Theory of Hydrogen Storage in Complex Hydrides

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Background and Model

- Experimental evidence has shown that mass transport of metal species may be rate-limiting in some hydrogen storage reactions[1]

- We model mass transport at the atomic level using density function theory calculations, studying point defect formation and mobility

  The activation energy for a flux of point defects, J, is
  $$E_{act} = -k_B \frac{\partial \ln|J|}{\partial (1/T)}$$

  The flux is calculated from $J = -D\nabla C$
  D: diffusivity of the defect
  C: concentration of the defect

- Calculated activation energies can be compared to experimentally obtained values to determine if mass transport is rate limiting and also used to screen candidate reactions for those that have low kinetic barriers

1. O. Kircher and M. Fichtner, J. Appl. Phys. **95**, **2004**, 7748.

Chemical Potential Gradients in Sodium Alanate
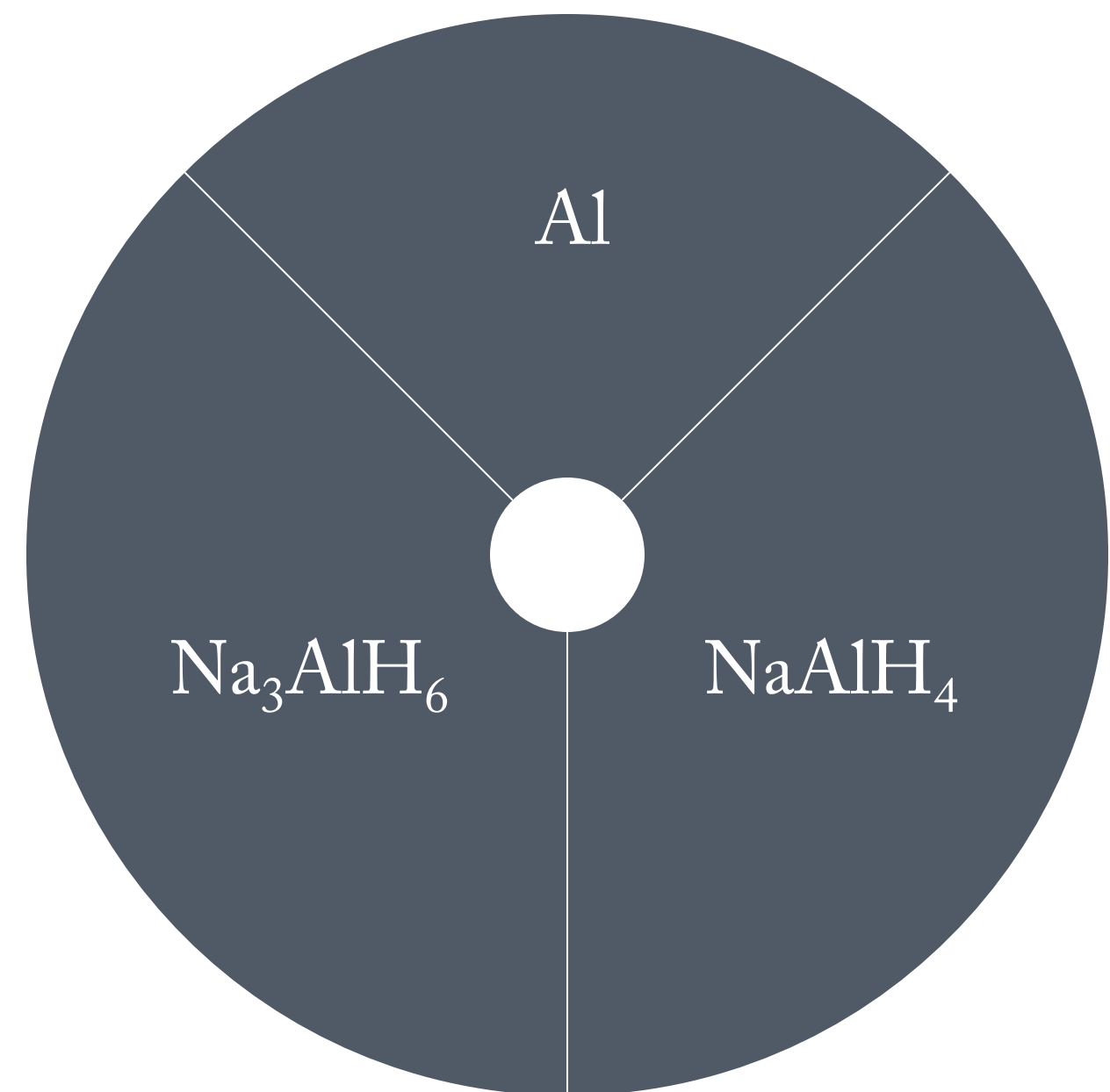
Tetrahydride/hexahydride interface

