

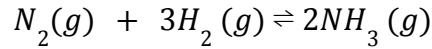
Simulation of Competitive Adsorption through Monte Carlo Simulations

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1. Introduction

The Haber-Bosch process has become well-known by allowing for the large-scale synthesis of ammonia. Historically, this process has had wide-ranging implications, from refrigeration to explosives manufacturing; most notably, this process has allowed for increased fertilizer production, contributing heavily to population growth by amplifying food production worldwide. However, the energy-intensive process accounts for a significant amount of energy consumption annually, prompting exploration into sustainable alternatives. Despite this, the Haber-Bosch process remains a fundamental chemical process crucial to global food networks today.

The Haber-Bosch process involves nitrogen gas and hydrogen gas, synthesizing these molecules into gaseous ammonia:



A key characteristic of this process involves competitive adsorption between nitrogen gas and hydrogen gas. The Haber-Bosch process involves the use of an iron catalyst, weakening the triple bond in the nitrogen molecule to allow for the forward reaction to occur. Not only is this catalyst inexpensive and abundant, but the lowering of the activation energy of the reaction significantly increases the reaction rate. The problem, however, results from the adsorption of hydrogen to the catalyst, slowing down the overall reaction. Hydrogen particles have a higher stoichiometric ratio in the Haber-Bosch process to produce the desired ammonia yield. To ensure maximum yield and minimize reaction runtime, it is therefore essential to understand competitive adsorption, which promotes binding or removal to our surface.

This project aims to utilize simulations to model the competitive adsorption between our two molecules of interest. In doing so, the goal of the project is to better understand the implications of maximizing nitrogen activation within the metal catalyst to increase the overall efficiency of the Haber-Bosch process, as well as to understand the chemical environments under which the process has optimal conditions.

2. Methodologies

This simulation involved the use of a Grand Canonical Monte Carlo simulation, as well as a Metropolis algorithm. Running the simulation can be broken down into smaller steps. First, the lattice was initialized, where a 4-by-4 grid was created to simulate 16 empty binding sites. After initializing empty coverage sites for both our nitrogen and hydrogen molecules, the simulation ran a function to decide whether or not to remove a particle. Although the decision to add or remove a particle was randomized, the acceptance of this decision was dependent on the acceptance probability.

$$acc = \min\left[1, \frac{N_a - N_s}{N_s + 1} \exp(-\beta[\Delta E - \mu s])\right] \quad (1)$$

$$acc = \min[1, \frac{N_s}{N_a - N_s + 1} \exp(-\beta[\Delta E + \mu_s])] \quad (2)$$

Equation 1 is the acceptance probability for adding a given particle, and Equation 2 is the acceptance probability for removing a given particle. In both equations, N_A represents the number of empty sites, N_s represents the number of sites occupied by species s , μ_s represents the chemical potential of species s , ΔE represents the change in energy of the system, and β represents the inverse temperature. If some randomized value between 0 and 1 was less than the acceptance probability, then the simulation would proceed with either adding or removing the particle from the given site.

$$\Delta E = \sum_i (N_i^A \epsilon_A + N_i^B \epsilon_B) + \frac{1}{2} \sum_{\langle i,j \rangle} (n_i^A n_j^A \epsilon_{AA} + n_i^B n_j^B \epsilon_{BB} + n_i^A n_j^B \epsilon_{AB} + n_i^B n_j^A \epsilon_{AB}) \quad (3)$$

In this context, Equation 3 shows that the acceptance probability is dependent on the change in total energy of the system, which varies with the epsilon values of the molecules. Therefore, running the Grand Canonical Monte Carlo simulation means that the optimization of molecular adsorption is dependent on the variation of the epsilon values, mu values, and temperature—trying different simulations at different values can provide useful insights into what conditions we aim to operate under.

