Project 1 – Monte Carlo Simulations

Introduction

The production of Ammonia is one of the most important industrial processes in human civilization. In addition to many other uses, ammonia is used as a fertilizer, and its mass production is one of the factors that allows for the industrial farming needed that the modern world relies on.

The current method for mass production of the Haber-Bosch process, which uses an iron catalyst to convert gaseous nitrogen and hydrogen to ammonia according to the following reaction:

$$3\mathrm{H}_2(g) + \mathrm{N}_2(g) \rightarrow 2\mathrm{NH}_3(g)$$

In order for this reaction to work at the scales needed, both nitrogen and hydrogen must interact with the catalyst, which serves to break H-H and N-N bonds to allow H and N atoms to come together to form ammonia. This project uses computational simulations to model the adsorption of these gases on the surface of this catalyst to make an attempt at determining the optimal conditions for this rection to take place under.

Methodology

To carry out these simulations, a grand Monte Carlo scheme on a square lattice was used. At each step in a given simulation, the program attempted to add or remove a particle from a random site on a pre-defined lattice. This move was accepted if a random number ranging from zero to 1 was less than the calculated acceptance probability, which is provided in equations 1 and 2 for particle addition and removal respectively. For these equations, β is the inverse temperature ($1/k_BT$), N_a and N_s are the number of empty sites and number of sites occupied by species s respectively, μ_s is the chemical potential of species s and ΔE is the change in energy (see equation 3) from the move.

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

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

The energy of a given lattice configuration if found by taking the sum of all adsorption energies (ϵ_i) and all interaction energies between nearest neighbor particles (ϵ_{ij}). These energies vary between the 5 scenarios tested and are provided in Table 1.

Table 1. Adsorption and interaction energies used in these simulations.

Scenario	ϵ_H	ϵ_N	ϵ_{third}	ϵ_{HH}	ϵ_{NN}	$\epsilon_{thirdthird}$	ϵ_{HN}	ϵ_{Hthird}	ϵ_{Nthird}
Ideal	-0.1	-0.1	-0.1	0.00	0.00	0.00	0.00	0.00	0.00
Repulsive	-0.1	-0.1	-0.1	0.05	0.05	0.05	0.05	0.05	0.05
Attractive	-0.1	-0.1	-0.1	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05
Immiscible	-0.1	-0.1	-0.1	-0.05	-0.05	-0.05	0.05	0.05	0.05
"Like dissolves unlike"	-0.1	-0.1	-0.1	0.05	0.05	0.05	-0.05	-0.05	-0.05

* All energies are given in units of eV

The chemical potentials for nitrogen and a third species are held constant, but the chemical potential of hydrogen is varied from -0.2 eV to 0 eV as part of the simulation process. Temperature ranges from 0.001 to 0.019 in units of T/k_B. At each combination, the simulation was allowed to run for 10,000 steps to equilibrate, and the average coverages of hydrogen, nitrogen, and a third species were calculated and recorded. These coverages were plotted on a grid using a color bar to indicate coverage. These plots were then examined to look at phases at different values of T and μ_H.

Because of the random nature of this method, the lattice configurations of a simulation at a given value of T and μ_H will cycle through several possible configurations around the same level of probability. To view this process, the code written to carry out these simulations allows a user to choose to generate a gif of different configurations at a specific T and μ_H. Examples of these animations for the ideal mixture scenario can be found in the folder titled "gifs" in the GitHub repository associated with this work.

Results

Ideal Mixture of Nitrogen and Hydrogen

The ideal mixture scenario assumes that the nitrogen and hydrogen do not interact with either themselves or each other. Because of this, only the adsorption energies of the gas particles contribute to total energy of the system. Because of this, the only factor that makes a particle of hydrogen more likely to bind than a particle of nitrogen is the value of μ_H. This is reflected in the phase diagrams of this system shown in Figure 1.

