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<div align="center">Water-Ammonia Binary System Fugacity Analysis</div>

Introduction and Background

In this project, I studied a binary mixture of ammonia and water. I chose these

components for the mixture because, when combined, they have a variety of relevant industrial

applications and contain interesting non-ideal behavior due to their strong unlike interactions. As

such, the mixture is not only important from a real-world standpoint, but also has unique

properties that yield more distinctive results than other systems with more ideal behavior.

In the real world, mixtures of water and ammonia have a large variety of applications,

including heating and refrigeration cycles, wastewater treatment, cleaning products, and fertilizer

production, among others. Since important properties, such as phase composition and energy

efficiency, depend on fugacity, a proper understanding of fugacity behavior in binary mixtures is

crucial for the development of reliable, safe, and effective processes.

Additionally, mixtures of water and ammonia exhibit strong non-ideal behavior. Both

ammonia and water are polar molecules capable of forming strong hydrogen bonds, leading to

unlike interactions that differ substantially from those in other binary systems. As such, the study

of this mixture successfully tests the limits of mixing rules, equations of state, and ideal

behavior, yielding rich results. Furthermore, the high nonideality of the mixture allows us to

explore the possibilities of using the binary mixing parameter k_{12} and evaluate its effect on the

mixing parameter a_{12} for quadratic mixing.

Methods

In this project, my goal was to evaluate the vapor-phase fugacity of a binary mixture of water and ammonia. To achieve this, I employed two methods: the Peng-Robinson (PR) equation of state with quadratic mixing rules, and generalized Lee-Kessler correlations for reduced temperature and pressure. I performed these calculations twice for each method, once under conditions close to ideality and once under nonideal conditions, to compare the Lewis fugacity rule with results from the PR equation of state. I produced my results using the following procedures.

To begin, I gathered physical property data for ammonia and water, including critical temperatures, critical pressures, and acentric factors, from Table A.1.2 in Koretsky's Engineering and Chemical Thermodynamics, 2nd ed. I then used the PR equation of state to find the pure-component PR parameter a_i for each component. This required the use of the Soave alpha function:

$$\alpha_i(T) = (1 + \kappa_i(1 - \sqrt{\tfrac{T}{T_{c,i}}})^2$$

where κ_i is fit to the acentric factor with:

$$\kappa_i = 0.37464 + 1.5422 * \omega - 0.26992 * \omega^2$$

I was then able to find the parameter a_i using the PR equation of state definition:

$$a_i(T) = 0.45724 \frac{R^2 T^2_{c,i}}{P_{c,i}} \alpha_i(T)$$

Next, I used this parameter, calculated for each component, to determine the mixing parameter a_{12}. Since the mixture of water and ammonia is highly unideal and asymmetric, it is most accurate to include the binary mixing parameter k_{12} when applying the binary mixing rule. To apply this, I took inspiration from Derjani, Figuiera, and Olivera-Fuentes' 2012 study on the

binary water and ammonia mixture, where they expressed the binary mixing parameter as a

linear function of temperature:

$$k_{ij}(T) = \mu_{ij} + \nu_{ij}T$$

where $\mu_{ij} = - 0.34918$ and $\nu_{ij} = 2.4467e - 4$.

Then, using quadratic mixing, I calculated a_{12} as follows twice: once including k_{12} and

once with $k_{12} = 0$:

$$a_{12}(T) = (1 - k_{12})(\sqrt{a_1 a_2})$$

Since the PR equation of state expresses the mixing parameter as a function of

temperature, I chose to calculate a_{12} at a variety of temperatures using this method, with a range

of 250 to 500 K.

Next, I used the equation for $ln\varphi_i$ for the PR equation of state to calculate the pure

species fugacity coefficients over a range of conditions. I measured the coefficients as functions

of pressure, temperature, and composition, each while holding the other conditions constant. To

do this, I first calculated a_{12} using the same process as before, along with the PR mixed

parameter b_{12}, found simply from:

$$b_i = 0.07780(\frac{RT_c}{P_c})$$

where R is the gas constant, and:

$$b_{ij} = y_i b_i + y_j b_j$$

where y_i and y_j are the mixture composition.

I also needed to calculate the compressibility factor, Z, which I accomplished by taking the largest real root of the cubic form of the PR equation of state, as follows:

$$f(Z) = Z^3 + \alpha Z^2 + \beta Z + \gamma = 0$$

where

$$\alpha = B - 1$$

$$\beta = A - 2AB - 3B^2$$

$$\gamma = B^3 + B^2 - AB$$

$$A = \frac{aP}{(RT)^2}$$

$$B = \frac{bP}{RT}$$

With these values, I had everything necessary to solve for the pure species fugacity coefficients for each component by applying the $ln\varphi$ formula for the PR equation of state, which is defined as:

$$ln\varphi_i = \frac{b_i}{b_m}(Z - 1) - ln(Z - B) - \frac{A}{2\sqrt{2}B}\left(\frac{2}{a_m}\sum_j y_j a_{ij} - \frac{b_i}{b_m}\right)ln\left(\frac{Z+(1+\sqrt{2})B}{Z+(1-\sqrt{2})B}\right)$$

I calculated the fugacity coefficients under a wide range of conditions, with my function of pressure ranging from 1 to 100 bar at 350 K and equimolar composition, my function of temperature ranging from 250 to 450 K at 20 bar and equimolar composition, and my function of composition ranging from 0 to 1 mol NH3/mol at 350 K and 20 bar.

