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Modelling of Ammonia Synthesis by Two Kinetic Equations

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CONTENT

1 INTRODUCTION

Ammonia is the crucial compound for industrial application, mainly for fertilizers production (e.g. nitric acid). Production of ammonia is an essential process in the modern society and gives a foundation for the growing global population. In 19th century the ammonia source was only saltpeter. In the beginning of the 20th century the world was facing a global starvation. Also, in these times new preparation way of ammonia synthesis was founded by Fritz Haber and Carl Bosch and many concepts still apply. In an industrial plant ammonia is typically produced at high pressure (above 100 bar) using iron-based catalyst. This process is also known as the Haber-Bosch process.

1.1 Catalysis

The whole synthesis could be written in one simple reaction **1** which is highly exothermic. The main source of nitrogen is air and hydrogen is produced by steam reforming of natural gas.

$$N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g) \qquad \mathbf{1}$$

Even though the Gibbs free energy of ammonia reaction is negative the reaction is not spontaneously. The limiting factor is the breakage of the bond in nitrogen and hydrogen which could be seen in the figure **1**. In the figure the blue curve illustrates energy diagram with an iron-based catalyst and the grey lines represent gas phase reactions.[1]

The catalytic reaction occurs on the surface of the solid catalyst. The outer atoms in the layer in solid have fewer neighbors. It means they are chemically unsaturated, and they may react with gaseous molecules. The whole mechanism of each reaction is called chemisorption which is formed between the surface and atoms of reactants. When the weak bonds are broken, atoms could migrate and react with other atoms to create ammonia molecule. Then ammonia molecule is detached from the surface.[2]

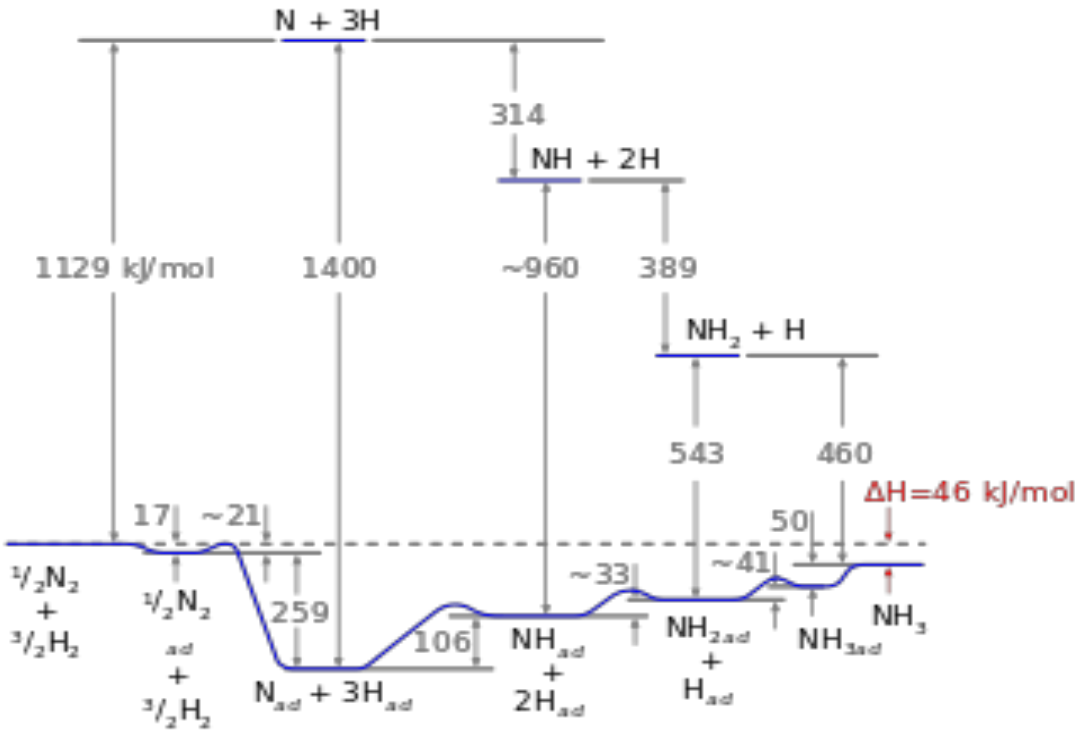

Figure 1 – Reaction mechanism and an energy diagram for ammonia synthesis.[1]

1.2 Kinetics

In this report was used two types of kinetic equations – Temkin-Pyzhnev's and Dyson-Simon's. Temkin-Pyzhnev's equation is original equation and Dyson-Simon's is slightly modified and it used thermodynamics from Gillespie which are known to be among the most accurate measured.

1.2.1 Temkin-Pyzhnev's Equation

Temkin and Pyzhnev formulated a kinetic equation for ammonia synthesis assuming that the rate determining step was the process of activated adsorption of nitrogen. A formula for the latter was postulated on a semi-empirical basis, and the equation for ammonia synthesis in a static system given as:[3]

$$r = k_1 \cdot p_{N_2} \cdot \left(\frac{p_{H_2}^3}{p_{NH_3}^2}\right)^{0.5} - k_2 \cdot \left(\frac{p_{NH_3}^2}{p_{H_2}^3}\right)^{0.5} \qquad 1$$

The formula **1** is connected with the stoichiometry which is shown in the reaction **1** and it is valid in pressure range 150-300 atm.[3]

The f is fugacity coefficient for component "i" and k_1 and k_2 are velocity constants. Their dependence on temperature are shown in the equation **2**[3], where T is in Kelvin and R is universal gas constant (8.314 $Jmol^{-1}K^{-1}$).

$$k_1 = 1.78954 \cdot 10^4 \cdot e^{\frac{-20800}{R \cdot T}}$$
$$k_2 = 2.5714 \cdot 10^{16} \cdot e^{\frac{-47400}{R \cdot T}} \qquad \mathbf{2}$$

Units of velocities constants are shown in the table **1**.

k1	$[\boldsymbol{mol \cdot h^{-1} \cdot m^{-3} \cdot atm^{-1}}]$
k2	$[mol \cdot h^{-1} \cdot m^{-3} \cdot atm^{0.5}]$

Table 1 – Overview of velocities constants units.

