

# INTERVAL ANALYSIS FOR COMPUTATIONAL CHEMISTRY

A THESIS

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**Bachelor of Science-Master of Science**

*in*

**CHEMISTRY**

*by*

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**March 2016**

# CERTIFICATE

This is to certify that **AKSHAY KRISHNA AK**, BS-MS (Chemistry), has worked on the project entitled '**INTERVAL ANALYSIS FOR COMPUTATIONAL CHEMISTRY**' under my supervision and guidance. The content of this report is original and has not been submitted elsewhere for the award of any academic or professional degree.

**April 2016**  
**IISER Pune**

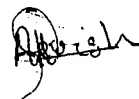


**Dr. A.P.J Jansen**

27 April 2016

# DECLARATION

I hereby declare that the matter embodied in the report entitled "**Interval Analysis for Computational Chemistry**" are the results of the investigations carried out by me at Shell Technology Center, Bangalore under the supervision of Dr. Tonek Jansen, Center for computational Expertise (CcoE) and the same has not been submitted elsewhere for any other degree.



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# ABSTRACT

A problem frequently encountered in all disciplines of science is to obtain all the solutions for a system of non-linear equations. A similar problem exists for reaction systems with many reactants, products, and intermediates. Such systems may have many steady states. Here one would like to have a list of all such steady states. Conventional methods rely on multiple initial start points, which means that they are initialization dependent and also might converge to trivial or unfeasible solutions. Such methods give one or a very limited set of steady states. The objective in thesis is to investigate how useful method of interval analysis is for determining the steady states of reaction systems. In particular, we are interested in solving kinetic equations of reactions involved in transition metal heterogeneous catalysis. The method of interval analysis can yield all steady states of a reaction system with mathematical certainty and are initialization independent. Here we will address how costly these methods are, and up to what size of the systems that one can reasonably handle.

# LIST OF SYMBOLS OR ABBREVIATIONS

## symbol

$\mathbb{R}$	Set of all Real Numbers
$\mathbb{IR}$	Set of all Interval Real Numbers
$x$	Real scalar
$x_i$	$i^{\text{th}}$ dimension of real vector
$[x]$	Real Interval
$\underline{x}$	Infimum of a Interval
$\bar{x}$	Supremum of a Interval
$\mathbf{x}$	Interval Vector
$\mathbf{A}$	Interval Matrix
$J$	Jacobian
$\theta$	Coverage over catalyst surface
$\alpha$	Flory-Schultz parameter

## Abbreviation

INTLAB	Interval laboratory
PROFIL	Programmer's Runtime Optimized Fast Interval Library
BIAS	Basic Interval Arithmetic Subroutine
IN/GB	Interval Newton Generalized Bisection



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# 1. INTRODUCTION

One of the relevant problems in mathematics is obtaining all solution for a system of nonlinear equations. It emerges just about in every one of the disciplines like engineering, physics, chemistry, economics and computer science. Most of the non-linear equations can't be solved analytically, so it is of utmost importance to try and develop better numerical algorithms. The main objective of this project is to understand how useful the method of interval analysis is for solving systems of nonlinear equations. In particular, we apply this method to study steady states of reactions in transition metal heterogeneous catalysis.

Section 1.1 gives background about the current methods to solve non-linear equations. Section 1.2 describes the importance and application of non-linear equations in chemistry.

## 1.1 Current Methods for Solving Non Linear Equations

The mathematical statement of the problem is considered: How to enclose all the solutions of a nonlinear system  $f(x) = 0$ , where  $x \in [\underline{x}, \bar{x}]$  and  $f : \mathbb{R}^n \rightarrow \mathbb{R}^m$ ,  $m < n$ ?

The most common method used to solve non-linear systems is the Newton method.<sup>1</sup> For an N dimensional equation ( $N=n=m$ ), Newton's method is given by

$$x_{i+1} = x_i - J_i^{-1}f(x_i) \quad (1.1)$$

Where  $i$  denotes the  $i^{\text{th}}$  dimension and  $J$  denotes the Jacobian. Even though the method is quadratically convergent, it has got major draw backs. The method doesn't converge to a solution unless the starting point is sufficiently close to a solution. The method fails to find multiple solutions, so one has to rely on multiple initial guesses. Even then there is no mathematical guarantee that all the solutions have been found out.

Several different methods exist for solving non-linear equations. But none except for homotopy based methods<sup>2-5</sup> can find multiple solutions. The basic idea in homotopy

based algorithm is to start from a solution and move along a path to next solution. Even though homotopy based method locates all solution in some cases, there is no mathematical guarantee that all solutions have been found. There are several other techniques to solve non-linear equation. These include techniques based on iterative programming, trust-region method, Halley method, Secant method and neural network based methods<sup>6--9</sup>.

## 1.2 Application in Chemistry

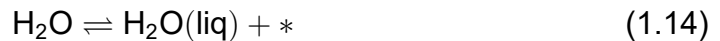
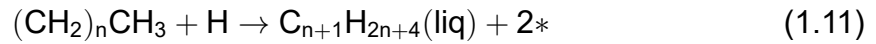
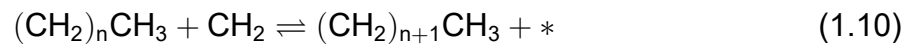
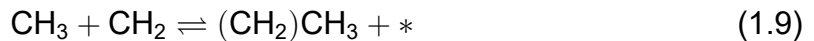
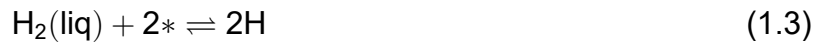
Non-linear equations are an integral part of chemistry. The problem of computing all steady states of a reaction system and reactive phase equilibrium has attracted significant attention from the research community.<sup>10</sup> The non-linear nature of rate equations and thermodynamic models in phase equilibrium makes computation difficult, since we don't know beforehand the number of solutions that exist, or if there exist any.<sup>11</sup> For solving such models we need a method which can be completely reliable, find out all solutions with mathematical and computational certainty. The standard local methods can give no such guarantee.

In the thesis we will be primarily focusing on solving non-linear rate equations using interval based methods(refer to chapter 2). Solving the rate equations gives important information regarding reaction mechanisms, transition states and the quality of underlying mathematical model. Computational methods like Density-functional Theory (DFT) have been widely used to study catalytic systems. But we can hardly predict anything about the kinetics by just looking at the DFT results. To get information regarding the kinetics, we try to solve the rate equations which are extremely non-linear in nature.

### 1.2.1 Fischer-Tropsch process

Fischer-Tropsch process is a set of reactions where carbon monoxide and hydrogen react to form hydrocarbons. Many mechanisms are suggested to explain the process.<sup>12</sup> But there is no clear consensus in literature regarding the correct mechanism. A reaction mechanism for Fischer Tropsch on a cobalt nanoparticle based on carbide model is given below. A \* denotes a vacant adsorption site. Non adsorbates are indicated by

adding a "(liq)" to the chemical formula.



Equations (1.10) and (1.11) represents chain growth and termination. Note that methane formation and chain termination reactions are not reversible. The mechanism of the reaction is dissociation of CO to form carbon followed by hydrogenation of carbon to form CH<sub>3</sub> to start chain growth with CH<sub>2</sub> as building blocks. The objective is to find out the coverages ( $\theta$ ) of these species on the catalyst surface at steady states using reliable interval computation.

The thesis is structured as follows. Chapter 2 provides the history and basic concepts in interval analysis. Chapter 3 discusses about the methods and methodology. An algorithm for non-linear equation solver based on interval analysis is presented in this chapter. Chapter 4 discusses the results obtained. Chapter 5 summarizes the thesis and draws conclusions. All other information that is required are given in Appendices. The appendices give details regarding the rate constants and rate equations used in the of Fischer Tropsch model.

## 2. BASICS OF INTERVAL ANALYSIS

This chapter introduces the main concepts of interval analysis. Section 2.1 gives a brief history of development of interval arithmetic. Section 2.2 introduces the concept of intervals and section 2.3 provides fundamentals of interval computation. A brief description of available platforms to execute interval arithmetic is provided in the last section.

### 2.1 History

Using intervals to solve problems is not a totally new marvel in science; it has existed under various names throughout history. A very old and famous example is that of Archimedes, who calculated the lower and upper bounds of  $\pi$  in the 3rd century. In the modern era, Ramon E Moore used intervals to investigate and keep track of errors in computers. In 1966, interval analysis rose to dominance after appearance of the book *Interval Analysis* by Moore.<sup>13</sup> In 1965 Eldon R. Hansen studied the use of interval arithmetic in linear algebra,<sup>14</sup> and later developed Hansen's method for global optimization. Alefeld, Krawczyk and Nickel played a crucial part in computer implementation of interval analysis. Interval analysis attracted a lot of interest among research community during the 1990's, and now it has its own journal called *Reliable Computing*.

### 2.2 Interval

An interval is a set of numbers that lies between two numbers. Mathematically, an interval  $[x]$  is a connected subset of  $\mathbb{R}$ . An interval will be denoted by  $[x]$ . The lower bound of an interval  $[x]$  will be denoted by  $\underline{x}$  and upper bound will be denoted by  $\bar{x}$ . Now we define an interval:

$$[x] = [\underline{x}, \bar{x}] = \{x \in \mathbb{R} : \underline{x} \leq x \leq \bar{x}\}$$

The set of all possible intervals on a real line is denoted as  $\mathbb{IR}$ :<sup>15</sup>

$$\mathbb{IR} = \{[\underline{x}, \bar{x}] : \underline{x} \leq \bar{x}; \quad \underline{x}, \bar{x} \in \mathbb{R}\}$$

A real number  $b$  will correspond to a interval with zero width. These are referred to as degenerate intervals.<sup>15</sup>

$$[b] = [\underline{b}, \bar{b}] \quad \text{where} \quad \underline{b} = \bar{b} = b$$

The elements of  $\mathbb{IR}$  follow the usual set relations defined by,

$$\begin{aligned} [x] = [y] &\Leftrightarrow \underline{x} = \underline{y} \text{ and } \bar{x} = \bar{y} \\ [x] \subseteq [y] &\Leftrightarrow \underline{y} \leq \underline{x} \text{ and } \bar{x} \leq \bar{y} \\ [x] \subset [y] &\Leftrightarrow [x] \subseteq [y] \text{ and } [x] \neq [y] \end{aligned}$$

Next section introduces interval analogue of real arithmetic operations.

