Investigation of adsorption of particles to a surface

Introduction:

The Haber-Bosch process is an industrial process to make ammonia by reacting hydrogen with nitrogen on an iron catalyst. Since these can only access the surface of the catalyst, how these gasses adsorb to the surface, entirely dictates the amount of ammonia formed. However, it's hard to predict how these molecules will adsorb to the surface. This can be visualized through molecular dynamics simulations. Using molecular dynamics we can create a small lattice, in this case 25 adsorption sites large, we can assume will effectively infinitely repeat until it becomes the macro system.

Montey Carlo Simulation:

The Montey Carlo Simulation is a methodology for simulating molecular dynamics using random numbers. With enough random numbers almost, any system can be molecular system can be visualized. However, if use of truly random numbers were implemented here there would not be any useful information since we would just have a random assortment of hydrogen and nitrogen affixed to our simulated lattice. We need to bias the lattices that are lower in energy.

The Metropolis Algorithm:

The metropolis algorithm takes a current lattice and proposes a random, but small change to that lattice. The algorithm then determines the change of energy that would result from moving to the new lattice. If the new lattice decreases energy the metropolis algorithm will move to it, but if it increases in energy the metropolis algorithm will still have a chance to move to it. This way the system will not get caught in a local minimum, but instead, theoretically proceed to the maximum minimum. The algorithm also saves data from each of the previous lattices so that the average state of the system can be calculated, since no system spends its entire time at the local minimum.

Methodolagy:

A metropolis algorithm was constructed that would analyze two different sizes of lattice. The adsorption site was square, and an atom adsorbed to it could interact with its 4 immediate neighbors. The simulation was run for 10,000 steps where each step one of three things could happen.

Addition of a particle: The algorithm would attempt to add either a nitrogen or hydrogen atom to the lattice. If this decreased the system energy the system would proceed to this

lattice, otherwise the system would accept the transition with the percentage chance: $\frac{N_a}{N_E+1} e^{-\beta(\Delta E-\mu_a)} * 100\%$ where N_a are the number of the particle to be added already attached to the lattice, N_E are the number of empty sites, β is 1 over the temperature in kelvin times the Boltzmann constant in electron volts, and μ_a is the chemical potential of the particle to be added.

Subtraction of a particle: The algorithm would attempt to remove a random particle from the system. If this decreased the system energy the system would proceed to this lattice, otherwise the system would accept the transition with the percentage chance: $\frac{N_E}{N_a+1} e^{-\beta(\Delta E+\mu_a)} * 100\%$. These variables are the same as the ones used above.

Swapping of two particles: The algorithm would attempt to swap two particles of different type at random. If this decreased the system energy the system would proceed to this lattice, otherwise the system would accept the transition with the percentage chance: $e^{-\beta\Delta E}\left(\frac{1}{N_E}\left(\frac{N_{a1}}{e^{\beta\mu_{a1}}}+\frac{N_{a2}}{e^{\beta\mu_{a2}}}\right)+N_E*\left(\frac{e^{\beta\mu_{a1}}}{1+N_{a1}}+\frac{e^{\beta\mu_{a2}}}{1+N_{a2}}\right)\right)*100\%$. Though this equation may look complicated it is merely the addition acceptance involving two different particles, added to the subtraction involving two different particles. This is because this step effectively removes two particles and adds them back to different locations.

During each of these steps the coverage of each particle on the lattice was recorded so that the average coverage at a given chemical potential and temperature could be calculated. The system was run with a temperature increasing from almost 0 K to 200 K and a hydrogen chemical potential ranging from -0.2 to 0. Nitrogen's chemical potential was held at a constant -0.1 since it makes up most of the atmosphere was assumed to be the chemical in excess.

The conditions of our system:

The system was run under 5 different sets of conditions. Where ϵA is the interaction energy of a particle with the lattice, ϵAA is the interaction energy of a particle with itself, and ϵAB is the interaction energy of a particle with the other particle:

Ideal Mixture of Nitrogen and Hydrogen:

ϵN=−0.1ϵN=−0.1 eV, ϵH=−0.1ϵH=−0.1 eV

ϵNN=0ϵNN=0 eV, ϵHH=0ϵHH=0 eV, ϵNH=0ϵNH=0 eV

Repulsive Interactions between Nitrogen and Hydrogen:

ϵN=−0.1ϵN=−0.1 eV, ϵH=−0.1ϵH=−0.1 eV

ϵNN=0.05ϵNN=0.05 eV, ϵHH=0.05ϵHH=0.05 eV, ϵNH=0.05ϵNH=0.05 eV

Attractive Interactions between Nitrogen and Hydrogen:

ϵN=−0.1ϵN=−0.1 eV, ϵH=−0.1ϵH=−0.1 eV

ϵNN=−0.05ϵNN=−0.05 eV, ϵHH=−0.05ϵHH=−0.05 eV, ϵNH=−0.05ϵNH=−0.05 eV

Immiscible Nitrogen and Hydrogen:

ϵN=−0.1ϵN=−0.1 eV, ϵH=−0.1ϵH=−0.1 eV

ϵNN=−0.05ϵNN=−0.05 eV, ϵHH=−0.05ϵHH=−0.05 eV, ϵNH=0.05ϵNH=0.05 eV

“Like Dissolves Unlike” Scenario:

ϵN=−0.1ϵN=−0.1 eV, ϵH=−0.1ϵH=−0.1 eV

ϵNN=0.05ϵNN=0.05 eV, ϵHH=0.05ϵHH=0.05 eV, ϵNH=−0.05ϵNH=−0.05 eV

The Ideal Mixture of Hydrogen and Nitrogen:

In this system there was assumed to be a negative energy associated with adsorbing to the surface, but none of the particles were assumed to interact with their neighbors.

