Grand Canonical Monte Carlo Simulation of Competitive Adsorption for the Haber-Bosch Process

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Introduction

The Haber-Bosch process is arguably the most important chemical reaction in modern agriculture. The amount of ammonia it is capable of producing allows for industrial farming on a scale capable of sustaining eight billion people. To aid in the optimization of this process, I have simulated the competitive adsorption of hydrogen and nitrogen onto a catalyst's surface using the Python coding language and the grand canonical Monte Carlo, a computational technique where the system is modelled as a rectangular lattice. A Metropolis algorithm is then utilized to determine if a particle is added or removed from the lattice, changing the lattice's energy, with this change in energy determining the likelihood of a particle's addition or removal. This is then repeated a set number of times. The technique was used to model multiple possible systems of interactions between hydrogen and nitrogen, with varying chemical potentials of hydrogen and temperatures. By exploring the generated phase diagrams and resulting final lattices, it is possible to determine the most optimal conditions with which to initialize the Haber-Bosch process.

Methodology

The grand canonical Monte Carlo was started by initializing a six-by-six array of values to represent the rectangular lattice. This array models the contents of each box on the lattice using a number, with 0 indicating that the box is empty, 1 indicating it contains a hydrogen, and 2 indicating it contains a nitrogen. This was performed using the Python package NumPy. Then, the directly adjacent boxes of each box of the lattice is determined. This allows for the modelling of the interactions between particles within adjacent boxes. In this case, the particle interacts with the four boxes along its sides. The boxes also interact periodically, meaning that the first box in a row or column interacts with the last box in that row or column, and vice versa.

The system then decides to either attempt to add or remove a particle from the lattice. This is determined randomly, with equal chance to attempt an addition or removal. If addition is chosen, and the lattice isn't full, then a random empty position on the lattice is selected. The system then randomly chooses to attempt to add hydrogen or nitrogen, then it calculates the system's change in energy from this addition based on the chemical potential of the added particle and the interaction energy of the particle with its neighbors. The probability of the addition being accepted is then calculated using Equation 1:

$$prob = \frac{N_0}{N_s+1} \times e^{-\beta(\Delta E-\mu_s)} \quad (1)$$

$$\beta = \frac{1}{k_B T} \quad (2)$$

where N_0 is the number of empty sites, N_s is the number of sites occupied by the species being added, β is the inverse absolute temperature, calculated as seen in Equation 2, ΔE is the difference in energy, and μ_s is the external chemical potential of the species being added. If the addition is accepted, then the position in the array is changed to the particle's number (1 for hydrogen, 2 for nitrogen).

For particle removal, the system randomly chooses an occupied position on the lattice, then calculates the change in energy if the particle is removed with the same calculation as in particle addition. The probability of the removal being accepted is calculated with Equation 3:

$$prob = \frac{N_s}{N_0+1} \times e^{-\beta(\Delta E+\mu_s)} \quad (3)$$

If the removal is accepted, the position in the array is changed to zero, indicating that it's empty. This algorithm is repeated 10000 times to generate a final lattice and track the coverage of every species on the lattice over the entire simulation.

This simulation was run with five different sets of possible interaction energies between and among particles of hydrogen and nitrogen: "ideal", "attraction", "repulsion", "immiscible", and "like-dissolves-unlike". The interaction parameters entered into the simulation for each can be seen in Table 1.

System	μ_{HH}	μ_{NN}	μ_{HN}
Ideal	0	0	0
Attraction	-0.05	-0.05	-0.05
Repulsion	0.05	0.05	0.05
Immiscible	-0.05	-0.05	0.05
Like-dissolves-unlike	0.05	0.05	-0.05

Table 1. The interaction energies between two hydrogens, two nitrogens, and hydrogen and nitrogen for every system simulated. All energies are in electron volts.

The "ideal" system had interaction energies of 0 between all particles, "attraction" had negative interaction energies between all particles, and "repulsion" had positive interactive energies between all particles. "Immiscible" had negative interaction energies for hydrogen and nitrogen when interacting with themselves, but positive energy when interacting with each other. The "like-dissolves-unlike" system had the opposite, positive

interaction energy when hydrogen interacted with another hydrogen, or nitrogen with nitrogen, but negative when hydrogen interacted with nitrogen.

