Profitability = f(G)

Computational Thermodynamics, Materials Design and Process Optimization

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Doctoral Thesis in Engineering Materials Science
Stockholm 2016
Abstract

The thesis starts by giving a motivation to materials modeling as a way to increase profitability but also a possibility decrease the environmental impact. Fundamental concepts of relevance for this work are introduced, this include the materials genome, ICME and of course the CALPHAD method. As a demonstration promising results obtained by an ICME approach using genetic algorithms and CALPHAD on the vacuum degassing process are presented. In order to make good predictive calculations and process models it is important to have good thermodynamic descriptions. Thus most part of the work has concerned the thermodynamic assessments of systems of importance for steelmaking, corrosion and similar processes. The main focus has been the assessment of sulfur-containing systems and thermodynamic descriptions of the Fe-Mn-Ca-Mg-S, Fe-Ca-O-S, Fe-Mg-O and Mg-Mn-O systems are presented. In addition, heat capacity measurements of relevance for the Mg-Mn-O system have been performed. To summarize the efforts some application examples concerning thermodynamic calculations related to steelmaking and inclusion formation are shown.
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This PhD project, the COMPASS project (Computational thermodynamics for steel and slag equilibria), was carried out in collaboration with the companies Ovako, Outokumpu, SSAB EMEA and Thermo-Calc Software. Most of the work was performed at Department of Materials Science and Engineering at KTH Royal Institute of Technology in Sweden while some parts of the work were performed at TU Delft in the Netherlands and TU Bergakademie Freiberg in Germany. Here the publications included in this thesis and the contributions by the author are listed.

**Paper 1: Process-time Optimisation of Vacuum Degassing using a Genetic Alloy Design Approach**
Contribution: Most of the modeling work and most of the writing.

**Paper 2: Thermodynamic Assessment of the Mn-S and Fe-Mn-S Systems**
Contribution: Most of the assessment work and most of the writing.

**Paper 3: Thermodynamic Assessment of the Fe-Ca-S, Fe-Mg-O and Fe-Mg-S Systems**
Contribution: Most of the assessment work of the Fe-Ca-S and Fe-Mg-S systems, some of the assessment work on the Fe-Mg-O system and large part of the writing.

**Paper 4: Thermodynamic Description of the Fe-Mn-Ca-Mg-S System**
D. Dilner CALPHAD 53 (2016) 55-61
Contribution: Sole author.

**Paper 5: Thermodynamics of the Mg-Mn-O System – Modelling and Heat Capacity Measurements**
Contribution: Experimental planning, most of the assessment work and most of the writing.

**Paper 6: Thermodynamic Description of the Fe-Ca-O-S system**
D. Dilner, M. Selleby, 2016, In manuscript.
Contribution: Most of the assessment work and most of the writing.

**Paper 7: Improving Steel and Steelmaking – Computational Thermodynamics using a Sulphide and Oxide database**
D. Dilner, L. Kjellqvist, H. Mao, M. Selleby, 2016, In manuscript.
Contribution: Large part of the calculations and most of the writing.

In addition to the papers included in the thesis, the following papers have been published during the course of the PhD studies:

*The influence of carbon vacancies on thermodynamic properties in TiZrC mixed carbides: ab initio study*

*Phase equilibria in the ZrO₂-MgO-MnO₁ₓ system*
Acknowledgements

I gratefully acknowledge my main supervisor Malin for all her support, many useful discussions and also for giving me the possibility to have large influence on the project. I would also like to thank my co-supervisor Mao for his support and many useful discussions about modeling. My co-author Lina at Thermo-Calc Software is acknowledged for her support and many discussions about the implementation of my research in their database. Many thanks to all my fellow PhD students, postdocs and senior researchers at KTH for many interesting discussions and joyful moments.

I would like to thank Sybrand for inviting me to TU Delft and thank all people there for being friendly and welcoming. I also would like to thank Olga for inviting me to TU Bergakademie Freiberg and for all support I got from her and other people conducting experimental work and drinking tea. I would also like to thank Tor-Björn at SSAB for introducing me to the world of steel.

I also acknowledge my friends and relatives for encouraging me over the course of my academic studies. A great thank to my mother Margareta for always encouraging me to seek knowledge. Finally, I would like to acknowledge my wife Annika for all her support and understanding during these five years.

När man tillverkar stål så använder man sig av en slagg, bestående av flytande oxider, för att skydda och rengöra det flytande stålet. Man kan jämföra stål och slagg med en salladsdressing där slaggen (olivoljan) flyter ovanpå stålet (vinägern). Olika ämnen löser sig i de olika vätskorna, exempelvis löser sig salt väl i vinäger medan många smak- och färgämnen löser sig bättre i olivolja. För den som vill ha mer information om ståltillverkning rekommenderas avsnittet om processer på Jernkontorets hemsida [2], där det även finns annan information om stål och stålindustrin. Vid ståltillverkning så vill man att föroreningar ska lösa sig i slaggen medan, ofta dyrbara, legeringsämnen ska lösa sig i stålet. Syftet med legeringsämnen är att förbättra någon egenskap i stålet, exempelvis korrosionsmotståndet eller hårdheten. Många föroreningar, t ex syre och svavel, löser sig i slaggen medan exempelvis nickel stannar i stålet. Det är dock inte alltid så enkelt, exempelvis så trivs koppar, som ofta betraktas som en förorening, bättre i stålet medan legeringsämnet krom gärna löser sig i slaggen. Det bör också påpekas att både koppar och svavel kan vara önskvärda i vissa stålsorter beroende på tillämpningsområde. Även om ståltillverkning inte sker under jämviktsförhållanden så spelar jämvikt en stor roll för förståelse av dessa fenomen. När det gäller stål så handlar jämvikt om var atomerna vill befinna sig men jämvikt kan lika gärna handla om mekanisk jämvikt, exempelvis att en boll hellre ligger i en dal än uppe på en bergstop. Då marken är ojämn så hindras ofta bollen att av sig själv rulla ner från bergstoppen utan man måste tillföra någon form av aktiveringsenergi för att den ska hamna.

Något som börjar få ökad spridning på senare år är flerskalig materialmodellering, ofta benämnd ICME (integrerad materialberäkningsteknik). Termodynamik och kinetik är vitalt för den typen av modellering och därför lanserade den amerikanska regeringen 2011

**Svenska referenser**


1. Background

Steel has been one of the foundations of modern society both literally and symbolically since the industrial revolution. It is the backbone in our trucks, skyscrapers, bridges, aircraft carriers and sometimes it is even part of our bodies. Not surprisingly steel is an important part of the world economy. This is particularly true for the Swedish economy, with several of its largest companies being either steel producers or having a large part of their purchase or sales related to steel.

Given the importance of steel one could believe that steelmaking is a lucrative business but this is however generally not the case. Even before the financial crisis in 2008 several steel companies were struggling with profitability problems. The financial crash led to a dramatic decrease in the steel price, as can be seen in Figure 1 and it still remains at the same low level, about 300 USD/tonne, August 2016. Low prices together with tougher competition on the market mean that steel companies always must think about reducing costs, preferably without decreasing the quality. The steel companies do not only compete about customers but also about raw materials, mostly alloying elements, slag formers and coal. The supply of many, for steel making important, raw materials is lower than the demand. Not only are the raw materials expensive, but the supply is in many cases controlled due to geopolitical reason. Many mineral deposits are located at sites with civil unrest, human rights problems or even armed conflicts. This makes the need to reduce the use of certain raw materials even larger. In some cases it is even desirable to replace one raw material with another. Raw material consumption is also related to several environmental problems. Most of them require large amounts of energy to be produced. Mining as well as recycling of several elements are problematic since they are hazardous to living organisms. From an environmental perspective this makes the interest to reduce the use, of at least some, raw materials significant. In addition, legislations due to health and environmental concerns may even cause some elements to be partly or completely banned in the future. For this reason it is beneficial or even crucial to be able to replace some raw materials. Companies that succeed to replace raw materials before they get banned will have an advantage.
Meeting competition could also be done by other means than reducing cost, e.g. by improving product quality and performance. In some cases this makes it possible to get a higher profit while sometimes it is simply a matter of survival of the company. Better product quality, e.g. corrosion resistance or higher strength, in many cases mean longer lifetime of the materials or lower weight and material need and thus less environmental impact. Another way to meet competition is to start producing more specialized products. This is already done in Sweden where no steel company produce steel products in the cheapest segments. By doing this it is possible to get higher margins but it also makes the need to be ahead of competitors more important. Making customized products makes it possible to get a higher profit and simultaneously satisfying specific customer needs. Of course this might be a difficult task, particularly if the customer demands higher performance than existing products.

