General Equation of State for Gaseous Environments

Allgemeine Zustandsgleichung für gasförmige Umgebungen

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Zusammenfassung

Für die Berechnung vieler numerischer Simulationen stellt die Zustandsgleichung ein Herzstück dar. Anwendungsgebiete sind breit gestreut und reichen von der chemischen Analyse von Verbrennungen bis hin zu Fragestellungen in der Atmosphärenphysik.

Die allgemeine Zustandsgleichung wurde für zunächst pure Gasumgebungen implementiert. Hiermit sollte es unter anderem zuverlässig und zügig möglich sein, das chemische Gleichgewicht bei Zwangsbedingungen von fixer Gastemperatur und -druck oder auch bei fixem totalen Systemvolumen und innerer Systemenergie zu lösen.

Um aus der Vielzahl an möglichen Lösungsansätzen hierfür den passenden zu finden, fand als erstes eine Literaturrecherche statt, die neue, sowie alte numerische Realisierungen des Problems betrachtete und kritisch bewertete. Als geeignet wurde eine stoichiometrische Methode befunden, die auf den optimierten Villars-Cruise-Smith Algorithmus beruht. Verglichen mit anderen Ansätzen liegen die Vorteile hier vor allem in der Schnelligkeit, mit der das chemische Gleichgewicht bestimmt wird, und dass in der Regel keine Konvergenzprobleme auftreten. Dies gilt sogar für Systeme, die kondensierte und flüssige chemische Spezies beinhalten. So könnte eine Lösung stets zuverlässig gefunden werden.

Ein Vergleich der Ergebnisse des implementierten stoichiometrischen Algorithmus mit Berechnungen von chemischen Gleichgewichten aus der Literatur zeigte in der Regel eine bemerkenswert gute Übereinstimmung. Auch extreme Umgebungen, bei denen besonders hohe und niedrige Drücke und Temperaturen herrschen, konnten im Allgemeinen reproduziert werden. Durch die numerische Abschätzung von anfänglichen Spezieshäufigkeiten („initial estimate“) war es außerdem möglich, die Geschwindigkeit des realisierten Codes, mit der eine Gleichgewichtszusammensetzung gefunden wurde, in vielen Fällen weiter zu verbessern. Es zeigte sich, dass besonders bei großen Systemen, die mehrere hundert Spezies beinhalten, häufig mehr als eine Halbierung der Berechnungszeit möglich war.

Abstract

An equation of state is the centrepice of many numerical simulations. Areas of application are widely spread, ranging from the chemical analysis of combustion, to issues in atmosphere physics.

For, initially, pure gaseous environments, the general equation of state was implemented. With this, it should be possible to reliably and rapidly determine the chemical equilibrium composition using the constraints of fixed gas temperature and pressure or of fixed total system volume and internal energy.

As a first step, in order to find the most suitable approach, a review of literature took place. New, as well as old, numerical algorithms to solve the equilibrium problem were considered and critically evaluated.

Based on the optimized Villars-Cruise-Smith code, the stoichiometric method was found appropriate for our purposes. In particular, compared with other approaches, the advantages are the speed of calculating the equilibrium and, furthermore, no convergence issues are known. This is true even for systems that include condensates and liquid chemical species. Hence, a solution can be reliably determined at all times.

The results of the implemented stoichiometric algorithm were compared with published calculations of chemical equilibrium compositions. Generally, a remarkably good consistency of them was found. In addition, environments with exceptional pressures and temperatures could be reproduced.

An initial estimate of the initial species abundance improved the performance to find the equilibrium composition. Especially in large systems, which take several hundred species into account, less than a half calculation time was achieved in many cases.

Contents

1 Motivation

An equation of state (EOS) is a substantial part of a variety of different (computer) simulations. For example, it is a centrepiece of atmospheric physics and chemistry as well as of the chemical analysis of combustions and propellants. All these examples have in common that a chemical equilibrium state has to be calculated based on an appropriate EOS for a given environment. Such an equilibrium can be regarded as the limiting case of a system of chemical reactions. A detailed description of this state would be difficult to implement because, apart from the fact that the microscopic data of the chemical reactions do not exist or are highly uncertain, the resulting numerical systems can be overwhelming. Nevertheless, the thermodynamic assumption of a local chemical equilibrium is particularly reliable in quasi-static systems like, e.g., stellar atmospheres. A proper definition of such an equilibrium is given in Section 2.1. Highly dynamic environments with, for instance, strong convective motions would require a time-dependent consideration of the problem. For the reasons mentioned above, the implementation of a chemical equilibrium-solving algorithm is a vital and powerful tool with a large range of application. Especially in complex simulations an outstanding feature is that a solution of the EOS has to be found in each iteration until convergence of the system is achieved, and concerning (spacially resolved) hydrodynamics, even at each grid cell. A rapid and reliable determination of an equilibrium state is, therefore, instrumental because a very small improvement in performance of the EOS-solving module can easily result in a significant drop in total simulation time.

Another essential requirement for this kind of code is robustness. Particularly in the context of time-consuming hydrodynamic simulations and very complex chemical systems, including several hundred different species, a reliable solution of the equilibrium state is needed. This way the loss of hours or even days of simulation time due to inaccurate calculations or even divergence caused by errors of the EOS could be prevented.

To support a more general applicability, the possibility to expand the code to handle solids, liquids, phase transitions and various types of EOS for, optionally, imperfect gas-mixtures is important. In the framework of this master thesis initially only ideal and pure gaseous systems were considered.

Furthermore, the algorithm should achieve a high level of accuracy. An inaccurately working code is, of course, practically worthless.

The first step to find an approach that meets exactly the above criteria was a review of literature, which is presented in Section 2.2. In the last decades, many different approaches and algorithms were developed to solve the chemical equilibrium problem. At this point, a critical evaluation of them is appropriate and presented in Section 2.3.

As a promising approach the method of optimized stoichiometry was identified and implemented. Some of the main features of the final code are listed in Chapter 3. In Chapter 4, a test of accuracy was done primarily by comparing its results to literature data. A number of well-defined and partially very simple test cases have been run. However, because they were of limited value in evaluating the robustness of the algorithm, further tests concerning extreme conditions were performed and described in Chapter 5.

After confidence in reliability and robustness was established, effort was put into improving the performance without changing the results (Chapter 6). Besides efficient coding, a review of literature was helpful. There are a number of published approaches to achieve a faster solution of the equilibrium problem. Notably among them, a numerical initial estimate of the equilibrium composition has turned out very promising. This way, a solution could be found several orders of magnitude faster than without such an initial estimate.

Only when all mentioned criteria are satisfyingly fulfilled, the implemented chemical equilibrium solver could be included as a module in a hydrodynamic or other simulation code.

2 Theory: Chemical Equilibrium

Undoubtedly, the determination of a chemical equilibrium composition is one of the most important applications of an equation of state of gaseous environments. The simplest EOS is the ideal gas law,

$$PV = nRT, \tag{2.1}$$

which relates the thermodynamic state variables gas pressure P, total volume V, number of moles n and temperature T. In this equation, R is the ideal gas constant.

Accordingly, the focus of this master thesis is on the calculation of a chemical equilibrium composition based on an initial state of the system using the ideal gas law. Unless stated otherwise, the following theoretical description of chemical equilibrium in Section 2.1 and of stoichiometry in Section 2.2.2 have been taken from Smith & Missen (1982) and Wong (2001).

In the last decades different numerical approaches were established to solve such an equilibrium state. The earliest ones were based on stoichiometric and non-stoichiometric equations. But, particularly, in the course of further technical development, advanced formulations of the equilibrium problem arose. For instance, it has become possible to take chemical reaction rates into account to apply detailed chemical kinetics. However, the computational effort required increases considerably. In this context, a more practical solution could be the assumption of rate-controlled constraint-equilibrium. According to this approach, the equilibrium problem is separated into different timescales, where the slow sequences can change the constraints and, therefore, require the use of reactions rates. However, the faster sequences can be calculated with help of carefully chosen contraints. At this point a stoichiometric algorithm could be one centre piece.

A selection of the most common old as well as new computational approaches of calculating the chemical equililibrium is presented in Section 2.2, including their advantages and disadvantages. Finally, a critical comparison of these algorithms concerning their applicability follows in Section 2.3.

2.1 Chemical Equilibrium

A closed thermodynamic system reaches the state of chemical equilibrium after a certain period of time. Distinctive for this state is a macroscopically unchanged system composition with no perceivable net change in the amounts of its species. It is a dynamic equilibrium because, from a microscopic perspective, there are still forward and reverse reactions but their time-averaged rates are equal.

Assuming a closed system, the conservation of mass constraint must be satisfied. A set of element-abundance equations, defined as

$$\sum_{i=1}^{N} a_{ki} n_i = b_k \qquad \text{with} \qquad k = 1, 2, ..., M, \tag{2.2}$$

correlates the fixed number of moles of the k^{th} element in the system, b_k, with the required chemical species i in such a way that there is neither loss nor increase in mass. Here, a_{ki} is the index of element k in the molecular formula of species i, n_i is the species number of moles, M the total number of elements and N the total number of species in the system. With the help of

$$\mathbf{A}\mathbf{n} = \mathbf{b}, \tag{2.3}$$

Equation 2.2 can be rewritten in vector-matrix notation, defining $\mathbf{A} = (\mathbf{a}_1, \mathbf{a}_2, ..., \mathbf{a}_N)$ as $(M \times N)$ formula matrix consisting of the formula vectors $\mathbf{a}_i$, $\mathbf{n} = (n_1, n_2, ...n_N)^T$ with $n_i \geq 0$ as species-abundance vector and $\mathbf{b} = (b_1, b_2, ..., b_M)^T$ as element-abundance vector. The important additional condition for the amount of the species,

$$n_i \geq 0 \qquad \text{with} \qquad i = 1, 2, ..., N, \tag{2.4}$$

is called non-negativity constraint. It states that a species is either present or it is not but it can never be negative.

According to the second law of thermodynamics, the entropy S cannot decrease in a closed and adiabatic system,

$$dS_{\mathrm{ad}} \geq 0, \tag{2.5}$$

and the Gibbs free energy G cannot increase in a system with constant temperature T and pressure P,

$$dG_{\mathrm{T,P}} \leq 0. \tag{2.6}$$

In these equations, d stands for an infinitesimal change in S and G.

In equilibrium, the entropy has thus its (local) maximum and the Gibbs free energy has its (global) minimum, i.e. $dG = 0$. It is defined as

$$dG = -SdT + VdP + \sum_{i=1}^{N} \mu_i dn_i \tag{2.7}$$

or for fixed temperature, pressure and chemical composition as

$$G = \sum_{i=1}^{N} \mu_i dn_i \tag{2.8}$$

with μ_i as the chemical potential

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_{j \neq i}} . \tag{2.9}$$

Hence, solving chemical equilibrium is a minimization problem. For fixed temperature and pressure, G_{min} has to be found.

But there are also other potential functions like the Helmholtz function A, the enthalpy H or the internal energy U that can be minimized to determine the equilibrium composition. They are connected to each other via Legendre transformations (see, e.g., Nolting, 2005). In these cases, other properties are kept constant. That is a fixed total volume and temperature for A_{min}, a fixed pressure and entropy for H_{min} and a fixed volume and entropy for U_{min}.

Such constant independent properties identify the thermodynamic state constraints for the system. Most frequently used are fixed temperature and pressure. Another important state constraint is the one of fixed total internal energy and total volume, but it is based on the (T,P)-constraint.

2.2 Solving Chemical Equilibrium

The following description of the most common different computational approaches to solve a chemical equilibrium is intended as an overview. It begins with the oldest and relatively simple non-stoichiometric and stoichiometric approaches and ends with the newer and advanced Rate-Controlled Constrained-Equilibrium approach. Especially the basic concept of stoichiometric algorithms is decribed in more detail. This is because the code we implemented is based on the stoichiometric Villars-Cruise-Smith (VCS) algorithm.

2.2.1 Non-Stoichiometrical Approach

Probably the most representative non-stoichiometric algorithms are the RAND (White et al., 1958), NASA (Gordon & McBride, 1971; Huff, 1951), Brinkley (Brinkley, 1947) and Blake (Freedman, 1982) algorithms.

Their basic principle is the formulation of the chemical equilibrium problem as a minimization of Gibbs free energy on the condition that (T,P)-constraints are used. The conservation of mass constraint is treated separately and is realized by the use of Lagrange multipliers $\boldsymbol{\lambda} = (\lambda_1, \lambda_2, ..., \lambda_M)^T$ (except for the Blake code):

$$\mathcal{L}(\mathbf{n}, \boldsymbol{\lambda}) \equiv \sum_{i=1}^{N} n_i \mu_i + \sum_{k=1}^{M} \lambda_k \left(b_k - \sum_{i=1}^{N} a_{ki} n_i \right). \tag{2.10}$$

The remaining variables are defined as above. The resulting set of $(M + N)$ non-linear equations,

$$\left(\frac{\partial \mathcal{L}}{\partial n_i} \right)_{n_{j \neq i}, \boldsymbol{\lambda}} = \mu_i - \sum_{k=1}^{M} a_{ki} \lambda_k = 0 \qquad \text{if} \qquad n_i > 0, \tag{2.11}$$

or

$$\left(\frac{\partial \mathcal{L}}{\partial n_i} \right)_{n_{j \neq i}, \boldsymbol{\lambda}} = \mu_i - \sum_{k=1}^{M} a_{ki} \lambda_k \geq 0 \qquad \text{if} \qquad n_i = 0, \tag{2.12}$$

and

$$\left(\frac{\partial \mathcal{L}}{\partial \lambda_k} \right)_{\lambda_{j \neq k}, \mathbf{n}} = b_k - \sum_{i=1}^{N} a_{ki} n_i = 0, \tag{2.13}$$

is solved by the Newton-Raphson method. Despite using the principle of non-stoichiometry, these algorithms can use stoichiometric coefficients (e.g., Brinkley method). Generally, non-stoichiometric codes require the solution of a set of $(M+N)$ non-linear equations on each iteration, with N as number of species and M as number of elements involed. For ideal systems, this may be reduced to $(M+\pi)$, with π as number of phases (Smith & Missen, 1982).

