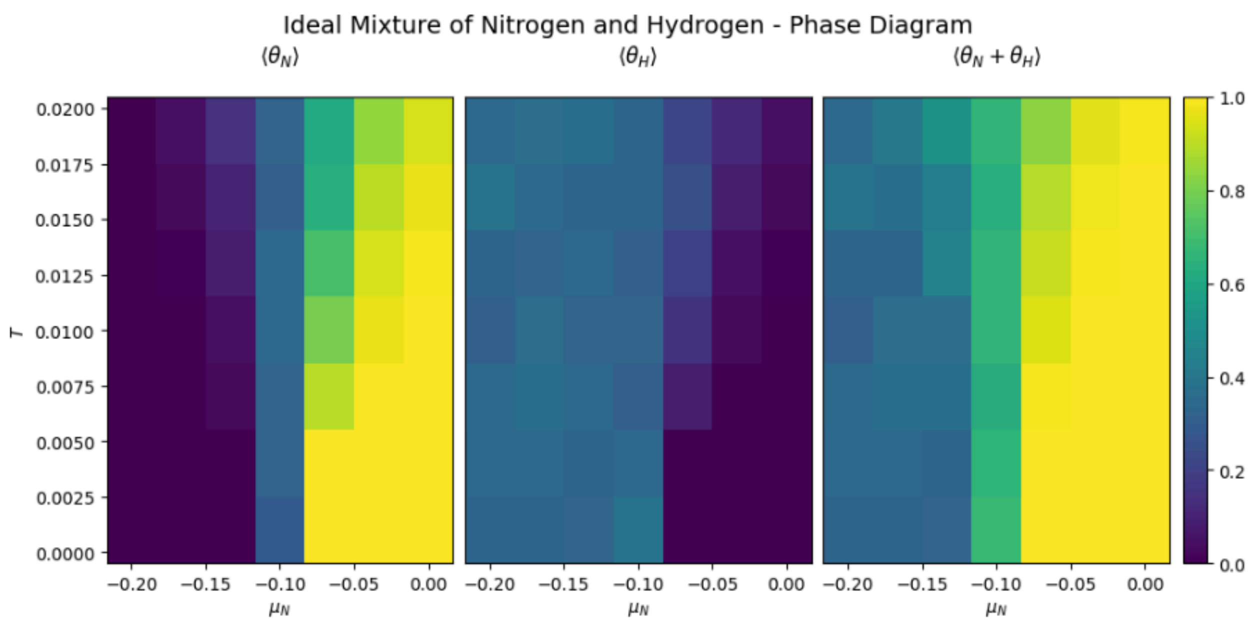
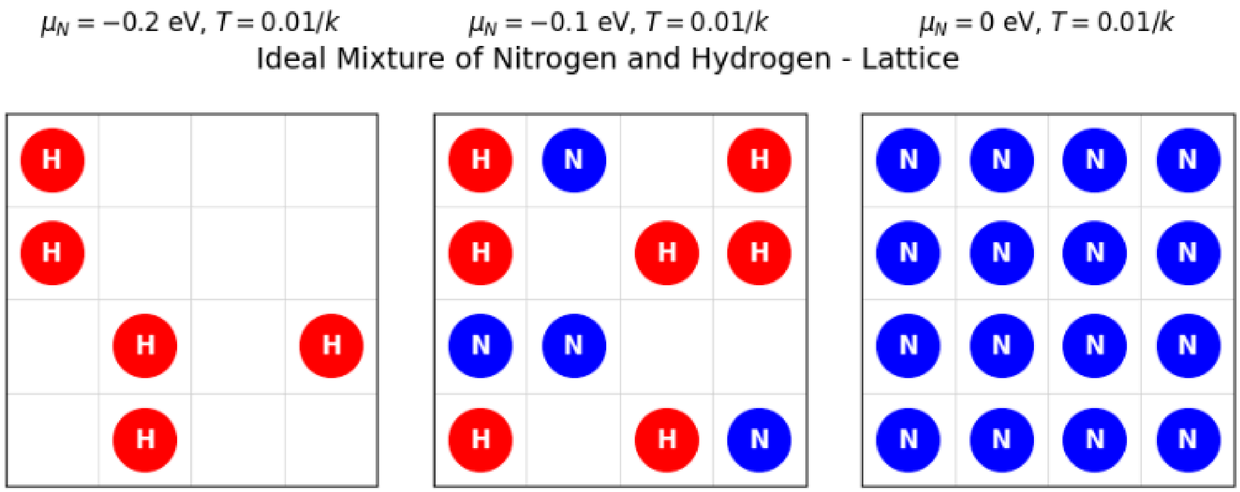
Adsorption Behavior Analysis
General Nitrogen and Hydrogen Adsorption