I then transitioned to my second method and calculated the same pure species fugacity coefficients using generalized correlations from the Lee-Kesler equation of state. I completed these calculations for two sets of conditions at a constant temperature of 500 K: 5 bar to represent a near-ideal system and 50 bar to represent a non-ideal system. Since I only calculated

four coefficients, two for each component under both sets of conditions, I manually calculated T_r and P_r retrieved data from Table C.7 and C.8 in Koretsky, rather than importing the tables as matrices and solving computationally. I used double linear interpolation computationally to approximate table readings and solved for coefficients using the equation:

$$log(\Phi_i) = log(\Phi_i^{(0)}) + \omega log(\Phi_i^{(1)})$$

I finished my procedure by calculating the mixture fugacities for each method and each component under each set of conditions, and comparing the errors between methods. For the PR equation of state, fugacities were calculated with:

$$f_i^{mix,PR} = y_i \Phi_i^{mix,PR} P$$

For the Lee-Kesler generalized correlations method, I assumed the Lewis fugacity rule, such that:

$$f_i^{mix,Lewis} \approx y_i f_i^{pure,LK} = y_i \Phi_i^{pure,LK} P$$

I compared the results of each method for each component under each set of conditions using the percent error formula:

$$\%error_i = \frac{f_i^{mix,Lewis} - f_i^{mix,PR}}{f_i^{mix,PR}} \times 100\%$$

Such a comparison allowed me to quantitatively evaluate the effectiveness of the Lewis rule under both near-ideal and non-ideal conditions.

All calculations in this study were performed using MATLAB, including the produced plots. To evaluate at various conditions, custom functions were created to evaluate PR parameters, solve the cubic PR equation of state, and interpolate generalized correlation table values. All numerical results were also generated from this script.

Results and Discussion

Figure 1 shows the mixing parameter a_{12} as a function of temperature given by the PR

equation of state over temperatures ranging from 250 to 500 K. We can see that the change as a

result of temperature is approximately linear, with a slight concavity upward. The plot also

compares the mixing parameter with and without the binary mixing parameter k_{12}, which is used

to correct the nonideality of unlike interactions. We can observe that the use of k_{12} is critical

when working with highly nonideal binary mixtures, as a_{12} values differed greatly between the

two conditions. Without accounting for the nonideality of unlike interactions, the mixture term is

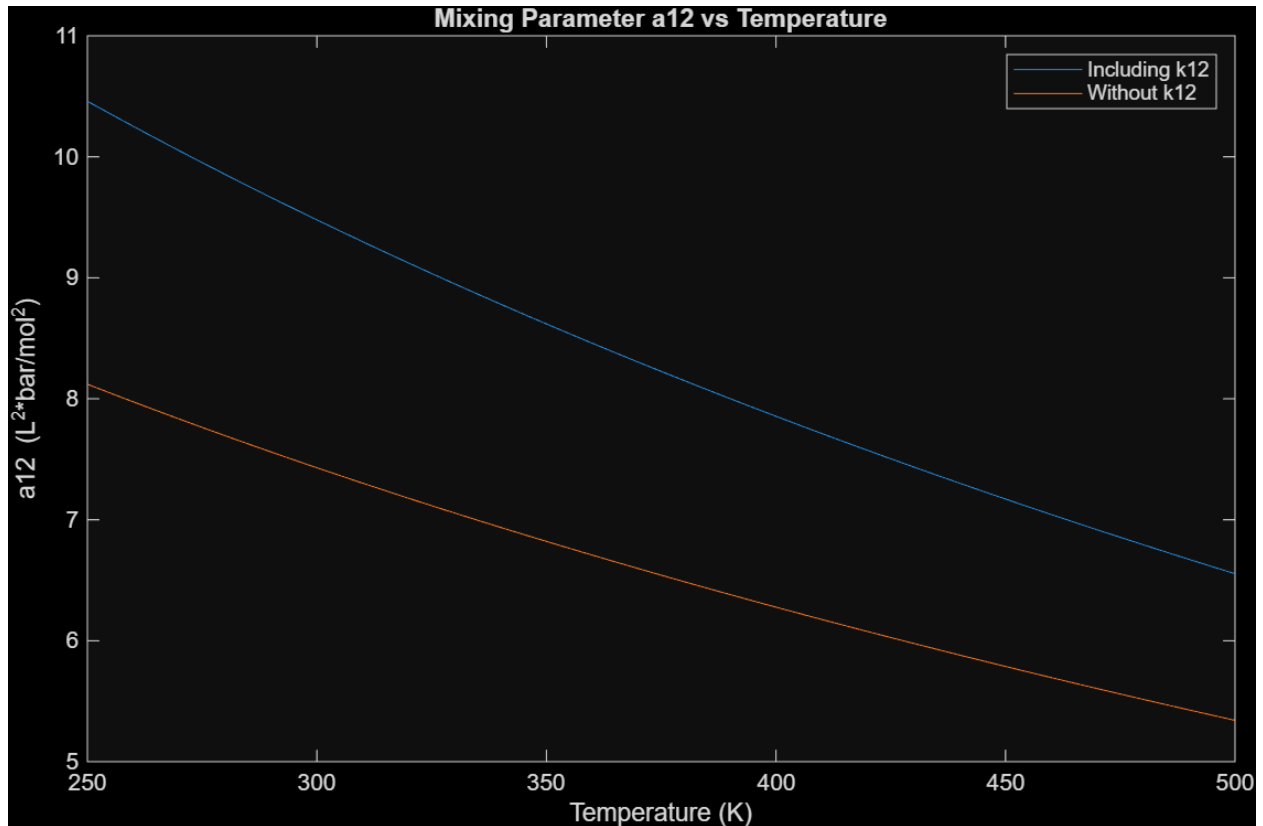highly inaccurate, with potentially dangerous consequences.

