Report on Adsorption Behavior of Nitrogen and Hydrogen: Implications for Ammonia Synthesis

by Brandon Salcedo-Lobato

Instructor: Robert Wexler

Computational Problem Solving in the Chemical Sciences CHEM 4050

Washington University in St. Louis

Fall 2024

Introduction:

This report investigates the adsorption behavior of nitrogen and hydrogen on a lattice under various interaction conditions: Ideal Mixture, Repulsive Interactions, Attractive Interactions, Immiscible, and "Like Dissolves Unlike" scenarios. By analyzing phase diagrams and lattice configurations for each parameter set, we aim to understand how different interaction energies and conditions influence adsorption patterns. These insights have direct implications for optimizing conditions in the ammonia synthesis process.

Methodology:

We used lattice-based Monte Carlo simulation to model the adsorption of nitrogen (θ_A) and hydrogen (θ_B) on a surface under varying temperatures (T) and chemical potential conditions (μ_A). The Monte Carlo algorithm is a computational technique that relies on random sampling to estimate complex system behaviors. In this simulation, it was used to model the probabilistic adsorption and desorption of nitrogen and hydrogen molecules on the lattice, allowing for the exploration of adsorption patterns under different interaction conditions.

Monte-Carlo Algorithm:

The Monte Carlo method employed here works by attempting random adsorption or desorption moves for nitrogen and hydrogen on a 2D lattice. Each move is evaluated using the Metropolis criterion, which compares the energy change resulting from the move to the thermal energy of the system. This approach enables the system to evolve toward equilibrium, with moves that lower the system's free energy more likely to be accepted. The algorithm accounts for the impact of temperature and chemical potential on adsorption behavior, simulating how these factors influence the coverage of nitrogen and hydrogen across the lattice.

Interaction Scenarios:

The simulation was run for different interaction scenarios between nitrogen and hydrogen:

- **Ideal Mixture**: No significant interactions between nitrogen and hydrogen.
- **Repulsive Interactions**: Nitrogen and hydrogen repel each other, discouraging co-adsorption.
- **Attractive Interactions**: Nitrogen and hydrogen attract each other, promoting co-adsorption.
- **Immiscible**: Nitrogen and hydrogen have high self-affinity but do not mix, leading to spatial separation.
- **Like Dissolves Unlike**: Hydrogen prefers adsorption over nitrogen.

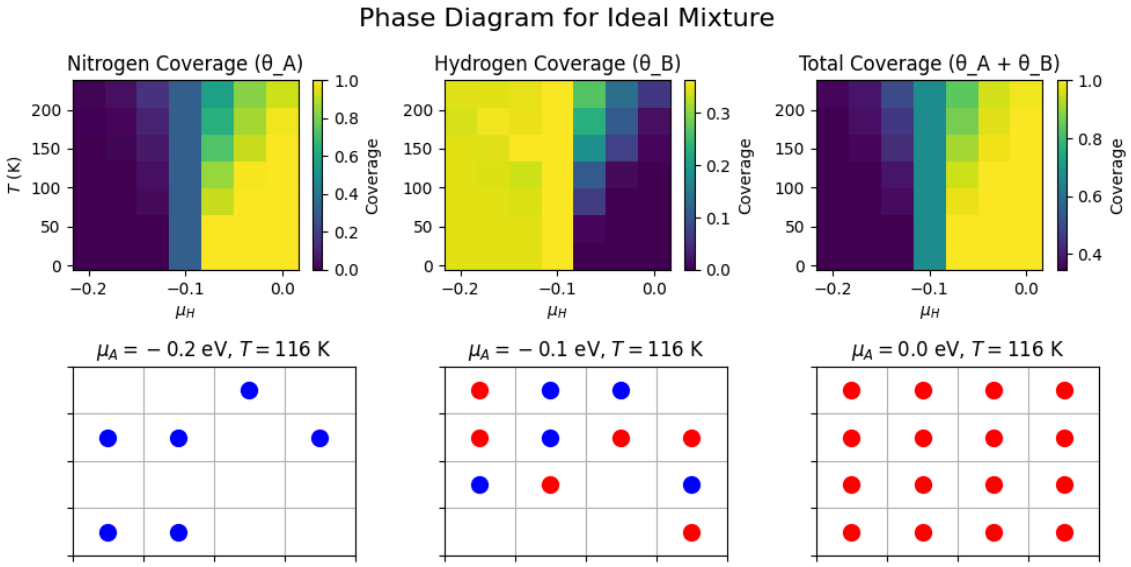
Data Collection:

For each scenario, phase diagrams were generated to show nitrogen and hydrogen coverage across a range of temperatures and chemical potentials. Lattice configurations were also captured at representative conditions (e.g., specific values of μ_A and T) to visualize how different interaction energies impact the spatial distribution of nitrogen and hydrogen on the lattice.

Results:

Ideal Mixture:

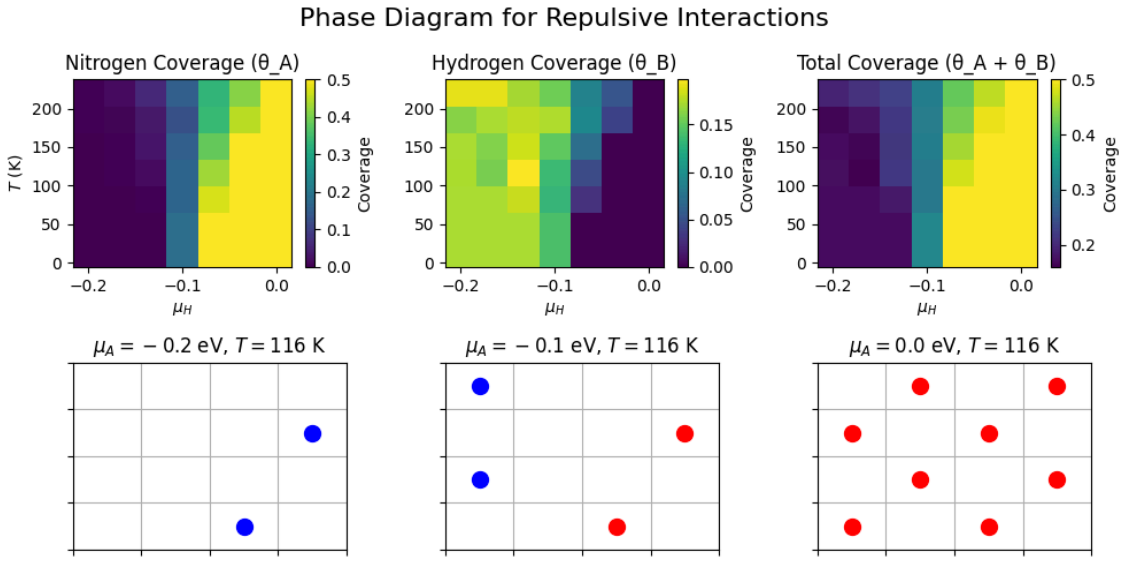
In the Ideal Mixture scenario (*Figure 1*) , both nitrogen and hydrogen display moderate coverage levels across a range of chemical potentials, but neither species reaches full coverage. This pattern suggests that the adsorption energies are balanced, with no strong preference for either nitrogen or hydrogen to dominate the lattice. The total coverage remains below 50%, indicating that the lattice is not fully occupied even under ideal mixing conditions. In an ideal mixture scenario, nitrogen and hydrogen co-adsorb without any significant interactions driving them together. This allows both gasses to coexist on the surface; however, without a strong driving force for increased coverage, the probability of nitrogen-hydrogen interaction remains low, limiting the potential for reactions such as ammonia synthesis.



(Figure 1. Phase Diagram for Ideal Mixture, μ_A = -0.2,-0.1,0 eV T=116K)

Repulsive Interactions:

The Repulsive Interactions (*Figure 2*) scenario shows that both nitrogen and hydrogen coverage are lower compared to the Ideal Mixture case. The repulsive interactions between nitrogen and hydrogen reduce the likelihood of co-adsorption, causing each atom to avoid regions where the other is present. As a result, the total coverage remains low, and the lattice is sparsely populated when both species are present. Repulsive interactions lead to a spatial separation that limits the coexistence of nitrogen and hydrogen on the surface. This configuration is unfavorable for ammonia synthesis because nitrogen and hydrogen are kept apart, reducing the likelihood of the necessary molecular interactions for ammonia formation.