$$\mu_{Na}^{TH} + \mu_{Al}^{TH} + 4\mu_{H}^{TH} = F(NaAlH_4)$$
$$3\mu_{Na}^{TH} + \mu_{Al}^{TH} + 6\mu_{H}^{TH} = F(Na_3AlH_6)$$
$$2\mu_{H}^{TH} = F(H_2)$$

Tetrahydride/aluminum interface

$$\mu_{Na}^{TA} + \mu_{Al}^{TA} + 4\mu_{H}^{TA} = F(NaAlH_4)$$
$$\mu_{Al}^{TA} = F(Al)$$
$$2\mu_{H}^{TA} = F(H_2)$$

Hexahydride/aluminum interface

$$3\mu_{Na}^{HA} + \mu_{Al}^{HA} + 6\mu_{H}^{HA} = F(Na_3AlH_6)$$
$$\mu_{Al}^{HA} = F(Al)$$
$$2\mu_{H}^{HA} = F(H_2)$$

Chemical potential gradients drive mass transport

$$\mu_{Na}^{TA} - \mu_{Na}^{TH} = -\frac{3}{2}\Delta F_{rxn}$$
$$\mu_{Al}^{TA} - \mu_{Al}^{TH} = \frac{3}{2}\Delta F_{rxn}$$

Formation Energies and Concentrations

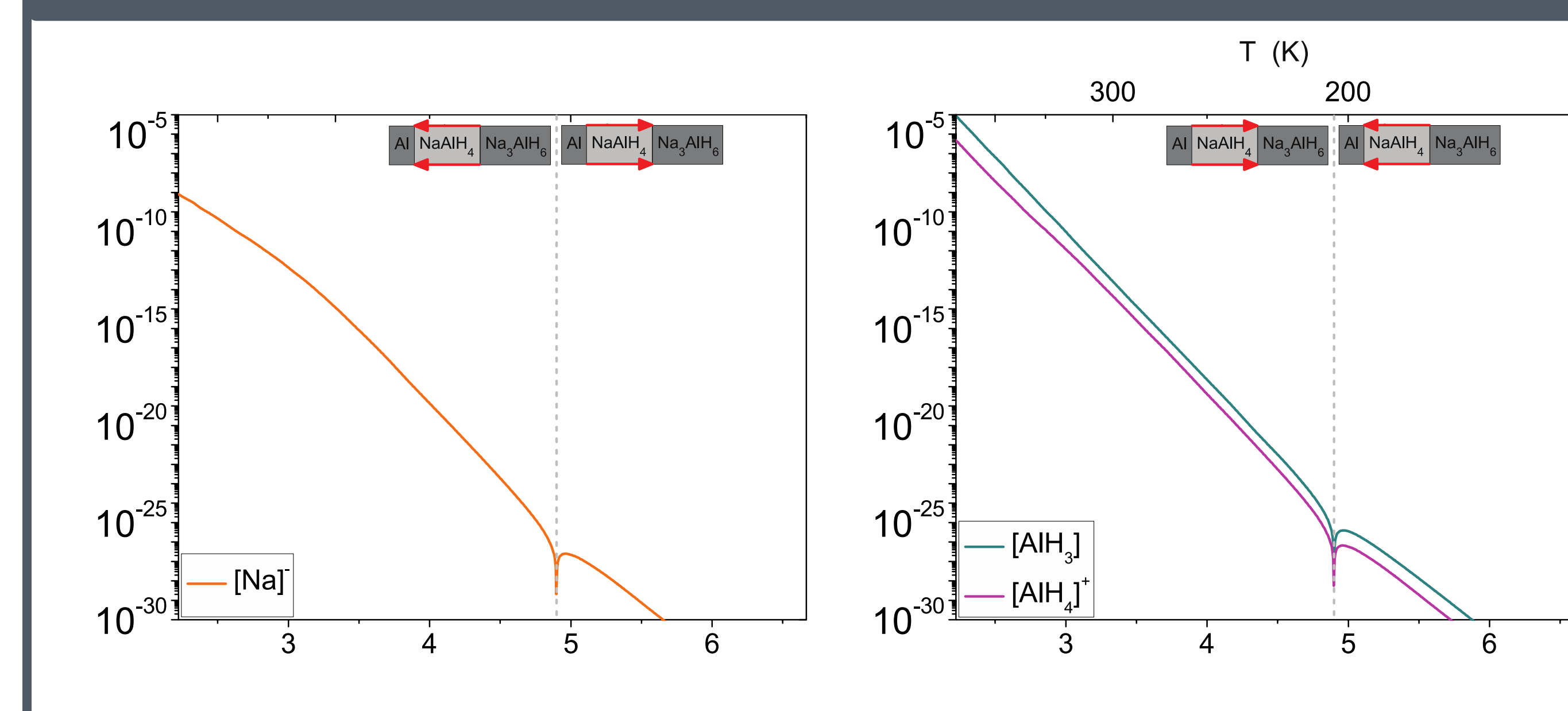$$\Delta F_{form} = \Delta F(supercell) - \sum_{i}^{elements} n_i \mu_i + q\varepsilon_F$$