Research and development is vital no matter if the ambition is developing a better product, implementing a cheaper process, replacing a raw material or designing a customized product. For a company that wants to take a lead position on the market, research and development is a key area but also a major cost. However, it is not only about cost but also about the time to develop a new product. In particular experimental work may be very expensive and time consuming. In order to save time and money modeling is an important tool in the development process. Several modeling tools are used today where the finite element method
(FEM) and computational fluid dynamics (CFD) are the two most well-known. In materials development, computational thermodynamics has become more important over the last decades since the birth of the CALPHAD method [2]. This may be used alone or combined with other models, like diffusion calculations or more specific calculations, concerned with for example bainite or martensite transformation. In its simplest form it can actually be used to calculate cost directly, based only on equilibrium calculation and raw material prices, as shown in Figure 2. Although, it should be emphasized that this is a very crude estimation neglecting all other factors influencing the cost. With that said in its simplicity it really demonstrates usability of the CALPHAD method for materials and process development. Lately, other methods like density functional theory (DFT) [3], molecular dynamics [4], Monte Carlo [5] and phase field [6] have gained more attention in materials development. It is also possible to combine several models in order to make calculations with the aim of designing a specific material or process. This thesis aims to describe how materials design can be used to reduce cost but also to describe computational thermodynamics, which is the key component upon which this type of holistic modeling is based. The research has been focusing on describing the thermodynamics of steel and slag, particularly related to sulfur, and demonstrating how this type of modeling can be utilized to design processes and materials.

![Figure 2](image2.png)

Figure 2 Equilibrium calculation using Thermo-Calc and the TCFE database [7] to calculate the cost of producing a duplex stainless steel with 50 % austenite with 20 % Cr and variable Mn and Ni contents. The red line indicates that the detrimental sigma phase is stable.
2. Materials and process design

The classic way to develop new materials is first to look at the processing and then at what microstructure that is obtained. A certain microstructure gives certain properties which give the performance of the final product. However, this approach is time consuming and might not lead to materials that can meet the challenges of tomorrow. Thus it is desirable to look from the opposite direction, how can we produce a material that meets specific demands in terms of performance? The idea is illustrated in Figure 3, based on Ref. [8] which is inspired by the reciprocity as suggested by Cohen [9]. The red arrow indicates the classic approach and the black arrow indicates the so-called materials by design approach.

![Diagram](image.png)

*Figure 3 The red arrow is the classic approach where a certain process yields a structure which has some properties that gives some performance. The black arrow shows the performance driven materials by design approach. The small arrows indicate which profession that is most involved in each step.*

This approach will likely increase the profitability in several ways, for example:

- The development cost of new materials will be reduced.
- Decreased development time gives competitive advantage.
- A tailored alloy does not need to overshoot in performance; it could thus be designed to minimize the use of expensive raw materials.
- The possibility of designing alloys for specific demands opens new markets.
Of course, as these ideas get more widespread they might turn into a necessity. Furthermore, if futuristic ideas, like a space elevator to replace costly launch vehicles to carry payload, should become reality, approaches like this is a requirement and not only a way to increase the profitability.

2.1 Materials Genome

For the reasons described in the introduction to this chapter several nations have launched programs aiming to stimulate the development of alloy design methods. Most well-known is the Materials Genome Initiative (MGI) [10], which was launched by the US government in 2011. The ambition is to shorten materials development times from 10-20 years to 3-5 years. In order to do so the idea is nothing less than to mimic the successful Human Genome Project. The original definition of the Materials Genome Initiative was viewed as too vague by Kaufman and Ågren [11] and they proposed that CALPHAD can be viewed as the materials genome, since both equilibria and diffusion data are crucial for materials modeling. It is apparent that CALPHAD is the backbone of the materials genome. Details about the CALPHAD method are given in Section 3.2. In the US, national institute of standards and technology (NIST) have taken the role to organize the efforts to collect thermodynamic and kinetic data, see Ref. [12] for details.

2.2 ICME

Indeed, these ideas have lately started to spread outside the computational materials science community. However, systematic ideas on alloy design have been around for over 20 years. Researchers at Northwestern University were the first to suggest and use such an approach. Their first efforts using this so called ‘Materials by Design’ approach was summarized in a paper by Olson in 1997 [8]. Despite the fact that most real materials are far from equilibrium, thermodynamic calculation using CALPHAD databases were the most important part of the design model. Already from the start the materials design philosophy was included in the teaching at Northwestern University. A good overview of the Integrated Computational Materials Engineering (ICME) and its relation to the Materials Genome can be found summarized in Ref. [13] and in more detail in Ref. [14]. Further on, in a paper by Xiong and Olson [15] the user level of materials design, integrated computational materials design (iCMD), is reviewed. In these papers Ferrium S53, the first ICME steel to obtain Accelerated Insertion of Materials (AIM) qualification is discussed. The total development
time was 8.5 years which is better than standard development times. The next alloy to be qualified was Ferrium M54 and this time it only took 6 years in total [15] and the time to market is thus approaching the objective of the MGI. A complete description of how these ideas are implemented is found in a paper by Campbell and Olson [16]. It starts by translating desired performance of a high performance stainless steel into properties. These properties are then related to different process steps and these are connected with various models which can be used to calculate the properties. Finally, conditions to meet each optimization criterion are checked to obtain an alloy with the desired properties. Later, other researchers have employed genetic algorithms to optimize materials properties [17,18]. Researchers at TU Delft combined genetic algorithms with CALPHAD modeling [19]. The basic idea in their work is the same as that at Northwestern University. The contrast between these works is that the latter involves human interaction to evaluate the optimization criteria in the design process. Using fully automatic optimization procedures, as employed at TU Delft among others, the human interaction will only be part of setting up the system and analyzing the results. Human interaction has the advantage that the user will obtain a better understanding along the way and also that problems are more easily found. On the other hand, a fully automatic optimizing procedure has the advantage of the possibility to search a large space of parameters and that it is in principle doing much of the work for you. The research group at TU Delft has also been utilizing their method to optimize the cost and performance of a ultra-high strength stainless steel [20].

In this context the book “Materials Selection for Mechanical Design” by Ashby [21] must be mentioned. It serves as a guide for students in mechanical engineering as well as materials science on materials selection. However, it is not true materials design in the sense that it only concerns optimizing performance by using existing materials with desirable properties.

2.3 Process modeling

Although processing is an essential part of ICME, see e.g. [16,19,20], the steelmaking process is payed little or no attention. However, several modeling methods related to secondary steelmaking exist, which are reviewed by Du [22]. Among these is an approach to combine computational fluid dynamics and thermodynamic models [23]. By analyzing the various conditions during the vacuum degassing it was possible to obtain increased understanding about the effect of the different process parameters. However, no efforts to
optimize the process systematically were made. Recently, researchers at École Polytechnique de Montréal have been implementing mesh-adaptive direct search to make optimization related to different process steps, including the blast furnace [24]. Materials development generally aims to create materials with as good properties as possible while keeping down the cost. Process development on the other hand generally aims to meet specifications, on composition and inclusions, to as low cost as possible. It should be mentioned that steel plants generally have quite good experience on how to meet these demands. However, one should realize that minor improvement could have an impact on the cost. For example lowering the loss of manganese by 10 kg per 100 ton heat would reduce cost by 200 000 USD per year for a steelmaker with an annual production of 1 000 000 tons. Further on, assuming full production, if the time in vacuum degassing would be reduced by 1 minute from 20 minutes this would mean 5 % increased capacity on existing equipment. As steelmaking is an investment heavy sector this could have a huge impact on the profitability. Thus implementing the ICME in the steelmaking process, or for that matter, processing of nonferrous alloys, has the possibility to greatly increase the profit to an almost neglectable cost. It should also be mentioned that the process route of completely new alloys might be unknown and thus be an obstacle to ICME designed alloys, which could be overcome by process design. Further on, while it might take time to get new alloys qualified, there are in many cases few external regulations that limit the possibilities to improve the processing.