The RAND, NASA and Brinkley methods differ from each other only in minor ways. They are computationally equivalent with only little difference in convergence and no significant advantage of one method over the other (Zeleznik & Gordon, 1960), especially, since the RAND and NASA methods utilize nearly identical equations (Gautam, 1979).

One big disadvantage is the requirement of matrix inversion at each iteration step. Hence, there is the possibility of non-trivial numerical problems when the coefficient matrix of the non-linear equations becomes numerically singular. This might occur whenever there is more than one phase (Smith & Missen, 1982). Additionally, the models converge slowly when many trace species are included (Ruda, 1982).

As mentioned by Smith & Missen (1982), there are a few other non-stoichiometric algorithms but with no particular advantage over the Brinkley, RAND and NASA algorithms. For example, Gautam (1979) showed that Powell's method (George et al., 1976) is slower than the RAND code.

2.2.2 Stoichiometrical Approach

The most important stoichiometric algorithm is the Villars-Cruise-Smith (VCS) algorithm (Smith & Missen, 1982) which is the basis of our code that has been implemented for this work. Other stoichiometric algorithms like Naphtali (1959, 1961) might not converge as quickly as the VCS method (Smith & Missen, 1982).

With this approach the result is essentially an unconstrained minimization problem.

A stoichiometric vector, ν_j, is nonzero and is defined by

$$\mathbf{A}\nu_j = \mathbf{0} \qquad \text{with} \qquad j = 1, 2, ..., R. \tag{2.14}$$

The maximum number of linearly independent solutions of this equation is given by

$$R = N - C. \tag{2.15}$$

C is the maximum number of linearly independent element-abundance equations and usually equal to the number of elements M:

$$C = \operatorname{rank}(\mathbf{A}) \leq M. \tag{2.16}$$

Using such a real stoichiometric vector ν_j and defining a set of real parameters ξ_j with $j = 1, 2, ...R$, a general compositional solution $\mathbf{n}$ of Equations 2.2 and 2.3 can be written as

$$\mathbf{n} = \mathbf{n}^0 + \sum_{j=1}^{R} \nu_j \xi_j. \tag{2.17}$$

The initial composition is representable by $\mathbf{n}^0$, which stands for any particular solution of Equation 2.17. The conservation of mass constraint is always satisfied because a pre-multiplication of Equation 2.17 by $\mathbf{A}$, in consideration of Equation 2.14, results in

$$\mathbf{An} = \mathbf{An}^0 + \sum_{j=1}^{R} \xi_j \mathbf{A} \nu_j = \mathbf{b}. \tag{2.18}$$

By means of a stoichiometric coefficient of the i^{th} species in the j^{th} stoichiometric vector, ν_{ij}, Equation 2.17 is rewritten to

$$n_i = n_i^0 + \sum_{j=1}^{R} \nu_{ij} \xi_j \qquad \text{with} \qquad i = 1, 2, ..., N. \tag{2.19}$$

Assuming a fixed $\mathbf{n}^0$, this coefficient ν_{ij} can be regarded as change in the number of moles of species i with respect to a unit change in ξ_j:

$$\left(\frac{\partial n_i}{\partial \xi_j} \right)_{\xi_{k \neq j}} = \nu_{ij}. \tag{2.20}$$

Based on these considerations, a set of linearly independent stoichiometric equations,

$$\sum_{i=1}^{N} A_i \nu_{ij} = 0 \qquad \text{with} \qquad j = 1, 2, ..., R, \tag{2.21}$$

is obtained, using the stoichiometric coefficients and replacing the formula matrix $\mathbf{A}$ in Equation 2.14 by the chemical formula A_i of the formula vectors $\mathbf{a}_i$. Such a set is not unique and relates all the species. Right after specifying a list of involved species, the R stoichiometric equations can be determined.

Therefore, a complete stoichiometric $(N \times R)$-matrix $\mathbf{N}$ is defined,

$$\mathbf{N} = (\boldsymbol{\nu}_1, \boldsymbol{\nu}_2, ..., \boldsymbol{\nu}_R), \tag{2.22}$$

with R columns consisting of arbitrarily chosen linearly independent stoichiometric vectors $\boldsymbol{\nu}_j$. The species of the system are separated into the component species C, the ones with linearly independent formula vectors, and into the $(N - C)$ remaining non-component species R.

The formula matrix $\mathbf{A}$ is reducible to the following matrix form,

$$\mathbf{A}^* = \begin{pmatrix} \mathbf{I}_C & \mathbf{Z} \\ \mathbf{0} & \mathbf{0} \end{pmatrix}, \tag{2.23}$$

with a $(C \times C)$-identity matrix $\mathbf{I}_C$ and the $(C \times R)$-matrix $\mathbf{Z}$. From this, $\mathbf{Z}$ is determinable and the complete stoichiometric matrix

$$\mathbf{N} = \begin{pmatrix} -\mathbf{Z} \\ \mathbf{I}_R \end{pmatrix} \tag{2.24}$$

can be obtained, where $\mathbf{I}_R$ is the $(R \times R)$-identity matrix. In conjunction with Equation 2.21, the set of chemical equations of the system is assignable as follows:

The sub-matrix $\mathbf{Z}$ is specified by

$$\mathbf{A}_C \mathbf{Z} = \mathbf{A}_R, \tag{2.25}$$

where $\mathbf{A}_C$ are the columns of $\mathbf{A}$ that are assigned to the component species and $\mathbf{A}_R$ to the noncomponent ones. Therefore, the stoichiometric basis $\mathbf{Z}$ can be identified directly by the formula matrix $\mathbf{A}$:

$$\mathbf{Z} = \mathbf{A}_C^{-1} \mathbf{A}_R \tag{2.26}$$

since

$$\mathbf{AN} = (\mathbf{A}_C, \mathbf{A}_R) \begin{pmatrix} -\mathbf{A}_C^{-1}\mathbf{A}_R \\ \mathbf{I}_R \end{pmatrix} = -\mathbf{A}_R + \mathbf{A}_R = \mathbf{0}. \tag{2.27}$$

As mentioned in Section 2.1, a minimization of the Gibbs free energy at fixed temperature and pressure will yield to the equilibrium composition of the system. In the stoichiometric formulation, G is a function of temperature, pressure and the parameter ξ. Hence, the system

$$\left(\frac{\partial G}{\partial \xi_j}\right)_{T,P,\xi_{i\neq j}} = \sum_{i=1}^{N} \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} \left(\frac{\partial n_i}{\partial \xi_j}\right)_{\xi_{i\neq j}} = 0 \qquad \text{with} \qquad j = 1, 2, ..., R, \tag{2.28}$$

must be solved. Finally, with Equations 2.20 and 2.9 this can be rewritten as

$$\sum_{i=1}^{N} \nu_{ij}\mu_i = 0 \qquad \text{with} \qquad j = 1, 2, ..., R. \tag{2.29}$$

The solution of such a set of $R = (N - M)$ non-linear equations is required on each iteration. In contrast to the non-stoichiometric formulation, the number of variables is always $(N - M)$, regardless of whether the systems are ideal. Hence, for non-ideal environments the stoichiometric algorithms will have fewer variables.

Additionally, the equilibrium conditions are represented by the non-linear equation

$$\mathbf{\Delta G} \equiv \left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \mathbf{N}^T \boldsymbol{\mu}(\boldsymbol{\xi}) = \mathbf{0} \tag{2.30}$$

as well and can also be used to solve the chemical equilibrium problem. This non-linear equation is solved by the Newton-Raphson method, using the superscript (m) as iteration-step index,

$$\delta\xi^{(m)} = -\left(\frac{\partial^2 G}{\partial \xi^2}\right)^{-1}_{n^{(m)}} \left(\frac{\partial G}{\partial \xi}\right)_{n^{(m)}}, \tag{2.31}$$

which represents a stoichiometric second-order method. Due to the fact that still R non-linear equations have to be solved on each iteration, an improvement can be useful. In particular, such an optimized stoichiometric approach is employed in the VCS algorithm. The resulting matrix can be approximated as a near-diagonal matrix by rearranging the species list and applying matrix operations. For instance, presuming a single ideal phase, Equation 2.31 can be rewritten to

$$\delta\xi^{(m)} \approx -\left(\frac{1}{n_{j+M}^{(m)}} + \sum_{k=1}^{M} \frac{\nu_{kj}^2}{n_k^{(m)}} - \frac{1}{n_t}\sum_{k=1}^{N} \nu_{kj}\right)^{-1} \frac{\Delta G_j^{(m)}}{RT} \quad \text{with} \quad j = 1, 2, ..., R, \tag{2.32}$$

where n_t is the total number of moles in the system with component species numbered from 1 to M and non-component ones from $M+1$ to N. For a detailed derivation see Smith & Missen (1982). This way, there is no need of time-consuming matrix inversions and no need for the solution of non-linear equations on each iteration anymore. Thus, further advantage over the non-stoichiometric algorithms is the handling of multiphases (Smith & Missen, 1982).

2.2.3 Chemical Kinetics Approach

Chemical kinetics deals with chemical reaction rates, using stoichiometric coefficients. To describe a combustion system, it relies on fluid dynamics and heat transfer (McAllister, 2011; Kee et al., 1996).

Most common is the general purpose CHEMKIN software. It is advertised as a very fast and robust tool that can manage thousands of reaction combinations (Reaction Design, 2013; Sandia National Laboratories, 2013). Another code is Cantera, but it is only capable of solving simple equilibrium systems (Goodwin, 2001).

As a big disadvantage, detailed chemical kinetics can easily exhaust computational systems depending on the number of species involved.

2.2.4 Element-Potential Method

For our purpose, an interesting algorithm could be the STANJAN code, which uses Lagrange multipliers to minimize the Gibbs free energy of the system (Reynolds, 1986). The mole fractions of each species is related to element potentials (= Lagrange multipliers). Hence, if the mole fraction of one dominant species in the system is estimated for each element, the element potential can be specified and, then, the mole fractions of all other species as well.

Only these element potentials plus the total number of moles in each phase are the variables that need to be adjusted to obtain the solution. In contrast to detailed chemical kinetics, an identification of a set of reactions is not required. Even for systems with a large number of species and multiphase systems, the resulting number of unknowns is comparatively small. Especially in combination with good initial guesses, this code converges very fast with high accuracy (Reynolds, 1986).

Unfortunately, since 1997, this code has been under license to Reaction Design, Inc. and is not freely available anymore.

Another code, based on the element-potential method, is CEQ (Pope, 2003). Newton's method, as employed by STANJAN to solve its non-linear equation system, is not guaranteed to converge if the initial guess is too far from the solution, because the iteration matrix can be singular. In this context, Pope (2004) prefered the method of Gibbs function continuation which can ensure convergence.

2.2.5 Rate-Controlled Constrained-Equilibrium Approach

For large chemical systems, the assumptions of rate-controlled constrained-equilibrium (RCCE) may result in an efficient determination of equilibrium compositions (Bishnu et al., 1997; Metghalchi, 2009; Keck, 1990). This method simplifies the kinetics of complex reacting systems by reducing the dimensions of the system-descriptive variables. Hence, the number of equations that need to be solved can be much smaller than the number of species. Additional and carefully specified constraints on the system are required, e.g. total moles and free valence of the radicals (Bishnu et al., 1997). It was shown that the performance of RCCE is very sensitive to the choice of constraints (Tang & Pope, 2004).

RCCE is based on the assumption that a relatively small number of rate-controlling reactions imposes slowly changing constraints in the allowed states of the system. The fast reactions relax the system to the constrained-equilibrium state. Their timescale is short compared to that on which the constraints are changing. Therefore, the system will relax to equilibrium through a sequence of RCCE states. Only the rates of reactions which slowly change the constraints are required.

For this reason, the calculations for small systems, in which the number of species is not much larger than the number of constraints, may take more CPU time than is required to integrate the full set of rate equations (Keck, 1990).

2.3 Critical Comparison of Chemical Equilibrium Approaches

Smith & Missen (1982) calculated a simple hydrazine combustion with the VCS and the RAND algorithms. Concerning the total computation time, there were no essential differences, despite of the need of about half as many iterations for the RAND code compared to the VCS approach. It must be mentioned, there is not inevitably a direct correlation between the CPU time required to achieve convergence and the corresponding number of iterations.

Wong (2001) provided a comparison of performance and robustness of the non-stoichiometric Blake, Bagheera and NASA codes with an extended version of the stoichiometric VCS algorithm (E-VCS). For the test problems with (U,V)-constraints, up to a moderate/large number of species were used with and without phase transitions. The result is that the NASA code needed less CPU time than the E-VCS, Blake and Bagheera codes but has its problems with an increasing number of condensing species. In this case, the E-VCS code is much more robust, faster and needs less iterations than all other tested algorithms. In systems with phase-transitions, the E-VCS code is slower than the NASA and Bagheera codes. Nevertheless, Wong (2001) showed, that for problems with (T,P)-constraints, the VCS algorithm should be faster than the NASA code, regarding results by Smith & Missen (1968). Smith & Missen (1968) combined the VCS method with a convergence forcer and a linear programming scheme and compared it to the RAND method. It turned out that, in 48 out of 50 tested systems, this VCS approach was faster than the RAND method. Additionally, the RAND algorithm fares inaccurately when the coefficient matrix of the non-linear equations approached singularity. VCS algorithms are independent of this non-stoichiometric problem because no set of non-linear equations has to be solved in each iteration. Due to the fact that the RAND code is computationally equivalent to the NASA approach, the lack of performance of Wong's E-VCS code could have been a result of the extension of the VCS algorithm, which was needed for the handling of the (U,V)-constraint.