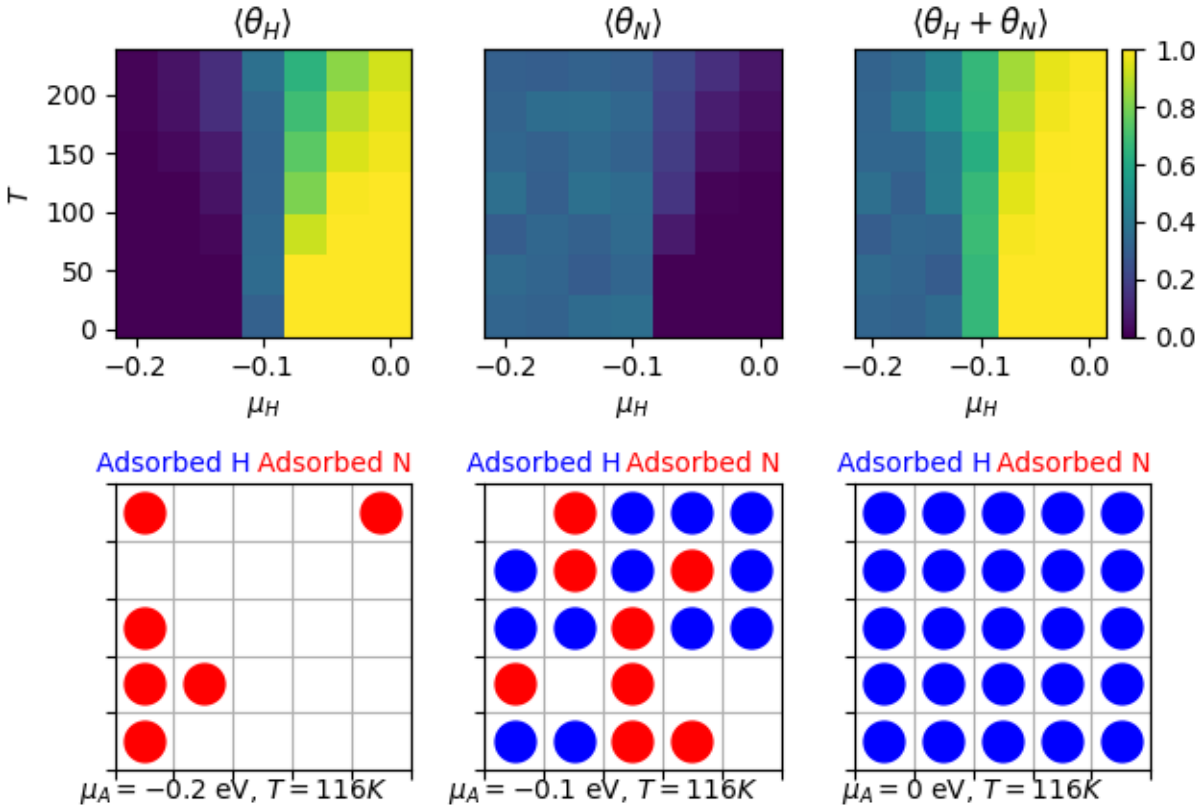

Figure 1: The adsorbing of Hydrogen and Nitrogen on a 5*5 grid in an ideal mixture scenario.

As can be seen as chemical potential of hydrogen approaches 0 the grid becomes fully saturated with it, since there is no thermodynamic reason to remove it. When chemical potential is larger than the binding energy almost no hydrogen is attached since it is far less likely to bind. Nitrogen occupies about half the sites as can be seen in the top middle graph, before hydrogen takes over since its chemical potential is the same as the adsorbing energy. This same trend extrapolates to the 10*10 grid as well (Figure 2).