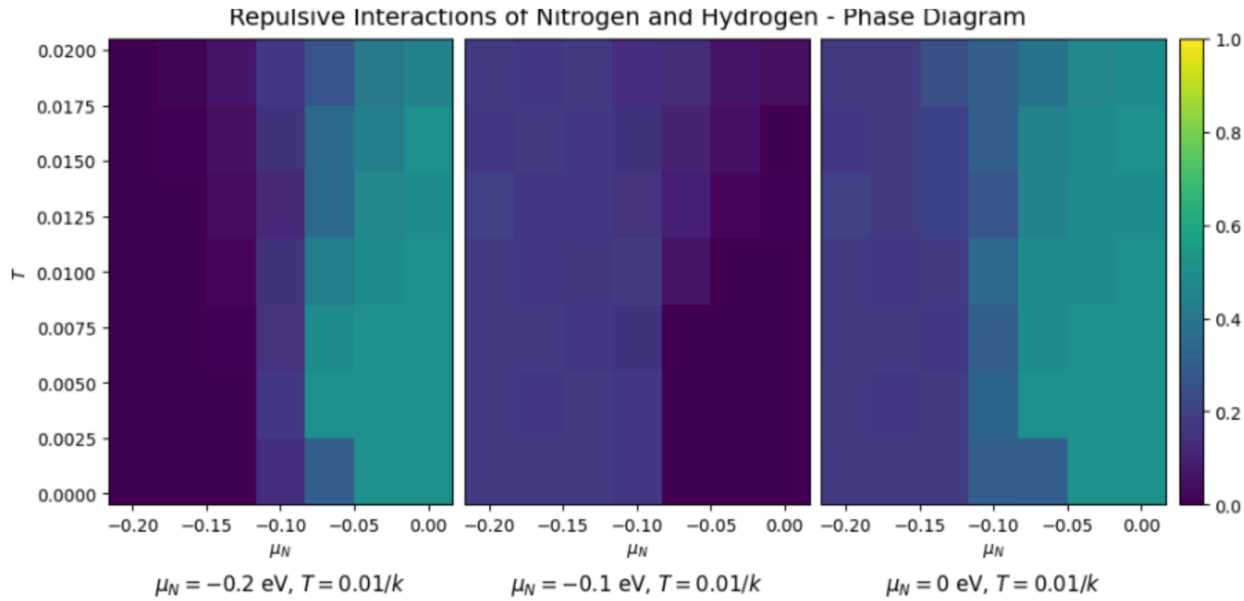
At constant temperature, as the chemical potential of nitrogen increases, the amount of nitrogen coverage also increases as the chance for a nitrogen atom to adsorb relative to a hydrogen atom increases. Unlike this, the increase in chemical potential of hydrogen at a constant temperature results in a decrease of hydrogen coverage as nitrogen atoms compete against hydrogen atoms to adsorb onto the lattice. Overall, an increase in the total chemical potential results in an increase in the total coverage as more nitrogen and hydrogen atoms are likely to adsorb to the surface until all sites in the lattice are covered. When the chemical potential is held constant, an increase in the temperature results in a smoother transition (ie smoother gradient on the colormap) for nitrogen, hydrogen, and total coverage. This is likely because a higher temperature results in a wider bell curve and therefore greater range of kinetic energies of the atoms, resulting in more overall possibilities for adsorption.