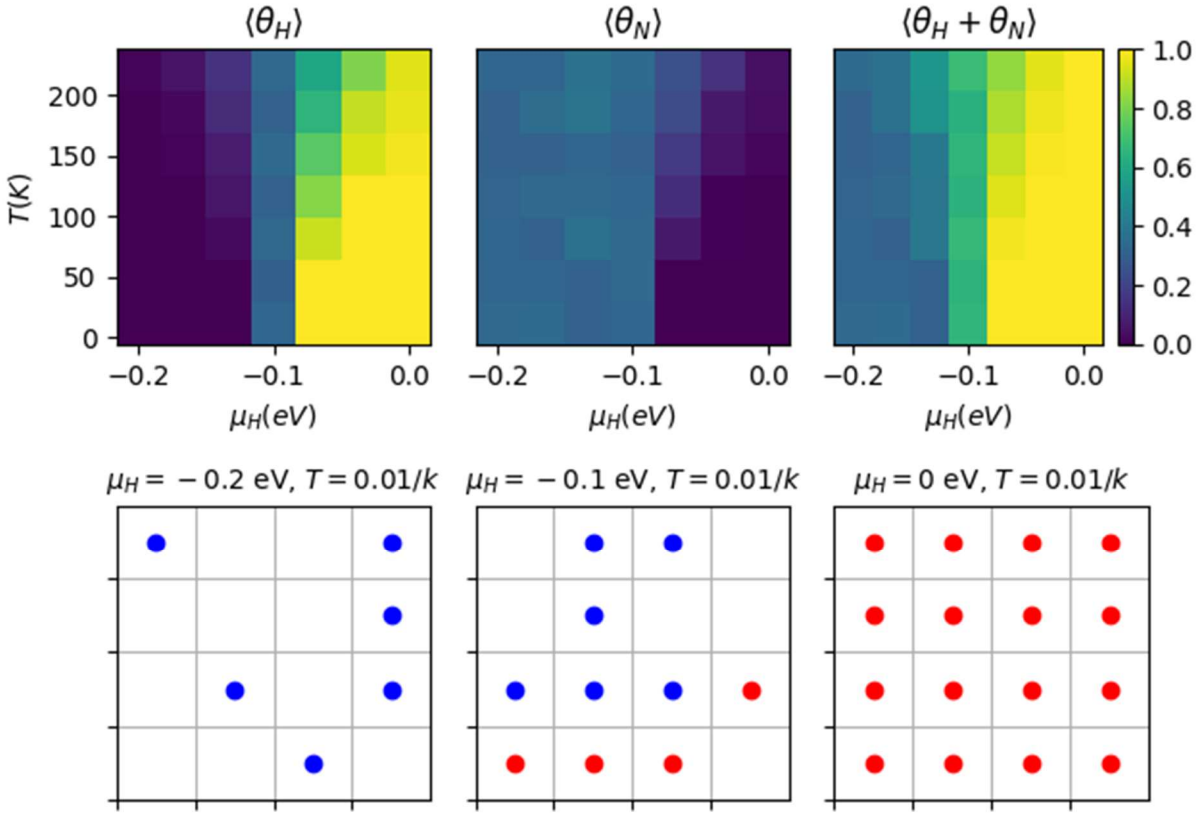

Figure 1. Phase diagrams and examples of lattice configurations for the ideal mixture scenario.

At values of $\mu_H < \mu_N$, only nitrogen is adsorbed at a coverage of about 0.4. When $\mu_H > \mu_N$, hydrogen is the predominant or only species adsorbed. This occurs because the higher value of μ_H relative to $,\mu_n$ results in a higher likelihood of hydrogen contacting the surface and adsorbing than the likelihood for the same to occur with nitrogen since it is thermodynamically preferred to have the hydrogen removed from the gas phase. Increasing the temperature did not affect the average coverages as much as altering the value of μ_H, but had the effect of reducing the mean coverage at a given value of μ_H.

Three species version

When a third species is added at the same chemical potential as nitrogen, it tends to follow the same trends as nitrogen does. This is because nitrogen in this scenario never had a mean coverage above 0.5 in the two species version and the particles do not interact with each other. Because the chemical potential used produces a lower coverage, there are enough sites for the third species to adsorb without competing with the nitrogen when hydrogen does not adsorb. As a result, the only real difference between the phase diagrams (see figure 2) for the two and three species versions of the ideal mixture scenarios that, at low μ_H, the total coverage is higher (around 0.6-0.8) because there is an additional species adsorbing in sites that would have otherwise remained empty.

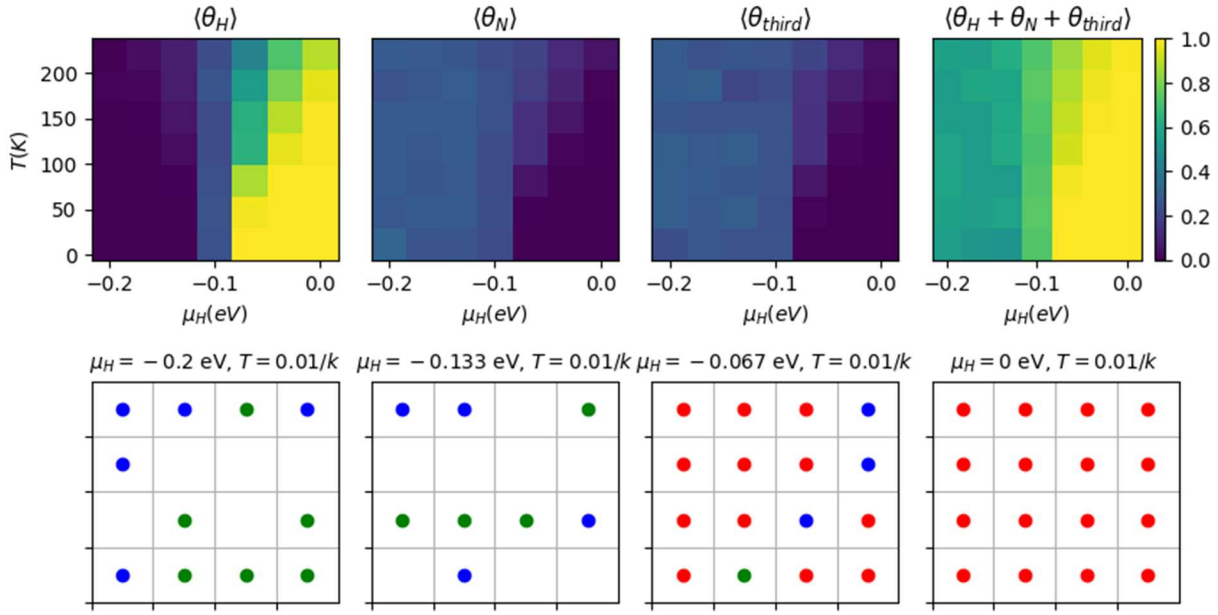

Figure 2. Phase diagrams and examples of lattice configurations for the three species version of the ideal mixture scenario.