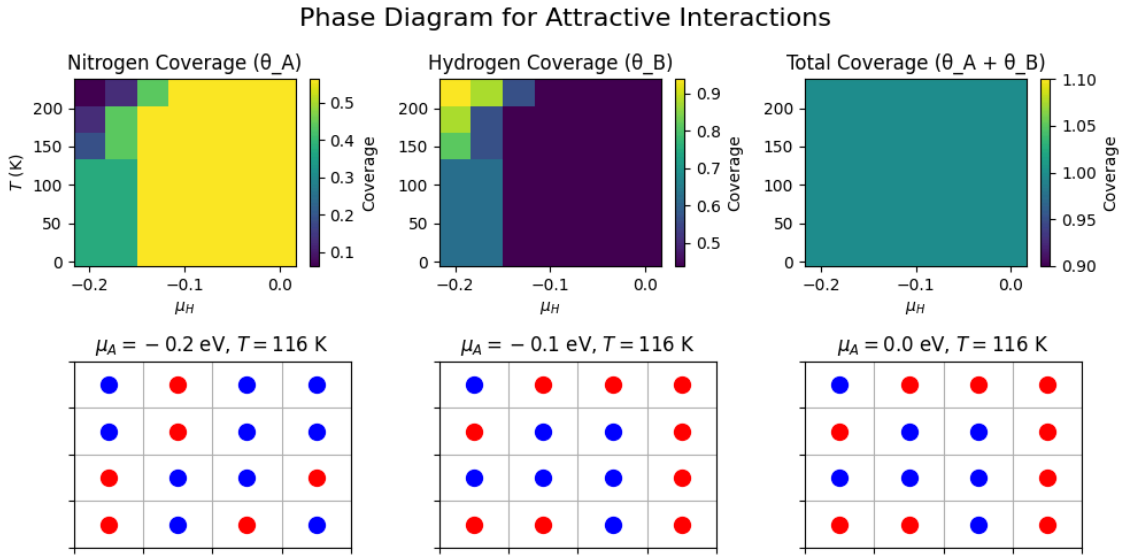


(Figure 2. Phase Diagram for Repulsive Interactions, μ_A = -0.2,-0.1,0 eV T=116K)

Attractive Interactions:

Under Attractive Interactions (*Figure 3.*), nitrogen and hydrogen both achieve higher coverage levels, especially at lower temperatures. This behavior indicates a cooperative effect, where the presence of one species promotes the adsorption of the other due to mutual attraction. The total coverage approaches 100%, suggesting that the lattice is nearly fully occupied when both gasses are present. This high-density occupation creates an environment conducive to nitrogen-hydrogen interaction. Attractive interactions increase the likelihood of co-adsorption, providing favorable conditions for nitrogen and hydrogen to interact closely on the surface. As a result, this scenario is beneficial for ammonia synthesis, as it maximizes the probability of

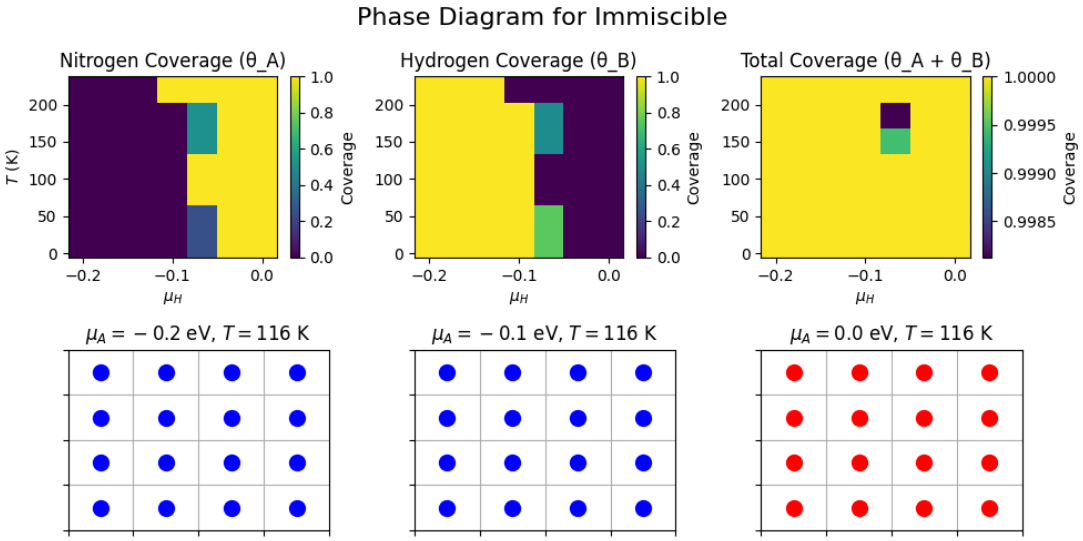
reaction by maintaining high coverage of both gasses.



