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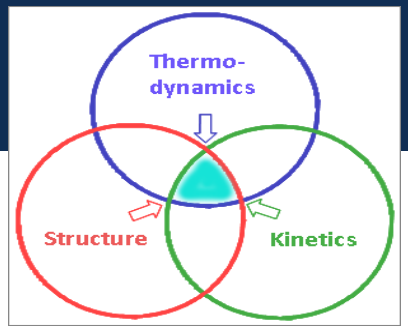
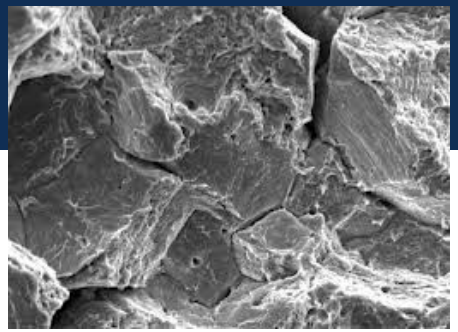
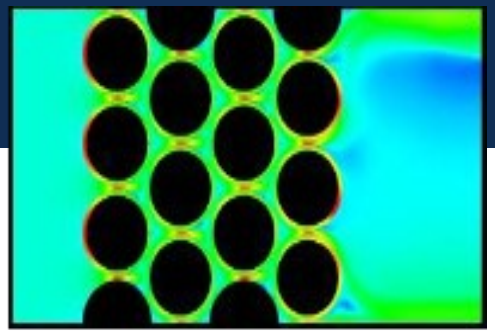


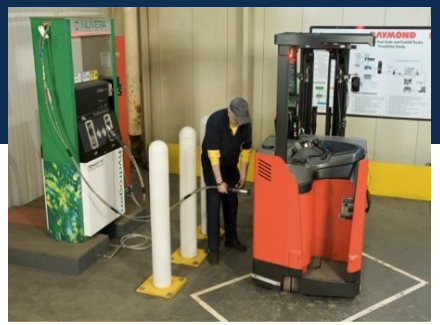
Multidisciplinary Research



Materials Science



Simulation and Optimization



Prototyping

Modeling Isotope Exchange in Palladium Hydride with Detailed Surface Reaction Chemistry

Maher Salloum, Scott James and David Robinson

2013 AIChE Annual Meeting
November 3-8, 2013, San Francisco, California, USA

U.S. DEPARTMENT OF ENERGY

National Nuclear Security Administration

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Overview

- Background and Motivation
- Palladium Hydride Surface Chemical Reactions
- Mathematical Model of Reactive Flow in a Porous Hydride Particles Bed
- Model Validation
- Effects of Temperature and Surface Adsorption Energy.
- Summary

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Background and Motivation

Metal hydrides are an important technology for energy storage

- Sandia National Laboratories have a vested interest in hydrogen storage and separation.
- Hydrogen isotopes can be used to study the separation chemical kinetics independently of solid transformations.
- Transport of hydrogen through palladium separation membranes is often limited by the surface reactions.
- In this study, we are interested in obtaining a better understanding of the PdH surface reactions kinetics and thermodynamics and their effects on the overall performance of a reactor bed.

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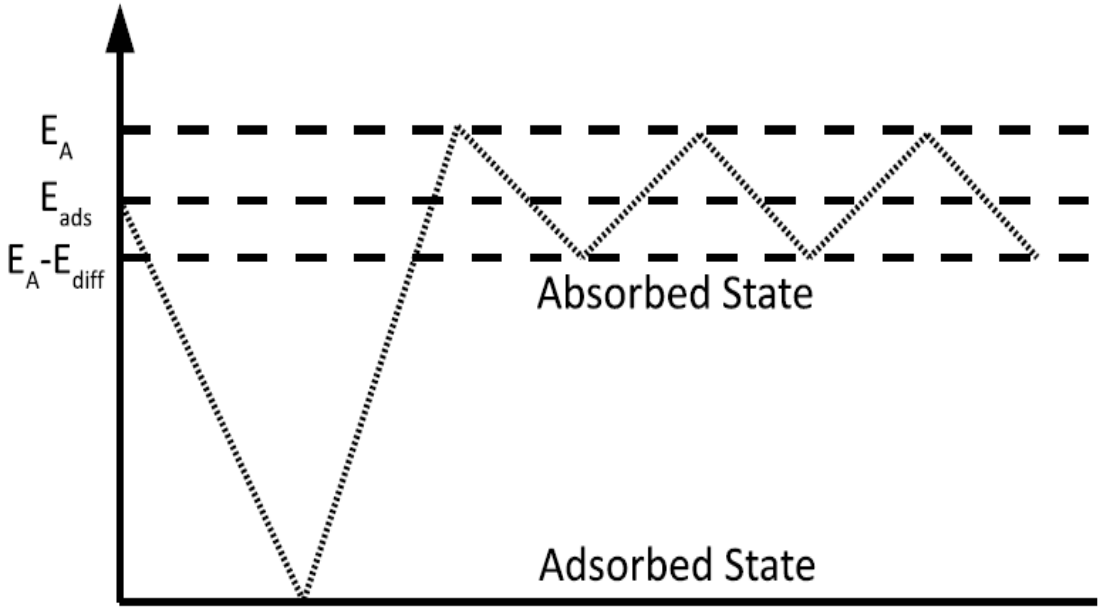
Background and Motivation

- We consider that at the surface level, the hydrogen transport is characterized by three energies: absorption energy E_{abs}, adsorption energy E_{ads} and diffusion energy E_{diff}.



