Kinetic Modeling of Low Temperature Water-Gas Shift Reaction using gPROMS

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Abstract:

The kinetics of water gas shift reaction was studied over commercial CuO/ZnO/Al2O3 in an integral fixed bed reactor. The experimental data were collected from literature. The CO conversion data in the temperature ranging from 180 ºC to 300 ºC were used for kinetic modeling. Surface redox and the Langmuir-Hinshelwood models as well as two empirical rate equation models, namely Moe and power law, were proposed to fit the experimental data. Using non-linear programming parameter estimation in gPROMS software, rate expressions were fitted to experimental data. The judgment among models was based on the statistical results. The surface redox mechanism was found to be the best model with apparent activation energy of 11.87 (kJ/mol). Also fitting of empirical models to experimental data showed that power law rate equation has a good fit in partial reaction order of 2.57, 2.02, -0.59 and -3.4 for CO, H2O, CO2 and H2 respectively with activation energy of 39.48 (kJ/mol). Using surface redox kinetic model as well as power law kinetic rate equation, the reactor was simulated to validate the results by comparison of experimental and predicted CO outlet conversion rates. The simulation results validated the model predictions of power law and surface redox models.

Keyword: WGSR, Kinetic Parameter Estimation, Cu-based Catalyst, gPROMS

1. Introduction

Water gas shift (WGS) reaction refers to an industrially important reaction in which carbon monoxide reacts with steam to produce hydrogen and carbon dioxide [1]:

\[ CO + H_2O \xrightarrow{\text{Catalysis}} CO_2 + H_2; \Delta H = -41.1 \text{ kJ mole}^{-1} \]  

(1)

It is a catalytically reversible, exothermic chemical reaction [2]. The water-gas shift reaction is a step used in production of ammonia, hydrogen, methanol and hydrocarbons. It is also utilized in petroleum refineries for several operations, namely hydrotreating and hydrocracking of petroleum fractions as well as recently in fuel cell applications, such as power generation and transportation. Considering the aforementioned industrial significance, the kinetic modeling of this reaction has been the subject of many investigations [3-5].

The WGS reaction is moderately exothermic (equation 1) and conversions are equilibrium-controlled. The equilibrium constant decreases with increasing temperature. Therefore, the reaction is thermodynamically favored at low temperatures. On the other hand, the reaction rate constant is increases with increasing temperature concluding that the reaction is kinetically favored at high temperatures. Accordingly, high conversions are favored at low temperatures and are not affected, significantly, by changes in total pressure[6, 7].
The exothermic nature of the WGS reaction leads the industrial shift reactors to be generally designed adiabatic, in which the temperature is increasing along the catalyst bed. These reactors are usually arranged in two stages if high purity hydrogen is needed. The first stage is run at high temperature called high temperature shift reaction (HTS). It is followed by cooling of the gases, steam is then added to the second stage and the residual CO is shifted over a low temperature shift (LTS) reaction [2, 8].

There are number of materials capable of catalyzing the water-gas shift reaction, which are divided in two main classes – that is – the iron-based catalysts and the copper-based catalysts. The iron-based catalysts, operating from about 320 to 450 °C, are the so-called high temperature shift (HTS) catalysts. There are quite a few of other catalysts investigated for HTS reaction, such as gold-based catalysts, platinum-based catalysts and ruthenium-based catalysts. Copper-based shift catalysts, having now acquired a wide acceptance in industries, are a more recent development. These are the so-called low temperature shift (LTS) catalysts approximately operated in the temperature ranges of 200 to 250 °C. Other catalysts such as nickel-based catalysts and iridium-based catalysts were investigated for LTS reaction. A further material receiving a considerable attention as an industrial water-gas shift catalyst is sulfided cobalt oxide-molybdenum oxide on alumina. It is reported that the activities of this catalyst at both high and low temperature ranges is pleasant [2, 9, 10].

Despite studying Cu-based catalysts for years as industrial LTS catalysts, the reaction mechanism and associated kinetic equations are still a heated controversy. In order to illuminate the behavior of the reaction over common industrial catalysts, many researchers have investigated the reaction mechanism and developed various models. The following four specific mechanisms were proposed for the WGS reaction: (1) the surface redox mechanism [11-18], (2) the associative mechanism[8, 19, 20], (3) the formate mechanism [11, 13, 21-23] and (4) more recently, the carbonate mechanism [17, 18, 24-27].