ΔF_{form}: formation energy
$\Delta F(supercell)$: change in supercell energy
$n_i\mu_i$: chemical potential of atoms in defect
$q\varepsilon_F$: charge of defect and Fermi level

$$C = N^{eq} N^{sites} e^{-\Delta F_{form}/k_B T}$$

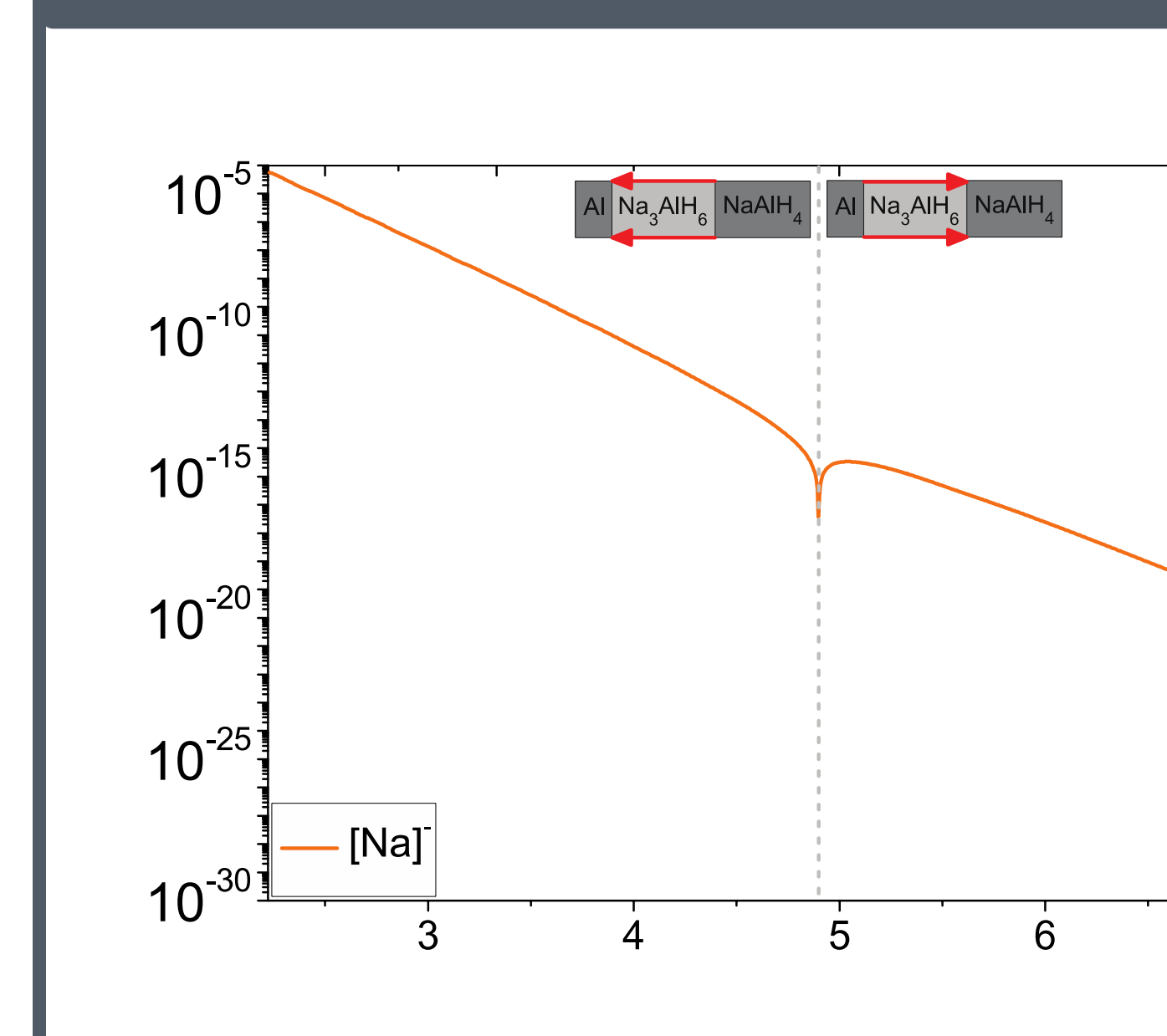N^{eq}: number of equivalent configurations
N^{sites}: number of sites

