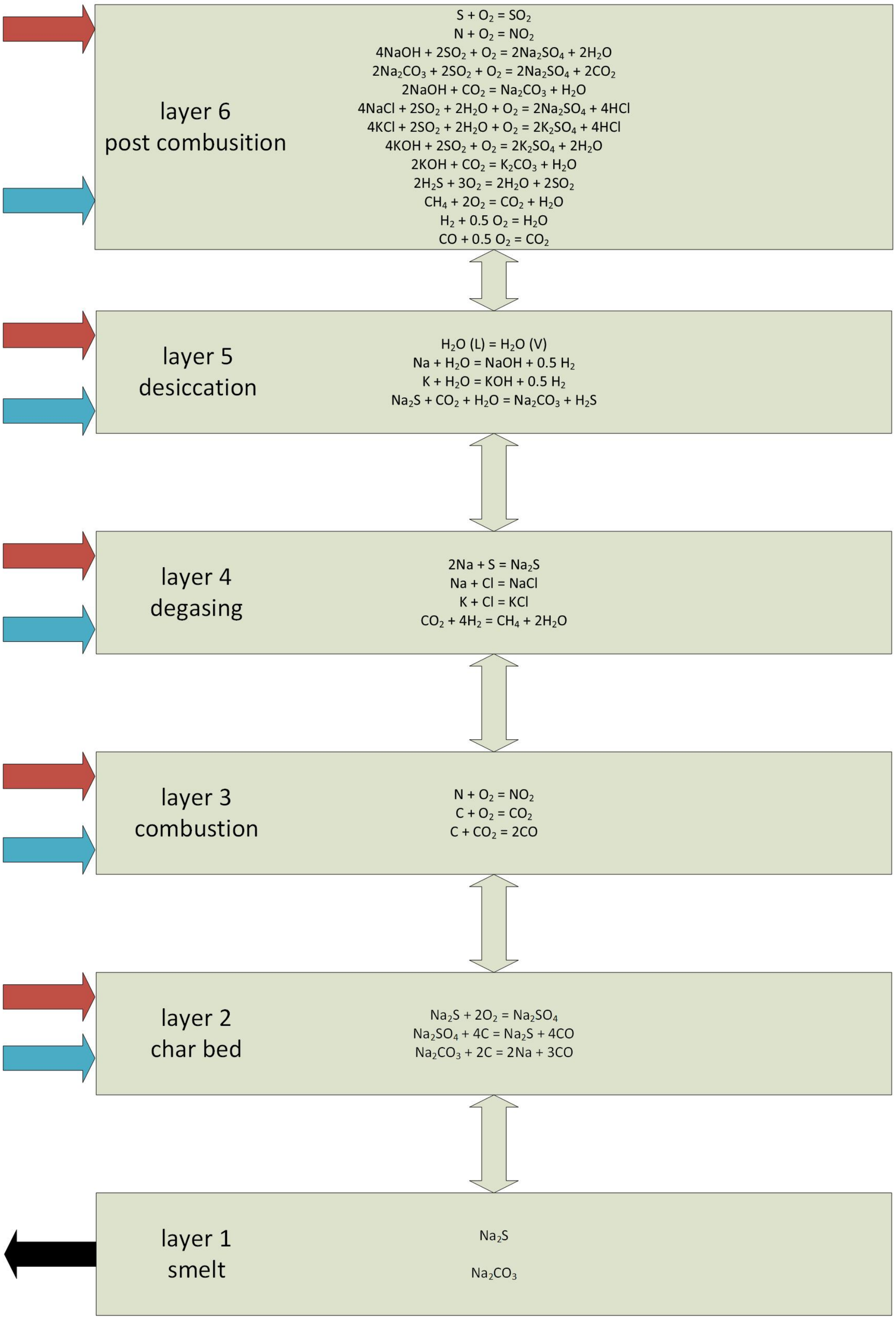
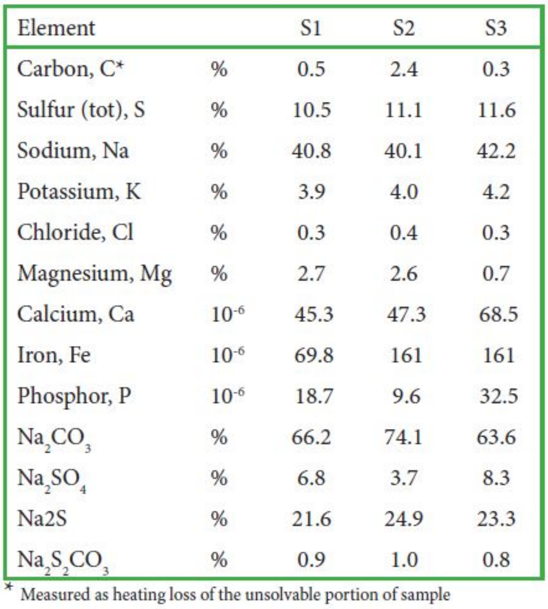


Figure 3.4: Structure of the model for black liquor

3.3 Oxidation/Reduction

Oxidation (reaction with oxygen, such as the combustion of carbon to carbon dioxide) and reduction (reaction in which oxygen is released) are two opposing processes. This makes it all the more difficult to run these two processes in one and the same boiler. Essential here is the melting bed which divides the boiler into two zones. The melt bed consists mainly of carbon, black liquor and melt. The aggregate state of the substances in the melt bed is liquid or solid. In order to obtain a constant bed, the same amount of melt must be discharged at the bottom as is supplied above. The added substances are black liquor drops from the added black liquor, residues from the boiler walls as well as from the super heaters that fall to the ground and inert substances. Measurements, see 3.5, have shown that the bed consists to a large extent of carbon, sodium carbonate $NaCO_3$, sodium sulphate Na_2SO_4, sodium sulphite Na_2S, sodium chloride $NaCl$ and smaller amounts of potassium salts and inert substances. The main task of the melt bed is the reduction of sodium sulphate to sodium sulphite.

$$Na_2SO_4 + 4C = Na_2S + 4CO$$



Element		S1	S2	S3
Carbon, C*	%	0.5	2.4	0.3
Sulfur (tot), S	%	10.5	11.1	11.6
Sodium, Na	%	40.8	40.1	42.2
Potassium, K	%	3.9	4.0	4.2
Chloride, Cl	%	0.3	0.4	0.3
Magnesium, Mg	%	2.7	2.6	0.7
Calcium, Ca	10^{-6}	45.3	47.3	68.5
Iron, Fe	10^{-6}	69.8	161	161
Phosphor, P	10^{-6}	18.7	9.6	32.5
Na_2CO_3	%	66.2	74.1	63.6
Na_2SO_4	%	6.8	3.7	8.3
Na2S	%	21.6	24.9	23.3
$Na_2S_2CO_3$	%	0.9	1.0	0.8

* Measured as heating loss of the unsolvable portion of sample

Figure 3.5: Measured char bed composition

The degree of reduction is usually given as the mole ratio of sodium sulphite to the sum of sodium sulphite and sodium sulphate. Typical reduction rates of modern boilers are approximately 95%. With increasing temperature of the melt the reduction rate increases and the SO_2 and H_2S emissions decrease. In modern boilers is therefore attempted to increase the char bed temperature. In addition to oxidation, carbon also plays an important role in reduction. The following 3 chemical reactions occur in the smelt:

$$Na_2S + 2O_2 = Na_2SO_4$$

$$Na_2SO_4 + 2C = Na_2S + 2CO_2$$

$$Na_2SO_4 + 4C = Na_2S + 4CO$$

The reduction process is relatively slow and requires a long stay in bed to achieve a high reduction rate. In order to achieve high reduction rates, a high carbon content on the surface of the carbon bed should be aimed at. Oxidation takes place mainly through the combustion of carbon. The oxygen for combustion comes from different sources. These are oxygen O_2 and elemental oxygen O, sodium sulphate Na_2SO_4, water vapour H_2O and carbon dioxide CO_2. The reaction with water vapour accounts for a third to a half of the reaction with carbon. The reason for this is the water stored in the black liquor which reacts with the carbon before it comes into contact with oxygen. [7] The main reactions are there:

$$C + O_2 = CO_2$$

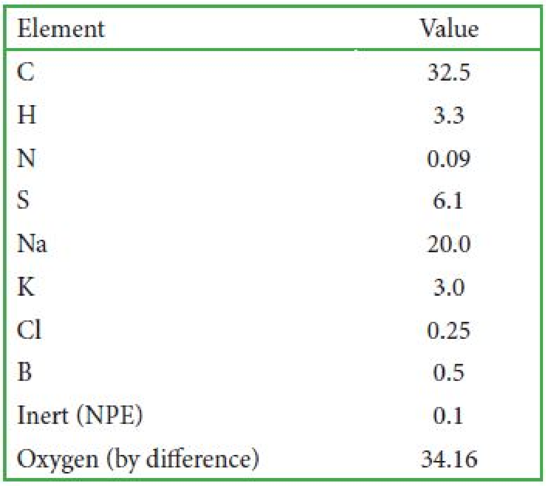
$$C + H_2O = H_2 + CO$$

$$C + 0.5O_2 = CO$$

3.4 Composition of black liquor

While typical biofuels consist of carbon C, hydrogen H_2, nitrogen N_2, sulphur S and oxygen O_2, the black liquor contains high amounts of ash, sodium Na, potassium K and chlorine Cl. The accurate analysis of the fuel is often difficult and less constant than in other fuels. Theoretically, the black liquor can be divided into 3 categories:

1. Organic substances (which burn completely)
2. Reactive inorganic substances that react to solid end products
3. Non-reactive substances flowing through the boiler without reaction



Element	Value
C	32.5
H	3.3
N	0.09
S	6.1
Na	20.0
K	3.0
Cl	0.25
B	0.5
Inert (NPE)	0.1
Oxygen (by difference)	34.16

Figure 3.6: Measured char bed composition in mass -%

Black liquor has a relatively low lower calorific value. Depending on the composition, this is in the order of about $12 MJ/Kg$. The reason is the high proportion of inorganic substances in the fuel. The high water content, the low calorific value and the high ash content make combustion difficult. A trend in recent years has therefore been to add dry black liquor to the normal black liquor to increase the calorific value and thus achieve higher temperatures and greater efficiency,see 3.7. In this diagram one can see the increase of the boiler efficiency with increasing black liquor dry solids (red line).

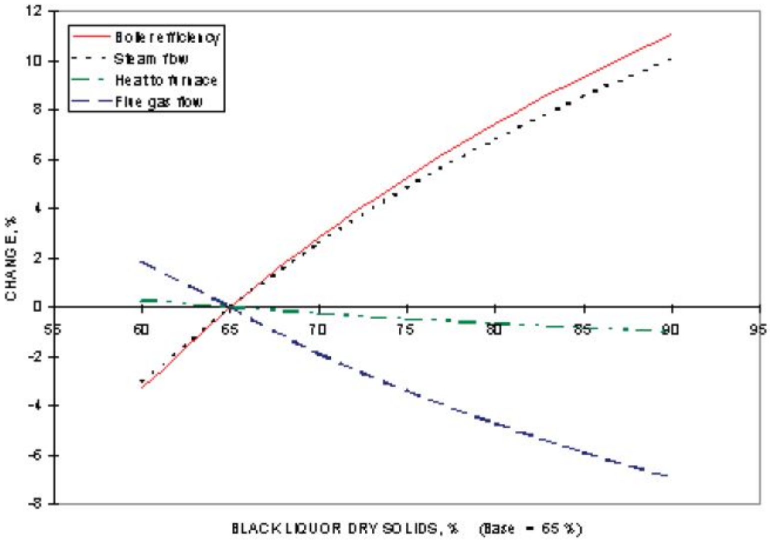


Figure 3.7: Effect of black liquor dry solids at amount of flue gas, boiler efficiency, steam flow and heat input to furnace.

The black liquor is sprayed into the boiler by several nozzles as fine droplets in order to increase the surface and thus the combustion rate or temperature. The average droplet diameter is about 2-3mm. The nozzles are distributed around the circumference and at a height that ensures that even unburned material reaches the char bed to react further. As with most fuels, the heat is released in 2 processes.

1. Release of volatile components
2. Reaction with oxygen (combustion)

3.5 Volatile matter

After the fuel has been sprayed into the hot boiler and the water has evaporated, the reactions begin with the lowest activation energy. For organic substances, this is the release of relatively light gases such as carbon dioxide, methane and hydrogen with respect to their molecular weight. The special feature of black liquor is the swelling of the particles during combustion in the boiler. No other industrial fuel swells as strongly as this one. The reason for this is the high content of volatile components and the suitable surface of the black liquor. The pyrolysis of black liquor is characterized by the swelling of the particles, the release of volatile components and the appearance of a flame around the droplets.

3.6 Combustion

Combustion starts as soon as the last volatile gases have escaped and oxygen comes into contact with the particles. In practice, however, both phenomena occur simultaneously or overlap. If there is a deficit of oxygen, the carbon reacts with carbon dioxide CO_2 and the water vapour H_2O and forms carbon monoxide CO. The carbon monoxide will react higher in the boiler with oxygen to carbon dioxide CO_2.

$$C + CO_2 = 2CO$$

$$C + H_2O = CO + H_2$$

3.7 Material flows

The material flows are not subdivided according to the substances, but only in the direction in which they flow. The black liquor is sprayed between the second and third air inlet and therefore flows downwards until it reaches the char bed. In addition, the superfluous melt flows downwards. Volatile gases as well as exhaust gases resulting from combustion or other reactions flow upwards and leave the boiler in the direction of the super heater surfaces above.

3.8 Simplifications / Assumptions

In order to depict certain phenomena in a model, various assumptions or simplifications are useful or even necessary. Especially in black liquor boilers there are countless chemical substances which react with each other under different conditions and thus make an exact representation of all occurring events virtually impossible. The difficulty, or more precisely the art, of simplifications is to choose them in such a way that the character of the phenomena is preserved and the error can be estimated, or rather kept within certain limits.

3.8.1 Layer model

The first assumption for the model is the so-called layer model.In the layer model, the boiler is cut into one or more layers with defined dimensions and regarded as submodels. Here a subdivision according to the respective reaction stages of the fuel is suitable. In addition, external influences must also be taken into account in the choice of layers, such as air and fuel supply or other inflows and outflows across system boundaries.

3.8.2 Assumption about gas dynamics

Gas dynamics play an important role in many processes, but their complexity makes them very computationally intensive and therefore time-consuming. If high gas velocities with simultaneous high turbulence occur, homogeneous mixtures are often assumed. Another common assumption is that the model is in a static state, i.e. that certain parameters do not change over time. Mathematically formulated are simpler algebraic equations that can be solved faster and more efficiently from equations that are initially temporally differential.