2.4 Process optimization using genetic algorithms

As could be realized from the previous section, the advantages with implementing an ICME approach on the steelmaking process are huge. This led to the idea to utilize the approach presented by Xu et al. [19] on the steelmaking process in a joint effort by KTH Royal Institute of Technology and TU Delft. It was decided to use the vacuum degassing process of a low alloyed steel as a demonstration, with the results presented in Paper I [25]. The aim with the vacuum degassing process is to reduce the content of impurity elements and inclusions. This is done by extensive stirring under low pressure with the aim to let nitrogen and hydrogen be removed by the gas flow while inclusions and sulfur are dissolved in the slag. It should be mentioned that the ambition at this stage was not to improve vacuum degassing but rather to confirm that years of industrial experience could be reproduced to show the possibilities with this approach.
As was mentioned in Section 2.2 the research group at TU Delft uses a genetic algorithm to design alloys. The principle behind the algorithm is quite simple. The different optimization parameters resemble genes which can take different expressions, combinations of 0 and 1 instead of A, C, G and T. In every iteration, a number of genomes, containing one gene for each parameter, are generated. During these iterations the genes can mutate and the fittest solutions are most likely to give an offspring, which will survive until the next iteration. The process models are embedded in the optimization algorithm.

![Flowchart of the optimization model](image)

As in earlier works, see e.g. Refs. [8,16,19,20], CALPHAD is the most important modeling tool. Given the complexity of the steelmaking process, which in principle has to be modeled for each steel plant individually, it is decided to use a simple model for the kinetics. As mentioned in the previous section, the objective of the steelmaking process is to produce steel with the correct composition to as low a cost as possible. However, estimating the cost of a process is not trivial as it not only involves raw materials and energy costs but also costs...
related to for example staff and investments. For this reason it was decided to use process time as the optimization criterion. Reducing the process time would mean that existing equipment is used more efficiently. As with many optimization problems several constraints will limit which solutions will be allowed. Neither viscosity of the slag nor the foaming height can be too high. In order to ensure sufficient mass transfer between the steel and the slag the later should be mostly liquid. The most important constraint is of course that the composition should fall within an allowed range when the degassing is completed. In order to calculate these constraints, different empirical models are used. In addition, a model is needed to calculate the process time, which is done by using an analytical expression [26] combined with the equilibrium composition calculated by computational thermodynamics. For more details about the models used see Paper I [25] or the original references [26–32]. The thermodynamic calculations were performed using Thermo-Calc [33] and a combination of the TCFE6 [7], SLAG3 [34] and SSUB4 [35] databases. A flowchart showing which models and constraints that are used is given in Figure 4.

Each optimization parameter could obtain 8 different values within its limit which means that over 16 million solutions would be possible. However, using genetic algorithms, less than 10000 iterations were needed to reach the optimal set-up. The results, which are in good agreement with industrial practice, are presented in Table 1. In particular the optimal solution obtained at 50 Pa pressure is in good agreement. The model seems to optimize the sulfur and nitrogen contents simultaneously. In Figure 5 the optimal solutions are tested at varying pressures. It can be seen that the intersections where the nitrogen removal becomes limiting are close to the pressure at which the solution was found. It can also be noted that the nitrogen removal is completely dominating at 200 Pa which means that the obtained solution will give much higher sulfur content in the steel, than would be possible if nitrogen was not considered, without significantly decreasing the process time. The reason for this is that the time rather than the sulfur content is the optimization variable.

The fact that the model managed to reproduce industrial experience is promising. Given the rather crude empirical models it is not certain that the current model setup would give reliable results in more extreme cases than vacuum degassing of low alloy steels. Thus to fully demonstrate the usefulness of the approach it needs to be tested using plant specific process models and full scale testing. The ideas are not restricted to vacuum degassing but can in principle be used for any process. A possible next step would be to calculate the cost using both raw material prices and a cost estimate for the time in vacuum degassing.
Table 1: Obtained optimal solutions at different pressures and normal industrial values in the bottom row.
†Indicates normal process time, i.e. longer than the minimum time.

<table>
<thead>
<tr>
<th>Pressure (Pa)</th>
<th>Time (s)</th>
<th>Al (mass%)</th>
<th>Ca (mass%)</th>
<th>Si (mass%)</th>
<th>Slag (kg)</th>
<th>Al₂O₃ (mass%)</th>
<th>MgO (mass%)</th>
<th>SiO₂ (mass%)</th>
<th>Temp. (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>429</td>
<td>0.010</td>
<td>0.005</td>
<td>0.243</td>
<td>1571</td>
<td>25.7</td>
<td>7.14</td>
<td>5.00</td>
<td>1922</td>
</tr>
<tr>
<td>75</td>
<td>479</td>
<td>0.019</td>
<td>0.005</td>
<td>0.243</td>
<td>1143</td>
<td>22.9</td>
<td>7.86</td>
<td>7.14</td>
<td>1964</td>
</tr>
<tr>
<td>100</td>
<td>562</td>
<td>0.023</td>
<td>0.005</td>
<td>0.243</td>
<td>1000</td>
<td>20.0</td>
<td>9.29</td>
<td>11.43</td>
<td>1973</td>
</tr>
<tr>
<td>200</td>
<td>1002</td>
<td>0.036</td>
<td>0.005</td>
<td>0.243</td>
<td>1286</td>
<td>20.0</td>
<td>8.57</td>
<td>15.71</td>
<td>1973</td>
</tr>
<tr>
<td>100</td>
<td>900-1200†</td>
<td>0.020-0.050</td>
<td>0-0.0010</td>
<td>0.20-0.30</td>
<td>1000</td>
<td>25.0-30.0</td>
<td>5.0-10.0</td>
<td>8.0-12.0</td>
<td>1950</td>
</tr>
</tbody>
</table>

Figure 5: Process time versus pressure in Pa for the optimal solutions found at P=50, 75, 100 and 200. Optimal solutions, where all constraints are fulfilled, can be found at 50, 75, 100 and 200 Pa (red dots). The black and red lines indicate the time needed for sulfur and nitrogen removal, respectively.
3. Computational thermodynamics

As mentioned in the previous chapter, computational thermodynamics is the key component of ICME. Not only can it be used to gain information about equilibria, it can also be an important part of diffusion calculations, phase field modeling and other models related to phase transformations. There are different methods to calculate equilibria. For reasons that will be described below minimizing Gibbs energy is the most common and used within the CALPHAD approach which is today widespread. This method will also be described in this chapter, as will the so-called ionic two-sublattice liquid model and compound energy model for spinel phases.

3.1 Thermodynamic principles and Gibbs energy

In order to understand CALPHAD and computational thermodynamics some thermodynamic basis is needed. In some sense all engineers have some knowledge about thermodynamics. Something which might strike you is how differently thermodynamics is taught in different majors. Students in mechanical engineering are focusing on the Carnot cycle, i.e. engines and heat pumps, and physics students are focusing on statistical mechanics, i.e. the probability of different states, and students in materials science and chemistry are focusing on Gibbs energy, although from slightly different angles. It should be emphasized that it is of course the same thermodynamics but just different focus and sometimes different representation. Before describing Gibbs energy some thermodynamic principles will be described.