Figure 2 shows the fugacity coefficients of ammonia and water in a mixture, as predicted

by the PR equation of state, for pressures ranging from 1 to 100 bar at 350 K and equimolar

composition. At low, near-ideal pressures, the mixture behaves as expected. Both ammonia and water have coefficients that begin near the ideal value of 1 and decrease smoothly as the pressure deviates from the ideal case. This is consistent with the expectation that intermolecular forces are weak at lower densities, and we can see that the PR equation of state accurately approximates the ideal gas limit.
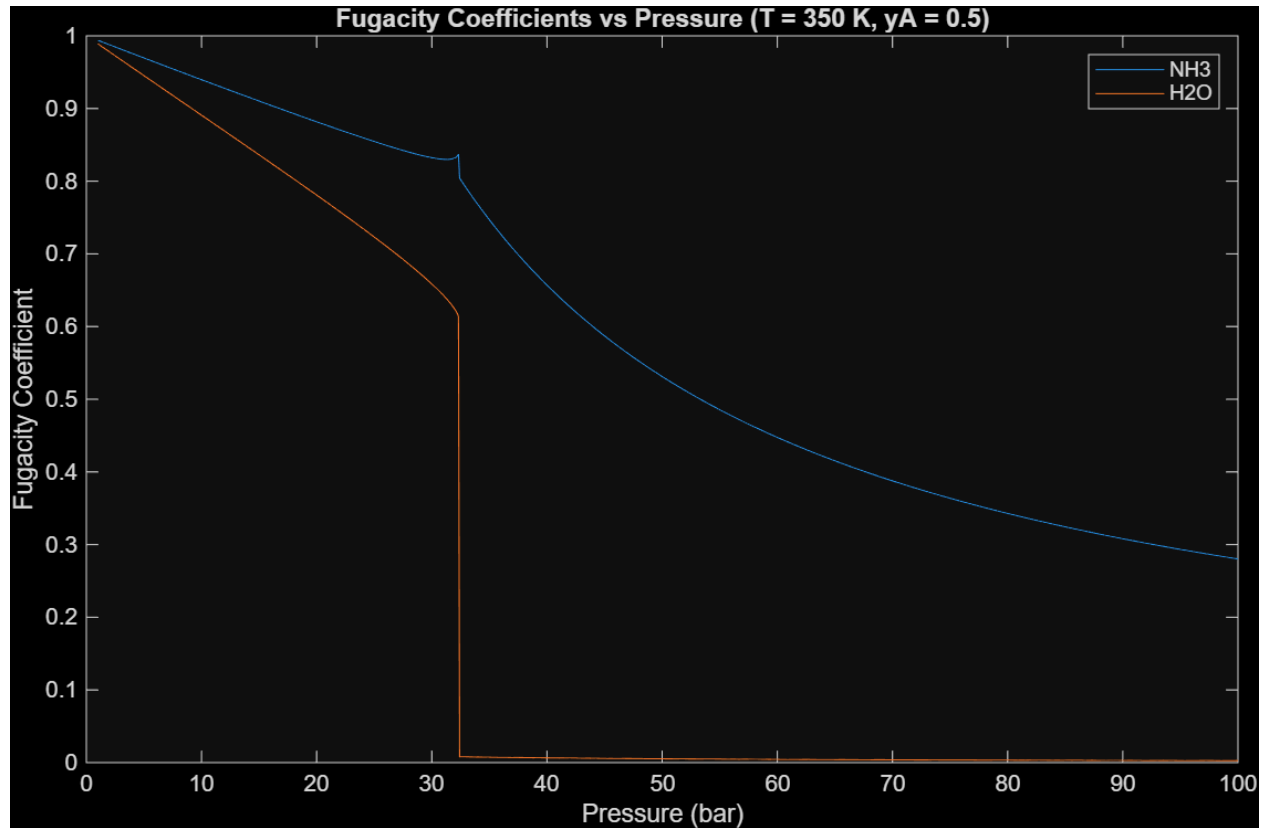
However, as the pressure increases, the PR model predicts extreme non-ideal behavior. Though ammonia's fugacity coefficient continues to decrease smoothly with pressure as expected, the coefficient of water, at around 33 bar, abruptly drops to approximately zero, and remains unexpectedly small throughout the rest of the pressure range. With further analysis, it becomes apparent that this decline is not due to incorrect math or condensation, which would occur at around 0.84 bar for water. Instead, it is a result of the instability of the PR equation of state when predicting the behavior of highly non-ideal systems. This failure is extremely fascinating! The term that causes the equation of state to fail as the system deviates from ideality is the logarithmic attraction term for the $ln\varphi$ formula for PR, which is as follows:

$$-\frac{A}{2\sqrt{2}B}\left(\frac{2}{a_m}\sum_j y_j a_{ij} - \frac{b_i}{b_m}\right)ln\left(\frac{Z+(1+\sqrt{2})B}{Z+(1-\sqrt{2})B}\right)$$
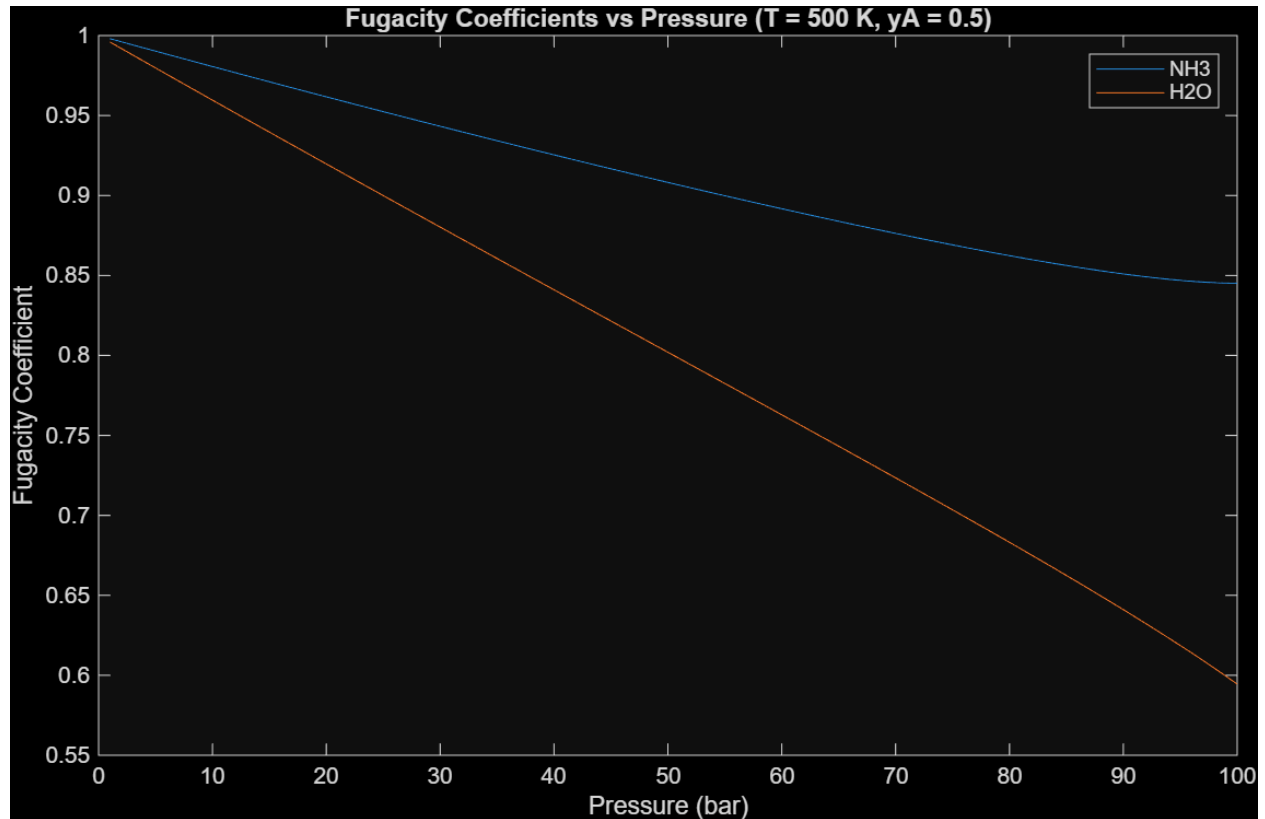
When the mixture becomes highly non-ideal, this expression becomes unstable. Since the term is negative, this instability causes $ln\Phi$ to approach $-\infty$, and therefore, causes Φ to approach zero. This happens because, for the mixture, the like interactions for water are incredibly strong, and, as a result, the mixture term a_{12} is skewed heavily toward the water term, affecting the compressibility factor Z such that, as the pressure increases, roots will become much less accurate. After a certain point, roots will become very close to each other or extremely small, which causes the logarithmic term to approach almost zero. The other parts of the