The general formula to calculate fugacity of component "i" could be seen in the formula **3**, where γ is fugacity coefficient, y_i is molar partial pressure and p is a total pressure in unit atm.

$$f_i = \gamma_i \cdot y_i \cdot p \qquad \mathbf{3}$$

1.2.2 Dyson-Simon's Equation

In order to dissociative chemisorption of nitrogen on the surface and that neither hydrogen nor ammonia affects the rate of nitrogen adsorption for the intrinsic rate of reaction which could be seen in the formula **4**. Different values are given for α in rate between 0.4 to 0.8 and it is constant. Dyson-Simon's formula was developed and slightly modified based on Temkin-Pyzhnev's expression with α 0.5. The first differences are that k is similar to reverse velocity constant k_2 and equilibrium constant in Dyson-Simon's equation K_A is squared. The reaction rate is shown in the formula **5**.[4]

$$r = k_1 \cdot p_{N_2} \cdot \left(\frac{p_{H_2}^3}{p_{NH_3}^2}\right)^{\alpha} - k_2 \cdot \left(\frac{p_{NH_3}^2}{p_{H_2}^3}\right)^{1-\alpha} \quad \textbf{4}$$

$$r = k \cdot \left[K_A^2 \cdot f_{N_2} \cdot \left(\frac{f_{H_2}^3}{f_{NH_3}^2}\right)^{0.5} - \left(\frac{f_{NH_3}^2}{f_{H_2}^3}\right)^{0.5}\right] \quad \textbf{5}$$

Where k is velocity constant, f_i is fugacities and K_A is equilibrium constant, which is calculated from the equation of Gillespsie and Beattieas described by Rase and Gaines. The formulas for equilibrium and velocity constants are shown in the equation **6**[4]. It could be noticed that the first difference is that equilibrium constant K_A is squared and according to formula **6** it is seen that k has almost same parameters as k_2 in Temkin-Pyzhnev's expression. It was used general equation **3** to evaluate fugacities and units are atm.

$$\log(K_A) = -2.691122 \cdot \log(T) - 5.519265 \cdot 10^{-5} \cdot T + 1.848863 \cdot 10^{-7} \cdot T^2 + \frac{2001.6}{T} + 2.6899 \quad \textbf{6}$$

$$k = 8.849 \cdot 10^{14} \cdot e^{\frac{-40765}{R \cdot T}}$$

Units of equilibrium and velocity constants are shown in the table **2**.

k	$\left[\boldsymbol{mol \cdot m^{-3} \cdot h^{-1} \cdot atm^{0.5}}\right]$
K_A	$[atm^{-1}]$

Table 2 – Overview of the units – velocity and equilibrium constants.

Fugacity coefficients where calculated by two options, which was used various equation of state – Peng-Robinson and UNIFAQ. By third option it was used description from article.

1.2.3 Fugacity Coefficients Variously Evaluated

Based on equation **3** there are several options how to evaluate fugacity coefficients. One option was to used their empirical expressions based on article[5] and their formulas is shown in the equation **7**[5]. For them it is used Newton's equation which has been proven to be accurate and has been used extensively to study the NH_3-H_2-N_2 system at high pressures. In the equation the temperature is in Kelvin and pressure is in atm.

In Aspen Plus V10 was chosen two equations of state – Peng-Robinson and UNIFAQ. Then fugacity coefficients were calculated at 200 bars as a function of temperature. Aspen does not use thermodynamic models that are tailor made for the NH_3-H_2-N_2 system such as Martin-Hou's equation of state even it works nicely overall for any chemical-engineering tasks.

$$\gamma_{H_2} = \exp\{\exp(-3.8402 \cdot T^{0.125} + 0.541) \cdot p - \ldots$$
$$\exp(-0.1263 \cdot T^{0.5} - 15.98) \cdot p^2 + \ldots$$
$$300 \cdot [\exp(-0.011901 \cdot T - 5.941)] \cdot \exp\left(\frac{p}{300}\right) - 1\}$$

$$\gamma_{N_2} = 0.93431737 + 0.3101804 \cdot 10^{-3} \cdot T + 0.295896 \cdot 10^{-3} \cdot p - \ldots \quad \textbf{7}$$
$$0.2707279 \cdot 10^{-6} \cdot T^2 + 0.4775207 \cdot 10^{-6} \cdot p^2$$

$$\gamma_{NH_3} = 0.1438996 + 0.2028538 \cdot 10^{-2} \cdot T - \ldots$$
$$0.4487672 \cdot 10^{-3} \cdot p - 0.1142945 \cdot 10^{-5} \cdot T^2 + \ldots$$
$$0.2761216 \cdot 10^{-6} \cdot p^1$$

In the figure **2** it is evaluated all fugacity coefficients. Red color is for hydrogen, blue is for nitrogen and black is for ammonia. By solid line is illustrated fugacity coefficients calculated by Dyson-Simon, dash dotted line imagine equation UNIFAQ and dash line is for Peng-Robinson equation. It could be seen that almost all fugacity coefficients correspond to each other for the component, but fugacity coefficient of hydrogen evaluated by Dyson-Simon lays away of the others. This impact is discussed below.