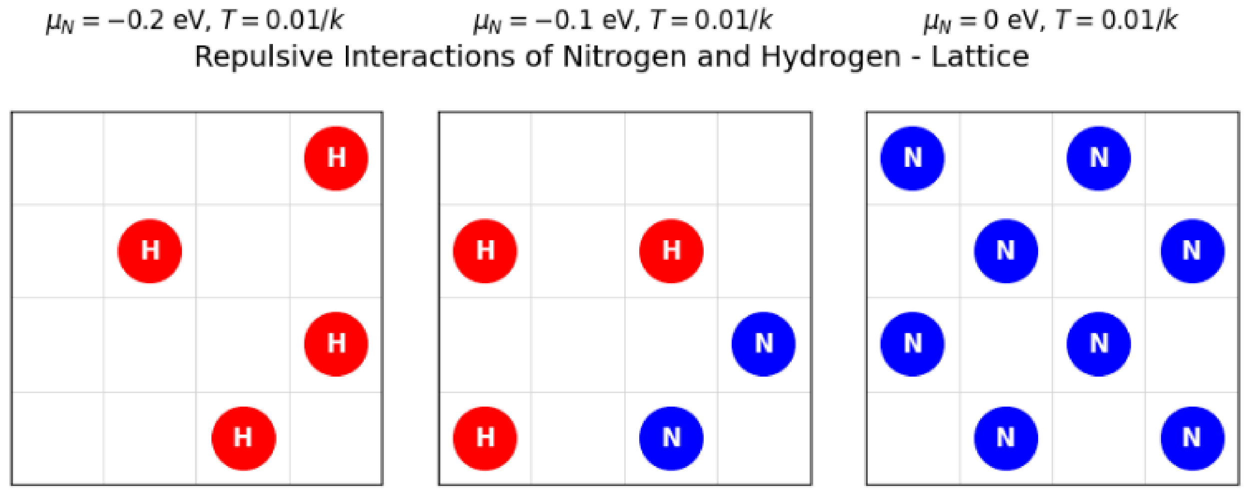
Adsorption Under Different Conditions
Under ideal conditions, there are no repulsive or attractive interactions between any atoms. For a constant temperature, an increase in the chemical potential results in an increase in nitrogen coverage and decrease in hydrogen coverage until 100% coverage is achieved. For a constant chemical potential, an increase in temperature results in a slight decrease in the total coverage, potentially because gases are more motivated to leave the lattice and escape as a gas. As shown by the lattice diagram, hydrogen is first to adsorb, followed by nitrogen adsorbing at empty sites, followed by the desorption of hydrogen and adsorption of nitrogen at the remaining sites.