To shed more light on this controversial issue, this paper aims to investigate the kinetic modeling of Cu-based catalyst in low temperature water gas shift reaction using gPROMS. Accordingly, two mechanistic models which have caught more attentions are proposed. In addition to mechanistic models, two practical empirical models are developed. Different models are implemented in gPROMS and their parameters are estimated using maximum likelihood estimation algorithm. Then, in order to validate parameter estimation statistical results, the experimental data are compared to model prediction result of ideal plug flow fixed bed reactor simulation. Backward finite difference approach is used for simulation tasks. Unlike the conventional software, gPROMS package - an equation-oriented modeling system - includes several features for parameter estimation and simulation tasks.

2. Model Development

The easiest method of illustrating the reaction in order for finding out the reaction rate and designing the reactors is provided by the kinetic models. Fundamentally, micro-kinetic approach and the empirical method are the two classes of kinetic expressions. The knowledge of elementary steps for the reaction and its energetics are the basics of the micro-kinetic method which can be applied for discovering the chemistry of the reaction in detail and estimating the surface coverage, reaction order and activation enthalpy. Furthermore, in spite of its computational intensity, the precise pathway and prediction of the reaction can be given by this method. Conversely, the experimental results are the basics of the empirical models which are not only commonly expressed in the Arrhenius model, but they can lay the ground for a comfortable computational method of predicting the reaction rate as well. In this study, the WGS reaction is discussed according to micro-kinetic approach as well as the empirical one [3].

Studying the reaction mechanisms of the WGS reaction is still on progress after more than one century of investigation. Associative and regenerative mechanisms are two main reaction pathways that have been proposed. The associative mechanism of the Langmuir-Hinshelwood (LH) type, proposed by Armstrong and Hilditch [28] in 1920 using a cop-per chromite based catalyst, consists of the adsorption of CO and H2O on a catalyst surface to produce an unspecified intermediate structure that subsequently decomposes into the reaction products. The regenerative mechanism of the Eley-Rideal type, also known as the surface redox (SR) mechanism, was originally described by Armstrong and Hilditch. The surface redox mechanism involves a catalytic cycle in which surface is oxidized by H2O and then reduced by CO to produce H2 and CO2, respectively [8].

There are many kinetic rate expressions published since the use of WGS reaction in the ammonia process. Literature results shows that some authors [29-32] proposed Langmuir-Hinshelwood model as appropriate mechanistic model while some others [13, 14, 33] proposed surface redox model as appropriate model for low temperature water gas shift reaction over commercial CuO/ZnO/Al2O3. Despite this disunity, the proposed mechanisms in this work is on the basis of Ayastuy et al.’s studies [30] who examined different mechanistic models concluding various rate equations for the low temperature WGS reaction over commercial CuO/ZnO/Al2O3 catalyst. In this work, two rival rate equations which have shown good fit between the experimental results and predictions of many studies are selected, namely Langmuir-Hinshelwood (LH) mechanism and surface redox (SR) mechanism.

The pathway of Langmuir-Hinshelwood (LH) mechanism is described via the following equations [30]:

\[
CO + S \leftrightarrow CO - S \quad (2)
\]

\[
H_2O + S \leftrightarrow H_2O - S \quad (3)
\]
The pathway of surface redox (SR) mechanism is described via the following equations [30]:

\[ \text{H}_2\text{O} + \text{S} \leftrightarrow \text{H}_2 + \text{O} - \text{S} \quad (8) \]

\[ \text{CO} + \text{O} - \text{S} \leftrightarrow \text{CO}_2 + \text{S} \quad (9) \]

The subsequent rate equation is then derived assuming the oxidation of surface, i.e. equation 8, to be the rate-determining step:

\[ (-r_{\text{CO}}) = -k \left( \frac{p_{\text{H}_2\text{O}}}{K_p} \right)^{\frac{p_{\text{CO}}}{p_{\text{H}_2\text{O}}}^{\frac{p_{\text{CO}_2}p_{\text{H}_2}}{p_{\text{CO}}}}} \quad (10) \]

where \((-r_{\text{CO}})\) is the rate of reaction, \(k\) is the reaction rate constant of the WGS reaction, \(p_i\) is the partial pressure of component \(i\), \(K_p\) is the equilibrium constant and \(K_i\) is the equilibrium adsorption constant of component \(i\).