5 simulations were run to replicate different conditions: an ideal mixture of Nitrogen and Hydrogen, repulsive interactions between Nitrogen and Hydrogen, attractive interactions between Nitrogen and Hydrogen, immiscible Nitrogen and Hydrogen, and a “Like Dissolves Unlike” scenario.

| | Ideal Mixture | Repulsive Interactions | Attractive Interactions | Immiscible | Like Dissolves Unlike |
|----------------------|---------------|------------------------|-------------------------|------------|-----------------------|
| ϵ_N (eV) | -0.1 | -0.1 | -0.1 | -0.1 | -0.1 |
| ϵ_H (eV) | -0.1 | -0.1 | -0.1 | -0.1 | -0.1 |
| ϵ_{NN} (eV) | 0 | 0.05 | -0.05 | -0.05 | 0.05 |
| ϵ_{HH} (eV) | 0 | 0.05 | -0.05 | -0.05 | 0.05 |
| ϵ_{NH} (eV) | 0 | 0.05 | -0.05 | 0.05 | -0.05 |

Table 1. Simulations Ran for Varying Parameters

As shown in Table 1, the epsilon values for the individual atoms of nitrogen and hydrogen are constant, whereas the ϵ_{NN} , ϵ_{HH} , and ϵ_{NH} values were varied across runs. During individual runs, the epsilon values were maintained for the entire simulation, while the μ_H value and temperature were changed – μ_H was varied from -0.2 eV to 0 eV, whereas temperature was varied from 0.001 to 0.019 eV (later adjusted to Kelvin). Furthermore, the μ_N value was kept constant due to excess nitrogen in the present conditions. Once the values had been initialized, the system was run for 10,000 steps, during which the system would attempt to either add or remove a particle 10,000 times. In doing so, this gives the system ample time to equilibrate. Once equilibrated, the results were plotted in both a color grid to indicate coverage across μ_H and temperature variation, as well as a lattice snapshot to depict a microscopic system snapshot after equilibration.

3. Results

3.1 Ideal Mixture of Nitrogen and Hydrogen

Within the first simulation, where hydrogen and nitrogen were initialized to have 0 interaction energies with their own respective molecules as well as other molecules, chemical potential appeared to contribute significantly to the adsorption and desorption of the molecules of interest. Since particle interactions were non-existent for this ideal scenario, it meant that the adsorption or desorption of one molecule was independent of nearby particles in the lattice. Looking at chemical potential, it can best be defined as the energy change that occurs when a particle is added to the system from a reservoir at a constant temperature. From Figure 1, we see that adjusting the μ_H value, we see that starting at a more negative chemical potential for hydrogen means that nitrogen has a higher affinity for binding to the lattice than hydrogen. This is because a more negative chemical potential indicates that desorption is more likely for sorbent particles, whereas a more positive chemical potential indicates a higher likelihood of adsorption. At a μ_H value of -0.2 eV, we observe only nitrogen adsorption and no hydrogen adsorption due to the chemical potential of hydrogen being lower. At a chemical potential of -0.1 eV for hydrogen, we observe roughly equal amounts of adsorption for the two molecules as they have the same