3.1.1 Probability and entropy

If you are rolling two pair of dice, the chance of getting 7 is much greater than the chance of getting 2 or 12, i.e. two ones or two sixes. However, the probability of getting 3 on one die and 4 on the other is equal to that of getting 2 or 12 but there are many other ways to get 7 which give a higher probability to get that number. If you had a large number of dice the average value would be close to 3.5, which is shown in Figure 6.
In a crystal consisting of A and B atoms there is a large number of possible ways the atoms can arrange themselves. Neglecting the interaction between the atoms it turns out that the probability of the atoms separating or ordering themselves is negligible. Just like the probability of getting an average of 6 or 1 if you roll a large number of dice. From probabilistic principles it is found that the number of possible states, $W$, for a mixture of A and B atoms can be calculated as:

$$W = \frac{N!}{n_A! n_B!}$$

where $N$ is the total number of atoms, $n_A$ and $n_B$ are the number of A and B atoms respectively. By using the number of states the entropy is defined as:

$$S = k_B \ln W$$

where $k_B$ is Boltzmann’s constant. Now we can calculate the entropy of mixing for the crystal of A and B atoms using the Stirling approximation:

$$S \approx -k_B N(x_A \ln x_A + x_B \ln x_B)$$
where \( x_A \) and \( x_B \) is the atomic fraction of A and B and N is the total number of atoms. Using one mole of atoms \( N=N_A \), Avogadro’s number, and since the gas constant is defined as expressed as \( R=N_A k_B \) the molar entropy of mixing becomes:

\[
S_M \approx -R(x_A \ln x_A + x_B \ln x_B)
\]

It is easily seen that the entropy of mixing reaches its maximum when \( x_A = x_B = 0.5 \). From this it can also be seen that it is almost impossible to get a completely pure metal as any impurity will give a drastic increase in entropy. In fact, in any isolated system, a spontaneous reaction will always lead to increased entropy, or at least constant entropy in the case of a reversible process. This is the second law of thermodynamics. It should be mentioned that the entropy can be much more than just entropy of mixing. A simplified way to see it is that the disorder in the universe always increases in some way, e.g. we can produce very pure metals but it requires a lot of energy which will lead to increased entropy. In this case we also have to consider the reaction in the power plant, e.g. the entropy increase caused by the use of fossil fuels which forms forming carbon dioxide, water vapor and cooling. If we instead use solar energy, were wind, water and bioenergy may be considered as indirect solar energy, the fusion reactions in the sun cause the entropy increase. These are called renewable energy sources, which is reasonable as we lack the possibility to control the reactions in the sun and given the lifetime of a star. Even fossil fuels can be considered as indirect solar energy, which has been stored for millions of years.

3.1.2 State functions and Gibbs energy

The entropy is a so called state function that describes the equilibrium state of a system. As stated in the previous section, the entropy change of a spontaneous reaction in an isolated system will always be larger than or equal to zero. Thus maximizing the entropy will tell us which reactions will occur. The classical way to define the entropy, assuming only pressure-volume work is performed, is from the differential, \( dS \), as follows:

\[
dS = (1/T)dU + (P/T)dV - \sum(\mu_i/T)dN_i
\]

where \( P \) is the pressure, \( V \) is the volume, \( \mu_i \) is the chemical potential of element i and \( N_i \) is the number of atoms of element i. However, if we are not speaking about a so called closed system the entropy increase of the reaction in principle refers to all connected reactions in the
universe. A closed system would require constant internal energy, constant volume and constant number of atoms. For the practical case, e.g. planning an experiment or understanding a metallurgical process, such conditions are hard to achieve and thus this approach becomes impractical. For this reason some other state function would be more suitable. By defining a function $F = U - TS$ one obtains a state function which describes the system at constant volume and temperature. $F$ is the so called Helmholtz energy, again assuming that only pressure-volume work is performed, and the differential is written as:

$$dF = -SdT -浦dV$$

As Helmholtz energy is a state function at constant volume, it is suitable to relate to so-called first principles calculations, like DFT. However, it turns out that it is quite hard to achieve constant volume experimentally. Pressure, unlike volume, is relatively easy to control experimentally. Thus the state function enthalpy defined as $H = U + PV$ is suitable. The change in enthalpy can be measured in a straight forward manner seen as change in heat due to a reaction. However, the enthalpy requires that the entropy of the system is kept constant. If we instead define a function $G = U + PV - TS = H - TS$ we get a state function which defines the system at constant pressure and temperature. This function is called Gibbs energy and its differential is written as:

$$dG = VdP - SdT + \sum \left( \frac{\mu_i}{T} \right) dN_i$$

In contrast to the entropy the Gibbs energy is minimized when equilibrium is reached. Any other thermodynamic quantities can be calculated from Gibbs energy, e.g. the entropy, enthalpy and pressure, but also the chemical potential, and heat capacity, $C_P$.

$$S = -\left( \frac{\partial G}{\partial T} \right)_{P,N_i}$$

$$H = G + TS = G - T\left( \frac{\partial G}{\partial T} \right)_{P,N_i}$$

$$V = \left( \frac{\partial G}{\partial P} \right)_{T,N_i}$$

$$\mu_i = \left( \frac{\partial G}{\partial N_i} \right)_{P,N_{\neq i}}$$

$$C_P = -T\left( \frac{\partial^2 G}{\partial T^2} \right)_{P,N_i}$$
Although Gibbs energy cannot be measured directly it is apparently a useful thermodynamic quantity. This is the reason why it is so frequently used in materials science and chemistry and to some extent in other fields as well. And it is the reason why it is probably the most suitable quantity to use in computational thermodynamics.

3.1.3 Regular solutions

In the previous subsection it was stated that equilibrium is obtained by minimizing Gibbs energy for a system at constant pressure and temperature. When dealing with reactions, like in chemistry, the Gibbs energy of formation is enough to establish if a reaction will occur or not, depending on whether $\Delta G$ is negative or positive. However, materials science often deals with alloys, i.e. solutions, in liquid and solid state. A common way to describe Gibbs energy of solutions is by using the well-known regular solution model. For a system which contains A and B atoms their partial Gibbs energies, $^\circ G_A$ and $^\circ G_B$, will define the baseline of the system. As described in the subsection about entropy, intermixing two species will increase the entropy. This is enough to describe so-called ideal solutions:

$$G_m = x_A^\circ G_A + x_B^\circ G_B - TS = x_A^\circ G_A + x_B^\circ G_B + RT(x_A \ln x_A + x_B \ln x_B)$$

For some type of systems this is actually enough to describe the molar Gibbs energy. In order for a system to be ideal the atoms must be very similar. The Hume-Rothery rules [36] gives an idea on the conditions which need to be fulfilled in order for the system to be reasonably ideal. This means that the atoms need to be similar in size and electronegativity and have the same crystal structure and valance. It should be noted that fulfilling these rules does not mean that the system will be ideal but rather that it cannot be ideal if they are not fulfilled. If the system is not ideal one has to handle the interaction energy, i.e. excess molar Gibbs energy, $G_m^E$, in some way. The easiest way to describe the excess Gibbs energy is by setting $G_m^E = x_A x_B L$. One thus has the regular solution model:

$$G_m = x_A^\circ G_A + x_B^\circ G_B - TS + G_m^E = x_A^\circ G_A + x_B^\circ G_B + RT(x_A \ln x_A + x_B \ln x_B) + x_A x_B L$$
For simple solution phases this works well in many cases. However, it might happen that the excess Gibbs energy cannot accurately be described using only a symmetric interaction parameter. For this reason Redlich-Kister polynomials [37] are widely used. Thus the interaction parameter for A and B will be defined in the following way:

\[ L_{A,B} = \sum (x_A - x_B)^v \cdot v L_{A,B} \]

In principle by using many polynomials it is possible to describe any behavior of the Gibbs energy. However, if more than first or possibly second order polynomials are needed it is generally an indication that a more advanced model is needed. These models will be described in the section about CALPHAD.

3.1.4 Thermoeconomics

Given the title of this thesis the concept thermoeconomics [38,39] has to be mentioned. In principle there is a price on energy and generally the more energy that is needed to produce a raw material or product the higher the price. As an example this is done on the relating financial terms to thermodynamics in the energy sector [40]. It should be emphasized that this is not thermoeconomics but instead computational thermodynamics, which is a tool that can be used for product and process development. The problem is that one also has to take sociological factors into account, i.e. supply and demand. How can oil price vary if it is related to a thermodynamic quantity and how can one explain the value of brands using thermodynamics? This can be compared with diffusion calculation where the Gibbs energy and mobility are used to model diffusivity, which by itself contains too little information. The difference is that sociologic factors are probably far more complicated to model than mobility, even though the latter is all but trivial. Thus one cannot say that profitability is a function of only Gibbs energy as other factors must be considered as well. Apart from the sociological factors this of course also includes other technical factors, like time and reliability of the equipment, as well as phenomenological factors, like mobility and heat transfer. Overall the title Profitability = f(G) suggests that this work is focusing on the Gibbs energy and how it can be used to increase profitability. But who knows, perhaps someday ICME will also include sociological models?
3.2 CALPHAD

As mentioned in the chapter about ICME, the CALPHAD method is an essential part of alloy design. It was first introduced in 1970 by Kaufman and Bernstein [2], and the meaning was simply “CALculation of PHAse Diagrams”. As the Gibbs energy can be used to calculate much more than just phase diagrams the meaning of the acronym was later changed to “Computer coupling of phase diagram and thermochemistry”, which is used in the full title of the CALPHAD journal. The calculation of the Fe-Ni phase diagram was published already in 1956 by Kaufman and Cohen [41] and can be considered to be the first CALPHAD assessment. It should be emphasized that CALPHAD is not a simulation method which can be used to obtain results by itself, like DFT or Monte Carlo. Nor is it an empirical model, at least not in the classical sense. Empirical models are often very limited and in principle anything can be fitted using the right polynomials. That does not mean that an empirical model cannot be good, it just means that they are only reliable within a defined range. CALPHAD do use experimental data to fit parameters but the parameters used are based on models which should be physically correct. Generally this means that one should avoid using too many parameters as that is usually a sign that the model is incorrect.