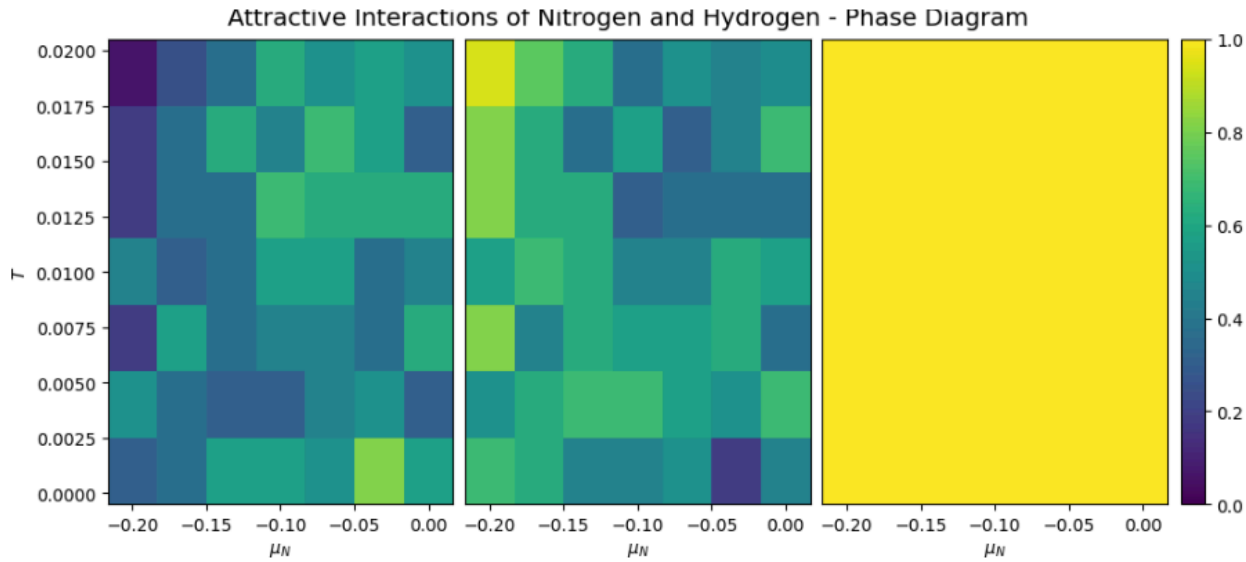


Under repulsive conditions, interactions between all nitrogen and hydrogen atoms are repulsive (ie positive interaction energy). For a constant temperature, an increase in the chemical potential results in an increase in nitrogen coverage and decrease in hydrogen coverage until approximately 60% total coverage is achieved. For a constant chemical potential, an increase in temperature results in a slight increase, then decrease in the total coverage, likely due to a shifting imbalance between the attraction of nitrogen and hydrogen atoms to each other versus to the lattice itself. As shown by the lattice diagram, hydrogen is first to adsorb, followed by nitrogen adsorbing at empty sites, followed by the desorption of hydrogen and adsorption of nitrogen at the remaining sites, similar to the ideal condition. However, 60% coverage is found by alternating nitrogen sites being occupied, and the same pattern is seen for hydrogen coverage, indicating repulsion between neighboring nitrogen atoms, neighboring hydrogen atoms, and between the nitrogen and hydrogen atoms. This inhibits adsorption of atoms to the surface as an increase in interactions reduces the likelihood that a particular atom will adsorb at a particular time. Compared to ideal conditions, less total coverage is achieved at the same temperature.



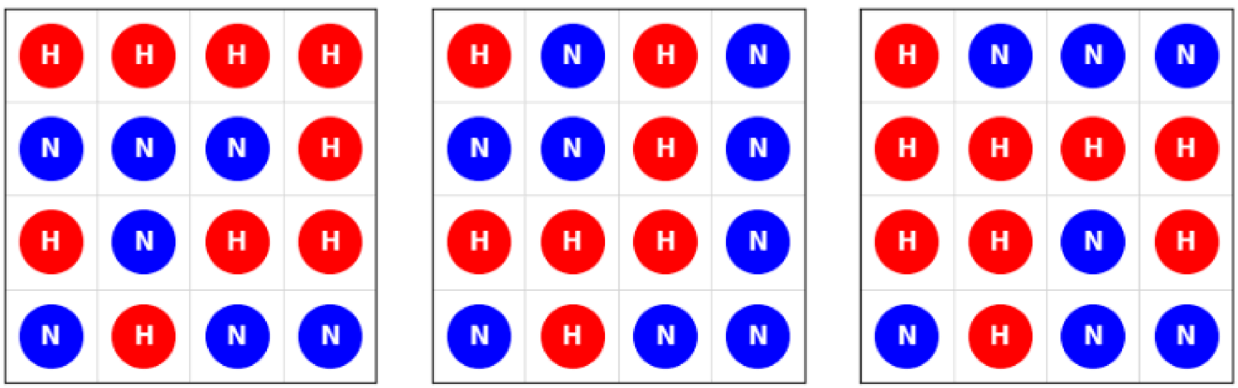


Under attractive conditions, interactions between all nitrogen and hydrogen atoms are attractive (i.e. negative interaction energy). For a constant temperature, an increase in the chemical potential results in a slight increase in nitrogen coverage and slight decrease in hydrogen coverage. For all temperatures and chemical potentials, the total coverage observed was 100%, indicating a high binding affinity of both nitrogen and hydrogen to the lattice. For a constant chemical potential, an increase in temperature does not show a direct relationship to nitrogen, hydrogen, or total coverage, indicating that there may be cooperativity between the attraction of the atoms to each other and to the lattice. In the lattice diagrams, slight clustering of nitrogen groups and hydrogen groups was observed, indicating more favorable attractive interactions between neighbors of the same element compared to different elements.

