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Bayesian characterization and forward propagation of the uncertainty in thermodynamic models for redox active materials

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Abstract

Demonstrating the thermodynamic efficiency of hydrogen conversion processes using various materials is a critical step in developing new technologies for storing concentrated solar energy, and is largely accomplished by using a thermodynamic model derived from experimental data. A main goal of this project is to calculate the uncertainty of the thermodynamic efficiency by calculating the uncertainty of the components that feed into the efficiency. Many different models and data sets were used to test the workflow. First, the models were fit to the data using a Bayesian Inference and a method called Markov Chain Monte Carlo (MCMC), which found the maximum a priori parameters, and a posterior probability distribution of the parameters. Next, the different models were compared to each other using model evidence values. It was found that for cleaner data sets, overfitting had not yet been reached, and the most complicated model was ideal, but on the noisier data sets, the less complex models were favored because the more complicated models resulted in overfitting. Next, forward propagation was used to calculate the enthalpy change and its associated uncertainty. A few variations on the models were tried, such as fitting in a different variable, producing negligible or negative effects on the fits of the models. Thus, the original models were used. A sensitivity analysis was performed, and used to calculate the model error. On the cleaner data sets, there was very minimal experimental noise, and thus, all resulting error was from the model. With consideration of the model error, the models fit the data very well, and the simpler model had a high model error, as expected. All these components will then be used to calculate the thermodynamic efficiency of the different materials.

I. INTRODUCTION

Finding a suitable functional redox material is a critical challenge to achieving scalable, economically viable technologies for storing concentrated solar energy in the form of a defected oxide. Demonstrating effectiveness for thermal storage or solar fuel is largely accomplished by using a thermodynamic model derived from experimental data. A main goal of this project is to be able to calculate the uncertainty of the thermodynamic efficiency by calculating the uncertainty of the components that feed into the efficiency. This will then enable us to determine the confidence needed in our experimental data in order to arrive at a desired level of accuracy for efficiency.

Figure (1) demonstrates an example of the type of redox reaction being tested. First, $MO_{x-\delta f}$ and sunlight produce oxygen and $MO_{x-\delta i}$. Then $MO_{x-\delta i}$ and water produce hydrogen and $MO_{x-\delta f}$, and the cycle is restarted.

A. Steps needed to calculate uncertainty of efficiency

First, a model, or a collection of models, is chosen to be tested. Then, Bayesian Inference and Markov Chain Monte Carlo (MCMC) are used to fit the models to the data. After that, different models are compared to each other using evidence values. Next, the uncertainty of derived quantitates, such as the enthalpy change, were calculated using forward proportion. Next, model error was determined. Finally, all these components of error will be brought together to calculate the uncertainty of the thermodynamic efficiency.

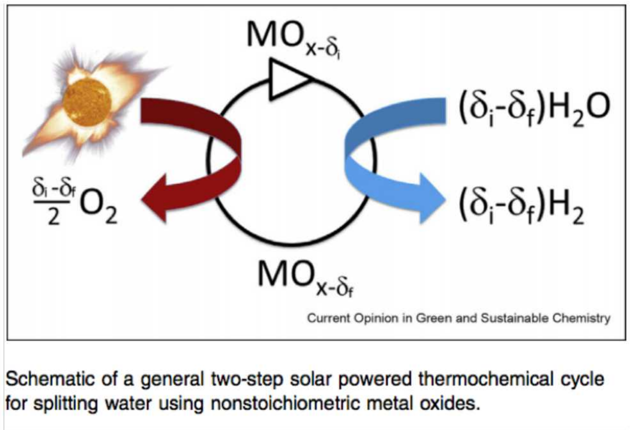


Figure 1: Example of a water splitting reaction with a redox active material M. Test material is exposed to sunlight, and oxygen is dispensed. Test material is then combined with water. Hydrogen is dispensed and the original material is retrieved.
McDaniel, Current Opinion in Green and Sustainable Chemistry. 2017

II. THE MODEL

Four models were used with an increasing number of parameters, ranging from 3 to 7 parameters.

$$\delta(p, T; \lambda) \tag{1}$$

where p is pressure, T is temperature, and λ are the parameters. The simplest model is linear, with exponential transforms, and the most complicated is a quadratic divided by a quadratic of the exponential transforms.

Four data sets were used to test the models. Three "clean" data sets were initially used while developing the workflow. However, these are not completely representative of real example data sets. Thus, a fourth, noisier data set was also considered.

