

# Thermodynamic Analysis of Ammonia Synthesis

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## Abstract

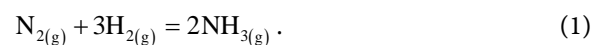
The paper researches the effect of temperature on ammonia synthesis. The ammonia synthesis reaction  $N_{2(g)} + 3H_{2(g)} = 2NH_{3(g)}$  is exothermic with a negative entropy change.  $\Delta G < 0$  condition is fulfilled at lower temperatures up to 464 K. It is a constant equilibrium of the ammonia synthesis reaction  $K'_p \gg 1$  at lower temperatures, which means that the  $NH_{3(g)}$  synthesis reaction is shifted in the direction of  $NH_{3(g)}$  formation (higher production of ammonia). The downside of lowering the temperature is that more ammonia is obtained, but the reaction rate slows down. Above 464K, the free enthalpy of the  $NH_{3(g)}$  synthesis reaction is greater than zero, so the reaction enters thermodynamically unfavorable conditions. By increasing the reaction temperature, the ammonia yield  $NH_{3(g)}$  decreases in the equilibrium mixture. At 400 K, it is 0.5128 kmol/kmol (51.28%) and at 900 K, the synthesis process  $NH_{3(g)}$  is practically complete.

## Keywords

Temperature, Thermodynamic Functions, Synthesis, Ammonia

## 1. Introduction

Ammonia is a colorless gas with a pungent odor. It dissolves well in water. At ambient temperature, ammonia  $NH_{3(g)}$  is stable. Ammonia is mainly used for the production of nitric acid and mineral fertilizers, carbamide, ammonium sulfate and others. Ammonia gas reacts quickly with sulfuric acid vapors  $SO_{3(g)}$  and  $H_2O_{(g)}$  creating ammonium sulfate  $(NH_4)_2SO_{4(s)}$  which is a high-quality artificial fertilizer. Gaseous ammonia is also used for the reduction of  $SO_{3(g)}$  and  $NO_{x(g)}$  in flue gases, and the reduction ranges from 77% - 97% [1]. In the literature [2]-[7] there are data on the synthesis of ammonia



These data are not complete. They relate to a certain temperature and pressure. Data on the effect of temperature on the composition of the equilibrium reaction mixture (1) are also incomplete. In engineering practice, the Haber-Bosch process is most often used for the production of ammonia [8] [9].

Knowledge of the value of thermodynamic functions  $\Delta H, \Delta S, \Delta G$  and  $K_p$ , as well as knowing the composition of the equilibrium reaction mixture (1) is the starting point in the design phase of devices and apparatus for the reduction of sulfur and nitrogen oxides in flue gases, the production of mineral fertilizers and polymer materials, which gives significance to this paper.

## 2. Mathematical Formulation

### Thermodynamic Functions

The enthalpy of a chemical reaction is defined as follows [10] [11]:

$$\Delta H = \sum_j b_j \cdot \Delta h_j - \sum_i b_i \cdot \Delta h_i, \quad (2)$$

of which:

- $b_i$  —the number of kilomoles of the  $i$ -th reactant components;
- $b_j$  —the number of kilomoles of the  $j$ -th component for products;
- $\Delta h_i$  —bond enthalpy of the  $i$ -th component;
- $\Delta h_j$  —bond enthalpy of the  $j$ -th component.

The dependence of reaction enthalpy on temperature is given by the expression:

$$\Delta H_T = \Delta H_{298} + \int_{298}^T \Delta c_{mp}(T) dT, \quad (3)$$

of which:

$$\Delta c_{mp} = \sum_j b_j \cdot c_{mpj} - \sum_i b_i \cdot c_{mpi}, \quad (4)$$

and represents the sum of the specific molar heat capacities of the components.

The dependence of molar heat capacity on temperature can be shown in the form of a polynomial:

$$c_{mp}(T) = a + b \cdot 10^{-3} \cdot T + c \cdot 10^5 \cdot T^{-2}, \quad (5)$$

of which:

- $a, b, c$  —polynomial coefficients that are determined experimentally,
- $T$ —absolute temperature.