Adapted from: Timothy L. Ward and Tien Dao. Model of hydrogen permeation behavior in palladium membranes. Journal of Membrane Science, 153(2):211–231, 1999.

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Objectives

- Our hypothesis is that we can have control over the energies E_{abs}, E_{ads} and E_{diff}.
- For example, destabilizing the PdH surface (*e.g.* by a near-surface alloy) decreases E_{ads} allowing a faster isotope exchange, hence a faster process.
- We would like to study the effects of varying these factors in a mathematical model of reactive flow in a porous PdH bed.
- Such model is useful in designing an optimal hydride bed operating at a given temperature, surface condition, etc.

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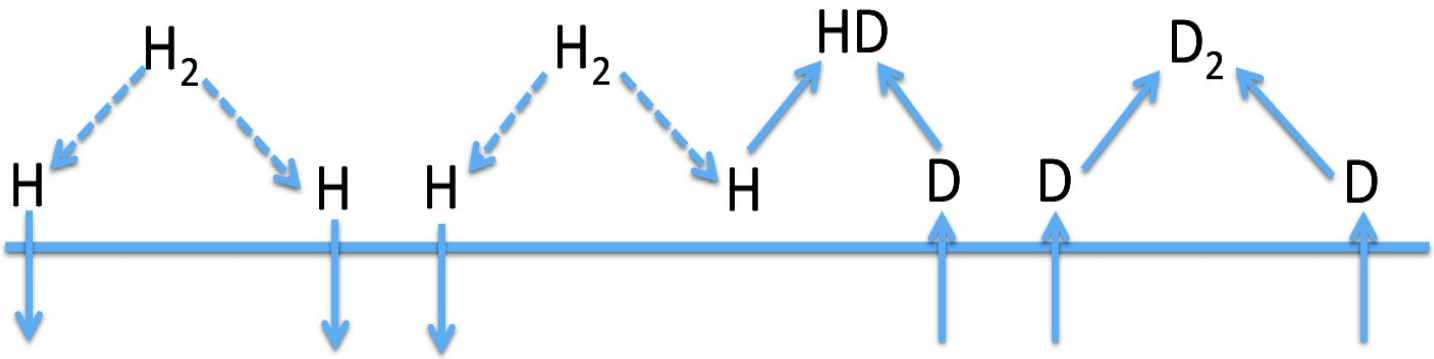
Surface Chemical Reactions



Adsorption of gases on the surface

Transport from surface to bulk

$$H_2 + 2V_s \rightleftarrows 2H_s$$

$$HD + 2V_s \rightleftarrows H_s + D_s$$

$$D_2 + 2V_s \rightleftarrows 2D_s$$

$$H_s + V_b \rightleftarrows H_b + V_s$$

$$D_s + V_b \rightleftarrows D_b + V_s$$

V = vacancy

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Molar Production Rates

For gas species, we derive the molar production rates as functions of the:

- Desorption attempt frequency ω_{des}
- Temperature T
- Adsorption energy E_{ads}
- Other species concentrations

For bulk species, we derive the molar production rates as functions of the:

- Surface-to-bulk attempt frequency ω_{sb}
- Bulk-to-surface attempt frequency ω_{bs}
- Temperature T
- Adsorption, absorption and diffusion energies (E_{ads}, E_{abs} and E_{diff})
- Other species concentrations

For surface species, we derive the molar production rates based on the chemical balances in terms of the bulk and gas species molar production rates.

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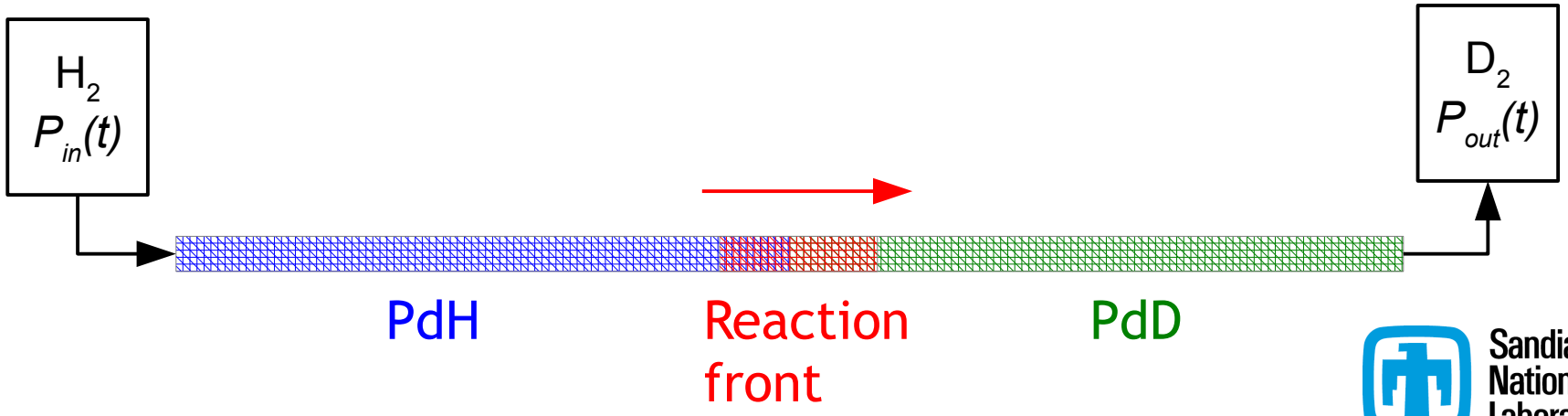
Mathematical Model of the Reactive Flow of Hydrogen Isotopes in a Porous PdH Particles Bed