In some instances, the STANJAN, and the NASA code as well, can fail in complex gas mixtures. A modification of both codes using RCCE assumptions showed that STANJAN is superior to NASA, concerning convergence and speed (Bishnu et al., 1997).
Regarding accuracy, RCCE methods should be not inferior to detailed chemical kinetics, as presented in Metghalchi (2009). Requirement for this is a careful selection of the constraints.

Unquestionably, the VCS approach is more likely a general purpose algorithm than the non-stoichiometric codes. In particular for multiphase systems with many condensed species, there is no risk of matrix singularities. Hence, it is a very robust and reliable algorithm usually with no convergence problems, in contrast to the non-stoichiometric approaches. In addition, the number of unknowns is less in systems with many elements and in systems which are non-ideal than in other methods.
The NASA code and the computationally equivalent Brinkley and RAND codes, are recommended for systems with purely gaseous species with no involved phase transitions. In such systems, the risk of convergence problems is minimized and a solution is found rather quickly with respect to computation time but also to number of iterations.
For environments with a very large number of species, detailed chemical kinetics need too much calculational effort. Generally, in these systems, methods that do not require an identification of a set of reactions absolutely should be prefered.
The very promising STANJAN solver, which is based on the element-potential method, is licensed as part of the CHEMKIN software and cannot be tested without funding. On the other hand, the CEQ code could be an alternative.
Additionally, a very good method could be the RCCE approach which reduces the effort even at very complex systems. But the associated code is very sophisticated, an implementation is, therefore, not easily feasible. In this case, it was considered to be better to spend time on the realization of a simpler reliable and fast algorithm where, if necessary, RCCE could be implemented as following step. To eventually do so, an algorithm based on the stoichiometric VCS approach was implemented.

3 Theory: The Stoichiometric Chemical Equilibrium Solver (StoiCES)

Based on the results of the literature review in Section 2.2 and 2.3, the Stoichiometric Chemical Equilibrium Solver (StoiCES) was implemented. The general principles of a stoichiometric approach to determine an equilibrium composition has been presented in Section 2.2.2. Just like the VCS algorithm, StoiCES uses optimized stoichiometry, which means that no matrix inversions and no solution of non-linear equations in each iteration are required. To implement this code, some further considerations were needed regarding the inclusion of thermodynamic data, the handling of different state constraints and efficiency. One focus was improvement of performance to find a solution as quickly as possible. A computational initial estimate and some adjustments of stoichiometric equations have been proven to be helpful in this context.
In this chapter, the main features of StoiCES are briefly summarized.

3.1 Thermodynamic Data

The thermodynamic data included was taken from the non-stoichiometric NASA program CEA, standing for Chemical Equilibrium with Applications (Gordon & McBride, 1994; McBride & Gordon, 1996). For gaseous as well as condensed species, this library provides the molecular weight, heat of formation and polynomial coefficients for a determination of the i^{th} species heat capacity $\frac{C_{p,i}^0}{R}$, enthalpy $\frac{H_i^0}{RT}$ and entropy $\frac{S_i^0}{R}$ at assigned temperatures. The superscript 0 indicates the respective value at its reference state, i.e. at 1bar and 298.15K.

In a perfect gas mixture, the chemical potential of species i is given by

$$\frac{\mu_i}{RT} = \frac{\mu_i^0}{RT} + \ln P_i. \tag{3.1}$$

Here, μ_i is a function of temperature and pressure, whereby the standard chemical potential μ_i^0, defined as

$$\frac{\mu_i^0}{RT} = \frac{H_i^0}{RT} - \frac{S_i^0}{R}, \tag{3.2}$$

that is a function of temperature T only. The standard chemical potential can be calculated with help of the provided thermodynamic data.

3.2 Thermodynamic State Constraints of Constant (U,V)

Many thermodynamic problems are located within a finite volume, for example a chemical analysis of a combustion within a vessel. The internal energy may be fixed as well, especially if adiabatic boundaries are considered. Thus, a calculation of the equilibrium composition, which is able to handle thermodynamic state constraints of constant internal energies and volume, extends the applicability of StoiCES.

To accomplish that, first, a pair of T and P is arbitrarily guessed. With help of the (T,P)-constraints, the appropriate Gibbs free energy is minimized and the equilibrium composition is determined. A comparison of the internal energy of this solution, U_{new}, to the initial internal energy U_{init}, shows whether T is too far from the equilibrium temperature. Since an adiabatic system in the equilibrium state is considered, the internal energy of the reactants equals the one of the product mixture. This is the case whenever $U_{\text{init}} = U_{\text{new}}$. This means a too high U_{new} indicates a too low guessed temperature and vice versa. As a result, the new T must be decreased or increased, respectively, which is realized by the application of a bisection method. Using the ideal gas law, the respective P can be determined. The new pair of temperature and pressure are now the current initial parameters for the (T,P)-constraints to estimate a new equilibrium composition. Only when there is a negligibly small difference in U_{new} and U_{init}, the right pair of T and P has been found.

3.3 Initial Estimate

Smith & Missen (1968) have shown that a good initial estimate (IE) of the equilibrium composition will achieve a faster solution with less iterations.

For this method, the initial species abundances $\mathbf{n}^0$ in Equation 2.17 are estimated consistent with the element abundances $\mathbf{b}$:

$$\min_{\boldsymbol{\mu}^* \in \mathbb{R}^n} \{\mathbf{n}^T \boldsymbol{\mu}^* \mid \mathbf{A}\mathbf{n} = \mathbf{b},\ n_i \geq 0\} \tag{3.3}$$

where $\boldsymbol{\mu}^*$ is the standard chemical potential. In StoiCES, this linear programming problem is solved by a simplex method (e.g., Press, 1992). The resulting composition within the solution space can be rewritten to

$$\mathbf{n} = \mathbf{n}^0 + \lambda d\mathbf{n}, \tag{3.4}$$

introducing the step-size parameter λ with $0 < \lambda \leq 1$ for which the most appropriate value is found by calculating

$$(dG/d\lambda) = \boldsymbol{\mu}^T d\mathbf{n} \tag{3.5}$$

in such a way that G is minimized. Following Smith & Missen (1968), if $(dG/d\lambda)_{\lambda=1} \leq 0$, the most favourable value of λ is obtained. If $(dG/d\lambda)_{\lambda=1}$ is positive, Equations 3.4 and 3.5 are recalculated with reduced step-size using $\lambda = 0.5$, in order to prevent overshooting. For the same reasons, $(dG/d\lambda)_{\lambda=0.5} > 0$ necessitates further reduction of λ, in this case to a value of 0.2. On the other hand, if $(dG/d\lambda)_{\lambda=0.5}$ is negative, determine

$$\beta = 0.5 \left(\frac{1 - (dG/d\lambda)_{\lambda=0.5}}{(dG/d\lambda)_{\lambda=1} - (dG/d\lambda)_{\lambda=0.5}} \right). \tag{3.6}$$

In the case of $\beta \leq 1$, this sets the new $\lambda = \beta$ value, and, if $\beta > 1$, the species abundances n_i calculated by $\lambda = 1$ are the best obtainable ones. A $(dG/d\lambda)_{\lambda=0.5} = 0$ indicates that $\lambda = 0.5$ is the preferred value.

Another way to determine the step-size parameter, is to halve λ iteratively for $(dG/d\lambda) < 0$ until G is minimized or until an arbitrarily set lower bound of $(dG/d\lambda)$ is reached, triggering an exit.

Both procedures are implemented in StoiCES. The initial estimate based on Smith & Missen (1968) is, hereafter, referred to as IE-SM, the other one as IE-Loop.

After the most reasonable λ is obtained, the estimated quantities of the possible composition result as the entries of the initial stoichiometric matrix. Thus, the closer it is to the actual equilibrium composition, the faster a solution is found.

4 Results: Accuracy

A prerequisite for the applicability of the implemented VCS algorithm StoiCES is the accuracy compared to literature data.

For this test, the thermodynamic data of the standard chemical potential, a set of initial element/species abundances supplemented by temperature and pressure for the (T,P)-constraints, or internal energy and volume for the (U,V)-constraints, needed to be identical to the original test cases to make the results comparable. For this reason, StoiCES used the same thermodynamic data. All data of StoiCES' resulting equilibrium composition was rounded to the same decimal as done in the literature with differences set into ratios:

$$\text{deviation} \equiv \frac{\text{result}_{\text{literature}} - \text{result}_{\text{StoiCES}}}{\text{result}_{\text{literature}}}. \tag{4.1}$$

The closer the deviation is to zero, the better the accuracy.

Unfortunately, some of the data in the literature was obviously flawed which is specifically mentioned in the corresponding test cases below. In addition, there can be no absolute confidence that there were no further deviations, typing mistakes or other errors in the literature. However, since StoiCES relies exactly the same thermodynamic data as CEA, a comparison to this extensively tested NASA-code should be particularly representative.

Differences in the assumed physical constants might have influenced the results. For example, over the last centuries, the values of the gas constant R have changed several times. It turned out that even a small difference in the fourth decimal of R can significantly affect the results. Unless the values of physical constants have been explicitly specified in the respective literature, the current values were assumed.

Start parameters:
T=3500K, P=51atm
Element abundances (in moles): H=2, O=1, N=1

Smith & Missen (1982)

Equilibrium	Literature	StoiCES	Deviation
H	2.482400e-02	2.482394e-02	2.42e-06
H_2	9.016901e-02	9.016914e-02	-1.44e-06
H_2O	4.779780e-01	4.779778e-01	4.18e-07
N	8.632234e-04	8.632236e-04	-2.32e-07
N_2	2.961622e-01	2.961622e-01	0
NH	4.230772e-04	4.230763e-04	2.13e-06
NO	1.672318e-02	1.672317e-02	5.98e-07
O	1.095514e-02	1.095512e-02	1.83e-06
O_2	2.277544e-02	2.277546e-02	-8.78e-07
OH	5.912673e-02	5.912687e-02	-2.37e-06
G/RT	-4.776137e+01	-4.776138e+01	-2.09e-07
total moles	1.638400e+00	1.638400e+00	0

Table 4.1: Test case 1 taken from Smith & Missen (1982) compared with StoiCES' results in mole fraction, Gibbs free energy G/RT and total moles.

4.1 Thermodynamic State Constraint of Constant (T,P)

4.1.1 Test Case 1: Hydrazine Combustion I

The first test case was a hydrazine combustion taken from Smith & Missen (1982, p. 138). It is presented in Table 4.1 and took 10 different species into account which were mixed compositions of the elements hydrogen, nitrogen and oxygen. The combustion started at a fixed temperature of 3500K and a fixed pressure of 51atm.

StoiCES achieved a difference to the values provided by Smith & Missen (1982) of a maximum of $\mathcal{O}(10^{-6})$. This is absolutely sufficient considering that it is compared to the seven significant decimals that were specified by them.

4.1.2 Test Case 2: Hydrazine Combustion II

Another hydrazine combustion is presented in Table 4.2, although this time, the initial chemical potentials were taken from Passy & Wilde (1968).

Start parameters:
T=3500K, P=51.02atm
Element abundances (in moles): H=2, O=1, N=1

	Passy & Wilde (1968)			**CEA**		
Equilibrium	Literature	StoiCES	Deviation	Literature	StoiCES	Deviation
H	0.0247	0.0248	-4.05e-03	0.0243	0.0243	0
H_2	0.0894	0.0902	-8.95e-03	0.0875	0.0875	0
H_2O	0.479	0.478	2.09e-03	0.479	0.479	0
N	0.000757	0.000863	-1.40e-01	0.000017	0.000017	0
N_2	0.2929	0.2962	-1.13e-02	0.2978	0.2978	0
NH	0.000369	0.000423	-1.46e-01	0.000009	0.000009	0
NO	0.01481	0.01672	-1.29e-01	0.01551	0.01551	0
O	0.01105	0.01095	9.05e-03	0.00988	0.00988	0
O_2	0.0232	0.0228	1.72e-02	0.0208	0.0208	0
OH	0.0594	0.0591	5.05e-03	0.0656	0.0656	0
total moles	1.6375	1.6384	-5.50e-04	1.6364	1.6364	0
U (in kJ/kg)				-109.43	-109.43	0
V (in m^3/kg)				0.28767	0.28767	0

Table 4.2: Test case 2 taken from Passy & Wilde (1968) recalculated with CEA and compared with StoiCES' results in mole fraction, total moles, internal energy U and volume V. StoiCES used the respective thermodynamic data.

It is conspicuous that there was a relatively high deviation up to $\mathcal{O}(10^{-1})$, especially in the mole fractions of nitrogen, nitrogen monohydride NH and nitrogen monoxide NO. Even older values of the gas constant could not improve the result and confirmed the trend. To review this test case, the same calculation was redone with CEA and StoiCES, but this time both were using CEA's thermodynamic data. It turned out that StoiCES did not deviate from CEA.

A comparison of the chemical potentials respectively, in accordance to Equation 3.1, showed the most notable differences were found for nitrogen and nitrogen monohydride:

CEA's chemical potentials of $\mu_{\mathrm{N}} = -2.134$ and $\mu_{\mathrm{NH}} = -11.402$ contrast with the ones of Passy & Wilde (1968), $\mu_{\mathrm{N}} = -5.914$ and $\mu_{\mathrm{NH}} = -14.986$.