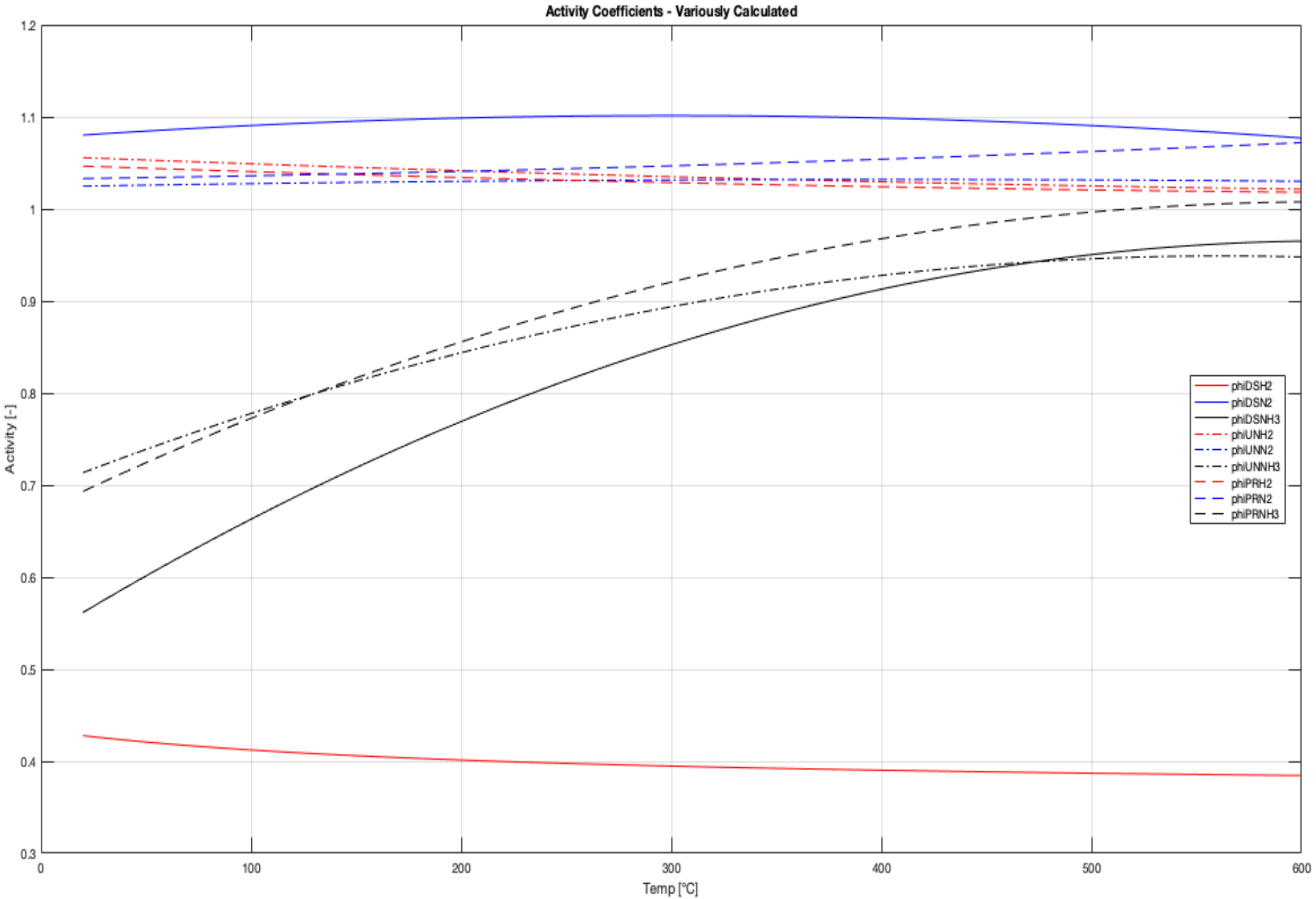

Figure 2 – All fugacity coefficients calculated variously.

2 MODEL

One dimensional model based on the following assumptions has been developed to explain ammonia synthesis:

- Steady state operation;
- External transport resistance between the catalyst particles and the gas phase are negligible;
- Adiabatic reactor without thermal lose;
- Axial dispersion is negligible;
- Pressure drop is not considered.

Then the differential equation for PFR is shown in the formula **8**, where n_i is mole flow of component "i", V is volume in units m^3, ν_i is stoichiometric coefficient for component "i" (stoichiometry is shown in the reaction **1**) and r is reaction rate.

$$\frac{dn_i}{dV} = \nu_i \cdot r \qquad \textbf{8}$$

To evaluate enthalpy balance it is needed to calculate reaction enthalpy. According to article[4] there is a general formula for reaction enthalpy as a function of temperature as well as pressure. This was clarified – reaction enthalpy was evaluated from the fused enthalpies for pure components and then it was used Kirchoff's law to obtain it at various temperature with using ideal gas equation of state. In the figure **3** it could be seen reaction enthalpy, where blue line is for reaction enthalpy calculated with using Kirchoff's law and orange line illustrates empirical equation based on article[4]. It could be noticed that the difference is really significant and for model was used the general empirical expression of reaction enthalpy. The reaction of ammonia synthesis is reversible reaction and according to the figure **3** the orange curve describes the reaction better – firstly ammonia is creating then it is consumed. This empirical equation was used in the model.