Results

All systems were simulated 49 times, all with a nitrogen chemical potential of -0.1 eV. The hydrogen chemical potential was varied uniformly between -0.2 and 0 eV, while the temperature, multiplied with the Boltzmann constant, was similarly varied between 0.001 and 0.019 eV/k. The resulting heat maps below are of the average coverage of each species for the final 1000 steps of the simulation, with a few select final lattices shown for comparison.

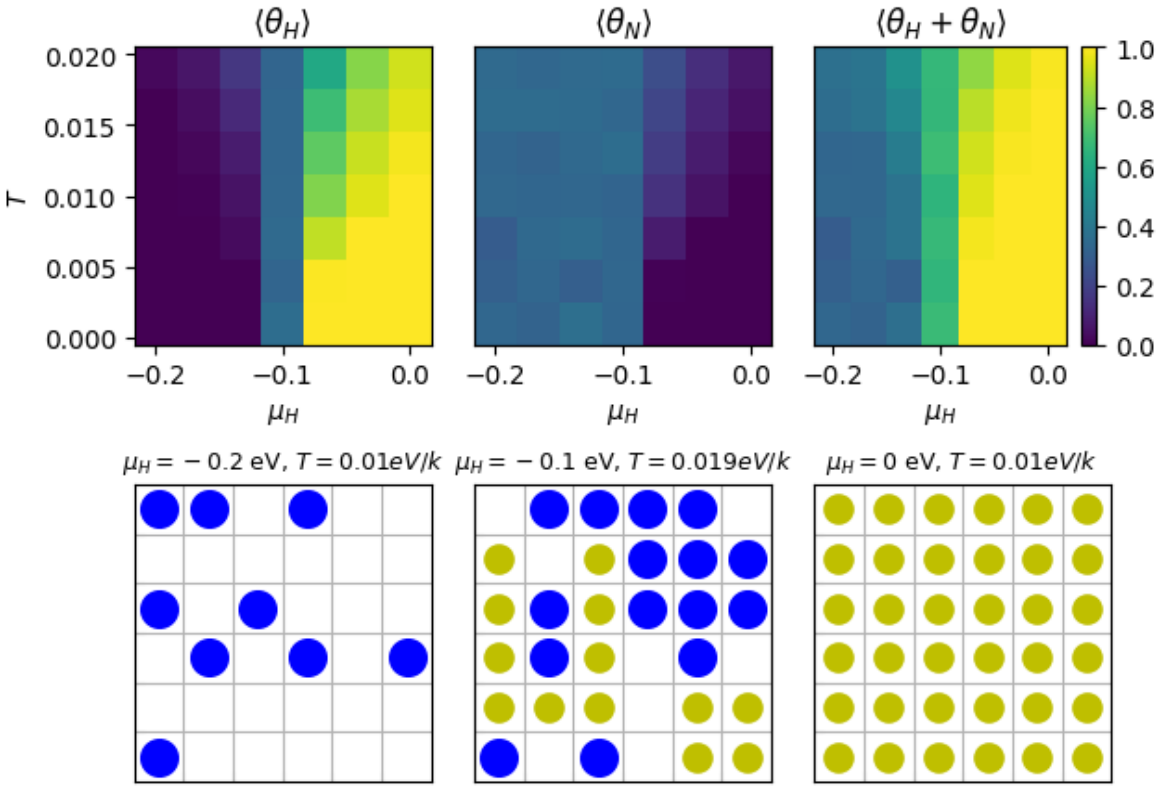

Figure 1. Heat maps and final lattice samples for the coverages of hydrogen and nitrogen in the "ideal" system.

For the "ideal" system, the ratio of hydrogen to nitrogen can be easily controlled by varying the chemical potential of hydrogen and the temperature, as seen in Figure 1. The best ratio of hydrogen to nitrogen for ammonia production is 3 to 1, so the best conditions to achieve this, assuming a nitrogen chemical potential of -0.1 eV, are a hydrogen potential of -0.07 eV and a temperature around 120 K.