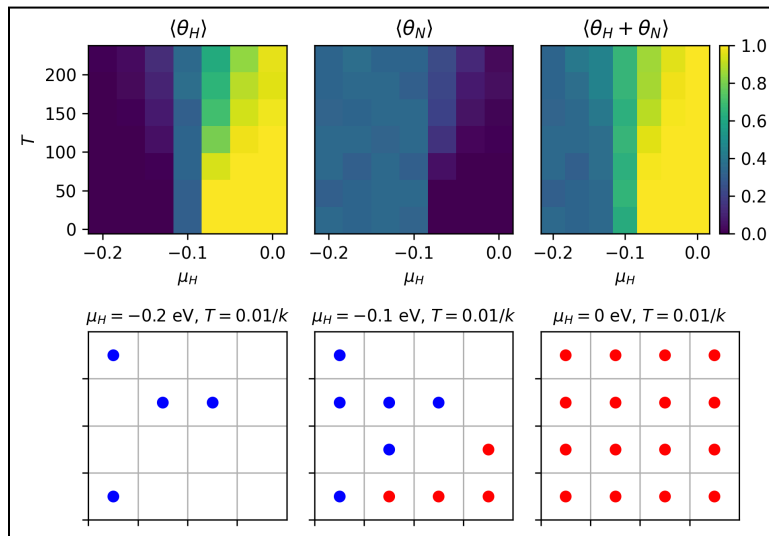


Figure 1. Coverage and Lattice Snapshot for the Ideal Mixture Simulation

chemical potential and therefore the same affinity for adsorption to the lattice. When the chemical potential for hydrogen was increased to 0 for hydrogen, hydrogen adsorption was dominant within the lattice due to the hydrogen now having the higher chemical potential. In general, increasing the chemical potential of hydrogen resulted in increased overall mean coverage of the lattice as well.

Looking at the effects of temperature on mean coverage, it was observed that increased temperature was generally associated with desorption, though these effects were less significant than varying the chemical potential. Most notably, at $\mu_H = -0.1$ eV, increasing the temperature from 0 to 200K had pronounced effects in reducing hydrogen adsorption and slightly increasing nitrogen adsorption. At other chemical potential values, this same effect was not observed as varying the temperature seemed to have negligible effects on overall coverage.

3.2 Repulsive Interactions between Nitrogen and Hydrogen

The repulsive interactions simulation involved setting all particle interactions to have an interaction energy of 0.05 eV. As shown in Figure 2, at a lower chemical potential for hydrogen, only nitrogen adsorption was observed. Similar to Figure 1, increasing the chemical potential of hydrogen to 0 eV had the effect of increasing hydrogen adsorption so that both molecules had roughly equal coverage across the lattice. At the highest chemical potential for hydrogen, 0 eV, only hydrogen adsorption was observed within the lattice, with minimal to no nitrogen adsorption. These results can be attributed to the same reasons cited in the ideal mixture simulation, in which a lower chemical potential contributes to desorption and a higher chemical potential leads to adsorption.

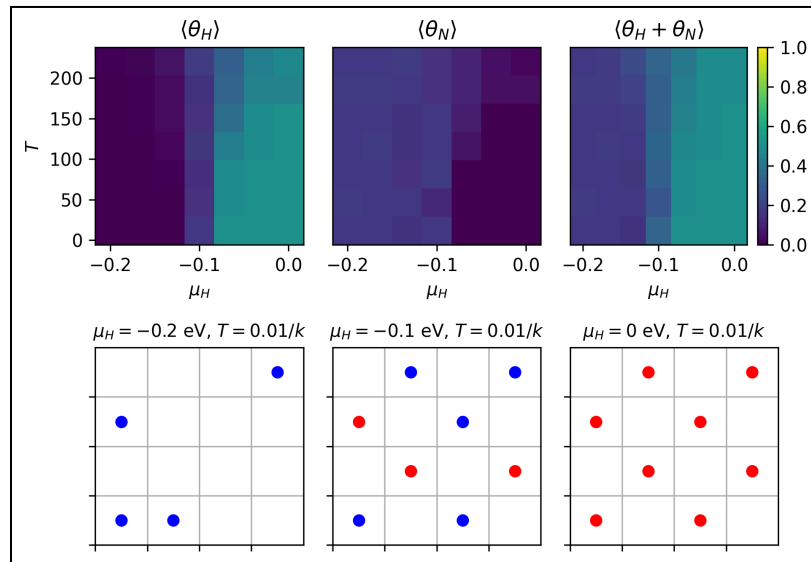


Figure 2. Coverage and Lattice Snapshot for the Repulsive Interactions Simulation

Notably, increasing chemical potential leads to increased coverage for hydrogen and increased overall mean coverage – however, the maximum for both appears to reach a value of 0.5. At equivalent and high chemical potentials, the molecules adsorb to the lattice in a checkerboard pattern. Due to repulsive interactions, molecular adsorption in adjacent sites would

lead to high energy. Thus, the checkerboard pattern can best be explained by a minimization of the energy of the system. Similar to the prior simulation, increasing the temperature only led to noticeable results at a chemical potential of -0.1 eV, by which hydrogen adsorption decreased and nitrogen adsorption slightly increased.