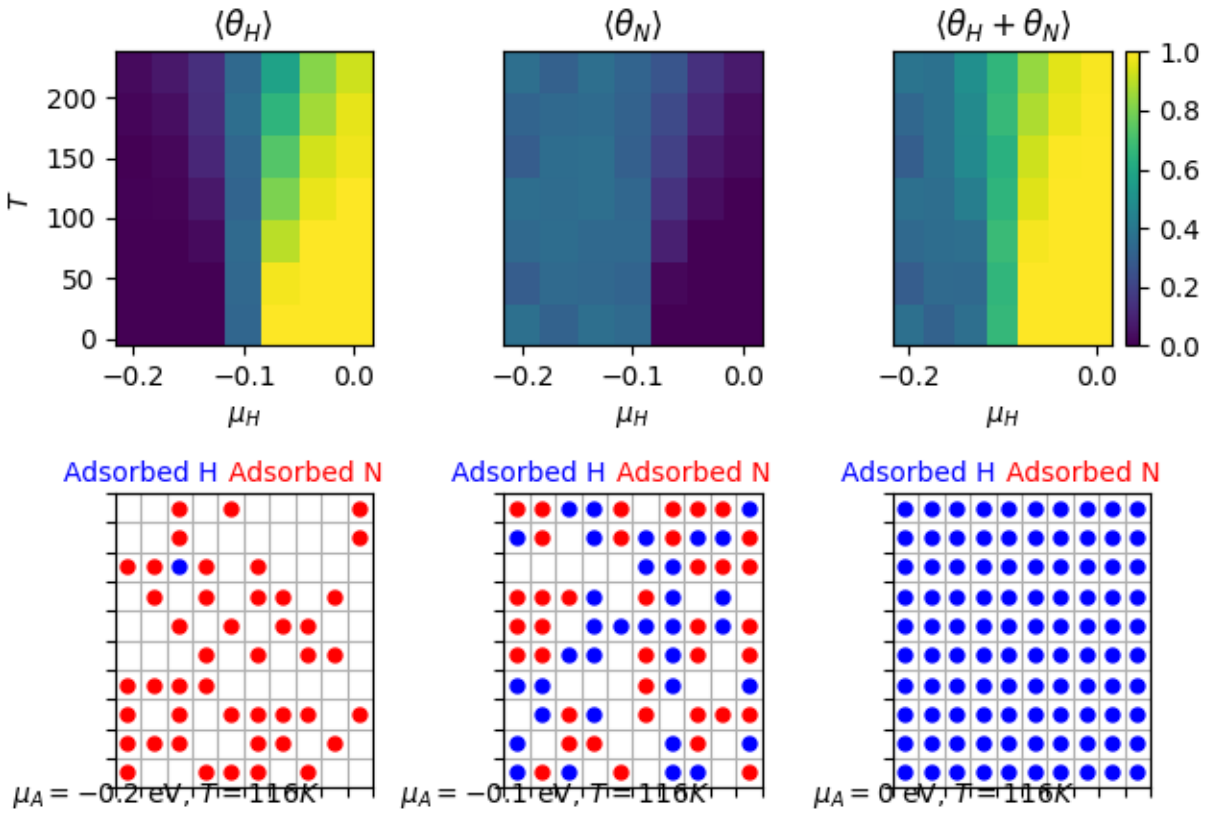

Figure 2: The adsorbing of Hydrogen and Nitrogen on a 10*10 grid in an ideal mixture scenario.

The Repulsive Mixture of Hydrogen and Nitrogen:

In this system there was assumed to be a negative energy associated with adsorbing to the surface, but a slightly smaller positive energy when particles were neighboring each other.

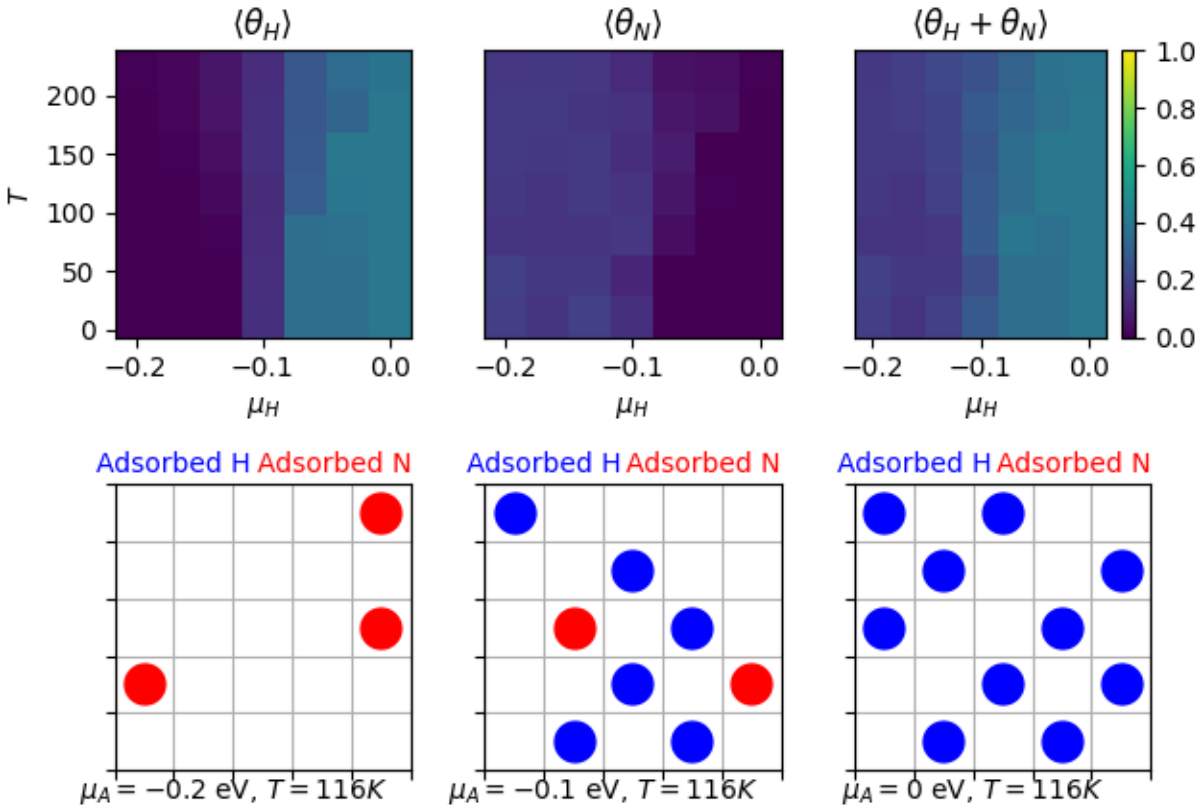

Figure 3: The adsorbing of Hydrogen and Nitrogen on a 5*5 grid in a repulsive mixture scenario.