3.8.3 Chemical reactions

Chemical reactions are strongly dependent on some parameters. Among the most important variables are temperature, mixture and time. These variables change temporally and spatially at each point in the black liquor boiler due to currents and therefore make an accurate analysis very difficult. One approach here would be to create a homogeneous mixture and, as a result, a homogeneous temperature distribution. This eliminates the local dependency or mathematically expressed derivative to the location. The temporal dependency can also be eliminated by sufficiently long residence times in a homogeneous room. The long residence time also simplifies the calculation of the amount of substance, since a chemical equilibrium can be assumed due to the homogeneity and the long residence time. The temperature dependence of the kinetics for some monomolecular reactions can be described with the Arrhenius approach.

$$k = A_{Arr} \cdot e^{\frac{-E_A}{R \cdot T}} \tag{3.1}$$

The chemical equilibrium is a reaction in which the forward and backward reactions are equally fast, i.e. the observable reaction speed for an external observer is zero although a reaction is taking place. The equilibrium constant is defined as follows by the law of mass action.

$$a \cdot A + b \cdot B = c \cdot C + d \cdot D \tag{3.2}$$

$$K = \frac{c_C^c \cdot c_D^d}{c_A^a \cdot c_B^b} \tag{3.3}$$

In formula 3.3 the base is the concentration of the species and the exponent the stoichiometric coefficient.

The amount of the equilibrium constant indicates on which side of the equation the chemical equilibrium is located. If the equilibrium constant is $K >> 1$, the equilibrium is on the side of the products. If $K << 1$, it is on the side of the educts.

3.8.4 Radiation model according to Scholand [6]

The Scholand radiation model explains a model that describes the radiation exchange of an enclosed gas with the surrounding walls. This model is used to calculate the radiation within a layer and the radiation exchange of all layers in the combustion chamber model.

If a grey and diffuse surface element is used, as shown in the figure 3.8 below, the net heat flux density is made up of the incoming and outgoing heat fluxes. The net heat flux density looks as follows:

$$\dot{q}_i = W_i - H_i \tag{3.4}$$

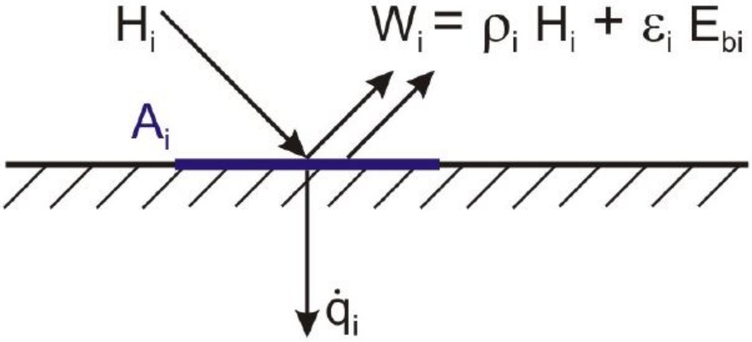


Figure 3.8: Exchange of heat on a small surface element A_1

The surface element receives the incoming heat flux density H_i from the other walls and the gas. One part of H_i gets reflected and another one is emmitted due to its temperature. Therefore the outgoing heat flux density W_i is made up of 2 parts and looks as follows

$$W_i = \varepsilon_i \cdot E_{bi} + \rho_i \cdot H_i \tag{3.5}$$

For a general surface the sum of the degree of reflection ρ ,the degree of emissivity ϵ and the degree of absorption α is one.

$$\alpha + \rho + \epsilon = 1$$

For a grey and diffuse surface element the degree of absorption (α) is zero and therefore the formula is

$$\rho + \epsilon = 1$$

so

$$\rho = 1 - \epsilon \tag{3.6}$$

E_{bi} is the blackbody emission of the surface with index i.

$$E_{bi} = \sigma \cdot T_i^4 \tag{3.7}$$

σ is the Stefan-Boltzmann constant and it is approximately $\sigma \approx 5.67040 \cdot 10^{-8} \frac{W}{m^2 K^4}$. T_i is the temperature on the inside of the wall of the combustion chamber. By inserting 3.6 and 3.4 in equation 3.5 under the condition of

$$\dot{q}_i = \frac{\dot{Q}_i}{A_i} \tag{3.8}$$

a definition for the net heat flux can be found

$$\dot{Q}_i = \frac{A_i \cdot \varepsilon_i \cdot (E_{bi} - W_i)}{1 - \varepsilon_i} \tag{3.9}$$

If it is assumed that the area A_i is divided into n individual areas A_j of the chamber,see 3.9 The incident radiant flux density H_i is calculated with

$$H_i = \epsilon_{gi} \sigma T_g^4 + \frac{1}{A_i} \sum_{j=1}^{n} A_j W_j F_{ji} \tau_{ji} \tag{3.10}$$

determined.

Where $\epsilon_{gi} \sigma T_g^4$ is the ingoing heat flux density of the surrounded gas and $\frac{1}{A_i} \sum_{j=1}^{n} A_j W_j F_{ji} \tau_{ji}$ the sum of the ingoing heat flux density of the walls.

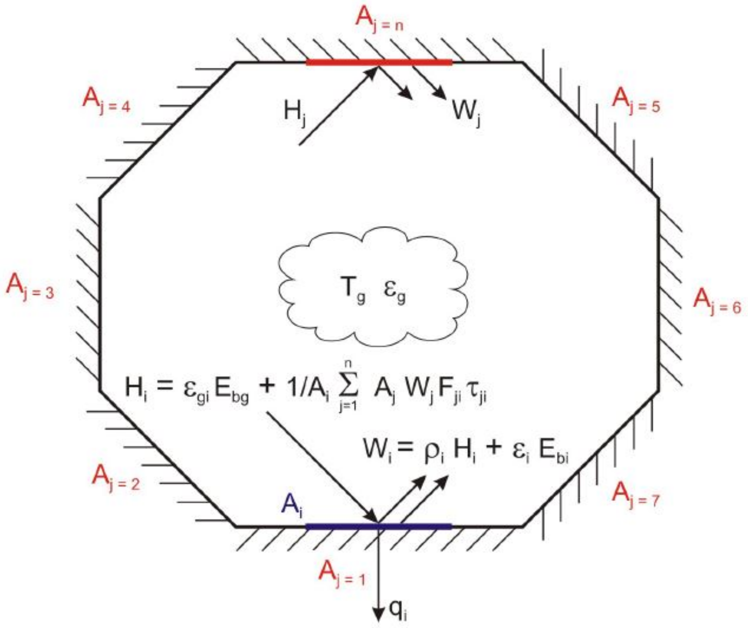


Figure 3.9: radiation exchange between a trapped gas and the surrounding walls

Inserting the incident flux density H_i, see 3.10, in the outgoing heat flux density W_i (3.5), one gets:

$$W_i = \varepsilon_i \sigma T_i^4 + \rho_i \epsilon_{gi} \sigma T_g^4 + \rho_i \frac{1}{A_i} \sum_{j=1}^{n} A_j W_j F_{ji} \tau_{ji} \tag{3.11}$$

$\varepsilon_i \sigma T_i^4$ is the emitted heat flux density of the surface, $\rho_i \epsilon_{gi} \sigma T_g^4$ is the reflected heat flux density of the gas inside the chamber and $\rho_i \frac{1}{A_i} \sum_{j=1}^{n} A_j W_j F_{ji} \tau_{ji}$ the sum of reflected heat flux densities of the other surfaces.

In the following is $E_{gi} = \epsilon_{gi} \sigma T_g^4$ the heat flux of the gas inside. F_{ji} is the so called form factor and includes the geometric properties of the surfaces A_i and A_j. In this case the form factors of [8] were used.

Moreover the reciprocal-law for grey gases is

$$A_i F_{ij} \tau_{ij} = A_j F_{ji} \tau_{ji} \tag{3.12}$$

the multiplication of the surface area, form factor and the degree of transmittance. The degree of transmittance is mostly measured or a value of experience. By inserting the formula 3.12 in 3.10 and 3.11 one gets a system of n equations with n unknowns. For a simpler use the equation 3.10 will be transformed to formulate a system of equations in a matrix-vector shape.

$$\sum_{j=1}^{n} \left(F_{ij} \tau_{ij} - \frac{\delta_{ij}}{\rho_i} \right) W_{ij} = -\frac{\varepsilon_i}{\rho_i} E_{bi} - \varepsilon_{gi} E_{bg} \tag{3.13}$$

Where δ_{ij} is the "Kronecker-Delta" and represents the elements of the identity matrix.

$$\delta_{ij} = 0\, for\, i \neq j$$

$$\delta_{ij} = 1\, for\, i = j$$

In matrix form the equation 3.13 looks like this.

$$\underline{\underline{M}} \cdot \underline{W} = \underline{C} \tag{3.14}$$

Solving this set of equations gives $\underline{W}$. Inserting the heat flux density in formula 3.9 gives the net heat flux of the cell. For the calculation all degrees of emittance ε_i and ε_g, Temperatures T_i of the cells and the gas T_g and the form factors F_{ij} must be known.

Consideration of adiabatic surfaces

A adiabatic surface describes a surface that lets no heat flux go trough it. Therefore the net heat flux of the specific surface ,indexed with an "a"), is

$$\dot{q_a} = 0 \tag{3.15}$$

Looking at 3.4 this indicates that the incoming heat flux density is equal to the outgoing.

$$H_a = W_a \tag{3.16}$$

With this condition also follows that the degree of emittance is zero $\varepsilon_a = 0$ and the degree of reflection is one $\rho_a = 1$.

Consideration of diatherm surfaces

A diatherm surface describes a surface that is completely transmissive for heat fluxes. It is often used to model openings in chambers or to model fictional borders of cells for example. The modelling of a fictional wall is necessary because it is easier to calculate energy balances. Diatherm walls are indexed with "d" and for the degree of reflection, emittance and transmittance one can say that

$$\rho_d = 0 \quad \varepsilon_d = 0 \quad \tau_d = 1 \tag{3.17}$$

Consequently all the heat flows are going through without interference and the equation 3.4 simplifies to

$$\dot{q_d} = -H_d \tag{3.18}$$

Use of diathermic surfaces for radiation exchange with an adjacent zone

With diathermic surfaces it is possible to break down a zone in a number of subzones or to treat them differently for other reasons. In this model with more cells in a reactor it is useful to create a radiation zone for every cell and connect them with diathermic surfaces.

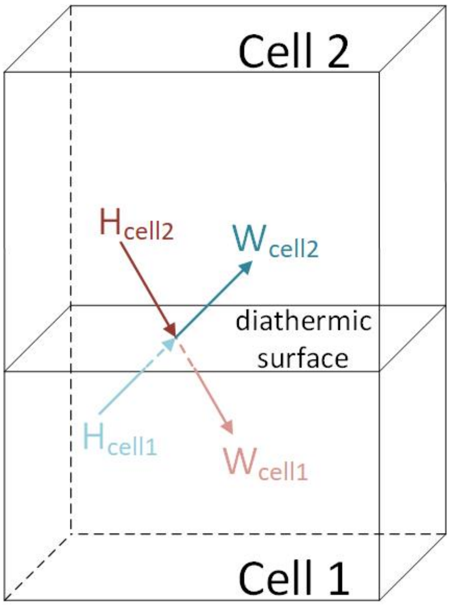


Figure 3.10: Division of a combustion chamber into two zones with exchange of radiation between the zones

In figure 3.10 one can see that the two cells are separated with a diathermic surface. This has the consequence that the outgoing flux of cell 1 called $\mathrm{H_{cell1}}$ is the ingoing flux of cell 2 called $\mathrm{W_{cell2}}$ and vice versa.

$$\begin{aligned} H_{cell1} &= W_{cell2} \\ H_{cell2} &= W_{cell1} \end{aligned} \tag{3.19}$$

Consideration of convection

Additionally to the radiation heat flux there are convective heat fluxes. To bring these into account, the energy balance for calculating the whole heat flux density is made around a surface element, like in figure 3.8.

$$\dot{q}_i = W_i - H_i + \dot{q}_{i,conv} \tag{3.20}$$

$\dot{q_{i,conv}}$ is therefore the convective part and can be described for straight walls in this manner

$$\dot{q}_{i,conv} = \alpha_i \cdot (T_i - T_g) \tag{3.21}$$

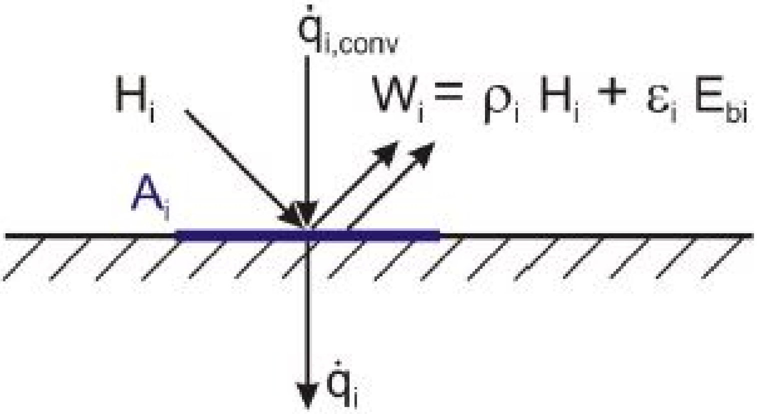


Figure 3.11: Exchange of radiational- and convective heat on a small surface element

Evaluation of the form factors according to [8]

In this chapter one finds the equations to calculate the form factors for the radiation model. The form factors depend on the geometry of the zone itself. In this case the cell has a cuboid shape and looks like figure 3.12

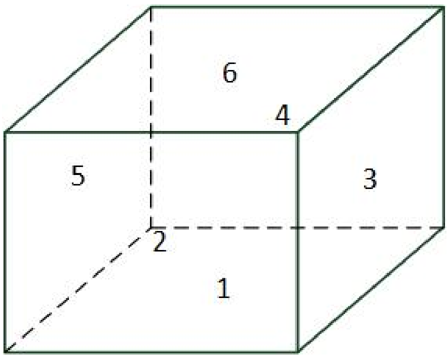


Figure 3.12: Numbering of the surfaces of the cuboid cell

For a stable computation without errors it is important to stay with the numbering of the surfaces, seen on 3.12) consistently.

For a cuboid there are 2 different orientations of two single surfaces possible. In the first case there are two finite surfaces with a right angle, see 3.13.