One of the main advantages with CALPHAD is that close to everyone within the community uses the same references for unary systems. In 1991 Dinsdale [42] published the unary descriptions established by the SGTE group. This means that higher order systems will be compatible under the condition that also lower order systems are compatible. However, a drawback with this is that all higher order systems must be re-assessed if the lower order systems were to be redefined. At present there is an effort to re-assess the unary descriptions with more physically correct models [43], both to get more accurate results but also to be able to make use of ab initio data to a larger extent. The first element to be re-assessed was Fe by Chen and Sundman [44]. However, as several elements of interest to this work are yet to be re-assessed the old unary descriptions are used. This is a disadvantage but as the application areas of the work are at higher temperatures this will probably not be a large problem in the near future.
3.2.1 Compound energy formalism

The compound energy formalism, at the time called the sub-lattice model, was first presented by Hillert and Staffansson in 1970 [45] as a model to be used for reciprocal systems. This subsection will present the general features about the compound energy formalism while modeling of ionic liquids will be discussed in further detail in the next subsection. In a more recent publication, Hillert [46] reviews the model now called the compound energy formalism. In fact the compound energy formalism is used to model solution phases with few exceptions. Having the regular solution in mind (Subsection 3.1.3) the idea is rather simple, to extend the regular solution model to more than one sublattice. For simplicity most of the discussion will focus on two sublattices, i.e. a (A,B)_(C,D) sublattice. This could for example represent a substitutional and an interstitial sublattice in an alloy or a cation and an anion sublattice in a salt. An important part of the model is the end-members defining the baseplane of the system, the so called surface of reference. The compound energies of these end-members have given the name to the model. It should be noted that while these end-members may exist experimentally there is no need for them to; in fact they might be impossible to obtain due to for example electroneutrality in some ionic phases. Secondly, just like in the regular solution model, a simple ideal configurational entropy is assumed. Further on, the excess Gibbs energy usually needs to be described to model the system. The general term description of molar Gibbs energy, \( G_m \), is given as:

\[
G_m = srf G_m - T \sum_{s} y_i^s \ln(y_i^s) + \text{phys} G_m + \text{E} G_m
\]

where the \( srf G_m \) is the surface of reference, \( \sum_{s} y_i^s \ln(y_i^s) \) the configurational entropy, \( \text{phys} G_m \) the physical contribution and \( \text{E} G_m \) the excess Gibbs energy. The physical contribution is usually the magnetic part of Gibbs energy. The excess Gibbs energy is described using interaction parameters using Redlich-Kister polynomials as in the regular solution model but for interaction on the different sublattices. The surface of reference and the configurational entropy are expressed as [46]:

\[
\begin{align*}
    srf G_m &= \sum_{s} \alpha_{s} y_i^s \\
    \text{phys} G_m &= -RT \sum_{s} \sum_{i} n_{s} y_i^s \ln(y_i^s)
\end{align*}
\]

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where \( y_i^s \) denotes site fraction of species \( i \) on sublattice \( s \), \( \Delta G_{end} \) denotes the end-member energy and \( n_s \) denotes the number of sites on every sublattice. At first this looks intimidating but one should be aware that it is in principle just the regular solution model. For the simplest system \((A,B)(C,D)\) this means that the Gibbs energy description can be written as:

\[
G_m = y_A y_c \Delta G_{A:C} + y_A y_D \Delta G_{A:D} + y_B y_c \Delta G_{A:D} + y_B y_D \Delta G_{B:D} \\
+ RT (y_A \ln y_A + y_B \ln y_B + y_C \ln y_C + y_D \ln y_D) + y_A y_B y_c L_{A:B:C} \\
+ y_A y_B y_D L_{A:B:D} + y_A y_C y_D L_{A:C:D} + y_B y_C y_D L_{B:C:D} + y_A y_B y_C y_D L_{A:B:C:D}
\]

where \( L_{A:B:C:D} \) is the reciprocal parameter. The next subsection will discuss the liquid model in further detail while Subsection 3.2.3 will discuss modeling of the spinel phase. As stated in the overview of the compound energy formalism [46] it can be used to model ordering in alloys. For further examples on how the compound energy formalism can be used more applications can be found in a paper by Frisk and Selleby [47].

3.2.2 Liquid modeling and the ionic two-sublattice liquid model

As described in the previous section, the compound energy formalism (CEF) is commonly used to describe solid solution phases within the CALPHAD community. However, when it comes to liquids different models are also used. The simplest way to model liquids is to assume that they behave as a regular solution, which works well for metallic liquids. However, the regular solution model cannot handle short range order. This can be addressed by adding associates, i.e. molecules or hypothetical molecules, to the regular substitutional solution in order to model short range order in liquids. This model is called the associate model [48] and it is used in for example an description of the Cu-Fe-S system [49]. Another way to model short range order in liquids is by considering the bonds between different species. This is done in the modified quasichemical model [50]. This model is widely used by the FACT group to model different ionic systems, commonly for materials processing applications. Yet another way to handle short range order in liquids is the Cell Model [51], which is used in the SLAG database [34], in which one considers mixtures of cells consisting of cations and anions. In some sense this model can be considered as a mixture between the modified quasichemical model and the associate model. In the present work the ionic two-sublattice liquid model is used which was originally developed as a purely mathematical
formalism [45], which is today known as the compound energy formalism. The ionic two-sublattice liquid model has been developed further since then. The idea behind this model follows the suggestion by Temkin [52] that one could consider an ionic liquid as having a cationic sublattice and an anionic sublattice. For ionic systems, this feels intuitively correct as it is reasonable that a positively charged ion wants to surround itself with negatively charged ions and vice versa. In its original form the ionic two-sublattice liquid model was used in thermodynamic assessments of for example the Fe-FeS [53], Mn-MnS [54] and Fe-Mn-S [55] systems. To model the complete Fe-S system Guillermet et al. [56] introduced charged vacancies on both sublattices. It was later concluded that the model becomes more self-consistent by restricting the vacancies to the anionic sublattice and having variable number of sites on the two sublattices [57]. In the same paper the model was compared with the associate model and it was concluded that the two are identical for binary systems while different for higher order systems. In fact the associate model needs more parameters in higher order systems. The excess Gibbs energy of the ionic two-sublattice liquid were then slightly modified by Sundman in 1991 [58] in order to be able to directly use the regular solution description of metallic systems to the ionic liquid model and vice versa. The ionic two-sublattice liquid model is expressed as [57,58]:

\[(C_{i}^{v})P(A_{v}^{-Q},V_{a}^{B})Q\]

where the site fractions P and Q are the average valence on the opposite sublattice, calculated using the following expressions:

\[P = \sum(-v_{i})y_{A_{i}} + Qy_{V_{a}}\]

\[Q = \sum v_{i}y_{C_{i}}\]