Repulsive interactions between nitrogen and hydrogen

In this scenario, it is assumed that all particles repel their neighbors. This means that both the adsorption energy and the specific site being considered affect the likelihood of adsorption and removal. Because of this, states with a high coverage are penalized more heavily due to the greater number of destabilizing neighbor interactions. This is reflected in the phase diagrams for the system (Figure 3)

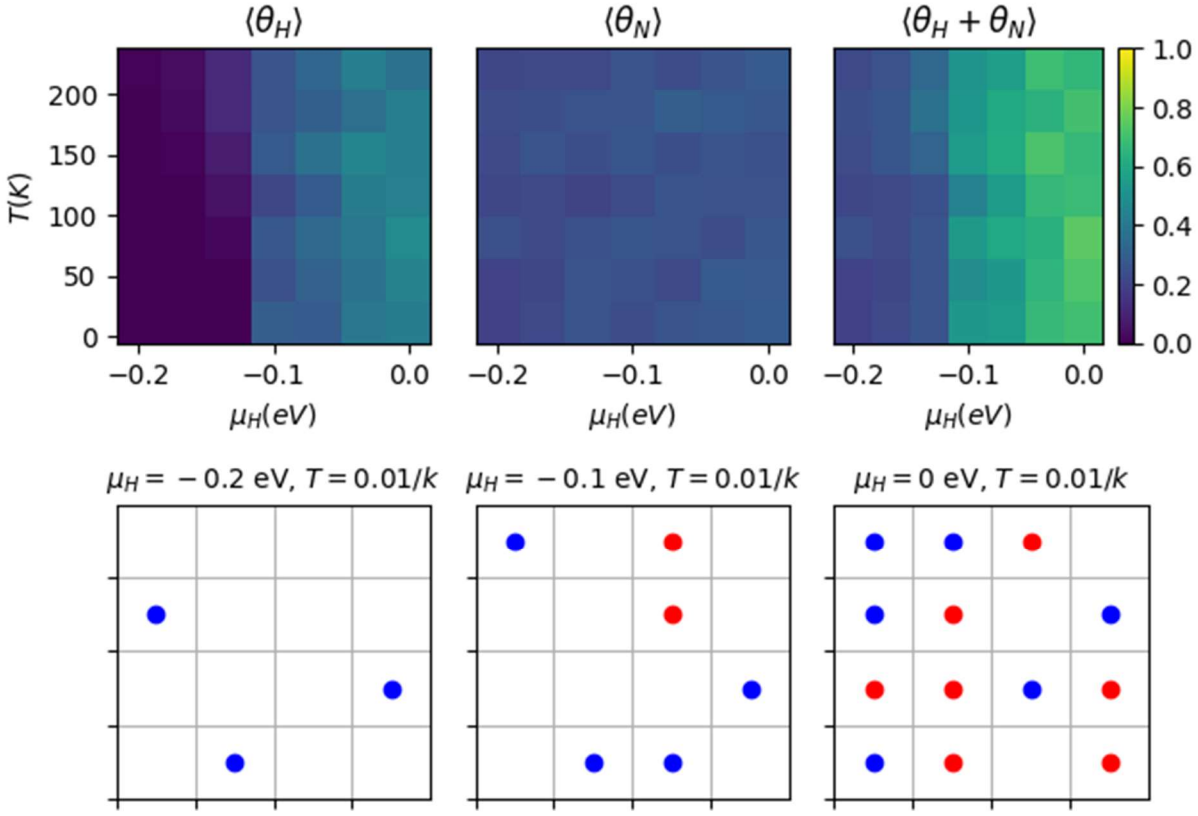

Figure 3. Phase diagrams and examples of lattice configurations for the scenario with repulsive interactions.

At values of $\mu_H < \mu_N$, only nitrogen is adsorbed at a coverage of about 0.4. When $\mu_H > \mu_N$, hydrogen becomes adsorbed at a coverage of about between 0.4 and 0.5 while the coverage of nitrogen is unchanged. Because the repulsive interactions between neighboring particles will begin to destabilize the system at higher coverages, there will consistently be open sites on the lattice, giving nitrogen more opportunities to adsorb even when μ_H is high.

This contrasts with the ideal mixture scenario where it is less likely for a particle to be removed at high coverage, reducing the number of available sites for new particles to bind. When μ_H is high in the ideal mixture scenario, hydrogen is more likely to bind to the surface than nitrogen, and once on, it is less likely to desorb, allowing for a coverage of 1.0. Here, the constant availability of sites means that nitrogen will have opportunities to bind, even if $\mu_H > \mu_N$.

Three species version

When a third species is added at the same chemical potential as nitrogen, it tends to follow the same trends as nitrogen in this scenario as well. This is because in this scenario, repulsive interactions make desorption more likely, while making it less favorable to produce states with high coverage. Because there are always open sites where the third species could adsorb, there is always the possibility for it to adsorb. The two main differences in the phase diagrams (see figure 4) for the two and three species versions of this scenario are that the coverage of nitrogen and the third species are lower for each (μ_H,T) combination than they were in the two species version, and that the coverage of hydrogen at high μ_H is lower nan it was in the two species version. Both of these can be explained by the fact that there is a maximum

number of particles that can be adsorbed without destabilization, and there are now more options for what particle to adsorb, lowering to coverage of each species.