3.3 Attractive Interactions between Nitrogen and Hydrogen

To run the simulation for the attractive interactions between all particles, all interactions were set to have an interaction energy of -0.05 eV. As shown in Figure 3, at a lower chemical potential for hydrogen, hydrogen adsorption was lower than nitrogen adsorption. At equivalent values of chemical adsorption and at a higher value of chemical adsorption for hydrogen, adsorption for both nitrogen and hydrogen was roughly equal. Total mean coverage for the lattice was independent of both chemical potential and temperature, being maximized throughout all conditions.

Unlike previous conditions, temperature seemed to have relevant effects at $\mu_H = -0.1$ eV, in which increasing temperature led to increased nitrogen adsorption and decreased hydrogen adsorption, though adjusting temperature had negligible effects at other chemical potentials. Due to attractive interactions being present, the lattice was completely occupied at all conditions, with only the type of molecular adsorption varying based on chemical potential levels. Overall, the presence of neighbors in adjacent binding sites lowers the overall energy under these conditions.

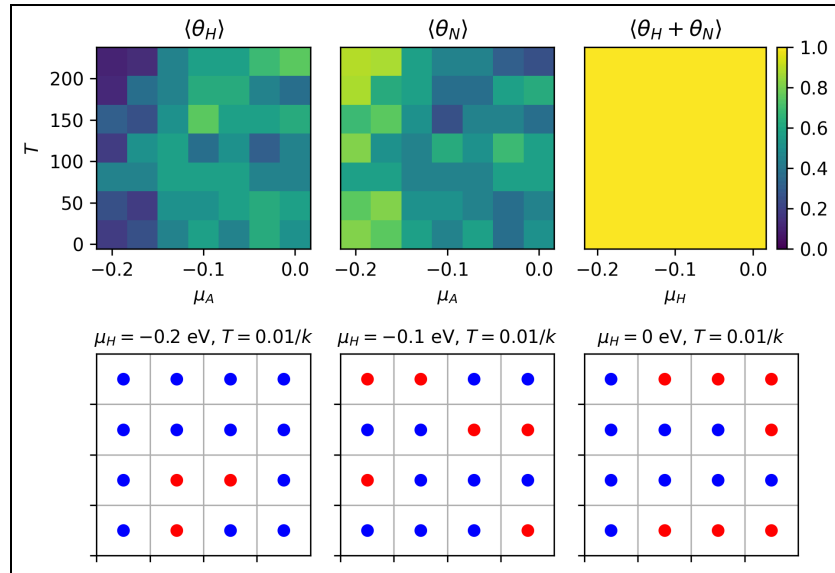


Figure 3. Coverage and Lattice Snapshot for the Attractive Interactions Simulation

3.4 Immiscible Nitrogen and Hydrogen

To simulate the conditions of immiscible nitrogen and hydrogen, the interaction energy between particles of the same type was set to -0.05 eV, whereas nitrogen and hydrogen had an interaction energy of 0.05 eV. That is, particles of the same type had attractive interactions, whereas particles of different types had repulsive interactions. The results can be observed in Figure 4 below. At $\mu_H = -0.2$ eV, only nitrogen adsorption is observed. When μ_H is increased to -0.1 eV, the lattice is occupied by about half nitrogen and half hydrogen molecules, where

adjacent sites are occupied by the same type of particles. This pattern alternates between particles of different types.