2.1. Analysis of the Models

Using the differential method as equation 14, the experimental reaction rates were obtained by calculating the CO conversion gradients versus \(W_{\text{cat}}/F_{\text{CO}}^{\text{feed}}\) at all points [6, 36], then fitted to the aforementioned kinetic rate expression.

\[ (-r_{\text{CO}}) = \frac{\delta \chi_{\text{CO}}}{\delta (W_{\text{cat}}/F_{\text{CO}}^{\text{feed}})} \quad (14) \]
The Arrhenius equation was applied in all rate expression to describe the variation of the rate constant with temperature:

\[ k = k_0 \exp\left(-\frac{E_a}{RT}\right) \]  \hspace{1cm} (15)

The Van’t Hoff expression was also used to describe the equilibrium constants of the adsorbed components as a function of temperature as following equation:

\[ K_i = K_{i,0} \exp\left(-\frac{\Delta H_i}{RT}\right) \]  \hspace{1cm} (16)

where \( K_{i,0} \) stands for the pre-exponential equilibrium adsorption constant of component \( i \).

The above-mentioned rate expressions were examined to find the most convenient fitness to the kinetic data. On the basis of maximum likelihood estimation algorithm [37, 38], MLE, the kinetic parameter estimation was executed using gPROMS software with MAXLKHD standard solver [39]. During solving a MLE problem, gPROMS tries to specify the uncertain physical models values as well as variance model parameters values, \( \theta \), which maximize the likelihood that the mathematical model will forecast the measurement values obtained from the experiments. Supposing independent, normally distributed measurement errors, \( \epsilon_{ijk} \), having means of zero as well as standard deviations, \( \sigma_{ijk} \), the optimum parameters were obtained by minimizing the subsequent objective function:

\[ \varnothing = \frac{N}{2} \ln(2\pi) + \frac{1}{2} \min_{\theta} \left\{ \sum_{i=1}^{NE} \sum_{j=1}^{NV_i} \sum_{k=1}^{NM_{ij}} \ln\left( \sigma_{ijk}^2 + \frac{(\tilde{z}_{ijk} - z_{ijk})^2}{\sigma_{ijk}^2} \right) \right\} \]  \hspace{1cm} (17)

where, \( N \) represents number of every measured variable over the experiments, \( \theta \) represents model parameters set going to be estimated, \( NE \) represents number of performed experiments, \( NV_i \) represents number of measured variables within the \( i^{th} \) experiment, \( NM_{ij} \) represents number of the \( j^{th} \) variable measurements within the \( i^{th} \) experiment, \( \sigma_{ijk}^2 \) represents the \( k^{th} \) measurement variance of variable \( j \) within experiment \( i \), \( \tilde{z}_{ijk} \) represents \( k^{th} \) measured value of variable \( j \) within experiment \( i \) and \( z_{ijk} \) represents \( k^{th} \) predicted value of variable \( j \) within experiment \( i \). The discrimination among the proposed models is then conducted based on (1) the suitability of fitting according to the weighted residuals and \( \chi^2 \) values so that a weighted residual less than \( \chi^2 \) value is considered good fit, (2) applying F-test in order that the highest calculated F-value corresponding to the model that best fits the experimental data and (3) \( \chi^2 \) values between experimental and predicted CO conversions. If any variance model is not chosen for the sensor, the aforementioned objective function, i.e. equation 17, will be turned to a recursive least squares parameter estimation [40].

All parameter estimation and simulations tasks where performed on an Intel® Core™ i7 CPU (Q740 - 1.73, 1.73) notebook with 4.00GB of RAM memory.

### 2.2. Modeling Procedure

The step by step procedure below shows how parameter estimation is performed in gPROMS to determine reaction kinetic constants [39]:

1. Construct a model of the process for which the measurements are being taken.
2. Define the parameters to be estimated and the variance model to be used for each measuring instrument.
3. Enter the experimental data sets.
4. Execute the estimation run.
5. Check the results in the detailed statistical analysis.