The molar Gibbs energy and molar excess Gibbs energy for the ionic two-sublattice liquid model are written as [58]:

\[G_{m} = \sum_{i} \sum_{j} y_{C_{i}}y_{A_{j}} \delta G_{C_{i}A_{j}} + Q y_{V_{a}} \sum_{i} y_{C_{i}} \delta G_{C_{i}} + Q \sum_{k} y_{B_{k}} \delta G_{B_{k}} + RT \left( P \sum_{i} y_{C_{i}} lny_{C_{i}} + Q \left( \sum_{j} y_{A_{j}} lny_{A_{j}} + y_{V_{a}} lny_{V_{a}} + \sum_{k} y_{B_{k}} lny_{B_{k}} \right) \right) + e G_{m}\]
\[ E_{Gm} = \sum_{i} \sum_{j_{1}}>i \sum_{k} y_{C_{i}j_{1}}y_{C_{i}j_{1}}L_{C_{i};A_{j1};A_{j2}} + \sum_{i} \sum_{j_{1}} \sum_{j_{2}>j_{1}} y_{C_{i}j_{1}}y_{A_{j1}}y_{A_{j2}}L_{C_{i};A_{j1};A_{j2}} + \\
\sum_{i} \sum_{j} \sum_{k} y_{C_{i}j}y_{A_{j}B_{k}}L_{C_{i};A_{j};B_{k}} + y_{Va} \sum_{i} \sum_{k} y_{C_{i}j}y_{C_{i}j}L_{C_{i};A_{j};Va} + \\
Qy_{Va} \sum_{i} \sum_{j_{2}>i} y_{C_{i}j_{1}}y_{C_{i}j_{1}}L_{C_{i};C_{i};Va} + Qy_{Va} \sum_{i} \sum_{k} y_{C_{i}j}y_{B_{k}}L_{C_{i};C_{i};Va} + \\
Q \sum_{k_{2}} \sum_{j_{2}>i} y_{B_{k_{1}}j_{1}}y_{B_{k_{2}}j_{2}}L_{B_{k_{1}};B_{k_{2}}}
\]

It should be noted that in the limit where \( \Delta G_{C:A}= G_{C:A}-(G_{B}+G_{C}) \) becomes zero the ionic liquid becomes identical to the regular solution of the C-A system [57] but where the interaction is between charged vacancies and neutral species instead of between the atoms directly. Moreover, it is identical to the associate model in the simple binary system [57]. However, it is not identical to the associate model for ternary systems. As stated earlier using the modifications by Sundman [58] the model also becomes identical to the regular solution model when \( y_{Va}=1 \), i.e. for pure metallic systems.

### 3.2.3 Spinel modeling

In this work two phases with spinel structures are modeled. They are also modeled using the compound energy formalism but as in the case with the ionic liquid model their modeling can be discussed in more detail. The spinel phase is a complex oxide mineral with cubic symmetry and the chemical formula \( \text{MgAl}_2\text{O}_4 \). The \( \text{Mg}^{+2} \)-ions are primarily dissolved on tetragonal sites and the \( \text{Al}^{+3} \)-ions primarily on the octahedral sites. This is referred to as the normal spinel with the arrangement \( (\text{Mg}^{+2})_{2}(\text{Al}^{+3})_{2}(\text{O}^{2-})_{4} \). As temperature increases some \( \text{Mg}^{+2} \)-ions and \( \text{Al}^{+3} \)-ions exchange sites with each other toward an inverse spinel which would have the arrangement \( (\text{Al}^{+3})_{1}(\text{Mg}^{+2},\text{Al}^{+3})_{2}(\text{O}^{2-})_{4} \). In the assessment of the \( \text{MgAl}_2\text{O}_4 \)-spinel phase by Hallstedt [59] an additional octahedral sublattice was introduce to represent the vacant octahedral sites. By using this sublattice it is possible to model oxygen deficiency in the spinel and the complete model used by Hallstedt [59] is:

\[
(\text{Mg}^{+2},\text{Al}^{+3})_{1}(\text{Al}^{+3},\text{Mg}^{+2},\text{Va})_{2}(\text{Va},\text{Al}^{+3},\text{Mg}^{+2})_{2}(\text{O}^{2-})_{4}
\]

In this work aluminum has not been considered and for this reason neither has \( \text{MgAl}_2\text{O}_4 \). However, the complex oxide phases with spinel structures exist in several systems including the Fe-O system [60], the Mn-O and Fe-Mn-O systems [61] as well as the Fe-Mg-O and Mg-Mn-O systems which are assessed in Paper 3 [62] and Paper 5. Details about these systems
will be given in the next chapter. The phase with the spinel crystal structure in all these systems can be modeled using the same model. In the assessment of spinel phases, the Gibbs energy of different reciprocal reactions is used to describe the end-members. However, when combining different systems one needs to consider that each system uses one end-member as reference and these may be have been chosen differently in different assessments which needs to be handled [63]. Commonly, the definition $G_{\text{Fe}^{2+}:\text{Fe}^{3+}:\text{Va}:\text{O}^2-} = 0$ as suggested by Sundman [60] is used a reference. In the assessment of a spinel phase the degree of inversion is an important parameter. The degree of inversion, $\xi$, is related to the site fractions and when considering only $(\text{Mg}^{2+},\text{Al}^{3+})_1(\text{Al}^{3+},\text{Mg}^{2+})_2(\text{O}^2-)_4$ the relations to the site fractions become $\xi = y^\prime_{\text{Al}}$ and $\xi = 2 - y^\prime_{\text{Mg}}$. In addition to the standard (cubic) spinel, a tetragonal spinel is present at lower temperatures in Mn-containing systems like Mn-O [61], Fe-Mn-O [61], Mn-Ni-O [64] and Mg-Mn-O which is described in Paper 5. In the Mn-O system the cubic spinel is referred to as $\beta$-$\text{Mn}_3\text{O}_4$ while the low temperature tetragonal spinel is referred to as $\alpha$-$\text{Mn}_3\text{O}_4$. The $\beta$-$\text{Mn}_3\text{O}_4$ most likely has a distribution of manganese cations with different valances similar to that in other cubic spinels [61,65]. However, the tetragonal $\alpha$-$\text{Mn}_3\text{O}_4$ probably only has Mn$^{2+}$-ions on the tetrahedral sites and Mn$^{3+}$, Mn$^{4+}$ on the octahedral sites. Thus a slightly different model is used and it can be argued whether the term degree of inversion can be used for this model as the manganese would not only need to change sublattice but also change oxidation state.
4. Thermodynamic descriptions

The focus of this work has been computational thermodynamics related to steelmaking and phenomena like corrosion. As was demonstrated in Section 2.4 process optimization is a suitable method to tailor a process to make a certain steel grade to as low cost as possible. In order to really be able to make good predictions the thermodynamic databases, just like the models used, should be as accurate as possible. The SLAG3 [34] database used has the advantage of using relatively simple models and is thus very comprehensive. Using more physically correct models would be more accurate but the development becomes more complicated and time-consuming. The TCOX database [66] is such a database utilizing the ionic two-sublattice model [57,58] for the liquid and other sublattice models for complex oxides. As a result of the more complicated models the database was lacking elements of importance for steelmaking as this work started. The major part of this work has been to describe the most important sulfur-containing system with the aim of extending the TCOX database with sulfur.

4.1 TCOX database

When the COMPASS project started the TCOX database contained descriptions of the most important alloying elements (Fe, C, Cr, Ni and Mn) and slag components (Al_2O_3, CaO, MgO and SiO_2). The thermodynamic descriptions in the TCOX database are based on extensive assessment work. A large part of this work have previously been performed at KTH Royal Institute of Technology, of which much can be found summarized in the PhD theses by Selleby [67], Jonsson [68], Hallstedt [69], Mao [70] and Kjellqvist [71].

Simultaneously with this project the Thermo-Calc Software company has made efforts along with other partners to include Y and Zr, in order to be able to perform calculations related to thermal barrier coatings, which are included in the current version. In addition, efforts are also being made to add F, Cu and Nb to the description. Fluorine is an element of great importance in slags, not at least in stainless steel production. In parallel to the development of TCOX, research is being conducted at KTH Royal Institute of Technology to describe vanadium-containing slags [72], which can be included in the database in the future. Further on, some improvements of the existing descriptions have been made. This includes the finalization of the assessment of the Fe-Mg-O system [62], which will be described further detail in Section 4.3.
4.2 Fe-Mn-Ca-Mg-S