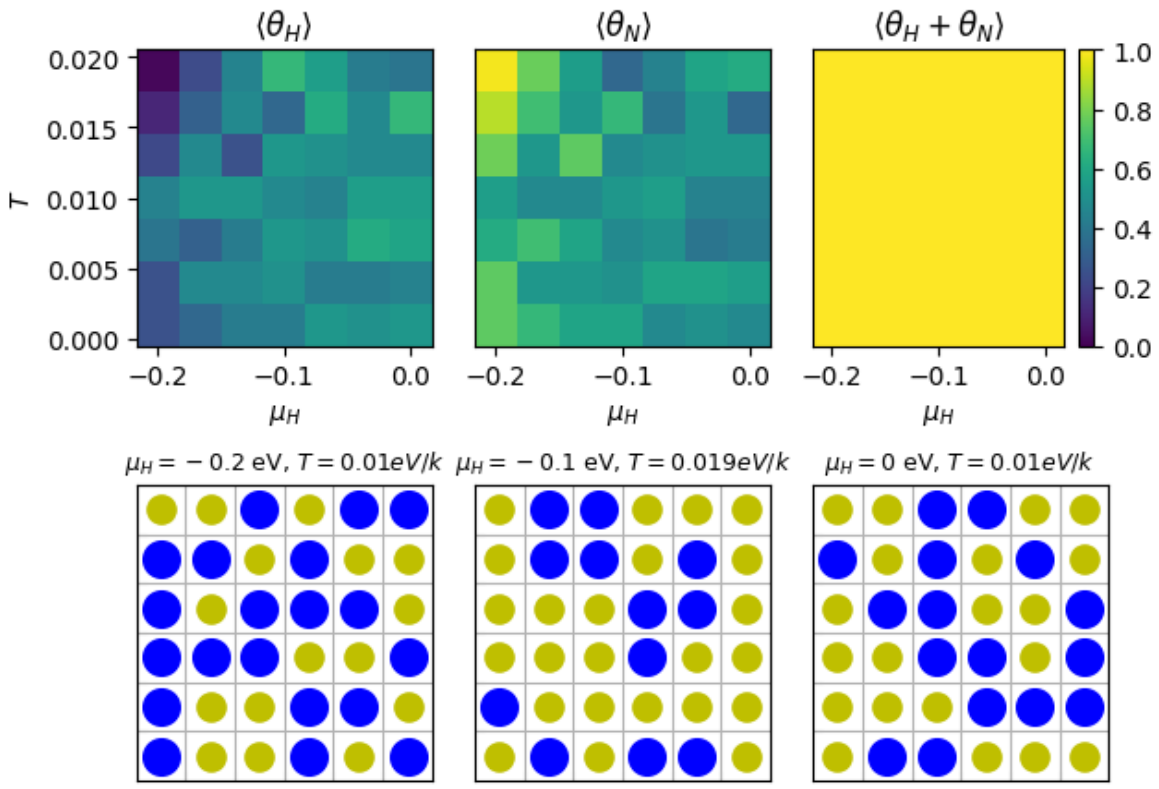

Figure 2. Heat maps and final lattice samples for the coverages of hydrogen and nitrogen in the "attraction" system.

If hydrogen and nitrogen interact attractively, the simulation results suggest that there is little possibility of controlling the ratio of hydrogen to nitrogen with the conditions tested. As seen in the heat maps in Figure 2, there is little correlation between the temperature, hydrogen chemical potential, and ratio of hydrogen to nitrogen. The only potential correlation is the amount of nitrogen on the lattice decreases as temperature decreases and hydrogen chemical potential increases, however it isn't defined enough to be considered particularly valuable, and operating the adhesion at temperatures near absolute zero would be hideously expensive.

