WASHINGTON UNIVERSITY IN SAINT LOUIS

Department of Chemistry

Simulations of Competitive Adsorption of Hydrogen and Nitrogen on a metal surface using Grand Canonical Monte Carlo Method

By

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Introduction

The Haber-Bosch process is a method for producing Ammonia from Nitrogen and Hydrogen while utilizing a metal surface as a catalyst. Several parameters, such as the type of catalyst, temperature, or pressure of the process, can vary to optimize the yield of ammonia.

$$N_2(g) + 3H_2(g) \underset{\text{T, P}}{\overset{\text{Catalyst}}{\rightleftarrows}} 2NH_3(g) \qquad \text{Eq.1}$$

In the following project, competitive adsorption of the reactants on a metal surface was simulated. To study the best way to optimize the reaction, the chemical potential of hydrogen and temperature of the reaction was varied, and its effects were analyzed by plotting phase diagrams as a function of chemical potential and temperature and several lattice configurations.

Methodology

This study was conducted by simulating competitive adsorption using the Grand Canonical Monte Carlo method (GCMC) and Metropolis algorithm in the programming language "python".

In the simulation, the energy of the system is given by *Eq.2*, in which it's the addition of the energy of adsorbate A and B at each site. The first sum iterates over all lattice sites, while the second sum iterates over the neighboring sites. The number of an adsorbate is equal to 1 if the site is occupied, and 0 if it's empty or occupied by a different particle.

$$E = \sum_i (n_i^A \epsilon_A + n_i^B \epsilon_B) + \frac{1}{2} \sum_{<i,j>} (n_i^A n_j^A \epsilon_{AA} + n_i^B n_j^B \epsilon_{BB} + n_i^A n_j^B \epsilon_{AB} + n_i^B n_j^A \epsilon_{AB}) \qquad \text{Eq.2}$$

The Metropolis Algorithm adapted for GCMC consists of adding a particle or removing a particle based on an acceptance criterion based on probabilities. *Eq.3* is the criteria to add a particle, while *Eq.4* is the criteria to remove a particle. N_a is the number of empty sites, while N_s is the number of sites occupied by a species s, with a chemical potential μ_s. Thermodynamic Beta includes the temperature and Boltzmann factor and is defined as $\beta = \frac{1}{K_B T}$.

$$acc = \min[\, 1, \frac{N_a - N_s}{N_s + 1} \exp(-\beta[\Delta E - \mu_s]) \,] \qquad \text{Eq.3}$$

$$acc = \min[\, 1, \frac{N_s}{N_a - N_s + 1} \exp(-\beta[\Delta E + \mu_s]) \,] \qquad \text{Eq.4}$$

During the simulation, a random empty site is chosen to add one of the adsorbates. Energy is calculated, and the criteria of *Eq.3* will decide if the move is accepted. Same procedure is done for removing a particle, but instead using *Eq.4*.

Results

An exploration of temperatures from 0 K to 220.5 K at different environments of interaction between the particles yielded a variety of phase diagrams. Lattice structures of three chemical potentials for hydrogen were plotted at a median temperature of 116 K.

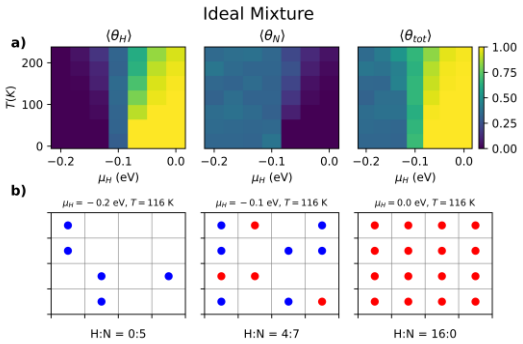

Figure 1. *Ideal Mixture interaction. a) Phase diagrams of mean coverage as a function of temperature and chemical potential. b) Lattice Structures at different chemical potentials*

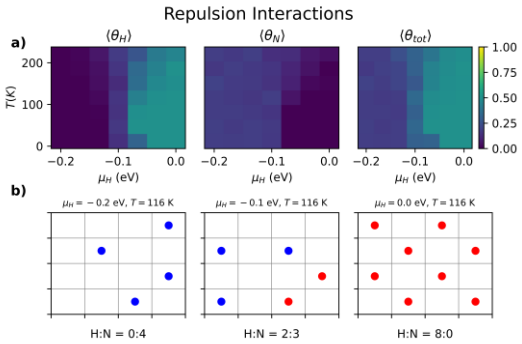

Figure 2. *Repulsion interaction. a) Phase diagrams of mean coverage as a function of temperature and chemical potential. b) Lattice Structures at different chemical potentials*