### 2.2.1 Interval Arithmetic

Let  $\star$  denote one of the real arithmetic operations addition (+), subtraction (-), multiplication (\*) or division (/). These real arithmetic operations can be defined on the elements of  $\mathbb{IR}$  by:<sup>16,17</sup>

$$[x] \star [y] = \{x \star y : x \in [x], y \in [y]\}$$

The definition holds true for all cases, except for operation  $[x]/[y]$  if  $0 \in [y]$ . It is possible to describe these operations in terms of the bounds on  $[x]$  and  $[y]$ . It is as follows:

$$\begin{aligned} [x] + [y] &= [\underline{x} + \underline{y}, \bar{x} + \bar{y}] \\ [x] - [y] &= [\underline{x} - \bar{y}, \bar{x} - \underline{y}] \\ [x] * [y] &= [\min\{\underline{x}\underline{y}, \underline{x}\bar{y}, \bar{x}\underline{y}, \bar{x}\bar{y}\}, \max\{\underline{x}\underline{y}, \underline{x}\bar{y}, \bar{x}\underline{y}, \bar{x}\bar{y}\}] \\ [x]/[y] &= [x] * [1/\bar{y}, 1/\underline{y}], \quad \text{if } 0 \notin [y] \end{aligned}$$

The operation  $[x]/[y]$  when  $0 \in [y]$  is dealt by using extended interval arithmetic.<sup>18</sup>

### 2.2.2 Interval Vectors

An interval vector  $[x]$  can be defined as a product of  $n$  closed Cartesian intervals. It will be a subset of  $\mathbb{R}^n$  and is defined as:<sup>17</sup>

$$[x] = [x_1] * [x_2] * \dots * [x_n], \quad \text{where } [x_i] = [\underline{x}_i, \bar{x}_i] \quad \text{for } i = 1, \dots, n.$$

The  $i^{\text{th}}$  component will be projection of  $[x]$  onto  $i^{\text{th}}$  axis. Interval vectors  $[x]$  are also referred to as  $N$  dimensional box and geometrically it can be interpreted as an  $N$ -dimensional rectangle. This definition can be extended to define an interval matrix

$\mathbf{B} = (B_{ij}) \in \mathbb{IR}^{n \times m}$  has interval elements  $B_{ij} \in \mathbb{IR}$ . Now we compare some properties of intervals,  $[x] \in \mathbb{IR}$  and interval vectors  $[\mathbf{x}] \in \mathbb{IR}^n$ .

Operation	Interval:	Interval Vector:
Midpoint	$\text{mid}([x]) = \frac{1}{2}(x + \bar{x})$	$\text{mid}([\mathbf{x}]) = [\text{mid}([x_1], \text{mid}[x_2] \dots \text{mid}[x_n])$
Width	$\text{wid}[x] = (\bar{x} - x)$	$\text{wid}([\mathbf{x}]) = \text{wid}([x_2] \dots \text{mid}[x_n])$

**Tab. 2.1:** Operations on intervals and interval vectors<sup>19,20</sup>

### 2.2.3 Interval Function

An interval function is a function that take and return intervals instead of real numbers. An interval function has the following property:

Consider a real function  $f: \mathbb{R}^n \rightarrow \mathbb{R}^m$ . The interval function  $\mathbf{F}: \mathbb{IR}^n \rightarrow \mathbb{IR}^m$  is an inclusion function of  $f$  only if,

$$f(x_1, x_2, \dots, x_n) \in \mathbf{F}([x_1], [x_2], \dots, [x_n])$$

Whenever  $x_i \in [x_i] \forall i = 1, 2, \dots, n$ .<sup>16,17</sup> An inclusion monotonic interval function  $\mathbf{F}([\mathbf{x}])$  obeys the property:<sup>16,18,21,22</sup>

$$[x_i] \subset [y_i] \quad (i = 1, 2, \dots, n) \implies \mathbf{F}([x_1], [x_2], \dots, [x_n]) \subset \mathbf{F}([y_1], [y_2], \dots, [y_n])$$

In a rational real function replacing the real variables and real arithmetic operations by corresponding intervals and interval operations one can obtain the inclusion monotonic interval extension for the function. If  $0 \notin \mathbf{F}([\mathbf{x}])$ , were  $\mathbf{F}([\mathbf{x}])$  is an inclusion monotone interval extension of  $f(\mathbf{x})$  then we can conclude that there is no root of  $f(\mathbf{x})=0$  in  $[\mathbf{x}]$ .

The interval function  $\mathbf{F}([\mathbf{x}])$  encloses the range of the function  $f(\mathbf{x}) \forall \mathbf{x} \in [\mathbf{x}]$ . But how good the bounds (tightness) are depends on the nature in which  $\mathbf{F}([\mathbf{x}])$  is expressed and evaluated. This is illustrated with an example, let  $f(\mathbf{x}) = x_3(x_2 - x_1) = x_3 * x_2 - x_3 * x_1$  then the interval analogue  $\mathbf{F}([\mathbf{x}]) = [x]_3([x]_2 - [x]_1)$  which can also be written as  $[x]_3 * [x]_2 - [x]_3 * [x]_1$ . Evaluating the function at  $[x]_3 = [x]_2 = [x]_1 = [1, 3]$  for the first form ( $[x]_3([x]_2 - [x]_1)$ ) gives  $[1, 3]([1, 3] - [1, 3]) = [1, 3] * (-2, 2) = [-6, 6]$  which is the range of  $f(\mathbf{x})$  over  $[\mathbf{x}]$ . Now evaluating the second expression ( $[x]_3 * [x]_2 - [x]_3 * [x]_1$ ) yields  $([1, 3] * [1, 3] - [1, 3] * [1, 3]) = [1, 9] - [1, 9] = [-8, 8]$  which encloses the range of  $f(\mathbf{x})$  over  $[\mathbf{x}]$  but is an overestimate. Overestimation happens because each time a variable occurs in an interval expression, interval arithmetic treats it as an independent variable, thereby failing to recognize the dependence. This is called the 'dependence problem' and it implies that the form of algebraic expression plays a role in the quality of result which is not the case in real arithmetic.



## 2.3 Implementation in Computers

There are many platforms that permit implementation of numerical application using interval arithmetic. In this section few of them are mentioned along with the one used in this thesis. Some of the available software's and compilers are:

**INTLAB:** INTerval LABortary(INTLAB) is an extension of MATLAB based on BLAS (Basic Linear Algebra Subprograms) routines.<sup>23</sup> For portability, speed and ease of use all the INTLAB codes are written in MATLAB.

**INTBIS:** It was designed to find out solutions for polynomial systems of equations. The codes were written in FORTRAN 77.<sup>24</sup>

**Boost:** It is a collection of C++ libraries that enables to perform interval arithmetic calculations.<sup>25</sup>

**PROFIL/BIAS:** Programmer's Runtime Optimized Fast Interval Library(PROFIL) is a portable C++ library that allows developing and implementing interval arithmetic in a smart and efficient way.<sup>26</sup> Interval algorithms in this thesis was developed with the help of this library. It supports both real data types and the corresponding interval ones. Some of the supported data types include: INT, REAL, VECTOR, INTERVAL, INTERVAL VECTOR, MATRIX, INTERVAL MATRIX and complex numbers. BIAS (Basic Interval Arithmetic Subroutine) provides an interface for computation of interval vectors/matrix operations. We use this library for implementation of interval arithmetic. An interval say  $[1.2345, 1.2346]$  will be represented as  $1.234[5,6]$  in PROFIL/BIAS. Intervals would be denoted by '[' ]' bracket.

## 3. INTERVAL ANALYSIS METHODS FOR NON-LINEAR EQUATIONS

The previous chapter introduced the basic concepts of interval analysis. This chapter primarily focuses on application of interval analysis for solving systems of non-linear equation. This goal is achieved by developing an Interval Newton/Generalized Bisection (IN/GB) method. Unlike the other real arithmetic methods, if implemented properly interval newton methods can find out all the solutions of an equation with mathematical and computational certainty.<sup>27</sup>

If a function is just continuous, a bisection type method would be an apt choice. For a differentiable function, Newton-type method is preferred. In section 3.1 interval bisection method is introduced. Bisection methods are computationally very expensive most of the times. To minimize the dependence on bisection method, the concept of contractors are defined in section 3.2. Finally section 3.3 we describe the algorithm for IN/GB method.

### 3.1 Interval Bisection Method

The problem we are addressing is to find out the solution set for  $f(\mathbf{x})=0$ . We know from section 2.2.3 that range of  $f(\mathbf{x})$  is a subset of the inclusion function  $\mathbf{F}[\mathbf{x}]$ . In the bisection method the initial domain, assuming to contain a solution, is bisected into two boxes along the component with highest width. The bisected boxes are further evaluated to contain any zero's; the box not containing the solution is discarded. The box containing the solution is further bisected until width of the solution box is less than a predefined tolerance given by the user.