The entropy of a reaction is defined by the expression:

$$\Delta S = \sum_j b_j \cdot s_j - \sum_i b_i \cdot s_i, \quad (6)$$

of which:

- $s_i$  —specific entropies and connections of the  $i$ -th component.
- $s_j$  —specific entropies and connections of the  $j$ -th component.

The dependence of reaction entropy on temperature is given by the expression:

$$\Delta S_T = \Delta S_{298} + \int_{298}^T \frac{\Delta c_{mp}(T)}{T} dT \quad (7)$$

The free enthalpy of reaction is defined by the expression:

$$\Delta G = \sum_j b_j \cdot \Delta g_j - \sum_i b_i \cdot \Delta g_i \quad (8)$$

of which:

$\Delta g_i$  —specific free enthalpies of the  $i$ -th component.

$\Delta g_j$  —specific free enthalpies of the  $j$ -th component.

The dependence of the free reaction enthalpy on the reaction enthalpy, temperature and entropy of the reaction is given by the expression:

$$\Delta G = \Delta H - T \cdot \Delta S \quad (9)$$

If reaction  $\Delta G > 0$  proceeds from right to left, *i.e.* in the direction of the formation of the reaction reactants. If reaction  $\Delta G < 0$  proceeds from left to right, *i.e.* in the direction of the formation of reaction products.

For a chemical reaction:

$$\sum_i a_i \cdot A_i = \sum_j b_j \cdot B_j \quad (10)$$

the chemical equilibrium constant expressed through partial pressures is:

$$K_p = \frac{\prod_j (p_{B_j})^{b_j}}{\prod_i (p_{A_i})^{a_i}}. \quad (11)$$

The value of the chemical equilibrium constant  $K'_p$  reduced to pressure  $p_0 = 1.013 \times 10^5$  Pa is determined by the expression:

$$K'_p = e^{-\frac{\Delta G}{R_u T}} = K_p \cdot p_0^{-\left(\sum_j b_j - \sum_i a_i\right)} \quad (12)$$

of which:

$$R_u = 8.314 \frac{\text{kJ}}{\text{kmol} \cdot \text{K}} \text{ —universal gas constant.}$$

Using numerical thermodynamic data for pure components that figure in the reaction  $\text{N}_{2(\text{g})} + 3\text{H}_{2(\text{g})} = 2\text{NH}_{3(\text{g})}$  at 298K and  $1.013 \times 10^5$  Pa (**Table 1** and **Table 2**) and using expressions from (2) to (12), it is possible to calculate the thermodynamic functions  $\Delta H, \Delta S, \Delta G, K'_p$  of the considered reaction depending on the reaction temperature.

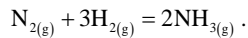
The results of the calculation of the thermodynamic functions  $\Delta H, \Delta S, \Delta G, K'_p, K_p$  are shown in **Table 3** and are in agreement with data from the literature [14] [15]. In the temperature interval 298 K to 1000 K, the thermodynamic

**Table 1.** Bond enthalpies, free enthalpies and components with entropy at  $1.013 \times 10^5$  Pa and 298 K [12].

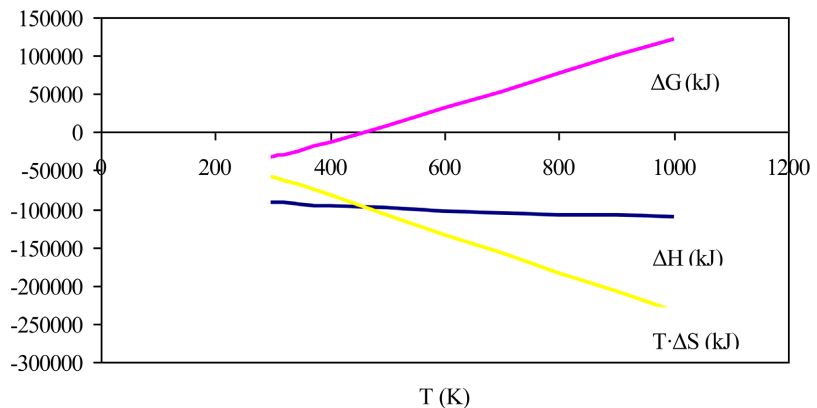
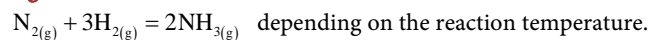
Substance	$\Delta h$ (kJ/kmol)	$\Delta g$ (kJ/kmol)	$s$ (kJ/kmol·K)
Nitrogen	0	0	191.50
Hydrogen	0	0	130.57
Ammonia	-46,110	-16,480	192.34