Mass Transport: $3NaAlH_4 \rightarrow Na_3AlH_6 + 2Al + 3H_2$

Largest defect fluxes through NaAlH₄

Largest defect flux through Na₃AlH₆

K. Michel and V. Ozolins, *J. Phys. Chem. C*, 115, **2011**, 21443.
K. Michel and V. Ozolins, *J. Phys. Chem. C*, 115, **2011**, 21454.
K. Michel and V. Ozolins, *J. Phys. Chem. C*, 115, **2011**, 21465.
K. Michel and V. Ozolins, *In Preparation*.

- The largest fluxes of metal containing defects in NaAlH₄ are negatively charged Na vacancies, neutral AlH₃ vacancies, and positive AlH₄ vacancies

- In Na₃AlH₆, negatively charged Na vacancies have the largest flux and this is larger than any in NaAlH₄

- The calculated activation energy for Na transport in Na₃AlH₆ during dehydrogenation is **70 kJ/mol**, compared to an overall activation energy of 80 kJ/mol H₂ measured experimentally in Ti-doped samples[2]

- Na vacancy transport is identified as the rate-limited step in the dehydrogenation of Ti-doped samples

2. K. Gross *et. al.* J. Alloy. Compd. 330, **2002**, 683

Mass Transport: $2Li_3AlH_6 \rightarrow 6LiH + 2Al + 3H_2$

Concentration gradients in Li₃AlH₆
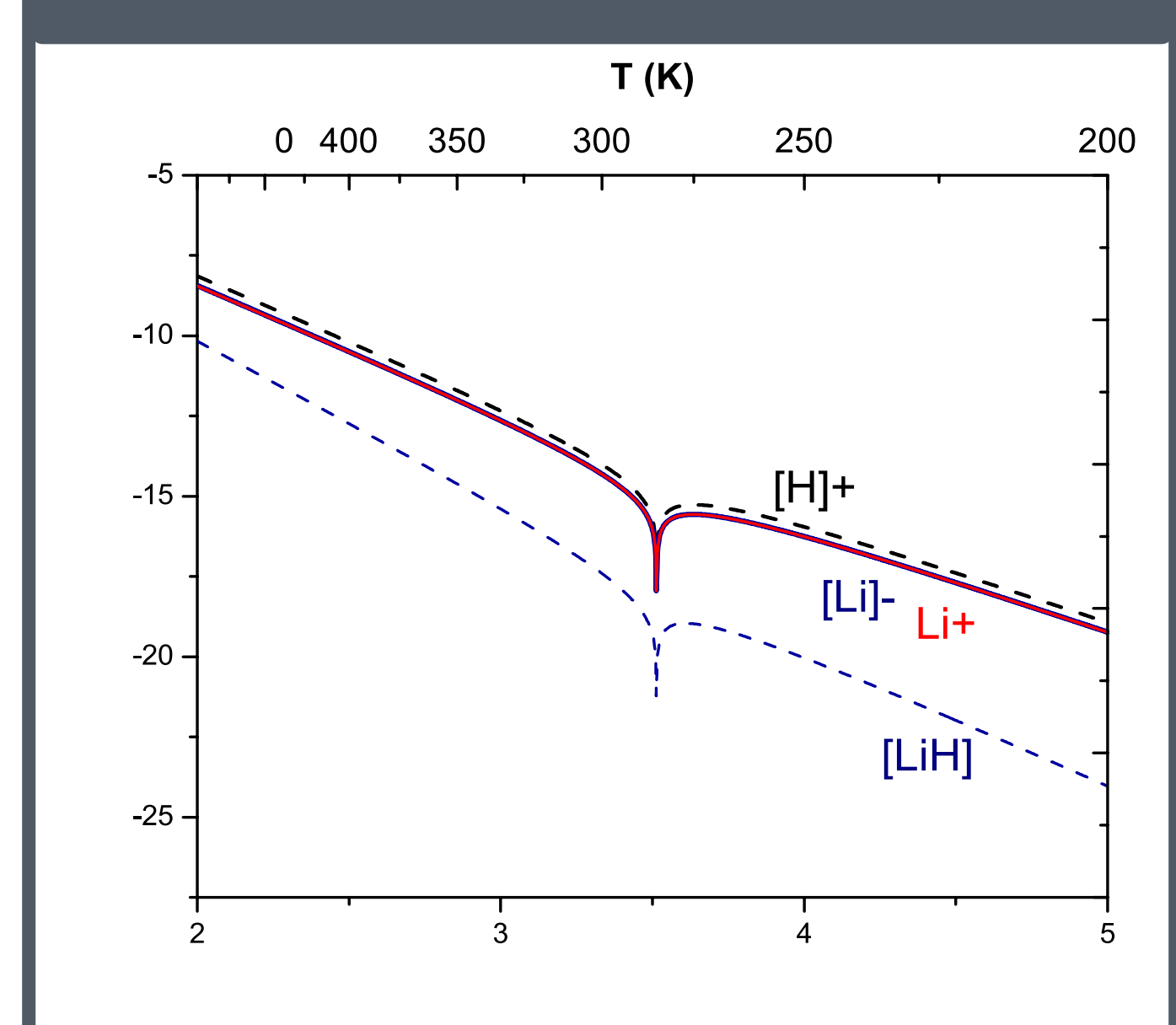
B. Rolih and V. Ozolins, *In Preparation*.