### 2.3. Data Collection

Kinetic data used in this study was gathered from Mendes et al. study. In their study an isothermally fixed bed reactor was used in order for kinetic study of the WGS reaction over a commercial Cu-based catalyst. Their experiments are designed in order that neither intra-particle resistances nor extra-particle resistances existed in the reactor. Experimental details are given in Mendes et al.’s publications [32, 41].
3. Results and Discussion

3.1. Reaction Kinetic Parameter Estimation

Considering the conversion data obtained from the literature, a total of 53 points were collected to yield experimental reaction rates data for water gas shift reaction. These data were reported for temperatures ranging 180-300 °C. The rate expressions were derived for each of the proposed reaction mechanism. The estimation of the kinetic model parameters from the sets of experimental data was executed in gPROMS. The temperature dependence of rate constants and adsorption coefficients were also considered. The statistical results of parameter estimation are presented in Table 1.

<table>
<thead>
<tr>
<th>Model</th>
<th>Objective Function</th>
<th>Weighted Residual</th>
<th>$\chi^2$ Value (95%)</th>
<th>No. of Parameter</th>
<th>F-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moe</td>
<td>79760.8</td>
<td>160144</td>
<td>67.5048</td>
<td>2</td>
<td>3.18</td>
</tr>
<tr>
<td>PL</td>
<td>-185.8</td>
<td>52.0746</td>
<td>61.6562</td>
<td>6</td>
<td>2.22</td>
</tr>
<tr>
<td>SR</td>
<td>-200</td>
<td>43.7768</td>
<td>65.1708</td>
<td>4</td>
<td>2.566</td>
</tr>
<tr>
<td>LH</td>
<td>-179.063</td>
<td>55.0109</td>
<td>61.6562</td>
<td>10</td>
<td>2.22</td>
</tr>
</tbody>
</table>

Furthermore, optimal parameter estimation results of different kinetic models, obtained with 95% confidence level, was investigated by using gPROMS and represented in Table 2. Moreover, comparisons of the experimental and predicted CO conversions for different models are presented in Figure 1. On the basis of weighted residuals and $\chi^2$ values it is concluded that the Moe model may be inadequate representation of physical system. Among rival models, the one with the highest F-value would be considered the best without guarantee; however, it would be statistically adequate. If two models have near F-value, due to similarity, the model with fewer parameters is better. Therefore, on the basis of F-value as well as $R^2$ values, it may be concluded that the surface redox model represents physical system of WGS re-action better than the other models. Comparison of results of this work and that of literature shows that although in this work the results of Langmuir-Hinshelwood and surface redox models are indistinguishable, on the basis of statistical results, the surface redox model shows the best fit to experimental data rather than the Langmuir-Hinshelwood model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SR Model</th>
<th>LH Model</th>
<th>Moe Model</th>
<th>PL Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation Energy ($\frac{1}{\text{mol}}$)</td>
<td>1.186794E+04</td>
<td>1.007200E+04</td>
<td>3.995844E+04</td>
<td>3.938268E+04</td>
</tr>
<tr>
<td>Arrhenius Constant ($\frac{\text{mol}}{\text{cat.h.Pa2}}$)</td>
<td>9.649790E-04</td>
<td>3.058140E-03</td>
<td>4.329751E-06</td>
<td>4.887043E+00</td>
</tr>
<tr>
<td>$\Delta H_{CO}$</td>
<td>-2.200790E+04</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\Delta H_{H2O}$</td>
<td>-</td>
<td>-6.941480E+03</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\Delta H_{CO2}$</td>
<td>-5.203140E+03</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\Delta H_{H2}$</td>
<td>-8.412750E+04</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$K_{CO}$</td>
<td>1.000000E-15</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$K_{H2O}$</td>
<td>3.595190E-03</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$K_{CO2}$</td>
<td>1.235247E-04</td>
<td>1.000000E-06</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$K_{H2}$</td>
<td>2.739000E-12</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
A brief compilation of power law model results in the literature and that of this work is shown in Table 3. The differences might be due to the reason that the majority of reported data in the literature were acquired at different range of temperatures and different catalyst formulation. For the similar operating conditions of this work and the work performed by Mendes et al., still some differences in the result exist. Even though, the results are comparable, the differences might be due to differences in algorithm of parameter estimation.