(Figure 3. Phase Diagram for Attractive Interactions, μ_A = -0.2,-0.1,0 eV T=116K)

Immiscible:

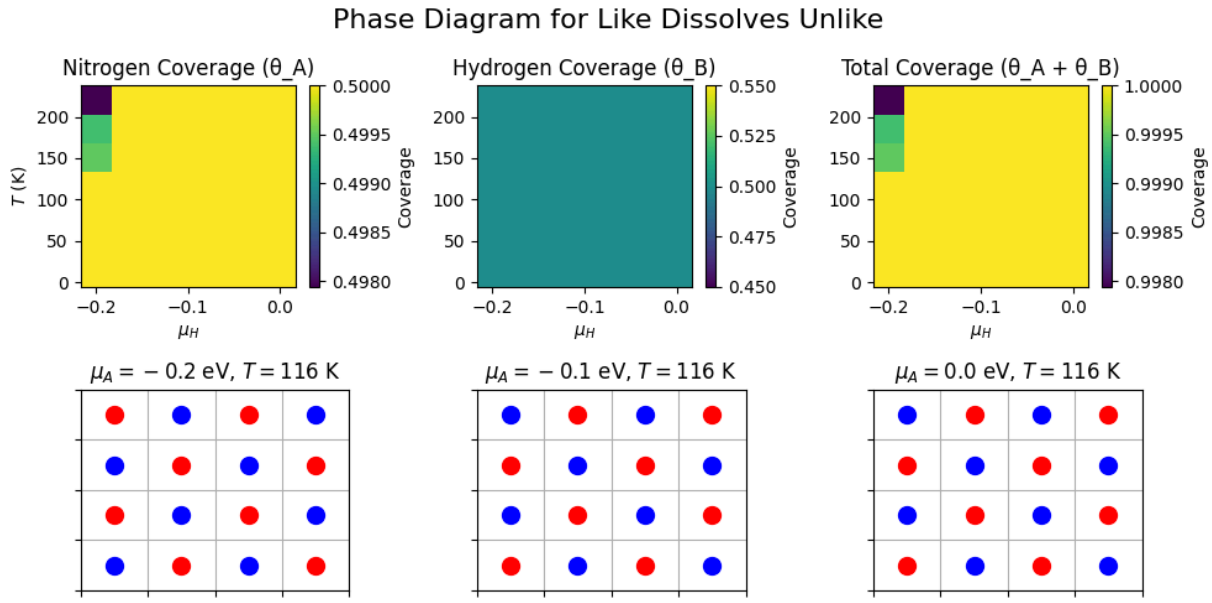
In the Immiscible scenario (*Figure 4.*), nitrogen and hydrogen each achieve high coverage individually, but they occupy separate regions of the lattice. This separation is due to immiscibility, where the presence of one species discourages adsorption of the other in adjacent sites, resulting in distinct regions dominated by either nitrogen or hydrogen. Although the total coverage is high, it consists of isolated regions of nitrogen and hydrogen rather than a uniform distribution. This spatial separation hinders direct interaction between nitrogen and hydrogen, which reduces the likelihood of reaction. Consequently, the immiscibility of nitrogen and hydrogen makes this configuration less suitable for ammonia synthesis, as the necessary molecular proximity for interaction and reaction is lacking.