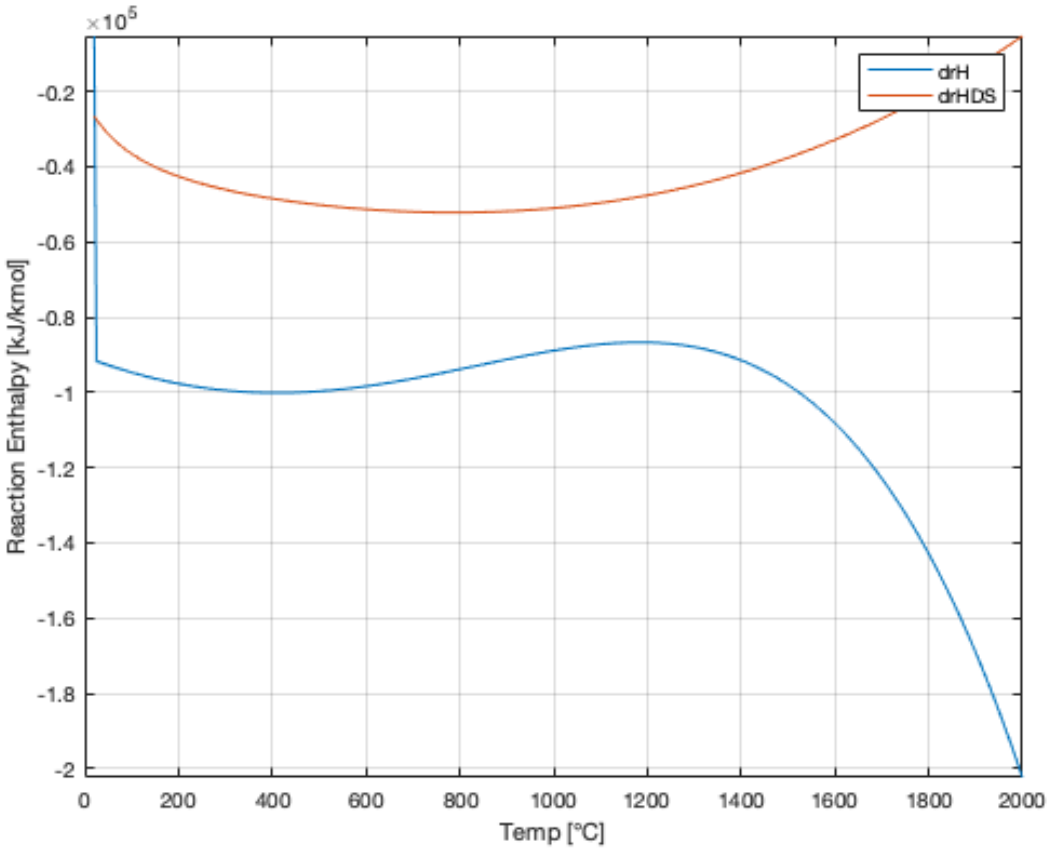

Figure 3 – Comparing reaction heat calculated by Kirchoff's law and evaluated by empirical expression based on article mentioned above.

The final equation for thermal balance is shown in formula **9**.

$$\frac{dT}{dV} = \frac{r \cdot \Delta_r H}{\sum_i n_i \cdot c_{pi}} \qquad \textbf{9}$$

3 RESULTS

Firstly, it was calculated reaction rate with fugacity coefficients equal to one (ideal behavior) to compare results. The inlet conditions are shown in the table **3**.

$\mathbf{t_{in}}$	350 °C
$\mathbf{n_{N2in}}$	1 [mol/hod]
$\mathbf{n_{H2in}}$	3 [mol/hod]
$\mathbf{n_{NH3in}}$	0.01 [mol/hod]
p	200 [atm]
$\boldsymbol{\upsilon_{N_2}}$	-1 [-]
$\boldsymbol{\upsilon_{H_2}}$	-3 [-]
$\boldsymbol{\upsilon_{NH_3}}$	+2 [-]

Table 3 – Overview of the inlet conditions for calculations.

3.1 Dyson-Simon's reaction rate

In the figure **4** is shown mole flow of all components for Dyson-Simon's reaction rate, where activity coefficients are neglected. It could be noticed that maximal conversion of nitrogen is 33.63 % and an equilibrium conversion is 64.05 %. It could be seen that reaction is fast – needed volume for reaction is approximately $5 \cdot 10^{-12}$ m^3.