- Zinkevich [6] and Panlener [4]: CeO_2, (Ceria) a material used for solar fuels by splitting water and carbon dioxide
- Goldyreva [1]: $Ca_{0.6-\gamma}Sr_{0.4}La_{\gamma}MnO_{3-\delta}$, a material for thermal storage
- SLMA3 [3]: a material similar to Ceria. This data sets is much noisier than the others

III. USING MCMC TO FIT THE MODEL

A. Bayesian inference

Bayesian Inference is a method for determining model parameters by calibrating against a set of data points. Bayes' formula is :

$$p(\theta|D, M) = \frac{p(D|\theta, M)p(\theta|M)}{p(D)} \tag{2}$$

where

- $p(\theta|D, M)$ is the posterior distribution and is how likely the specific parameters are given the data. The most probable parameters can be found by maximizing the posterior and are known as the maximum a posteriori (MAP) parameters.
- $p(D|\theta, M)$ is the likelihood and is the probability of the data given the particular model with certain parameters.

- $p(D|\theta, M)$ is the prior. It is based on the prior knowledge of the problem, and a uniform prior is used for this problem because there is very minimal prior knowledge about the problem and a uniform distribution is the most general.
- $p(D)$ is the model evidence. When fitting the model to the data, it can be viewed as a normalizing factor. It comes into play when comparing different models to each other, in the sense that a higher evidence value implies better support for the model. This will be discussed further.

B. Markov Chain Monte Carlo

Markov Chain Monte Carlo (MCMC) is a algorithm to sample from a parameter space and finds a posterior probability distribution of parameters. At the maximum of the posterior distribution there is the maximum a posteriori (MAP) parameters.

1. How MCMC works?

First, start at a given point and find the posterior probability using Equation (2). Select a second point based on a Gaussian proposal distribution and again find the posterior probability. Then calculate α as the posterior of the new divided the old posterior:

$$\alpha = \frac{p(new|D)}{p(old|D)}. \tag{3}$$

If $\alpha > 1$, the new point is more likely and accept the new point. If $\alpha < 1$, then accept the new point at a probability of α. Continue this process for the desired amount of samples. This process will explore all areas of the given space, while focusing on areas that are more likely and have larger posteriors.

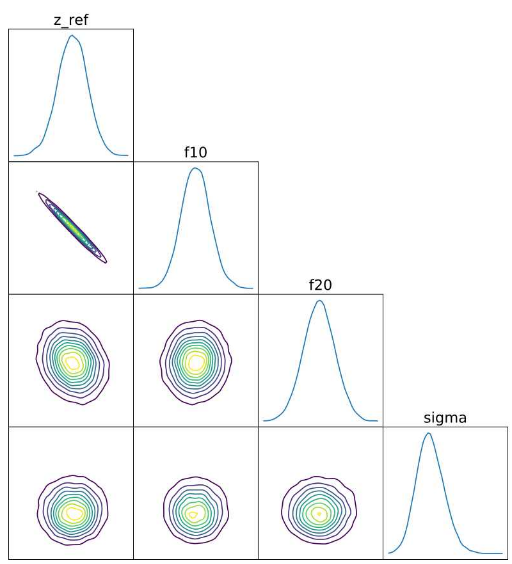
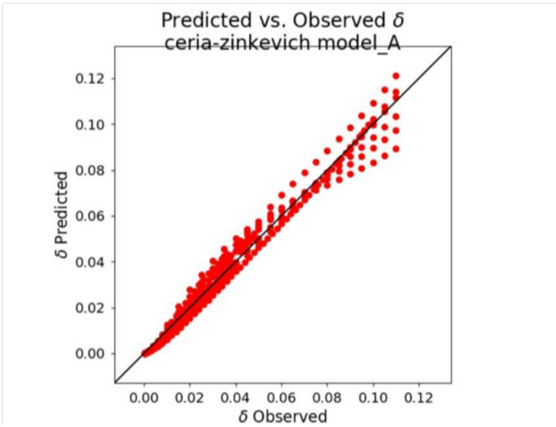


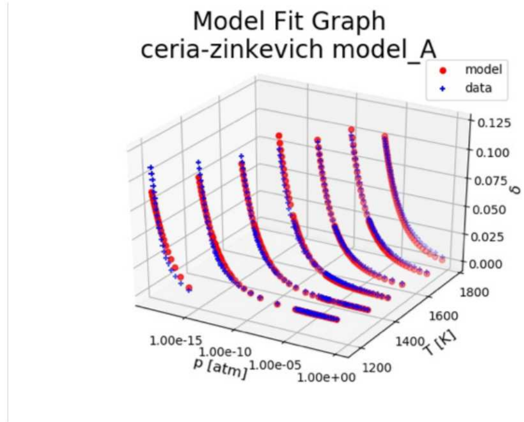
Figure 2: Goldyreva Model A Posterior Plots for all Parameters and Correlations Between Parameters. Diagonals show the marginalized posteriors for each variable. Off-diagonals show marginalized correlations between two variables.

2. MCMC gives a probability distribution of the model parameters.

In Fig (2), the marginalized posterior plots are on the diagonals. These graphs show the most likely set of parameters, and also a distribution of how likely other sets of parameters are. These plots are marginalized,

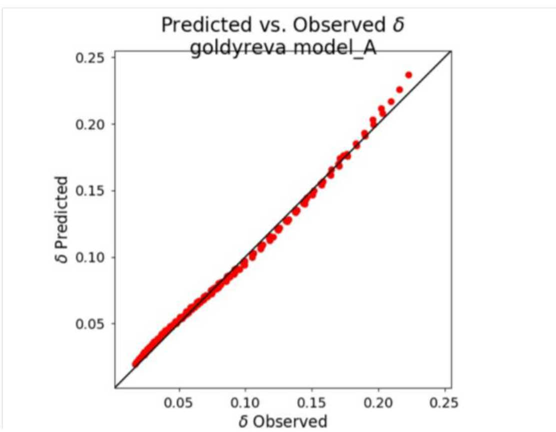


a: Ceria-Zinkevich Predicted vs. Observed δ

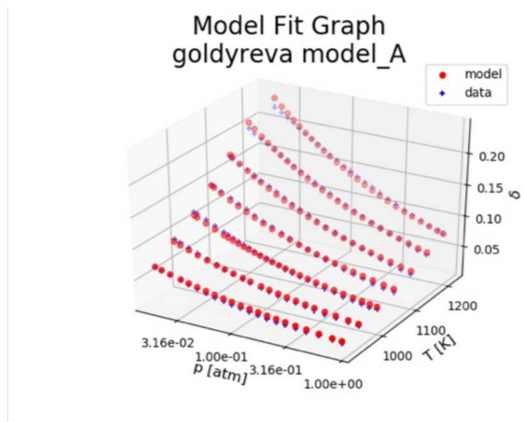


b: Ceria-Zinkevich 3D fit graph

Figure 3: Ceria-Zinkevich Fit Graphs



a: Goldyreva Predicted vs. Observed δ



b: Goldyreva 3D fit graph

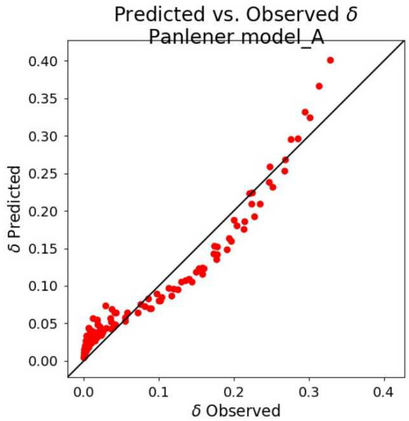
Figure 4: Goldyreva Fit Graphs

which means that for each parameter, they display the posteriors averaged over all other parameters. The off-diagonals of Fig (2) shows the correlations between parameters. The correlation between z_{ref} and f_{10} is very long, skinny, and negatively sloped. This means that those two parameters are very heavily negatively correlated. All other correlations between pairs of variables are circular, meaning that the other parameters are only weakly correlated to each other.

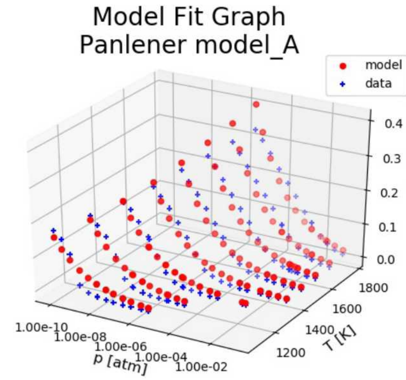
C. Examples of the model fits

Good fitting for all models of Ceria-Zinkevich and Goldyreva were obtained. The simpler two models were also fitting for Panlener, but the more complicated models are not yet converging, cannot obtain a solution that is consistent through different runs.

Examples of the fits are shown in Figures (3), (4), and (5). These plots show how well the models are fitting the data. On the first plots (a)s, the observed δ is on the x-axis, and the predicted delta is on the y-axis. Thus, "perfect" would be the 45° lines, shown by the black line. The other graphs, (b)s demonstrate how the model fits the data in the 3D space.

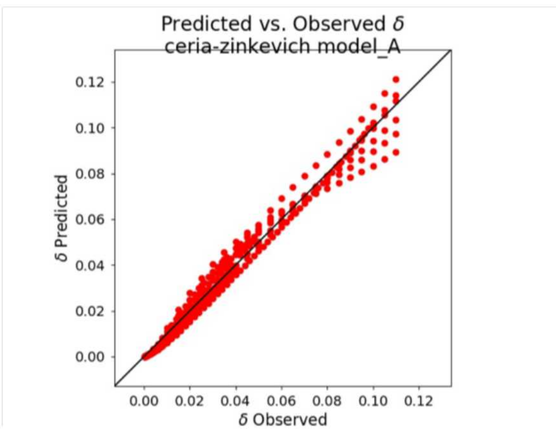


a: Panlener Predicted vs. Observed δ

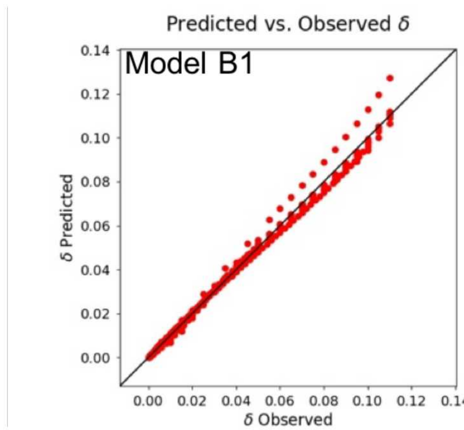


b: Panlener 3D fit graph

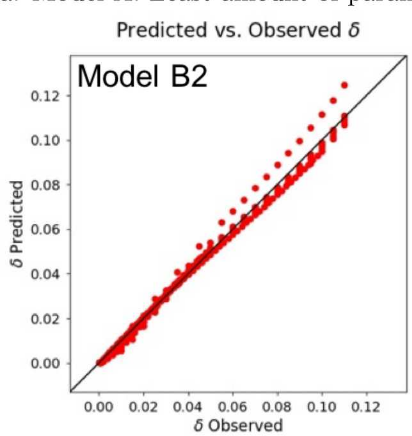
Figure 5: Panlener Fit Graphs



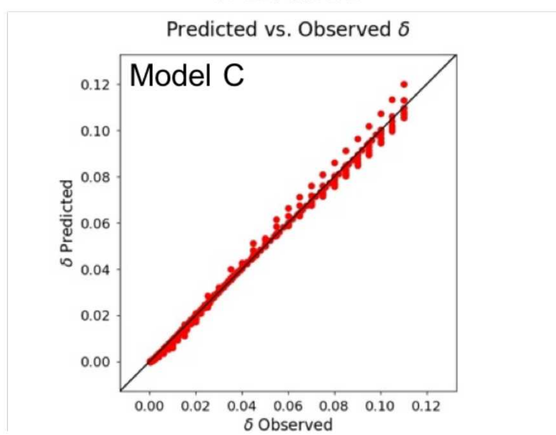
a: Model A: Least amount of parameters



b: Model B1



c: Model B2



d: Model C: Largest amount of parameters

Figure 6: Ceria-Zinkevich model fits for all models
These figures show different models fitted on the same data set. The number of parameters increases with each model and a noticeable improvement of the fits occur.

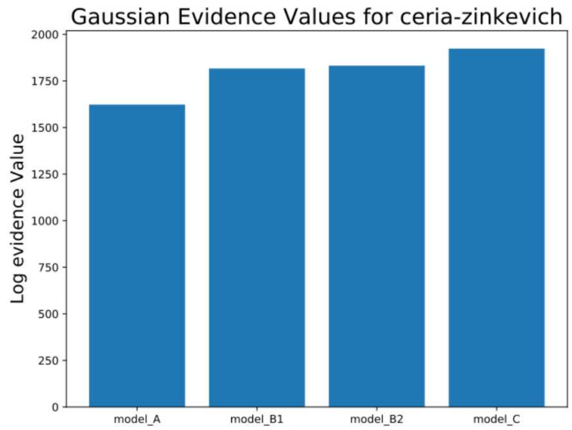


Figure 7: Log Evidence Values for Ceria Zinkevich
Higher log evidence indicated improved fit. Each model shown is increasing the number of parameters and increasing log evidence indicates better fitting. The peak has not yet been reached, and thus overfitting has not yet occurred.

IV. COMPARING MODELS

Four different models were used with increasing number of parameters. Thus, comparing the models to each other is an important task to see which model is best. Figure (6) shows all the models fits of the Ceria-Zinkevich data set. Notice how as the number of parameters increase, the predicted δ values become much more similar to the observed values. However, it is possible that the models with more parameters are overfitting the data. Model evidence is a way to quantitatively compare different models to each other.

A. Using model evidence

1. What is model evidence?

One way to compare different models is to utilize model evidence, which is calculated by:

$$p(D) = \int p(D|\theta, M)p(\theta|M)d\theta \tag{4}$$

It can be shown that log evidence is the difference between the model fit and the model complexity. Increasing the number of parameters will increase the model fit. However, increasing the number of parameters will also increase the model complexity. Thus, finding the maximum evidence will give the best fit without overfitting.

2. Model Evidence for the models and data sets

The model evidence values for all model of the Ceria-Zinkevich data set are shown in Figure (7).The evidence values are increasing, meaning that the fit is improving. The evidence values have not yet begun to decrease, which means that overfitting has not yet occurred.

Comparing the graphs in Figure (6) to the evidence values shown in Figure (7), you can see that the fit of the models is improving and the evidence values are increasing.

V. FITTING WITH NOISY DATA

One problem with the data sets used so far, is that they were very "clean", meaning that there is very minimal noise in the data. However, most data sets that will be used in practice are not clean. They are

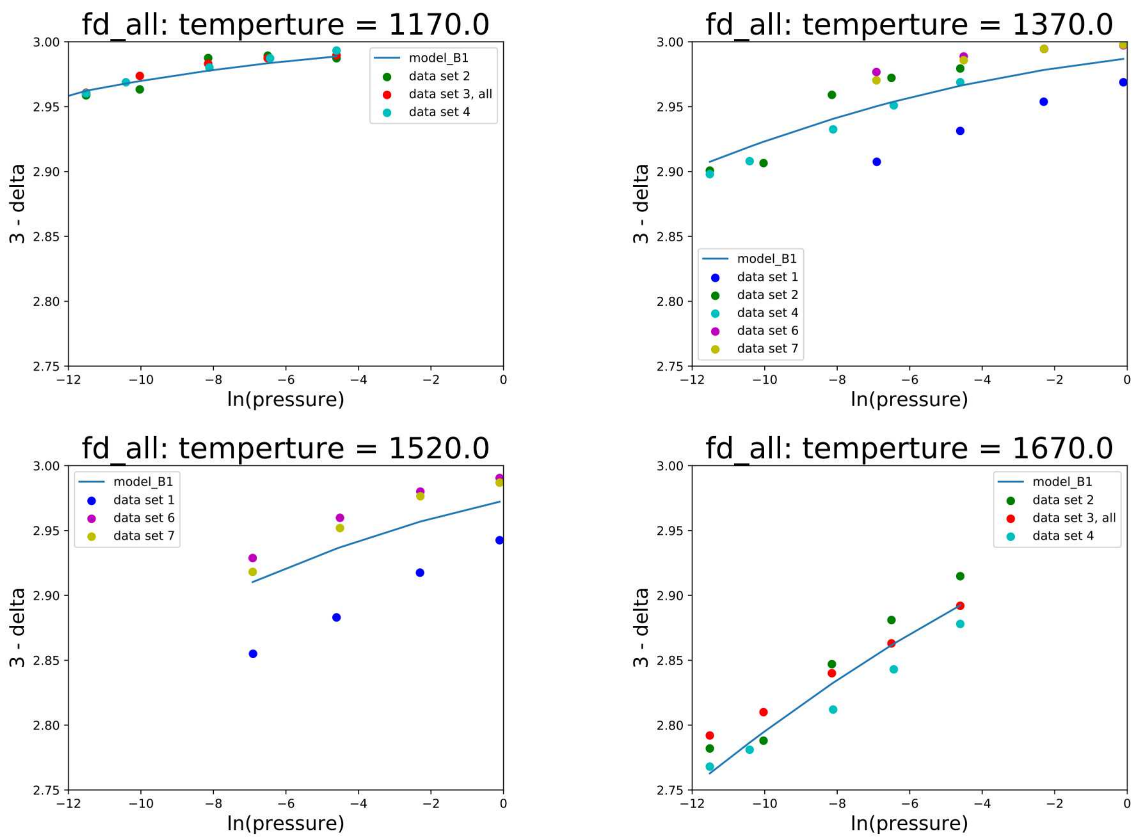


Figure 8: Model B1 fitted to all the noisy data over shown over representative temperatures. The different colors of the data points represent different experiments of this material.

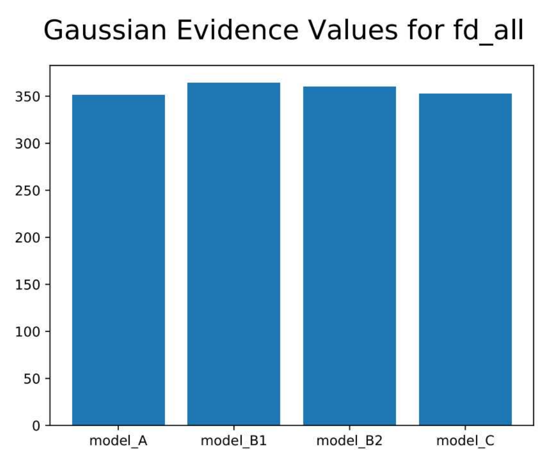


Figure 9: Log Evidence of all models fitted over all noisy data sets. Notice how Model B1 has the highest log evidence value, implying that model B1 is fitting the data the best.

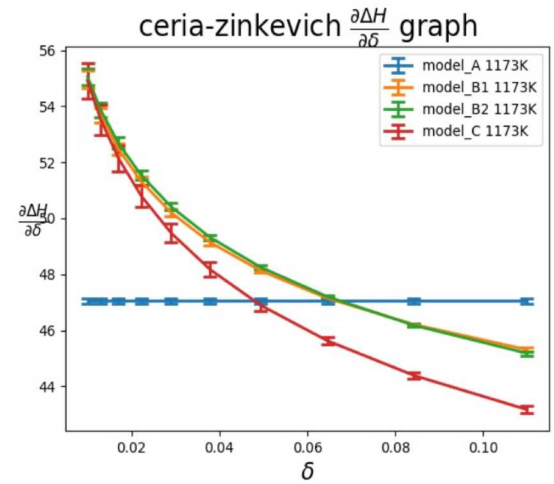


Figure 10: Ceria Zinkevich Enthalpy Derivative

very messy, thus this workflow needs to be tested on a noisy data set. The noisy data set used is from SLMA3, a material that is similar to the ceria in Zinkevich.

Fig (8) shows all the data from the noisy data set. The different colors represent different tests, varying by location, date, and sample tested. In many cases, there are some samples tested at the same pressure and temperature, but with different δ values. This could have been caused by a variety of reasons and is the reason why this data set is messy. This data set is a good example of some of the error that can occur in a typical data set.

A. The fit

The simpler models are fitting the noisy data well, but the more complicated models are not converging, not giving consistent answers between runs. Models A and B1 are fitting this data pretty nicely. Model B1 is as shown in Fig (8). Fig (9) shows the log Evidence values of all the models over all the noisy data sets. The log evidence peaks at model B1, implying that model B1 has the best fit to the data. This means that model A is not capturing all the behavior and models B2 and C are overfitting the data.

VI. CALCULATE DERIVED QUANTITIES AND THEIR UNCERTAINTIES

A. Forward propagation

Forward propagation is a way to calculate derived quantities and their uncertainties based on the MCMC chains. The MCMC algorithm produces a probability distribution, as seen in the diagonals of Figure (2). Samples are then randomly drawn from this posterior, and used to calculated certain quantities. Based on all these samples, mean and standard deviations of the derived quantities are obtained.

B. Enthalpy change

Forward propagation was used to calculate a few desired quantities, the enthalpy derivative and the average enthalpy change. Figure (10) shows the derivative of the enthalpy for the Ceria-Zinkevich data set, and Figure (11) shows the average enthalpy change. The error bars show one standard deviation, and all are less than 3%. Both of the quantities are relevant in calculating the thermodynamic efficiency.

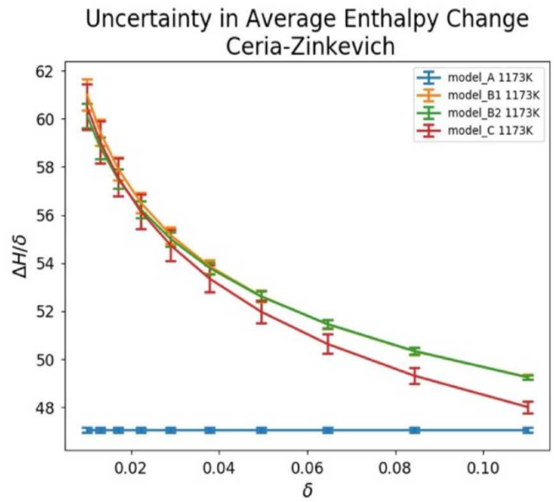


Figure 11: Ceria Zinkevich Average Enthalpy Change

VII. MODEL ERROR

The Ceria-Zinkevich data set is a very "clean" data set, with very minimal experimental error. However, Fig (6) shows that there is error between the fitted model and the data. This error is caused by the error in the model, not in the data. This section will discuss how the uncertainty from the model error was quantified.

A. Sensitivity Analysis

The first step in calculating the model error is to perform a sensitivity analysis and create a surrogate model. A sensitivity analysis helps to determine the which parameters have more or less effects on the output of the model. Fig (12) shows the results of the sensitivity analysis for model A on the Ceria-Zinkevich data set. z_{ref} (Param #1) is the most sensitive parameter because the largest part of the graph is blue. This means that small changes of z_{ref} contribute more change in δ, the output variable, than any other parameter.

The x-axis is the index number of the inputs. The order of the input variables (p and T) are increasing pressures, and then increasing temperatures. In this graph, where there are the more extreme decreases in z_{ref} is where the temperatures change. Within each of these parts, the pressure is also increasing, and the sensitivity of z_{ref} is increasing with pressure. Based this graph, z_{ref} is most significant. f_{20} (Param #3, the red) is more significant at the lower temperatures and pressures, and f_{10} (Param #2, the green) is the opposite, more significant at higher temperatures and pressures.

B. Calculating model error

Earlier in the project, when fitting the models to the data, it was assumed that each parameter was a single, determined value. To calculate the model error, a parameter, or set of parameters, will now be treated as a distribution. To start they will be assumed to be gaussian distributions, and thus both the mean and standard deviations will be inferred. The spread of the model predictions for realizations of these parameter from their inferred distributions then cover the model error in this particular model representation.

Because z_{ref} is the most sensitive parameter, z_{ref} will be first parameter that is assumed to be a distribution. Figure (13) shows the model error at every tested temperature. The error bars show 2 standard deviations and they encapsulate most of the observed data values. Figure (13) shows three types of errors:

1. the surrogate error is the error produced by making the surrogate model
2. the posterior uncertainty is the uncertainty from performing MCMC
3. the model error is the sigma that is inferred when z_{ref} is assumed to be a gaussian

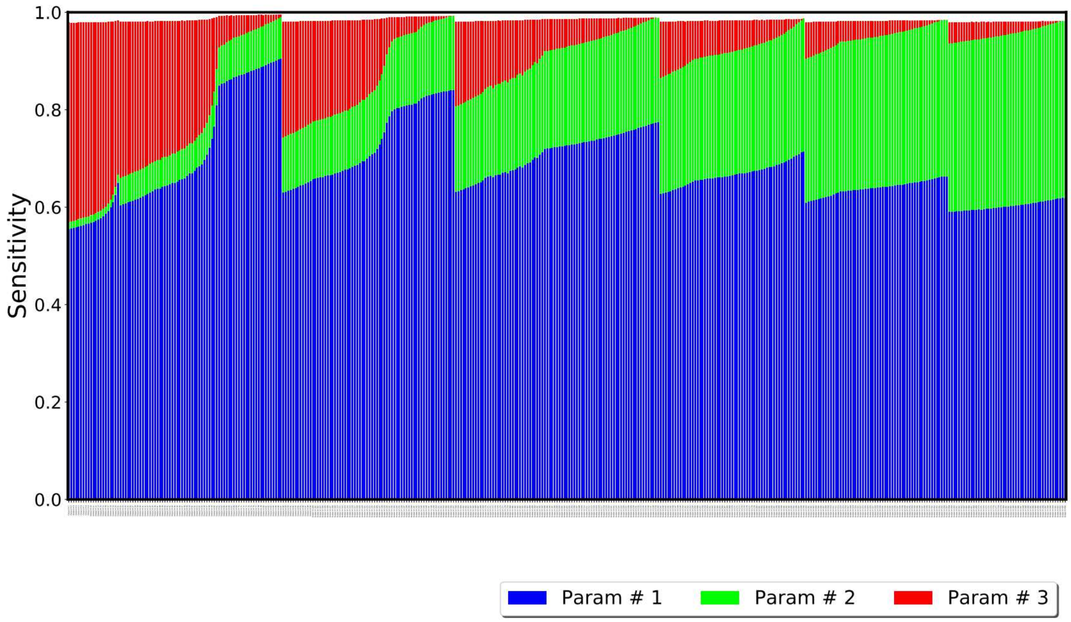
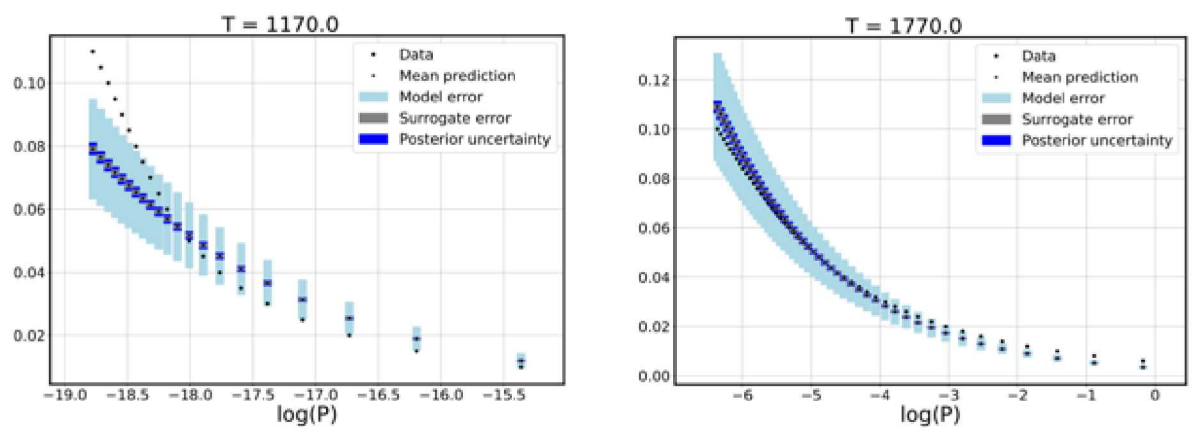


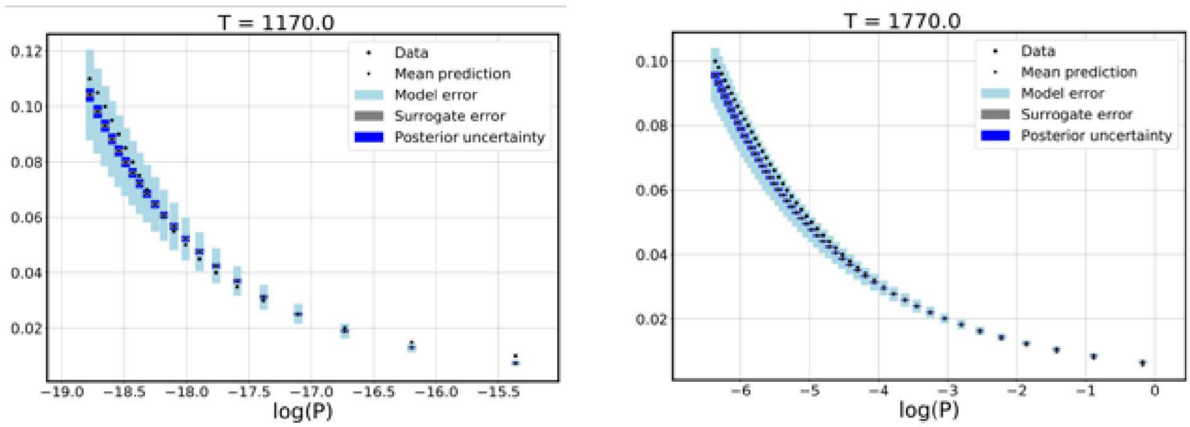
Figure 12: Main Sensitivity Analysis for Model A on Ceria-Zinkevich data set. x-axis is the index number of each sample. The samples are ordered by increasing pressure, and then increasing temperature. Param #1 is z_{ref}, Param #2 is f_{10}, and Param #3 is f_{20}.



a: Lowest tested temperature

b: Highest tested temperature

Figure 13: Model Error of Ceria-Zinkevich for Model A



a: Lowest tested temperature

b: Highest tested temperature

Figure 14: Model Error of Ceria-Zinkevich for Model B1

Ideally Model B1 should have less model error because the model fits the data better, as seen in Figure (6). This can be seen by comparing Figures (13) and (14). Figure (14) shows the model error for Model B1. The model error is encapsulating most of the data, and the error bars are smaller than those of model A, meaning that Model B1 is a more exact model.

VIII. FURTHER WORK

Further work in this project includes actually computing the thermodynamic efficiency and its uncertainty, further computing the model error, and exploring other areas of the project.

Using all these components discussed in this paper, the thermodynamic efficiency and its uncertainty will be calculated. Uncertainty comes from both the data, the MCMC chain, and the model error. All these uncertainties will be sent through a particular equation and the efficiency will be calculated.

Currently, model error has only been calculated by varying the most sensitive parameter, z_{ref}. Further exploration on other parameters will help determine which are more and less important, and to better quantify the model error. Also, performing these calculations on the other models and data sets will help better characterize the models.

Once the thermodynamic efficiency is calculated, back propagation then then be use in order to determine the confidence need in the data in order to determine a desired level of accuracy of the efficiency. This will allow new material to be tested with minimal cost because the minimum level of confidence in the data will be known.

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This paper describes objective technical results and analysis. Any subjective views or opinions that might

be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

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