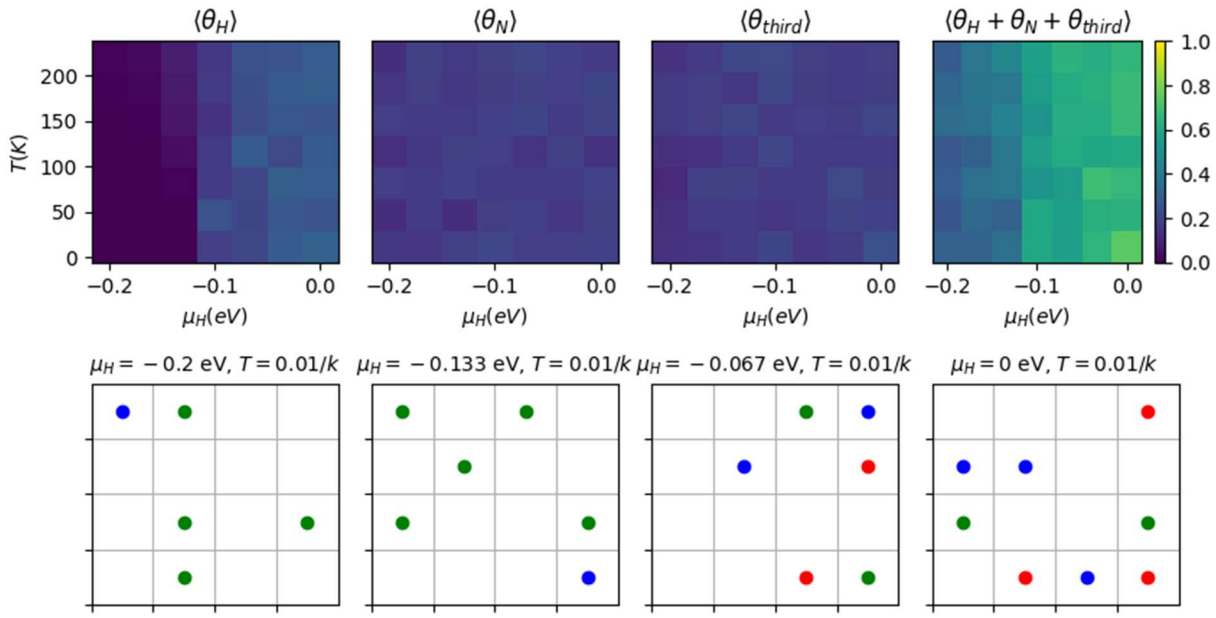

Figure 4. Phase diagrams and examples of lattice configurations for the three species version of the repulsive interaction scenario.

Attractive interactions between nitrogen and hydrogen

In this scenario, it is assumed that all particles are attracted to their neighbors. This means that states with a high coverage are more likely than low coverage phases due to the greater number of stabilizing neighbor interactions.

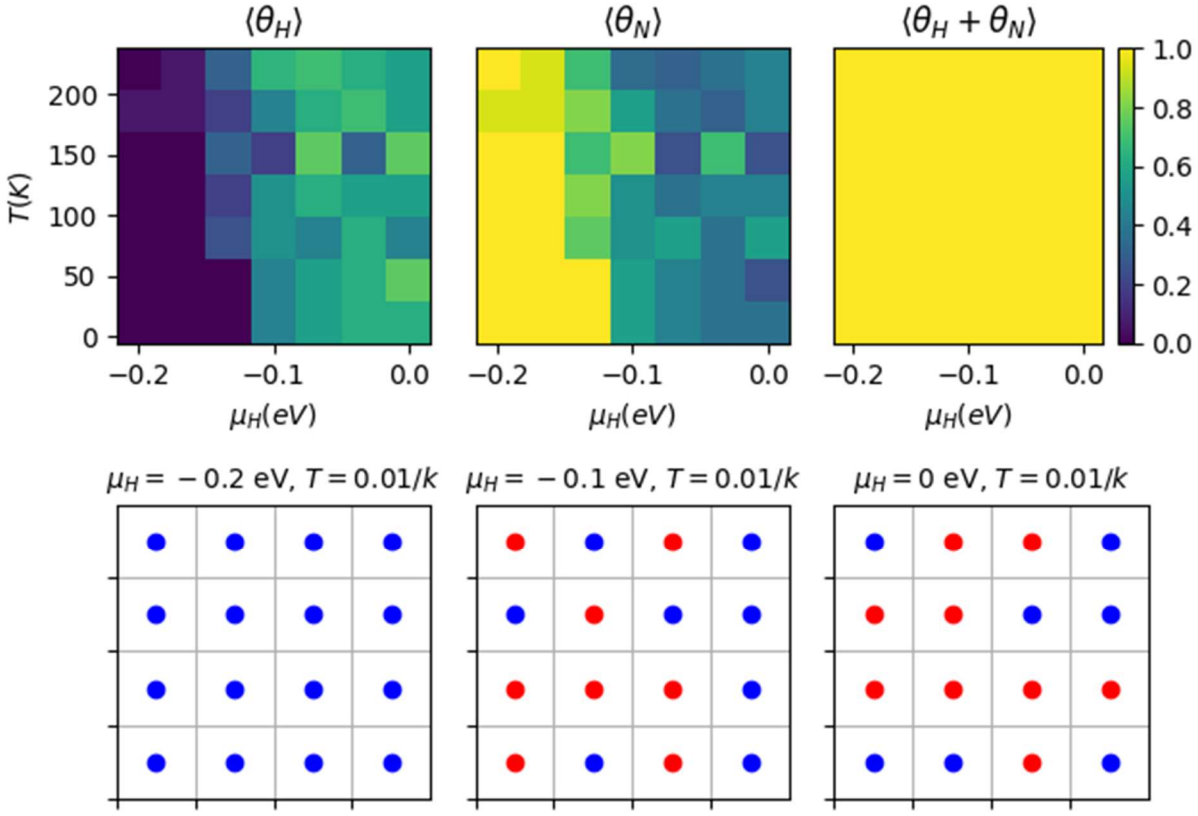

Figure 4. Phase diagrams and examples of lattice configurations for the scenario with attractive interactions between nitrogen and hydrogen.