As can be seen, the particles tend to form a checkerboard pattern. This is because although the positive energy of having a neighbor is less than the negative energy of adsorbing, once a pattern begins to emerge adsorbing anywhere would result in 4 neighbors. Another important thing to note is that even when hydrogen has too large a chemical potential to adsorb nitrogen still only takes up 25% of the spots on average rather than the 50% it did before. This is because the checkerboard pattern effectively blocks half the sites, so nitrogen is still taking up half the available sites as is expected. The 10*10 grid shows no abnormalities from the 5*5 grid's prediction (Figure 4).

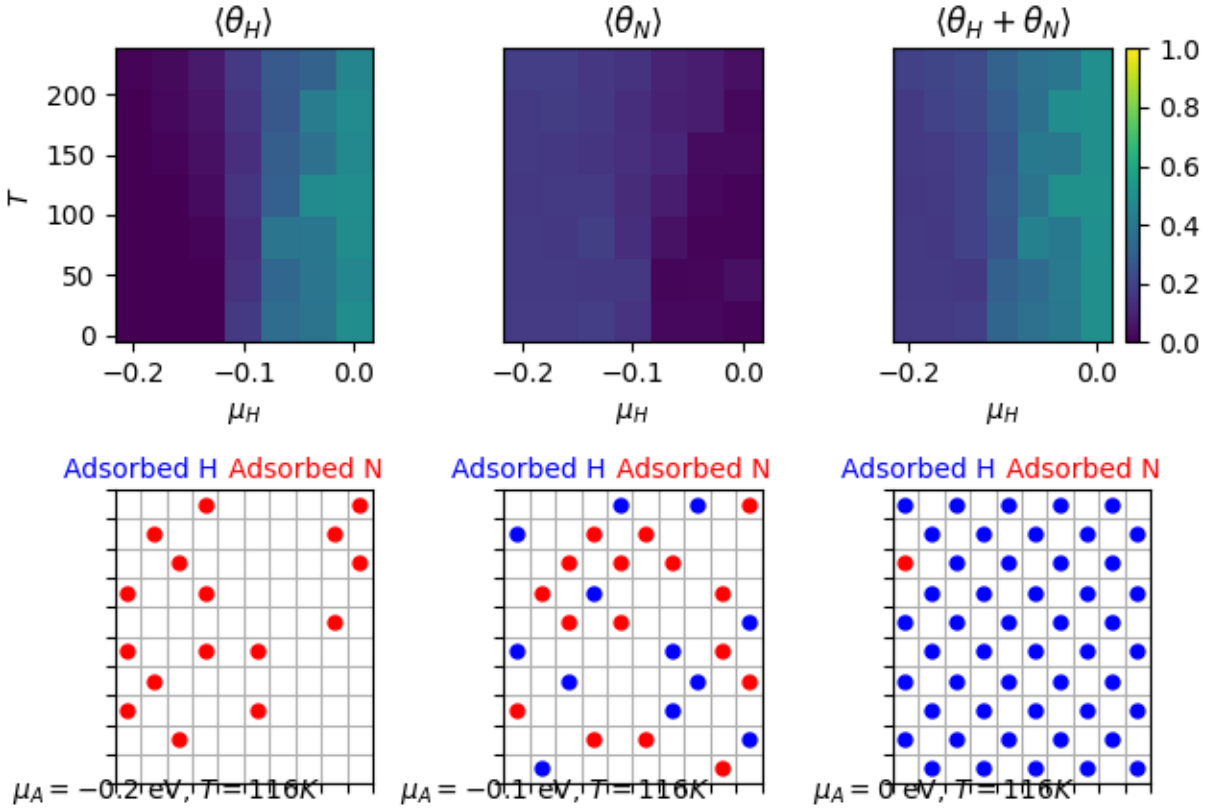

Figure 4: The adsorbing of Hydrogen and Nitrogen on a 10*10 grid in a repulsive mixture scenario.

The Attractive Mixture of Hydrogen and Nitrogen:

In this system there was assumed to be a negative energy associated with adsorbing to the surface, and another negative energy when particles were neighboring each other.