This explains how the equilibrium mole fractions of N and NH could differ so much considering the results of Passy & Wilde (1968) and CEA and, furthermore, illustrates nicely the strong impact of the thermodynamic data on the equilibrium composition. Therefore, it is of critical importance to gather reliable laboratory or theoretical data in order to find reasonable results.

Start parameters:
T=2200K, P=40atm
Element abundances (in moles): H=8, O=10, C=3

Smith & Missen (1982)

Equilibrium	Literature	StoiCES	Deviation
CO	2.637254e-03	2.637369e-03	-4.36e-05
CO_2	1.082671e-01	1.082670e-01	9.24e-07
H	2.325215e-05	2.325451e-05	-1.01e-04
H_2	6.872857e-04	6.873310e-04	-6.59e-05
H_2O	1.468280e-01	1.468279e-01	6.81e-07
O	1.635950e-05	1.636117e-05	-1.02e-04
O_2	1.487093e-03	1.487162e-03	-4.64e-05
OH	6.912399e-04	6.912822e-04	-6.12e-05
total moles	2.705033e+01	2.705034e+01	-3.70e-07
inert gas	7.393624e-01	7.393624e-01	0

Table 4.3: Test case 3 taken from Smith & Missen (1982) compared with StoiCES' results in mole fraction, total moles and mole fraction of inert gas.

Nevertheless, the assumption of the same chemical potentials should result in sufficient consistency of the final composition. Since this was not the case while using the μ_i of Passy & Wilde (1968) and old values of the gas constant R, and due to the fact that StoiCES was capable to reproduce the equilibrium compositions of the hydrazine combustions calculated by CEA and Smith & Missen (1982), it seems reasonable to assume the use of erroneous data employed by Passy & Wilde (1968). An indication of this might be found in Ruda (1982) as well, were the hydrazine combustion was recalculated using the same initial temperature and standard chemical potentials as Passy & Wilde (1968). Only the pressure differed slightly and was 51.2atm. It turned out that the equilibrium moles of Ruda (1982) had deviations from the results of Passy & Wilde (1968) as well. With the exception of hydrogen, molecular nitrogen N_2 and oxygen, their respective differences were of a similar magnitude to that ones of StoiCES in Table 4.2.

4.1.3 Test Case 3: Propane Combustion I

The propane combustion results as shown in Table 4.3 were obtained from Smith & Missen (1982, p. 97) and contained the presence of molecular nitrogen N_2 as inert gas. 8 species, composed of hydrogen, oxygen and carbon, were present in equilibrium.

Start parameters:
T=2200K, P=40atm
Element abundances (in moles): H=8, O=10, N=40, C=3

	Ruda (1982)			**Dinkel & Lakshmanan (1977)**		
Equilibrium	Literature	StoiCES	Deviation	Literature	StoiCES	Deviation
CO	0.0819268	0.0815966	4.03e-03	0.0815971	0.0815966	6.62e-06
CO_2	2.9180737	2.9184034	-1.13e-04	2.9184028	2.9184034	-6.85e-08
H	0.0006811	0.0006540	3.98e-02	0.0006540	0.0006540	0
H_2	0.0204434	0.0200734	1.81e-02	0.0200735	0.0200734	5.48e-06
H_2O	3.971582	3.971900	-8.01e-05	3.9718994	3.9718996	-1.51e-07
N_2	19.986533	19.9866657	-6.35e-06	19.9866573	19.9866657	-1.35e-07
NO	0.0269337	0.0266859	9.20e-03	0.0266857	0.0266859	-7.87e-06
O	0.000459	0.000443	3.50e-02	0.0004428	0.0004429	-2.57e-04
O_2	0.0338415	0.0335841	7.61e-03	0.0335845	0.0335841	1.31e-05
OH	0.0152673	0.0154001	-8.70e-03	0.0154000	0.0154001	-7.14e-06
G/RT	-777.6387	-777.6387	0	-777.6387	-777.6387	0
total moles	27.057600	27.055397	8.13e-05	27.05539731	27.05539694	-9.98e-08

Table 4.4: Test case 4 taken from Ruda (1982) and Dinkel & Lakshmanan (1977) compared with StoiCES' results in moles, Gibbs free energy G/RT and total moles.

Though the resulting differences of StoiCES were slightly worse than in test case 1, there still existed a consistency with the equilibrium composition provided by Smith & Missen (1982). Additionally, it was shown that StoiCES is capable to include inert species.

4.1.4 Test Case 4: Propane Combustion II

Test case 4 in Table 4.4 concerned another propane combustion which was taken from Ruda (1982). In addition to test case 3, the presence of molecular nitrogen and nitrogen monoxide was taken into account.
This time, StoiCES' results differed with a maximum of $\mathcal{O}(10^{-2})$ from Ruda's composition. But using Ruda's quote of her reference test case from Dinkel & Lakshmanan (1977) and comparing StoiCES' results to it, it turned out that there was a significant better and sufficient match of 7 decimals to the results of Dinkel & Lakshmanan (1977).

4.1.5 Test Case 5: Methane and Water Reaction

In the methan and water reaction from Ruda (1982), with inital parameters and results presented in Table 4.5, there was a too large deviation $\mathcal{O}(10^{-1})$ regarding the equilibrium

Start parameters:
T=1095K, P=1atm
Element abundances (in moles): H=14, O=3, C=2

	Ruda (1982)			**CEA**		
Equilibrium	Literature	StoiCES	Deviation	Literature	StoiCES	Deviation
CH_4	0.1722	0.2015	-1.70e-01	0.0237	0.0237	0
CO	1.5174	1.4820	2.33e-02	1.7493	1.7493	0
CO_2	0.3107	0.3165	-1.87e-02	0.2270	0.2270	0
H_2	5.7942	5.7121	1.42e-02	6.1558	6.1558	0
H_2O	0.8612	0.8850	-2.76e-02	0.7968	0.7968	0
G/RT	-79.3605	-79.3597	1.01e-05			
total moles	8.6558	8.5971	6.78e-03	8.9526	8.9526	0
U (in kJ/kg)				-3904.98	-3904.98	0
V (in m^3/kg)				9.33945	9.33945	0

Table 4.5: Test case 5 taken from Ruda (1982) recalculated with CEA and compared with StoiCES' results in moles, Gibbs free energy G/RT, total moles, internal energy U and volume V. StoiCES used the respective thermodynamic data.

composition.

Like test case 2, a recalculation with CEA and its thermodynamic data showed an exact agreement of the results of CEA and StoiCES and showed the capability to reproduce such a simple reaction. Here too, a verification of Ruda's results was not successful with the provided thermodynamic data.

4.1.6 Test Case 6: Gas-Water Reaction

StoiCES' results of a gas-water reaction, which initial data has been taken from Dinkel & Lakshmanan (1975), were in accordance with their results (Table 4.6). There was only a negligibly small difference $\mathcal{O}(10^{-7})$ in Gibbs free energy.

4.1.7 Test Case 7: Claus Furnace I

The claus furnace combustion from Ruda (1982) is presented in Table 4.7. It considered 8 equilibrium species composed of hydrogen, oxygen, nitrogen and sulfur.

StoiCES' results differed only slightly from Ruda's. Regarding the mole fraction of sulfur dioxide SO_2, which featured the strongest deviation of $\mathcal{O}(10^{-3})$, StoiCES had actually the same value as the resulting equilibrium composition provided by Bonsu (1981).

Start parameters:
T=1371K, P=2atm
Element abundances (in moles): H=2, O=1, C=1

Dinkel & Lakshmanan (1975)

Equilibrium	Literature	StoiCES	Deviation
CO	0.59417	0.59417	0
CO_2	0.40583	0.40583	0
H_2	0.40583	0.40583	0
H_2O	0.59417	0.59417	0
G/RT	-82.80798	-82.80796	2.42e-07
total moles	2.00000	2.00000	0

Table 4.6: Test case 6 taken from Dinkel & Lakshmanan (1975) compared with StoiCES' results in moles, Gibbs free energy G/RT and total moles.

Start parameters:
T=800K, P=1atm
Element abundances (in moles): H=2, O=1, N=3.76, S=0.3

Ruda (1982)

Equilibrium	Literature	StoiCES	Deviation
H_2O	0.28304	0.28304	0
H_2S	0.05139	0.05136	5.84e-04
N_2	0.62869	0.62868	1.59e-05
S_2	0.01098	0.01098	0
S_4	0.00013	0.00013	0
S_6	0.00013	0.00013	0
S_8	0.00000	0.00000	0
SO_2	0.02565	0.02568	-1.17e-03
G/RT	-110.48998	-110.48998	0
total moles	2.99003	2.99040	-1.24e-04

Table 4.7: Test case 7 taken from Ruda (1982) compared with StoiCES' results in mole fraction, Gibbs free energy G/RT and total moles.

Start parameters:
T=800K, P=1atm
Element abundances (in moles): H=4, O=2, N=7.52, S=2

	Ruda (1982)			**CEA**		
Equilibrium	Literature	StoiCES	Deviation	Literature	StoiCES	Deviation
H_2	0.00020	0.00020	0	0.00020	0.00020	0
H_2O	0.21922	0.21540	1.74e-02	0.21707	0.21707	0
H_2S	0.09009	0.09365	-3.95e-02	0.09262	0.09262	0
N_2	0.58311	0.58140	2.93e-03	0.58259	0.58259	0
S_2	0.04783	0.05260	-9.97e-02	0.04993	0.04993	0
S_6	0.01130	0.00752	3.35e-01	0.00923	0.00923	0
S_8	0.00120	0.00229	-9.08e-01	0.00195	0.00195	0
SO_2	0.04505	0.04693	-4.17e-02	0.04641	0.04641	0
G/RT	-230.12109	-230.07059	2.19e-04			
total moles	6.44320	6.46715	-3.72e-03	6.45393	6.45393	0
U (in kJ/kg)				-1573.15	-1573.15	0
V (in m^3/kg)				2.06178	2.06178	0

Table 4.8: Test case 8 taken from Ruda (1982), recalculated with CEA and compared with StoiCES' results in mole fraction, Gibbs free energy G/RT, total moles, intenal energy U and volume V. StoiCES used the respective thermodynamic data.

4.1.8 Test Case 8: Claus Furnace II

The data of the claus furnace combustion quoted in Table 4.8 originated from Ruda (1982). As distinguished from test case 7, other element abundances were assumed and the species S_4 was replaced by H_2. Obviously, there was a typing error in Ruda's specification of the initial moles of nitrogen. Following Equation 2.2, her 3.76 moles of nitrogen conflicted with the resulting mole fractions of N_2=0.58311 at 6.4432 total moles. Since, in this test case, N_2 was the only species that contained nitrogen, it was assumed there are 7.52 initial moles of nitrogen instead of 3.76 moles.

In order to resolve the unsatisfactory match of StoiCES' and Ruda's equilibrium composition, which had a too large difference of a maximum of $\mathcal{O}(10^{-1})$, the same calculation was compared to CEA using its thermodynamical data. As before, there was no notable deviation between StoiCES and CEA, hence, with Ruda's given data a validation of her results was not feasible.

4.1.9 Test Case 9: Claus Furnace III

Table 4.9 contains results from a third claus furnace combustion based on Ruda (1982). The same element abundances, temperature and pressure as in test case 8 were used, but this time, 24 species were included instead of 8. Again, there seems there have been typing errors in the provided data by Ruda (1982). The initial moles of oxygen are most likely 2 moles rather than the listed 4 moles. This consideration follows the same logic as applied in test case 8. Furthermore, Ruda's standard chemical potential of oxygen had a sign error and should be positive.

Compared to Ruda's equilibrium composition, the results of StoiCES were acceptable with a deviation of mostly $\mathcal{O}(10^{-4})$. The mole fraction of O_2 differed very strongly with $\mathcal{O}(10^{2})$. Although this relative error may seem high, the absolute error remain tiny regarding that the corresponding equilibrium mole fraction was less than 10^{-20} and there was still an agreement of 20 significant decimals with Ruda (1982). Nevertheless, a review with CEA was advisable and showed a remarkable good consistency between StoiCES and CEA even at very low species abundances.

Regarding the equilibrium mole fraction of S_4, there was a notable difference between CEA and Ruda (1982). Like in test case 2, reason was the use of quite different chemical potentials, that was $\mu_{S_4} = -18.054$ used by CEA and $\mu_{S_4} = 21.723$ used by Ruda (1982).

4.2 Thermodynamic State Constraint of Constant (U,V)

4.2.1 Test Case 10: Hydrogen-Oxygen Detonation

The results of the hydrogen-oxygen detonation in Table 4.10 were based on Gubin & Shargatov (2013, Table 2). The species abundances, originally given as volume percentage, have been converted to moles for the purpose of recalculation. In this test case, fixed internal energy and volume were assumed and the respective temperature and pressure had to be determined.