At values of $\mu_H < \mu_N$, nitrogen is the primary adsorbate with a coverage between about 0.7 and 1.0. When $\mu_H \geq \mu_N$, hydrogen and nitrogen are adsorbed at similar coverages with hydrogen becoming slightly more prevalent as μ_H increases. At all values of T and μ_H the total coverage is 1.0. Because all neighboring particles attract and stabilize each other, states with high total coverages are favored, which is why the total mean coverage is always 1.0.

The mixture of nitrogen and hydrogen that forms at $\mu_H > -0.1$ can be explained as follows. Because all particles are stabilized by their neighbors regardless of particle type, adsorbed particles are much less likely to desorb at high coverages. As a result of this, at high values of μ_H, once a nitrogen adsorbs to the surface, it is harder to replace in the simulation than it was in the ideal mixture scenario since the ΔE associated with desorption is greater and less favorable than it was in the ideal mixture scenario. As a result of this, the mean coverage of nitrogen is always nonzero because it does not remain desorbed long enough to be fully replaced by hydrogen.

Three species version

When a third species is added at the same chemical potential as nitrogen, the phase diagrams for it and nitrogen are similar to one another but differ from the phase diagram of nitrogen in the two species. In this scenario, all neighbor particles have attractive interactions between them regardless of species. Because of this, all particles that adsorb are stabilized. Since there are now three options for adsorbates, the coverage of any one species will decrease when compared to the results of the two species scenario. This can be seen in the diagrams in figure 4

which show that, while the total coverage is always 1.0, the coverage of non-hydrogen species are never at 1.0 even when μ_H.

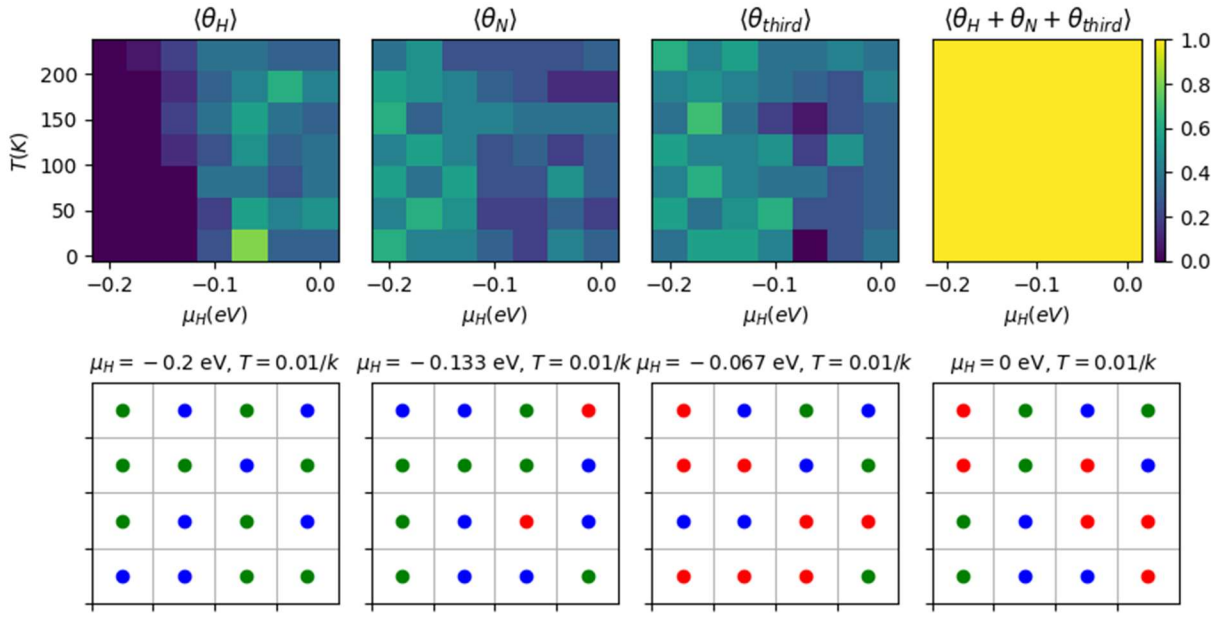

Figure 4. Phase diagrams and examples of lattice configurations for the three species version of the attractive interaction scenario.

Immiscible nitrogen and hydrogen

In this scenario, it is assumed that particles are attracted to other particles of the same type but repelled by other types of particles. The results of this are that clusters of a single type of particle should form on the surface which is reflected in the lattices shown in Figure 5.