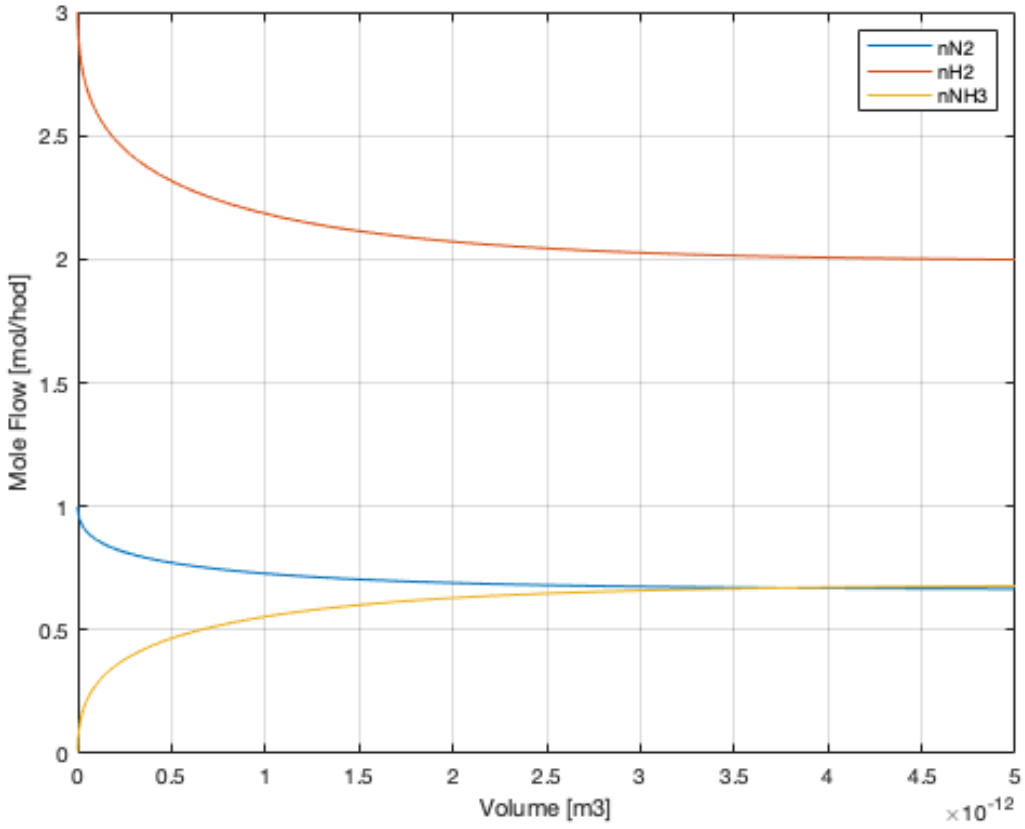

Figure 4 – Mole flow of all components for Dyson-Simon's reaction rate[4].

According to the fast reaction in the figure **4** and **5** it is seen that majority of reaction is held in the beginning of reactor – the derivation is sharp. In the $0.5 \cdot 10^{-12}$ m^3 is produced almost 50 % of ammonia and then it is increasing up to mentioned conversion of nitrogen above (33.63 %). In the figure **5** he maximum temperature released by the reaction is 492.89 °C. Also, in the $0.5 \cdot 10^{-12}$ m^3 the temperature is increased about 100 °C.

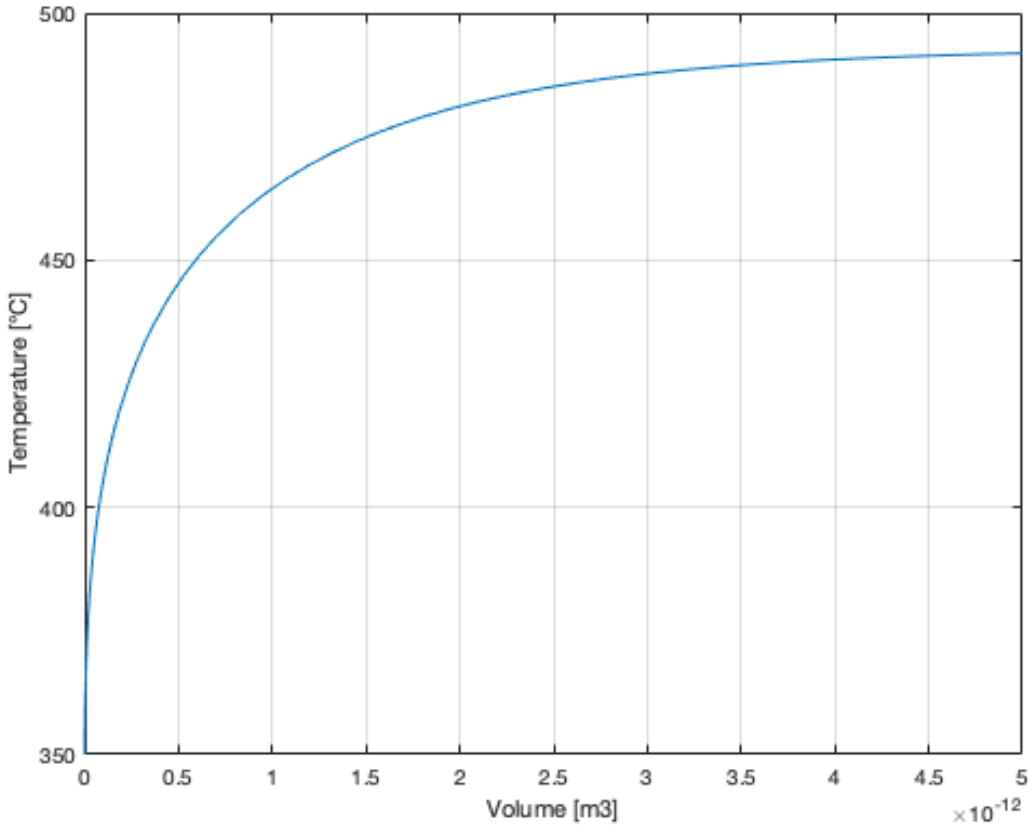

Figure 5 – Temperature along the volume of reactor for Dyson-Simon's reaction rate[4].

3.2 Temkin-Pyzhnev's reaction rate

Secondly it was used Temkin-Pyzhnev's reaction rate with ideal behavior. In the figure **6** could be seen mole flow of all components. It could be noticed that needed volume for reaction is approximately $3 \cdot 10^{-12}$ m^3. It means that the reaction is also as fast as in Dyson-Simon's reaction rate. Also, the conversion of nitrogen is 20.53 %, which is less in comparing Dyson-Simon's equation. Equilibrium conversion is 26.95 %.