equation remain stable and do not collapse. In other words, the mixing rules for the PR equation of state are too simple to model the system accurately at highly non-ideal and asymmetrical cases, leading to Φ values that do not represent the physical reality.
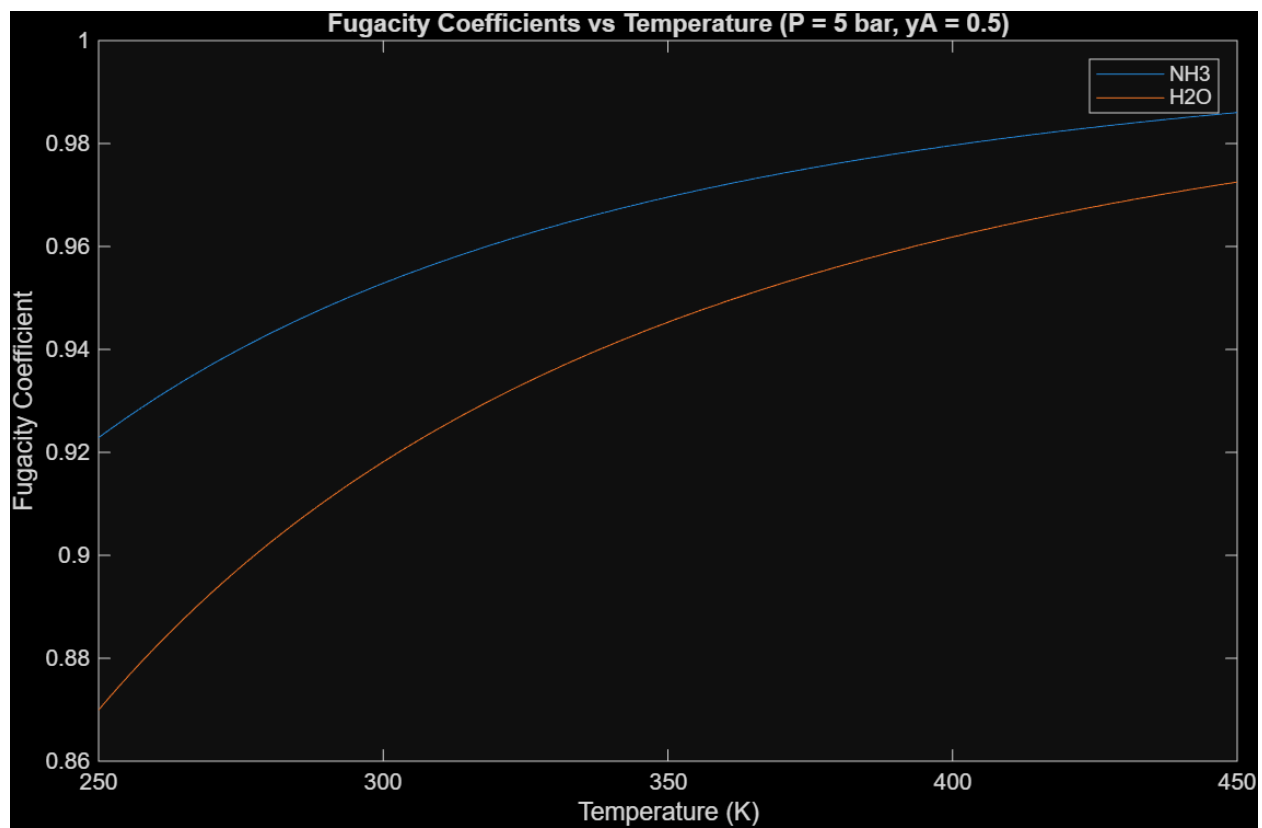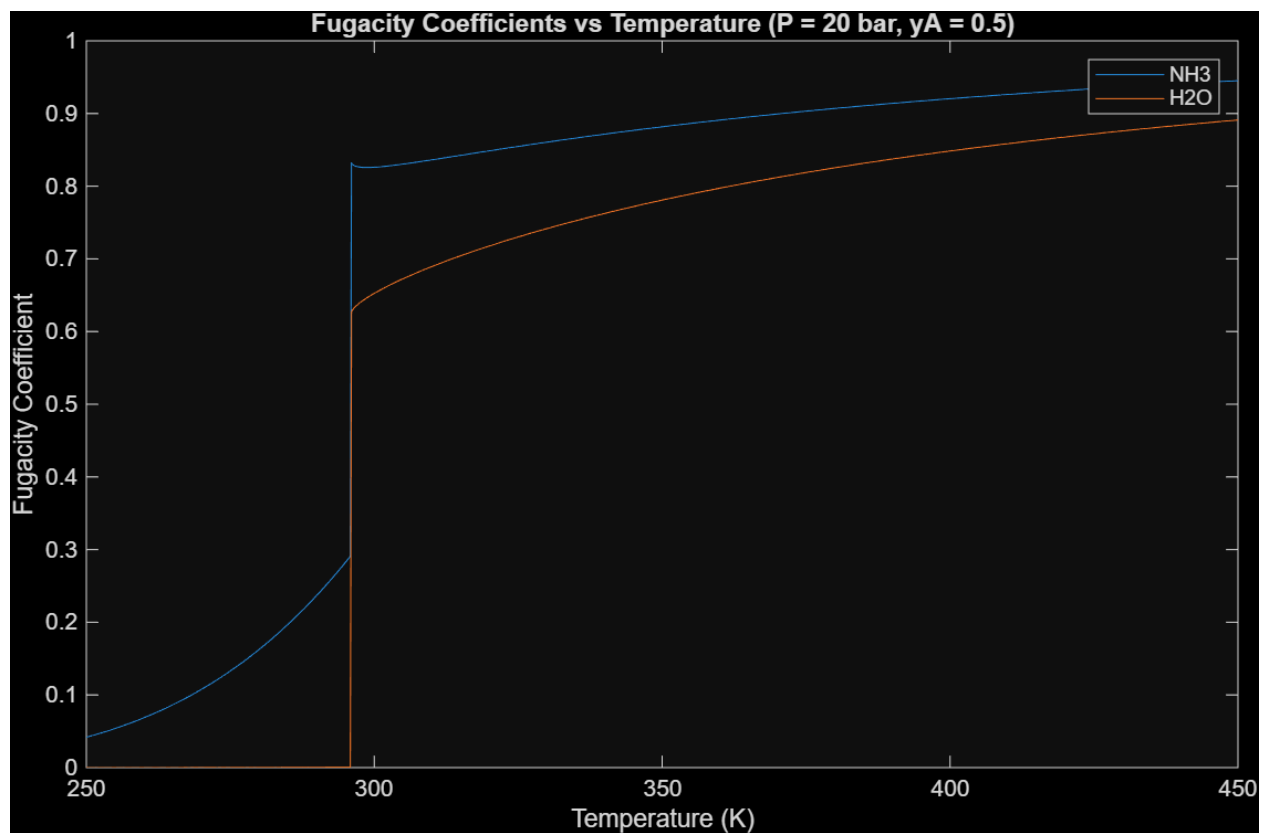
This complex chain of instability begins at a surprisingly simple point: k_{12} the binary mixing parameter. In this project, the binary mixing parameter was fit to the system using a previously conducted study. However, this