The interval bisection method is accurate and robust, but computationally very expensive. The efficiency of bisection highly relies on the plane along which bisection is performed. A better choice for bisection is given by Ratshek and Rokne, 1995 and Ratz and Csendes,<sup>28</sup> 1995. But when the dimensionality (number of variables) of a problem is large, bisection should be used only as a last resort. This is because the complexity of bisection algorithm is exponential in nature. This problem is also known as 'curse

of dimensionality'. In order to overcome the problem, we introduce the concept of contractors in the next section.

## 3.2 Contractors

A contractor is an operator which acts on an interval  $[x]$  to replace it with a smaller interval  $[x^*]$  such that  $[x^*] \subset [x]$ . Using a contractor reduces the complexity of the algorithm by giving a better bound on the solution set without relying on the bisection method. In the coming sections we will briefly describe some of the contractors used.

### 3.2.1 Gauss Seidel Contractor

Interval Gauss Seidel method is an interval analogue of the real Gauss Seidel method. Systems of linear interval equations can be represented in the matrix form as,

$$[\mathbf{A}][\mathbf{q}] - [\mathbf{b}] = 0 \quad (3.1)$$

where the matrix  $[\mathbf{A}]$  denotes a square interval matrix,  $[\mathbf{q}]$  and  $[\mathbf{b}]$  denote interval vectors. Interval matrix  $[\mathbf{A}]$  can be written as a sum of a diagonal matrix and a matrix with zero's on its diagonal

$$[\mathbf{A}] = \text{diag}[\mathbf{A}] + \text{extdiag}[\mathbf{A}] \quad (3.2)$$

substituting equation(3.2) in equation(3.1) gives

$$\text{diag}([\mathbf{A}])[\mathbf{q}] + \text{extdiag}([\mathbf{A}])[\mathbf{q}] = [\mathbf{b}] \quad (3.3)$$

Assuming that  $[\mathbf{A}]$  is invertible, we have

$$[\mathbf{q}] = (\text{diag}([\mathbf{A}]))^{-1}([\mathbf{b}] - \text{extdiag}([\mathbf{A}])[\mathbf{q}]) \quad (3.4)$$

$$C_{GS} : \rightarrow [\mathbf{q}] \cap (\text{diag}([\mathbf{A}]))^{-1}([\mathbf{b}] - \text{extdiag}([\mathbf{A}])[\mathbf{q}]) \quad (3.5)$$

$C_{GS}$  is known as the Gauss-Seidel contractor. Gauss Seidel contractor might not necessarily contract a given interval, the method is efficient when the interval matrix  $[\mathbf{A}]$  is close to identity matrix.<sup>17</sup>

The efficiency of Gauss - Seidel contractor could be improved by preconditioning the matrix  $[\mathbf{A}]$ . The preconditioned Gauss-Seidel contractor is denoted by  $C_{GSP}$ . This provides a tighter bound for the solutions. A simple way to precondition the matrix  $[\mathbf{A}]$  is to multiply it with the inverse of the matrix generated by computing the midpoints of

$[\mathbf{A}]$ , i.e,  $B=(\text{mid}[\mathbf{A}])^{-1}$ . The matrix  $[\mathbf{A}]$  and  $[\mathbf{b}]$  are replaced  $[\mathbf{A}]'=B^{-1}[\mathbf{A}]$  and  $[\mathbf{b}]'=B^{-1}[\mathbf{b}]$ . The algorithm for the preconditioned Gauss-Seidel contractor is provided in table 3.1.

Algorithm $C_{\text{GSP}}$	
1	$B = \text{mid}([\mathbf{A}]);$
2	$[\mathbf{A}]' = B^{-1}([\mathbf{A}]);$
3	$[\mathbf{b}]' = B^{-1}[\mathbf{b}];$
4	$C_{\text{GS}}([\mathbf{A}][\mathbf{q}] - [\mathbf{b}]' = 0);$
5	$[\mathbf{b}] = B[\mathbf{b}]' \cap [\mathbf{b}];$
6	$[\mathbf{A}] = B[\mathbf{A}]' \cap [\mathbf{A}];$

Tab. 3.1: Preconditioned Gauss Seidel Method

### 3.2.2 Interval Newton Contractor

Consider a real function  $f: \mathbf{x} \rightarrow \mathbb{R}$  which is a continuously differentiable over its domain with  $x_0 \in \mathbf{x}$  such that  $f(x_0) = 0$ . Let's assume that the derivative of function  $f'(x) \neq 0$  over  $X$  and its inclusion function  $F'(\mathbf{x})$  exists. By applying the Mean Value Theorem for any  $x \in \mathbf{x}$  we get

$$f(x) = f(x_0) + f'(c)(x - x_0) \quad (3.6)$$

for some  $c$  between  $x$  and  $x_0$ . Solving for  $x_0$  gives:

$$x_0 = x - \frac{f(x)}{f'(c)} \in x - \frac{f(x)}{F'(\mathbf{x})} \quad (3.7)$$

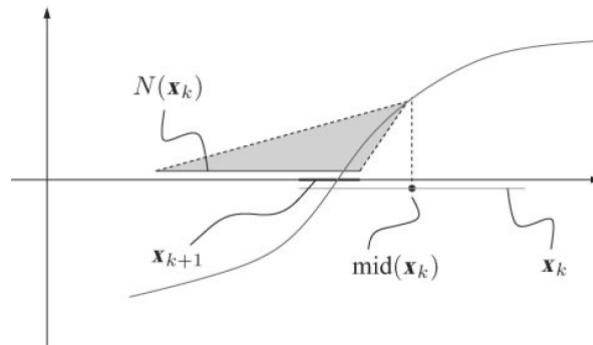
From the definition of inclusion function (section 2.2.3 )  $f'(c) \in F'(\mathbf{x})$ . Now we define function

$$N(x, \mathbf{x}) = x - \frac{f(x)}{F'(\mathbf{x})} \quad (3.8)$$

Since we said that  $x_0 \in \mathbf{x}$  and from equation we know that  $x_0 \in N(x, \mathbf{x})$ . This implies that  $x_0 \in N(x, \mathbf{x}) \cap \mathbf{x}$  for all  $x \in \mathbf{x}$ . The new interval we obtained can be iterated again to get a tighter enclosure, the sequence would be as follows:

$$\mathbf{x}_{m+1} = N(\mathbf{x}_m) \cap \mathbf{x}_m \quad m = 0, 1, 2, 3, \dots \quad (3.9)$$

The figure 3.1 given below represents one iteration of newton contractor.



**Fig. 3.1:** One iteration of interval newton contractor<sup>15</sup>

The equation (3.9) not only gives a tight bound to the solution but also provides an existence and uniqueness test. If  $N(x_m) \cap x_m = \phi$  then there is no solution in this interval  $x_m$ . If  $N(x_m) \subset x_m$  then there is a unique root of  $f(x)$  in  $x_m$ . In the below table 3.2 we describe a brief algorithm for multidimensional Newton contractor.  $\mathbf{J}([x])$  denotes interval analogue of the Jacobian matrix.

<b>Algorithm <math>C_{\text{Newton}}</math></b>	
1	$\mathbf{x}^* = \text{mid}([x]);$
2	$\mathbf{A} = \mathbf{J}([x])$
3	$[\mathbf{q}] = [x] - \mathbf{x}^*$
4	$C_{\text{GSP}}(\mathbf{A}\mathbf{q} + \mathbf{f}(\mathbf{x}^*) = 0)$
5	$[x] = [x] \cap ([\mathbf{q}] + \mathbf{x}^*)$

**Tab. 3.2:** Newton Contractor<sup>17</sup>

### 3.3 Algorithm

We briefly describe the Interval Newton Generalized Bisection (IN/GB) algorithm that was developed to solve system of non-linear equations. If executed properly only mode of failure is an excessive computational requirement. The method described in this section is a serial version.

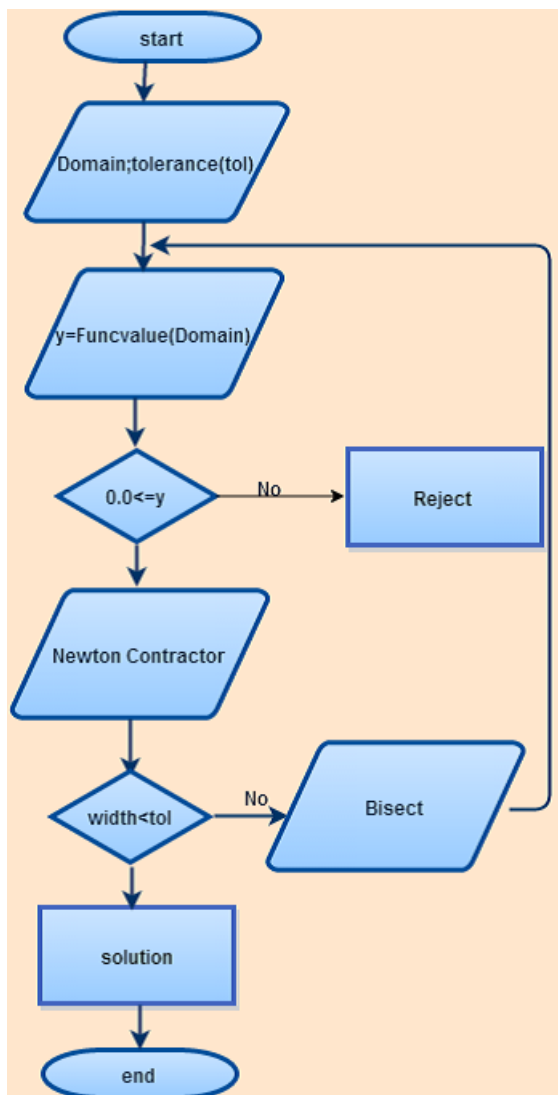
1. Input the domain space where you want to search for solutions. Provide a tolerance value (tol), which represents the smallest allowable box dimension.
2. Evaluate the function over the given domain.
3. Check if root lies in the obtained function range.
  - (a) If No, reject that domain space
  - (b) If Yes, Call the Newton contractor to converge to the solution.