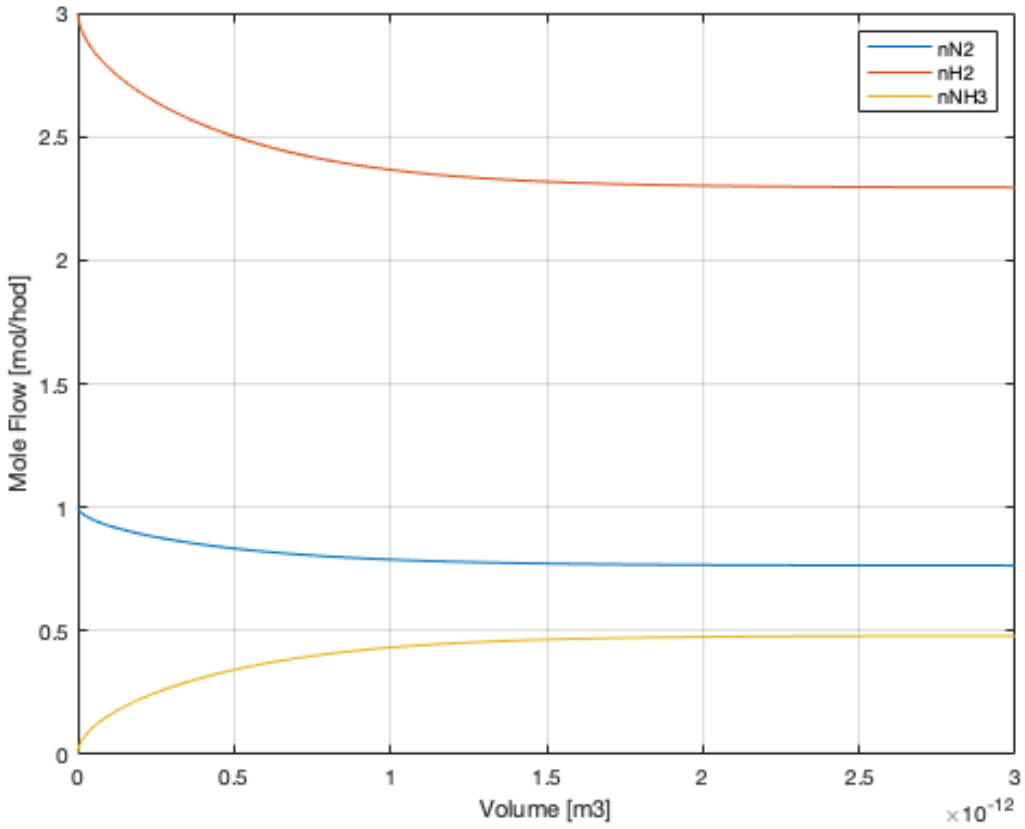

Figure 6 – Mole flow of all components for Temkin-Pyzhnev's reaction rate[3].

According to the figure **6** and **7** it could be noticed that the derivation at the beginning is not straight as in Dyson-Simon's expression and it is slightly increasing along in the reaction volume. The maximum temperature is 448.63 °C which is less about 50 °C to Dyson-Simon's formula. In order to the temperature difference it is caused by different produced amount of ammonia.

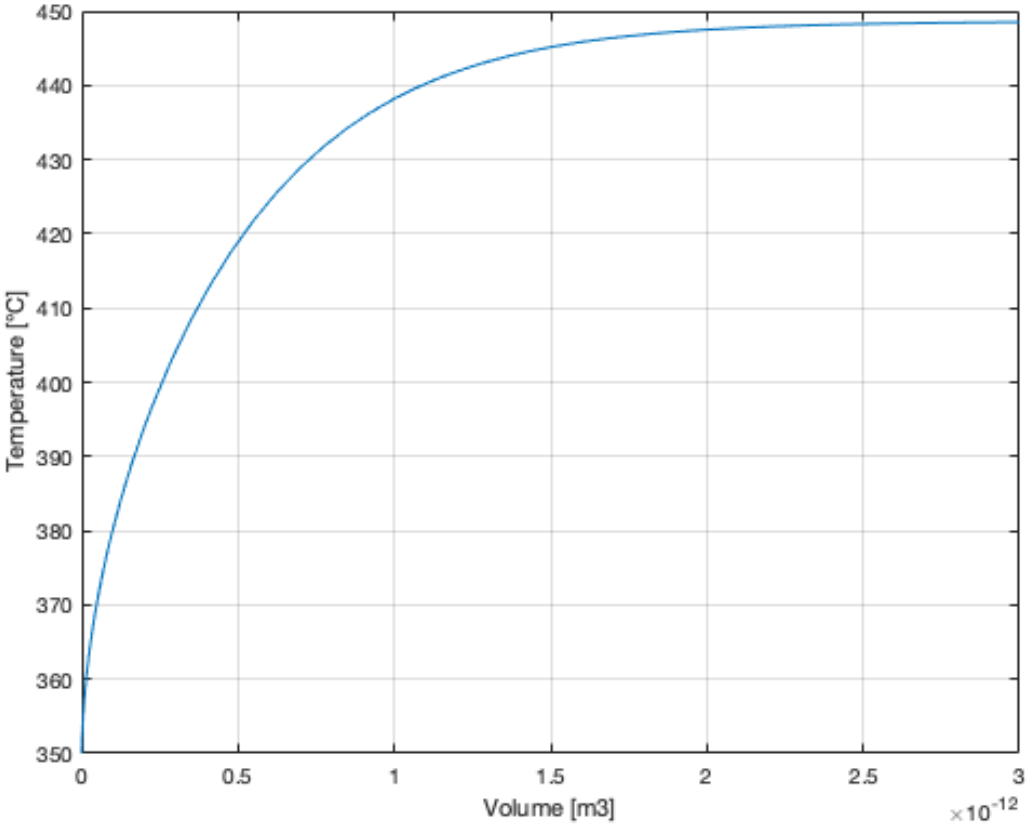

Figure 7 – Temperature along the volume of reactor for Temkin-Pyzhnev's reaction rate[3].