Since Gubin & Shargatov (2013) provided no specification on the used thermodynamic data, their equilibrium composition can be considered as indicative only. Therefore, the

Start parameters:
T=800K, P=1atm
Element abundances (in moles): H=4, O=2, N=7.52, S=2

	Ruda (1982)			**CEA**		
Equilibrium	Literature	StoiCES	Deviation	Literature	StoiCES	Deviation
H	4.128e-14	4.128e-14	0	4.084520e-14	4.084520e-14	0
H_2	2.040e-04	2.040e-04	0	2.012169e-04	2.012169e-04	0
H_2O	2.197e-01	2.197e-01	0	2.237905e-01	2.237905e-01	0
H_2S	9.010e-02	9.009e-02	1.11e-04	8.689377e-02	8.689377e-02	0
N_2	5.827e-01	5.827e-01	0	5.844649e-01	5.844649e-01	0
NH_3	6.922e-09	6.923e-09	-1.44e-04	6.633945e-09	6.633945e-09	0
NO	2.386e-16	2.386e-16	0	2.152229e-16	2.152229e-16	0
O	4.394e-24	4.394e-24	0	4.534701e-24	4.534701e-24	0
O_2	1.983e-23	3.074e-21	-1.54e+02	3.268221e-21	3.268221e-21	0
OH	1.506e-14	1.506e-14	0	1.983937e-14	1.983937e-14	0
S	2.060e-12	2.060e-12	0	2.127177e-12	2.127177e-12	0
S_2	4.692e-02	4.689e-02	6.39e-04	4.180412e-02	4.180412e-02	0
S_2O	1.514e-03	1.513e-03	6.61e-04	1.209778e-03	1.209778e-03	0
S_3	4.139e-03	4.135e-03	9.66e-04	4.505701e-03	4.505701e-03	0
S_4	4.424e-21	4.419e-21	1.13e-03	5.721087e-04	5.721087e-04	0
S_5	1.445e-03	1.443e-03	1.38e-03	5.813613e-03	5.813613e-03	0
S_6	5.339e-03	5.330e-03	1.69e-03	5.420529e-03	5.420529e-03	0
S_7	2.186e-03	2.211e-03	-1.14e-02	1.422329e-03	1.422329e-03	0
S_8	1.450e-03	1.447e-03	2.07e-03	9.585052e-04	9.585052e-04	0
SH	4.484e-08	4.483e-08	2.23e-04	1.673900e-07	1.673900e-07	0
SN	5.036e-14	5.034e-14	3.97e-04	3.871899e-14	3.871899e-14	0
SO	1.593e-07	1.593e-07	0	1.668523e-07	1.668523e-07	0
SO_2	4.440e-02	4.439e-02	2.25e-04	4.294257e-02	4.294257e-02	0
SO_3	7.925e-11	7.924e-11	1.26e-04	8.507275e-11	8.507275e-11	0
G/RT	-230.1378	-230.1380	-8.69e-07			
total moles	6.45207	6.45279	-1.12e-04	6.4332350	6.4332350	0
U (in kJ/kg)				-1579.16	-1579.16	0
V (in m^3/kg)				2.05517	2.05517	0

Table 4.9: Test case 9 taken from Ruda (1982) recalculated with CEA and compared with StoiCES' results in mole fraction, Gibbs free energy G/RT, total moles, internal energy U and volume V. StoiCES used the respective thermodynamic data.

Start parameters:
U=-206kJ/kg, $V=1/\rho$=2.063132m^3/kg
Species abundances (in moles): H_2=3.214359, H_2O=1.156798,
H_2O_2=2.682071e-05, HO_2=2.896637,
O_2=9.923664, OH=2.564473
H=1.561791e-01, O=7.241593e-02

Gubin & Shargatov (2013)

Equilibrium	Literature	StoiCES	Deviation
H	0.036692	0.036385	8.37e-03
H_2	0.075516	0.075794	-3.68e-03
H_2O	0.271771	0.269886	6.94e-03
H_2O_2	0.000006	0.000006	0
HO_2	0.000068	0.000062	8.82e-02
O	0.017013	0.016584	2.52e-02
O_2	0.023314	0.022713	2.58e-02
OH	0.060248	0.063778	-5.86e-02
T (in K)	3505	3497	2.28e-03
P (in bar)	9.602	9.590	1.25e-03

Table 4.10: Test case 10 taken from Gubin & Shargatov (2013) compared with StoiCES' results in moles, temperature T and pressure P.

difference which were in $\mathcal{O}(10^{-3})$ and $\mathcal{O}(10^{-2})$ are actually very good.

4.2.2 Test Cases 11-14: Various Test Cases Using CEA

Test cases 11-14 contained a hydrazine combustion (test case 11), propane combustion (test case 12), methane and water reaction (test case 13) and a claus furnace (test case 14). The fixed initial internal energies and volumes and the species abundances as well are listed in Table 4.11. StoiCES' results were compared to CEA and respective temperatures and pressures are presented in Table 4.12.

Due to the fact that StoiCES relied on exactly the same thermodynamic data as CEA, these (U,V)-test cases should be particularly representative. In the previous section, it has been shown that StoiCES is able to reproduce CEA's equilibrium compositions for given element abundances, temperatures and pressures concerning such low-species test cases. Therefore, matching temperatures and pressures of StoiCES and CEA in Table 4.12 implied identical equilibrium compositions. In all test cases, StoiCES showed no deviation from CEA. Accordingly, it was shown that StoiCES is capable to accurately

Test case	Start parameters
11	U=-67 kJ/kg V=0.3 m^3/kg Species abundances (in moles): H=0.040, H_2=0.143, H_2O=0.783, N=0.000, N_2=0.487, NH=0.00, NO=0.025, O=0.016, O_2=0.034, OH=0.107
12	U=-780 kJ/kg V=0.6 m^3/kg Species abundances (in moles): O=0.00, CO_2=3.00, CO=0.10, H_2O=4.00, H_2=0.02, O_2=0.04, OH=0.02, H=0.00
13	U=-435 kJ/kg V=90 m^3/kg Species abundances (in moles): CO=1.5, CO_2=0.3, H_2O=0.9, H_2=6.0, CH_4=0.2
14	U=-245 kJ/kg V=2.5 m^3/kg Species abundances (in moles): SO_2=0.07, H_2S=0.15, H_2O=0.85, S_2=0.03, S_4=0.01, S_6=0.01, S_8=0.01, N_2=1.88

Table 4.11: Initial internal energy U, volume V and species abundances for test cases 11-14.

Test case	CEA	StoiCES	Deviation
11	P=49.684bar	P=49.684bar	0
	T=3501.76K	T=3501.76K	0
12	P=21.928bar	P=21.928bar	0
	T=3638.63K	T=3638.63K	0
13	P=0.22082bar	P=0.22082bar	0
	T=2229.23K	T=2229.23K	0
14	P=2.9733bar	P=2.9733bar	0
	T=2472.82K	T=2472.82K	0

Table 4.12: Respective equilibrium temperatures T and pressures P for test cases 11-14 with start parameters given in Table 4.11.

determine equilibrium compositions using fixed internal energy and volume constraints.

5 Results: Robustness

Besides accuracy, robustness is an important criterion concerning reliability of the implemented code. Requirements for StoiCES are a broad band intended applications. Therefore, it must be able to handle extreme environments and a large number of species without convergence problems or large deviations from the literature.

In this chapter, all calculated test cases were recalculated by CEA which provided the reference equilibrium compositions.

5.1 A Large Number of Species

In order to verify whether StoiCES is capable to find accurate equilibrium compositions for very large systems, a test case was calculated which took 411 different gaseous species into account that were composed of 16 elements. In Appendix A, the full list of species and element abundances can be found. A fixed temperature of 3000K and a fixed pressure of 1bar were assumed. A recalculation was done with CEA and compared to StoiCES' equilibrium mole fractions of all species. This was an advanced test because, in addition to the large number of species, a wide range of equilibrium abundances were considered with mole fractions varying from $\mathcal{O}(10^{-1})$ down to $\mathcal{O}(10^{-93})$.

In this test, StoiCES faced no convergence problems and its agreement with CEA was remarkable. Only the trace species B_4H_{12}, C_8H_{18} (isooctane) and $C_{12}H_{10}$ (biphenyl) differed slightly in $\mathcal{O}(10^{-7})$ from CEA. Regarding their very low equilibrium mole fractions of $\mathcal{O}(10^{-46})$, $\mathcal{O}(10^{-78})$ and $\mathcal{O}(10^{-63})$ their relative errors were tiny. The equilibrium abundances of all other 408 species were determined without any deviation from CEA and even very small trace species were calculated reliably.

5.2 Extreme Environments

It was shown that StoiCES is capable of calculating the equilibrium composition of the large 411-species test case at a moderate fixed temperature of 3000K and pressure of 1bar. To investigate its accuracy concerning extreme environments the temperature and pressure ranges were extended to their limits. Again, the equilibrium mole fractions of the large test case were determined by StoiCES and CEA. It was assumed that species with mole fraction of less than $1 \cdot 10^{-40}$ were absent in the equilibrium composition and were, although calculated, excluded from the analysis. The simple reason for this is that the numerical uncertainties that might arise during the calculation, e.g., from the relative error due to the machine precision and to the limited accuracy of physical constants, are bigger than the values of such low trace species.

5.2.1 Whole Range of Temperatures

Figure 5.1 shows StoiCES accuracy compared to CEA's results for the large test case which was calculated with a fixed pressure of 1bar and a number of fixed temperatures. Here, the thermodynamic data provided by CEA set the upper and lower limit of the used temperature range. Since StoiCES is not set up to extrapolate the included data, various temperatures from 200K to 6000K were used.

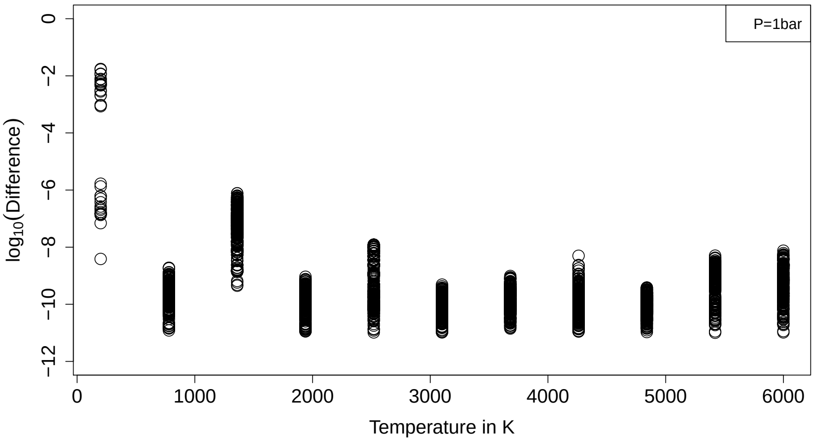

Figure 5.1: StoiCES results from the large test case concerning 11 temperatures from 200K to 6000K in steps of 580K at a fixed pressure of 1bar. Species with differences to CEA's equilibrium abundances are plotted.

As presented in Figure 5.1, the maximum deviation from CEA in $\mathcal{O}(10^{-2})$ was found at 200K. At this low temperature, only 39 species were present in the equilibrium composition. This is a very small number compared to the total number of species that were considered. Consequently, 372 trace species had mole fractions lower than $1 \cdot 10^{-40}$.

A good agreement to CEA's results was found with StoiCES for all other temperatures between 780K and 6000K where, furthermore, most species, i.e., 290-377, were present in equilibrium. Here, differences were predominantly below $\mathcal{O}(10^{-8})$.

It thus seems that there was a correlation between the accuracy of StoiCES and the high number of absent species in the equilibrium at 200K. A single difference in a trace species seems small, but, in accordance to the conservation of mass constraint, the element abundances of the whole system stay fix. Therefore, and only if the number is large enough, even tiny deviations in the mole fractions of minor species can result in significant differences of the final equilibrium composition.

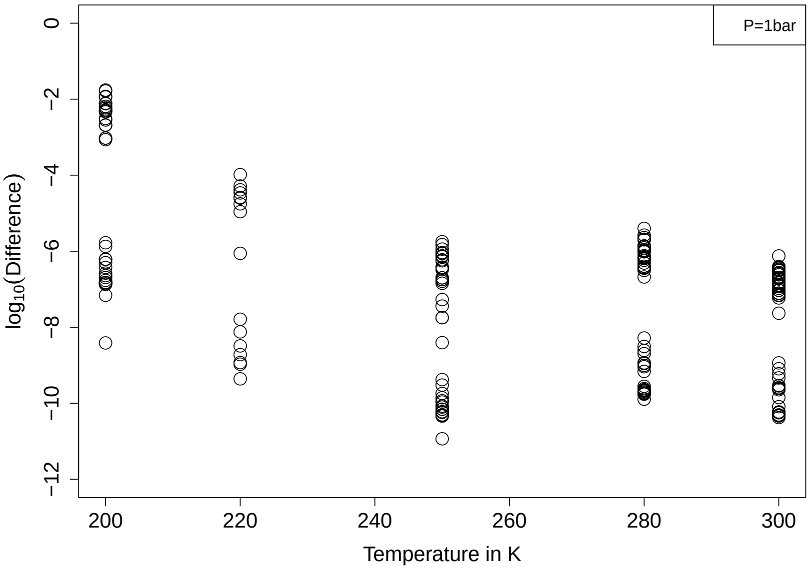

Figure 5.2: StoiCES results from the large test case concerning 5 temperatures from 200K to 300K at a fixed pressure of 1bar. Species with differences to CEA's equilibrium abundances are plotted.

In Figure 5.2, the resulting differences of further variations of low temperatures between 200K and 300K are plotted. Here, always less than 70 species were present in equilibrium. Compared with Figure 5.1, only the compositions of 200K and 220K deviate with a maximum of $\mathcal{O}(10^{-2})$ and $\mathcal{O}(10^{-4})$ more than the results of the higher temperatures. This could indicate that, concerning this lower range of validity of the thermodynamic data, there are differences within small numeric components of CEA and StoiCES to handle it. The finally employed thermodynamic data is based on polynoms, which resulted from fitting data of the JANAF Thermochemical Tables. Regarding the lower bound of 200K, their physical representability is possibly worse than in the range of higher temperatures. The assumption, that CEA and StoiCES cope with such a critical situation of the data in a different way is justified, because even slightly higher temperatures result in a significant increase in consistency of the equilibrium compositions.

Nevertheless, StoiCES accuracy in comparison to CEA regarding all temperatures above 220K is remarkable.