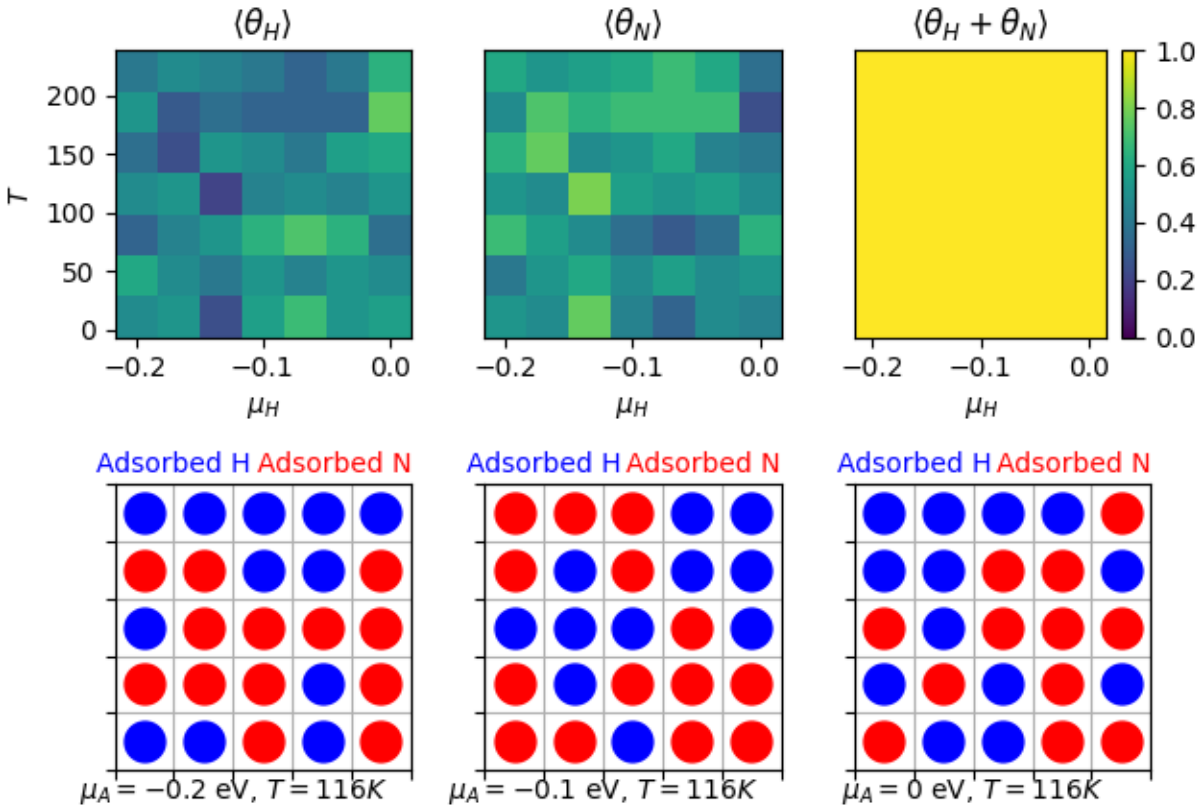

Figure 5: The adsorbing of Hydrogen and Nitrogen on a 5*5 grid in an attractive mixture scenario.

In this scenario it doesn't matter what the potential of hydrogen is, the result is still a mixture of hydrogen and nitrogen. This is because once a particle binds next to even one adjacent particle. The energy cost to remove them is so large that it pretty much won't happen. Once more neighbors appear, all those neighbors are also effectively stuck to the lattice. This scenario again shows no difference between the 5*5 and 10*10 matrix (Figure 6).