- We consider a high length-to-width ratio bed (length = 2 cm and diameter = 2 mm) such that it can be modeled as a one-dimensional domain.
- The bed initially contains palladium deuteride (PdD) powder particles (particle radius = 1 μm).
- H_2 gas is injected in the bed
- The H_2 gas sweeps the bed transforming the the PdD into PdH while D_2 gas is collected at the reactor outlet.



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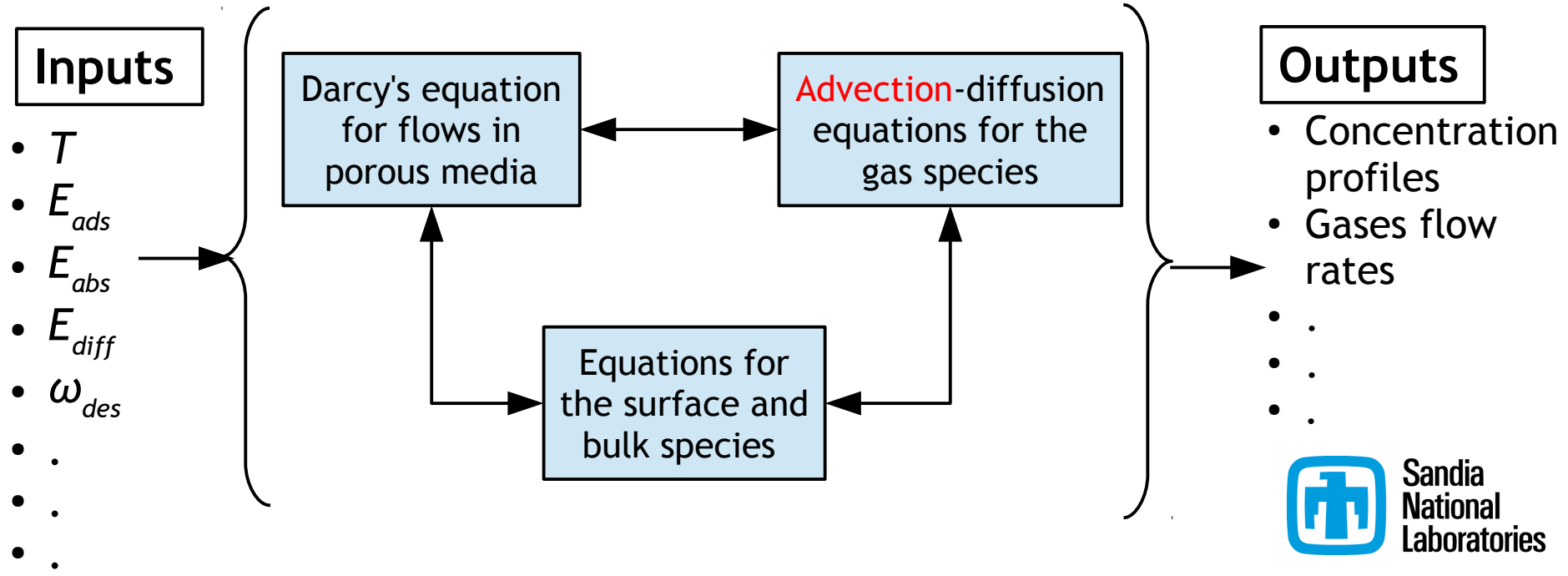
Mathematical Model of the Reactive Flow of Hydrogen Isotopes in a Porous PdH bed

- The isotope exchange in metal hydrides involves multiscale multiphysics transport phenomena.
- The derived molar production rates are used as inputs to a set of coupled and nonlinear ordinary, and partial differential equations.
- Given the bed aspect ratio, we neglect the heat conduction and assume a constant temperature throughout the bed.