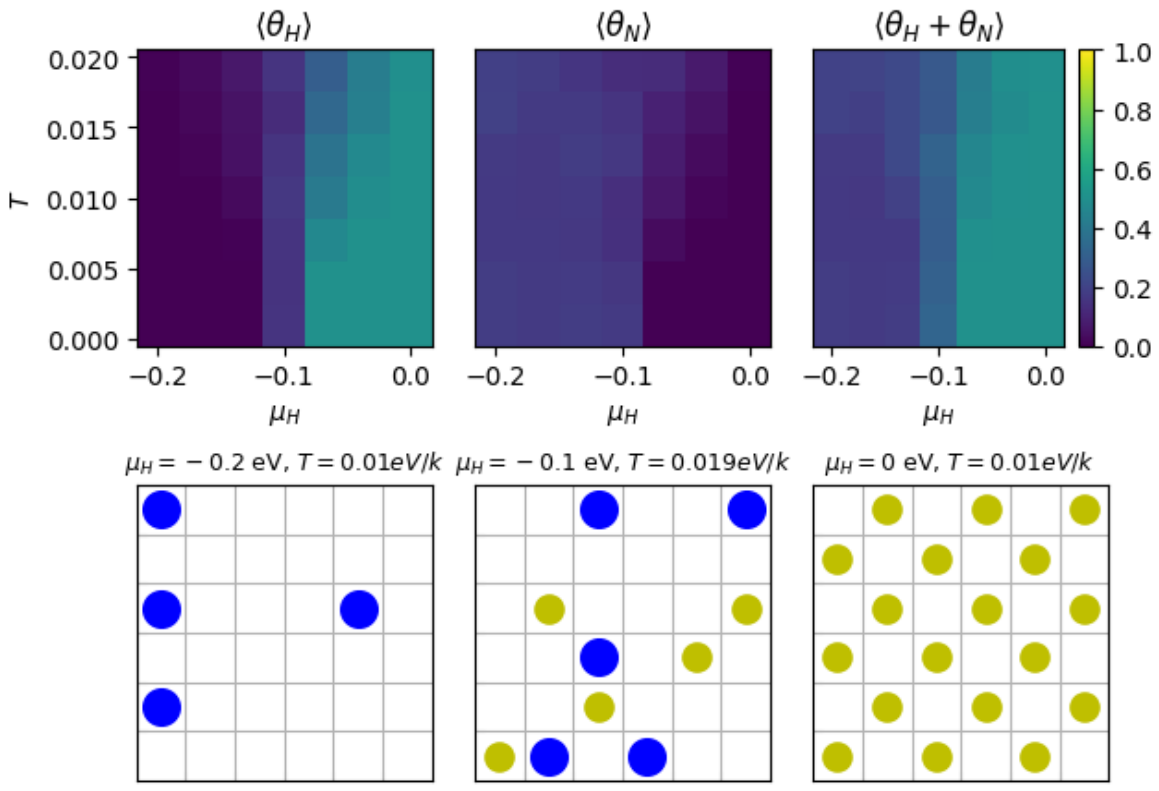

Figure 3. Heat maps and final lattice samples for the coverages of hydrogen and nitrogen in the "repulsion" system.

If hydrogen and nitrogen repulse both themselves and each other, then the ratio between the two is similar to that of the "ideal" system. The same recommendation from the "ideal" system is valid here as well: μ_H = -0.07 eV and T = 120 K. However, the "repulsion" system has only around half as many adhered particles for any set of parameters as the "ideal" system. Experimental testing would be needed to discern which system hydrogen and nitrogen follows, and thus whether or not a larger surface would be necessary to obtain the same amount of adhered particles.

