

Thermodynamic analysis of methane synthesis by hydrogenation of carbon dioxide

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Abstract

In this study, a thermodynamic analysis of methane synthesis by hydrogenation of carbon dioxide was performed. Although the standard Gibbs potential of this reaction, known as the Sabatier reaction, is negative, methane synthesis under standard conditions does not occur due to kinetic limitations. To overcome these kinetic limitations, a significant increase in temperature and pressure is necessary along with a catalyst additive. Therefore, further thermodynamic analysis of the Sabatier reaction was carried out for the real conditions of this reaction, temperature $T_r = 673.15$ K and pressure $P_r = 3$ MPa. The calculations showed that under real conditions the Sabatier reaction has exothermic enthalpy $\Delta_r H = -181$ kJ/mol, and negative Gibbs potential $\Delta_r G = -84$ kJ/mol. Thus, methane synthesis reaction from carbon dioxide and hydrogen at elevated temperature T_r and pressure P_r is energetically and thermodynamically favorable. In addition, the equilibrium constant of this reaction K_{eq} is 3.24×10^6 . This great value of the K_{eq} indicates that under real conditions the Sabatier reaction is strongly shifted to the methane synthesis.

Keywords: Sabatier reaction; Reaction conditions; Thermodynamic analysis; Enthalpy; Entropy; Gibbs potential; Equilibrium constant

1. Introduction

Recently, the process of methane synthesis from carbon dioxide and hydrogen, known as the Sabatier reaction, has attracted much interest for the following reasons [1, 2]. Firstly, this reaction can be used to purify hydrogen from traces of carbon dioxide and also carbon oxide. Secondly, the optimization and scaling of this process will allow the conversion of large volumes of carbon dioxide into a synthetic fuel, methane, using renewable energy. Thus, there is a prospect of decreasing the CO_2 concentration in Earth's atmosphere and reducing the effect of global warming. Thirdly, further improvement and widespread use of the Sabatier process can reduce the use of fossil fuels by replacing them with carbon-neutral synthetic methane. Fourthly, the synthesis of methane by hydrogenation of carbon dioxide allows the production of rocket fuel on Mars and other planets. Therefore, combining this reaction with the electrolysis process of water to produce hydrogen and oxygen can facilitate long-term space exploration missions by space agencies such as NASA.

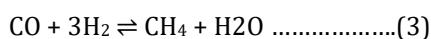
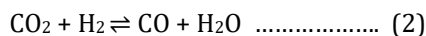
The Sabatier reaction is expressed by the following equation:



At normal or slightly increased temperatures and pressures, the rate of direct reaction probable is negligible, and the process is shifted to the left. To ensure the conversion of CO_2 to CH_4 , the reaction should be carried out at elevated temperatures and pressures in the presence of a catalyst [2-5]. Studies have shown that a high yield of synthetic methane, over 90% of the theoretical yield, can be achieved if the reaction temperature is about $400^\circ C$ (673.15 K) and the pressure is about 3 MPa [4]. As catalysts, Ni and Ru on alumina and some others are used [2, 5].

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The Sabatier reaction most likely occurs in two stages [2, 5]. In the first stage, carbon dioxide is reduced with hydrogen to carbon monoxide (equation 2), and in the second stage, carbon monoxide is converted to methane (equation 3).



It was found that the Sabatier reaction is exothermic [2]. Several references indicated that the standard enthalpy of reaction ($\Delta_r H^\circ$) is -165 kJ/mol CH_4 or -41.25 kJ/mol H_2 when formed water is in the gaseous (vapor) state [2, 6-9]. The standard Gibbs potential of this reaction was also estimated [10]. Unfortunately, for the case, when the formed water vapor condenses into liquid, the calculation of the standard enthalpy and potential of the reaction was not performed. However, thermodynamic analysis requires the calculation of three thermodynamic functions, enthalpy, entropy, and Gibbs potential, and not only for standard temperature and pressure but also for real conditions occurring at high temperature and pressure. For this purpose, a complete thermodynamic analysis of the Sabatier reaction was carried out under standard and real reaction conditions.

2. Results and Discussion

2.1. Thermodynamic analysis of Sabatier reaction at standard conditions

Using reference books, the standard enthalpies of formation ($\Delta_f H^\circ$) and the standard enthalpies (S°) for reagents and products of the Sabatier reaction were found (Table 1).

Table 1 Standard thermodynamic functions (TDF)

Substance	$\Delta_f H^\circ$, kJ/mol	S° , J/mol K
CO_2 gas	-393.51	213.6
H_2 gas	0	130.6
CH_4 gas	-74.85	186.19
H_2O gas (vapor)	-241.84	188.74
H_2O liquid	-285.83	69.96

2.1.1. Thermodynamic analysis in the case of the gaseous (vapor) state of the formed water

The standard enthalpy of reaction (1) was calculated using the equation:

$$\Delta_r H^\circ(\text{g}) = \Delta_f H^\circ(\text{CH}_4, \text{g}) + 2\Delta_f H^\circ(\text{H}_2\text{O}, \text{g}) - \Delta_f H^\circ(\text{CO}_2, \text{g}) - 4\Delta_f H^\circ(\text{H}_2, \text{g}) \dots\dots\dots(4)$$

The standard entropy of this reaction was calculated, as follows:

$$\Delta_r S^\circ(\text{g}) = S^\circ(\text{CH}_4, \text{g}) + 2S^\circ(\text{H}_2\text{O}, \text{g}) - S^\circ(\text{CO}_2, \text{g}) - 4S^\circ(\text{H}_2, \text{g}) \dots\dots\dots (5)$$

In addition, the Gibbs potential of the reaction was found:

$$\Delta_r G^\circ(\text{g}) = \Delta_r H^\circ(\text{g}) - T_0 \Delta_r S^\circ(\text{g}) \dots\dots\dots (6)$$

where $T_0 = 298.15$ K is the standard temperature.