3.3 Development of Dyson-Simon's Model

In this project was decided to develop Dyson-Simon's reaction rate because it contains the fugacity coefficients and also are known empirical formulas of all Dyson-Simon's fugacity coefficients. In this chapter it is added fugacity coefficients, which are discussed above, in the model and it will be seen how they influence the conversion of ammonia.

3.3.1 Summarizing All Results

In the figure **8** it is shown changeover of all components in the reaction with used all various fugacity coefficients mentioned above. Solid curve is for fugacity coefficients provided by Dyson-Simon, dash-dotted illustrate UNIFAQ equation of state and dash line belongs to Peng-Robinson equation. Red color imagine hydrogen, blue means nitrogen and black illustrate ammonia. Also, it could be noticed that results for used UNIFAQ and Peng-Robinson are overlapped. It means that ammonia conversion could be same. The conversion of UNIFAQ's fugacity coefficients is 34.24 % and for coefficients evaluated by Peng-Robinson is 33.83 %. Equilibrium conversion with using UNIFAQ is 66.41 % and with Peng-Robinson is 65.87 %. In order to the conversion obtained by ideal behavior of the system (33.63 %) is almost same even it was used various fugacity coefficients described by two equations of state. It means that these two options are not suitable for the ammonia modelling.

Furthermore, coefficients designed by Dyson-Simon gives different results – conversion of nitrogen is just 20.98 % which is less than for ideal behavior (fugacity coefficients equal to one with conversion 33.63 %). Equilibrium conversion is 41.82 %. All curves have same profile.

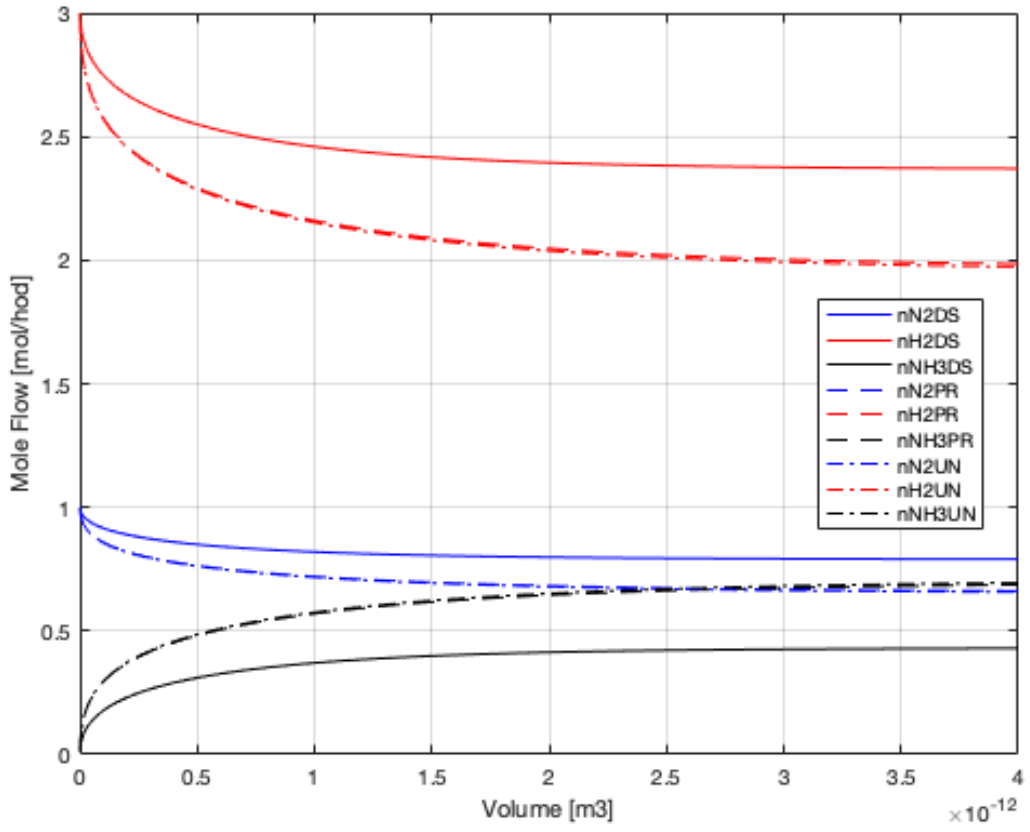

Figure 8 – Changeover of all components with all fugacity coefficients used.

In the figure **9** is shown temperature profiles for all three options. Blue line means model with used Dyson-Simon's fugacity coefficients, red illustrate Peng-Robinson's coefficients and orange is for UNIFAQ. UNIFAQ's and Peng-Robinson's results overlap again and profile of used Dyson-Simon's coefficients are different even that the curve profile looks similar for all options. When it is used UNIFAQ's coefficients maximum temperature is 495.62 °C, for Peng-Robinson it is 493.78 °C and Dyson-Simon it is 437.45 °C. The temperature profile of equations of state is reasonable according to the almost same ammonia conversion.