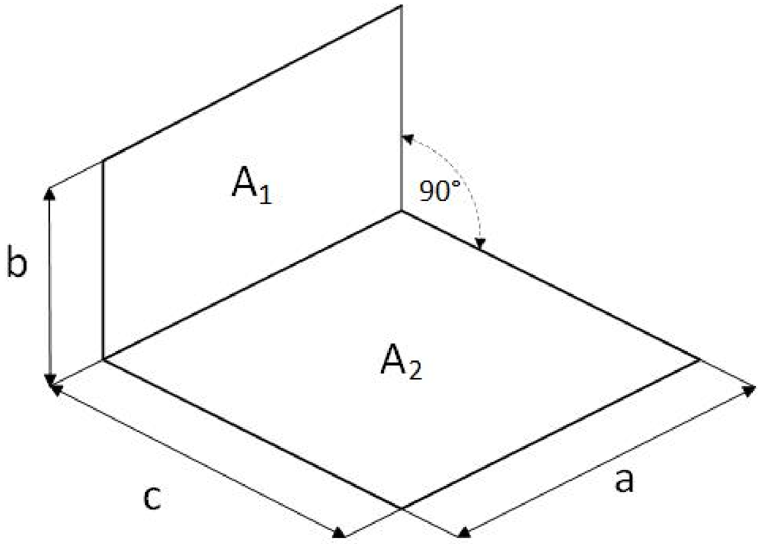


Figure 3.13: Form factor for two surfaces in a right angle

$$B = \frac{b}{a} \quad C = \frac{c}{a}$$

$$F_{ij} = \frac{1}{\pi B}\Bigg\{B\,arctan\frac{1}{B} + C\,arctan\frac{1}{C} - \sqrt{B^2+C^2}\,arctan\frac{1}{\sqrt{B^2+C^2}} + \frac{1}{4}\Bigg[B^2\,ln\frac{(1+B^2+C^2)B^2}{(B^2+C^2)(1+B^2)} + C^2\,ln\frac{(1+B^2+C^2)C^2}{(B^2+C^2)(1+C^2)} - ln\,\frac{1+B^2+C^2}{(1+B^2)(1+C^2)}\Bigg]\Bigg\} \tag{3.22}$$

In the second case there are two finite surfaces in a distance, see 3.13.

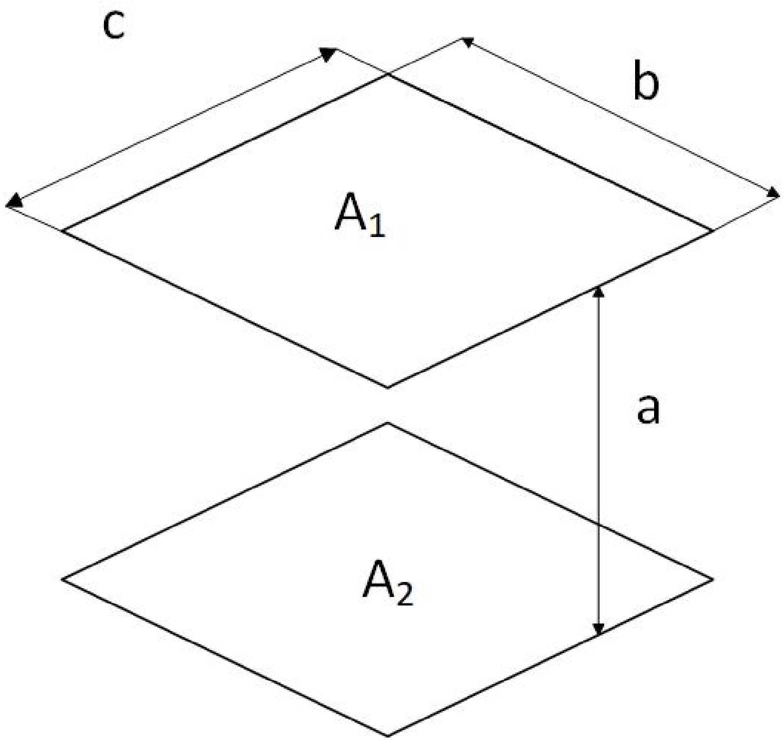


Figure 3.14: Form factor for two surfaces in a distance

$$B = \frac{b}{a} \quad C = \frac{c}{a} \tag{3.23}$$

$$\begin{aligned} F_{ij} = \frac{1}{\pi}\Big[&\frac{1}{BC} ln\Big(\frac{(1+B^2)(1+C^2)}{1+B^2+C^2}\Big) - \frac{2}{B} arctan\, C - \frac{2}{C} arctan\, B \\ &+ \frac{2}{C}\sqrt{1+C^2}\, arctan \frac{B}{\sqrt{1+C^2}} + \frac{2}{B}\sqrt{1+B^2}\, arctan \frac{C}{\sqrt{1+B^2}}\Big] \end{aligned} \tag{3.24}$$

4 Calculation procedure

Before the calculation is carried out, it must be determined which parameters are known and which conditions are specified. With this information and simplifications, which were made at the model, now further unknown quantities can be calculated. The rough procedure is as follows:

1. Establishing the N chemical equations and creating a matrix of stoichiometric coefficients
2. Specification of a temperature in the layer
3. Calculate resulting substance quantity
    - Determine all mole fractions using chemical run numbers (one mole fraction per species)
    - From the stoichiometric matrix, construct the system of equations for the chemical equilibrium (N equations)
    - Calculate the n equilibrium constants at a given temperature
    - Solve the system of equations for the running numbers, put them back into the mole fractions and thus determine the resulting amount of material of each species.
4. For the first law of thermodynamics calculate the unknown heat fluxes
    - Convection Q_{konv}
    - Radiation using the Scholand model
    - Inflowing and outflowing enthalpies of the individual substances
5. Calculate the first law of thermodynamics for all given temperatures
6. Determine the temperature that meets the first law of thermodynamics

4.1 Approaches/Solutions

In stoichiometry, the following case generally exists: Given are N components (also called species) which react according to an initially unknown reaction scheme. An important question arises here: How many reaction equations are required at least to explain the mole change of all components? This is referred to as a set of key reactions. Conversely, if one has a set of reactions: Does this set of intuitively formulated reaction equations contain all key reactions or even those that are not relevant for calculating them? In this case, the second question is whether the intuitively formulated model reaction equations contain a complete set of key reactions. At the same time, this raises another question: Do these formulated key equations suffice to describe the real chemical system? As a first step, therefore, the reactions set up for a sufficient minimum description are sought. Mathematically, this means finding a set of linearly independent equations. To control this, the matrix of stoichiometric coefficients (4.1) is established and the rank R_ν of this matrix is calculated. [1]

Reaction/Species	Species 1	Species 2	Species 3	Species 4	Species 5
Reaction 1					
Reaction 2					
Reaction 3					

Table 4.1: Stoichiometric matrix

The rank R_β is also calculated from the element species matrix 4.2.

Element/Species	Species 1	Species 2	Species 3	Species 4	Species 5
Element 1					
Element 2					
Element 3					

Table 4.2: Element species matrix

A prerequisite for the success of a complete response scheme is that the set of $N - R_(\beta)$ contains key reactions. (N...number of equations) This means that $R_\nu = N - R_\beta$ must be used to obtain a solution for the amount of substance. With an extensive system, it can happen that reactions are overlooked. In this case the result is $R_\nu < N - R_\beta$. Or the reverse case is when too many reactions exist and thus linear dependent equations exist. This would result in $R_\nu > N - R_\beta$. In a reacting system, the molar change of a component is usually caused by several partial reactions. The amount of the reactions is M, where mostly $M > R_\nu$. If the magnitude of the j-th reaction to δn with Δn is given, the so-called reaction run number can be defined as the reaction-specific quantity. [1]

$$\delta n_{ij}/\nu_{ij} = \varepsilon_j(kmol) = (n_{ij,0} - n_{ij})/\nu_{ij} \tag{4.1}$$

The running number measures the progress of the j-th reaction. It changes one unit when the reaction progresses by one turnover. The total mole-change of a component is composed of the amounts of all M reactions in which the species reacts.

$$\Delta n = \sum_{j=1}^{M} \delta n_{ij} = \sum_{j=1}^{M} \nu_{ij} \cdot \varepsilon \; for \; i = 1...N \tag{4.2}$$

From a mathematical point of view, this equation represents an inhomogeneous system of equations consisting of N balance equations and M unknown. However, the coefficient matrix of this system of equations is the transposed matrix of the stoichiometric coefficients. This one has the rank R_ν. To calculate the M running numbers from the N equations one only needs to consider R_ν linearly independent and one can omit the remaining $N - R_\nu$ equations. However, if only the key reactions are taken into account in the reaction profile, then $M = R_\nu$ and the solution is unique. [1].

Once the reaction scheme has been checked for completeness and solubility, the system of equations for the calculation of the resulting substance quantities is established. For this purpose, the individual mole fractions are set up for each substance as a function of the reaction run numbers of the respective reaction. The mole fraction X denotes the ratio of the quantity of substance of the individual substance to the total quantity of substance, i.e. the sum of all substances.

$$X = \frac{n_i}{\sum_1^{Species} n_i} \tag{4.3}$$

The reaction run numbers ε_i indicates the change in the quantity of the individual substances and must be completed in the mole fraction. The program HSChemistry is used to determine the equilibrium constants of the individual reaction equations within a temperature range of $273K$ - $2273K$ and store them in an Excel table. The temperature distances are $\Delta T = 100K$. Intermediate values are interpolated linearly. In the case of the condition $0 <= \varepsilon <= 1$ (molar conversion), ε must therefore refer to the component that is the first to be consumed completely in the reaction sequence, but this depends not only on the stoichiometry of the reaction but also on the composition of the initial mixture. The generalized method looks as follows: [2]

$$y = \frac{n_i^0 + \nu_i \cdot \varepsilon}{\sum n_i^0 + \nu_i \cdot \varepsilon} \tag{4.4}$$

$$K_p = p^{\sum \nu_i} \prod_i y_i^{\nu_i} = p^{\sum \nu_i} \prod_i (\frac{n_i^0 + \nu_i \cdot \varepsilon}{\sum n_i^0 + \nu_i \cdot \varepsilon})^{\nu_i} \tag{4.5}$$

Using a Newton algorithm solver, the system of equations (one equation for every species) is solved in Matlab. The difficulty lies in finding good starting values for the reaction run numbers of the algorithm that calculates the correct solution quickly. For the calculation, a (previously determined) set of random number sets is generated in a certain range. The area is delimited by the following thoughts: The maximum reaction run number ε_{max} is reached when one of the starting materials (i.e. substances with stoichiometric coefficients <0) is exhausted for the first time. The minimum value ε_{min} when the quantity of one of the products ($\nu > 0$) disappears for the first time. Let n be the starting material with $i = n$ and $n_n = 0$ for the formula of epsilon:

$$\varepsilon_{max} = \frac{-n_{n,0}}{\nu_n} \tag{4.6}$$

If m is the product whose substance quantity becomes zero at a greater value of ε than the other products,with $i = m$ follows:

$$\varepsilon_{min} = \frac{-n_{m,0}}{\nu_m} \tag{4.7}$$

With the limits of ε_{max} and ε_{min} several random number sets are generated and made available to the solver. Then, for each solution of ε, the corresponding amount of substance is calculated and stored. After the calculation, the final substance quantities are further restricted. The material values are excluded which are negative and the most frequent values are used for the following calculation. The temperature is determined using the first law of thermodynamics for open systems. Since the structure consists of several identical cells, only one cell is treated in the following.

$$\begin{aligned} 0 = &\dot{Q}_{Brennstoff} + \dot{Q}_{Luft} + \dot{Q}_{ein\ oberer\ Stoffstrom} + \dot{Q}_{ein\ unterer\ Stoffstrom} \\ &- \dot{Q}_{aus\ oberer\ Stoffstrom} - \dot{Q}_{aus\ unterer\ Stoffstrom} - \dot{Q}_{Konvektion} - \dot{Q}_{Strahlung} \end{aligned} \tag{4.8}$$

To quantify the enthalpies, these are calculated from the data determined for the molar heat capacity $\mathrm{c_p}$. The values for *cp* are in turn determined from the value table of the HSChemistry program. The individual c_p values are determined for each substance and for a temperature range of 273K - 2273K in 100K steps and stored in an Excel table. The *cp* values are determined using the Kelley polynomial, with different coefficients (A,B,C,D) tabulated for each substance or temperature range.

$$c_p(T) = A + B \cdot 10^{-3} \cdot T + C \cdot 10^5 \cdot T^{-2} + D \cdot 10^{-6} \cdot T^2 \tag{4.9}$$

The molar enthalpy of the substance can be determined from the heat capacity and the temperature.

$$H(T) = H_f(298.15) + \int_{298.15}^{T} cpdT + \sum H_{tr} \tag{4.10}$$

Where H_f is the standard enthalpy of formation at $298.15K$ and H_{tr} the enthalpy of formation at crystal lattice changes or aggregate changes.

The control volume is placed directly at the boundaries of the cell. The fuel and air flows are external incoming material quantities, independent and may vary for each cell. The out flowing amount of material is the amount of material that leaves the cell after the reaction, up or down and enters the next cell Q_{aus}. Inflowing substance quantities are the substance quantities that enter from the cell above or below Q_{ein}. The red arrows symbolize heat flows. By convection with the colder wall, the heat flow $Q_{convection}$ is emitted. $Q_{radiation}$ is the net heat flux that is transmitted by the radiation into the neighbouring cell or radiated from the neighbouring cell. Depending on the cell temperature, this can be positive or negative. To determine the inflowing fuel or air heat flows, the quantities of material (mole) are multiplied by the respective molar enthalpy (KJ/mol). As shown in the drawing 4.1, there are 2 material flows that connect the

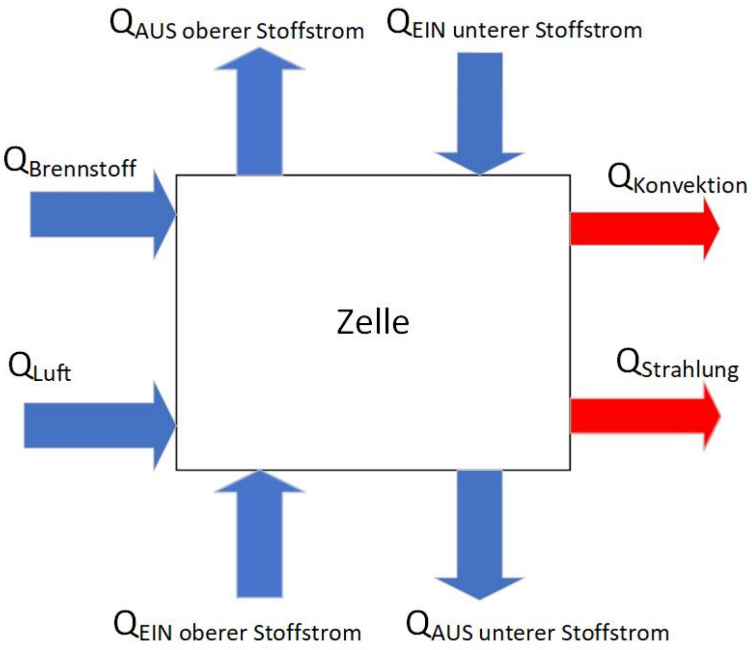


Figure 4.1: 1 st law of thermodynamic for one cell

individual cells with each other. One is directed upwards for substances flowing upwards according to the model, such as exhaust gases, and the other is directed downwards to describe the substances flowing downwards. The exact material flows flowing upwards or downwards must be determined before the start of the calculation. In the program, the substances contained in the b-vector are transferred upwards to the next cell, while all other substances are transported by default to the lower neighbouring cell. The convective heat loss is controlled via

$$Q_{konv} = \alpha \cdot A_i \cdot (T - T_{wall}) \tag{4.11}$$

The wall temperature is given for simplicity's sake, since it can be measured well in real boilers and some comparative values exist. The temperature T is the temperature that prevails in the cell. Alpha is the heat transfer coefficient and depends on factors such as the flow velocity, the geometry and the material properties of the fluid. The calculation of the heat transfer is not dealt with in detail here, since it can vary greatly depending on the boiler and requires its own consideration. The side surface of each cell is used as the surface, as these are open at the top and bottom, except for the "bottom cell". The convective heat loss can be easily quantified with the values for α, the area A_i and the temperatures.