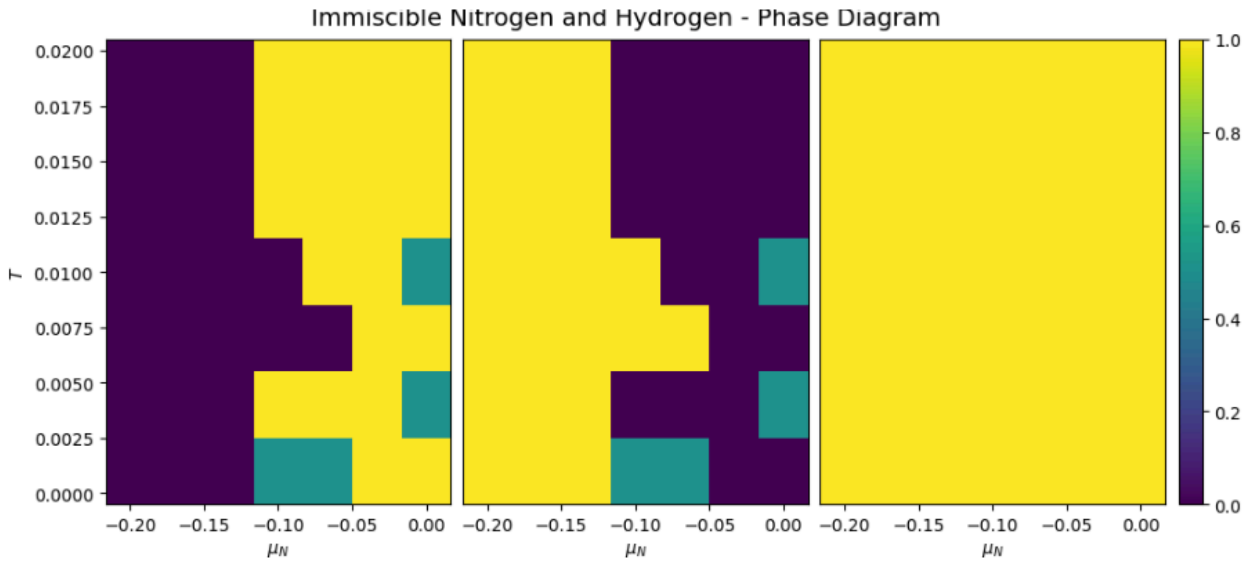


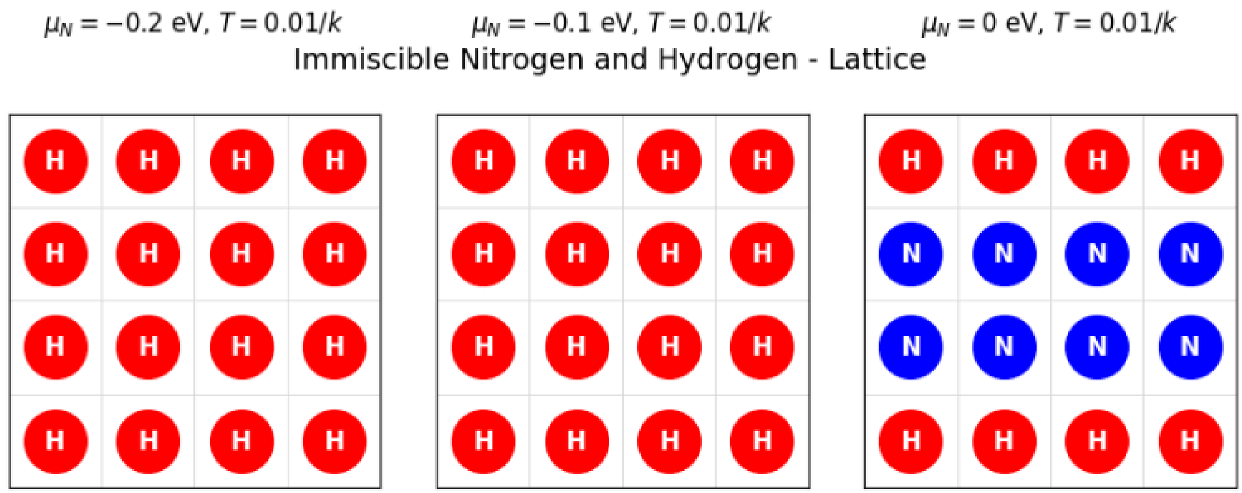
$\mu_N = -0.2$ eV, $T = 0.01/k$ $\mu_N = -0.1$ eV, $T = 0.01/k$ $\mu_N = 0$ eV, $T = 0.01/k$