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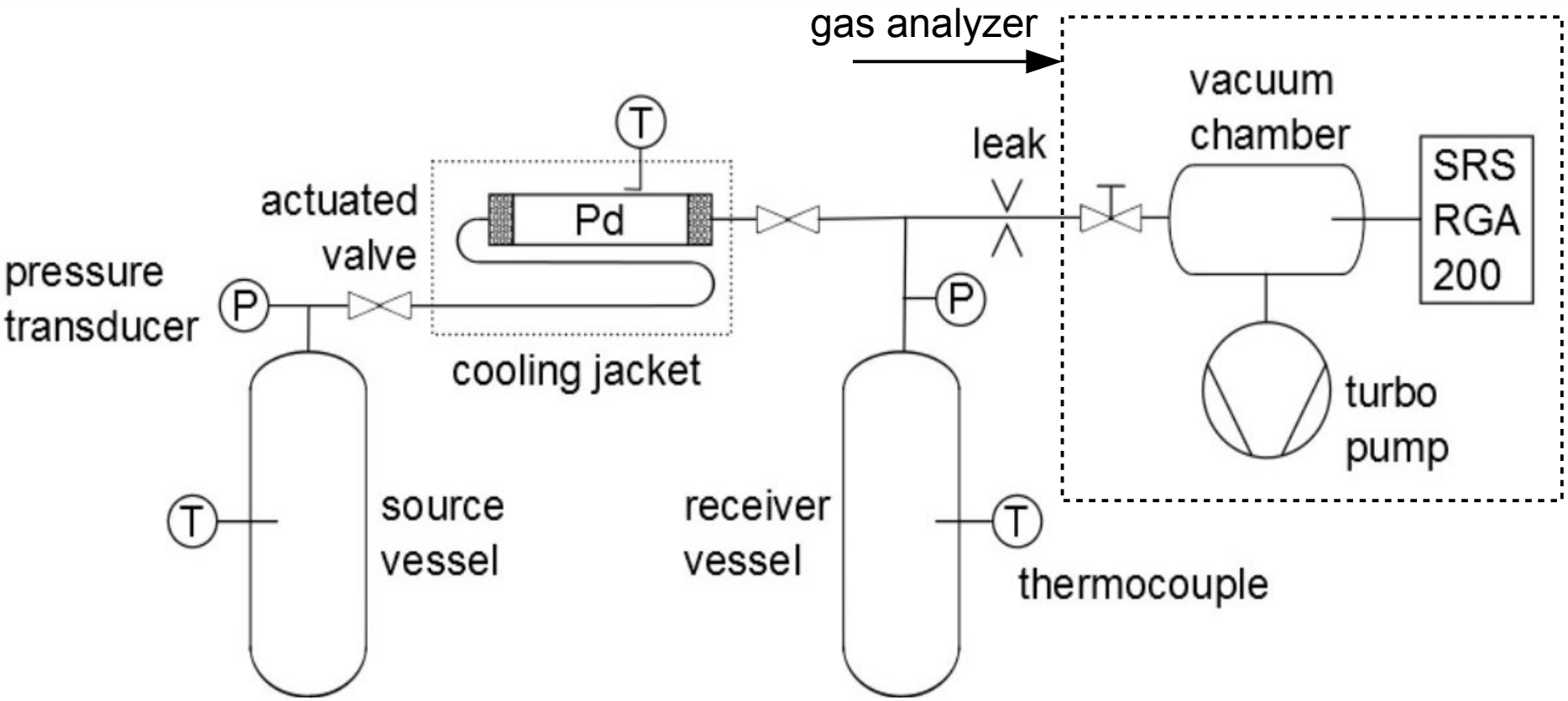
Setup of the Isotope Exchange Experiment