The calculation of the radiation requires more effort than convection. Essentially, this is calculated using Scholand's net radiation model. Scholand's model describes the radiation exchange of a closed space containing a gas. In the model of the black liquor boiler it is used for the heat exchange of individual cells with different temperatures, see chapter 3.8.4

With the now known net radiant heat $Q_{radiation}$ which connects the individual cells, can be used in the first main sentence. According to the formula for the first main set, zero should come out, which will not be the case with the previously assumed temperatures. The difference to zero is stored together with the temperature in a matrix, see 4.3.

Temperature	Difference
800	$-8 \cdot 10^7$
1000	$-4 \cdot 10^3$
1200	$5 \cdot 10^2$

Table 4.3: Example of the Difference depending on the temperature

The process of calculating the amount of substance and then the first main clause is repeated for one cell until all temperatures in the temperature range have been used. In the following, the sign change of the differences in the matrix is searched for and interpolated linearly. The resulting temperature is stored as the cell temperature and used for further calculations that include the cell temperature. All cell temperatures are calculated according to this principle. Once these are known, the resulting quantities of substances are exchanged between the cells and fuel or air, depending on the model, is refilled. After 2 calculation runs, the first calculation of the net heat radiation between the individual cells takes place. This is done first with the calculation of the form factors, see chapter 3.8.4 and in the second step a system of matrices is created from the general equation. With this system of equations, the radiant flux density W can be determined, through which the net radiant heat can be inferred. After the first calculation of the radiant heat, the cell temperature is determined anew for all cells. The radiation term $Q_{Strahlung}$ is stored and compared with the following value. If the difference is less than a certain value $\Delta Q_{Strahlung}$ given at the beginning, the calculation is terminated and the results of the temperatures and mass quantities of the individual cells are output.

4.2 A closer look at the matlab-code

The chapter 4.1 gave a more general look at the basic understanding of the mathematical procedure itself. In this chapter the focus is more on the coding side of the model. It is an object-oriented program consisting of two objects:

1. Object "Zelle"
2. Object "Reaktor"

The object "Zelle" is defined as one layer of the model. Its properties are:

- Temperature
- n-Vector
- nu-matrix
- geometry of one cell (depth,width,height)
- "Schichtindex" is the index of the specific layer
- alpha the heat transfer coefficient
- degree of emittance of the walls
- degree of emittance, reflection and transmittance of the gas

The object "Reaktor" contains all the objects "Zelle" and connects them. The main program with all the initial values and the general structure is called "Main".

To get a better understanding on the structure of the code and how it works a flow diagram was made, see 4.2.There are two major structures which are very important:

1. The order of the species in stoichiometric matrix
2. The order of the species inside the matlabcode, see 4.5

The n-vector contains all the amounts of substances (in mole) that go into the chamber. Its order is the exact same order as the one in the stoichiometric matrix. All indexes of the following calculation are based on this particular order (4.5).
An example of an stoichiometric matrix and the associated n-vector.

Reaktions/ Species	C	O2	CO2	N2
1				
2				
3				

$$\rightarrow n = \begin{pmatrix} C \\ O_2 \\ CO_2 \\ N_2 \end{pmatrix}$$

Table 4.4: The stoichiometric matrix for the example and the associated n-vector

One can see now that the carbon is on position 1, oxygen on position 2 and so on. To link up the right data (e.g. enthalpies) to the species, one must take the order of the species in the matlab-code into account, see 4.5. The v-vector links this both orders together. In the example the v-vector would look like this.

$$n = \begin{pmatrix} C \\ O_2 \\ CO_2 \\ N_2 \end{pmatrix} \rightarrow v = \begin{pmatrix} 1 \\ 24 \\ 3 \\ 22 \end{pmatrix}$$

Index	Species	Index	Species	Index	Species	Index	Species	Index	Species
1	C	7	HCl	13	KOH	19	Na_2CO_3	25	S
2	CO	8	H_2	14	K_2CO_3	20	Na_2SO_4	26	SO_2
3	CO_2	9	H_2O	15	K_2SO_4	21	NaOH		
4	Cl	10	H^2S	16	Na	22	N_2		
5	CH_4	11	K	17	NaCl	23	NO_2		
6	C_2H_6	12	KCl	18	Na_2S	24	O_2		

Table 4.5: Order of the species in the matlab-code

The b_strom-vector gives information about the species that flow upwards and must be changed manually. The number in the vector indicates the position of the substance in relation to the n-vector. For example, if one wants the carbon dioxide CO_2 and the nitrogen N_2 to flow upwards the b_strom-vector looks as follows.

$$b_{strom} = \begin{pmatrix} 3 & 4 \end{pmatrix}$$

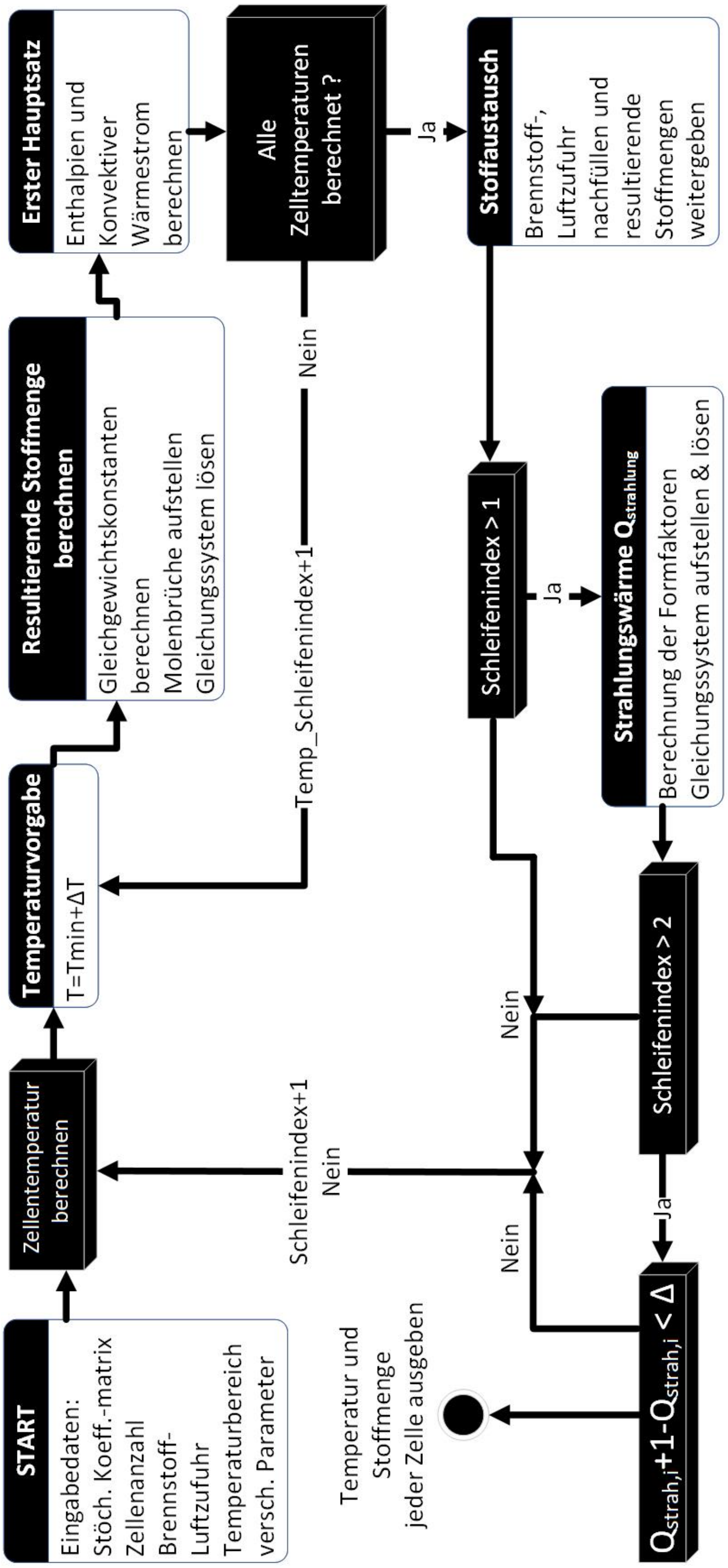


Figure 4.2: The underlying structure of the matlab-code

At the beginning the input data must be filled out completely to ensure proper function. Table 4.6, shows the needed information together with the units.

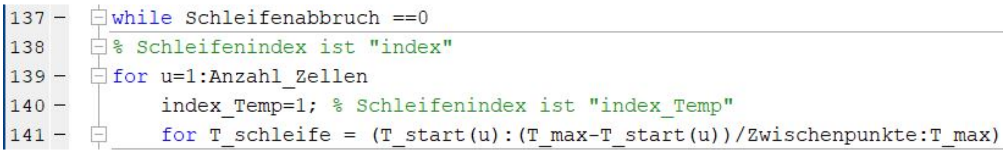
Name	Unit	Name	Unit
nu_matrix	-	Zwischenpunkte	-
b_strom	-	T_Wand	K
v	-	T_Luft	K
Anzahl_Zellen	-	T_Br	K
n_brennstoff	mol	e	-
n_luft	mol	e_g	-
t b h	m	t_g	-
alpha	W/m^2 K	g_g	-
T_max	K	delta_Temp	K
T_start	K	Q_strah_delta	W

Table 4.6: Input data and units

nu_matrix	...	The stoichiometric matrix (see 4.1)
b_strom	...	The vector with the placings of the species in the n-Vector that flow upwards (all the other species flow downwards)
v	...	This vector connects the order of the species in the matlab code together with the order of the species in the stoichiometric matrix
Anzahl_Zellen	...	Number of cells
n_brennstoff	...	Contains the amounts of fuel entering the cells
n_luft	...	Contains the amount of air (oxygen and nitrogen) entering the cells
t,b,h	...	depth (t), width (b) and height (h) of one cell
alpha	...	The heat transfer coefficient between the gas and the wall
T_max	...	The upper temperature limit for the calculation
T_start	...	The lower temperature limit for the calculation
Zwischenpunkte	...	The number of intermediate points between T_start and T_max
T_wand	...	Temperature of the chamberwall
T_Luft	...	The temperature of the air entering the cell
T_Br	...	The temperature of the fuel entering the cell
e	...	degree of emittance of the walls
e_g	...	degree of emittance of the gas
t_g	...	degree of transmittance of the gas
g_g	...	degree of reflection of the gas
delta_Temp	...	the maximum allowed temperature difference between two comparing temperatures of two calculation cycles
Q_strah_delta	...	the maximum allowed heat flow difference between two comparing heat fluxes of two calculation cycles

After assigning the relevant data to the variables the calculation starts by giving the object "Zelle" the information it needs, see 4.2.

For calculating the temperature of the cell a for-loop is made to go through all cells separately starting with cell number 1, the bottom of the chamber. Another for-loop is made to use all the preset temperatures for the interpolation later on. The subdivision of the temperature vector can be seen in figure 4.4.



```
while Schleifenabbruch ==0
% Schleifenindex ist "index"
for u=1:Anzahl_Zellen
    index_Temp=1; % Schleifenindex ist "index_Temp"
    for T_schleife = (T_start(u):(T_max-T_start(u))/Zwischenpunkte:T_max)
```

Figure 4.3: The first two for-loops

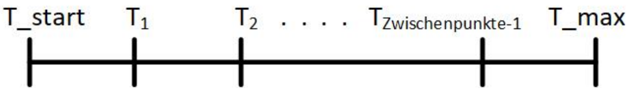
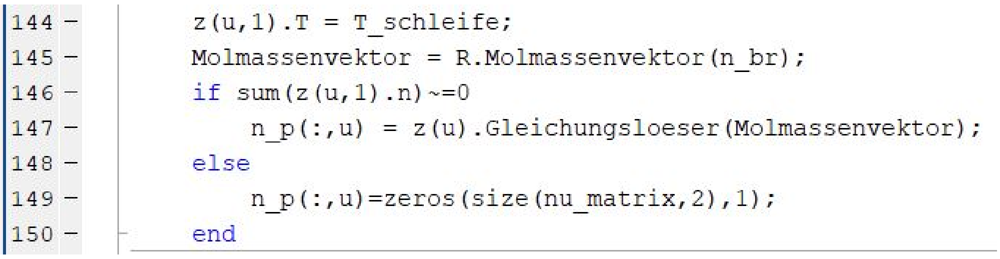


Figure 4.4: The subdivision of the temperature vector

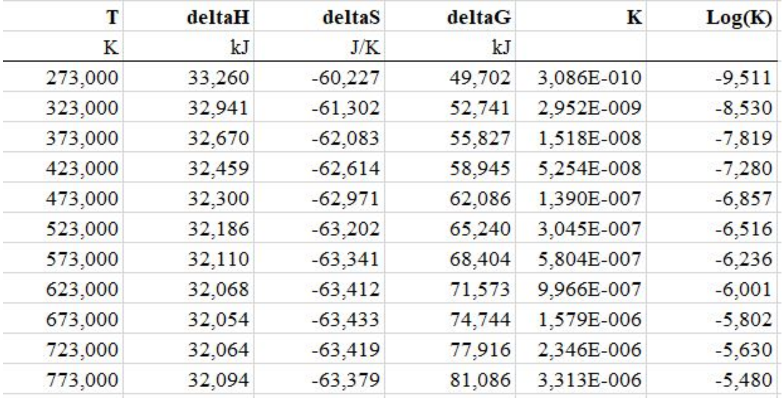
The preset temperature can now be used to calculate the resulting substance quantity of the individual cell. A if-loop keeps the program from calculating the resulting amount of substance if there is no substance at all, see 4.5, line 146.



```
144 -       z(u,1).T = T_schleife;
145 -       Molmassenvektor = R.Molmassenvektor(n_br);
146 -       if sum(z(u,1).n)~=0
147 -           n_p(:,u) = z(u).Gleichungsloeser(Molmassenvektor);
148 -       else
149 -           n_p(:,u)=zeros(size(nu_matrix,2),1);
150 -       end
```

Figure 4.5: Calculating the resulting amount of substance

The function "Gleichungsloeser" is located in the object "Zelle" and calculates the resulting substances based on the chemical reactions respectively on the stoichiometric matrix. To solve the set of equations a Newton-Rhapson-algorithm is used. Therefore a set of starting points is pre generated, as mentioned in 24. Looking at one of the equations in the set, see 4.5, one realizes that the equilibrium constant (K_p), which depends on the temperature, is unknown. The equilibrium constant is extracted from an Excel sheet, see 4.6 and is linearly interpolated. To avoid difficulties the maximum value of K can be set to a certain value. The default value is 10^8.