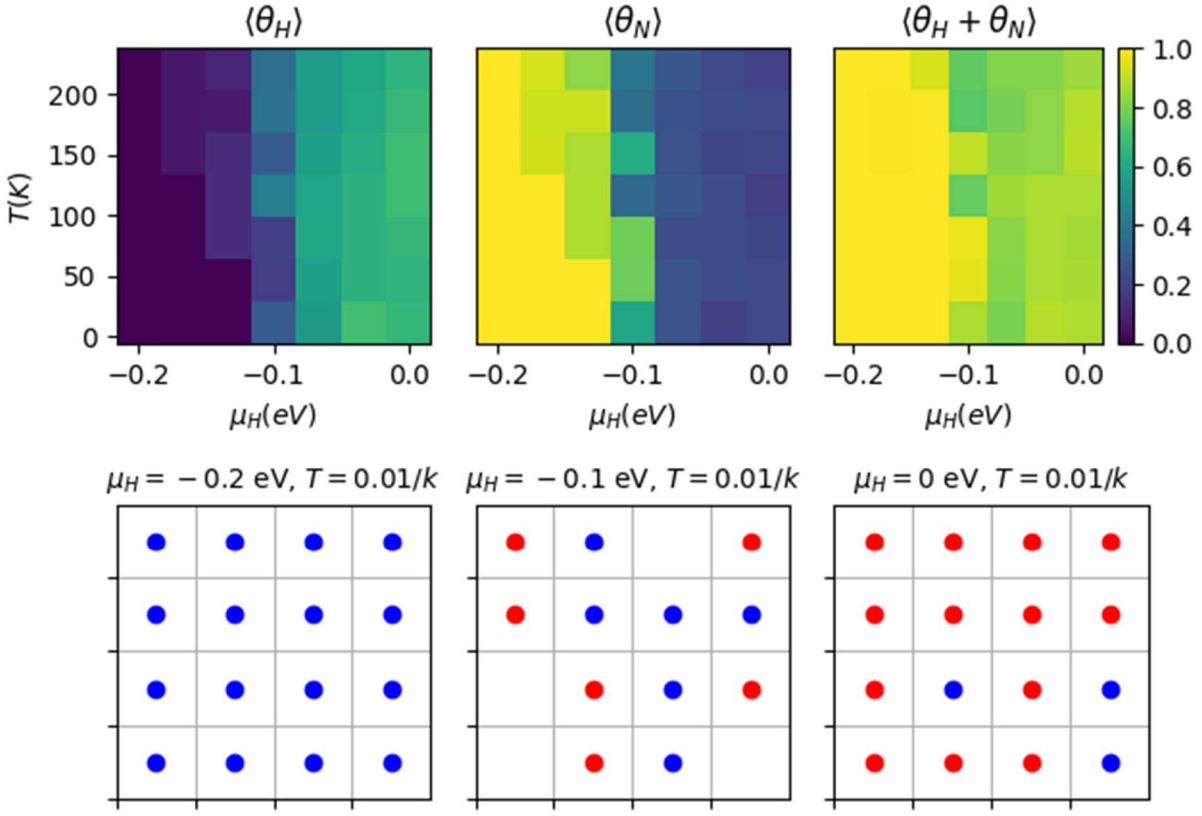

Figure 5. Phase diagrams and examples of lattice configurations for the scenario with repulsive interactions between nitrogen and hydrogen, but attractive interactions between particles of the same type.

At low values of μ_H, nitrogen is adsorbed with a high coverage ranging from 0.8 to 1 depending on μ_H and temperature. This is because at these values of μ_H, hydrogen is less able to adsorb, and nitrogen can maximize its attractive interactions with itself. However, as μ_H increases, more hydrogen can adsorb, introducing repulsive interactions that destabilize the system and lower the total coverage.

The phase diagrams of this scenario differ from those of the purely repulsive and attractive scenarios because it contains two types of interparticle interactions. As with the purely attractive scenario, when nitrogen is the primary adsorbate, coverage is high because all neighbor interactions are stabilizing. Unlike the purely attractive scenario, adding hydrogen destabilizes the system and lowers total coverage. However, because the two species can form clusters with stabilizing interactions, the coverage still remains above 0.5, resulting in a difference between this scenario and the one with purely repulsive interactions.

Three species version

In this scenario, adding a third species produces significant deviation from the phased diagram behavior of the two species version. The region of $\mu_H$values which produce a total coverage of 1.0 extends to higher values than it does in the two species version. Additionally, at lower values of μ_H in many (μ_H,T) pairs, only nitrogen or the third species will be adsorbed at a coverage of 1.0. This is because each species repels all other species, meaning that whichever of the two gains the highest coverage first will force any new particles of the other species off.

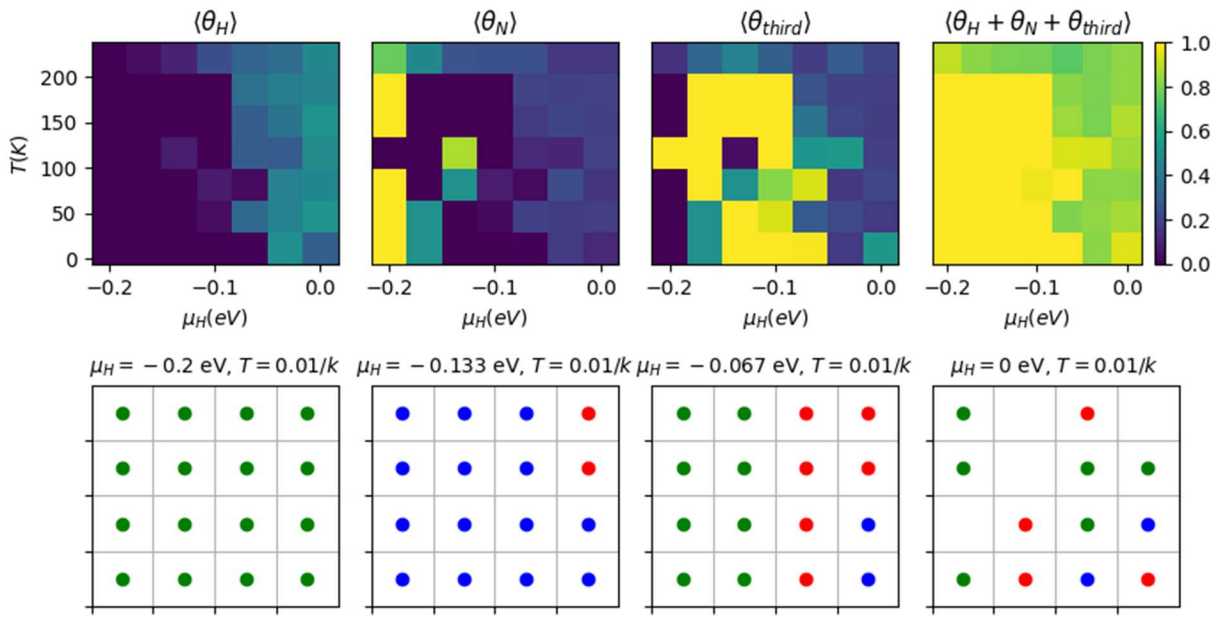

Figure 5. Phase diagrams and examples of lattice configurations for the three species version of the immiscible scenario.