**Table 3:** Literature values for the power law kinetic model of WGS reaction over commercial CuO/ZnO/Al₂O₃

<table>
<thead>
<tr>
<th>Reference</th>
<th>Parameter Estimation Algorithm</th>
<th>Eₐ (kJ/mol)</th>
<th>Orders of Reaction</th>
<th>Pressure and Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ovesen et al. (1996)</td>
<td>TPD spectra</td>
<td>86.5</td>
<td>1</td>
<td>5 bar, 180-220 ºC</td>
</tr>
<tr>
<td></td>
<td></td>
<td>78.2</td>
<td>1</td>
<td>20 bar, 180-220 ºC</td>
</tr>
<tr>
<td>Koryabkina et al. (2003)</td>
<td>iterative fitting correction</td>
<td>79</td>
<td>0.8</td>
<td>1 atm, 190 ºC</td>
</tr>
<tr>
<td>Ayastuy et al. (2005)</td>
<td>LMNR</td>
<td>79.7</td>
<td>0.48</td>
<td>3 bar, 180-217 ºC</td>
</tr>
<tr>
<td>Mendes et al. (2010)</td>
<td>GA</td>
<td>35.0</td>
<td>0.85</td>
<td>1 bar, 180-300 ºC</td>
</tr>
<tr>
<td>this work</td>
<td>MLE</td>
<td>39.48</td>
<td>2.57</td>
<td>1 bar, 180-300 ºC</td>
</tr>
</tbody>
</table>
Figure 1. Parity plots of experimental and predicted CO conversions for: (a) Moe model, (b) power law model, (c) surface redox model, (d) Langmuir-Hinshelwood model

3.2. Kinetic Models Validation

The surface redox model and empirical power law model were used to simulate the performance of fixed bed reactor in order to validate the kinetic models results. The validation is based on steady state mass conversion law as well as corresponding boundary conditions. The assumptions of ideal gas behavior, isothermally operated fixed bed reactor without axial and radial dispersion, negligible external and internal resistances for mass and heat transfer as well as pressure drop athwart the bed and reaction occurs on the catalyst surface are considered in this model validation. The mass balance equation then is given by:

$$\frac{d}{dx}(u_p) - \rho_b RT(r_i v_i) = 0$$  \hspace{1cm} (18)

The corresponding boundary condition is:

$$p_i(0) = R y^0_i$$  \hspace{1cm} (19)

where $P_i$ is the partial pressure of component $i$, $P_t$ is the total pressure of gas mixture, $u$ is the superficial velocity of gas mixture, $\rho_b$ is the bulk density of the solid catalyst, $R$ is the universal gas constant, $T$ is the temperature, $y^0_i$ is the molar fraction of component $i$ in the feed, $r_i$ stands for the reaction rate of component $i$, $v_i$ is the stoichiometric coefficient of component $i$ and $i$ refers to the $i^{th}$ component. The simulation of reactor model together with the corresponding boundary condition, i.e. equations 18 and 19,
is numerically implemented by gPROMS software with DASOLV standard solver which is based on backward differentiation formula (PSE 2012). The simulation and experimental results have been shown by Figure 2. It can be concluded from Figure 2 that the fixed bed reactor model shows pretty well fit to the experimental outlet CO conversion rate values. Also, as represented by Figure 2, CO conversion rates predicted using SR model shows better fit to the experimentally measured CO conversion rates compared to the power law model.

![Figure 2](image.jpg)

**Figure 2.** Experimental versus predicted CO conversion rates using: (a) power low model (b) surface redox model

### 4. Conclusions

In this study kinetics of low temperature WGS reaction over a Copper based catalyst was investigated. The kinetic parameters for empirical models including Moe and Power Low rate equations as well as mechanistic models consisting of surface redox and Langmuir-Hinshelwood mechanisms were determined using gPROMS software. Carbon monoxide kinetic rate and its conversion were predicted by means of estimated parameters. On the basis of statistical results, it can be concluded that surface redox mechanism model showed the best fit to experimental data among all mechanistic and empirical models. Furthermore, parameters of power law empirical model were significantly obtained. The simulation of fixed bed reactor validated the model predictions of power law and surface redox models.