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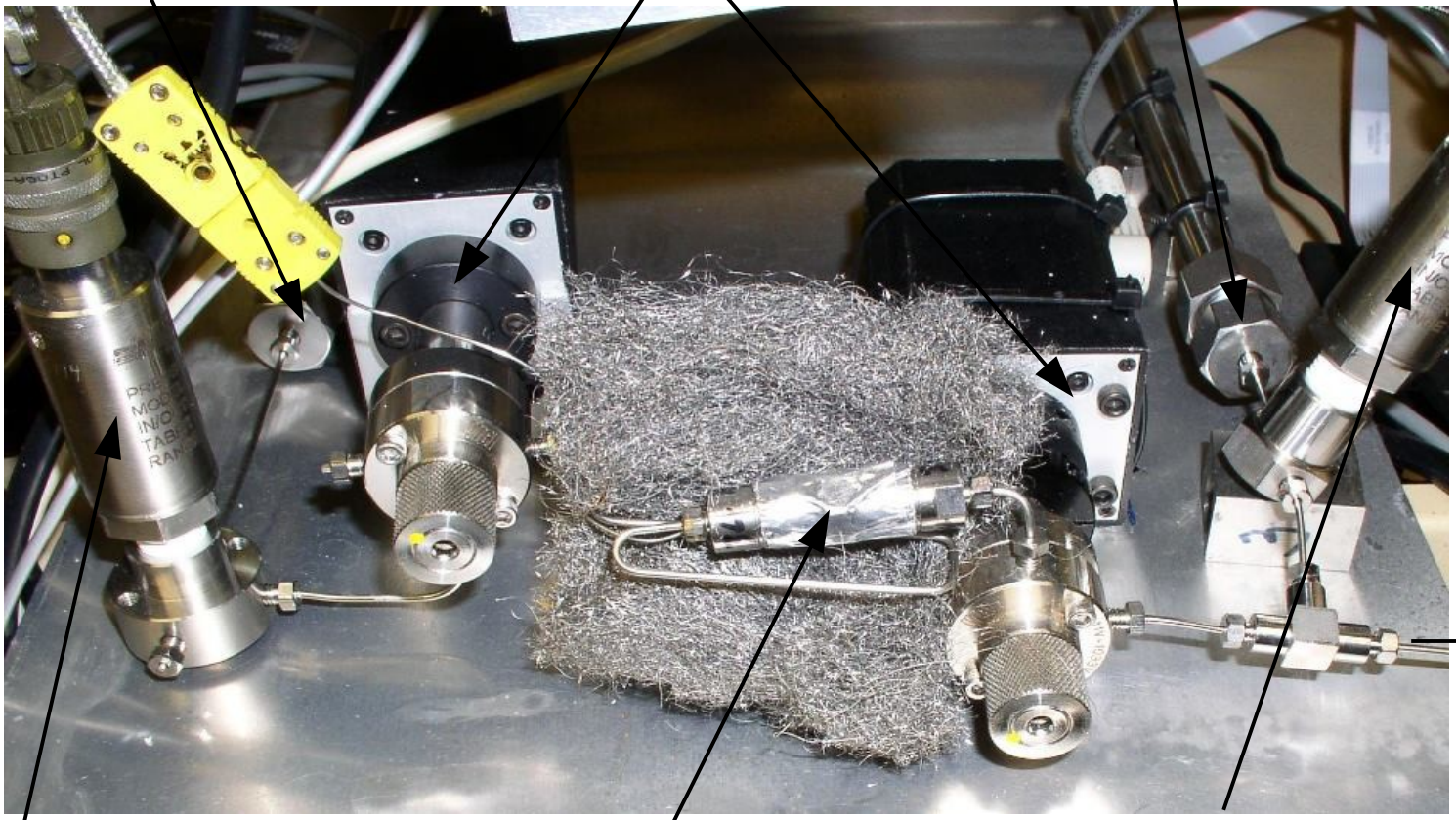
Setup of the Isotope Exchange Experiment



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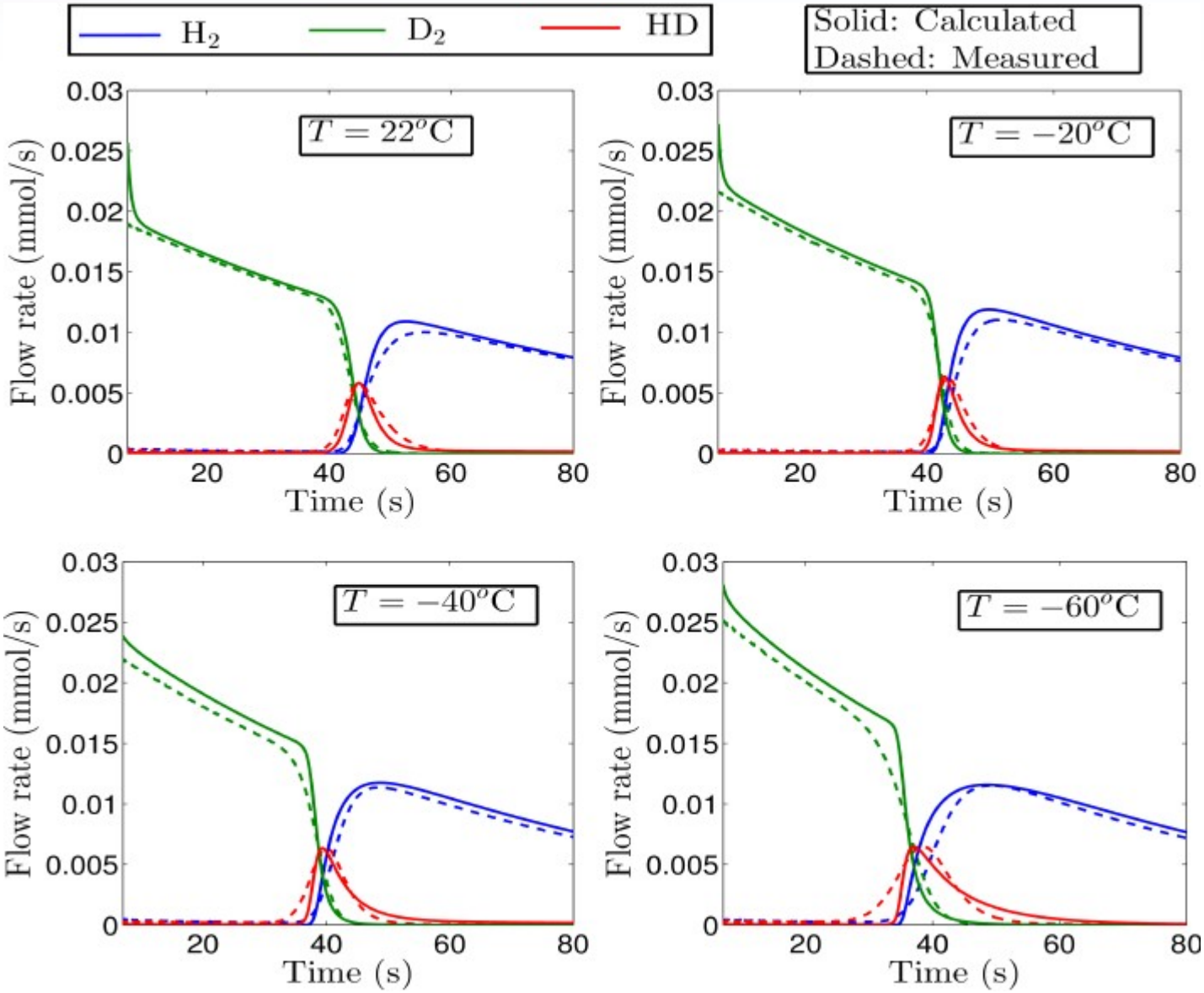
Model Validation