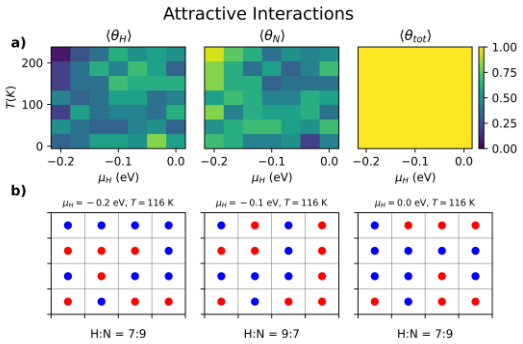

Figure 3. *Attractive interactions. a) Phase diagrams of mean coverage as a function of temperature and chemical potential. b) Lattice Structures at different chemical potentials*

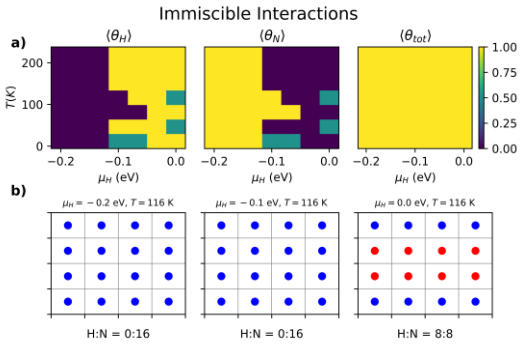

Figure 4. *Immiscible interactions. a) Phase diagrams of mean coverage as a function of temperature and chemical potential. b) Lattice Structures at different chemical potentials*

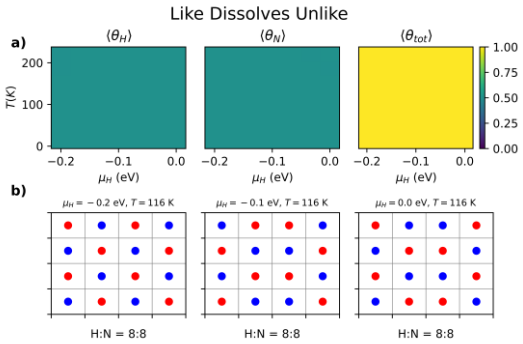

Figure 5. *Like dissolves unlike interactions. a) Phase diagrams of mean coverage as a function of temperature and chemical potential. b) Lattice Structures at different chemical potentials*

Tables summarizing the conditions needed for the reaction to be optimized were created. Lattice structures with a Hydrogen to Nitrogen ratio of "3.0" or "3:1" was considered the preferred condition based on the chemical reaction of the Haber-Bosch process. Ratios between 2 and 4 were also considered optimal. The parameters that yielded the optimal results were summarized in the following tables:

Ideal Mixture			
μ (eV)	**Temperature (K)**	**H:N Ratio**	**θ (%)**
-0.07	116.0	4.0	93.75
-0.07	185.7	2.5	87.5

Table 1. *Ideal Mixture interaction.*

Repulsion Interactions			
μ (eV)	**Temperature (K)**	**H:N Ratio**	**θ (%)**
-0.1	185.7	2.0	37.5
-0.07	150.9	2.5	43.75
-0.07	220.5	2.0	37.5

Table 2: *Repulsive interaction.*

Attractive Interactions			
μ (eV)	**Temperature (K)**	**H:N Ratio**	**θ (%)**
-0.1	150.9	2.2	100.0
-0.07	185.7	2.2	100.0

Table 3: *Attractive interaction.*

For the range of temperature specified (0-220 K), no parameters were found in which the ratio was optimal for Immiscible and Like Dissolves Unlike interactions.

Discussion

During the simulation, the chemical potential for Nitrogen (μ_N) was kept constant with a value of -0.1 eV. The chemical potential for Hydrogen was varied (μ_H) with values ranging from -0.2 eV to 0 eV. The chemical potential can be described as a tendency of a substance to move from one place to another. In the context of a gas molecule adsorbing to a lattice site, a low chemical potential indicates that the molecule is less favorable to adsorb in the lattice.