4. Check whether width of solution box is less than given tolerance.

(a) If No, bisect the box into two and repeat steps from 2.

(b) If Yes, store the box in solution list and stop.

Below we represent a flow chart for the algorithm.



**Fig. 3.2:** Represents flow chart for Interval Newton/Bisection Method.

## 4. RESULTS

### 4.1 PUMA problem

After developing the IN/GB algorithm we need to benchmark it. For this we test it on the following problem, called Puma arose from inverse kinematics of 3R robot, commonly used to benchmark non-linear system solvers:

$$x_1^2 + x_2^2 - 1 = 0 \quad (4.1a)$$

$$x_3^2 + x_4^2 - 1 = 0 \quad (4.1b)$$

$$x_5^2 + x_6^2 - 1 = 0 \quad (4.1c)$$

$$x_7^2 + x_8^2 - 1 = 0 \quad (4.1d)$$

$$0.004731 * x_1 * x_3 - 0.3578 * x_2 * x_3 - 0.1238 * x_1 \quad (4.1e)$$

$$-0.001637 * x_2 - 0.9338 * x_4 + x_7 - 0.3571 = 0$$

$$0.2238x_1x_3 + 0.7623x_2x_3 + 0.2638x_1 - 0.07745x_2 - 0.6734x_4 - 0.6022 = 0 \quad (4.1f)$$

$$x_6x_8 + 0.3578x_1 + 0.004731x_2 = 0 \quad (4.1g)$$

$$-0.7623x_1 + 0.2238x_2 + 0.3461 = 0 \quad (4.1h)$$

$$x_1, \dots, x_8 \in [-1, 1]. \quad (4.1i)$$

In the above form it is a well-determined set of 8 equations and 8 variables with 16 solutions. We ran the code taking a domain ranging from [-10, 10] for all the variables. The tolerance set was 0.0001. We obtain all the 16 solutions in 92.3 seconds without using a preconditioned interval newton method. Table 4.1 and 4.2 represents the literature reported solutions for this problem. Table 4.3 and 4.4 gives the solutions obtained using Interval Newton/Generalised bisection method.

From the results of PUMA problem, we can conclude that the algorithm can provide all the solutions for a set of non-linear equations. We can also infer from the tables that the interval analysis solution encloses the actual solution. This is true for all the 16

	solution 1	solution 2	solution 3	solution 4	solution 5	solution 6	solution 7	solution 8
x1	0.16443	0.16443	0.16443	0.16443	0.16443	0.16443	0.16443	0.16443
x2	-0.98638	-0.98638	-0.98638	-0.98638	-0.98638	-0.98638	-0.98638	-0.98638
x3	0.23961	0.23961	0.23961	0.23961	-0.95472	-0.95472	-0.95472	-0.95472
x4	-0.97086	-0.97086	-0.97086	-0.97086	0.29747	0.29747	0.29747	0.29747
x5	0.99763	-0.99763	-0.99763	0.99763	0.91115	-0.91115	-0.91115	0.91115
x6	0.06872	-0.06872	0.06872	-0.06872	-0.41206	0.41206	-0.41206	0.41206
x7	-0.6155	-0.6155	-0.6155	-0.6155	0.99132	0.99132	0.99132	0.99132
x8	-0.78813	0.78813	-0.78813	0.78813	0.13145	-0.13145	0.13145	-0.13145

**Tab. 4.1:** Actual solutions for PUMA problem

	solution 9	solution 10	solution 11	solution 12	solution13	solution 14	solution 15	solution 16
x1	0.67155	0.67155	0.67155	0.67155	0.67155	0.67155	0.67155	0.67155
x2	0.74095	0.74095	0.74095	0.74095	0.74095	0.74095	0.74095	0.74095
x3	-0.23961	-0.23961	-0.23961	-0.23961	0.95472	0.95472	0.95472	0.95472
x4	-0.97086	-0.97086	-0.97086	-0.97086	0.29747	0.29747	0.29747	0.29747
x5	-0.95791	0.95791	0.95791	-0.95791	-0.12877	0.12877	0.12877	-0.12877
x6	-0.28704	0.28704	-0.28704	0.28704	0.99167	-0.99167	0.99167	-0.99167
x7	-0.5279	-0.5279	-0.5279	-0.5279	0.96931	0.96931	0.96931	0.96931
x8	0.8493	-0.8493	0.8493	-0.8493	-0.24583	0.24583	-0.24583	0.24583

**Tab. 4.2:** Actual solutions for PUMA problem

	solution 1	solution 2	solution 3	solution 4	solution 5	solution 6	solution 7	solution 8
x1	0.1644[28,36]	0.1644[28,36]	0.1644[28,36]	0.1644[28,36]	0.1644[28,36]	0.1644[28,36]	0.1644[28,36]	0.1644[28,36]
x2	-0.9863[85,94]	-0.9863[85,94]	-0.9863[85,94]	-0.9863[85,94]	-0.9863[85,94]	-0.9863[85,94]	-0.9863[85,94]	-0.9863[85,94]
x3	0.2396[10,20]	0.2396[10,20]	0.2396[10,20]	0.2396[10,20]	-0.9547[23,32]	-0.9547[23,32]	-0.9547[23,32]	-0.9547[23,32]
x4	-0.9708[59,69]	-0.9708[59,69]	-0.9708[59,69]	-0.9708[59,69]	0.2974[89,98]	0.2974[89,98]	0.2974[89,98]	0.2974[89,98]
x5	0.9976[29,38]	-0.9976[29,38]	-0.9976[29,38]	0.9976[29,38]	0.9107[71,16]	-0.9107[71,16]	-0.9107[71,16]	0.9107[71,16]
x6	0.0687[21,31]	-0.0687[21,31]	0.0687[21,31]	-0.0687[21,31]	-0.4128[45,55]	0.4128[45,55]	-0.4128[45,55]	0.4128[45,55]
x7	-0.6154[18,11]	-0.6154[18,11]	-0.6154[18,11]	-0.6154[18,11]	0.9913[44,53]	0.9913[44,53]	0.9913[44,53]	0.9913[44,53]
x8	0.7881[35,45]	0.7881[35,45]	-0.7881[35,45]	0.7881[35,45]	0.1312[06,16]	-0.1312[06,16]	0.1312[06,16]	-0.1312[06,16]

**Tab. 4.3:** Interval Analysis solution for PUMA problem

	solution9	solution 10	solution 11	solution 12	solution13	solution 14	solution 15	solution 16
x1	0.67155[21,74]	0.67155[21,74]	0.67155[21,74]	0.67155[21,74]	0.67155[21,74]	0.67155[21,74]	0.67155[21,74]	0.67155[21,74]
x2	0.7409[47,57]	0.7409[47,57]	0.7409[47,57]	0.7409[47,57]	0.7409[47,57]	0.7409[47,57]	0.7409[47,57]	0.7409[47,57]
x3	-0.2396[01,10]	-0.2396[01,10]	-0.2396[01,10]	-0.2396[01,10]	0.9547[23,32]	0.9547[23,32]	0.9547[23,32]	0.9547[23,32]
x4	-0.9708[69,78]	-0.9708[69,78]	-0.9708[69,78]	-0.9708[69,78]	0.2974[60,70]	0.2974[60,70]	0.2974[60,70]	0.2974[60,70]
x5	-0.9579[18,27]	0.9579[18,27]	0.9579[18,27]	-0.9579[18,27]	-0.1287[41,50]	0.1287[41,50]	0.1287[41,50]	0.1287[41,50]
x6	-0.2870[36,46]	0.2870[36,46]	-0.2870[36,46]	0.2870[36,46]	0.9912[00,95]	-0.9912[00,95]	0.9912[00,95]	-0.9912[00,95]
x7	-0.5278[68,16]	-0.5278[68,16]	-0.5278[68,16]	-0.5278[68,16]	0.9692[85,95]	0.9692[85,95]	0.9692[85,95]	0.9692[85,95]
x8	0.8493[04,13]	-0.8493[04,13]	0.8493[04,13]	-0.8493[04,13]	-0.2459[33,43]	0.2459[33,43]	-0.2459[33,43]	0.2459[33,43]

**Tab. 4.4:** Interval Analysis solution for PUMA problem

solutions. Depending on the tolerance given one can go arbitrarily close to the solution. Next we apply the method to solve kinetic equations in catalysis to figure out the steady states at equilibrium.