Gas Flow Rates at the Bed Outlet ($E_{ads,H}$ = 23.22 kJ.mol^{-1})



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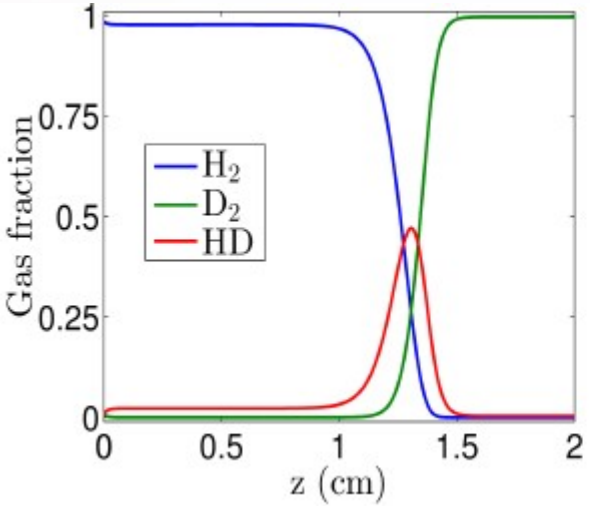
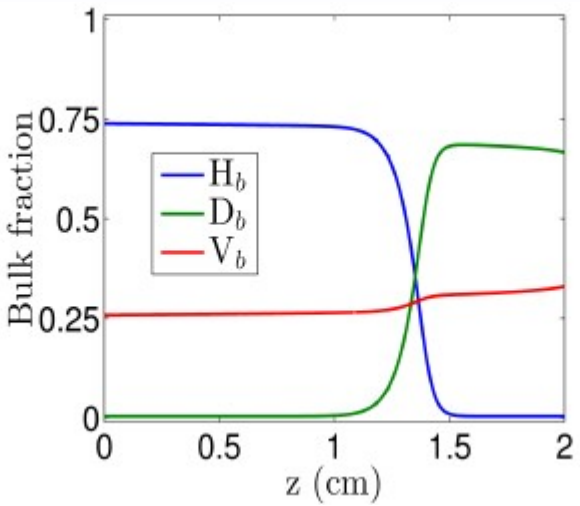
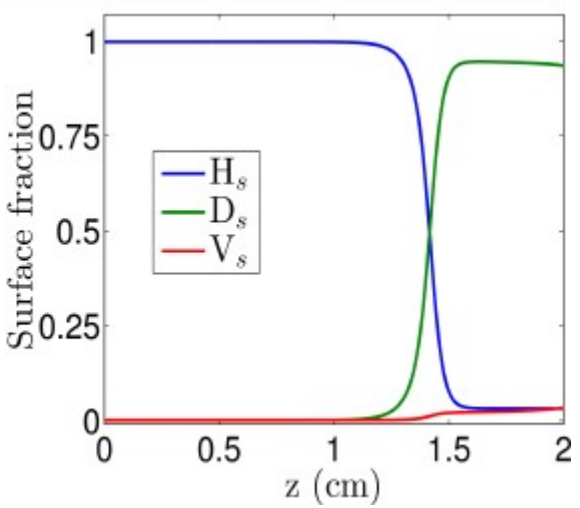
Concentration Profiles in the bed during the Isotope Exchange