In steels, it is important to predict sulfide formation as sulfides have a large impact on the properties. They are usually undesirable as they have a negative impact on the mechanical properties, in particular the toughness, and they can also give rise to pitting corrosion in stainless steels. However, in some cases sulfur is added on purpose to improve the machinability of certain steel grades. A lot of research has been done to investigate sulfide formation in steel, see e.g. [73–75]. For low-alloy steels, and in to some extent even stainless steels, the Fe-Mn-Ca-Mg-S system is the most important metal-sulfur system. Although it is obvious that iron is important in steel it should be mentioned that FeS, if formed, gives rise to hot-shortness due to its low melting temperature. Early steelmakers started using manganese to avoid formation of FeS. For several reasons manganese is still today a common alloying element and thus MnS is found in many steels. To obtain better mechanical properties, in particular toughness, calcium can be added to the steel to form CaS instead of MnS. Many steel plants use MgO linings in their ladles and considering that MgS has a complete mutual solubility with MnS, magnesium should be included in a description of sulfides. Of the binary metal-sulfur sub-systems the Fe-S [53,56] and Mn-S [54,76,77] systems have been assessed using the ionic two-sublattice model prior to this work. Additionally, the Ca-S [78], Fe-S [79] and Mn-S [80] systems have been assessed using the modified quasi-chemical model. Of the ternary sub-systems only the Fe-Mn-S [55,76,77,80] system has been assessed using the ionic two-sublattice liquid model prior to this work. Besides the Fe-S system, which was accepted from Lee et al. [49], all sulfur sub-systems have been assessed as part of this work. The stable FeS-sulfide has the NiAs-structure and its mineral name is pyrrhotite. Paper 2 [81] includes the assessment of the Mn-S system and Paper 3 [62] includes the assessments of Ca-S and Mg-S. MnS, CaS and MgS all have the NaCl-structure and is referred to as alabandite which is the mineral name of MnS. The MnS-alabandite was assessed taking heat content and heat capacity measurements [82–85] into consideration while CaS- and MgS-alabandite were assessed using the Neumann-Kopp approximation due to lack of high temperature heat capacity data. The Mn-S system was optimized using experimental data with the exception of the liquid phase at sulfur contents over 50 at%, were the liquid was assumed to behave similar as in the Fe-S system [49]. However, the liquid in Ca-S and Mg-S system were approximated using parameters from the Ca-O [86] and Mg-O [87] systems respectively. The calculated phases diagram of the binary metal-sulfur systems are shown in Figure 7.
Figure 7 Binary metal-sulfur systems, a) Fe-S calculated using parameters from Ref. [49], b) Mn-S from Paper 2 [81], c) Ca-S from Paper 3 [62] and d) Mg-S from Paper 3 [62].

In sulfide systems, just like for oxide, carbide and nitride systems, a good way to represent a system is pseudobinary phase diagrams. In these the different equilibria are plotted along a fixed sulfur content or activity. They are commonly used in handbooks, such as the Slag Atlas [88]. In this work all pseudobinary phase diagrams for the Fe-Mn-Ca-Mg-S system have been assessed at fixed sulfur content. This includes the FeS-MnS from Paper 2 [81], FeS-CaS and FeS-MgS from Paper 3 [62] and CaS-MnS, CaS-MnS and MgS-MnS from Paper 4 [89]. In addition, the FeS-MnS pseudobinary has also been assessed in equilibrium with iron, in principle a fixed sulfur activity. The pseudobinary phase diagrams with fixed sulfur content and fixed sulfur activity assessed in this work are shown in Figure 8 and Figure 9, respectively.
When thermochemical data are available for a system it is a great advantage since this can make the description more accurate. For the Fe-Mn-S system activity data for different parts of the system is found in the literature [101–104]. Additionally, activity measurements have been reported in the CaS-MnS pseudobinary system [105]. The calculated activity in that pseudobinary section from the assessment in Paper 4 is shown together with experimental data in Figure 10.
Experimental data for isothermal sections in the ternaries are only found for the Fe-Mn-S system. Due to the absence of experimental information in the remaining systems no values are set for reciprocal liquid parameters in these systems. The calculated isothermal sections at steelmaking temperature (1600°C) are shown in Figure 11 using results from Papers 2, 3 and 4.

Just like with pseudobinary sections, pseudoternary sections offer a great way to represent sulfide systems. Skinner and Luce [94] reports experimental data for several isothermal pseudoternary sections for the Fe-Mn-Ca-Mg-S system. These are used for the assessment work in Paper 4 [89] and presented in Figure 12. Only a few parameters were needed to fit these systems as the interpolation of the low order systems generally give quite good results.
Figure 11 Isothermal section at 1600°C for the a) Fe-Mn-S, b) Fe-Ca-S, c) Fe-Mg-S, d) Ca-Mn-S, e) Ca-Mg-S and f) Mn-Mg-S systems.
Figure 12 Calculated pseudoternary isothermal sections from Paper 4 [89] of the a) CaS-FeS-MgS at 800°C, b) CaS-FeS-MnS at 800°C, c) CaS-MgS-MnS at 600-1000°C and d) FeS-MnS-MgS at 900-1100°C with experimental data [94].

4.3 Fe-Mg-O and Mg-Mn-O

Given the fact that MgO is a common material used for lining in ladles the Fe-Mg-O system is of great importance for calculations related to steelmaking. This system was already included in the TCOX database but during this project it was fully assessed and published in Paper 3 [62]. The major challenge in this system is the spinel phase which is discussed in Section 3.2.3. The degree of inversion of the MgFe\textsubscript{2}O\textsubscript{4} spinel fitted using experimental data which shown Figure 13. It can be seen that the spinel has an inverse structure at room temperature and gradually transforms toward a normal structure as the temperature increases.

Several thermochemical data were used in this assessment together with phase diagram data. In Figure 14 are experimental phase diagram data are shown together with the calculated
phase diagram in air. In addition, the FeO-MgO pseudobinary and the isothermal section at 1600°C are shown in Figure 15 and Figure 16, respectively. The agreement with the experimental data is generally good for the Fe-Mg-O system.

Figure 13 Degree of inversion in MgFe$_2$O$_4$-spinel calculated using the description in Paper 3 [62] together with experimental data [106–112].
Figure 14 Calculated MgO-FeO\textsubscript{x} phase diagram in air from Paper 3 [62] with experimental data [113–116]. The dashed lines represent the MgO-Fe\textsubscript{2}O\textsubscript{3} phase diagram calculated by setting the oxygen activity to a very high value.

Figure 15 Calculated MgO-FeO pseudobinary from Paper 3 [62] with experimental data [117–121].
A part of the PhD studies were performed at TU Bergakademie Freiberg with the ambition to investigate the thermodynamics of Mg-Mn-Zr-O system. This system is of great importance for the ZrO$_2$-reinforced metal-matrix composite steel, which are proposed by Biermann et al. [124]. In Paper 5 a thermodynamic description of the Mg-Mn-O system and experimental heat capacity of MgMn$_2$O$_4$ and Mg$_6$MnO$_8$ are presented. Like in the Fe-Mg$_2$O$_4$ system the largest challenge in the assessment of the Mg-Mn-O is modeling the spinel phase. However, in this system two spinels are present, the normal cubic spinel at high temperatures and a tetragonal spinel at low temperatures. In this work the heat capacities of the tetragonal MgMn$_2$O$_4$-spinel and Mg$_6$MnO$_8$ were measured as that had not been done previously. The measured and calculated heat capacity is shown in Figure 17. As for the FeMg$_2$O$_4$-spinel the degree of inversion at different temperatures for the tetragonal MgMn$_2$O$_4$-spinel is used in the assessment, which is shown in Figure 18 with experimental data Refs. [125–127]. The phase diagram data presented in a separate publication by the group at TU Bergakademie Freiberg [128] as well as other phase diagram data [129–132] are used in the assessment which is shown in Figure 19 displaying the phase diagram in air. For the equilibria between halite and cubic spinel it should be mentioned that it is chosen to trust the results which suggests a higher Mg solubility despite that earlier studies report a lower Mg solubility in the spinel. The

Figure 16 Calculated isothermal MgO-Fe$_2$O$_3$-FeO section at 1600°C from Paper 3 [62] with experimental data [122,123].
reason for this decision is that x-ray diffraction (XRD) showed that the samples with lower Mg solubility were not cubic. Overall, the work in Paper 5 is an important step toward a larger thermodynamic description related to ZrO$_2$-reinforced metal matrix composites.

Figure 17 Calculated and measured heat capacity from Paper 5 for a) MgMn$_2$O$_4$ spinel and b) Mg$_6$MnO$_8$.