## 4.2 CO oxidation with NO

The reaction of carbon monoxide with nitrogen monoxide occurs in catalytic converters. A catalytic converter is device used to reduce the emissions from internal combustion engines. It converts harmful gases like CO and NO to harmless CO<sub>2</sub> and N<sub>2</sub> via redox



reaction with help of a catalyst. The reaction between CO and NO is given below:



Steps involved:

1. Adsorption of CO and NO
2. Desorption of NO
3. Dissociation of NO
4. Formation and immediate desorption of CO<sub>2</sub>
5. Formation and immediate desorption of N<sub>2</sub>

The kinetic rate equation for the process is given below:

$$\frac{d[\text{N}]}{dt} = k_2[\text{NO}][\text{Z}] - k_4[\text{N}]^2 \quad (4.3a)$$

$$\frac{d[\text{NO}]}{dt} = k_5[\text{Z}] - k_6[\text{NO}] - k_2[\text{NO}][\text{Z}] \quad (4.3b)$$

$$\frac{d[\text{CO}]}{dt} = k_1[\text{Z}] - k_3[\text{CO}][\text{O}] \quad (4.3c)$$

$$\frac{d[\text{O}]}{dt} = k_2[\text{Z}] - k_3[\text{CO}][\text{O}] \quad (4.3d)$$

$$[\text{N}] + [\text{NO}] + [\text{CO}] + [\text{O}] + [\text{Z}] = 1 \quad (4.3e)$$

In the above set of equations the square brackets indicate the surface coverage of the molecule over the catalyst. [Z] denotes the free surface area on the catalyst. By setting the differential values to 0 the set of equations becomes a set of non-linear equations. The values of rate constants have to be chosen as  $k_1 = 0.8, k_2 = 0.2, k_3 = k_4 = k_5 = 10, k_6 = 0.25$ . The simulation details are given in table 4.5. Actual solutions obtained via Mathematica and Interval analysis based solutions are given in table 4.6

Trial	1	2
Number of solution obtained	2	2
Tolerance	0.0001	0.000001
Time taken(s)	5.88	8.15

**Tab. 4.5:** Simulation Details of IN/GB algorithm for obtaining steady states

	IN/GB solution 1	IN/GB solution 2	Actual solution 1	Actual solution 2
[N]	0	0	0	0
[NO]	0	0	0	0
[CO]	0.999	0	1	0
[O]	0	0.999	0	1
[Z]	0	0	0	0

**Tab. 4.6:** Comparison of IN/GB solutions and actual solutions for steady states of CO oxidation with NO

From table 4.6 we can infer that the actual solutions obtained via Mathematica and the solutions obtained from Interval analysis are same. The steady state values indicate a clear case of catalyst poisoning taking place due to either carbon monoxide or oxygen.

### 4.3 Fischer Tropsch: Methanation Problem

In section 1.2.1 we introduced the Fischer-Tropsch process. The equations (1.2-1.14) are the steps involved in the reaction. One can study the kinetics of methane formation if the equations (1.9-1.11) are neglected. The neglected equations corresponds to the hydrocarbon chain growth. To obtain the list of all steady states involved in methane formation, we use the IN/GB method. The methanation process is studied using a set of both fictitious and real rate constants. The rate equations and rate constants for the steps involved are given in the appendix A.

#### 4.3.1 Fictitious rate constants :

The fictitious rate constants are given random values between 1 and 2. This was done because we wanted the rate constants to be of the same order of magnitude as the real rate constants vary several orders of magnitude. The steady state solutions are obtained by solving the rate equations simultaneously using the IN/GB method. The results obtained and simulation details are given below:

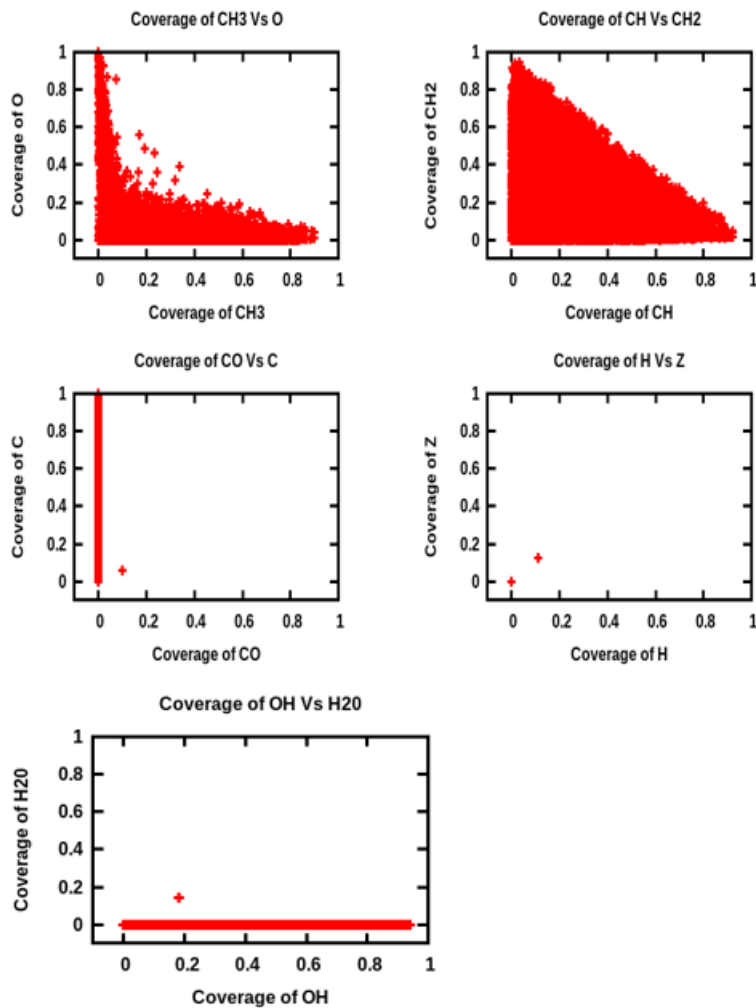
Tolerance(tol)	Number of solution boxes(N)	Time taken(s)
0.05	1820837	2457.3
0.1	68871	107.28
0.2	3098	5.2
0.3	211	0.54

**Tab. 4.7:** Simulation details for IN/GB algorithm for Fischer-Tropsch

From the above table we can infer that:

1. As the tolerance (width of solution box) decreases the number of solution boxes increases
2. As tolerance decreases the computational time increases drastically.

The computation become so expensive that we fail to get results for any tolerance value less than 0.05. Unless the tolerance is decreased further, we cannot conclusively say anything about the number of solutions and the exact value of the solutions. To go to lower tolerances using IN/GB method, the algorithm must be parallelized But here we take another approach, that is to combine the IN/GB method with classical newton to get a faster convergence to the solution. This is done by taking the midpoint of solution boxes obtained from 0.05 tolerance as a starting point for classical newton. The time taken to run this simulation was 4.3 hours. Below we plot the results obtained for the coverages:



**Fig. 4.1:** Solutions for methanation problem with fictitious rate constants.

In the above figure 'Z' denotes the coverage of vacant space( $\theta_*$ ) on the catalyst surface. From the above graph of coverage of Z, we can infer that the steady state value of  $\theta_*$  is either 0 or 0.1239 . The value of  $\theta_* = 0$  implies that there is catalyst poisoning taking place. During poisoning the entire surface of the catalyst is covered with one or more elements thereby making the catalyst ineffective. The chemical compounds/elements that cause poisoning are Carbon, CH, CH<sub>2</sub>, CH<sub>3</sub>, Oxygen and OH which can be seen from Fig 4.1.

The other value  $\theta_*$  takes is 0.1239. The corresponding coverages of other components are given in table 4.7. This solution is different from rest of the other solutions because this is a reactive steady state. A reactive steady state can be identified by having a non-zero value for  $\theta_*$ . This means that there is probability for reactions to take place, as there are vacant sites on the catalyst surface. In table 4.8 we compare the reactive steady state solution obtained by IN/GB method and another one using a kinetic ordinary differential equation (ODE) solver.

Chemical species	Coverage from interval analysis	Coverage from kinetic ODE solver
C	0.05822	0.112
CH	0.03631	0.007
CH <sub>2</sub>	0.01178	0.002
CH <sub>3</sub>	0.00883	0.001
CO	0.10093	0.146
H	0.10984	0.1077
H <sub>2</sub> O	0.14616	0.115
O	0.22357	0.1619
OH	0.18035	0.124
Z(Vacancy)	0.12395	0.121

**Tab. 4.8:** Comparison of solution from interval analysis method and kinetic ODE solver

From the table (4.8) we can clearly see that the interval analysis solution clearly differs from the solution obtained from an ODE solver. By substituting the values back in the equation we see that the solution obtained from ODE solver is not an exact solution but a very good approximation. This is the added advantage of interval analysis, not only it finds all the solution but finds them with mathematical certainty.

### 4.3.2 Real rate constants

The real rate constants and rate equations are given in Appendix A. Same as the case with the fictitious rate constants, the maximum tolerance we could go upto was 0.05 using IN/GB method. Any tolerance below that becomes computationally very

expensive to compute. Like in the previous case we combine the IN/GB method with classical newton to get a better convergence to the solution. The time taken to run this simulation was 3.8 hours. The coverages obtained at steady states are plotted in the graphs below:

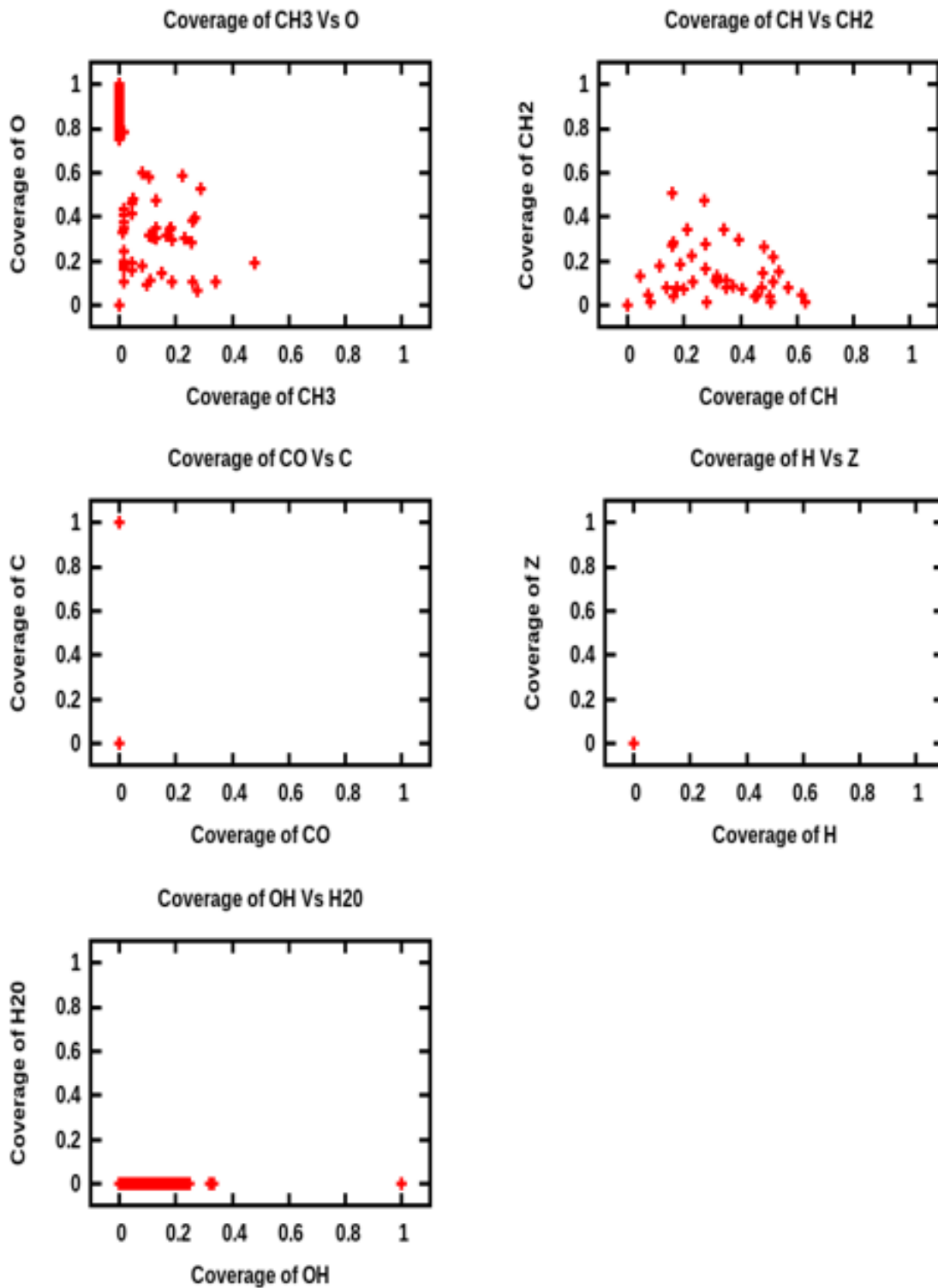


Fig. 4.2: Solution for methanation problem with real rate constants

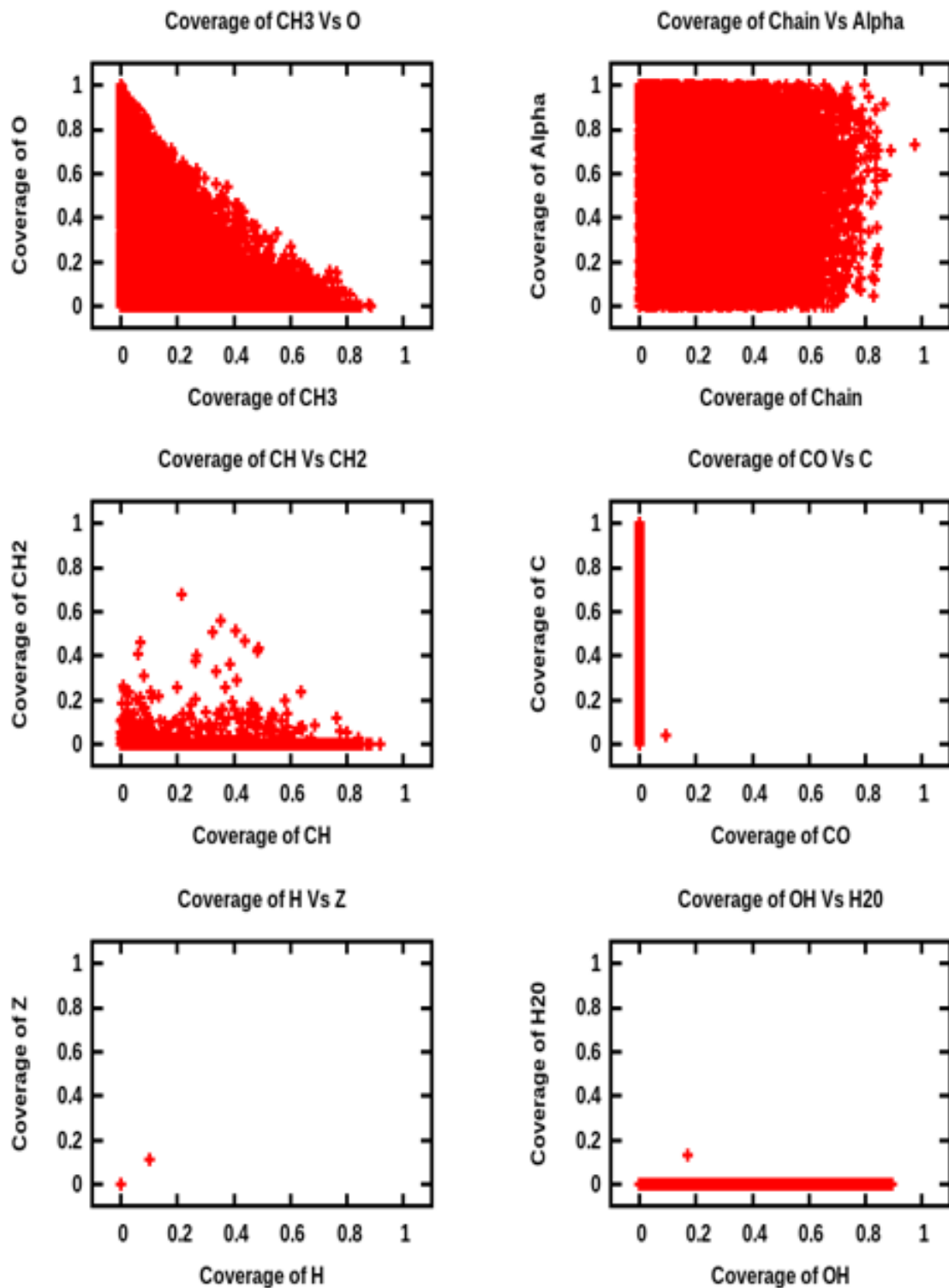
The following information can be inferred from the graphs. The coverage of  $\theta_*$  (denoted by Z in graphs) is always 0, which means that there is no reactive steady state. The coverages of  $\theta_{CO}$ ,  $\theta_H$ ,  $\theta_{H_2O}$  are also negligible. The coverage of CO, H<sub>2</sub>O are negligible due to high desorption rate. The hydrogen available would have been used for methane generation and formation of CH<sub>x</sub> species. Hence the coverage hydrogen is low. At the steady state species like Carbon, Oxygen and OH can completely cover the catalyst surface ( $\theta=1$ ).

## 4.4 Fischer Tropsch:Chain Growth Problem

In the methanation problem we neglected equation (1.9-1.11). These equations correspond to hydrocarbon chain growth. Now we include the chain growth phenomenon and solve for the steady states. If chain length is included the set of rate equations in Fischer Tropsch becomes infinite. By assuming a Flory-Schultz distribution<sup>29</sup> for the chain length the set of rate equations are decoupled. This results in a finite set of rate equations and a quadratic equation for the Flory-Schultz parameter  $\alpha$ . The full set of rate equations and rate constants are given in Appendix B.

### 4.4.1 Fictitious rate constants

Just like in the methanation problem we solve for the steady states using fictitious as well as real rate constants. The fictitious rate constants are given randomly between 0 and 2. We use the IN/GB combined with newton algorithm to solve the set of rate equations which comprises of 12 equations and 12 variables. The domain for all the variables are kept between 0 and 1. The time taken to run the simulation is 12.3 hours. Compared to methanation problem the time taken to run the simulation is quite high. This is because we have 12 variables to solve compared to the 10 variables in methanation. The results obtained are plotted below:



**Fig. 4.3:** Solutions for chain growth problem with fictitious rate constants.

From the graph of coverage of  $\theta_*$  (denoted by Z in graphs) we can infer that there exist a reactive steady state. All the other steady state values depict catalyst poisoning taking place, i.e., value of  $\theta_* = 0$ . The catalyst poisoning is caused by the coverages

of Carbon, CH, CH<sub>2</sub>, CH<sub>3</sub>, OH, Oxygen and hydrocarbon chain. The reactive steady state obtained is given below:

Chemical Species	coverage
C	0.043369
CH	0.056271
CH <sub>2</sub>	0.019927
CH <sub>3</sub>	0.006641
CO	0.093672
H	0.100341
H <sub>2</sub> O	0.135775
O	0.256633
OH	0.171109
Z(Vacancy)	0.115095
chain	0.00116703
$\alpha$	0.149459