5.2.2 Extreme Pressures

Another way to verify StoiCES' robustness is to extend the pressure range. Due to the StoiCES implementation, the lower pressure limit was given by 10μbar. The maximum pressure was defined in order to prevent unphysical solutions. For instance, it is assumed that hydrogen may metallize at certain pressures. Liu et al. (2012) suggested such a transformation at 4Mbar for a temperature of 300K. For higher temperatures of about 3000K, this could occur at an even lower pressure of 1.4Mbar (Weir et al., 1996). Those extreme environments require specialized EOS (see, e.g., McMahon et al., 2012). Thus, an appropriate upper pressure limit of 1Mbar limits the full application range of StoiCES. The large test case was, therefore, solved for pressures ranging from 10μbar to 1Mbar, assuming fixed temperatures of 200K, 3000K and 6000K for each pressure. Figure 5.3 shows the appeared differences to CEA's results in mole fractions of the respective equilibrium compositions.

For the moderate and high temperatures of 3000K and 6000K, there were only slight deviations in the compositions with maximum differences of $\mathcal{O}(10^{-8})$ and $\mathcal{O}(10^{-7})$. Even at very high pressures, CEA's equilibrium compositions could be reproduced reliably in these test cases. For those temperatures, more than 250 species were always present in the equilibrium (see Figure 5.4).

In contrast, for the low temperature of 200K, StoiCES' mole fractions differed from CEA's up to $\mathcal{O}(10^{-1})$. Across the whole pressure range, there were less than 40 species present

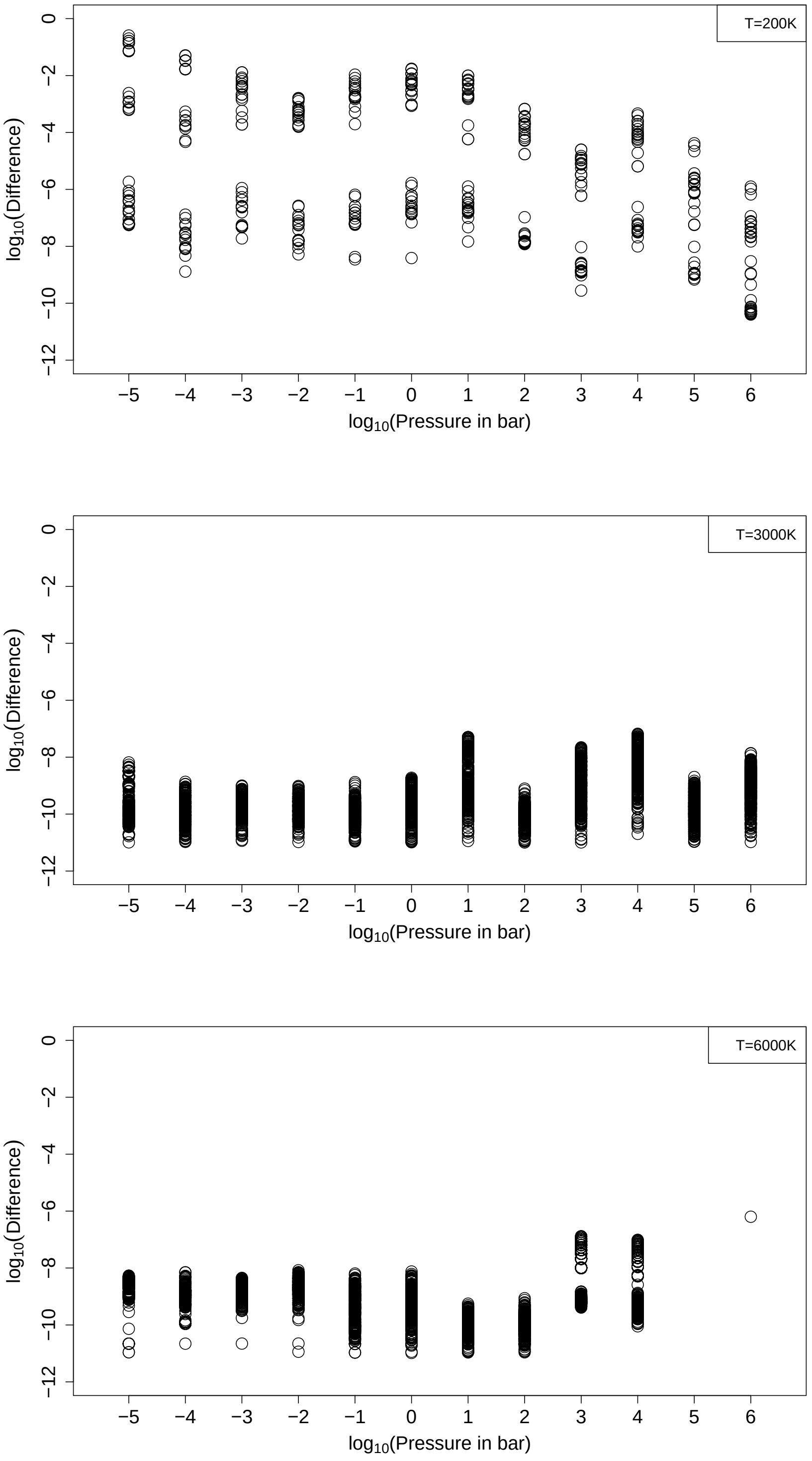

Figure 5.3: StoiCES results from the large test case concerning 12 pressure values from 10μbar to 1Mbar for 200K, 3000K and 6000K, respectively. Species with differences to CEA's equilibrium abundances are plotted.

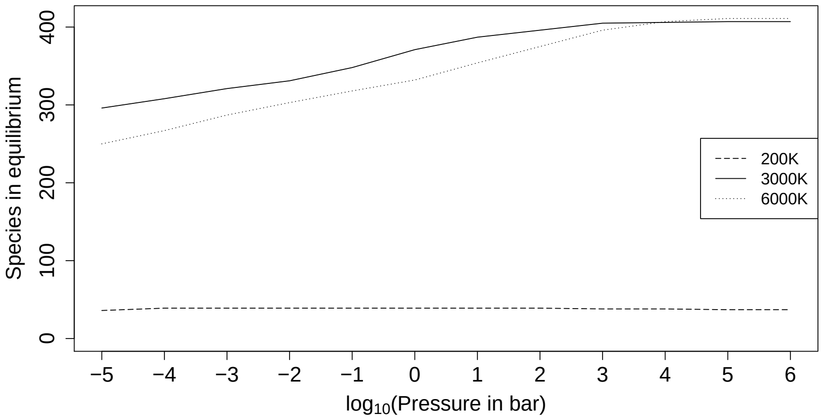

Figure 5.4: Number of species that were present in the respective equilibrium compositions of the large test case, with presence defined by mole fractions greater than $1 \cdot 10^{-40}$.

in the final compositions. As previously mentioned in Section 5.2.1, the total sum of the tiny deviations of the very small trace species with mole fractions of lower than $1 \cdot 10^{-40}$ was still big enough to influence the other species amounts of the equilibrium composition in a significant way. Additionally, this temperature represents the lower range of validity of the thermodynamic data which CEA and StoiCES seem to cope with in different ways. This low temperature test case was challenging and it shows the tremendous impact of even the slightest differences in species abundances in environments with an exceptional large number of very low trace species. Furthermore, the physical accuracy of the thermodynamic data was likely limited by possible fitting uncertainties. Nevertheless, StoiCES was able to reproduce such systems within one order of magnitude.

6 Results: Performance

After confidence in accuracy and robustness of StoiCES has been achieved, the next essential step was to increase its speed. To evaluate and compare the performance, the number of iterations and the CPU time required to calculate the chemical equilibrium composition using fixed (T,P)-constraints and given initial element abundances was measured. Selection and reading in of the thermodynamic data, as well as data output were deliberately excluded from the timing. Even small temporal fluctuations in computation time were minimized by considering the averaged time of 100,000 calulations.

Due to the current implementation of StoiCES, three different procedures were compared for the performance test. The first one used optimized stoichiometry as presented in Section 2.2.2. In addition to that, the second and third methods calculated an initial estimate of the species abundances and were based on IE-SM and IE-Loop which have been introduced in Section 3.3.

All calculations were carried out on a 2.5GHz Intel Core i5 CPU.

6.1 Performance Tests

In Table 6.1 and 6.2, total 20 test cases were compared in iterations and calculation time for determination of the equilibrium compositions. The start parameters of test cases 1-9 were in accordance with the respective ones presented in Chapter 4, but, this time, StoiCES' thermodynamic data were used. The initial temperatures, pressures, element abundances of test cases 10-20 are listed in Table 6.3.

In most test cases, the usage of an initial estimate decreased the number of iterations that were required to find a solution. This effect was particularly pronounced in big systems with several hundred species.

The impact of the IE on the low-species test cases 1-9 was rather small because, from the

Test case	Species	no IE	IE-SM	IE-Loop
1	10	**1.359e-04s** 36 iterations	**1.216e-04s** 33 iterations $\lambda = 0.200$	**1.221e-04s** 33 iterations $\lambda = 0.250$
2	10	**1.348e-04s** 36 iterations	**1.208e-04s** 33 iterations $\lambda = 0.200$	**1.220e-04s** 33 iterations $\lambda = 0.250$
3	8	**9.713e-05s** 31 iterations	**1.171e-04s** 40 iterations $\lambda = 0.200$	**1.175e-04s** 40 iterations $\lambda = 0.250$
4	10	**1.505e-04s** 38 iterations	**1.611e-04s** 45 iterations $\lambda = 0.200$	**1.600e-04s** 44 iterations $\lambda = 3.125\text{e-}02$
5	5	**4.488e-05s** 15 iterations	**5.315e-05s** 12 iterations $\lambda = 0.933$	**5.251e-05s** 12 iterations $\lambda = 1.000$
6	4	**3.873e-05s** 8 iterations	**3.455e-05s** 5 iterations $\lambda = 0.507$	**4.464e-05s** 5 iterations $\lambda = 1.000$
7	8	**1.091e-04s** 22 iterations	**8.522e-05s** 18 iterations $\lambda = 1.000$	**8.547e-05s** 18 iterations $\lambda = 1.000$
8	8	**1.478e-04s** 46 iterations	**1.491e-04s** 48 iterations $\lambda = 0.625$	**1.491e-04s** 46 iterations $\lambda = 1.000$
9	24	**6.716e-04s** 95 iterations	**6.215e-04s** 96 iterations $\lambda = 0.625$	**5.092e-04s** 74 iterations $\lambda = 1.000$
	total:	**1.530e-03s** 327 iterations	**1.464e-03s** 330 iterations	**1.363e-03s** 305 iterations

Table 6.1: CPU time and iterations required by StoiCES to calculate the chemical equilibrium compositions of various test cases including the final value of the step-size parameter λ.

Test case	Species	no IE	IE-SM	IE-Loop
10	411	**1.588e-01s** 653 iterations	**6.652e-02s** 245 iterations $\lambda = 0.200$	**6.572e-02s** 239 iterations $\lambda =$4.883e-04
11	411	**1.959e-01s** 862 iterations	**9.152e-02s** 383 iterations $\lambda = 0.200$	**7.756e-02s** 310 iterations $\lambda =$ 1.355e-20
12	411	**1.282e-01s** 460 iterations	**7.795e-02s** 256 iterations $\lambda = 0.200$	**6.287e-02s** 180 iterations $\lambda =$ 3.052e-05
13	411	**1.396e-01s** 518 iterations	**6.407e-02s** 220 iterations $\lambda = 0.910$	**6.928e-02s** 249 iterations $\lambda =$ 7.813e-03
14	411	**2.558e-01s** 1074 iterations	**2.360e-01s** 1117 iterations $\lambda = 1.000$	**1.364e-01s** 559 iterations $\lambda = 0.125$
15	411	**4.102e-01s** 1828 iterations	**3.011e-01s** 1378 iterations $\lambda = 1.000$	**2.811e-01s** 1333 iterations $\lambda =$ 4.768e-07
16	252	**4.985e-02s** 617 iterations	**3.094e-02s** 398 iterations $\lambda = 0.200$	**2.011e-02s** 228 iterations $\lambda =$ 3.906e-03
17	252	**4.230e-02s** 525 iterations	**3.391e-02s** 418 iterations $\lambda = 0.200$	**2.642e-02s** 307 iterations $\lambda = 0.250$
18	252	**3.611e-02s** 438 iterations	**3.181e-02s** 367 iterations $\lambda = 0.200$	**3.106e-02s** 355 iterations $\lambda =$ 1.953e-03
19	252	**3.658e-02s** 441 iterations	**3.132e-02s** 366 iterations $\lambda = 0.571$	**2.897e-02s** 331 iterations $\lambda = 1.000$
20	252	**5.919e-02s** 750 iterations	**3.568e-02s** 453 iterations $\lambda = 0.200$	**3.488e-02s** 436 iterations $\lambda =$ 4.547e-13
	total:	**1.513s** 8166 iterations	**1.001s** 5601 iterations	**8.344e-01s** 4527 iterations

Table 6.2: CPU time and iterations required by StoiCES to calculate the chemical equilibrium compositions of various test cases including the final value of the step-size parameter λ.

Test case	Temperature	Pressure	Element abundances
10	6000K	1bar	Appendix A
11	5000K	$1 \cdot 10^{-2}$bar	
12	4000K	$1 \cdot 10^{1}$bar	
13	3000K	$1 \cdot 10^{3}$bar	
14	2000K	$1 \cdot 10^{4}$bar	
15	500K	$1 \cdot 10^{-3}$bar	
16	6000K	$1 \cdot 10^{4}$bar	Appendix B
17	4000K	$1 \cdot 10^{3}$bar	
18	3000K	$1 \cdot 10^{-1}$bar	
19	2000K	$1 \cdot 10^{-2}$bar	
20	500K	$1 \cdot 10^{1}$bar	

Table 6.3: Initial temperatures and pressures of the performance tests 10-20 in Table 6.2. The full list of element abundances and the respective species can be found in the Appendix A and B.

start, the equilibrium composition was determined quickly. Nevertheless, an improvement of performance could be achieved even here.