- Negatively charged Li vacancies and positively charged H vacancies and interstitial Li have the largest concentration gradients
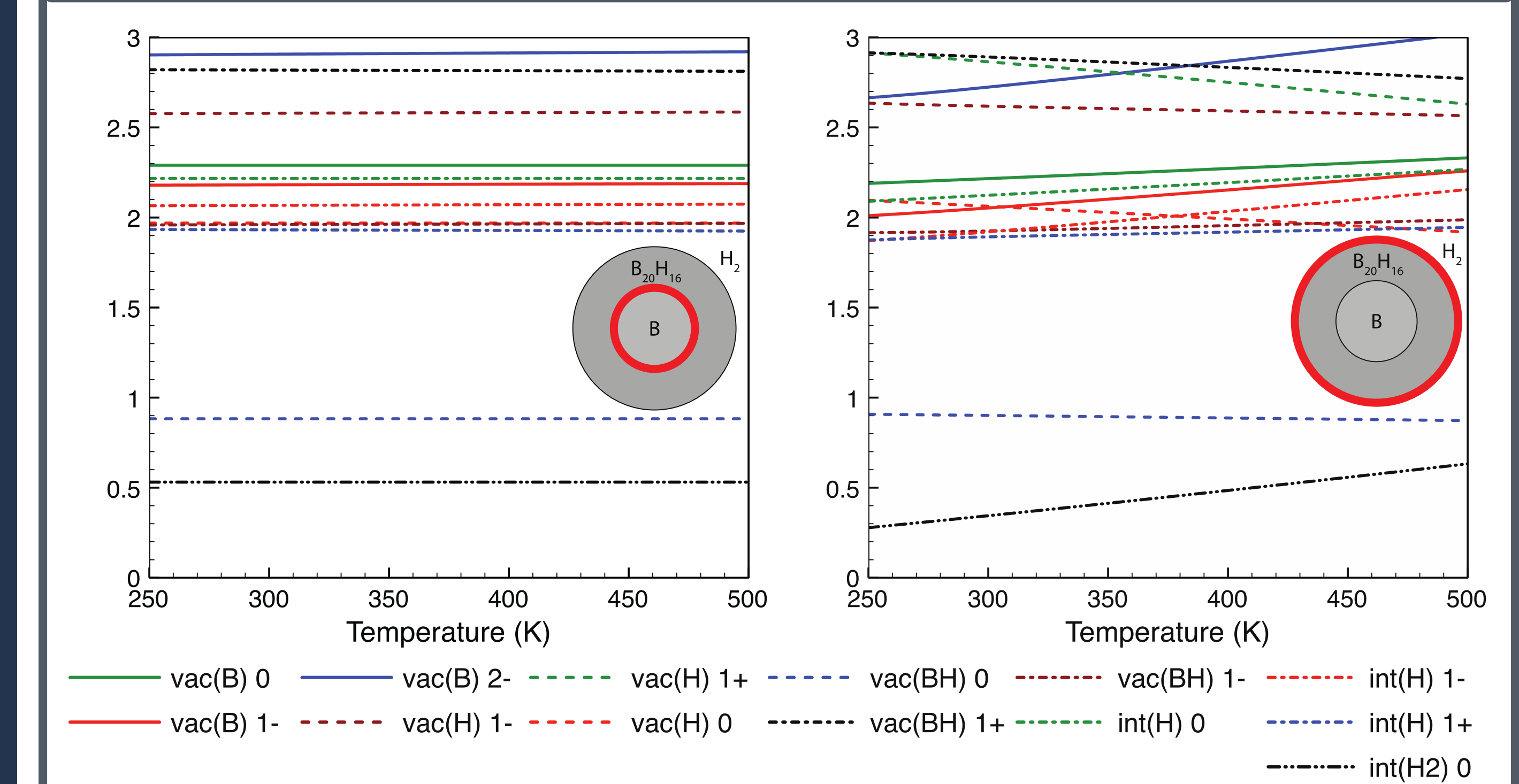
- Metal transport will be dominated by Li-containing defects

- The formation enthalpies of these Li defects are both **86 kJ/mol** so that with the addition of the diffusion barrier, will likely match well with the experimental activation energy for the reaction, 100 kJ/mol[3]

3. R.A. Varin and L. Zbroniec J. Alloy. Compd. 509, **2010**, S736

Mass Transport: $B_{20}H_{16} \rightarrow 20B + 8H_2$

Defect formation energies in B₂₀H₁₆

vac(B) 0 — vac(B) 2- — vac(H) 1+ — vac(BH) 0 — vac(BH) 1- — int(H) 1-
vac(B) 1- — vac(H) 1- — vac(H) 0 — vac(BH) 1+ — int(H) 0 — int(H) 1+
int(H2) 0

- The lowest formation energy of all defects is of neutral H₂ as an interstitial defect. This type will dominate mass transport and is sufficient for carrying the reaction to completion.

- The formation enthalpy of interstitial H₂ is 51 kJ/mol under dehydrogenation conditions and 3 kJ/mol for rehydrogenation. The diffusion barrier can be added to obtain the activation energy.