### Acknowledgements

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### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>a, b, c, d</td>
<td>Apparent Reaction Orders for CO, H₂O, CO₂ and H₂ Respectively</td>
</tr>
<tr>
<td>Eₐ</td>
<td>Activation Energy for The WGS Reaction [J·mol⁻¹]</td>
</tr>
<tr>
<td>i</td>
<td>Species Involved in The Reaction (CO, H₂O, CO₂, or H₂)</td>
</tr>
<tr>
<td>k</td>
<td>Rate Constant for The WGS Reaction [mol·g₉cat⁻¹·h⁻¹·Pa⁻n]</td>
</tr>
<tr>
<td>k₀</td>
<td>Pre-Exponential Factor of The Rate Constant [mol·g₉cat⁻¹·h⁻¹·Pa⁻n]</td>
</tr>
<tr>
<td>Kᵢ</td>
<td>Adsorption Equilibrium Constant of Species i [Pa⁻¹ or Pa⁻¹.5]</td>
</tr>
<tr>
<td>Kᵢ₀</td>
<td>Pre-Exponential Adsorption Equilibrium Constant of Species i [Pa⁻¹ or Pa⁻¹.5]</td>
</tr>
<tr>
<td>Kₚ</td>
<td>Equilibrium Constant for The WGS Reaction</td>
</tr>
<tr>
<td>Pᵢ</td>
<td>Partial Pressure of Component i [Pa or bar]</td>
</tr>
<tr>
<td>R</td>
<td>Total Pressure [Pa or bar]</td>
</tr>
<tr>
<td>R</td>
<td>Ideal Gas Constant [J·mol⁻¹·K⁻¹]</td>
</tr>
<tr>
<td>rᵢ</td>
<td>Rate of Consumption or Formation of Species i [mol·g₉cat⁻¹·h⁻¹]</td>
</tr>
<tr>
<td>S</td>
<td>Catalyst Active Site</td>
</tr>
<tr>
<td>T</td>
<td>Absolute Temperature [K]</td>
</tr>
<tr>
<td>uₛ</td>
<td>Superficial Velocity [m·s⁻¹]</td>
</tr>
</tbody>
</table>
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\[ \frac{W_{\text{cat}}/P_{\text{feed}}^{\text{feed}}}{x} : \text{Space Time [g}_{\text{cat}}\cdot\text{h-mol}^{-1}] \]

\[ X_i : \text{Axial Coordinate of The Reactor [m]} \]

\[ Y_{i0} : \text{Conversion of Component i} \]

\[ y_i^0 : \text{Feed Molar Fraction of Component} \]

**Greek letter**

\[ \beta : \text{Term for The Backward Reaction or Approach to Equilibrium} \]

\[ \Delta H_i : \text{Heat of Adsorption of Component i [J-mol}^{-1}] \]

\[ \Delta H_i^0 : \text{Standard Heat of Reaction [J-mol}^{-1}] \]

\[ v_i : \text{Stoichiometric Coefficient of Species i} \]

\[ \rho_b : \text{Catalyst Bulk Density [kg-m}^{-3}] \]

**Statistical Acronyms**

\[ \theta : \text{Parameter Estimation Objective Function} \]

\[ \chi^2 : \text{Statistical Chi Squared} \]

\[ \varepsilon : \text{Difference Between The Experimental and The Model Predicted Values} \]

\[ z_i : \text{Model Predicted Value in Parameter Estimation} \]

\[ \bar{z}_i : \text{The Experimental Values} \]

\[ \sigma_i : \text{Standard Deviation} \]

\[ N : \text{Number of Experimental Data Points} \]

\[ NE : \text{number of experiments performed} \]

\[ NM_{ij} : \text{number of measurements of the j}^{\text{th}} \text{ variable in the i}^{\text{th}} \text{ experiment} \]

\[ NV_i : \text{number of variables measured in the i}^{\text{th}} \text{ experiment} \]

\[ R^2 : \text{Statistical R Squared} \]

**Abbreviations**

\[ \text{GA} : \text{Genetic Algorithm} \]

\[ \text{HTS} : \text{High Temperature Shift} \]

\[ \text{LTS} : \text{Low Temperature Shift} \]

\[ \text{LH} : \text{Langmuir-Hinshelwood} \]

\[ \text{MLE} : \text{Maximum Likelihood Estimation} \]

\[ \text{PL} : \text{Power Law} \]

\[ \text{SR} : \text{Surface Regeneration or Surface Redox} \]

\[ \text{WGS} : \text{Water-Gas Shift} \]

\[ \text{WR} : \text{Weighted Residuals} \]

5. References:


