

Bayesian Regression of Thermodynamic Models of Redox Active Materials

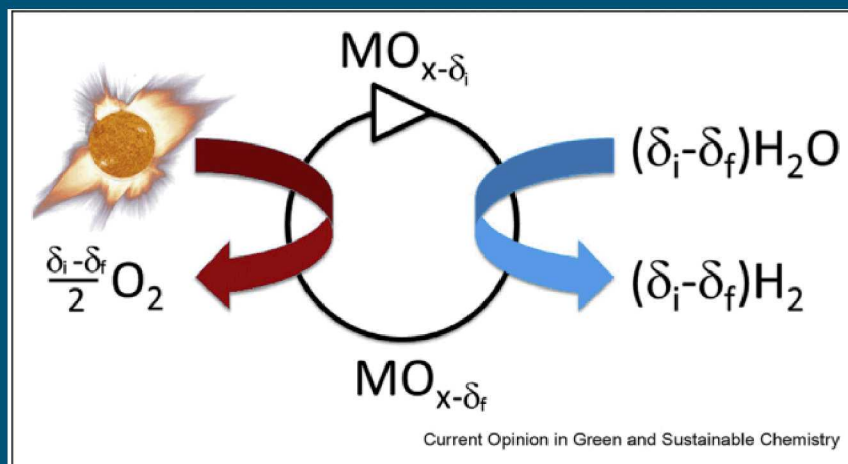
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In collaboration with:

Bert Debuschere (Sandia National Laboratories)
and Ellen Stechel (Arizona State University)

Introduction:

- Find a suitable functional redox material for storing concentrated solar energy
- Demonstrate effectiveness for thermal storage or solar fuel using a thermodynamic model derived from experimental data.
- Calculate the uncertainty of components that feed into thermodynamic efficiency to quantify the uncertainty of the efficiency



Schematic of a general two-step solar powered thermochemical cycle for splitting water using nonstoichiometric metal oxides.

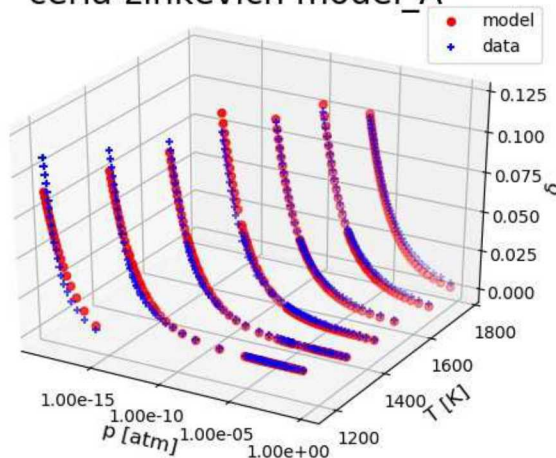
The Model

- Four models

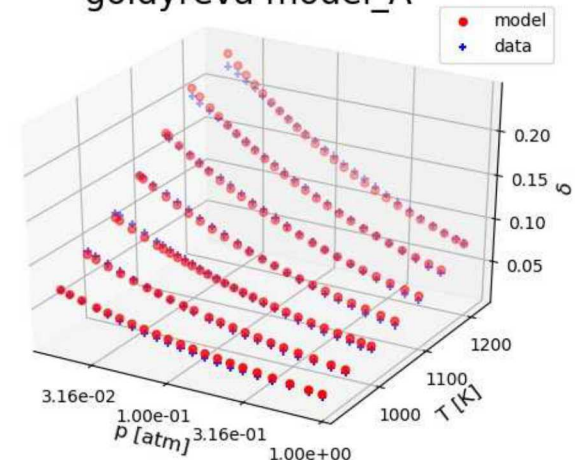
$$\delta(p, T; c)$$

- Pressure (p), Temperature (T), Parameters (c)
- Three data sets:
 - Zinkevich and Panlener: CeO_2 , a material used for solar fuels by splitting water and carbon dioxide
 - Goldyreva: $\text{Ca}_{0.6-y}\text{Sr}_{0.4}\text{La}_y\text{MnO}_{3-\delta}$, a material for thermal storage

Model Fit Graph
ceria-zinkevich model_A



Model Fit Graph
goldyreva model_A



Steps to Calculate Uncertainty of Efficiency

Fitting the model to the data, using MCMC



Compare Models using Evidence values



Use Forward Propagation to Find the Uncertainty of Enthalpy Change



Use Enthalpy Change with Uncertainty to Calculate Efficiency

Bayesian Inference: Basics

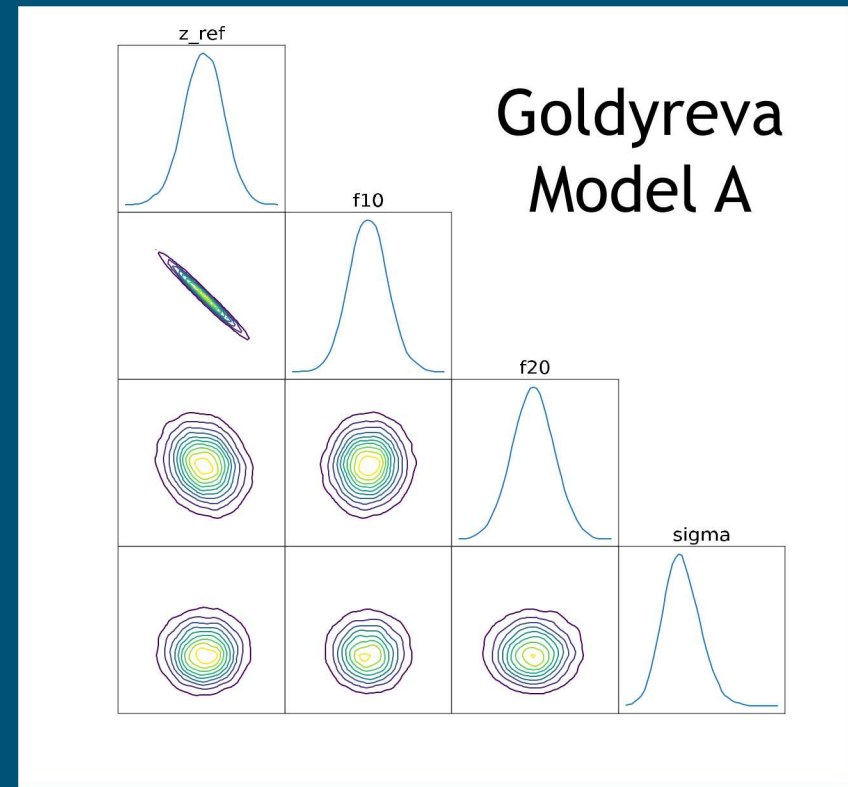
- Bayes' Formula

$$\underbrace{P(\mathbf{c}|\mathcal{D})}_{\text{Posterior}} = \frac{\underbrace{P(\mathcal{D}|\mathbf{c})}_{\text{Likelihood}} \underbrace{P(\mathbf{c})}_{\text{Prior}}}{\underbrace{P(\mathcal{D})}_{\text{Evidence}}} \propto P(\mathcal{D}|\mathbf{c})P(\mathbf{c})$$

- Likelihood is the probability of the data given the parameters
- The prior is our prior beliefs about the posterior knowledge (uniform of our problem)
- Evidence can be viewed as a normalizing factor here
- Posterior measures how likely that particular set of parameters fits the data

Use Markov Chain Monte Carlo to get a probability density of posteriors

- Use Markov Chain Monte Carlo (MCMC) to sample the parameter space to get Maximum a posteriori (MAP) parameters and distribution
- Diagonals show the marginalized posterior distributions
- Off diagonals show the correlations between parameters.

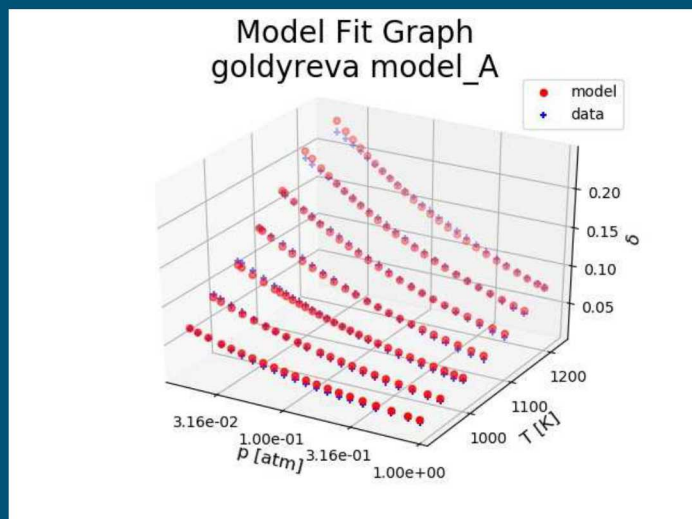
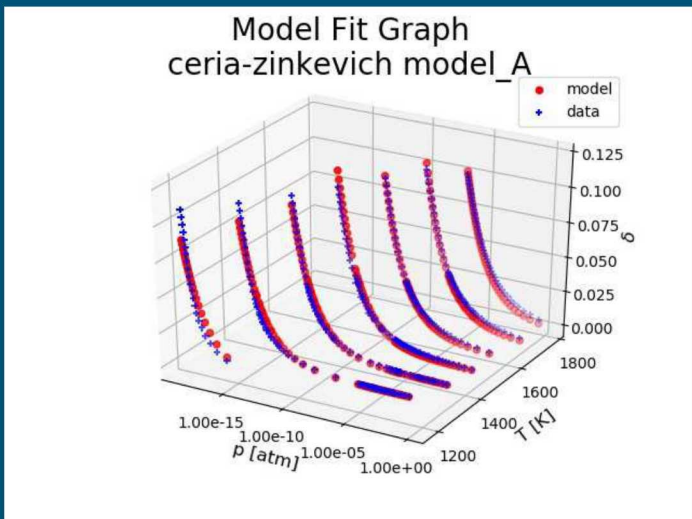
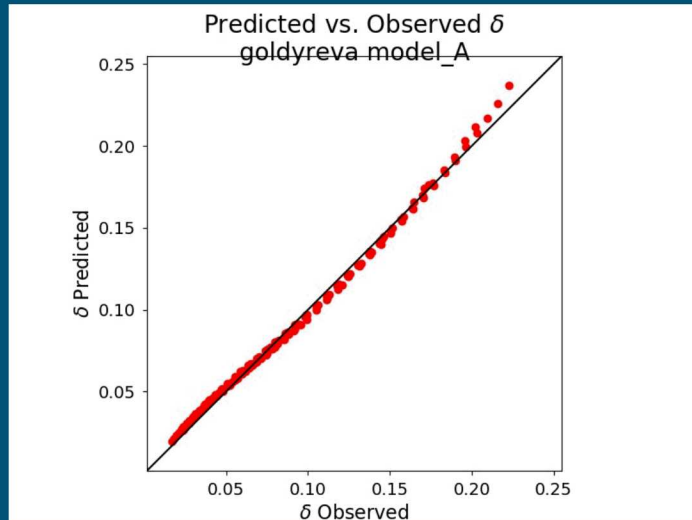
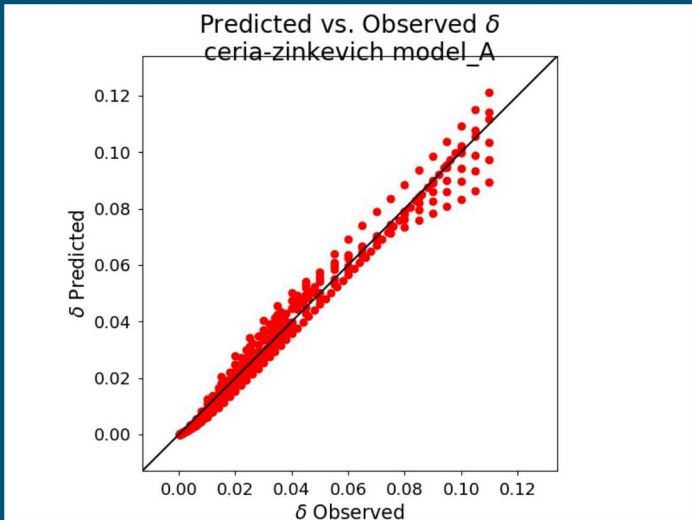




Using MCMC, Models are Fitting Both Data Sets Well

Ceria-Zinkevich

Goldyreva



Slide 10

MOU24 Will these be too small/too busy??

Microsoft Office User, 7/25/2018

MOU30 Could improve title

Microsoft Office User, 7/25/2018

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Fitting the model to the data, using MCMC



Compare Models using Evidence values

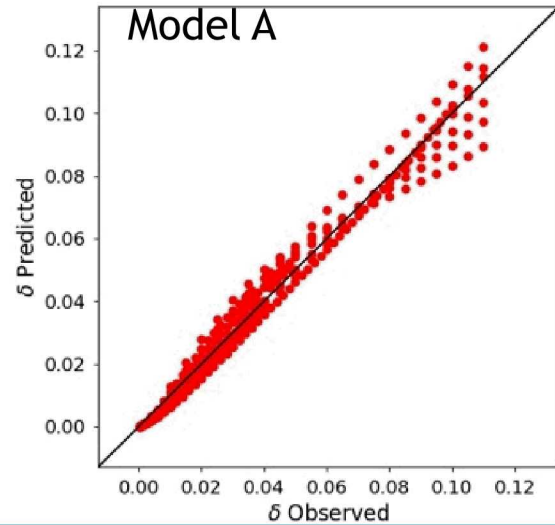
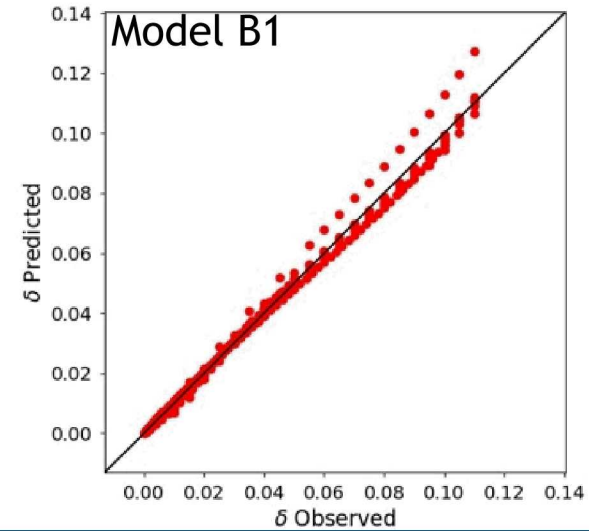
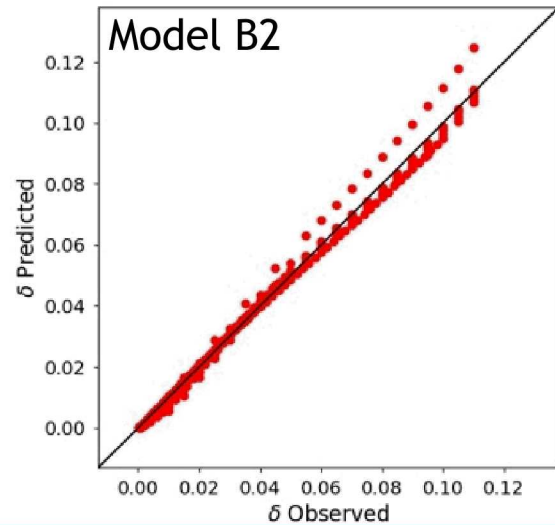
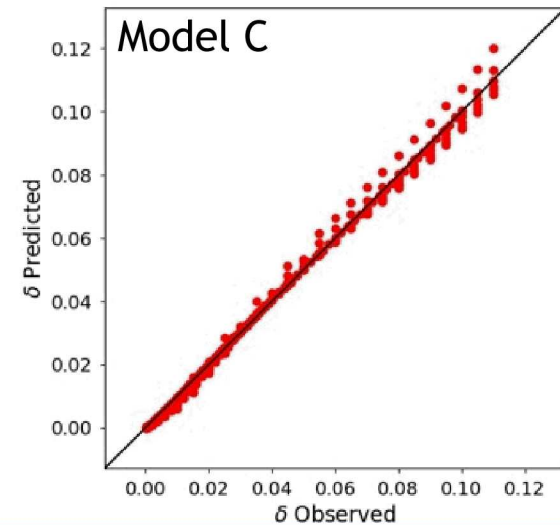


Use Forward Propagation to Find the Uncertainty of Enthalpy Change



Use Enthalpy Change with Uncertainty to Calculate Efficiency

Comparing Different Models: Ceria-Zinkevich Examples

Predicted vs. Observed δ Predicted vs. Observed δ Predicted vs. Observed δ Predicted vs. Observed δ 

Using Model Evidence to Compare Different Models

- Bayes' Formula

$$\underbrace{P(\mathbf{c}|\mathcal{D})}_{\text{Posterior}} = \frac{\underbrace{P(\mathcal{D}|\mathbf{c})}_{\text{Likelihood}} \underbrace{P(\mathbf{c})}_{\text{Prior}}}{\underbrace{P(\mathcal{D})}_{\text{Evidence}}} \propto P(\mathcal{D}|\mathbf{c})P(\mathbf{c})$$

- Use evidence values to compare different models
- Formula to calculate evidence

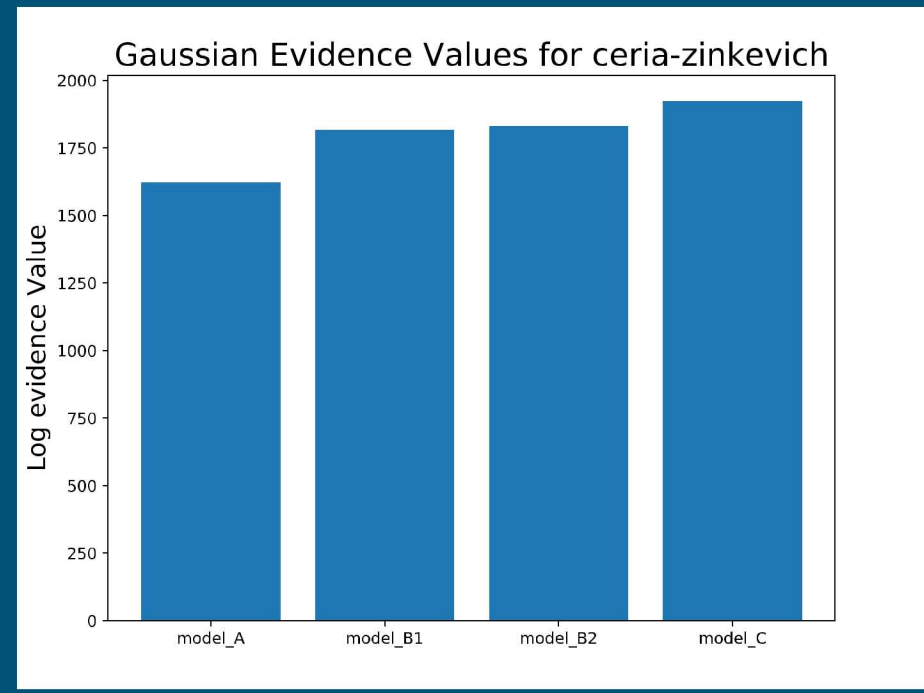
$$P(\mathcal{D}) = \int p(\mathcal{D}|c)p(c)dc$$

- Calculated in a variety of methods



Model Evidence for Ceria-Zinkevich Data Set

- These values were calculated using Gaussian estimation
- Higher evidence value means better fit to the data
- All are increasing, overfitting has not yet occurred



Slide 14

MOU6 Need better word than goodness.

Microsoft Office User, 7/24/2018

MOU21 If I don't include this slide, I could include these graphs on the previous slide

Microsoft Office User, 7/24/2018

MOU27 Will probably omit for final presentation

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MOU31 Break into 3 slides: models, equation, and evidence graph

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Steps to Calculate Uncertainty of Efficiency

Fitting the model to the data, using MCMC



Compare Models using Evidence values



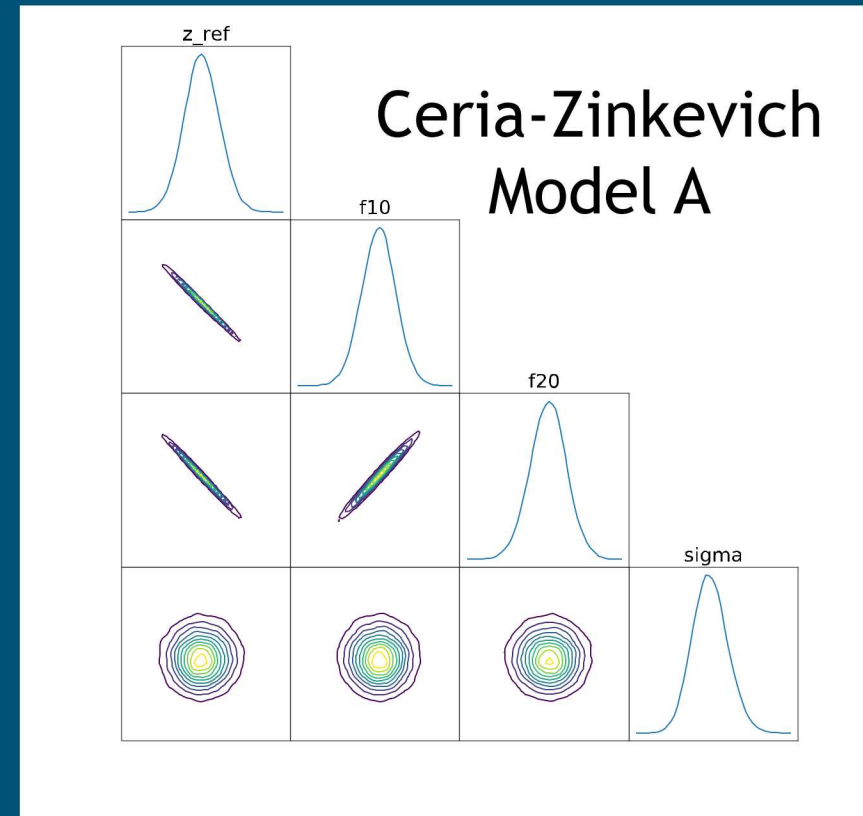
Use Forward Propagation to Find the Uncertainty of Enthalpy Change



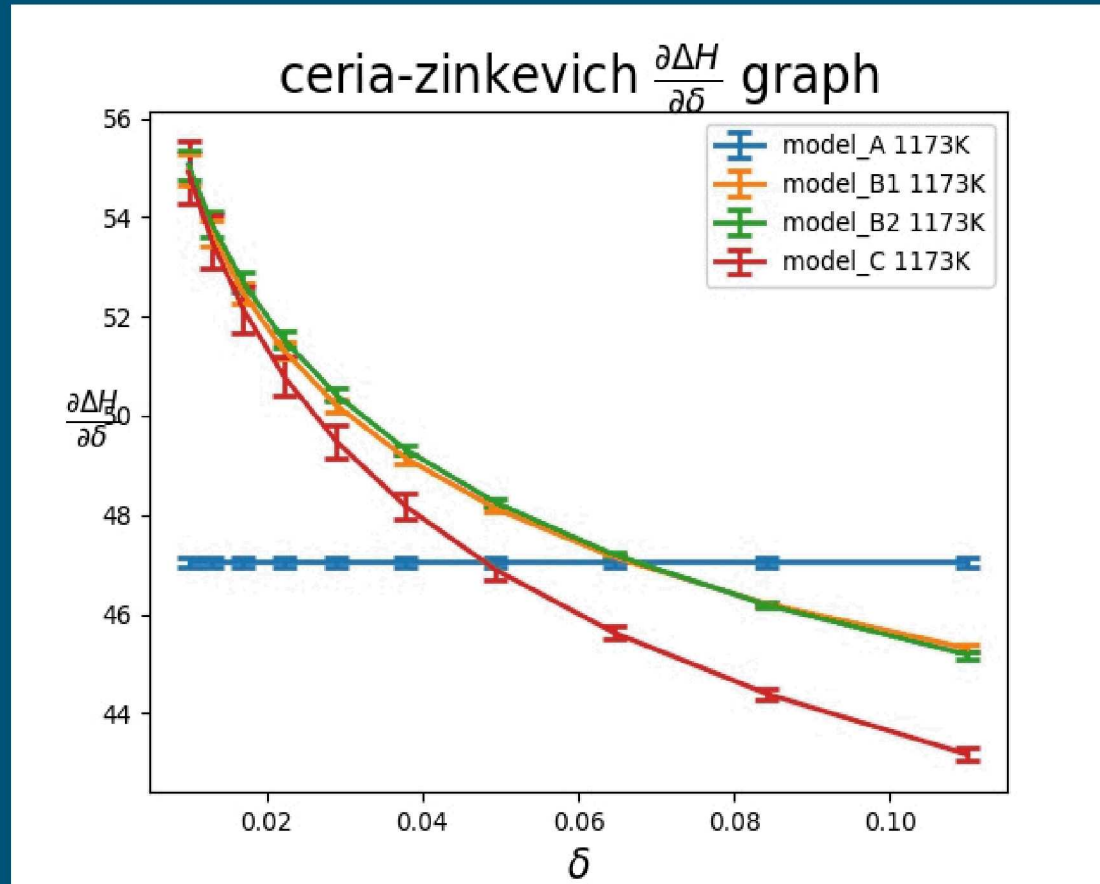
Use Enthalpy Change with Uncertainty to Calculate Efficiency

Forward Propagation of Uncertainty using Posterior Distribution

- Take samples from posterior distribution
- Calculate desired quantity with those parameters
- Find mean and standard deviation of calculated quantity

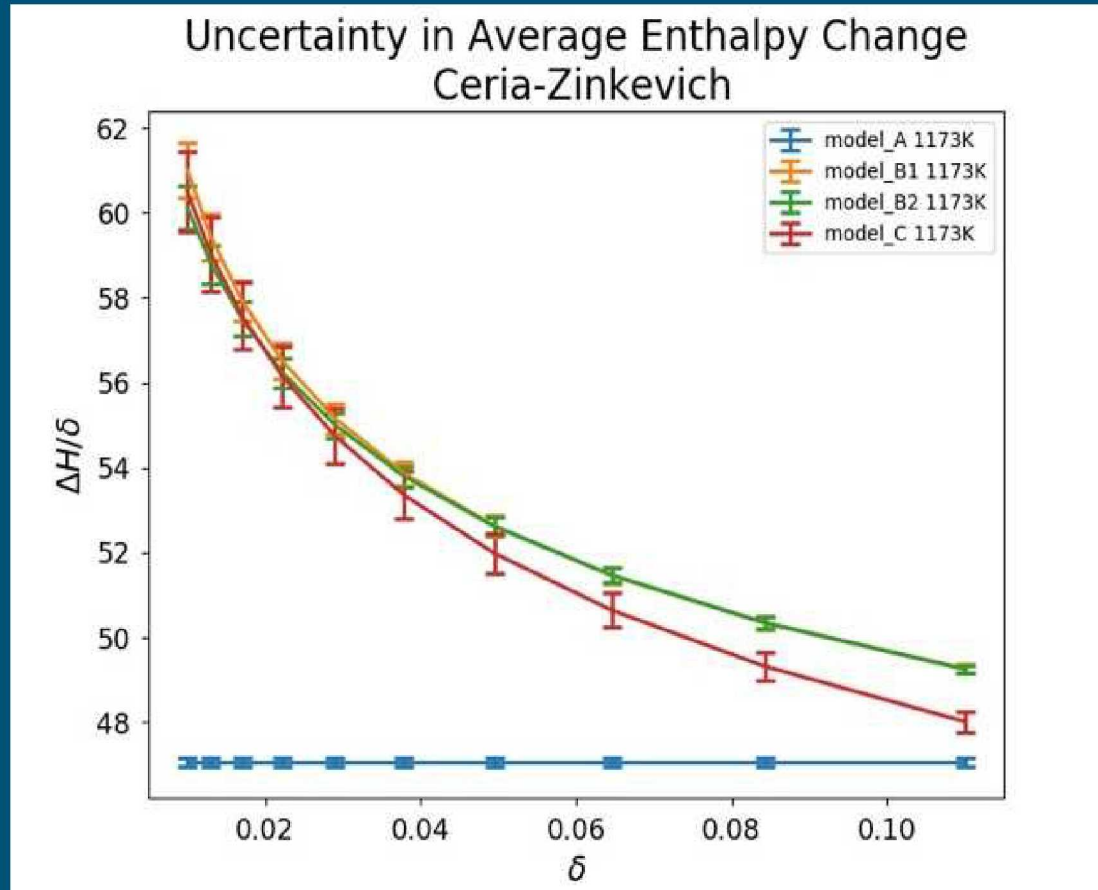


Calculate Enthalpy Derivative using Forward Propagation



- Error bars show 1 standard deviation
- May need change in enthalpy to calculate model efficiency
- Maximum error was less than 3%

Calculate Average Enthalpy Change using Forward Propagation



- Error bars show 1 standard deviation
- May need change in enthalpy to calculate model efficiency
- Maximum error was less than 2%

Steps to Calculate Uncertainty of Efficiency

Fitting the model to the data, using MCMC



Compare Models using Evidence values



Use Forward Propagation to Find the Uncertainty of Enthalpy Change



Use Enthalpy Change with Uncertainty to Calculate Efficiency

Next Steps - Calculating Efficiency

- Use the calculated enthalpy change to calculate the thermodynamic efficiency
- Use the calculated uncertainty of the enthalpy change to determine the uncertainty of the efficiency

Uncertainty Quantification Toolkit (UQTk) Tutorial

- Built using the Uncertainty Quantification Toolkit (UQTk)
- Will develop into a tutorial for the toolkit
 - Code was developed with generalization in mind
 - Will be made available to others in the hydrogen community

<http://www.sandia.gov/UQToolkit/>

The logo for the Uncertainty Quantification Toolkit (UQTK) features the letters 'UQTK' in a bold, black, sans-serif font. The letters are set against a white background that is framed by a thick black border. The 'U' and 'Q' are the largest characters, while the 'T' and 'K' are smaller and positioned to the right.

Slide 26

MOU15 Write a little better. Not paragraph form

Microsoft Office User, 7/24/2018

Conclusions

- Bayesian inference allows us to determine the confidence in the inferred parameters.
- Forward propagation allows us to determine the uncertainty in the derived quantities.
- Our workflow allows us to predict the uncertainty of the thermodynamic efficiency of a hydrogen conversion process based on new material.
- The tutorial shares this work with the hydrogen community.

Acknowledgements

Thank you Ellen Stechel and Anthony McDaniel for the model and work on the problem. Thank you Bert Debusschere for mentoring. Funding was provided by the DOE Workforce Development for Teachers and Scientists (WDTS) program as well as the DOE Office of Energy Efficiency and Renewable Energy (EERE).

Goldyreva, et al. *J. of Alloys and Compounds*, 638, 44-49, 2015.

McDaniel, *Current Opinion in Green and Sustainable Chemistry*, 4, 37- 43. 2017

Panlener, R. J., et al. *J. of Physics and Chemistry of Solids*, 36(11), 1213-1222, 1975.

Zinkevich, et al. *Solid State Ionics* 177, 989-1001, 2006.