**Table 2.** Numerous values of  $a$ ,  $b$ ,  $c$  coefficients for determining the value of heat capacities of components [13].

Substance	$a$	$b$	$c$	Temperature range (K)
Nitrogen	27.884	4.270	–	298 - 2500
Hydrogen	27.298	3.266	0.502	298 - 3000
Ammonia	29.768	25.121	–1.549	298 - 1800

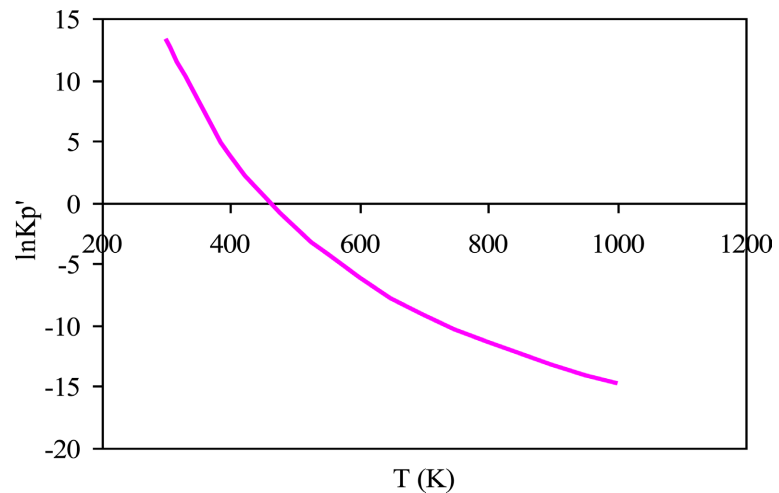
**Table 3.** Values of enthalpy, entropy and free enthalpy of the reaction temperature

$T$ (K)	$\Delta H$ (kJ)	$\Delta S$ (kJ/K)	$\Delta G$ (kJ)	$K'_p$ -	$K_p$ (Pa <sup>-2</sup> )	$\ln K'_p$ -
298	-92,220	-198.53	-33,058	$6.23 \times 10^5$	$6.07 \times 10^{-5}$	13.34
300	-92,018	-196.10	-33,187	$6.01 \times 10^5$	$5.85 \times 10^{-5}$	13.31
400	-95,819	-208.03	-12,604	$4.43 \times 10^1$	$4.31 \times 10^{-9}$	3.79
500	-99,224	-216.10	8827	$1.20 \times 10^{-1}$	$1.16 \times 10^{-11}$	-2.12
600	-102,246	-221.87	30,874	$2.05 \times 10^{-3}$	$2.0 \times 10^{-13}$	-6.19
700	-104,892	-226.10	53,378	$1.04 \times 10^{-4}$	$1.01 \times 10^{-14}$	-9.17
800	-107,165	-229.24	76,224	$1.05 \times 10^{-5}$	$1.03 \times 10^{-15}$	-11.46
900	-109,066	-231.54	99,325	$1.72 \times 10^{-6}$	$1.67 \times 10^{-16}$	-13.27
1000	-110,597	-233.21	122,612	$3.94 \times 10^{-7}$	$3.84 \times 10^{-17}$	-14.75

**Figure 1.** Determination of the reaction area for an exothermic reaction

functions  $\Delta H$  and  $\Delta S$  are negative, so the sign  $\Delta G$  is determined by the relative ratio of the enthalpy and entropy terms (Equation (9)) (Figure 1). This means that reaction temperature is a decisive factor for the thermodynamic balance of the synthesis reaction  $\text{NH}_{3(\text{g})}$ . In the temperature interval of 298 K to 464 K, the equilibrium constant of the considered reaction is very large  $K'_p \gg 1$ , which means