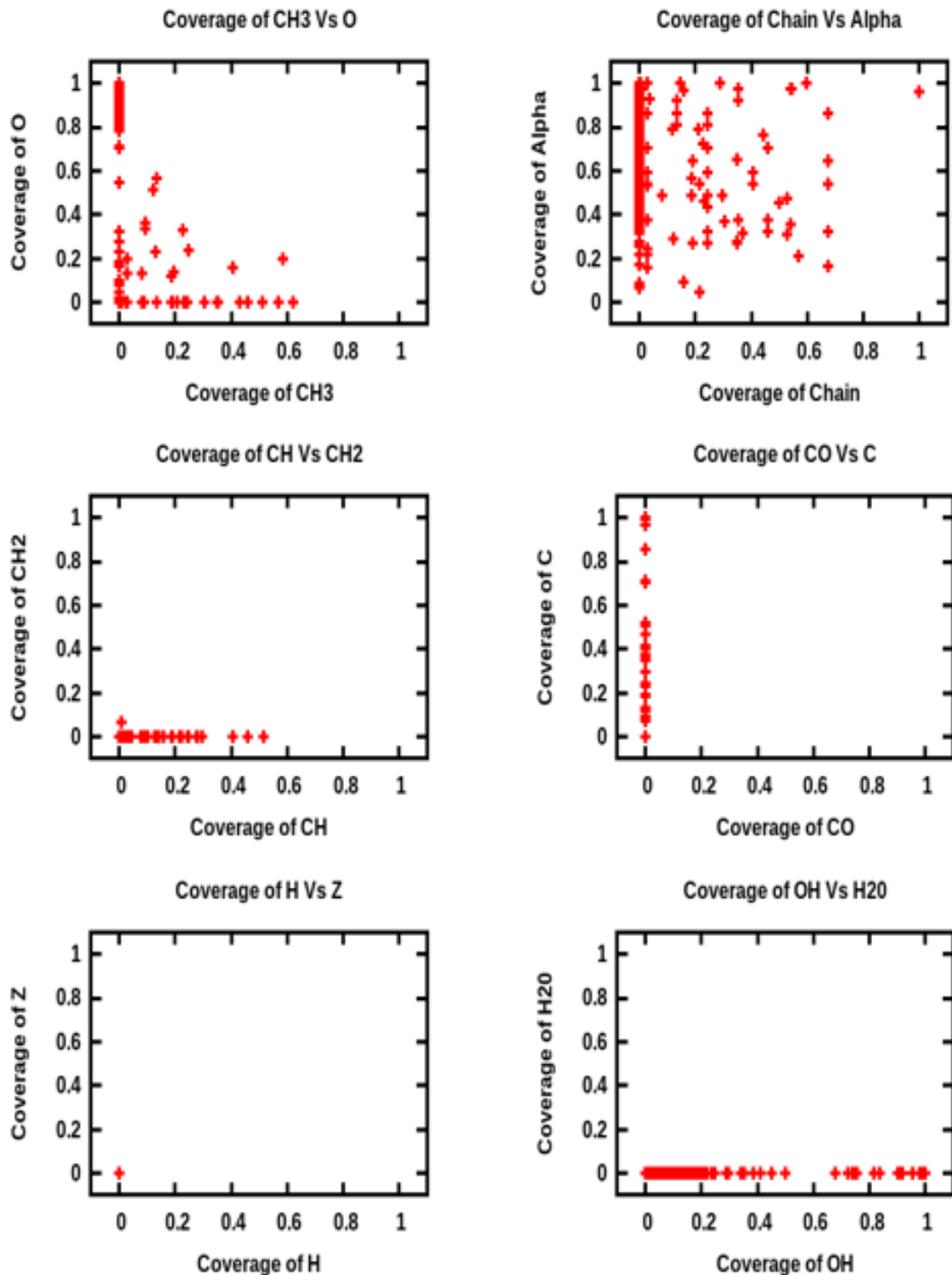
**Tab. 4.9:** Reactive steady state for Fischer Tropsch with fictitious rate constants

The value of Flory-Schultz parameter  $\alpha$  obtained for reactive steady state was 0.149459. Smaller value of  $\alpha$  means that the probability of chain growth is less. From the above table we can see that the coverage of hydrocarbon chain is the least. The coverage of oxygen is the highest followed by OH, H<sub>2</sub>O, H, CO, CH, CH<sub>2</sub>, CH<sub>3</sub>, chain.

#### 4.4.2 Real rate constants

The rate equations and rate constants for Fischer Tropsch process is given in Appendix B. The IN/GB combined with newton algorithm was used to solve the set of rate equations which comprises of 12 equations and 12 variables. The domain for all the variables are kept between 0 and 1. The time taken to run the simulation is 10.2 hours. The results obtained are plotted below:





**Fig. 4.4:** Solutions for chain growth problem with real rate constants.

From the graph of Z (vacant space) we can infer that there are no reactive steady states. The outcome of this reaction is always catalyst poisoning due to Carbon,  $\text{CH}_3$ , CH, chain, Oxygen and OH. Surprisingly the coverage of  $\text{CH}_2$  is low compared to  $\text{CH}_3$  and CH groups. For value of coverage of chain equal to 1, we get the  $\alpha$  value to be 1

as expected. But we cannot conclude that higher value for  $\alpha$  means higher coverage for chain. Most of the steady states have very high value for  $\alpha$ . The coverages for H<sub>2</sub>O is very low because its rate of desorption is very high. It is not very clear among the scientific community what actually causes catalyst deactivation in Fischer Tropsch process. Salib and co-workers published a review stating the importance of the role of carbon in deactivating the CO catalyst.<sup>30</sup> Huffman et al. showed that it is possible to oxidize cobalt particles under the conditions of Fischer Tropsch process.<sup>31</sup> Sadeqzadeh et al. advocates for deactivation done by both Carbon and Oxygen.<sup>32</sup> From the solutions of carbide model mechanism for Fischer Tropsch process using IN/GB combined with Newton method we can conclusively say that carbon, carbonaceous species and oxygen play a crucial role in deactivating the catalyst. Moreover the model also predicts deactivation due to deposition of OH species. The above results seem to favor carbide mechanism as an appropriate mechanism for Fischer Tropsch process.

## 5. CONCLUSION

We have described here a new method to figure out all solutions for a set of non-linear equations. The method is based on interval analysis, to be more precise an Interval Newton /Generalized bisection(IN/GB) method which provides all solutions with mathematical certainty. The IN/GB methods works really well for small chemical systems as it can be seen from the results of oxidation of CO with NO The method also works well for systems with a finite number of solutions with many variables. IN/GB method becomes computationally very expensive for ill-defined systems, i.e. , situations where the number of solutions are infinite. In such cases the interval newton contractor fails and the method heavily relies on bisection. This makes it computationally very expensive, as bisection algorithms have an exponential complexity. The rate equations corresponding to Fischer-Tropsch process belonged to this category. In such cases we can combine the IN/GB method with classical newton so as to get a faster convergence to solutions. Classical newton method is faster than the interval counterpart, but the interval counterpart is more reliable. The computational time for interval methods can be significantly decreased by parallelizing the algorithm, as interval methods are highly parallelization As a modeler there is an option choose between a fast method which may give incomplete answers or a slow method which guarantees accurate results. Further advancements in the software and hardware to implement interval based methods, along with the rapidly increasing computational power, would make interval analysis based methods an invaluable tool for computational chemistry.

# Appendices

## Appendix A

Full list of rate equations for methanation:

- CO:

$$\begin{aligned} \frac{d\theta_{CO}}{dt} = & W_{CO,ads} \theta_* - W_{CO,des} \theta_{CO} \\ & - W_{CO,diss} \theta_{CO} \theta_* + W_{CO,frm} \theta_C \theta_O \end{aligned} \quad (A.1)$$

$W_{CO,ads}$  and  $W_{CO,des}$  are rate constants of adsorption and desorption of CO from a site.  $W_{CO,diss}$  and  $W_{CO,frm}$  are rate constants of dissociation and formation of CO.

- Carbon:

$$\begin{aligned} \frac{d\theta_C}{dt} = & W_{CO,diss} \theta_{CO} \theta_* - W_{CO,frm} \theta_C \theta_O \\ & - W_{C,hydr} \theta_C \theta_H + W_{CH,dehydr} \theta_{CH} \theta_* \end{aligned} \quad (A.2)$$

$W_{C,hydr}$  is the rate constant of hydrogenation of a carbon atom, and  $W_{CH,dehydr}$  is the rate constant of dehydrogenation from CH group.

- CH:

$$\begin{aligned} \frac{d\theta_{CH}}{dt} = & W_{C,hydr} \theta_C \theta_H - W_{CH,dehydr} \theta_{CH} \theta_* \\ & - W_{CH,hydr} \theta_{CH} \theta_H + W_{CH_2,dehydr} \theta_{CH_2} \theta_* \end{aligned} \quad (A.3)$$

$W_{CH,hydr}$  is the rate constant of hydrogenation of CH and  $W_{CH_2,dehydr}$  is the rate constant of dehydrogenation of CH<sub>2</sub> group.

- CH<sub>2</sub>:

$$\begin{aligned} \frac{d\theta_{CH_2}}{dt} = & W_{CH,hydr} \theta_{CH} \theta_H - W_{CH_2,dehydr} \theta_{CH_2} \theta_* \\ & - W_{CH_2,hydr} \theta_{CH_2} \theta_H + W_{CH_3,dehydr} \theta_{CH_3} \theta_* \end{aligned} \quad (A.4)$$

$W_{\text{CH}_2,\text{hydr}}$  is the rate constant of hydrogenation of  $\text{CH}_2$  and  $W_{\text{CH}_3,\text{dehydr}}$  is the rate constant of dehydrogenation of  $\text{CH}_3$

- $\text{CH}_3$  :

$$\begin{aligned} \frac{d\theta_{\text{CH}_3}}{dt} = & W_{\text{CH}_2,\text{hydr}} \theta_{\text{CH}_2} \theta_{\text{H}} - W_{\text{CH}_3,\text{dehydr}} \theta_{\text{CH}_3} \theta_* \\ & - W_{\text{CH}_3,\text{hydr}} \theta_{\text{CH}_3} \theta_{\text{H}} \end{aligned} \quad (\text{A.5})$$

$W_{\text{CH}_3,\text{hydr}}$  is the rate constant of hydrogenation of  $\text{CH}_3$ , but note that there is no rate constant  $W_{\text{CH}_4,\text{dehydr}}$  because methane formed by hydrogenation immediately desorbs.