K. Michel, Y. Zhang, and C. Wolverton, *In Preparation*.

Nucleation Model (Future Work)

Initial configuration
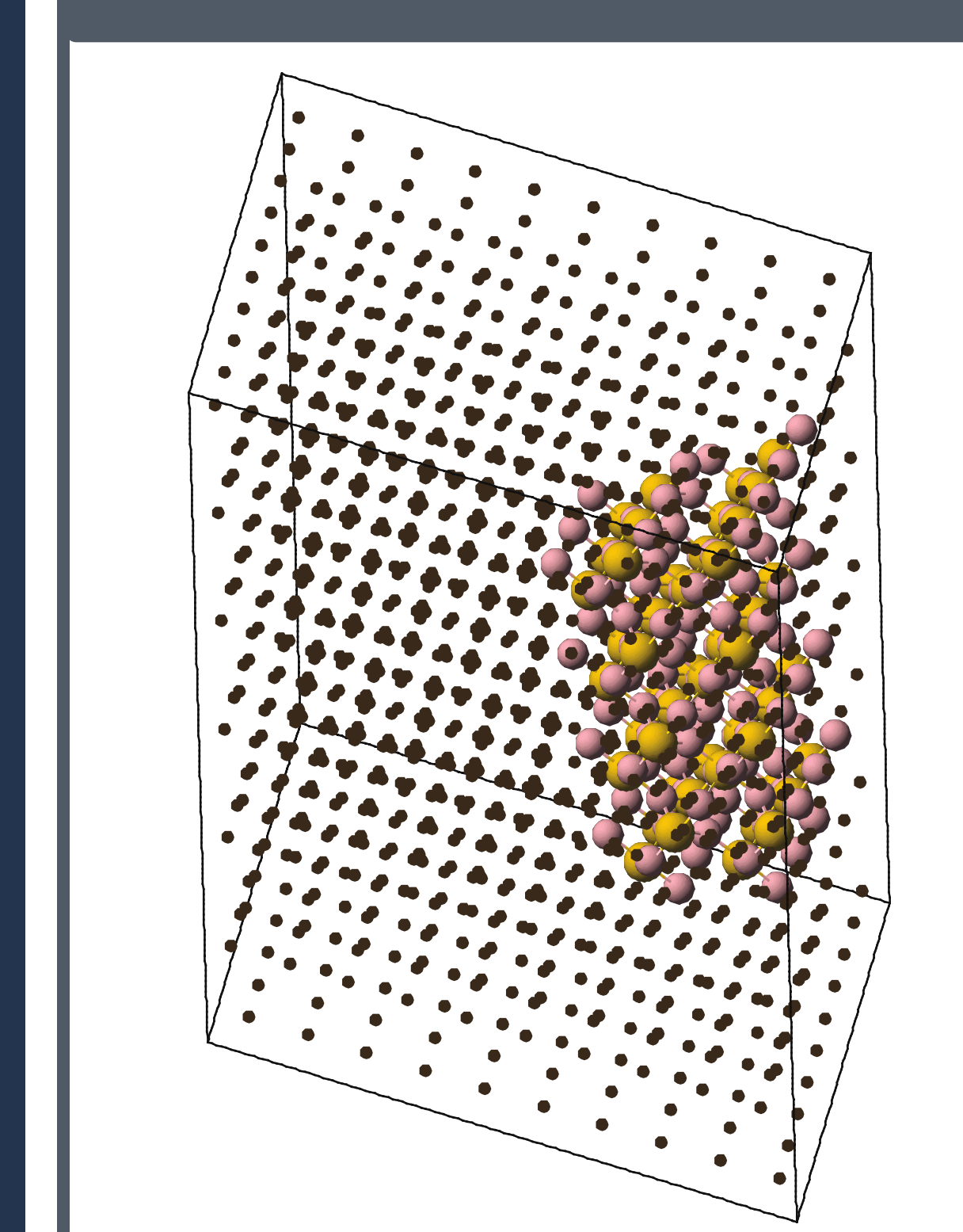
- Model nucleus as a particle of one phase embedded in another (left image)

- Develop classical potential suited to each system from more accurate first-principles calculations of bulk and interface structures

- Using stochastic methods, search for the ground-state configuration of the nucleus

- Run more accurate first-principles calculations on the interfaces that are found most often since these should be the ones that are lowest in energy

- Use the interfacial and bulk energies to obtain the nucleation barrier and compare to experimental activation energies

Acknowledgement

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