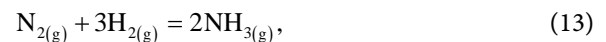
that the reaction is shifted in the direction of product formation  $\text{NH}_{3(\text{g})}$ . At a reaction temperature above 464 K, the chemical equilibrium constant  $K'_p \ll 1$ , so the equilibrium of the reaction shifts in the direction of the formation of reactants of the reaction (Figure 2). These considerations are in line with Le Chatelier's principle. For an exothermic reaction ( $\Delta H < 0$ ), a decrease in temperature shifts the equilibrium of the reaction to the product side.



**Figure 2.** Dependence of the reaction equilibrium constant  $\text{N}_{2(\text{g})} + 3\text{H}_{2(\text{g})} = 2\text{NH}_{3(\text{g})}$  from the temperature.

### 3. Calculation of the Composition of the Equilibrium Mixture of the Synthesis Reaction $\text{NH}_{3(\text{g})}$

Balance equations of reactants in the reaction:



can be written as follows:

$$\text{nitrogen } n_{\text{N}_{2(\text{g})}} = a - y, (\text{kmol}), \quad (14)$$

$$\text{hydrogen } n_{\text{H}_{2(\text{g})}} = b - 3y, (\text{kmol}), \quad (15)$$

$$\text{ammonia } n_{\text{NH}_{3(\text{g})}} = 2y, (\text{kmol}), \quad (16)$$

of which:

$a$ —The number of kilomoles of nitrogen entering the reaction (13);

$b$ —The number of kilomoles of hydrogen reacting (13);

$2y$ —The number of kilomoles of ammonia in the mixture after establishing chemical equilibrium.

The total number of kilomoles in the mixture at any conversion time is equal to:

$$\begin{aligned} n_{\Sigma} &= n_{\text{N}_{2(\text{g})}} + n_{\text{H}_{2(\text{g})}} + n_{\text{NH}_{3(\text{g})}}, \\ n_{\Sigma} &= (a - y) + (b - 3y) + 2y = a + b - 2y. \end{aligned} \quad (17)$$

The mole fraction of the components in the mixture after the establishment of chemical equilibrium amounts to:

$$y_{\text{N}_2(\text{g})} = \frac{n_{\text{N}_2(\text{g})}}{n_{\Sigma}} = \frac{a-y}{a+b-2y}, (\text{kmol/kmol}), \quad (18)$$

$$y_{\text{H}_2(\text{g})} = \frac{n_{\text{H}_2(\text{g})}}{n_{\Sigma}} = \frac{b-3y}{a+b-2y}, (\text{kmol/kmol}), \quad (19)$$

$$y_{\text{NH}_3(\text{g})} = \frac{n_{\text{NH}_3(\text{g})}}{n_{\Sigma}} = \frac{2y}{a+b-2y}, (\text{kmol/kmol}). \quad (20)$$

The partial pressures of the components in the equilibrium mixture are:

$$p_{\text{N}_2(\text{g})} = y_{\text{N}_2(\text{g})} \cdot p = \frac{a-y}{a+b-2y} \cdot p, (\text{Pa}), \quad (21)$$

$$p_{\text{H}_2(\text{g})} = y_{\text{H}_2(\text{g})} \cdot p = \frac{a-3y}{a+b-2y} \cdot p, (\text{Pa}), \quad (22)$$

$$p_{\text{NH}_3(\text{g})} = y_{\text{NH}_3(\text{g})} \cdot p = \frac{2y}{a+b-2y} \cdot p, (\text{Pa}), \quad (23)$$

of which:

$p$ —total pressure in the reactor space after equilibrium is established, (Pa).