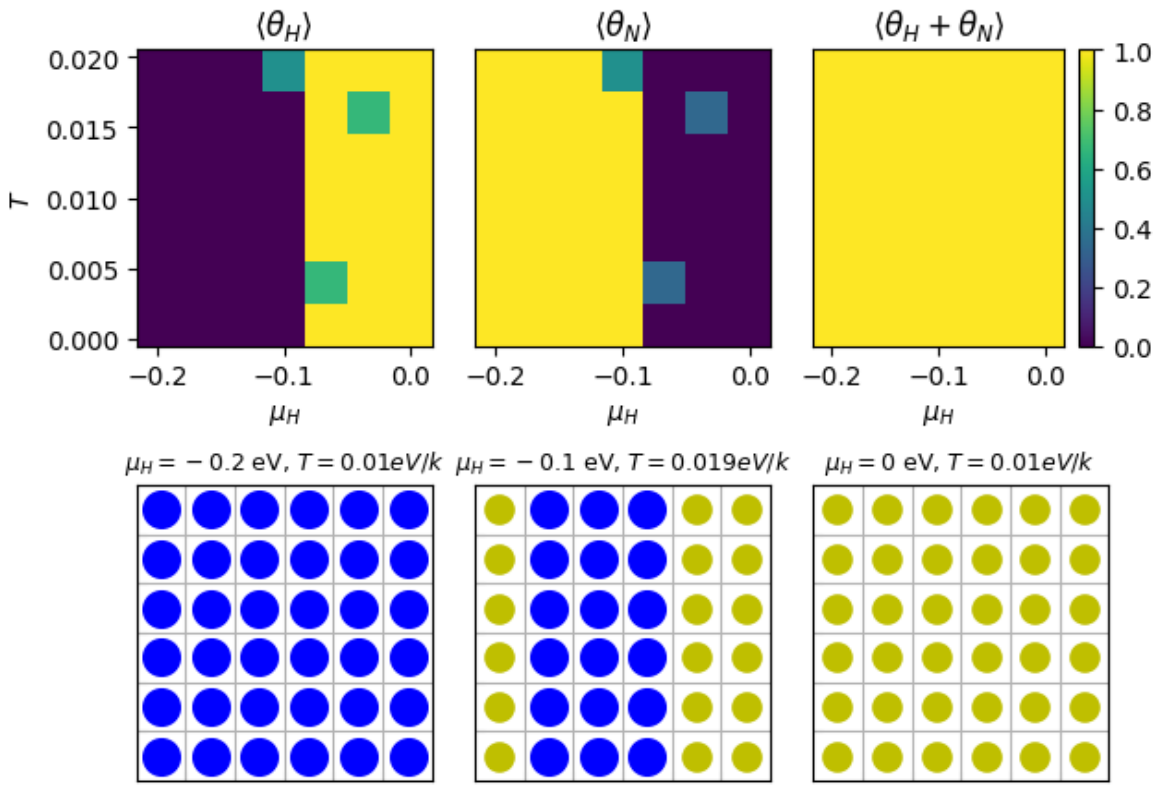

Figure 4. Heat maps and final lattice samples for the coverages of hydrogen and nitrogen in the "immiscible" system.

If hydrogen and nitrogen are immiscible, then it is unlikely that a favorable ratio of the two can be achieved. In all but 3 of the 49 simulations, only one of the two elements was bound to the entire lattice at the end of the simulation. If these elements are immiscible with each other, then another approach should be taken to better optimize the Haber-Bosch process.