To interpret the results, and to hypothesize on factors that can improve the conditions of the reaction, chemical and thermodynamic properties should be employed. At constant temperature, chemical potential is defined in *Eq.5*. This equation relates how a change of pressure affects the chemical potential of a substance and can be used to analyze the phase diagrams. Le Chatelier's principle, which governs how equilibrium is shifted based on changes in the conditions can be applied to the chemical reaction of the Haber-Bosch process described in *eq.1* to determine the validity of the results.

$$\mu = \mu^o + RTln(\frac{P}{P^o}) \qquad \text{Eq.5}$$

The perfect conditions for the reaction to occur are when the lattice sites have a ratio of 3 hydrogen molecules to 1 nitrogen molecule, as that follows the stoichiometry of the chemical reaction in *Eq.1*. However, even without that optimal condition the reaction can still proceed, as long as there is at least one 3:1 ratio of particles neighboring each other. The lattice structure acts as a catalyst as it provides higher surface area with active sites in which molecules can bind and react with their neighbors, so its effectiveness outside of the 3:1 ratio depends on the physical parameters such as pressure and temperature that will affect the kinetics of the reaction.

A. Ideal Mixture

The phase diagram for the ideal mixture of nitrogen and hydrogen is shown in *Figure 1*. Under this setup, there are no attractive or repulsive interactions between the adsorbates on the surface. Therefore, they adsorb independently of each other. Neighboring atoms do not have an effect on their distribution along the lattice sites. The only condition that affects the lattice coverage is the chemical potential of hydrogen.

It is expected that at low μ_H the lattice sites will have more nitrogen and less hydrogen. The phase diagrams show the expected result, with the coverage of hydrogen increasing with an increase of μ_H and the opposite trend occurs with the coverage of nitrogen. It is worth noting that when $\mu_H = \mu_N$ the lattice sites, the lattice sites will be occupied with 50% nitrogen and 50% hydrogen. At the moment the chemical potential of hydrogen surpasses nitrogen, the lattice sites will include more hydrogen molecules.

Temperature has minimal effects on the adsorption of the molecules. With increasing temperature, there is a chance that hydrogen can adsorb into the surface of the molecule, even at low chemical potentials. Furthermore, with an increase in temperature, the total coverage of the lattice also increases.

Table 1 shows that for an ideal mixture, the chemical potential of hydrogen must be higher than nitrogen to facilitate hydrogen adsorption, and high temperature to increase the coverage of the lattice structure.

B. Repulsive Interactions

If the energies of the particles are set to be completely repulsive, it will result in lattice structures with low coverage as seen in *Figure 2*, as it is energetically favorable to not have molecules in neighboring sites. Similarly to the ideal mixture condition, an increase in μ_H will result in lattice structures that favor hydrogen adsorption. Temperature has a similar effect, in which it increases the chance of having hydrogen molecules adsorb in the lattice, even at values in which μ_H is lower than μ_N .

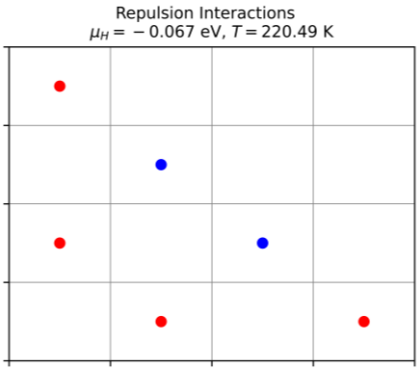

Figure 7. *Example of a lattice structure in the repulsive interaction regime*

Table 2 shows some conditions in which the ratio of hydrogen to nitrogen is favorable, but it has a very low coverage due to its repulsive interactions, as every other site is unoccupied. Even high temperatures can't overcome the repulsive energies between the molecules as seen in *figure 7*. Repulsive interactions will not induce a reaction in which the lattice structure acts as an optimal catalyst for the Haber-Bosch reaction.

C. Attractive Interactions

In the attractive regime, the energies of the molecules are set in a way that the molecules will be stabilized by having a neighbor in its lattice site. As a result, every lattice structure will be completely covered with mostly a 1:1 ratio as shown in the phase diagram in *Figure 3*. However, *Table 3* indicates that at some temperatures and chemical potentials, there are some structures that will form optimal conditions for catalyzing the reaction. As an example, at approximately 185 K, and with μ_H of -0.07, the lattice created has a ratio of 11:5. In another words, the lattice has three 3:1 clusters facilitating the reaction.