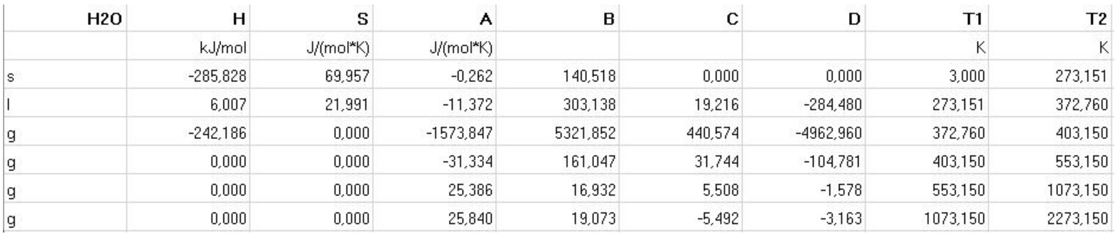
T	deltaH	deltaS	deltaG	K	Log(K)
K	kJ	J/K	kJ		
273,000	33,260	-60,227	49,702	3,086E-010	-9,511
323,000	32,941	-61,302	52,741	2,952E-009	-8,530
373,000	32,670	-62,083	55,827	1,518E-008	-7,819
423,000	32,459	-62,614	58,945	5,254E-008	-7,280
473,000	32,300	-62,971	62,086	1,390E-007	-6,857
523,000	32,186	-63,202	65,240	3,045E-007	-6,516
573,000	32,110	-63,341	68,404	5,804E-007	-6,236
623,000	32,068	-63,412	71,573	9,966E-007	-6,001
673,000	32,054	-63,433	74,744	1,579E-006	-5,802
723,000	32,064	-63,419	77,916	2,346E-006	-5,630
773,000	32,094	-63,379	81,086	3,313E-006	-5,480

Figure 4.6: The excel-sheet for reading out the equilibrium constant

For the solver the equations were adjusted to give zero. The solution are the run numbers ε_i for every species. With the definition of the run number it is possible to calculate the resulting amount of substances for all species.

$$n_i = n_i^0 + \nu_i \cdot \varepsilon_i \tag{4.12}$$

The next step is to determine the equation for the first law of thermodynamics of the cell for the given temperature. To do so one has to compute the enthalpies H_i and the convective heat flux Q_{konv} first. Q_{konv} can be calculated using formula 4.11. For the enthalpies an excel sheet with a certain temperature range is used to compute the heat capacity at constant pressure c_p, see formula 4.9.



H2O	H	S	A	B	C	D	T1	T2
	kJ/mol	J/(mol*K)	J/(mol*K)				K	K
s	-285,828	69,957	-0,262	140,518	0,000	0,000	3,000	273,151
l	6,007	21,991	-11,372	303,138	19,216	-284,480	273,151	372,760
g	-242,186	0,000	-1573,847	5321,852	440,574	-4962,960	372,760	403,150
g	0,000	0,000	-31,334	161,047	31,744	-104,781	403,150	553,150
g	0,000	0,000	25,386	16,932	5,508	-1,578	553,150	1073,150
g	0,000	0,000	25,840	19,073	-5,492	-3,163	1073,150	2273,150

Figure 4.7: The excel-sheet for reading out the heat capacity at constant pressure

Figure 4.7 presents variable data for H_2O. The first column shows the state of aggregation and the second column the corresponding enthalpies of transformation in $\frac{KJ}{mol}$. The third column is the entropy, but it is not used in this context. More important are the columns 4 to 7 with the coefficients A,B,C,D for the Kelley equation (4.9) to calculate the local c_p ($\frac{J}{molK}$) at the given temperature. The last two columns are the temperature ranges for the values in the row. With the information from the excel-sheet and 4.10 one can calculate the molar enthalpy (in $\frac{J}{mol}$).

The resulting heat flux of a material flow that leaves the system border is determined by multiplication of the molar mass with the related specific enthalpy H.

Looking at figure 4.1 the first law of thermodynamics, for one given temperature, can be evaluated using 4.8. Attention should be paid to the fact that for the bottom cell and the top cell the equation for the first law of thermodynamic is a bit different. For example at the bottom cell there is no $Q_{EIN\,oberer\,Stoffstrom}$ and no $Q_{AUS\,unterer\,Stoffstrom}$, see 3.4.

By repeating the calculation with every temperature of the temperature vector and plotting every temperature with the difference of the first law of thermodynamics in a x-y diagram one gets 4.8.

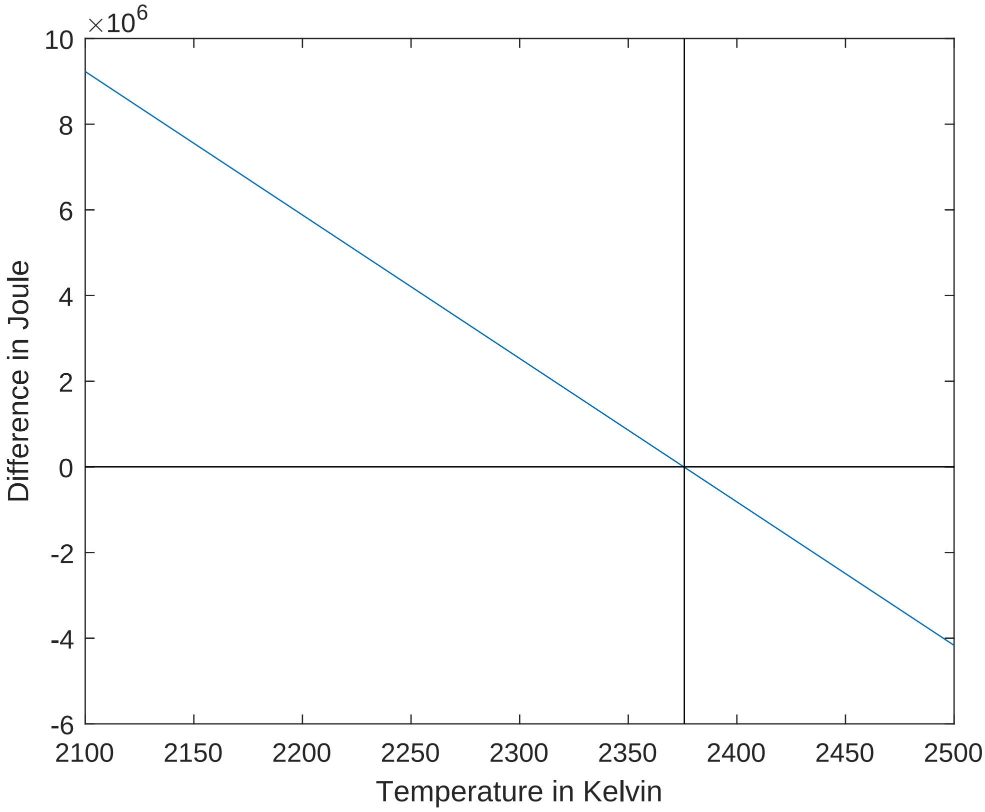


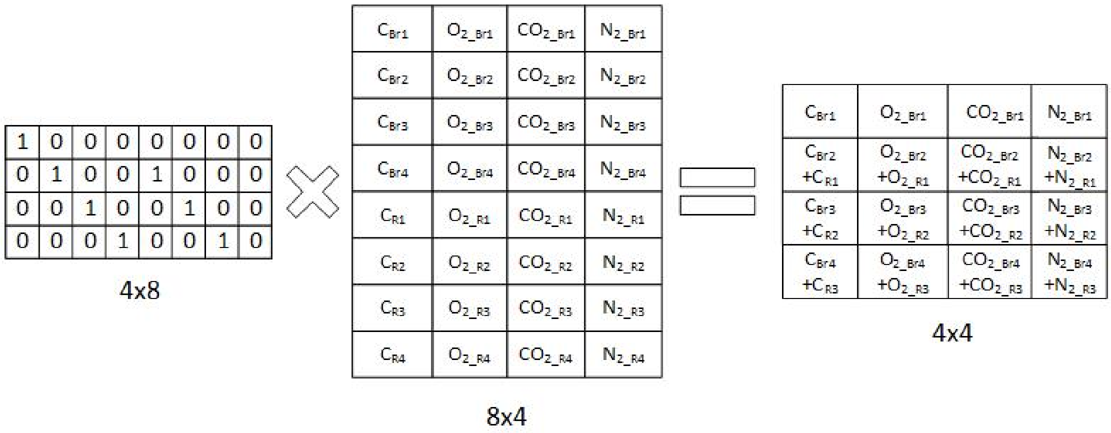
Figure 4.8: Plotting the "difference" over the temperature

Since in the first law of thermodynamics the result must be zero, the point of intersection of the blue line with the x-axis is the desired temperature. In the case of figure 4.8 the temperature is approximately 2375 Kelvin.

After determination of the temperature the next step is to exchange the molar masses of the cells in regard to the flow direction.

The goal is to find some kind of matrix that gives the cells the reaction products of the cell above or underneath and at the same time fills in the fuel/air from the outside. So the first step is to separate the reaction products and the fuel/air and create a matrix with the fuel/air supply and the reaction products for every species and for every cell. The result must be a matrix , for example for the upward flow, with the first row consisting of just the fuel/air supply (index Br). The second row must consist of the fuel/air supply for the second cell (index Br2) plus the reaction products of cell 1 (index R1) and so on. For the downward flow it is the other way around.

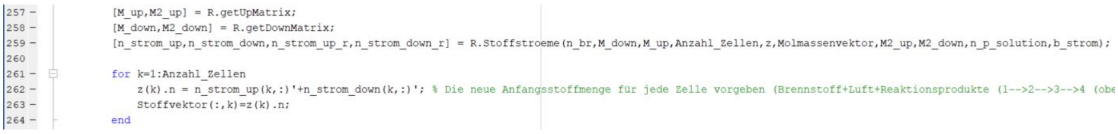
With this information, a distribution matrix for the upward (M_up) and downward (M_down) flow can be generated. Figure 4.9 shows such a system in regards to the upward flow. The system of substances is equal to the order of the stoichiometric matrix and it consists of 4 cells. Keep in mind that in this example all 4 species flow upwards, so the matrix consists of all 4 species and gets multiplied by the matrix called M_up.



$$\underbrace{\begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 \end{bmatrix}}_{4x8} \times \underbrace{\begin{bmatrix} C_{Br1} & O_{2\_Br1} & CO_{2\_Br1} & N_{2\_Br1} \\ C_{Br2} & O_{2\_Br2} & CO_{2\_Br2} & N_{2\_Br2} \\ C_{Br3} & O_{2\_Br3} & CO_{2\_Br3} & N_{2\_Br3} \\ C_{Br4} & O_{2\_Br4} & CO_{2\_Br4} & N_{2\_Br4} \\ C_{R1} & O_{2\_R1} & CO_{2\_R1} & N_{2\_R1} \\ C_{R2} & O_{2\_R2} & CO_{2\_R2} & N_{2\_R2} \\ C_{R3} & O_{2\_R3} & CO_{2\_R3} & N_{2\_R3} \\ C_{R4} & O_{2\_R4} & CO_{2\_R4} & N_{2\_R4} \end{bmatrix}}_{8x4} = \underbrace{\begin{bmatrix} C_{Br1} & O_{2\_Br1} & CO_{2\_Br1} & N_{2\_Br1} \\ C_{Br2}+C_{R1} & O_{2\_Br2}+O_{2\_R1} & CO_{2\_Br2}+CO_{2\_R1} & N_{2\_Br2}+N_{2\_R1} \\ C_{Br3}+C_{R2} & O_{2\_Br3}+O_{2\_R2} & CO_{2\_Br3}+CO_{2\_R2} & N_{2\_Br3}+N_{2\_R2} \\ C_{Br4}+C_{R3} & O_{2\_Br4}+O_{2\_R3} & CO_{2\_Br4}+CO_{2\_R3} & N_{2\_Br4}+N_{2\_R3} \end{bmatrix}}_{4x4}$$

Figure 4.9: Example for the multiplication with the M_up Matrix

One can see that the resulting matrix is the one which was wanted in the first place. The function who creates the M_up or the M_down matrix is called getUpMatrix or getDownMatrix and is located in the object "Reaktor". Line 262 in figure 4.10 delivers the new starting values for the n-vector in the object "Zelle".

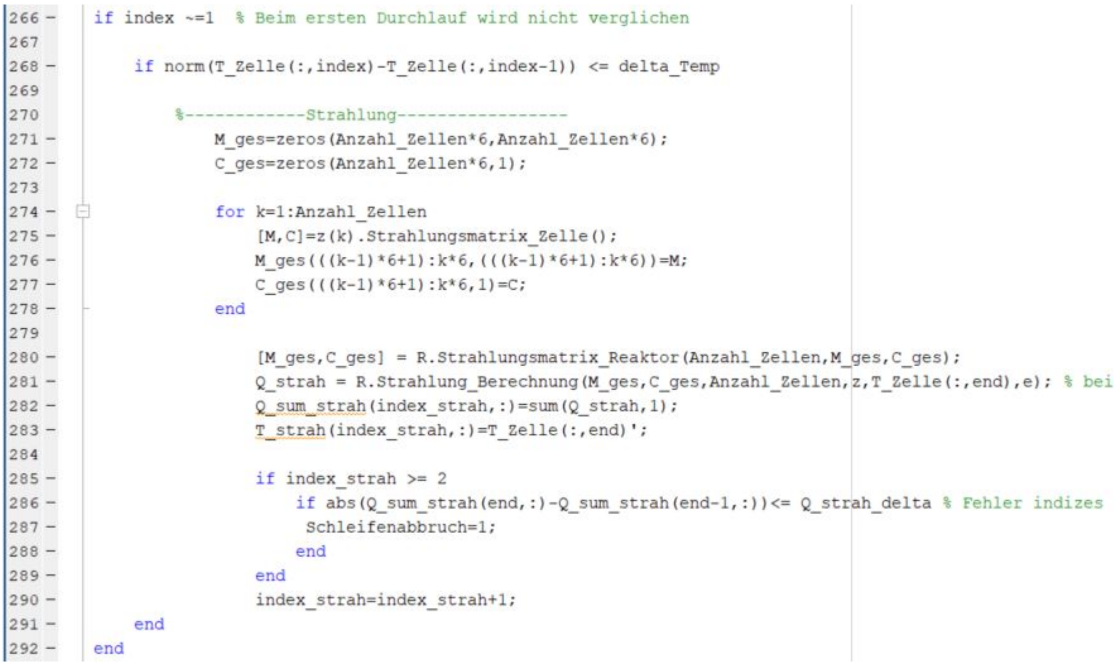


```
257 -          [M_up,M2_up] = R.getUpMatrix;
258 -          [M_down,M2_down] = R.getDownMatrix;
259 -          [n_strom_up,n_strom_down,n_strom_up_r,n_strom_down_r] = R.Stoffstroeme(n_br,M_down,M_up,Anzahl_Zellen,z,Molmassenvektor,M2_up,M2_down,n_p_solution,b_strom);
260
261 -          for k=1:Anzahl_Zellen
262 -              z(k).n = n_strom_up(k,:)'+n_strom_down(k,:)'; % Die neue Anfangsstoffmenge für jede Zelle vorgeben (Brennstoff+Luft+Reaktionsprodukte (1-->2-->3-->4 (obe
263 -              Stoffvektor(:,k)=z(k).n;
264 -          end
```

Figure 4.10: Code for the exchange of the cells

If all cell temperatures have been calculated at least 2 times and if the temperature difference of the mean value of all cells is below a certain value delta_temp, the radiation term Q_{Strah} is calculated.