A step-size parameter $\lambda = 1.000$ implied that the estimated initial moles based on the solution of the simplex method were the favourable ones which minimized the Gibbs free energy. Consequently, a variation of λ was no longer required in such cases.

In test cases 3, 4 and regarding IE-SM in test cases 8 and 9, an initial estimate resulted in an increase of iterations compared to the calculation without any IE. This might seem suspicious but it is attributable to the fact that StoiCES starts from the assumption that the initial moles of each species are 1 mole if no IE is used. Here, the blanket inital moles were closer to the equilibrium moles than the estimated ones and, hence, the IE led to more iterations.

Unfortunately, the averaged time of 100,000 calculations is still subjected to small fluctuations in CPU time. These are only in the magnitude of mostly $\mathcal{O}(10^{-6})$ but could influence the resulting speed considering the particular short times of $\mathcal{O}(10^{-5})$ and $\mathcal{O}(10^{-4})$ that were common in test cases 1-9. However, general tendencies could be identified.

Despite of almost equal iterations of all three methods in test case 5, IE-SM and IE-Loop required slightly more CPU time than the determination of the equilibrium composition without any initial estimate. This is substantiated by the fact that the simplex method and the identification of the most favourable value of the parameter λ requires additional calculation time. Especially within the IE-Loop method, the search for λ can be relatively time-consuming compared to IE-SM which provides only four different values of

λ, namely 1.0, 0.5, 0.2 and β. On the contrary, the IE-Loop halves λ iteratively and, hence, the smaller the final λ the longer it takes to determine its value and the respective corresponding standard chemical potentials. This was indicated in, e.g., test cases 1-3. Although the usage of IE-Loop and IE-SM required equal number of iterations, the identification of the best λ took slightly more time within the IE-Loop method.

The sum of the total CPU times in Table 6.1 shows that, as a whole, an IE accelerated the determination of a solution concerning the chemical equilibrium problem. This is actually true despite the application of an IE resulted in more iterations in a few cases.

The test cases 10-20 in Table 6.2 with its several hundred species are more representative of real systems than the low-species test cases 1-9 and, therefore, are more crucial. Here, a distinct improvement of speed and number of iterations could be achieved by an initial estimate. In test cases 10-13 and 16, the CPU time was more than halved due to either IE-SM or IE-Loop.

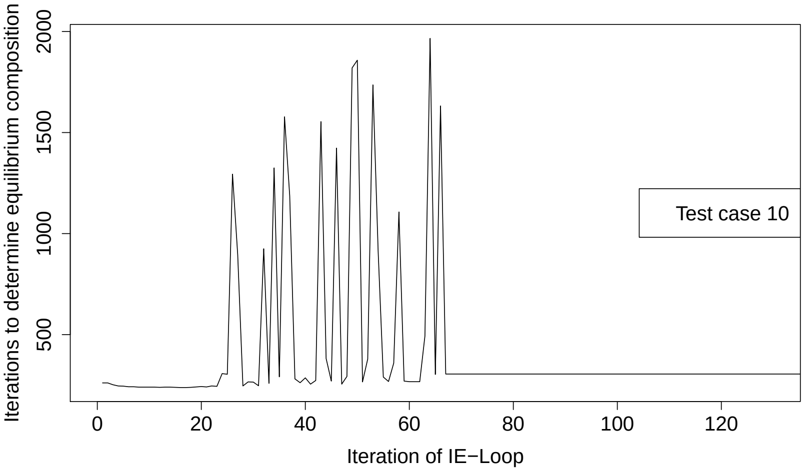

Figure 6.1: Influence of the iteration of the IE-Loop, which halved λ repeatedly, on the total number of iterations that were necessary to determine the equilibrium composition. The 11^{th} iteration of the IE-Loop resulted in a $\lambda = 4.883 \cdot 10^{-4}$ and, in this test case 10, it was the fastest way to find the final composition.

In this context, the right choice of λ is a decisive criterion for the quality of the initial estimate. In Figure 6.1, there is an impressive example of this. In every iteration of the IE-Loop, λ was halved and each value of it influenced the final number of iterations that were required to determine the equilibrium composition. Thus, it may occur that an unfavourable choice of λ result in more iterations and CPU time until a solution to the equilibrium problem is found. Concerning the IE-Loop method, in all 20 test cases in Table 6.1 and 6.2, the respective best value of λ were selected manually. Therefore, it can be regarded as an optimum result based on an iteratively halved λ. Unfortunatly, a pattern could not be identified here and, hence, the most favourable λ remains difficult to predict. At this point, the criterion for the final value of it had to be chosen carefully within the IE-Loop method to prevent an unnecessary time-consuming search for the appropriate value of λ and, simultaneously, to achieve a reliable decrease in calculation time and iterations. It turned out to be promising to stop the λ-halving after an arbitrarily set lower bound of $(dG/d\lambda)$ was reached. For Figure 6.2, lower bounds were varied from $1 \cdot 10^{-1}$ to $1 \cdot 10^{-20}$ and the respective results considering the total number of iterations to solve the chemical equilibrium compositions of test cases 10-20 were compared.

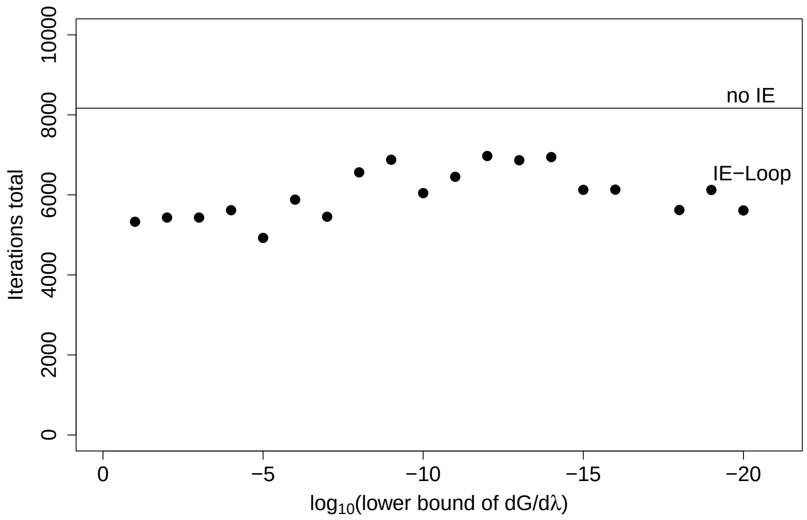

Figure 6.2: Resulting sum of iterations of test cases 10-20 until the equilibrium compositions were found using the IE-Loop method with various lower bounds of $(dG/d\lambda)$.

The minimum number of iterations was achieved at a lower bound of $1 \cdot 10^{-5}$. This value would be a good compromise between the elapsed time until a reasonable λ is found and the resulting number of iterations, which, with 4925, were considerably below the 8166 iterations that were needed by StoiCES without any IE and were only slightly above the best obtained value of 4527.

In individual cases, the application of an initial estimate bears the risk of an increase in the number of iterations, but, considering the majority of the studied cases, the benefits outweigh this.

The IE-SM method does not always provide the optimum results in performance improvement, though it turned out as a quite reliable approach to accelerate the calculation time.

Regarding the very low-species test cases 1-9, the initial moles taken directly from the simplex method were in many cases already the best ones.

Undoubtedly, the IE-Loop is very promising, as far as the termination condition for the λ-search is selected cleverly. In large systems with several hundred species which require up to thousands of iterations until the equilibrium composition is found, an adjustment of the lower bound of $(dG/d\lambda)$ may be useful to achieve the individual optimum acceleration of the calculation time.

7 Summary

An algorithm was implemented to determine the chemical equilibrium composition of initially only gaseous environments. It is based on the optimized stoichiometric VCS method, which has proven to be suitable for the problem at hand. It is able to find solutions quick and reliable and, additionally, it can be extended to handle condensated species in chemical equilibrium. Even in big systems that include several hundred species, there are no known convergence issues. The final code StoiCES allows for either fixed temperatures and pressures or fixed energy and volume of the system as constraints.

To check the accuracy of StoiCES, a comparison to literature test cases took place. A complex part of this was to evaluate the influence of different thermodynamic data and physical constants on the results. Nevertheless, StoiCES is in accordance with literature data considering (T,P)- and (U,V)-constraints.

The robustness tests, which assumed environments with temperatures from 200K-6000K and pressures from 10μbar-1Mbar, showed a generally very good aggreement with the reference compositions calculated by CEA. Only at the lower range of validity of the thermodynamic data, there were deviations in $\mathcal{O}(10^{-1})$. Here, more than 90% of the species had equilibrium abundances of lower than 10^{-40} moles. This indicates that, in those rather extreme systems, both algorithms handle minor species and physical less accurate data in different ways. A reasonable improvement of StoiCES might be to implement the possibility to skip the very low amount species during the calculation. This may accelerate the convergence of StoiCES.

The upper limit of 6000K and the lower limit of 200K were restricted to the available thermodynamic data of most species. An extrapolation of the data to higher or lower temperatures could technically expand the applicability of StoiCES but with possible loss in reliability. Especially in astrophysics, much hotter or colder systems are of particular importance. An implementation of this and evaluation how far the extrapolation of this non-linear problem is reasonable at a satisfactory level could be interesting for this field. In all test cases, a perfect equation of state was assumed. In this context, the addition of other environments like non-ideal gases which require a more detailed EOS and, in a few cases, adapted chemical potentials could achieve an improvement considering the handling of real systems. On those grounds, the inclusion of solids, liquids and even phase-transitions would improve StoiCES significantly. First test cases that took, initially, a mixture of pure gaseous and pure solid species into account were already promising. A refinement of StoiCES dealing with these single species phases and the implementation of the possibility of condensation or melting should be regarded as a next step.

Furthermore, the code assumes a stationary chemical equilibrium. Though in certain dynamic areas of astrophysical environments, it can occur that an equilibrium may never be reached because the environing thermo- and hydrodynamic conditions change faster than the chemical system can adapt. Turbulent parts of, e.g., a convective atmosphere do strive to an equilibrium, but the system continuously reconfigures itself on short timescales. In these cases, a time-dependent treatment of the chemical non-equilibrium would be required. A promising approach for this purpose would be the one of rate-controlled constraint-equilibrium where only the slow reactions and their species abundances need to be calculated time-dependent and explicitly. Concerning the remaining reactions, chemical equilibrium is assumed. This way, the effort of the time-dependent consideration of this non-equilibrium problem could be decreased for the most part. In the scope of further development, StoiCES could provide the basis for such an approach.

The application of an initial estimate of the initial moles could decrease the number of iterations and CPU time until a solution of the chemical equilibrium problem was found. In many test cases, the speed was more than doubled. Considering that especially in hydrodynamic simulations, the equilibrium composition need to be determined up to millions of times, this enormous acceleration of the calculation time is extremely worthwhile. Two different methods were compared. The IE-SM is based on Smith & Missen (1968) and in particular in systems with a few hundred species, it decreases the CPU time most reliably. Here, the step-size parameter λ, which influences the quality of the initial estimate, is allowed to take only four different values into account. This can be regarded as an advantage because, this way, the possibly time-consuming search for the most favourable λ can be reduced. On the other hand, the resulting quality of the IE is limited. A finer

λ-variation could be achieved by an iteratively halving of it which was realized by the IE-Loop method. It is important to select the lower bound of the termination condition within the determination of the appropriate λ in a clever way. Thus, an improvement compared to the IE-SM method could be attained in many cases.

A quick and on the fly calculated initial estimate can prevent the usage of partial pressure tables. Such tables can be regarded as a library of initial species abundances depending on various pressures. Their reading in takes additional time or, alternatively, a loading in the main memory would decrease the computing performance. Additionally, the applicability of these tables concerning systems which take several hundred species into account are not optimal. Especially in combination with hydrodynamics, in those simulations there are no spatially constant element abundances. In general, each grid cell provides different element compositions, varied from spatial point to point depending on the thermal history of the gas.

Furthermore, the usage of big tables are excluded from calculations that run on a Graphics Processing Unit (GPU). Due to such an architecture, a bottleneck would easily arise while copying the table data on the GPU. Basically, StoiCES provides good preconditions to run on those units because the stoichiometric approach requires only simple matrix calculations. This is, incidentally, another advantage over the non-stoichiometric algorithms with its matrix inversions at each iteration step.

All this underlines the enormous benefit of an included initial estimate. Therefore, the calculation time can be significantly accelerated while remaining independent of respective tables with their limited exactness but instead with a precise solution adapted to the individual case.

Another valuable feature of StoiCES' modular implementation is that this algorithm could be easily included in existing simulation codes. It can be regarded as a kind of library, where only, in the case of (T,P)-constraints, temperature, pressure, element abundances and a list of species is needed to be handed over. As a result, StoiCES returns the equilibrium properties like the chemical composition.

Appendix A

Considered Element Abundances of the Large Test Cases

List of initial elements and their abundances used for the large 411 species test cases in Chapter 5 and 6:
H (moles=1), He (moles=2), C (moles=1), N (moles=1), O (moles=2), S (moles=1), B (moles=1), Be (moles=1), F (moles=1), Ne (moles=2), Na (moles=3), Mg (moles=2), Ti (moles=1), Si (moles=1), P (moles=1), Cr (moles=1).