Attractive Interactions of Nitrogen and Hydrogen - Lattice

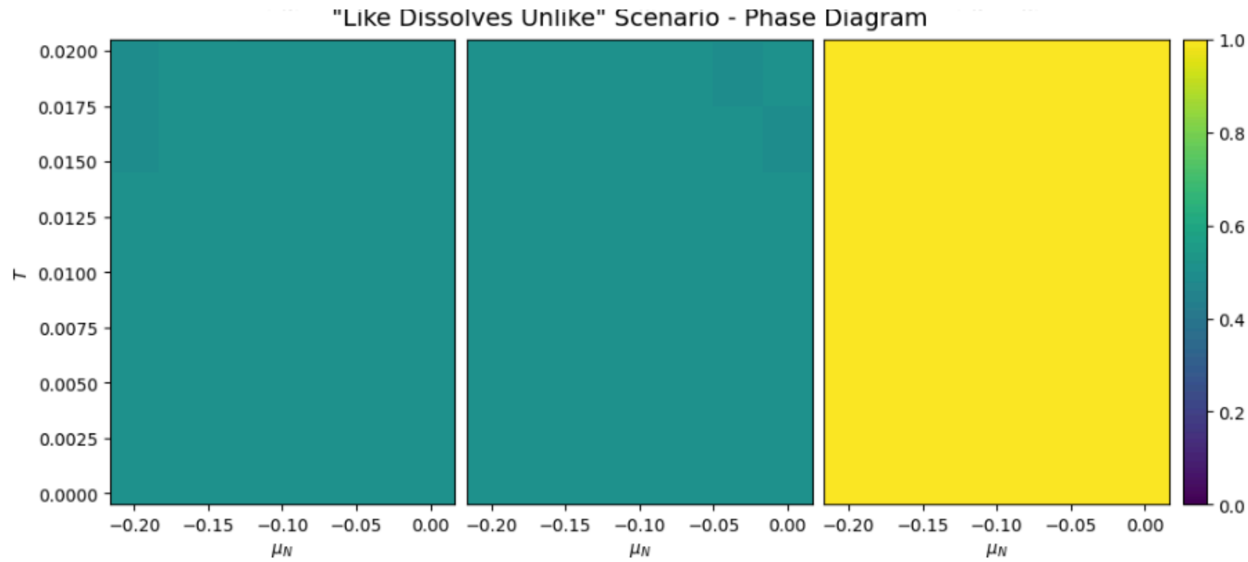


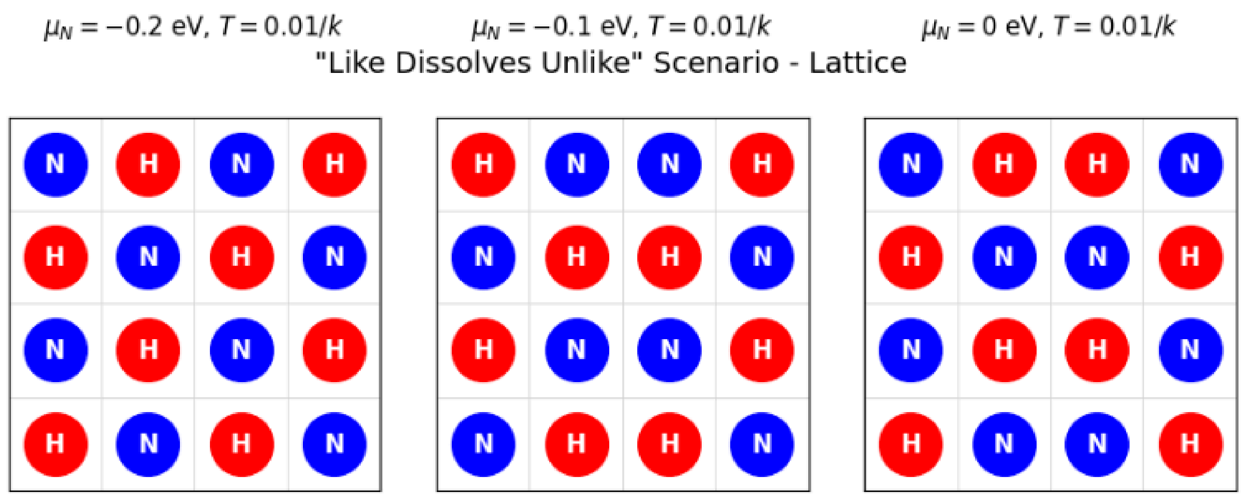
Under immiscible conditions, atoms of the same element experience attractive interactions, while atoms of different elements experience repulsive interactions. For a constant temperature, an increase in the chemical potential results in a change from all sites being occupied by hydrogen to all sites being occupied by nitrogen at around mu = -0.125 eV. For very low temperatures and very high chemical potentials, some 50% nitrogen / 50% hydrogen adsorptions were observed. As with the attractive condition, for all temperatures and chemical potentials, the total coverage observed was 100%, indicating a high binding affinity of both nitrogen and hydrogen to the lattice. For a constant chemical potential, an increase in temperature has no effect on the coverage apart from the previously discussed low temperature or high chemical potential cases. In the lattice diagrams, significant clustering of nitrogen groups and hydrogen groups was observed, indicating much more favorable attractive interactions between neighbors of the same element compared to different elements.