The chemical equilibrium constant of the reaction (13) is determined using the expression:

$$K_p = \frac{p_{\text{NH}_3(\text{g})}^2}{p_{\text{N}_2(\text{g})} \cdot p_{\text{H}_2(\text{g})}^3}, (\text{Pa}^{-2}). \quad (24)$$

By changing Equations (21) to (23) into Equation (24) and solving for the unknown  $y$ , the equation is obtained:

$$Ay^4 + By^3 + Cy^2 + Dy + E = 0, \quad (25)$$

of which:

$$A = 27p^2K_p - 16,$$

$$B = (a+b) \cdot (16 - 27p^2K_p),$$

$$C = 9bp^2K_p \cdot (b+3a) - 4 \cdot (a+b)^2,$$

$$D = -b^2p^2K_p \cdot (9a+b),$$

$$E = ab^3p^2K_p.$$

By substituting the solution of Equation (25) into expressions (21) to (23), the numerical values of the mole fractions of the components in the equilibrium mixture are obtained. Degree of responsiveness of reactants  $\text{N}_{2(\text{g})}$  and  $\text{H}_{2(\text{g})}$  is determined using the expression:

$$\eta_{\text{N}_2(\text{g})} = \frac{a-(a-y)}{a} = \frac{y}{a}, (\text{kmol/kmol}) \quad (26)$$

$$\eta_{\text{H}_2(\text{g})} = \frac{b - (b - 3y)}{b} = \frac{3y}{b}, (\text{kmol/kmol}) \quad (27)$$

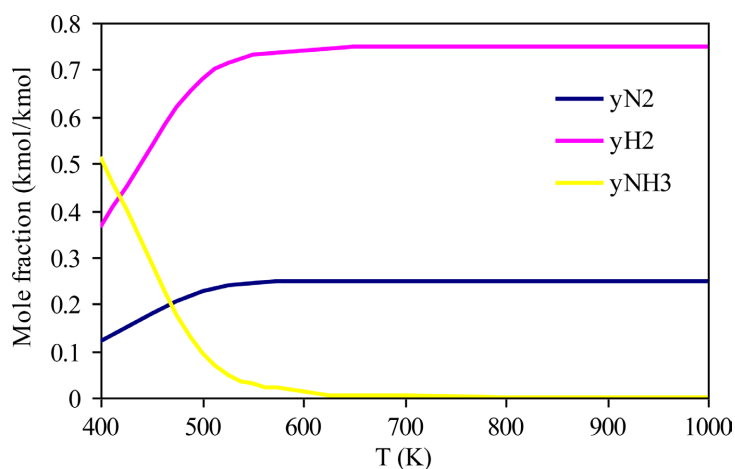
#### 4. The Results of the Calculation of the Composition of the Equilibrium Mixture of the Reaction



The results of the calculation of the composition of the equilibrium mixture at the stoichiometric ratio of reactants, at  $T = 400 \text{ K}$  and pressure  $p = 1.013 \times 10^5 \text{ Pa}$  are shown in **Table 4** and the graphic dependence in **Figure 3**.

**Table 4.** Composition of the equilibrium reaction  $\text{N}_{2(\text{g})} + 3\text{H}_{2(\text{g})} = 2\text{NH}_{3(\text{g})}$  mixture at the stoichiometric number of moles of reactants ( $a = 1 \text{ kmol}$ ,  $b = 3 \text{ kmol}$ ) at pressure  $1.013 \times 10^5 \text{ Pa}$ .