In the first step the M-matrix and the C-vector are created and manipulated according to the model. The system of equations $M \cdot W = C$ (3.14) was then set up as shown in Figure 4.11 and the radiation flux density W was resolved accordingly.



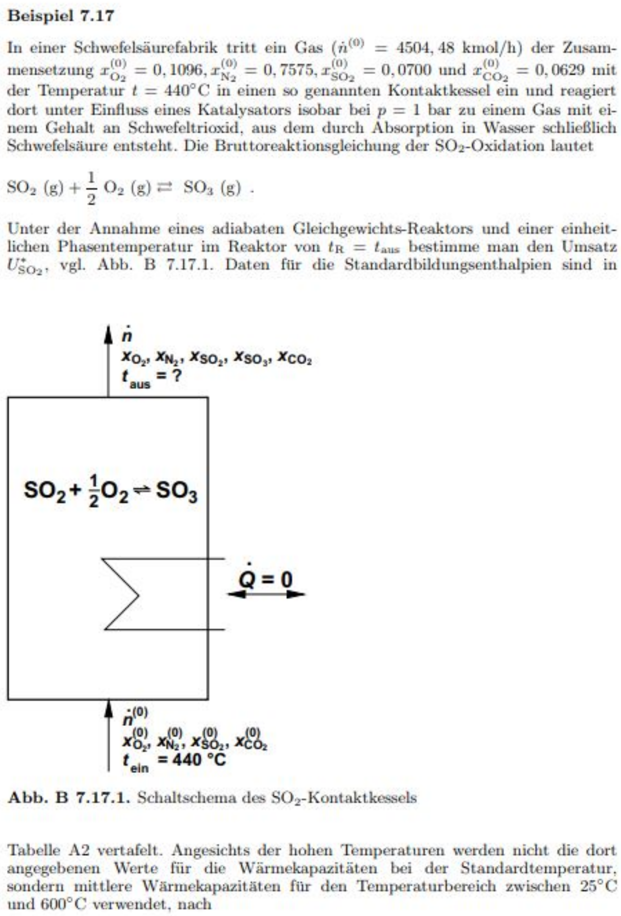
```
266  if index ~=1  % Beim ersten Durchlauf wird nicht verglichen
267
268      if norm(T_Zelle(:,index)-T_Zelle(:,index-1)) <= delta_Temp
269
270          %------------Strahlung-----------------
271              M_ges=zeros(Anzahl_Zellen*6,Anzahl_Zellen*6);
272              C_ges=zeros(Anzahl_Zellen*6,1);
273
274              for k=1:Anzahl_Zellen
275                  [M,C]=z(k).Strahlungsmatrix_Zelle();
276                  M_ges(((k-1)*6+1):k*6,(((k-1)*6+1):k*6))=M;
277                  C_ges(((k-1)*6+1):k*6,1)=C;
278              end
279
280                  [M_ges,C_ges] = R.Strahlungsmatrix_Reaktor(Anzahl_Zellen,M_ges,C_ges);
281                  Q_strah = R.Strahlung_Berechnung(M_ges,C_ges,Anzahl_Zellen,z,T_Zelle(:,end),e); % bei
282                  Q_sum_strah(index_strah,:)=sum(Q_strah,1);
283                  T_strah(index_strah,:)=T_Zelle(:,end)';
284
285                  if index_strah >= 2
286                      if abs(Q_sum_strah(end,:)-Q_sum_strah(end-1,:))<= Q_strah_delta % Fehler indizes
287                       Schleifenabbruch=1;
288                      end
289                  end
290                  index_strah=index_strah+1;
291      end
292  end
```

Figure 4.11: Code for the calculation of the radiation

If the radiation term has been calculated twice (line 285) and the difference between these two terms is below a tolerance Q_strah_delta (line 286), the whole calculation is stopped and the results are saved.

5 Verifying the model and comparison

In general, a model or the results of the model should be reviewed to ensure its accuracy. Such models are often compared with existing examples/models. In this case, an existing example was first recalculated with the data available there. Specifically, it was an example from the book [3]. This has the advantage that the calculation can be better understood, since the correct steps are already known and intermediate results can be compared.



Beispiel 7.17

In einer Schwefelsäurefabrik tritt ein Gas ($\dot{n}^{(0)} = 4504,48$ kmol/h) der Zusammensetzung $x_{O_2}^{(0)} = 0,1096$, $x_{N_2}^{(0)} = 0,7575$, $x_{SO_2}^{(0)} = 0,0700$ und $x_{CO_2}^{(0)} = 0,0629$ mit der Temperatur $t = 440°C$ in einen so genannten Kontaktkessel ein und reagiert dort unter Einfluss eines Katalysators isobar bei $p = 1$ bar zu einem Gas mit einem Gehalt an Schwefeltrioxid, aus dem durch Absorption in Wasser schließlich Schwefelsäure entsteht. Die Bruttoreaktionsgleichung der SO_2-Oxidation lautet

$$SO_2\ (g) + \frac{1}{2}\ O_2\ (g) \rightleftarrows\ SO_3\ (g)\ .$$

Unter der Annahme eines adiabaten Gleichgewichts-Reaktors und einer einheitlichen Phasentemperatur im Reaktor von $t_R = t_{aus}$ bestimme man den Umsatz $U_{SO_2}^{*}$, vgl. Abb. B 7.17.1. Daten für die Standardbildungsenthalpien sind in

Abb. B 7.17.1. Schaltschema des SO_2-Kontaktkessels

Tabelle A2 vertafelt. Angesichts der hohen Temperaturen werden nicht die dort angegebenen Werte für die Wärmekapazitäten bei der Standardtemperatur, sondern mittlere Wärmekapazitäten für den Temperaturbereich zwischen 25°C und 600°C verwendet, nach

Figure 5.1: Example of a contact boiler for sulfuric acid taken from [3]

Figure 5.1 shows a example in book [3] for calculating the equilibrium temperature and the conversion in a contact boiler with sulphur dioxide, oxygen and sulphur trioxide. The input parameters are:

- the inlet temperature $t_{ein} = 440°$
- the chemical equation of $SO_2 + O_2 = SO_3$
- the mole fraction of SO_2, O_2, SO_3 and CO_2
- the whole molar flux $\dot{n}^{(0)} = 4504.48$ kmol/h
- the pressure $p = 1\ bar$
- the isobaric heat capacities for the species (also taken from [3])

$c_p^{ig} / \left(\frac{J}{mol\ K}\right)$	SO_2	SO_3	N_2	O_2	CO_2
	48,7	66,4	31	31,9	48

After entering and adjusting the data in matlab, the code found the right solutions for the temperature $t_{aus} = 597.4°$ and molar mass flows of each species.

The second test included the comparison with the commercial program "Aspen". The model consisted of two adiabat series-connected Gibbs-Reactors, each with a fuel and air supply and the same reaction equations:

$$C + O_2 = CO_2$$
$$0.5N_2 + O_2 = NO_2$$

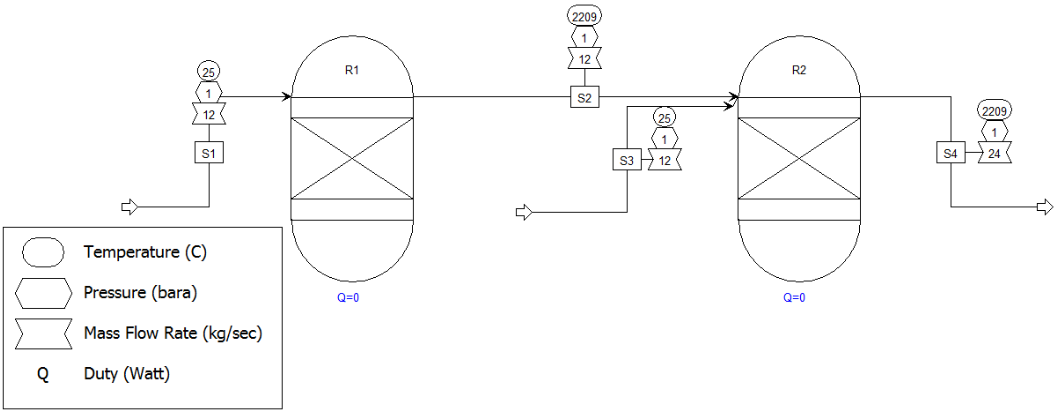


Figure 5 shows the structure of the two reactors connected in series. Both reactors are fed with the same fuel, see below.

$$n = \begin{pmatrix} 80\,mole \\ 80\,mole \\ 0\,mole \\ 296\,mole \\ 0\,mole \end{pmatrix} = \begin{matrix} C \\ O_2 \\ CO_2 \\ N_2 \\ NO_2 \end{matrix}$$

The material quantity results of the two examples look as follows (all quantities in mole):

Species/ Programm	C	O_2	CO_2	N_2	NO_2
Aspen	$4.23 \cdot 10^{-12}$	$4.23 \cdot 10^{-12}$	79.999996	296	$6.634 \cdot 10^{-6}$
Matlab	0.547	0.547	79.45	296	$5.546 \cdot 10^{-5}$

One can clearly see the difference between the remaining carbon and oxygen quantities. This is due to the limitation of the equilibrium constants in the matlab code for the chemical reactions ($K_{max} = 100000$ instead of e.g. $K_C \approx 10^{10}$). Tests have shown that in this case a higher equilibrium constant also affects the remaining amount of substance. The upper limit was introduced because otherwise the equation solver cannot find a reliable solution due to the very high equilibrium constants at some temperatures. The temperature in the program Aspen is 2209 °C, the matlab-code calculates a solution of 2198 °C. The difference of 11 °C can with high probability be attributed to the difference of the equilibrium constants and the other material values for H and c_p.

5.1 Verifying the radiation model

Both models mentioned in the previous chapter 5 were calculated without the influence of radiation. This is due to the incorrect radiation calculation. According to the plan, the radiation model should be included in the program but could not be corrected even after a long search due to technical reasons and a certain time pressure. The main problem lies in setting up the M matrix see 3.14. This essentially consists of the entries of 3.13. Where F_{ij} represents the formfactors, τ_{ij} the degree of transmission of the gas and ρ_i the degree of reflection of the wall i. τ_{ij} of the gas was assumed with $\tau = 0.7$ in every section. ρ_i was set for every wall to $\rho = 0.7$. The form factors, see 3.8.4, were checked so that $\sum_{i=1}^{6} F_i = 1$.

After checking the values of the M matrix the matlab function for the radiation was tested with different numbers of cells and temperatures. Following a few test runs with results to be assessed as realistic (order of magnitude was appropriate and opposite walls had the same heat flows), there were however cases, with which the equation solver calculated no or not useful values (order of magnitude $Q_{wand} \approx 10^{30} kW$ or partly complex values). Therefore it cannot be excluded that it comes to errors within the radiation calculation. The exact cause of this error could not be found however due to the complexity in the equation system. For time reasons, the focus was placed on the correct calculation of the amount of substance and thus the cell temperature. Nevertheless, the program code is retained so that future work on the radiation code can be carried out.

6 Summary

English version

In general, boilers are complex. With some simplifications models can be developed that allow good approximations for real applications. The black liquor boiler is a level of complexity higher with the simultaneous oxidation and reduction in the same boiler and the many related chemical reactions. It is not easy to find suitable simplifications here and it is often necessary to fall back on existing models or simplifications as these types of models are relatively rare. This work was planned to become a model for the black liquor boiler, but due to the high complexity some problems like for example the high number of reactions and the resulting equations could not always be solved and therefore no constantly satisfactory solutions could be calculated. A much more general approach was then chosen, allowing for different material flows, cell counts, fuel feeds, etc.. This makes it possible to simply extend the model and test it again and again until one is created that describes the black liquor boiler. In this work it was not possible to deal with it in more detail, since an extension would go beyond the scope. Nevertheless, the matlabcode and the model itself provide a good basis for further work.

The model is very general and can be manipulated for various applications in the boiler area. Each model consists essentially of:

1. A variable Number of cells
2. One variable fuel-air supply per cell
3. An upward and downward mass flow for different material flow directions
4. A set of reaction equations for all cells
5. A set of input parameters

To use it for black liquor boilers the 5 points have to be changed. Input data generally includes heat transfer coefficients, dimensions, wall temperatures and the temperature range.

German version

Im Allgemeinen sind Kessel ein relativ komplexes Konstrukt. Mit einigen Vereinfachungen können jedoch gute Modelle entwickelt werden, die gute Annäherungen für reale Anwendungen ermöglichen. Der Schwarzlaugekessel ist eine weitere Komplexitätsstufe höher, da die gleichzeitige Oxidation und Reduktion im gleichen Kessel und die vielen damit verbundenen chemischen Reaktionen stattfinden. Es ist nicht einfach, hier geeignete Vereinfachungen zu finden und oft ist es notwendig, auf bestehende Modelle oder Vereinfachungen zurückzugreifen, da diese Arten von Modellen relativ selten sind. Diese Arbeit sollte zu einem Modell für den Schwarzlaugekessel werden, aber aufgrund der hohen Komplexität konnten einige Probleme wie z.B. die hohe Anzahl der Reaktionen und die damit verbundenen Gleichungen nicht immer gelöst werden und somit konnten keine konstant zufriedenstellenden Lösungen berechnet werden. Aufgrund dessen wurde ein viel allgemeinerer Ansatz gewählt, der unterschiedliche Materialflüsse, Zellenzahlen, Kraftstoffzuführungen usw. berücksichtigt. Dadurch ist es möglich, das Modell einfach zu erweitern und immer wieder zu testen, bis eines entsteht, das den Schwarzlaugekessel beschreibt. In dieser Arbeit war es nicht möglich, näher darauf einzugehen, da eine Erweiterung den Rahmen sprengen würde. Dennoch bieten der Matlabcode und das Modell selbst eine gute Grundlage für die weitere Arbeit.