linear fit is far too simple for the complexity of the water-ammonia system, and when conditions are extrapolated too far from conditions under which the empirically derived linear fit was created, the binary mixing parameter is no longer able to accurately correct the nonideal behavior of the mixing parameter a_{12}, leading to the deviation of the model from physical behavior as previously discussed. This beautiful result not only reinforces the extreme significance of including a mixing parameter for non-ideal systems but also demonstrates how a single, simple quantity can cause the collapse of a complex system of equations.
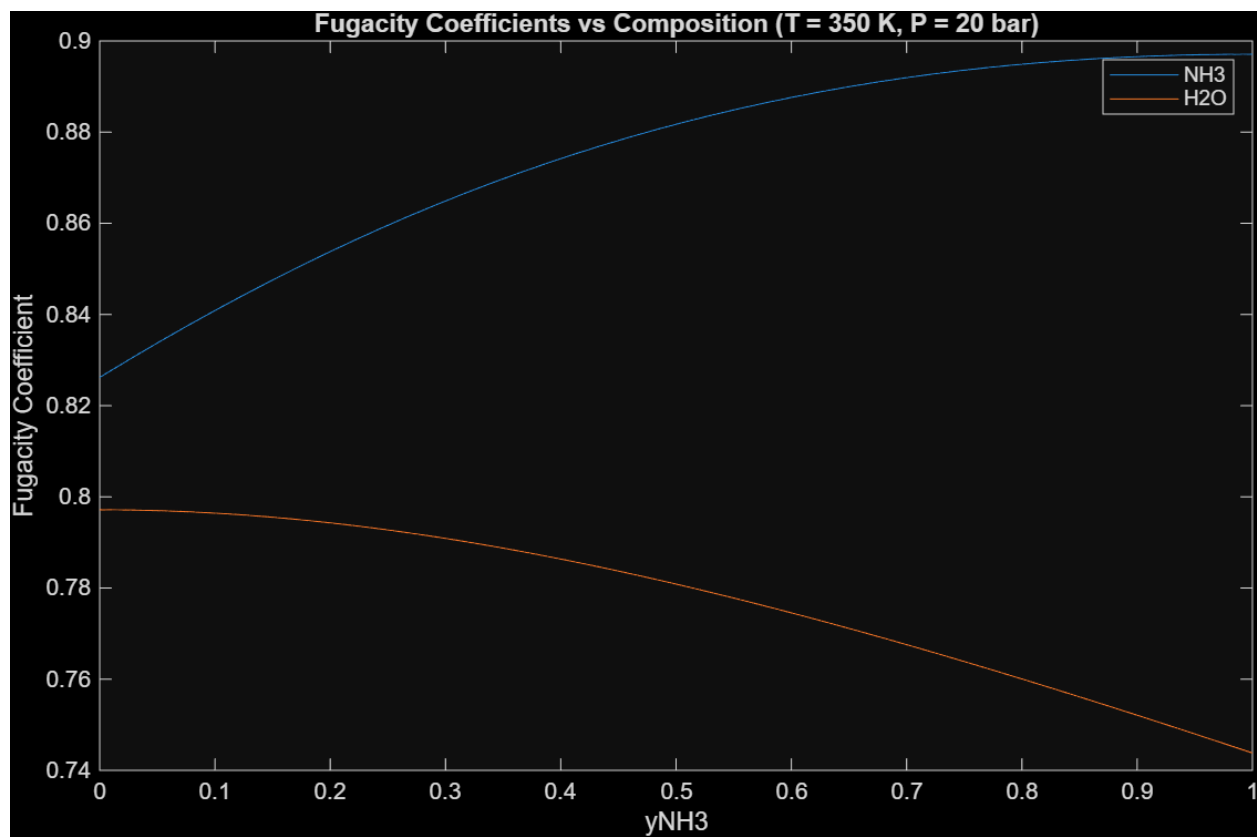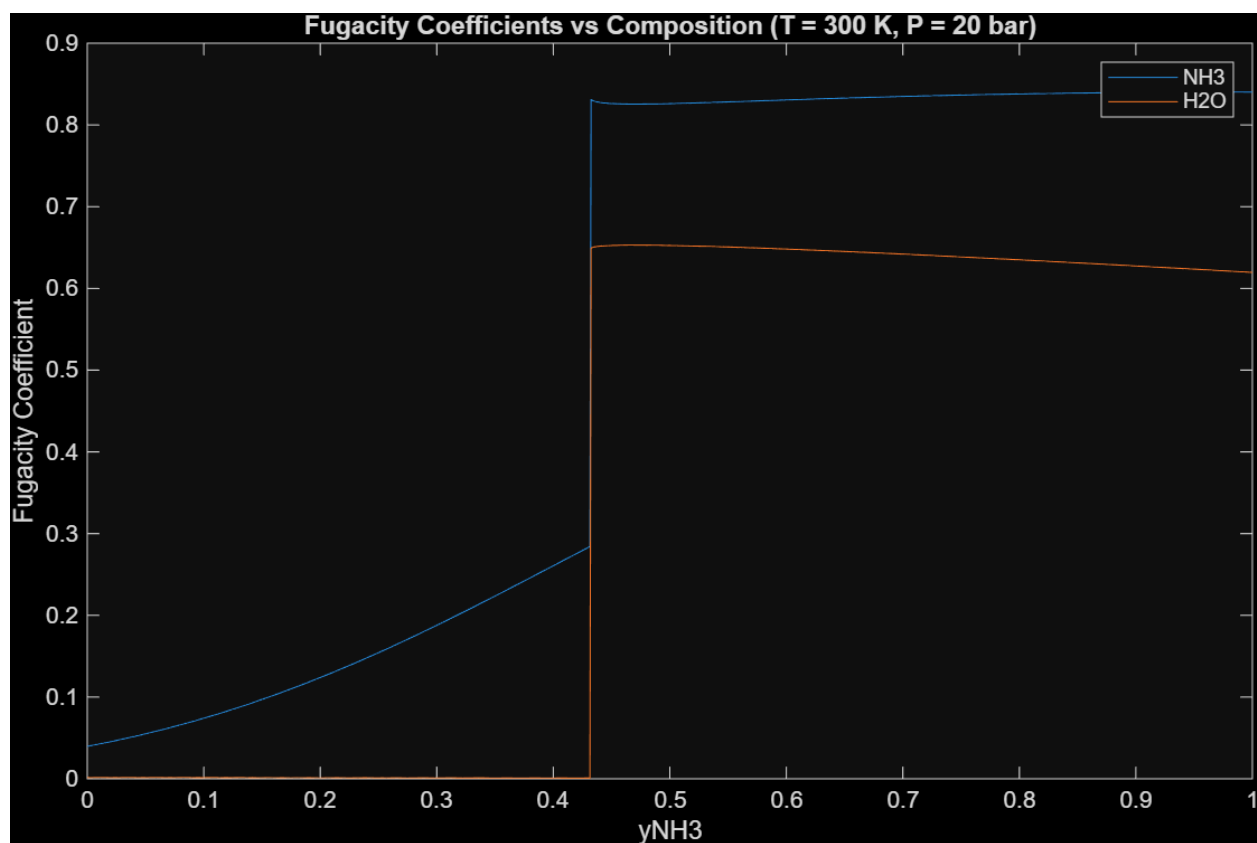
This issue can be easily resolved by adjusting the temperature constant to a more ideal value as pressure changes. This change is evident in Figure 3, which plots the same values at a constant temperature of 500 K. At this temperature, both coefficients continue to decrease smoothly over the range, as expected for the system. There are no sudden collapses or failures for the PR equation of state for these conditions.