Under "like dissolves unlike" conditions, atoms of the same element experience repulsive interactions, while atoms of different elements experience attractive interactions. For a constant temperature, an increase in the chemical potential has no discernable effect on the ratio of adsorption by nitrogen or hydrogen. Instead, 50% nitrogen / 50% hydrogen adsorptions were observed with 100% total coverage, indicating a high binding affinity of both nitrogen and hydrogen to the lattice. For a constant chemical potential, an increase in temperature results in no discernable change in the coverage of either atom or total coverage, indicating low optimization potential. In the lattice diagrams, almost no clustering of nitrogen groups and hydrogen groups was observed.





Comparison Between Parameter Sets
Key Differences
Out of all tested conditions, 100% coverage was achieved in all conditions except repulsive conditions, which observed a maximum of 60% total coverage. As a result, a positive interaction energy points toward lower adsorption onto the lattice. Likewise, out of all conditions, only the "like dissolves unlike" condition consistently showed 50% nitrogen / 50% hydrogen adsorption, while the immiscible only achieved this state under low temperature and high chemical potential. Lastly, the immiscible and "like dissolves unlike" conditions showed sharp changes in nitrogen and hydrogen coverage for a change in chemical potential, while the remaining conditions showed gradual changes in the relative coverage of nitrogen and hydrogen.

Observed Differences
Out of the tested conditions, repulsive interactions result in the least overall coverage, likely due to repulsive forces between neighboring atoms effectively lowering the probability of atoms adsorbing to the surface of the lattice. In contrast, attractive interactions result in clustering and

cooperative adsorption. Immiscible interactions result in two distinct compositions for adsorption that are highly dependent on chemical potential. The "like dissolves unlike" condition results in balanced 50 % nitrogen / 50% hydrogen adsorption, almost no clustering, and is temperature- and chemical potential- independent, making it the most ideal condition for efficient ammonia adsorption onto the lattice.

Implications for Ammonia Synthesis
Connection to Industrial Process
By optimizing reaction conditions, the most effective method of adsorption of atoms to a lattice surface can be achieved. As a result, if the surface acts as a catalyst for a reaction, as in ammonia production, finding the most efficient adsorption conditions would significantly increase the reaction rate and efficiency. By examining the conditions between atoms, such as repulsive and attractive interactions, we can observe multiple resulting effects, such as clustering, competitive adsorption, incomplete coverage, and gradual versus drastic shifts in the adsorbates on the lattice.

Optimization Strategies
To achieve a "like dissolves unlike" condition for synthesis, there must be repulsion between atoms of the same element and attraction between atoms of different elements. This means the interaction energy between two nitrogen atoms or two hydrogen atoms is positive, and the interaction energy between a nitrogen and hydrogen atom is negative. As a result, nitrogen and hydrogen will both adsorb onto the lattice while avoiding forming clusters. In an industrial setting, this could look like engineering the surface of the lattice or suspending the lattice in a fluid to induce repulsions between like atoms and encourage attractions between unlike atoms.