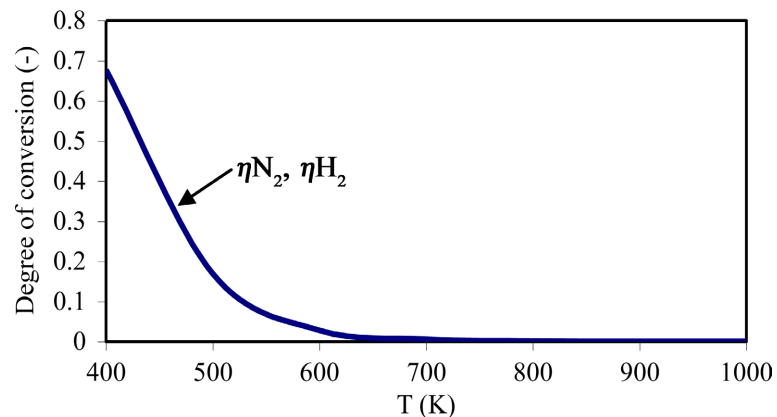
$T(\text{K})$	$y_{\text{N}_2}$ (kmol/kmol)	$y_{\text{H}_2}$ (kmol/kmol)	$y_{\text{NH}_3}$ (kmol/kmol)	$\eta_{\text{N}_2}$ (kmol/kmol)	$\eta_{\text{H}_2}$ (kmol/kmol)
400	0.1218	0.3654	0.5128	0.6779	0.6779
500	0.2269	0.6808	0.0922	0.1690	0.1690
600	0.2464	0.7393	0.0143	0.0282	0.0282
700	0.2492	0.7475	0.0033	0.0066	0.0066
800	0.2498	0.7493	0.0010	0.0020	0.0020
900	0.2499	0.7496	0.0005	0.0010	0.0010
1000	0.2499	0.7486	0.0005	0.0010	0.0010



**Figure 3.** Mole fraction of components in the equilibrium reaction mixture  $\text{N}_{2(\text{g})} + 3\text{H}_{2(\text{g})} = 2\text{NH}_{3(\text{g})}$  depending on the temperature.

It can be seen that ammonia synthesis starts at lower temperatures. At 400 K, the mole fraction of ammonia in the equilibrium mixture is 0.5128 kmol/kmol. At higher temperatures, the mole fraction of ammonia decreases, while at 900 K, the mole fraction of ammonia is equal to 0.0005 kmol/kmol. The degree of conversion

(reaction)  $N_{2(g)}$  and  $H_{2(g)}$  depending on the temperature is shown in **Figure 4**. Apparently, the increase in the reaction temperature and mole fraction shares  $N_{2(g)}$  and  $H_{2(g)}$  in the equilibrium reaction  $N_{2(g)} + 3H_{2(g)} = 2NH_{3(g)}$  mixture, the degree of conversion of the reactants decreases. At 400 K, the degree of conversion of reactants is as much as 0.6779 kmol/kmol, and at 900 K, the degree of conversion is 0.0010 kmol/kmol. This practically means that the synthesis process  $NH_{3(g)}$  at 900 K is completed because it amounts to only 0.0005 kmol/kmol.



**Figure 4.** Degree of conversion  $N_{2(g)}$  and  $H_{2(g)}$  in the equilibrium reaction mixture  $N_{2(g)} + 3H_{2(g)} = 2NH_{3(g)}$  depending on the temperature.

## 5. Conclusion

The paper presents the thermodynamic analysis of ammonia synthesis and the following conclusions were reached:

- The ammonia synthesis reaction is exothermic with a negative entropy change in the temperature interval of 298 - 1000 K
- The sign of the free enthalpy of the  $\Delta G$  reaction is determined by the ratio of the enthalpy and entropy term (Equation (9)), which means that the reaction temperature for is a decisive factor for the thermodynamic balance of the synthesis reaction  $NH_{3(g)}$
- Constant balance reactions synthesis of ammonia is much larger than 1 ( $K'_p \gg 1$ ) at lower temperatures what means that the reaction synthesis continued in direction of the reaction products. Above 464 K, a free synthesis reaction enthalpy is higher than zero, thus reaction enters the thermodynamic unfavorable conditions
- By increasing reaction temperature, the ammonia yield in equilibrium mixture decreases. At 400 K it amounts to 0.5128 kmol/kmol (51.28%) and at 900 K, the synthesis process is practically finished
- Due to the slow speed of the ammonia synthesis reaction, industrial catalysts are used in practice to achieve sufficient activity at higher temperatures (>464 K) [14] [16]

This paper can be used like initial basis of phase designing devices and apparatus in various branches process techniques, chemical engineering as well as for

a better understanding of the process of combustion and synthesis of the multi-component systems.

Further research into ammonia synthesis should be directed at determining the speed of the considered reaction. It is also necessary to investigate the influence of different industrial catalysts on the speed of the ammonia synthesis reaction and their application in industrial practice.

## Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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