Figure 18 Calculated degree of inversion versus temperature together with experimental data [125–127].
4.4 Fe-Ca-O-S

The Fe-Ca-O-S system is essential to describe desulfurization of steel. The sub-system Fe-Ca-O has previously been assessed [86] and the sub-system Fe-Ca-S has been assessed as part of this work and is presented in Paper 3 [62]. Assessments of the Fe-O-S and Ca-O-S systems are presented in in Paper 6. For the Fe-O-S system several experimental studies are found while the experimental information in the Ca-O-S system is limited. In Figure 20 the calculated pseudobinaries CaO-CaS and FeO-FeS are shown. The information in the Ca-O-S system is limited to the eutectic point reported by Ref. [133]. However, due to the relative similar degree of ionization the liquid can probably be assumed to be ideal. In the Fe-O-S system some studies, see e.g. [134–137], report phase diagram data. Additionally, a lot of activity data is found for this system, see e.g. [137–145]. One type of activity data is the potential phase diagram data obtained at P(SO₂)=1 at different temperatures [138–141,145]. The calculated potential diagrams for both the Fe-O-S and the Ca-O-S systems are presented.
in Figure 21. It should be noted that no ternary interaction parameter was needed for the liquid in the Fe-O-S system which demonstrates the usefulness of the ionic two-sublattice liquid model. Moreover, it demonstrates one of the true strength in CALPHAD that a good model and reliable descriptions of low order systems should give good extrapolation in higher order systems.

Figure 20 Calculated pseudobinaries of the a) FeO-FeS system with experimental data [134,135] and b) CaO-CaS with experimental data [133,146].

Figure 21 Calculated potential phase diagram at $a_{SO_2}=1$ for the a) Fe-O-S system with experimental data [138–141,145] and b) Ca-O-S system.
5 Applications

In this chapter several application examples will be given to demonstrate the usability of the TCOX database and the results obtained in this study. Moreover, this will give an idea of what kind of equilibrium calculations that is possible to perform related to steelmaking and sulfide formation. It should be noted that these examples concern equilibria and not multi-scale modeling of the type discussed in Chapter 2. However, as mentioned in the discussion about ICME it should be emphasized that equilibrium calculations are the basis for more advanced models. The results presented here summarize the results in Paper 7.

5.1 Applications of TCOX in its present state

As mentioned in Section 4.1 the TCOX database contains the most important oxide systems for steelmaking applications. To demonstrate the use of the database some are presented in this section. It is important to be able to predict the oxygen content in the liquid steel. In an experimental study the oxygen content in pure iron is measured after it has been equilibrated with MgAl$_2$O$_4$ spinel for 30 minutes at 1600°C [147]. In Figure 22 the calculated oxygen and magnesium content in liquid steel is shown together with experimental results. One thing of great interest in stainless steel production is chromium recovery from the slag. It is measured with different SiO$_2$ additions [148] and in addition the slag melting temperature is measured, the results are shown in Figure 23 and Figure 24, respectively.

![Figure 22](image)

Figure 22 The calculated and experimental oxygen (red) and magnesium (black) content in liquid steel in equilibrium with MgOAl$_2$O$_3$ spinel using a) Al$_2$O$_3$ crucible and b) MgO crucible.
Figure 23 Calculated chromium recovery as function of SiO₂ content together with experimental data [148].

Figure 24 Calculated slag melting temperature as function of SiO₂ together with experimental data [148].
5.2 Application of sulfide descriptions

As a large part of the work has been focusing on describing sulfide systems and therefore some calculations related to sulfide formation are performed. As much attention has been paid to the Fe-Mn-Ca-Mg-S system in this work it is natural to make a calculation related to sulfide formation in low alloy steels. Not many papers which report equilibration trials concerning sulfide formation in steels are found. A study performed related to MnS formation in Si-steel [149] is used to compare the results for low alloy steels with experimental results, as can be seen in Figure 25. In stainless steels sulfides can also be of importance and for this reason some calculations related to them are made as well. Since Cr and Ni are major alloying elements in stainless steels preliminary descriptions were made to include these elements in the sulfide database. In many cases parameters from the Fe-Me-S systems could likely give a good estimate for these systems. For example, Oikawa et al. [75] suggest that one could approximate the Cr-Mn-S system based on the Fe-Mn-S system. The calculated chromium content in MnS in a stainless steel with 13 % Cr and 0.3 % S is shown in Figure 26 together with experimental data [150]. The sulfur descriptions in their current state can be used for calculations related to sulfides in both low alloy and stainless steels.

Figure 25 Calculated mass fraction MnS in a Si-steel a) without Ca and b) with Ca. The solid vertical line indicates the highest temperature where MnS is observed and the dotted vertical line the lowest temperature without any MnS observation from the experimental study of this steel [149].
Figure 26 Calculated chromium content in MnS as function of Mn content at two different temperatures together with experimental results [150].

5.3 Sulfur in steelmaking

The ambition of this work has been to include sulfur in the TCOX database. For this reason the sulfur descriptions are combined with the TCOX database. At this stage only a few parameters are estimated, in principle missing sulfide end-members, in order to be able to combine the descriptions. In a study [151] the sulphur content in a steel in equilibrium with different slags is measured at different sulphur partial pressures. As can be seen in Figure 27 the agreement with the experimental results is quite good. Another study [152] investigates the sulphur solubility in the CaO-Al₂O₃-CaF₂ system. The calculations shown in Figure 28 are in good agreement with experimental results. Given that few parameters have been set in order to combine the TCOX database with the sulfide descriptions the results are really good. This does not only demonstrate the usability of the descriptions but also demonstrates that the ionic two-sublattice liquid model is indeed powerful when it comes to extrapolating to higher order system.
Figure 27 Calculated sulphur content at different sulphur partial pressure for four different slags, obtained at log(PO$_2$)=-10.28.

Figure 28 Calculated (solid lines) and experimental (dotted lines) sulphur solubility in the CaO-Al$_2$O$_3$-CaF$_2$ system.
6 Conclusions and future work

Modeling of materials is a powerful tool in order to improve the profitability at steelmaking companies. Already today the ICME approach and the materials genome are showing their usefulness with real applications. It will most likely have even more impact in the future. The core of the materials genome, and thus ICME, is the CALPHAD method. As part of this work the ICME approach has been applied on the vacuum degassing process combining CALPHAD and genetic algorithms. In that model the process time is optimized since is it closely related to the cost. The results are really promising but it would be very interesting to try the methodology at a steel plant. However, the ideas do not necessarily have to involve the vacuum degassing but could equally well be used on another process, for example argon oxygen decarburization (AOD) or electric arc furnace (EAF).

Given the importance of having good thermodynamic databases a major part of this work has involved assessment of sulfur-containing systems of importance for steels. The Fe-Mn-Ca-Mg-S system has been described fully. Moreover, the approximate descriptions of other metal-sulfur systems have been added to this description. Finally, the Fe-Ca-O-S system has been described fully. Generally, the thermodynamic descriptions fit well with experimental data. However, in some cases experimental data is lacking and efforts should be made to get more information about these systems. In addition to the sulfur-containing systems, the Fe-Mg-O and Mg-Mn-O systems have been assessed during this work. Having reliable descriptions of these systems is important for the usability of the TCOX database.

The sulfur description done in this work is validated using experimental results. In addition, calculations using the current description in TCOX are compared with experimental results. On top of this, the sulfur descriptions are combined with the TCOX database to obtain a preliminary description containing both oxygen and sulfur. The results of the sulfide and oxide calculations agree well with experimental results. Combining the sulfur descriptions with the TCOX database also gives good agreement with experimental results. Thanks to the efforts in this work the next release of TCOX database will include sulfur. Additionally, it will also include fluorine, niobium and cupper, thanks to parallel efforts. Moreover, efforts are made to add vanadium as well. The natural next step is to add nitrogen as it is an important element to consider in the steelmaking process. Since it does not dissolve in the slag it would probably be relatively easy. In addition, phosphorus should be added as this is also an
important element in the steelmaking process but that will probably be more complicated considering the different oxidation states of phosphorus. Of course, minor alloying elements like titanium and molybdenum should also be included in the description.

To conclude, CALPHAD is an important modeling tool for materials development and it is one of the cornerstones in ICME. Using this approach it is possible to develop better materials and processes faster which is a key to profitability. Thus one can say that profitability is indeed a function of Gibbs energy. Of course other factors have to be involved as well of which some can be handled using ICME. Finally, it must be emphasized that it is up to the steel producers to use the ideas as well as the results presented in this thesis and other sources to increase their profitability and to make a better world. This would benefit their stock owners and customers but also the rest of society.
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