Similar behavior can be seen in Figures 4 and 5, which plot the fugacity coefficients as a function of temperature at constant pressure and composition, with temperatures ranging from 250 to 450 K. Figure 4, with a pressure of 20 bar, shows the same collapsing behavior as is observed in Figure 2 because of its highly unideal nature, leading to unstable Z roots. As shown in Figure 3, this collapse can be avoided by decreasing the constant pressure to a more ideal value. In Figure 5, this pressure is lowered to 5 bar, and no collapses are observed.

Fugacity Coefficients vs Temperature (P = 20 bar, yA = 0.5)

Fugacity Coefficients vs Temperature (P = 5 bar, yA = 0.5)

The same behavior is maintained for plots of the fugacity coefficient as a function of composition. Note that, in Figure 6, the model collapses for compositions where the mole fraction of water exceeds the mole fraction of ammonia, and that, in Figure 7, this collapse can be resolved by moving the system closer to ideality, with a temperature of 350 K rather than 300K.

Fugacity Coefficients vs Composition (T = 300 K, P = 20 bar)

Fugacity Coefficients vs Composition (T = 350 K, P = 20 bar)

For the pure-component fugacities calculated using the Lee-Kessler generalized correlation tables, we observed the expected results for both sets of conditions tested. In the near-ideal case, at 350 K and 5 bar, both components exhibited pure coefficients consistent with ideal behavior. Water had a coefficient of 0.97899, while ammonia had a coefficient of 0.99293. For the non-ideal case, both of these coefficients dropped significantly below one, which is logical for a mixture with such nonideality. Water had a coefficient of 0.54777, while ammonia had a coefficient of 0.92842. Unlike the predictions from the PR equation of state, the generalized correlation tables showed no collapses or unstable behavior. This model also reveals the relative strength of interactions in the system. Since water has very strong hydrogen bonding, its fugacity coefficient drops substantially faster than that of ammonia, which has weaker and less polar hydrogen bonds.

When evaluating the fugacity from the generalized correlation coefficient values, the Lewis fugacity rule was applied. This was compared with the fugacity calculated using coefficient values obtained from the PR equation under conditions where the model is accurate and stable. For the ideal state, the Lewis assumption performed well for both components. Coefficients from each method were extremely similar, with the water values having a % error of 0.07723% and ammonia values having a % error of 0.27035%. Such an agreement between the methods is expected, since both models are accurate in near-ideal cases.

In the non-ideal state at 50 bar, the Lewis rule was far less accurate. Compared to the PR equation of state method, which is more reliable in non-ideal cases while stable, the fugacities calculated using the Lewis fugacity rule had a % error of 93.16985% for water and 89.77698% for ammonia. These differences result from the Lewis rule's complete neglect of mixture interactions, which, for this binary system, are highly significant in fugacity calculations. The

results of this comparison confirm that the Lewis rule should be applied only to systems with near-ideal behavior and with negligible intermolecular interactions.

Conclusion

This study examined fugacity behavior for a binary mixture of water and ammonia using both the PR equation of state with binary mixing and the Lee-Kessler correlations with the Lewis fugacity rule. The analysis demonstrated that this binary mixture is highly non-ideal and exhibits asymmetric, strong interactions. The immense strength of water's like bonds in comparison to other interactions in the system produces substantial deviations from ideality for both methods studied.

The PR equation of state was unable to entirely capture the behavior of the mixed system and can only provide reasonable predictions at low pressures and high temperatures, where the mixture is near the ideal-gas limit. At elevated pressures, low temperatures, and compositions with substantial water content, the model exhibits severe instability and even collapses completely in some cases. The lack of stability in the compressibility factor leads to models that do not accurately represent the physical behavior of the system, and such failures are significant in that they highlight a limitation of the PR equation of state for highly asymmetric mixtures, as well as the importance of using a proper binary mixing value to correct non-ideal mixing behavior.

The Lee-Kessler generalized correlations, in contrast, produced physically accurate results under both near-ideal and non-ideal conditions. However, when calculating fugacities using the Lewis rule, the results at non-ideal conditions deviated by almost 100% for each component from the behavior expected according to the PR model. This is because mixture effects and strong unlike interactions are not accounted for in pure fluid behavior. As such, the

Lewis rule should be applied only to systems with near-ideal behavior. In this study, near-ideal conditions yielded results that were extremely similar between the two methods, with a maximum error of less than 1%.

Overall, this project successfully demonstrated the importance of selecting appropriate models, especially when dealing with systems that deviate significantly from ideality. The results emphasize that while cubic equations of state are useful for many engineering calculations, caution is essential when applying them to mixtures with strong bonding and asymmetry. In such circumstances, it may be necessary to use more advanced models to ensure that processes and simulations mimic real physical behavior.

References

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