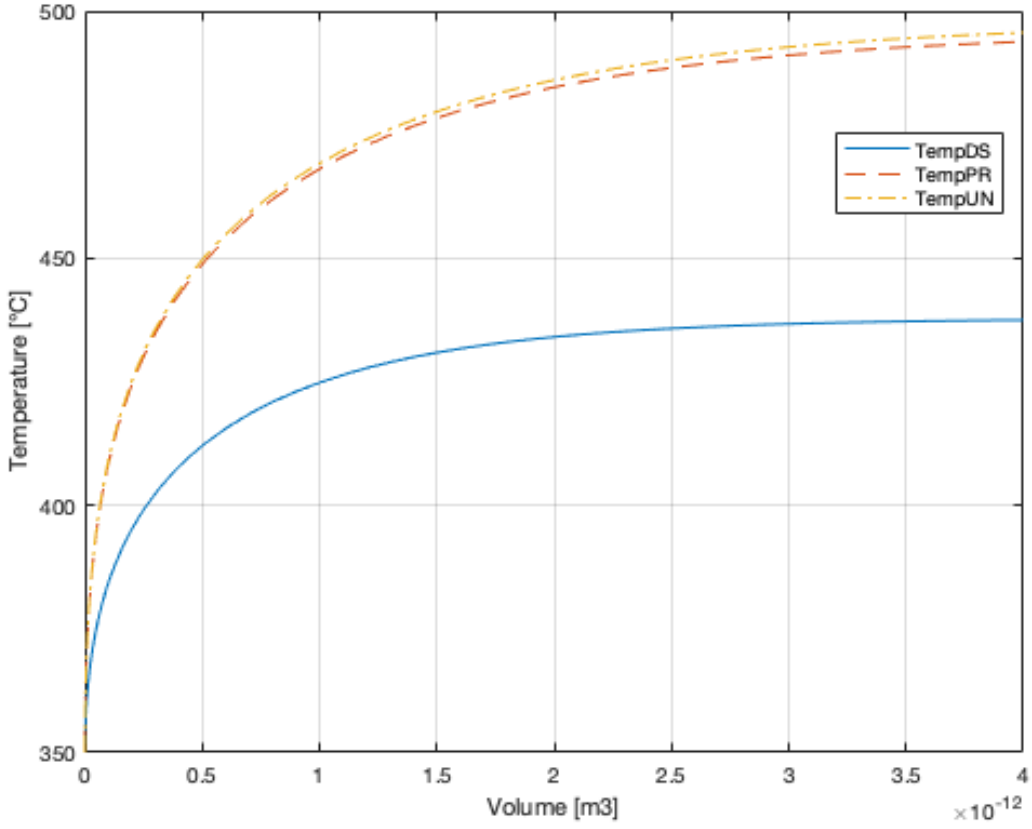

Figure 9 – Temperature profile for all fugacity coefficients.

4 CONCLUSION

The aim of this project is to create a model for ammonia synthesis which for is used two types of kinetic equations – Temkin-Pyzhnev's[3] and Dyson-Simon's[4] equations. Dyson-Simon's is slightly modified form of Temkin-Pyzhnev's expression. Then it was chosen Dyson-Simon's expression and it was developed by adding fugacity coefficients. Also, reaction heat evaluated from empirical equation taken from article[4] is totally difference of calculated reaction heat based on Kirchoff's law using an ideal equation of state. According to the figure **3** it is seen that empirical formula described reaction heat correctly. Furthermore, empirical formula for fugacity coefficients designed by Dyson and Simon[5] are quite similar to coefficients described by UNIFAQ and Peng-Robinson equations but coefficients for hydrogen are totally different. For Dyson-Simon the average value is 0.4 and for equations of state is approx. 1.05. In order to compare both kinetic equations in ideal option (fugacity coefficients equal to one) it was chosen Dyson-Simon's expression for model development because it contains fugacity coefficients and also are known empirical formulas of all Dyson-Simon's fugacity coefficients. When fugacity coefficients were calculated by UNIFAQ and Peng-Robinson equation the mole changeover of all components and temperature profile are overlapped. Nitrogen conversion for both are 34 % and maximum temperature is 493.78 °C for system described by Peng-Robinson and for UNIFAQ system it is 495.62 °C. It could be noticed that the conversion for both is a little bit higher than for ideal system (33.63 %). It means that these two options are not suitable for ammonia modelling. On the other hand, if Dyson-Simon's fugacity coefficients are used the nitrogen conversion is 20.98 % which is less than for ideal system (33.63 %). It corresponds to the industrial conversion. Temperature at equilibrium is 437.45 °C. This various result is caused by different fugacity coefficient of hydrogen.

LIST OF TABLES

LIST OF FIGURES

LITERATURE

[1] http://people.idsia.ch/~juergen/haberbosch.html.
[2] Z. Lendzion-Bieluń, R. Pelka and W. Arabczyk, *Catalysis Letters* **2009**, *129*, 119-123.
[3] E. P. Carvalho, C. Borges, D. Andrade, J. Y. Yuan and M. A. S. S. Ravagnani, *Applied Mathematics and Computation* **2014**, *237*, 330-339.
[4] M. R. Panahandeh, J. Fathikaljahi and M. Taheri, *Chemical Engineering & Technology* **2003**, *26*, 666-671.
[5] D. C. Dyson and J. M. Simon, *Industrial & Engineering Chemistry Fundamentals* **1968**, *7*, 605-610.