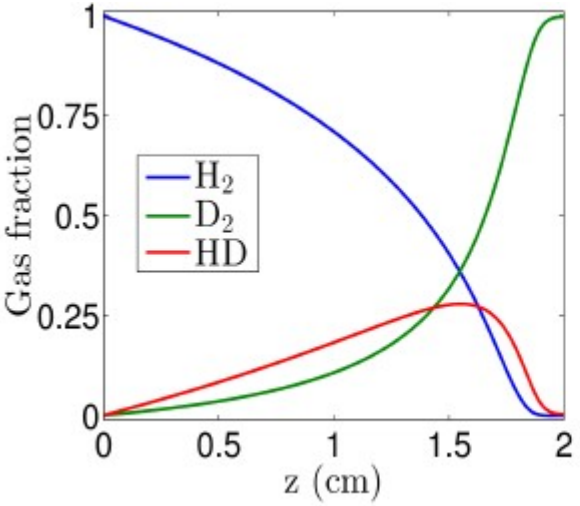
T=20°C

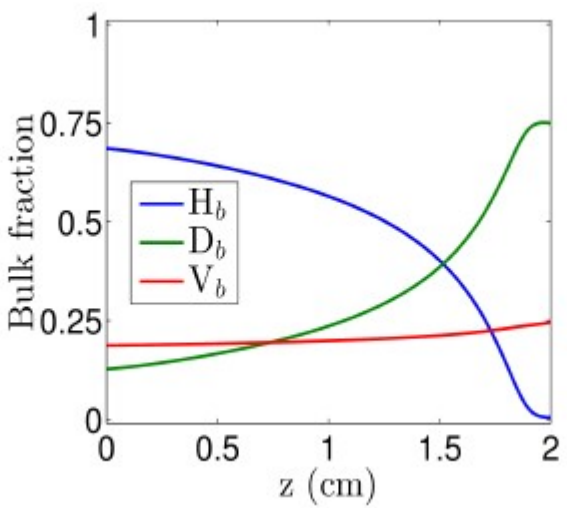


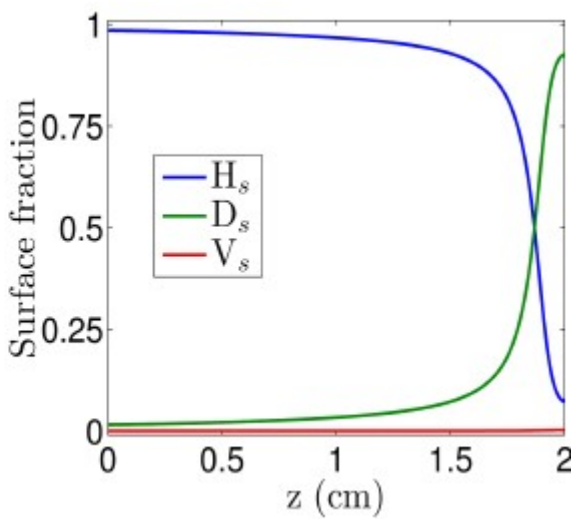




T=-60°C







Time = 20 s

$E_{ads,H}$ = 25.10 kJ.mol^{-1}

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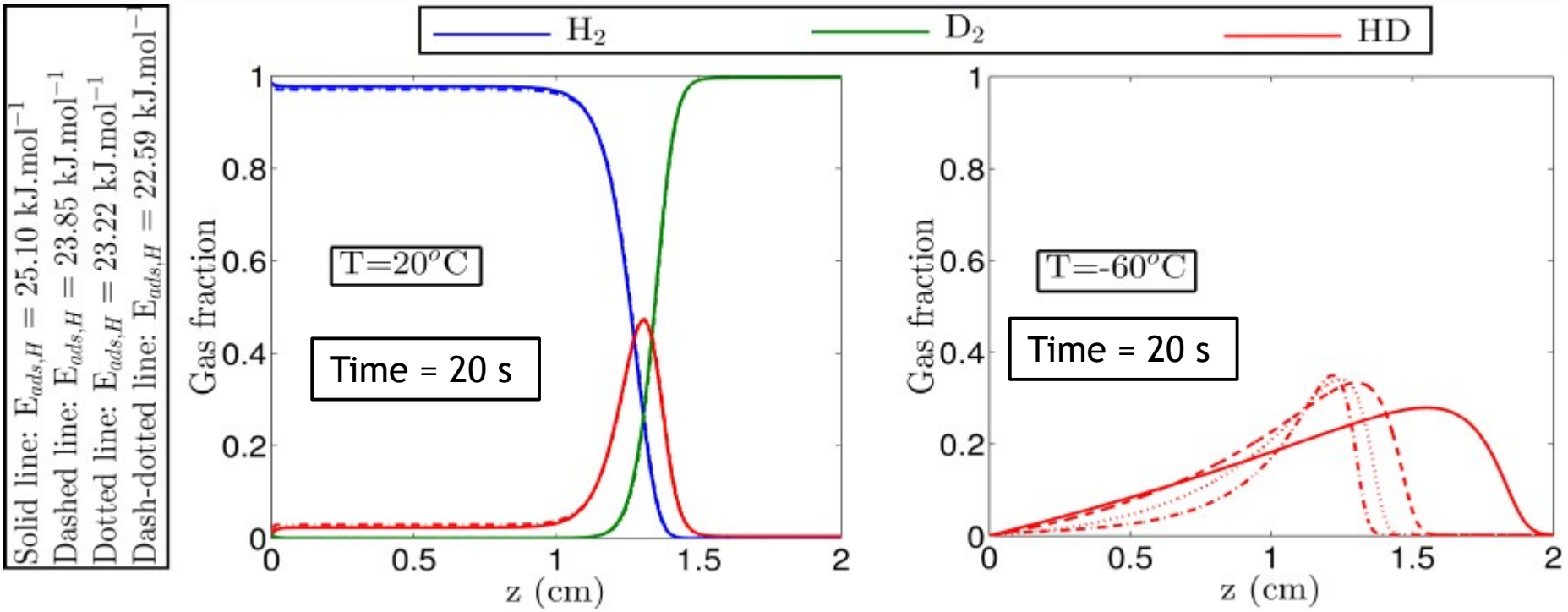
Parametric Study

Concentration Profiles in the bed during the Isotope Exchange



- The concentration profiles are highly dependent on the H_2 adsorption energy at low temperatures.
- The HD concentration profile width is related to the reaction kinetics speed.
- The reaction kinetics slow down with temperature and H_2 adsorption energy.