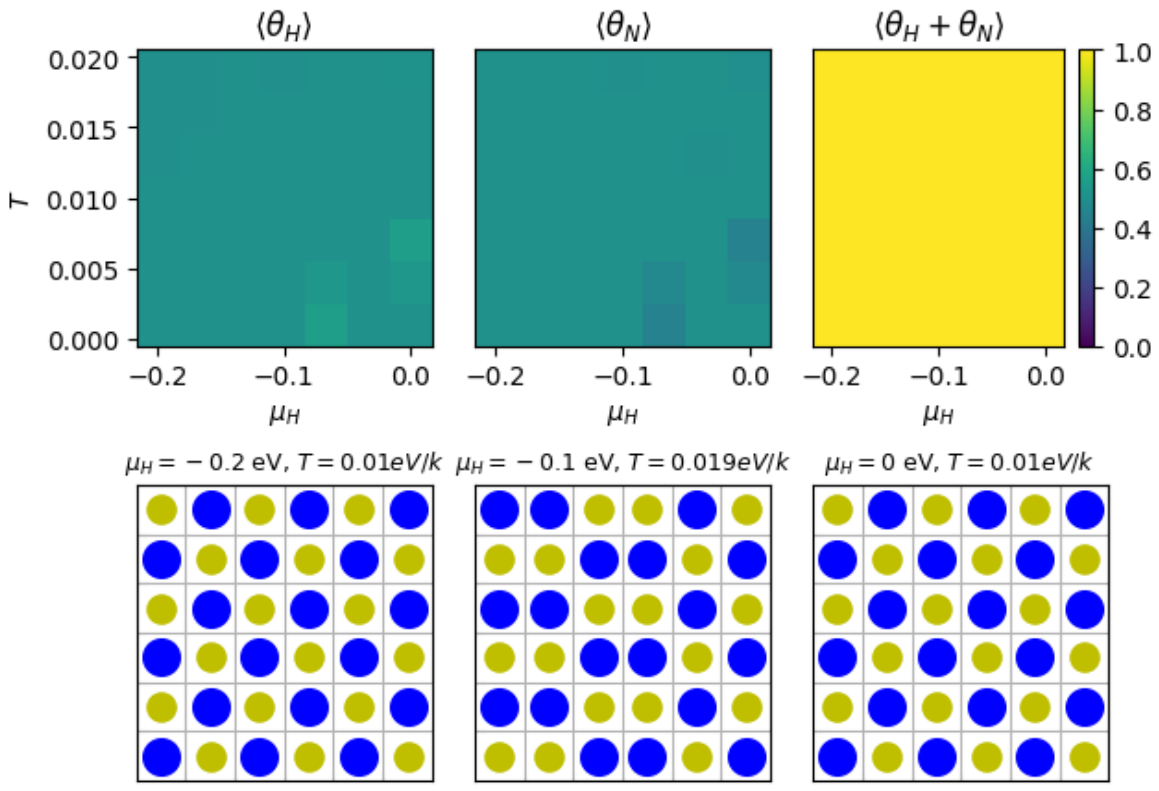

Figure 5. Heat maps and final lattice samples for the coverages of hydrogen and nitrogen in the "like-dissolves-unlike" system.

If hydrogen and nitrogen interact attractively with each other, but repulse particles of the same element, then it is unlikely that a lattice will achieve any ratio of hydrogen to nitrogen other than 1:1. There are a few cases where the coverage of hydrogen was higher than the coverage of nitrogen, all at temperatures approaching absolute zero and at less negative chemical potentials for hydrogen. It could be possible to achieve a better ratio with much more excess hydrogen, however, since hydrogen is our limiting reactant, it needs to be decided whether this would be worth the cost.

Discussion

There is one clear trend within the heat maps of almost every interaction system shown above: as the chemical potential of hydrogen becomes more positive, the amount of hydrogen adsorbed increases, while the amount of nitrogen adsorbed decreases. This is thermodynamically logical, as the less negative that hydrogen's chemical potential is, the more favorable the addition of hydrogen to the lattice is and the less favorable its removal becomes.

The decrease of nitrogen's coverage on the lattice as hydrogen's chemical potential increases is most prevalent when the chemical potential of hydrogen is greater than the

chemical potential of nitrogen. This suggests that the ratio of hydrogen to nitrogen adsorbed on the lattice varies logistically with the difference between both elements' chemical potentials, where the largest change in the coverage ratio occurs when the chemical potentials are almost equal to each other.

The effect of the temperature on the simulation is harder to determine. From analyzing Equations 1 and 3, an increase in temperature should result in increased volatility of the simulation. Effectively, when the temperature increases, the likelihood of a particle being adsorbed increases in unfavorable circumstances and decreases in favorable circumstances. This is reflected in the heat maps from the simulations. For example, for the "ideal" and "repulsion" systems, the ratio of hydrogen to nitrogen on the lattice increases at a slower rate with increasing hydrogen chemical potential when the temperature is high. The increased temperature lowers the favorability of hydrogen adsorption when μ_H is high but raises it when μ_H is low.

This temperature phenomenon can also be seen in the "immiscible" system, where 2 of the 3 final lattices with both hydrogen and nitrogen present were at high temperatures. With this in mind, running the adsorption at high temperatures can aid in achieving a 3:1 hydrogen to nitrogen ratio when the interaction system would not favor this ratio, such as in the "immiscible" system.

Conclusion

The Grand Canonical Monte Carlo simulation suggests different strategies to obtain the best adhesion ratios depending on the interactions between hydrogen and nitrogen. If they do not interact at all or interact repulsively, then temperatures of 120 K and slightly more positive values for the chemical potential of hydrogen produce a hydrogen to nitrogen ratio near 3:1, arguably the best possible for the Haber-Bosch process. If both elements attract each other, regardless of if they attract or repulse themselves, then temperatures approaching absolute zero and a much higher chemical potential of hydrogen are needed to obtain any ratio above 1:1. If hydrogen and nitrogen are immiscible, then extremely high temperatures will be needed to have even a chance of producing a favorable hydrogen to nitrogen ratio.

Since there is no set of parameters that would produce the best hydrogen to nitrogen ratio for every tested interaction system, it is recommended that an experiment is conducted to determine the interaction energies of both hydrogen and nitrogen, both with themselves and each other. With these determined, this report and the accompanying program can be utilized to obtain the most reasonable parameters for adsorption to better improve our current Haber-Bosch production line. Since the program can accept custom inputs outside of those in Table 1, it can give the ideal temperatures and chemical potentials once those have been determined, limiting the amount of trial and error needed during the experimental phase of this optimization, and thus the cost required to carry out the necessary research.