- Oxygen :

$$\begin{aligned} \frac{d\theta_{\text{O}}}{dt} = & W_{\text{CO},\text{diss}} \theta_{\text{CO}} \theta_* - W_{\text{CO},\text{frm}} \theta_{\text{O}} \theta_{\text{C}} \\ & - W_{\text{OH},\text{form}} \theta_{\text{O}} \theta_{\text{H}} + W_{\text{OH},\text{diss}} \theta_{\text{OH}} \theta_* \end{aligned} \quad (\text{A.6})$$

$W_{\text{OH},\text{form}}$  and  $W_{\text{OH},\text{diss}}$  are rate constants of formation and dissociation of OH.

- OH :

$$\begin{aligned} \frac{d\theta_{\text{OH}}}{dt} = & W_{\text{OH},\text{form}} \theta_{\text{O}} \theta_{\text{H}} - W_{\text{OH},\text{diss}} \theta_{\text{OH}} \theta_* \\ & - W_{\text{H}_2\text{O},\text{form}} \theta_{\text{OH}} \theta_{\text{H}} + W_{\text{H}_2\text{O},\text{diss}} \theta_{\text{H}_2\text{O}} \theta_* \end{aligned} \quad (\text{A.7})$$

$W_{\text{H}_2\text{O},\text{form}}$  and  $W_{\text{H}_2\text{O},\text{diss}}$  are rate constants of formation and dissociation of water.

- $\text{H}_2\text{O}$  :

$$\begin{aligned} \frac{d\theta_{\text{H}_2\text{O}}}{dt} = & W_{\text{H}_2\text{O},\text{form}} \theta_{\text{OH}} \theta_{\text{H}} - W_{\text{H}_2\text{O},\text{diss}} \theta_{\text{H}_2\text{O}} \theta_* \\ & + W_{\text{H}_2\text{O},\text{ads}} \theta_* - W_{\text{H}_2\text{O},\text{des}} \theta_{\text{H}_2\text{O}} \end{aligned} \quad (\text{A.8})$$

$W_{\text{H}_2\text{O},\text{ads}}$  and  $W_{\text{H}_2\text{O},\text{des}}$  are rate constants of adsorption and desorption of water.

- AtomicHydrogen ::

$$\begin{aligned} \frac{d\theta_{\text{H}}}{dt} = & W_{\text{H},\text{ads}} \theta_* \theta_* - W_{\text{H},\text{des}} \theta_{\text{H}} \theta_{\text{H}} \\ & - \sum_0^3 W_{\text{CH}_k,\text{hydr}} \theta_{\text{H}} \theta_{\text{CH}_k} + \sum_1^3 W_{\text{CH}_k,\text{dehydr}} \theta_* \theta_{\text{CH}_k} \\ & - W_{\text{OH},\text{form}} \theta_{\text{H}} \theta_{\text{O}} + W_{\text{OH},\text{diss}} \theta_* \theta_{\text{OH}} \\ & - W_{\text{H}_2\text{O},\text{form}} \theta_{\text{H}} \theta_{\text{OH}} + W_{\text{H}_2\text{O},\text{diss}} \theta_* \theta_{\text{H}_2\text{O}} \end{aligned} \quad (\text{A.9})$$

$W_{H,ads}$  and  $W_{H,des}$  are rate constants of adsorption and desorption of hydrogen.

These are the set of rate equations for the methanation problem. To obtain the steady state solutions we set the left hand side of all these equations equal to zero and solve using IN/GB method. An additional constraint is given as:

$$\theta_{CO} + \theta_C + \theta_{CH} + \theta_{CH_2} + \theta_{CH_3} + \theta_O + \theta_{OH} + \theta_H + \theta_* = 1 \quad (\text{A.10})$$

This ensures that the individual coverages of different groups on the catalyst surface doesn't exceed unity.

Rate constants for methanation:

Symbol	Real rate constant	Fictitious rate constant
$W_{CO,ads}$	194732	1.23
$W_{CO,des}$	$1.6128 \cdot 10^8$	1.5
$W_{CO,diss}$	$1.85931 \cdot 10^6$	1.75
$W_{CO,frm}$	$6.4532 \cdot 10^6$	1.6
$W_{C,hydr}$	$1.11941 \cdot 10^7$	1.434
$W_{CH,hydr}$	$1.80017 \cdot 10^8$	1
$W_{CH_2,hydr}$	22210.6	1.95
$W_{CH_3,hydr}$	42349.9	1.1
$W_{CH,dehydr}$	$1.08346 \cdot 10^8$	1.8
$W_{CH_2,dehydr}$	$6.23561 \cdot 10^6$	2
$W_{CH_3,dehydr}$	80341	1.33
$W_{OH,form}$	$2.07595 \cdot 10^7$	1.5
$W_{OH,diss}$	$3.34319 \cdot 10^9$	1.6
$W_{H_2O,form}$	0	1.7
$W_{H_2O,diss}$	$1.80298 \cdot 10^{16}$	1.8
$W_{H_2O,ads}$	487.709	1.43
$W_{H_2O,des}$	$5.22427 \cdot 10^{11}$	1.22
$W_{H,ads}$	$5.59524 \cdot 10^8$	1.54
$W_{H,des}$	668002	1.43

**Tab. A.1:** Methanation rate constants

## Appendix B

If we include chain growth in the rate equations it forms an infinite set. So we need a method to decouple the equations. Below we describe a method to do so:

$$\theta_{(\text{CH}_2)_k\text{CH}_3} = \alpha \theta_{(\text{CH}_2)_{k-1}\text{CH}_3} \quad (\text{B.1})$$

for  $k \geq 2$ . Using this above rule we define:

$$\theta_{\text{chain}} = \sum_1^{\infty} \theta_{(\text{CH}_2)_k\text{CH}_3} \quad (\text{B.2})$$

$\theta_{\text{chain}}$  refers to the coverage of chain on catalyst surface. The rate equations for this coverage is given by:

$$\begin{aligned} \frac{d\theta_{\text{chain}}}{dt} = & W_{\text{grow}} \theta_{\text{CH}_3} \theta_{\text{CH}_2} - [1 - \alpha] W_{\text{shrink}} \theta_{\text{chain}} \theta_* \\ & + W_{\text{term}} \theta_{\text{chain}} \theta_{\text{H}} \end{aligned} \quad (\text{B.3})$$

Since a new coverage  $\theta_{\text{chain}}$  is introduced it affects some of the other rate constants. Equation (A.4) becomes

$$\begin{aligned} \frac{d\theta_{\text{CH}_2}}{dt} = & W_{\text{CH,hydr}} \theta_{\text{CH}} \theta_{\text{H}} - W_{\text{CH}_2,\text{dehydr}} \theta_{\text{CH}_2} \theta_* \\ & - W_{\text{CH}_2,\text{hydr}} \theta_{\text{CH}_2} \theta_{\text{H}} + W_{\text{CH}_3,\text{dehydr}} \theta_{\text{CH}_3} \theta_* \\ & - W_{\text{grow}} \theta_{\text{CH}_3} \theta_{\text{CH}_2} - W_{\text{grow}} \theta_{\text{CH}_2} \theta_{\text{chain}} \\ & + \alpha W_{\text{shrink}} \theta_* \theta_{\text{chain}} + [1 - \alpha] W_{\text{shrink}} \theta_{\text{chain}} \theta_* \end{aligned} \quad (\text{B.4})$$

equation (A.5) becomes

$$\begin{aligned} \frac{d\theta_{\text{CH}_3}}{dt} = & W_{\text{CH}_2,\text{hydr}} \theta_{\text{CH}_2} \theta_{\text{H}} - W_{\text{CH}_3,\text{dehydr}} \theta_{\text{CH}_3} \theta_* \\ & - W_{\text{CH}_3,\text{hydr}} \theta_{\text{CH}_3} \theta_{\text{H}} \\ & - W_{\text{grow}} \theta_{\text{CH}_3} \theta_{\text{CH}_2} + [1 - \alpha] W_{\text{shrink}} \theta_{\text{chain}} \theta_* \end{aligned} \quad (\text{B.5})$$



equation (A.9) becomes

$$\begin{aligned}
 \frac{d\theta_H}{dt} = & W_{H,ads} \theta_* \theta_* - W_{H,des} \theta_H \theta_H \\
 & - \sum_0^3 W_{CH_k,hydr} \theta_H \theta_{CH_k} + \sum_1^3 W_{CH_k,dehydr} \theta_* \theta_{CH_k} \\
 & - W_{OH,form} \theta_H \theta_O + W_{OH,diss} \theta_* \theta_{OH} \\
 & - W_{H_2O,form} \theta_H \theta_{OH} + W_{H_2O,diss} \theta_* \theta_{H_2O} - W_{term} \theta_H \theta_{chain}
 \end{aligned} \tag{B.6}$$

the constraint becomes

$$\theta_{CO} + \theta_C + \theta_{CH} + \theta_{CH_2} + \theta_{CH_3} + \theta_O + \theta_{OH} + \theta_H + \theta_* + \theta_{chain} = 1 \tag{B.7}$$

The additional rate constants for chain growth are given below:

Symbol	Real rate constant	Factual rate constant
$W_{grow}$	11393573.55	1.78
$W_{shrink}$	392940.4467	0.75
$W_{termination}$	6746.548178	1.28

**Tab. B.1:** Rate constants for chain growth

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