Temperature had no effect on the adsorption of molecules to the lattice as the mean coverage remained constant throughout the simulation and only varied with changing chemical potential. Due to both attractive and repulsive potentials present in this simulation, the mean coverage was maximized, though the location of molecular adsorption was dependent on the same molecule type being adjacent to each other in binding sites.

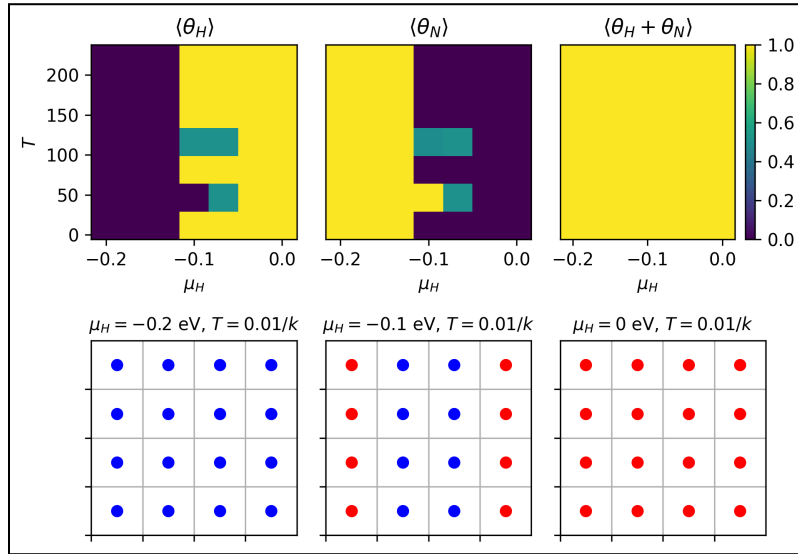


Figure 4. Coverage and Lattice Snapshot for the Immiscible Nitrogen and Hydrogen Simulation
3.5 “Like Dissolves Unlike” Scenario

The “Like Dissolves Unlike” condition was simulated by setting the interaction energy between particles of the same type to 0.05 eV and particles of different types to -0.05 eV. This means that repulsive interactions were established between particles of the same type, and attractive interactions were established between particles of different types. The results are shown in Figure 5.

Unlike past scenarios, the results were observed to be independent of both temperature and chemical potential. The mean coverage of both hydrogen and nitrogen across the lattice was 0.5 throughout all temperature and chemical potential conditions, meaning that half the binding sites in the lattice were occupied by hydrogen and half by nitrogen. The mean coverage of the entire lattice was maximized throughout all parameter conditions as well. The lattice snapshot was consistent throughout all conditions, showing hydrogen and nitrogen adsorption in a checkerboard pattern. Due to repulsive interactions between like particles and attractive interactions between different particle types, the system energy was minimized when molecules were horizontally adjacent to binding sites occupied by different particle types.