Das Modell ist sehr allgemein gehalten und kann für verschiedene Anwendungen im Kesselbereich manipuliert werden. Jedes Modell besteht im Wesentlichen aus:

1. Einer variablen Anzahl an Zellen
2. Eine Brennstoff- und Luftzufuhr pro Zelle
3. Ein auf- und abwärts gerichteter Massenstrom
4. Ein chemisches Gleichungssystem für alle Zellen
5. Eine Anzahl von Eingabeparametern

Um einen Schwarzlaugenkessel zu berechnen, müssen zumindest diese 5 Punkte verändert werden. Die Eingabedaten umfassen allgemeine Parameter wie den Wärmeübergangskoeffizient, die Geometrie, die Wandtemperaturen und ein Temperaturbereich.

7 Outlook and improvements

In principle, any model can be improved at will. However, the question is to what extent such a change in the model affects other parameters such as computing time, susceptibility to failure and complexity. An important aspect that could not be dealt with due to the great effort involved is radiation. In the program such a calculation was integrated however this is not correct and delivers obviously wrong values for the radiant heat. The error probably lies in the structure of the equation system for the radiant flux density W. In the beginning, the model was designed for the black liquor boiler. After some implementations and experiments, the calculation of the amount of substance became a problem. Due to the size of the chemical system and the resulting mathematical equation system, no satisfactory solutions for the run numbers could be found in each step. The model was then modified so that different chemical systems and sizes could be calculated. This means that for future work on the model, the stoichiometric matrix must be changed in terms of entries (columns and rows must be adapted to the chemical equations) and a solution to the problem of calculating the resulting amount of substance must be found in order to implement the black liquor boiler in the model.

Another point is the technical optimization of the program. How exactly such an optimization looks like or at which program parts it seems meaningful cannot be said at the moment. However, there is a high probability that one will be able to further improve the performance.

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List of Figures

List of Tables

8 Attachment

Temperature, enthalpy, entropy and the equilibrium constant of all reactions for the black liquor boiler for a temperature range of 273K-2273K

$Na_2S + 2O_2(g) = Na_2SO_4$

T K	**deltaH** kJ	**deltaS** J/K	**deltaG** kJ	**K**	**Log(K)**
273,000	-1021,460	-355,763	-924,337	7,475E+176	176,874
473,000	-1022,154	-358,395	-852,633	1,467E+094	94,166
673,000	-1006,567	-329,121	-785,069	8,668E+060	60,938
873,000	-1000,418	-321,158	-720,047	1,221E+043	43,087
1073,000	-992,558	-313,088	-656,615	9,275E+031	31,967
1273,000	-970,724	-293,856	-596,645	3,048E+024	24,484
1473,000	-993,425	-309,877	-536,976	1,105E+019	19,044
1673,000	-986,421	-305,414	-475,464	7,019E+014	14,846
1873,000	-980,116	-301,850	-414,751	3,695E+011	11,568
2073,000	-974,503	-299,000	-354,676	8,665E+008	8,938
2273,000	-969,575	-296,728	-295,112	6,059E+006	6,782

$Na_2SO_4 + 4C = Na_2S + 4CO(g)$

T K	**deltaH** kJ	**deltaS** J/K	**deltaG** kJ	**K**	**Log(K)**
273,000	578,653	710,892	384,580	2,570E-074	-73,590
473,000	582,071	721,669	240,721	2,596E-027	-26,586
673,000	565,020	689,975	100,666	1,535E-008	-7,814
873,000	555,249	677,337	-36,067	1,439E+002	2,158
1073,000	542,823	664,571	-170,261	1,946E+008	8,289
1273,000	515,886	640,982	-300,084	2,062E+012	12,314
1473,000	533,166	653,051	-428,778	1,608E+015	15,206
1673,000	520,493	644,980	-558,558	2,760E+017	17,441
1873,000	508,295	638,090	-686,848	1,434E+019	19,157
2073,000	496,551	632,131	-813,857	3,228E+020	20,509
2273,000	485,225	626,914	-939,750	3,960E+021	21,598

$Na_2CO_3 + 2C = 2Na + 3CO(g)$

T	**deltaH**	**deltaS**	**deltaG**	**K**	**Log(K)**
K	kJ	J/K	kJ		
273,000	798,650	543,588	650,251	3,744E-125	-124,427
473,000	805,019	561,677	539,346	2,714E-060	-59,566
673,000	797,197	548,408	428,118	5,874E-034	-33,231
873,000	787,045	534,991	319,998	7,109E-020	-19,148
1073,000	774,704	522,352	214,220	3,721E-011	-10,429
1273,000	730,121	483,174	115,040	1,902E-005	-4,721
1473,000	715,967	472,840	19,474	2,039E-001	-0,691
1673,000	702,775	464,435	-74,224	2,078E+002	2,318
1873,000	690,847	457,692	-166,411	4,378E+004	4,641
2073,000	680,478	452,425	-257,399	3,065E+006	6,486
2273,000	671,958	448,494	-347,470	9,676E+007	7,986

$0.5N_2(g) + O_2(g) = NO_2(g)$

T	**deltaH**	**deltaS**	**deltaG**	**K**	**Log(K)**
K	kJ	J/K	kJ		
273,000	33,260	-60,227	49,702	3,086E-010	-9,511
473,000	32,300	-62,971	62,086	1,390E-007	-6,857
673,000	32,054	-63,433	74,744	1,579E-006	-5,802
873,000	32,203	-63,247	87,418	5,876E-006	-5,231
1073,000	32,551	-62,890	100,032	1,349E-005	-4,870
1273,000	32,980	-62,524	112,574	2,401E-005	-4,620
1473,000	33,448	-62,183	125,044	3,676E-005	-4,435
1673,000	33,938	-61,872	137,449	5,107E-005	-4,292
1873,000	34,437	-61,590	149,794	6,640E-005	-4,178
2073,000	34,939	-61,335	162,086	8,231E-005	-4,085
2273,000	35,440	-61,104	174,330	9,851E-005	-4,007

$C + O_2(g) = CO_2(g)$

T	**deltaH**	**deltaS**	**deltaG**	**K**	**Log(K)**
K	kJ	J/K	kJ		
273,000	-393,484	2,952	-394,290	2,806E+075	75,448
473,000	-393,613	2,598	-394,842	4,047E+043	43,607
673,000	-393,910	2,085	-395,313	4,838E+030	30,685
873,000	-394,326	1,544	-395,675	4,749E+023	23,677
1073,000	-394,750	1,107	-395,938	1,889E+019	19,276
1273,000	-395,165	0,753	-396,123	1,800E+016	16,255
1473,000	-395,578	0,451	-396,242	1,128E+014	14,052
1673,000	-396,007	0,178	-396,305	2,369E+012	12,375
1873,000	-396,463	-0,079	-396,315	1,131E+011	11,053
2073,000	-396,959	-0,331	-396,274	9,683E+009	9,986
2273,000	-397,511	-0,584	-396,182	1,274E+009	9,105

$C + CO_2(g) = 2CO(g)$

T K	**deltaH** kJ	**deltaS** J/K	**deltaG** kJ	**K**	**Log(K)**
273,000	172,081	174,613	124,411	1,562E-024	-23,806
473,000	173,571	179,039	88,886	1,525E-010	-9,817
673,000	173,136	178,342	53,112	7,540E-005	-4,123
873,000	171,742	176,545	17,618	8,826E-002	-1,054
1073,000	169,883	174,635	-17,500	7,112E+000	0,852
1273,000	167,746	172,811	-52,242	1,393E+002	2,144
1473,000	165,449	171,136	-86,634	1,182E+003	3,072
1673,000	163,043	169,605	-120,706	5,875E+003	3,769
1873,000	160,552	168,199	-154,485	2,035E+004	4,309
2073,000	157,983	166,896	-187,993	5,462E+004	4,737
2273,000	155,336	165,677	-221,249	1,216E+005	5,085

$2Na + S = Na_2S$

T K	**deltaH** kJ	**deltaS** J/K	**deltaG** kJ	**K**	**Log(K)**
273	-366,15	-38,61	-355,61	1,1125E+68	68,046
473	-374,67	-60,808	-345,9	1,5937E+38	38,202
673	-376,63	-64,36	-333,31	7,4509E+25	25,872
873	-377,05	-64,944	-320,35	1,4766E+19	19,169
1073	-375,53	-63,429	-307,47	9,32E+14	14,969
1273	-363,57	-53,47	-295,5	1,3377E+12	12,126
1473	-333,22	-31,857	-286,29	14229000000	10,153
1673	-333,64	-32,124	-279,9	549270000	8,7398
1873	-334,75	-32,745	-273,42	42249000	7,6258
2073	-336,87	-33,813	-266,77	5279200	6,7226
2273	-340,32	-35,398	-259,86	937990	5,9722

$Na + Cl(g) = NaCl$

T K	**deltaH** kJ	**deltaS** J/K	**deltaG** kJ	**K**	**Log(K)**
273,000	-532,421	-144,358	-493,012	2,181E+094	94,339
473,000	-535,219	-151,892	-463,374	1,500E+051	51,176
673,000	-534,791	-151,184	-433,044	4,106E+033	33,613
873,000	-533,366	-149,361	-402,974	1,298E+024	24,113
1073,000	-530,757	-146,693	-373,356	1,503E+018	18,177
1273,000	-499,091	-117,469	-349,553	2,210E+014	14,344
1473,000	-496,140	-115,312	-326,285	3,728E+011	11,572
1673,000	-493,634	-113,714	-303,391	2,974E+009	9,473
1873,000	-491,694	-112,615	-280,766	6,772E+007	7,831
2073,000	-490,487	-111,999	-258,313	3,232E+006	6,509
2273,000	-490,180	-111,854	-235,935	2,645E+005	5,422

$K + Cl(g) = KCl$

T K	**deltaH** kJ	**deltaS** J/K	**deltaG** kJ	**K**	**Log(K)**
273,000	-557,992	-147,183	-517,811	1,214E+099	99,084
473,000	-560,444	-154,441	-487,393	6,740E+053	53,829
673,000	-559,914	-153,548	-456,576	2,754E+035	35,440
873,000	-558,479	-151,711	-426,035	3,114E+025	25,493
1073,000	-529,442	-123,729	-396,680	2,053E+019	19,312
1273,000	-525,629	-120,466	-372,277	1,892E+015	15,277
1473,000	-522,423	-118,119	-348,433	2,275E+012	12,357
1673,000	-520,082	-116,623	-324,972	1,403E+010	10,147
1873,000	-518,866	-115,930	-301,730	2,603E+008	8,415
2073,000	-519,033	-116,008	-278,549	1,046E+007	7,019
2273,000	-520,839	-116,833	-255,277	7,360E+005	5,867

$CO_2(g) + 4H_2(g) = CH_4(g) + 2H_2O$

T K	**deltaH** kJ	**deltaS** J/K	**deltaG** kJ	**K**	**Log(K)**
273,000	-265,610	-457,146	-140,809	8,791E+026	26,944
473,000	-246,099	-392,902	-60,256	4,516E+006	6,655
673,000	-227,692	-361,471	15,578	6,178E-002	-1,209
873,000	-202,111	-328,215	84,421	8,879E-006	-5,052
1073,000	-175,752	-301,042	147,265	6,767E-008	-7,170
1273,000	-148,786	-278,003	205,111	3,828E-009	-8,417
1473,000	-121,401	-258,025	258,670	6,706E-010	-9,174
1673,000	-93,743	-240,420	308,479	2,332E-010	-9,632
1873,000	-65,929	-224,716	354,964	1,258E-010	-9,900
2073,000	-38,058	-210,578	398,470	9,092E-011	-10,041
2273,000	-10,183	-197,741	439,282	8,021E-011	-10,096

$Na + H_2O = NaOH + 0.5H_2(g)$

T K	**deltaH** kJ	**deltaS** J/K	**deltaG** kJ	**K**	**Log(K)**
273,000	-133,202	33,178	-142,259	1,666E+027	27,222
473,000	-142,243	1,584	-142,992	6,199E+015	15,792
673,000	-136,529	11,485	-144,258	1,576E+011	11,198
873,000	-145,849	-0,640	-145,291	4,943E+008	8,694
1073,000	-155,278	-10,361	-144,161	1,043E+007	7,018
1273,000	-164,972	-18,641	-141,242	6,252E+005	5,796
1473,000	-175,091	-26,020	-136,764	7,084E+004	4,850
1673,000	-185,794	-32,829	-130,872	1,220E+004	4,086
1873,000	-197,241	-39,287	-123,656	2,811E+003	3,449
2073,000	-209,592	-45,548	-115,170	7,985E+002	2,902
2273,000	-223,006	-51,722	-105,442	2,650E+002	2,423

$K + H_2O = KOH + 0.5H_2(g)$

T K	**deltaH** kJ	**deltaS** J/K	**deltaG** kJ	**K**	**Log(K)**
273,000	-132,209	35,820	-141,988	1,478E+027	27,170
473,000	-144,640	-4,413	-142,553	5,544E+015	15,744
673,000	-146,593	-6,434	-142,262	1,103E+011	11,043
873,000	-147,824	-6,688	-141,986	3,135E+008	8,496
1073,000	-156,985	-16,133	-139,675	6,310E+006	6,800
1273,000	-166,465	-24,229	-135,622	3,676E+005	5,565
1473,000	-176,516	-31,556	-130,034	4,089E+004	4,612
1673,000	-187,393	-38,474	-123,026	6,942E+003	3,841
1873,000	-199,349	-45,218	-114,656	1,577E+003	3,198
2073,000	-212,643	-51,956	-104,939	4,410E+002	2,644
2273,000	-227,530	-58,805	-93,866	1,436E+002	2,157

$Na_2S + CO_2(g) + H_2O = Na_2CO_3 + H_2S(g)$

T K	**deltaH** kJ	**deltaS** J/K	**deltaG** kJ	**K**	**Log(K)**
273,000	-98,568	-9,012	-96,107	2,457E+018	18,390
473,000	-113,652	-56,279	-87,032	4,092E+009	9,612
673,000	-121,236	-69,601	-74,395	5,952E+005	5,775
873,000	-131,081	-82,159	-59,356	3,563E+003	3,552
1073,000	-140,546	-91,969	-41,863	1,092E+002	2,038
1273,000	-127,990	-79,901	-26,277	1,198E+001	1,078
1473,000	-163,992	-105,630	-8,399	1,986E+000	0,298
1673,000	-169,936	-109,411	13,109	3,897E-001	-0,409
1873,000	-176,264	-112,982	35,351	1,033E-001	-0,986
2073,000	-182,995	-116,395	58,291	3,397E-002	-1,469
2273,000	-190,154	-119,690	81,901	1,311E-002	-1,882

$CO(g) + H_2O = CO_2(g) + H_2(g)$

T K	**deltaH** kJ	**deltaS** J/K	**deltaG** kJ	**K**	**Log(K)**
273,000	9,845	102,235	-18,065	2,863E+003	3,457
473,000	-3,563	59,858	-31,876	3,315E+003	3,520
673,000	-14,863	40,375	-42,035	1,832E+003	3,263
873,000	-28,574	22,521	-48,235	7,697E+002	2,886
1073,000	-41,789	8,884	-51,321	3,152E+002	2,499
1273,000	-54,624	-2,089	-51,965	1,357E+002	2,132
1473,000	-67,167	-11,243	-50,606	6,233E+001	1,795
1673,000	-79,462	-19,071	-47,556	3,054E+001	1,485
1873,000	-91,539	-25,891	-43,045	1,587E+001	1,201
2073,000	-103,414	-31,916	-37,252	8,685E+000	0,939
2273,000	-115,101	-37,299	-30,321	4,976E+000	0,697