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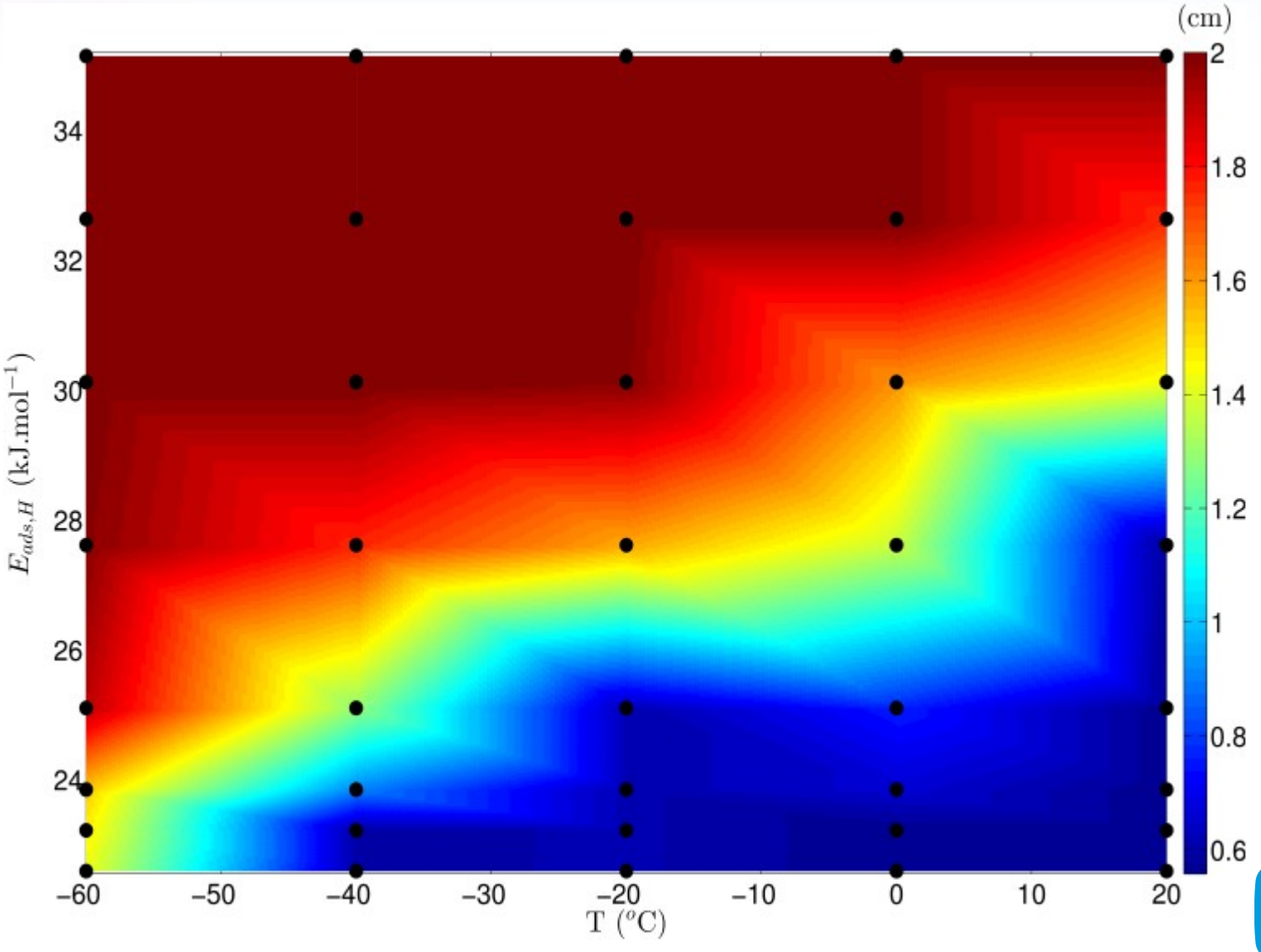
Parametric Study

Reaction Front Thickness



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Conclusion

- We developed a multiphysics mathematical model of the hydrogen isotope exchange in palladium hydride.
- The numerical formulation of the model is general and can account for temperature variations and different bed geometries and aspect ratios.
- A unique feature in the formulation is that it allows to account for all absorption, adsorption and diffusion activation energies that can be adjusted depending on the state of the metal surface.
- The results predicted by the model are insensitive to the H_2 surface adsorption energy ($E_{ads,H}$) at high temperatures.
- The results are highly dependent on $E_{ads,H}$ at low temperatures ($T \leq 40^{o}C$).

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Acknowledgments

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Thank you for your attention!

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