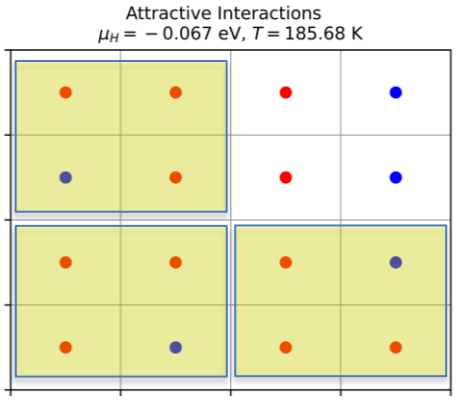

Figure 8. *Example of a lattice structure in the attractive interaction regime*

Overall, the attractive regime does not propitiate an adequate environment for ammonia production reaction as it's very likely to end up with a 1:1 ratio, however there are ranges of chemical potential and temperature that will favor ammonia production.

D. Immiscible Interactions

Immiscible interactions indicate that there are attractive interactions with adsorbates of the same kind and repulsive interactions between hydrogen and nitrogen. As the chemical potential of hydrogen increases, adsorption of hydrogen will be preferred as shown in *Figure 4.*

It is important to highlight that even though there are immiscible interactions, there is still a chance for both particles to be in the structure due to the randomness of the algorithm, however, they will form clusters of the same kind, and neighbors will not be two different molecules. However, because of the strong immiscible interactions, it is more likely to only have one type of molecule in the lattice structure and similar to the trend with the other types of environment, the chemical potential of hydrogen is a strong factor in indicating hydrogen adsorption to a lattice site.

Because of the clustering of like molecules, or having lattice structures completely conformed of one type of molecule, immiscible interactions are not favorable for ammonia production.

E. Like Dissolves Unlike

In "Like dissolved unlike" condition, the energetics favored mixing between hydrogen and nitrogen, as there are weak repulsive forces with like particles, and weak attractive forces with unlike particles. As a result, *Figure 5* shows a 50% coverage for hydrogen and nitrogen, with lattices existing in a 1:1 ratio, most likely alternating the type of molecule with its neighbors.

This is the most favorable, as it is more likely to form an arrangement in which Nitrogen will be surrounded by Hydrogen molecules, especially after adjusting the chemical potential to facilitate the adsorption of hydrogen inside the lattice

F. Implications for Haber-Bosch reaction

The results indicate that the chemical potential for hydrogen is pivotal to optimize the reaction. Temperature is also a factor. The reaction described in *Eq.1* is exothermic, and there are fewer gas molecules on the product side than the reactant. According to Le Chatelier's principle, by increasing the pressure at the beginning of the process, the equilibrium will be shifted forward, favoring the production of ammonia. This is validated in the results as in all interaction schemes, an increase of μ_H also increases hydrogen adsorption, which is needed to ensure there are enough moles of hydrogen to react with one mole of nitrogen. *Eq.5* further validates an increase of pressure as more favorable conditions, as an increase in P will increase μ_H . However, as the results summarized in *Tables 1 -3* show, the most optimal configurations do not have a chemical potential for hydrogen that ensures only hydrogen is able to adsorb into the lattice sites.

Because the reaction is exothermic, low temperatures are favored according to Le Chatelier's principle, however as shown in the phase diagrams of *Figures 1-6*, the lattice sites might be unoccupied and the reaction will proceed slowly. Therefore, moderately high temperatures could improve the kinetics of the reaction, however, it will result in a lower yield of ammonia. Due to the financial and global need for ammonia, quick production of ammonia might be more favorable, than increasing the yield at slower rates.

Conclusion

The ideal mixture could result in favorable conditions in which the lattice is able to catalyze the reaction, however, that is because of the randomness of the algorithm, and the conditions to set up an ideal mixture can't be effectively implemented in the industry. Repulsive interactions represent a regime that will result in no neighbors in their lattice sites, effectively eliminating any use of a lattice structure as a catalyst for the reaction. Attractive interactions represent a regime that could be favorable to ammonia production, but overall there is a large

likelihood of random configurations that might not satisfy the 3:1 ratio adequately. Immiscible Interactions are not favorable as the molecules will cluster with the same kind, and don't allow for any interaction with molecules of a different kind, which is essential for a chemical reaction to happen. Like dissolves unlike interactions are the most favorable, as it promotes an equal distribution of hydrogen and nitrogen in the lattice, but without clustering of the same type of molecules. The likelihood of 3 molecules of hydrogen to be neighboring one molecule of nitrogen is increased.

According to the phase diagrams, and validated by Le Chatelier's principle, and the thermodynamic definition of chemical potential, an increase of pressure and lower temperature will favor the production of ammonia. However, there must be a balance in the industry between increasing the kinetics and yield of the reaction.