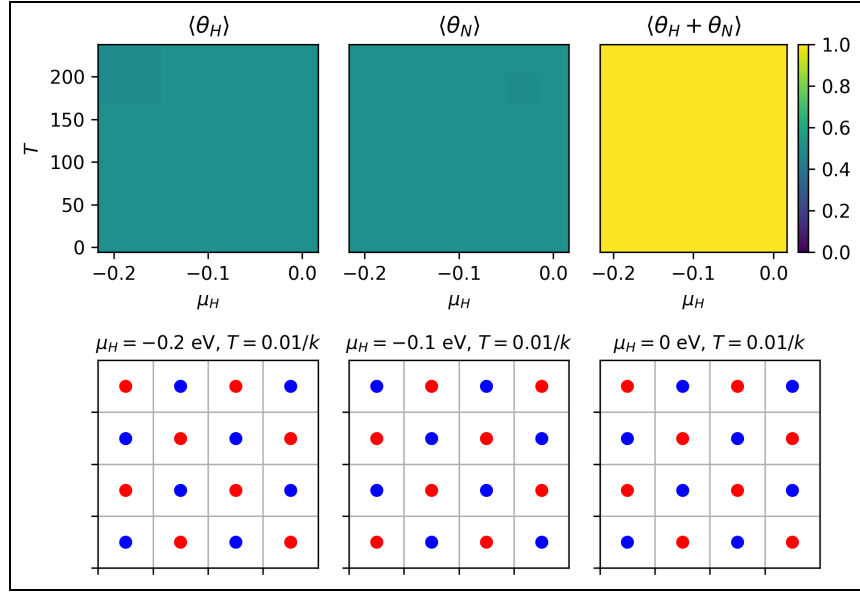


Figure 5. Coverage and Lattice Snapshot for the “Like Dissolves Unlike” Simulation

4. Discussion

4.1 Chemical Potential Effects

Throughout all five simulation conditions, the chemical potential of hydrogen, μ_H , was varied from -0.2 eV to 0 eV. On average, increasing this chemical potential also increased hydrogen adsorption to the lattice. This effect can best be attributed to the definition of chemical potential, which is the energy change that occurs when a particle is added to the system from a reservoir at a constant temperature. That is, a higher chemical potential is associated with greater binding. In the ideal mixture, repulsive interactions, and immiscible hydrogen and nitrogen scenarios, increasing this potential led to significant increases in hydrogen adsorption. Since μ_N was held constant in this simulation, in most scenarios, nitrogen adsorption was dependent on hydrogen adsorption. In Figures 1, 2, and 4, we observe that increasing μ_H resulted in decreased mean coverage of nitrogen on the lattice. This was due to either hydrogen having a higher affinity for binding, hydrogen having a strong preference for binding sites away from nitrogen, or a combination of both. In Figure 3, the nitrogen adsorption decreased slightly when μ_H was increased, though attractive forces appeared to be more significant.

For the like-dissolves-unlike scenario, increasing the chemical potential did not lead to increased hydrogen adsorption. In this simulation, particle interaction energies were the dominant force, having more significant effects than the chemical potential itself. Mean coverage for hydrogen remained constant throughout the changing chemical potential. Thus, chemical potential is an important factor in determining the amount of nitrogen adsorption present, but it is not the only factor, nor is it the dominant factor when μ_N is held constant.

4.2 Temperature Effects

Throughout all conditions, temperature was varied from 0.001 to 0.019 eV, which was converted to kelvin during the visualization phase. On average, changing the temperature of the

process had limited effects on both hydrogen and nitrogen adsorption. Temperature is seen to be involved in the acceptance probability equation, being related to the inverse of β . However, the only scenarios where increasing temperature had discernible effects were the ideal mixture, the attractive interaction mixture, and the repulsive interaction mixture. In each of these cases, increasing the temperature from 0 to 200K only had noticeable effects at one chemical potential value. In Figures 1 and 2, increasing temperature at $\mu_H \approx -0.1$ eV resulted in higher nitrogen adsorption, though this trend was not observed at different chemical potentials along the same chemical interaction conditions. In Figure 3, this same trend was observed but at $\mu_H = -0.2$ eV. For all conditions where temperature variation led to pronounced results, it is important to note that only a small increase in adsorption was noted for nitrogen.

The effects of temperature on hydrogen desorption and nitrogen adsorption suggest that a higher temperature is preferred when making the Haber-Bosch process more efficient. In Figure 2, we observe higher nitrogen adsorption when the temperature is increased and repulsive interactions are present. This trend can likely be attributed to the fact that nitrogen experiences increased kinetic energy at increased temperatures, therefore being able to overcome the repulsive interactions between the hydrogen particles. Similarly, in Figure 3, increasing temperature also led to observed nitrogen adsorption at a lower hydrogen chemical potential. This effect can likely be attributed to increased particle interactions at higher temperatures and kinetic energies – since nitrogen is present in excess, greater particle interactions on the lattice means that there is a higher likelihood of nitrogen adsorption. However, further simulations should be done to explain why this trend is only observed at specific chemical potential values.