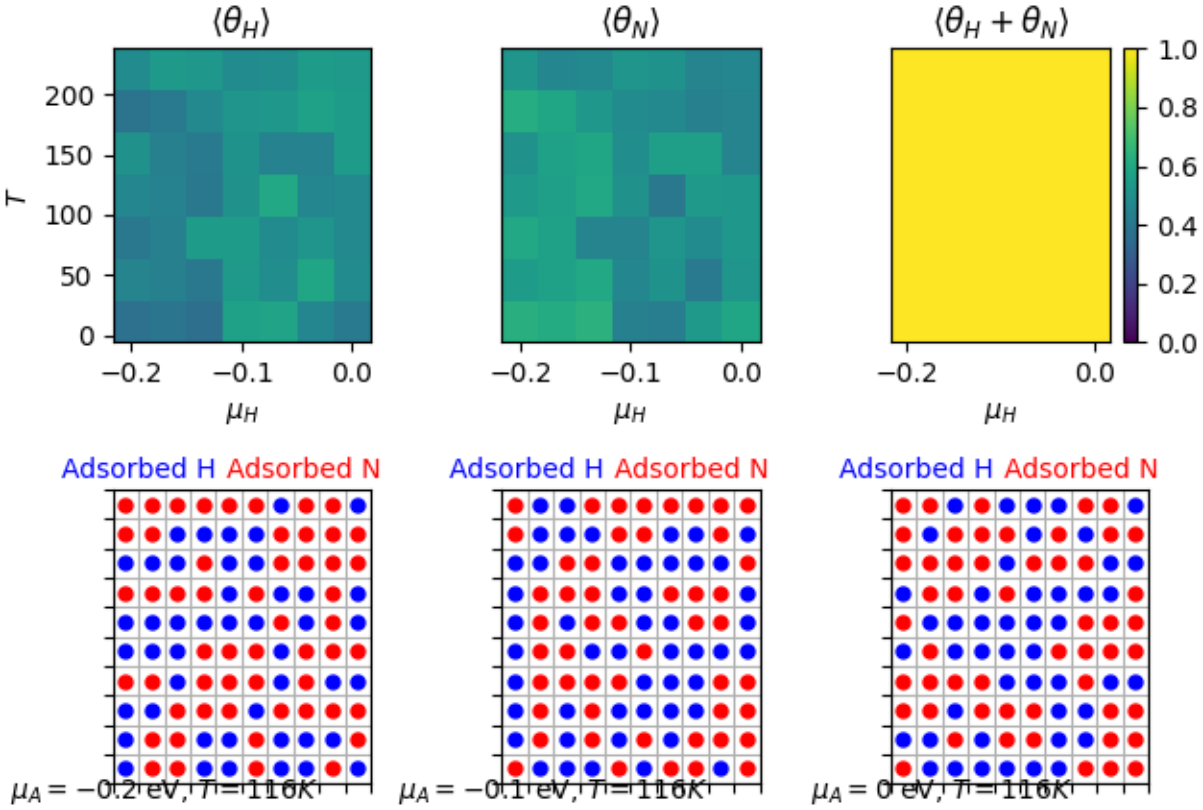

Figure 6: The adsorbing of Hydrogen and Nitrogen on a 10*10 grid in an attractive mixture scenario.

The Immiscible Mixture of Hydrogen and Nitrogen:

In this system there was assumed to be a negative energy associated with adsorbing to the surface, and another negative energy when particles were neighboring each other but only if those particles were the same, otherwise there was a positive energy.

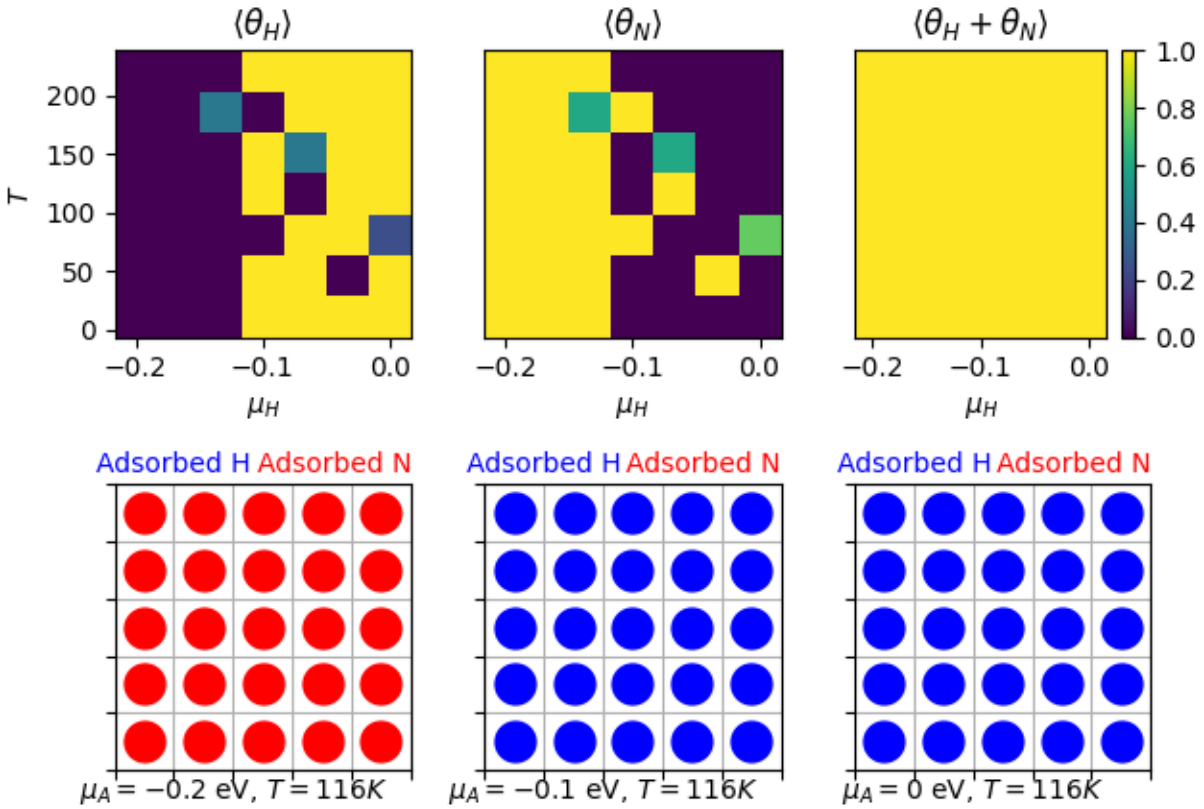

Figure 7: The adsorbing of Hydrogen and Nitrogen on a 5*5 grid in an immiscible mixture scenario.

In this scenario there is always total coverage of the system again because once a particle is neighboring itself it becomes nye impossible to remove from the lattice. However, the main difference is that the system is entirely dominated by one particle most of the time. This is because once one type of particle saturates a lot of the lattice, it can “bully” the other particles off of it. There are some cases though where both particles control part of the board as can be seen in the 10*10 matrix (Figure 8). In the middle grid each particle has “strongholds” where it is very hard to remove them, so they begrudgingly share the lattice space. This also seems to be more likely on a larger board since there is more space for two separate “strongholds” form.