<u>"Like dissolves unlike" scenario</u>

In this scenario, particles repel other particles of the same type, but attract particles of a different type. This should result in lattice configurations where clusters of one particular species do not form which is reflected in the lattices shown in figure 6.

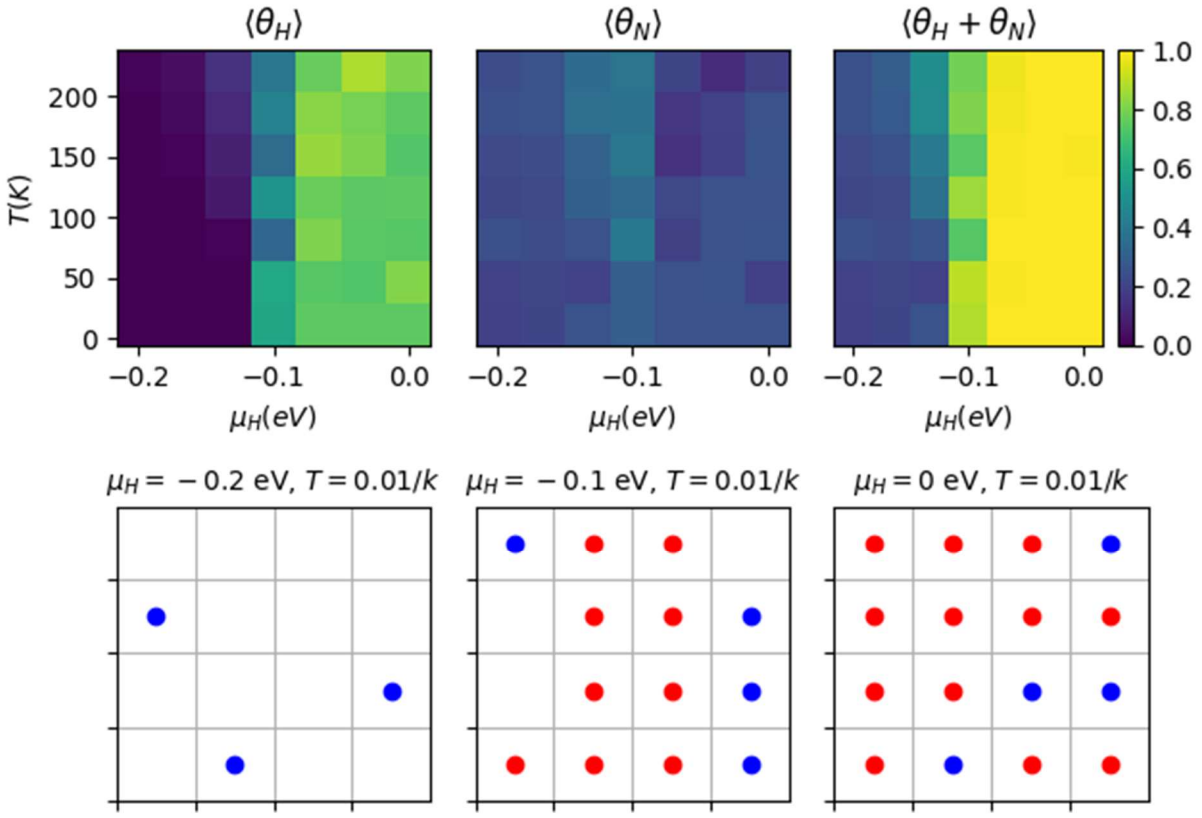

Figure 6. Phase diagrams and examples of lattice configurations for the scenario with attractive interactions between nitrogen and hydrogen, but repulsive interactions between particles of the same type.

At low values of μ_H, nitrogen is the primary adsorbate at a coverage of about 0.4. This is because at these values of μ_H, hydrogen does not adsorb very well, so nitrogen almost exclusively experiences destabilizing neighbor interactions, causing it to essentially experience the same conditions as in the purely repulsive scenario. At higher values of μ_H, hydrogen is adsorbed with a coverage around 0.7 - 0.8, while nitrogen adsorbs at around 0.2-0.3. at values of μ_H greater than -0.1, the total coverage is always 1.0. By allowing both hydrogen and nitrogen to adsorb, the number of repulsive interactions can be minimized, and the number of attractive interactions maximized. Hydrogen is the primary adsorbate at high μ_H even though (in theory), the way to optimize neighbor interactions would be to fill every other site with hydrogen and the rest with nitrogen. This indicates that at high enough chemical potential, destabilization from neighbor interactions can be overcome.