4.3 Implications

The presence of the iron catalyst in the Haber-Bosch process is primarily to promote N_2 adsorption, though the presence of H_2 on the surface is also necessary for ammonia synthesis. Therefore, in a competitive adsorption scenario, it is important to maximize nitrogen adsorption while ensuring proper conditions for hydrogen interactions as well. For instance, in Figure 4, we observe that nitrogen adsorption completely occupies the lattice – however, this is also a condition where nitrogen and hydrogen are immiscible. Therefore, while it appears to be ideal, it is important to recognize the limited hydrogen and nitrogen interactions that would occur to synthesize ammonia. An ideal scenario would involve high attraction between particles of different types, as well as high nitrogen adsorption affinity.

Though the simulations demonstrate that there is no end-all-be-all solution to the problem of maximizing Haber-Bosch efficiency, the results provide unique implications for controllable factors to help reduce inefficiencies. For instance, lowering μ_H so that $\mu_H < \mu_N$ is a key factor that can increase nitrogen adsorption, since nitrogen chemical potential is held constant. For the purposes of this simulation, it is stated that nitrogen is present in excess, which is something that should be maintained throughout the Haber-Bosch process to maximize nitrogen adsorption. An important factor to note, however, is that we also fix μ_N to ensure that the chemical potential isn't too strong to the point where nitrogen cannot desorb from the lattice. There is an important balance that is maintained by fixing this chemical potential. Another important factor to control

is temperature – although temperature has less pronounced effects than varying μ_H , increasing temperature was shown to increase nitrogen adsorption at lower and medium values of μ_H . Additionally, increasing temperature can increase the interactions that occur between hydrogen and nitrogen, helping with the ammonia synthesis pathway. Finally, to ensure that interactions occur, ϵ_{NH} should be set to some negative value to indicate attractive interactions between the particles.

Practically, it is important to understand the cost of implementing these conditions within the Haber-Bosch pathway. For instance, if temperature is increased in these conditions, it would likely be energetically inefficient if this results in only a fractional amount of increased nitrogen adsorption. Making changes to the iron catalyst could also be a way of increasing ammonia output – as stated earlier, however, the iron catalyst is chosen for its abundance and cost-efficiency. Therefore, while another catalyst might work better, making drastic changes to the industrial process might not be worth the resources invested to make only slight improvements to the process.

5. Conclusion

The Haber-Bosch process remains an integral part of food networks today, highlighting the importance of its current contributions. To minimize its carbon emissions and energy usage while also maximizing its ammonia output, ensuring that the iron catalyst is being put to use is important. The primary goal of the iron catalyst is to weaken the triple bond in N_2 to ensure that the ammonia product can be formed. However, it is also important for the bond in H_2 to be weakened and for hydrogen and nitrogen to have stabilizing interactions. The challenge lies in ensuring maximal nitrogen adsorption to our catalyst while ensuring that our reactants can still properly react to form our product.

We conclude that the best conditions for ammonia synthesis occur when $\mu_H < \mu_N$, where nitrogen has a higher affinity for binding to our metal catalyst lattice. Although adjusting the temperature had less pronounced effects than varying our hydrogen chemical potential, the reaction should be run at high temperatures to promote nitrogen adsorption, as well as particle-particle interactions to form ammonia. Most importantly, an attractive interaction potential should be established between our two particles to ensure that they interact and that the lattice mean coverage is maximized.

Future simulations could examine the effects of different lattice arrangements and their effects on competitive adsorption. Making changes to the metal catalyst, such as lattice size or particle binding affinity for a particular metal, is also a reasonable next step. The results of our simulations, however, provide key insights into how to best maximize the output of the Haber-Bosch process.