(Figure 4. Phase Diagram for Immiscible, μ_A = -0.2,-0.1,0 eV T=116K)

“Like Dissolves Unlike”:

In the "Like Dissolves Unlike" scenario (*Figure 5.*), hydrogen achieves higher coverage than nitrogen, while nitrogen coverage remains very low. This pattern suggests that hydrogen strongly prefers adsorption, effectively inhibiting nitrogen adsorption. As a result, the total coverage is dominated by hydrogen, with nitrogen making only a minimal contribution. In this scenario, the selective adsorption of hydrogen reduces the presence of nitrogen on the lattice, leading to an imbalance that is suboptimal for ammonia synthesis. The lack of sufficient nitrogen limits the potential for reaction with hydrogen, thus reducing the overall efficiency of the synthesis process.



(Figure 4. Phase Diagram for Immiscible, μ_A = -0.2,-0.1,0 eV T=116K)

Discussion:

Physical Interpretation of Results

The adsorption behavior of nitrogen and hydrogen on the lattice varies significantly across different interaction types, reflecting how thermodynamic principles influence coverage and spatial distribution. In the Ideal Mixture scenario, nitrogen and hydrogen adsorb in a balanced manner without a strong preference for co-adsorption. This results in moderate coverage for both species, with neither achieving high occupancy of the lattice. The lack of significant interactions means that nitrogen and hydrogen can coexist without driving each other to higher adsorption levels, which limits their potential for interaction.

In contrast, Repulsive Interactions create spatial separation between nitrogen and hydrogen, as each species avoids regions where the other is present. This reduces total coverage and limits the coexistence of both gasses on the surface, decreasing the probability of nitrogen-hydrogen interactions. Attractive Interactions, however, encourage co-adsorption by lowering the free energy of the system when both species are present together. This cooperative effect leads to

high coverage and a densely populated lattice where nitrogen and hydrogen are in close proximity, maximizing the likelihood of interaction—an arrangement that is particularly advantageous for reactions that require both species to be close, such as ammonia synthesis.

The Immiscible scenario, on the other hand, leads to high coverage but in isolated patches, where nitrogen and hydrogen occupy separate regions of the lattice. This spatial separation reduces the chances of direct nitrogen-hydrogen interaction, making it less effective for processes that rely on both gasses being in the same region. Finally, the Like Dissolves Unlike scenario favors hydrogen adsorption over nitrogen, resulting in an imbalance where hydrogen dominates the lattice while nitrogen is mostly excluded. This limits nitrogen's availability on the surface and reduces the potential for ammonia synthesis due to a lack of sufficient nitrogen coverage.

Implications for Ammonia Synthesis

For the ammonia synthesis process, it is essential for nitrogen and hydrogen to be in close proximity on the catalyst surface to maximize the probability of interaction. Based on the simulation results, Attractive Interactions provide the most favorable condition for ammonia synthesis, as they promote high co-adsorption and increase the likelihood of nitrogen-hydrogen interactions by maintaining a high-density lattice. In contrast, Repulsive Interactions and Immiscible conditions are less favorable because they create spatial separation between nitrogen and hydrogen, which reduces the chances of interaction. The Like Dissolves Unlike and Ideal Mixture scenarios offer some potential but fail to achieve the necessary balance or level of co-adsorption to make them as effective as the Attractive Interactions scenario.

Suggested Strategies for Optimization

To optimize conditions for ammonia synthesis, several strategies can be considered. First, designing catalysts that induce attractive interactions between nitrogen and hydrogen would promote co-adsorption and increase the chances of interaction. Controlling chemical potentials to achieve balanced and moderate coverage of both nitrogen and hydrogen would ensure that both gasses are available on the surface without one species dominating the lattice. Lastly, maintaining a temperature range that favors adsorption without leading to excessive desorption

would create a stable environment conducive to interaction. By implementing these strategies, it is possible to create optimal conditions that maximize the efficiency of ammonia synthesis through improved adsorption and co-adsorption behavior.

Conclusion:

Our study demonstrates that attractive interactions between nitrogen and hydrogen create the optimal conditions for ammonia synthesis by maximizing co-adsorption. Catalysts that promote such interactions and optimized temperature and chemical potentials could significantly enhance the efficiency of ammonia production. Future research may involve testing real catalyst materials under these optimized conditions to validate simulation predictions.