This scenario differs from the immiscible scenario in that this scenario penalizes states with one primary adsorbate while the immiscible scenario rewards those states. This can be seen in the phase diagrams in figures 4 and 5 because in figure 5, $< \theta_N >$ is maximized at 1.0 when μ_H is too low for hydrogen to adsorb at significant levels, while in figure 6, $< \theta_N >$ remains at less than half regardless of μ_H. Additionally, in the immiscible scenario, $< \theta_{total} >$ decreases with increasing μ_H while in this scenario, it increases. The lattice configurations also differ between scenarios. With the immiscible set of interactions, adsorbates formed single species clusters, which can be seen in the example lattices provided in figure 5. In the “like dissolves

unlike" scenario, the species should be intermixed, with no significant clusters, which can be seen in figure 6.

Three species version

The largest difference between the three and two species versions of this scenario is that all (μ_H, T) samples to produce a total coverage of 1.0. This is because the presence of the third species ensures that there is always a way to generate configurations that maximize the number of attractive neighbor interactions. This can be seen in the lattice configurations for low μ_H provided in figure 7. Hydrogen does not adopt a configuration with coverages as high as in the two species set for higher μ_H values because having two extra species to compete against lessens the effect of having a higher chemical potential.

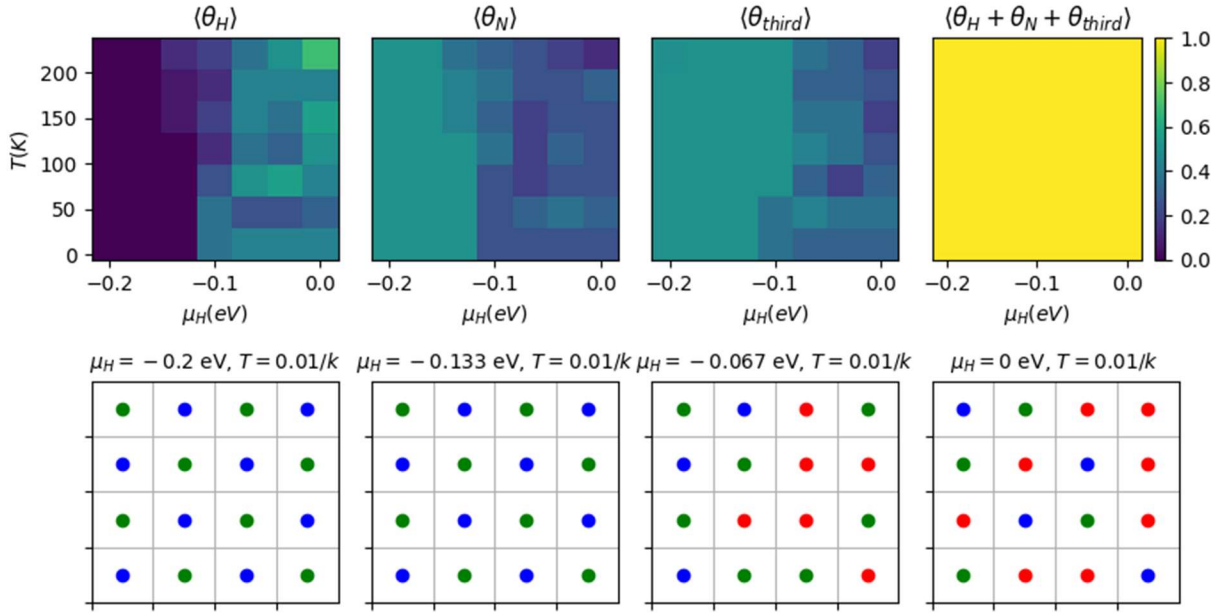

Figure 7. Phase diagrams and examples of lattice configurations for the three species version of the "like dissolves unlike" scenario.

Discussion

In all scenarios, despite differences in interaction energies, a couple of trends are present. First, hydrogen does not adsorb at significant levels- if at all- at values of μ_H below -0.1 eV. This holds true even for sets where the coverage of other species were well below 1.0 at those values of μ_H, and there were open lattice sites that it could have adsorbed to. This suggests that the chemical potential of hydrogen must be > -0.1 eV in order for ammonia to be produced since both hydrogen and nitrogen must be adsorbed.

The second general trend is that increased temperature reduces the coverage of the primary adsorbate at the corresponding μ_H value if the difference in coverage is large. This does not always affect the total coverage, because the coverage of the less prevalent adsorbate will increase in these scenarios. This is because a higher temperature makes it easier for particles to exist in gas phase because the total energy of the system is increased. The most obvious examples of this are the hydrogen coverage in figure 1 at low μ_H for and in the nitrogen coverage for the same at high μ_H. From the stoichiometry of the reaction that produces ammonia from H_2 and N_2, it the ideal ratio of H to N on the surface is 3:1, meaning hydrogen should be the primary adsorbate for optimal ammonia production. In all scenarios besides the ideal mixture, the

difference between the coverage of hydrogen and the coverage of other species is not large enough to be significantly affected by an increase in temperature.

Conclusion

Based on trends in adsorption behavior, the optimum conditions should be to have high chemical potential for hydrogen and elevated temperature. Because it is not possible to tell which scenario is the most accurate example of adsorption in this system without experimental exploration of the coverage, a general solution is needed. For all systems, hydrogen is only the primary adsorbate when $\mu_H > \mu_N$. Because (as previously mentioned) the optimal ratio of adsorbed hydrogen to adsorbed nitrogen is 3:1, hydrogen needs to be the primary adsorbate. This elevated chemical potential could be achieved by running the reaction at high pressure, or at least ensuring that the partial pressure of gaseous hydrogen is higher than the partial pressure of gaseous nitrogen. The reaction should also be run at elevated temperatures, because in many scenarios, there is only a minimal effect on adsorption due to temperature, and in the scenarios where temperature has a greater effect, higher temperature prevents hydrogen from occupying an excessive number of sites at the values of μ_H needed.