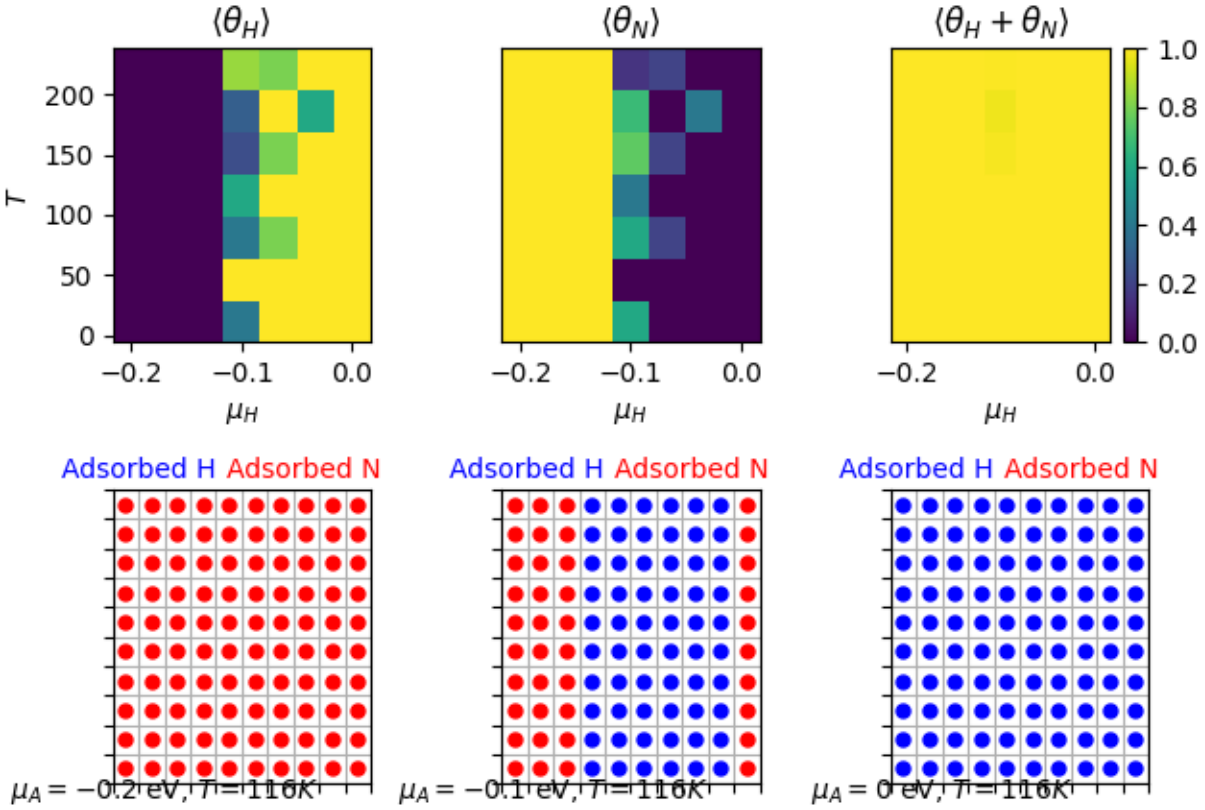

Figure 8: The adsorbing of Hydrogen and Nitrogen on a 10*10 grid in an immiscible mixture scenario.

The Like Dissolves Unlike Mixture of Hydrogen and Nitrogen:

In this system there was assumed to be a negative energy associated with adsorbing to the surface, and another negative energy when particles were neighboring each other but only if those particles were different, otherwise there was a positive energy.