$C + H_2O = CO(g) + H_2(g)$

T	**deltaH**	**deltaS**	**deltaG**	**K**	**Log(K)**
K	kJ	J/K	kJ		
273,000	181,926	276,848	106,346	4,471E-021	-20,350
473,000	170,009	238,897	57,010	5,054E-007	-6,296
673,000	158,273	218,717	11,077	1,381E-001	-0,860
873,000	143,168	199,067	-30,618	6,794E+001	1,832
1073,000	128,094	183,518	-68,821	2,242E+003	3,351
1273,000	113,122	170,722	-104,207	1,889E+004	4,276
1473,000	98,282	159,893	-137,241	7,365E+004	4,867
1673,000	83,580	150,534	-168,262	1,795E+005	5,254
1873,000	69,013	142,308	-197,530	3,230E+005	5,509
2073,000	54,569	134,980	-225,245	4,744E+005	5,676
2273,000	40,235	128,379	-251,570	6,049E+005	5,782

$S + O_2(g) = SO2(g)$

T	**deltaH**	**deltaS**	**deltaG**	**K**	**Log(K)**
K	kJ	J/K	kJ		
273,000	-296,509	12,065	-299,803	2,332E+057	57,368
473,000	-302,067	-2,414	-300,925	1,717E+033	33,235
673,000	-305,762	-9,037	-299,680	1,826E+023	23,262
873,000	-308,290	-12,337	-297,520	6,356E+017	17,803
1073,000	-310,603	-14,725	-294,803	2,252E+014	14,353
1273,000	-312,806	-16,609	-291,663	9,306E+011	11,969
1473,000	-314,928	-18,158	-288,182	1,660E+010	10,220
1673,000	-316,989	-19,470	-284,416	7,600E+008	8,881
1873,000	-319,004	-20,608	-280,406	6,617E+007	7,821
2073,000	-320,985	-21,613	-276,181	9,114E+006	6,960
2273,000	-322,942	-22,514	-271,767	1,761E+006	6,246

$4NaOH + 2SO_2(g) + O_2(g) = 2Na_2SO_4 + 2H_2O$

T	**deltaH**	**deltaS**	**deltaG**	**K**	**Log(K)**
K	kJ	J/K	kJ		
273,000	-1064,138	-569,454	-908,677	7,532E+173	173,877
473,000	-1060,477	-543,756	-803,281	5,199E+088	88,716
673,000	-1071,430	-557,821	-696,016	1,061E+054	54,026
873,000	-1046,029	-524,927	-587,768	1,483E+035	35,171
1073,000	-1012,812	-490,847	-486,133	4,650E+023	23,667
1273,000	-929,428	-418,989	-396,054	1,789E+016	16,253
1473,000	-896,372	-394,875	-314,721	1,450E+011	11,161
1673,000	-862,849	-373,538	-237,920	2,685E+007	7,429
1873,000	-828,824	-354,330	-165,165	4,041E+004	4,607
2073,000	-794,285	-336,811	-96,076	2,637E+002	2,421
2273,000	-759,234	-320,671	-30,348	4,983E+000	0,697

$2Na_2CO_3 + 2SO_2(g) + O_2(g) = 2Na_2SO_4 + 2CO_2(g)$

T K	**deltaH** kJ	**deltaS** J/K	**deltaG** kJ	**K**	**Log(K)**
273,000	-707,657	-252,490	-638,728	1,666E+122	122,222
473,000	-706,570	-249,939	-588,349	9,516E+064	64,978
673,000	-685,970	-209,183	-545,190	2,081E+042	42,318
873,000	-685,156	-208,727	-502,937	1,245E+030	30,095
1073,000	-680,470	-203,892	-461,694	3,003E+022	22,478
1273,000	-690,809	-214,270	-418,043	1,428E+017	17,155
1473,000	-692,264	-215,332	-375,080	2,004E+013	13,302
1673,000	-693,722	-216,260	-331,919	2,313E+010	10,364
1873,000	-695,223	-217,107	-288,581	1,119E+008	8,049
2073,000	-696,801	-217,907	-245,079	1,499E+006	6,176
2273,000	-698,483	-218,681	-201,420	4,257E+004	4,629

$2NaOH + CO_2(g) = Na_2CO_3 + H_2O$

T K	**deltaH** kJ	**deltaS** J/K	**deltaG** kJ	**K**	**Log(K)**
273,000	-178,240	-158,482	-134,974	6,724E+025	25,828
473,000	-176,953	-146,908	-107,466	7,392E+011	11,869
673,000	-192,730	-174,319	-75,413	7,139E+005	5,854
873,000	-180,437	-158,100	-42,415	3,452E+002	2,538
1073,000	-166,171	-143,477	-12,220	3,935E+000	0,595
1273,000	-119,309	-102,360	10,994	3,539E-001	-0,451
1473,000	-102,054	-89,772	30,179	8,506E-002	-1,070
1673,000	-84,563	-78,639	47,000	3,408E-002	-1,468
1873,000	-66,800	-68,611	61,708	1,901E-002	-1,721
2073,000	-48,742	-59,452	74,502	1,326E-002	-1,877
2273,000	-30,376	-50,995	85,536	1,082E-002	-1,966

$4NaCl + 2SO_2(g) + 2H_2O + O2(g) = 2Na_2SO_4 + 4HCl(g)$

T K	**deltaH** kJ	**deltaS** J/K	**deltaG** kJ	**K**	**Log(K)**
273,000	-321,013	-31,396	-312,442	6,113E+059	59,786
473,000	-348,356	-118,413	-292,346	1,938E+032	32,287
673,000	-344,332	-106,593	-272,595	1,443E+021	21,159
873,000	-367,528	-136,817	-248,086	7,000E+014	14,845
1073,000	-387,174	-157,172	-218,529	4,356E+010	10,639
1273,000	-473,189	-238,720	-169,298	8,858E+006	6,947
1473,000	-495,765	-255,199	-119,857	1,781E+004	4,251
1673,000	-517,938	-269,315	-67,374	1,270E+002	2,104
1873,000	-539,936	-281,736	-12,244	2,195E+000	0,341
2073,000	-561,808	-292,832	45,232	7,247E-002	-1,140
2273,000	-583,616	-302,875	104,819	3,900E-003	-2,409

$4KCl + 2SO_2(g) + 2H_2O + O_2(g) = 2K_2SO_4 + 4HCl(g)$

T	**deltaH**	**deltaS**	**deltaG**	**K**	**Log(K)**
K	kJ	J/K	kJ		
273,000	-318,398	-21,254	-312,595	6,541E+059	59,816
473,000	-345,219	-106,613	-294,792	3,609E+032	32,557
673,000	-366,317	-143,095	-270,014	9,094E+020	20,959
873,000	-366,587	-146,005	-239,125	2,037E+014	14,309
1073,000	-498,378	-274,166	-204,197	8,737E+009	9,941
1273,000	-524,016	-296,157	-147,007	1,078E+006	6,033
1473,000	-481,307	-263,841	-92,670	1,934E+003	3,286
1673,000	-509,818	-281,992	-38,046	1,542E+001	1,188
1873,000	-538,154	-297,991	19,984	2,771E-001	-0,557
2073,000	-566,364	-312,302	81,038	9,075E-003	-2,042
2273,000	-594,510	-325,264	144,815	4,697E-004	-3,328

$H_2(g) + 0.5O_2(g) = H_2O$

T	**deltaH**	**deltaS**	**deltaG**	**K**	**Log(K)**
K	kJ	J/K	kJ		
273,000	-292,628	-188,066	-241,286	1,481E+046	46,170
473,000	-280,029	-148,079	-209,988	1,554E+023	23,192
673,000	-268,660	-128,504	-182,177	1,383E+014	14,141
873,000	-254,460	-110,022	-158,411	3,014E+009	9,479
1073,000	-240,528	-95,648	-137,898	5,171E+006	6,714
1273,000	-226,831	-83,940	-119,975	8,382E+004	4,923
1473,000	-213,347	-74,100	-104,198	4,958E+003	3,695
1673,000	-200,062	-65,642	-90,244	6,574E+002	2,818
1873,000	-186,968	-58,248	-77,870	1,485E+002	2,172
2073,000	-174,057	-51,697	-66,888	4,848E+001	1,686
2273,000	-161,322	-45,832	-57,146	2,058E+001	1,313

$2KOH + CO_2(g) = K_2CO_3 + H_2O$

T	**deltaH**	**deltaS**	**deltaG**	**K**	**Log(K)**
K	kJ	J/K	kJ		
273,00	-201,02	-174,03	-153,51	2,36780E+29	29,37
473,00	-191,64	-142,97	-124,01	4,97070E+13	13,70
673,00	-192,24	-146,69	-93,52	1,81700E+07	7,26
873,00	-194,56	-152,10	-61,78	4,97390E+03	3,70
1073,00	-181,49	-138,66	-32,71	3,91290E+01	1,59
1273,00	-137,25	-100,98	-8,70	2,27610E+00	0,36
1473,00	-118,99	-87,65	10,12	4,37500E-01	-0,36
1673,00	-100,95	-76,17	26,48	1,49000E-01	-0,83
1873,00	-83,09	-66,08	40,68	7,33310E-02	-1,13
2073,00	-65,36	-57,09	52,99	4,62150E-02	-1,34
2273,00	-47,74	-48,98	63,58	3,45780E-02	-1,46

$4KOH + 2SO_2(g) + O_2(g) = 2K_2SO_4 + 2H_2O$

T K	**deltaH** kJ	**deltaS** J/K	**deltaG** kJ	**K**	**Log(K)**
273,00	-1167,80	-581,18	-1009,10	1,24590E+193	193,10
473,00	-1148,60	-518,16	-903,56	6,17560E+99	99,79
673,00	-1153,70	-532,11	-795,54	5,63770E+61	61,75
873,00	-1137,60	-519,32	-684,27	8,82710E+40	40,95
1073,00	-1111,90	-492,90	-583,04	2,42940E+28	28,39
1273,00	-1080,40	-466,06	-487,14	9,78110E+19	19,99
1473,00	-981,34	-392,60	-403,05	1,96690E+14	14,29
1673,00	-954,13	-375,27	-326,30	1,54400E+10	10,19
1873,00	-927,30	-360,12	-252,79	1,12340E+07	7,05
2073,00	-900,82	-346,69	-182,14	3,88890E+04	4,59
2273,00	-874,67	-334,64	-114,03	4,17440E+02	2,62

$2H_2S(g) + 3O_2(g) = 2H_2O + 2SO_2(g)$

T K	**deltaH** kJ	**deltaS** J/K	**deltaG** kJ	**K**	**Log(K)**
273,00	-1138,10	-441,01	-1017,70	5,55630E+194	194,74
473,00	-1110,40	-354,29	-942,85	1,35070E+104	104,13
673,00	-1084,70	-309,86	-876,16	1,01930E+68	68,01
873,00	-1053,50	-269,27	-818,44	9,43010E+48	48,98
1073,00	-1023,60	-238,35	-767,81	2,40350E+37	37,38
1273,00	-994,66	-213,64	-722,69	4,53560E+29	29,66
1473,00	-966,60	-193,16	-682,07	1,54640E+24	24,19
1673,00	-939,25	-175,74	-645,23	1,40300E+20	20,15
1873,00	-912,48	-160,63	-611,62	1,14420E+17	17,06
2073,00	-886,21	-147,30	-580,86	4,33920E+14	14,64
2273,00	-860,36	-135,39	-552,61	5,01480E+12	12,70

$CH_4(g) + 2O_2(g) = CO_2(g) + 2H_2O$

T K	**deltaH** kJ	**deltaS** J/K	**deltaG** kJ	**K**	**Log(K)**
273,00	-904,90	-295,12	-824,33	5,46830E+157	157,74
473,00	-874,02	-199,41	-779,70	1,29190E+86	86,11
673,00	-846,95	-152,54	-744,29	5,92060E+57	57,77
873,00	-815,73	-111,87	-718,06	9,28810E+42	42,97
1073,00	-786,36	-81,55	-698,86	1,05630E+34	34,02
1273,00	-758,54	-57,76	-685,01	1,28910E+28	28,11
1473,00	-731,99	-38,38	-675,46	9,01140E+23	23,96
1673,00	-706,51	-22,15	-669,45	8,00790E+20	20,90
1873,00	-681,94	-8,27	-666,44	3,86840E+18	18,59
2073,00	-658,17	3,79	-666,02	6,07570E+16	16,78
2273,00	-635,11	14,41	-667,86	2,23430E+15	15,35

$C_2H_6(g) + 3.5O_2(g) = 2CO_2(g) + 3H_2O$

T K	**deltaH** kJ	**deltaS** J/K	**deltaG** kJ	**K**	**Log(K)**
273,00	-1581,50	-388,90	-1475,30	1,99130E+282	282,30
473,00	-1534,70	-243,97	-1419,30	5,62570E+156	156,75
673,00	-1494,50	-174,36	-1377,20	7,87430E+106	106,90
873,00	-1448,30	-114,14	-1348,60	5,01140E+80	80,70
1073,00	-1404,70	-69,13	-1330,50	5,96000E+64	64,78
1273,00	-1363,10	-33,61	-1320,30	1,52090E+54	54,18
1473,00	-1323,30	-4,51	-1316,60	4,93560E+46	46,69
1673,00	-1284,70	20,05	-1318,20	1,45180E+41	41,16
1873,00	-1247,20	41,24	-1324,40	8,68790E+36	36,94
2073,00	-1210,50	59,84	-1334,60	4,27350E+33	33,63
2273,00	-1174,60	76,38	-1348,20	9,66960E+30	30,99

$CO(g) + 0.5O_2(g) = CO_2(g)$

T K	**deltaH** kJ	**deltaS** J/K	**deltaG** kJ	**K**	**Log(K)**
273,00	-282,78	-85,83	-259,35	4,23870E+49	49,63
473,00	-283,59	-88,22	-241,86	5,15150E+26	26,71
673,00	-283,52	-88,13	-224,21	2,53300E+17	17,40
873,00	-283,03	-87,50	-206,65	2,31960E+12	12,37
1073,00	-282,32	-86,76	-189,22	1,62980E+09	9,21
1273,00	-281,46	-86,03	-171,94	1,13700E+07	7,06
1473,00	-280,51	-85,34	-154,80	3,09050E+05	5,49
1673,00	-279,52	-84,71	-137,80	2,00800E+04	4,30
1873,00	-278,51	-84,14	-120,91	2,35720E+03	3,37
2073,00	-277,47	-83,61	-104,14	4,21030E+02	2,62
2273,00	-276,42	-83,13	-87,47	1,02380E+02	2,01