Considered Species of the Large Test Cases

List of the 411 considered species used for the large test cases in Chapter 5 and 6:
B, BC, BC_2, BF, BFOH, $BF(OH)_2$, BF_2, BF_2OH, BF_3, BH, BHF, BHF_2, BH_2, BH_2F, BH_3, BH_4, BH_5, BH_3NH_3, BN, BO, BOF, BOF_2, BOH, BO_2, $B(OH)_2$, BS, BS_2, B_2, B_2C, B_2F_4, B_2H, B_2H_2, B_2H_3, B_2H_3 (db), B_2H_4, B_2H_4 (db), B_2H_5, B_2H_5 (db), B_2H_6, B_2O, B_2O_2, B_2O_3, $B_2(OH)_4$, B_2S, B_2S_2, B_2S_3, B_3H_7 (C_{2v}), B_3H_7 (C_s), B_3H_9, $B_3N_3H_6$, $B_3O_3F_3$, B_4H_4, B_4H_{10}, B_4H_{12}, B_5H_9, Be, BeF, BeF_2, BeH, BeH_2, BeN, BeO, BeOH, $Be(OH)_2$, BeS, Be_2, Be_2F_4, Be_2O, Be_2OF_2, Be_2O_2, Be_3O_3, Be_4O_4, C, CF, CF_2, CF_3, CF_4, CH, CHF, CHF_2, CHF_3, CH_2, CH_2F, CH_2F_2, CH_3, CH_3F, CH_2OH, CH_3O, CH_4, CH_3OH, CH_3OOH, CN, CNN, CO, COF_2, COHF, COS, CO_2, COOH, CP, CS, CS_2, C_2, C_2F, C_2F_2, C_2F_3, C_2F_4, C_2F_6, C_2H, C_2HF, C_2HF_3, C_2H_2 (acetylene), C_2H_2 (vinylidene), $C_2H_2F_2$, CH_2CO (ketene), $O(CH)_2O$, $HO(CO)_2OH$, C_2H_3 (vinyl), C_2H_3F, CH_3CN, CH_3CO (acetyl), C_2H_4, C_2H_4O (ethylen-o), CH_3CHO (ethanal), CH_3COOH, $OHCH_2COOH$, C_2H_5, C_2H_6, $CH_3N_2CH_3$, C_2H_5OH, CH_3OCH_3, $CH_3O_2CH_3$, CCN, CNC, OCCN, C_2N_2, C_2O, C_2S_2,

C_3, C_3H_3 (1-propynl), C_3H_3 (2-propynl), C_3H_4 (allene), C_3H_4 (propyne), C_3H_4 (cyclo-), C_3H_5 (allyl), C_3H_6 (propylene), C_3H_6 (cyclo-), C_3H_6O (propylox), C_3H_6O (acetone), C_3H_6O (propanal), C_3H_7 (n-propyl), C_3H_7 (i-propyl), C_3H_8, C_3H_8O (1-propanol), C_3H_8O (2-propanol), CNCOCN, C_3OS, C_3O_2, C_3S_2, C_4, C_4H_2 (butadiyne), C_4H_4 (1,3-cyclo-), C_4H_6 (butadiene), C_4H_6 (1-butyne), C_4H_6 (2-butyne), C_4H_6 (cyclo-), C_4H_8 (1-butene), C_4H_8 (cis-2-buten), C_4H_8 (tr-2-butene), C_4H_8 (isobutene), C_4H_8 (cyclo-), $(CH_3COOH)_2$, C_4H_9 (n-butyl), C_4H_9 (i-butyl), C_4H_9 (s-butyl), C_4H_9 (t-butyl), C_4H_10 (n-butane), C_4H_{10} (isobutane), C_4N_2, C_5, C_5H_6 (1,3-cyclo-), C_5H_8 (cyclo-), C_5H_{10} (1-pentene), C_5H_{10} (cyclo-), C_5H_{11} (pentyl), C_5H_{11} (t-pentyl), C_5H_{12} (n-pentane), C_5H_{12} (i-pentane), $CH_3C(CH_3)_2CH_3$, C_6H_2, C_6H_5 (phenyl), C_6H_5O (phenoxy), C_6H_6, C_6H_5OH (phenol), C_6H_{10} (cyclo-), C_6H_{12} (1-hexene), C_6H_{12} (cyclo-), C_6H_{13} (n-hexyl), C_6H_{14} (n-hexane), C_7H_7 (benzyl), C_7H_8, C_7H_8O (cresol-mx), C_7H_{14} (1-heptene), C_7H_{15} (n-heptyl), C_7H_{16} (n-heptane), C_7H_{16} (2-methylh), C_8H_8 (styrene), C_8H_{10} (ethylbenz), C_8H_{16} (1-octene), C_8H_{17} (n-octyl), C_8H_{18} (n-octane), C_8H_{18} (isooctane), C_9H_{19} (n-nonyl), $C_{10}H_8$ (naphthale), $C_{10}H_{21}$ (n-decyl), $C_{12}H_9$ (o-bipheny), $C_{12}H_{10}$ (biphenyl), Cr, CrN, CrO, CrO_2, CrO_3, F, FCN, FCO, FO, FO_2 (FOO), FO_2 (OFO), F_2,F_2O, F_2O_2, FS_2F, H, HBO, HBO_2, HBS, HCN, HCO, HCCN, HCCO, HF, HNC, HNCO, HNO, HNO_2, HNO_3, HOF, HO_2, HPO, HSO_3F, H_2, HBOH, HCHO (formaldehy), HCOOH, H_2F_2, H_2O, H_2O_2, H_2S, H_2SO_4, H_2BOH, $HB(OH)_2$, H_3BO_3, $H_3B_3O_3$, $H_3B_3O_6$, H_3F_3, $(HCOOH)_2$, H_4F_4, H_5F_5, H_6F_6, H_7F_7, He, Mg, MgF, MgF_2, MgH, MgN, MgO, MgOH, $Mg(OH)_2$, MgS, Mg_2, Mg_2F_4, N, NCO, NF, NF_2, NF_3, NH, NHF, NHF_2, NH_2, NH_2F, NH_3, NH_2OH, NO, NOF, NOF_3, NO_2, NO_2F, NO_3, NO_3F, N_2, NCN, N_2F_2, N_2F_4, N_2H_2, NH_2NO_2, N_2H_4, N_2O, N_2O_3, N_2O_4, N_2O_5, N_3, N_3H, Na, $NaBO_2$, NaCN, NaF, NaH, $NaNO_2$, $NaNO_3$, NaO, NaOH, Na_2, Na_2F_2, Na_2O, Na_2O_2, $Na_2O_2H_2$, Na_2SO_4, Na_3F_3, Ne, O, OH, O_2, O_3, P, PF, PF_2, PF_3, PF_5, PH, PH_2, PH_3, PN, PO, POF_3, PO_2, PS, P_2, P_2O_3, P_2O_4, P_2O_5, P_3, P_3O_6, P_4, P_4O_6, P_4O_7, P_4O_8, P_4O_9, P_4O_{10}, S, SF, SF_2, SF_3, SF_4, SF_5, SF_6, SH, SN, SO, SOF_2, SO_2, SO_2F_2, SO_3, S_2, S_2F_2, S_2O, S_3, S_4, S_5, S_6, S_7, S_8, Si, SiC, SiC_2, SiF, SiF_2, SiF_3, SiF_4, SiH, SiHF, $SiHF_3$, SiH_2, SiH_2F_2, SiH_3, SiH_3F, SiH_4, SiN, SiO, SiO_2, SiS, SiS_2, Si_2, Si_2C, Si_2F_6, Si_2N, Si_3, Ti, TiO, TiO_2.

Appendix B

Considered Element Abundances of the Large Performance Test Cases

List of initial elements and their abundances used for the large 252 species test cases in Chapter 6:

H (moles=2), C (moles=1), O (moles=2), S (moles=1), B (moles=1), F (moles=1), Ne (moles=1).

Considered Species of the Large Test Cases

List of the 252 considered species used for the large test cases in Chapter 6:

B, BC, BC_2, BF, BFOH, $BF(OH)_2$, BF_2, BF_2OH, BF_3, BH, BHF, BHF_2, BH_2, BH_2F, BH_3, BH_4, BH_5, BO, BOF, BOF_2, BOH, BO_2, $B(OH)_2$, BS, BS_2, B_2, B_2C, B_2F_4, B_2H, B_2H_2, B_2H_3, B_2H_3 (db), B_2H_4, B_2H_4 (db), B_2H_5, B_2H_5 (db), B_2H_6, B_2O, B_2O_2, B_2O_3, $B_2(OH)_4$, B_2S, B_2S_2, B_2S_3, B_3H_7 (C_{2v}), B_3H_7 (C_s), B_3H_9, $B_3O_3F_3$, B_4H_4, B_4H_{10}, B_4H_{12}, B_5H_9, C, CF, CF_2, CF_3, CF_4, CH, CHF, CHF_2, CHF_3, CH_2, CH_2F, CH_2F_2, CH_3, CH_3F, CH_2OH, CH_3O, CH_4, CH_3OH, CH_3OOH, CO, COF_2, COHF, COS, CO_2, COOH, CS, CS_2, C_2, C_2F, C_2F_2, C_2F_3, C_2F_4, C_2F_6, C_2H, C_2HF, C_2HF_3, C_2H_2 (acetylene), C_2H_2 (vinylidene), $C_2H_2F_2$, CH_2CO (ketene), $O(CH)_2O$, $HO(CO)_2OH$, C_2H_3 (vinyl), C_2H_3F, CH_3CO (acetyl), C_2H_4, C_2H_4O (ethylen-o), CH_3CHO (ethanal), CH_3COOH, $OHCH_2COOH$, C_2H_5, C_2H_6, C_2H_5OH, CH_3OCH_3, $CH_3O_2CH_3$, C_2O, C_2S_2, C_3, C_3H_3 (1-propynl), C_3H_3 (2-propynl), C_3H_4 (allene), C_3H_4 (propyne), C_3H_4 (cyclo-), C_3H_5 (allyl), C_3H_6 (propylene), C_3H_6 (cyclo-), C_3H_6O (propylox), C_3H_6O (acetone), C_3H_6O (propanal), C_3H_7 (n-propyl), C_3H_7 (i-propyl), C_3H_8, C_3H_8O (1-propanol), C_3H_8O (2-propanol), C_3OS,

C_3O_2, C_3S_2, C_4, C_4H_2 (butadiyne), C_4H_4 (1,3-cyclo-), C_4H_6 (butadiene), C_4H_6 (1-butyne), C_4H_6 (2-butyne), C_4H_6 (cyclo-), C_4H_8 (1-butene), C_4H_8 (cis-2-buten), C_4H_8 (tr-2-butene), C_4H_8 (isobutene), C_4H_8 (cyclo-), $(CH_3COOH)_2$, C_4H_9 (n-butyl), C_4H_9 (i-butyl), C_4H_9 (s-butyl), C_4H_9 (t-butyl), C_4H_{10} (n-butane), C_4H_{10} (isobutane), C_5, C_5H_6 (1,3-cyclo-), C_5H_8 (cyclo-), C_5H_{10} (1-pentene), C_5H_{10} (cyclo-), C_5H_{11} (pentyl), C_5H_{11} (t-pentyl), C_5H_{12} (n-pentane), C_5H_{12} (i-pentane), $CH_3C(CH_3)_2CH_3$, C_6H_2, C_6H_5 (phenyl), C_6H_5O (phenoxy), C_6H_6, C_6H_5OH (phenol), C_6H_{10} (cyclo-), C_6H_{12} (1-hexene), C_6H_{12} (cyclo-), C_6H_{13} (n-hexyl), C_6H_{14} (n-hexane), C_7H_7 (benzyl), C_7H_8, C_7H_8O (cresol-mx), C_7H_{14} (1-heptene), C_7H_{15} (n-heptyl), C_7H_{16} (n-heptane), C_7H_{16} (2-methylh), C_8H_8 (styrene), C_8H_{10} (ethylbenz), C_8H_{16} (1-octene), C_8H_{17} (n-octyl), C_8H_{18} (n-octane), C_8H_{18} (isooctane), C_9H_{19} (n-nonyl), $C_{10}H_8$ (naphthale), $C_{10}H_{21}$ (n-decyl), $C_{12}H_9$ (o-bipheny), $C_{12}H_{10}$ (biphenyl), F, FCO, FO, FO_2 (FOO), FO_2 (OFO), F_2, F_2O, F_2O_2, FS_2F, H, HBO, HBO_2, HBS, HCO, HCCO, HF, HOF, HO_2, HSO_3F, H_2, HBOH, HCHO (formaldehy), HCOOH, H_2F_2, H_2O, H_2O_2, H_2S, H_2SO_4, H_2BOH, $HB(OH)_2$, H_3BO_3, $H_3B_3O_3$, $H_3B_3O_6$, H_3F_3, $(HCOOH)_2$, H_4F_4, H_5F_5, H_6F_6, H_7F_7, Ne, O, OH, O_2, O_3, S, SF, SF_2, SF_3, SF_4, SF_5, SF_6, SH, SO, SOF_2, SO_2, SO_2F_2, SO_3, S_2, S_2F_2, S_2O, S_3, S_4, S_5, S_6, S_7, S_8.

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Erklärung

Ich bestätige, dass die vorliegende Arbeit von mir selbständig verfasst wurde und ich keine anderen als die angegebenen Hilfsmittel - insbesondere keine im Quellenverzeichnis nicht benannten Internet - Quellen - benutzt habe und die Arbeit von mir vorher nicht einem anderen Prüfungsverfahren eingereicht wurde. Die eingereichte schriftliche Fassung entspricht der auf dem elektronischen Speichermedium. Ich bin damit einverstanden, dass die Masterarbeit veröffentlicht wird.

Hamburg, den 25.11.2013