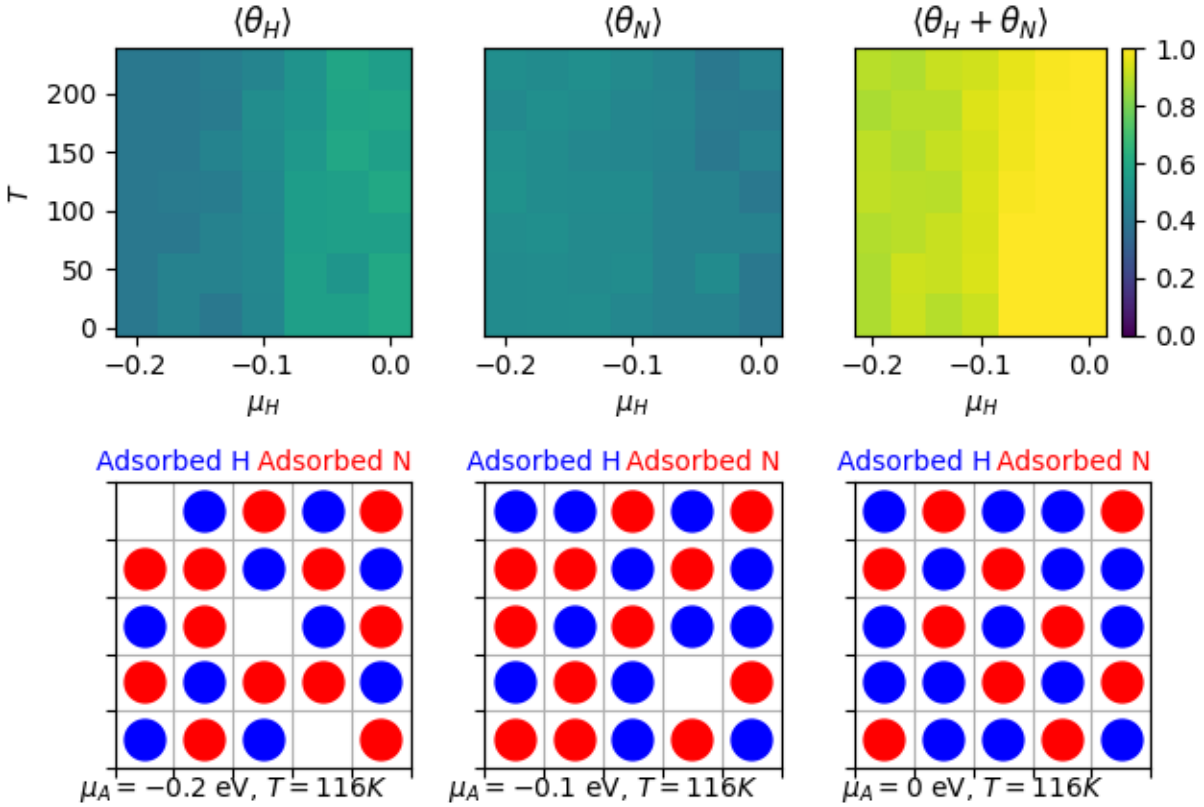

Figure 9: The adsorbing of Hydrogen and Nitrogen on a 5*5 grid in an in a like dissolves unlike mixture scenario.

Here we see the checkerboard pattern sort of emerge again, but it isn't perfect and as expected it is filled with alternating particles. Since each particle wants to be near as many different particles as possible this makes sense. One unusual thing is that the grid doesn't have total coverage as it did for all other attractive scenarios. This is likely because some spots have too many neighbors of both particle types that it becomes unfavorable for either particle. This weirdly didn't happen as much in the 10*10 grid.

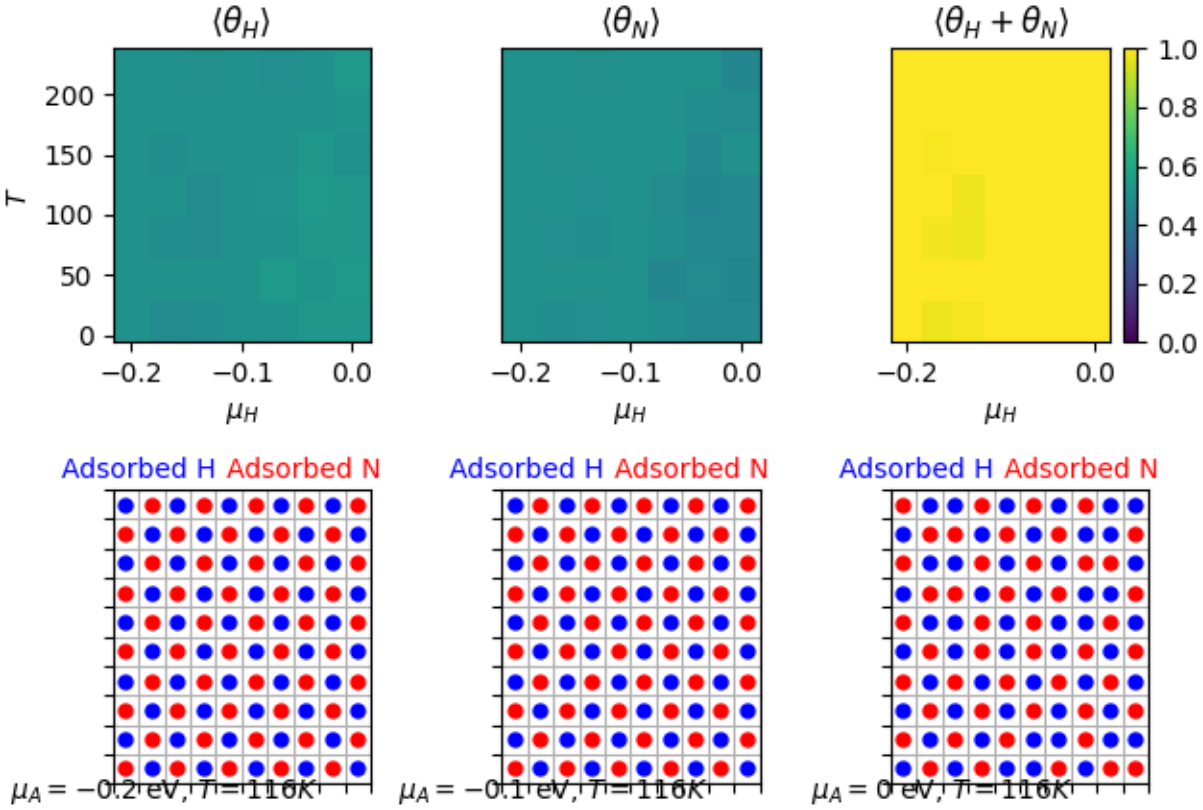

Figure 9: The adsorbing of Hydrogen and Nitrogen on a 10*10 grid in an in a like dissolves unlike mixture scenario.

Conclusions:

These simulations are useful for industry because they allow you to simulate a system under various conditions prior to constructing it. It also allows you to see what system is the most favorable for your purposes. In this case I believe that should the like dissolves unlike scenario be accurate, it would be the best for ammonia assembly.