Substituting the values of the required TDF from Table 1 into these equations, the standard TD functions of the Sabatier reaction were obtained (Table 2).

Table 2 TDF of the reaction (1) at standard conditions: at $T_0 = 298.15$ K and $P_0 = 0.1$ MPa

TDF	Values for the case of gaseous H ₂ O formation	Values for the case of liquid H ₂ O formation
$\Delta_r H^\circ$ (g), kJ/mol	-165.00	-253.00
$\Delta_r S^\circ$ (g), J/mol K	-172.33	-409.89
$\Delta_r G^\circ$ (g), kJ/mol	-113.62	-130.79

2.1.2. Thermodynamic analysis in the case of the liquid state of the formed water

The calculations were performed using similar equations with the difference that standard TDF of liquid (l) water was used instead of gaseous (g) water.

$$\Delta_r H^\circ(l) = \Delta_f H^\circ(\text{CH}_4, \text{g}) + 2\Delta_f H^\circ(\text{H}_2\text{O}, \text{l}) - \Delta_f H^\circ(\text{CO}_2, \text{g}) - 4\Delta_f H^\circ(\text{H}_2, \text{g}) \dots\dots\dots(7)$$

$$\Delta_r S^\circ(l) = S^\circ(\text{CH}_4, \text{g}) + 2S^\circ(\text{H}_2\text{O}, \text{l}) - S^\circ(\text{CO}_2, \text{g}) - 4S^\circ(\text{H}_2, \text{g}) \dots\dots\dots (8)$$

$$\Delta_r G^\circ(l) = \Delta_r H^\circ(l) - T_s \Delta_r S^\circ(l) \dots\dots\dots (9)$$

The calculation results are presented in Table 2. When the resulting water is liquid, the exothermic thermal effect of the reaction is higher than in the case of gaseous water. The same relationship is observed for the Gibbs potential of the Sabatier reaction. A more negative value of the Gibbs potential means that the process that forms liquid water is more favorable than the process that produces gaseous water.

Despite the negative value of the Gibbs potential, the process of carbon dioxide hydrogenation under standard conditions, $T_0 = 298.15$ K and $P_0 = 0.1$ MPa, cannot be implemented, due to kinetic limitations [5]. As the temperature rises, the reaction rate increases, especially in the presence of a catalyst [2-5]. In addition, the elevation of pressure shifts the equilibrium of reaction (1) to the right and increases the yield of methane [10, 11].

2.2. Thermodynamic analysis of catalyzed Sabatier reaction at high temperature and pressure

These calculations were carried out for real conditions of the Sabatier reaction, $T_r = 673.15$ K and $P_r = 3$ MPa in the catalyst presence, when the reaction rate is high enough to ensure a high methane yield. Under these conditions, the formed water is in a gaseous state.

As is known, enthalpy is almost independent of pressure and the main influence on the enthalpy value is exerted by temperature. The enthalpy value of a gaseous substance at pressure P_r and temperature T_r was found using the equation:

$$\Delta H(P_r, T_r) = \Delta H^\circ(g) + \int_{T_0}^{T_r} C_p dT \dots\dots\dots(10)$$

where C_p is the specific heat capacity of the gas, which depends on temperature; $T_0 = 298.15$ K is the standard temperature, and $T_r = 673.15$ K is the reaction temperature.

The C_p values of gaseous CO_2 , H_2 , and H_2O are functions of temperature:

$$C_p(T) = a + bT + c/T^2 \dots\dots\dots (11)$$

where a , b , and c are coefficients, the values of which can be found in reference books.

On the other hand, the temperature dependence of C_p for gaseous CH_4 is the following:

$$C_p(T) = a + bT + cT^2 + dT^3 \dots\dots\dots (12)$$

where a , b , c , and d are coefficients, the values of which are given in reference books.

Unlike enthalpy, the entropy depends on both pressure and temperature. The value of enthalpy at pressure $P_r = 3$ MPa and standard temperature $T_0 = 298.15$ K was calculated using the equation:

$$S(P_r, T_o) = S^o(g) - R \ln(P_r/P_o) \dots\dots\dots (13)$$

where pressure $P_o=0.1$ MPa, and $R=8.3145$ (J/mol K) is the gas constant.

The calculated values of $S(P_r, T_o)$ at $P_r=3$ MPa for the studied substances are shown in Table 3.

Table 3 Entropy values of substances at $P_r=3$ MPa and $T_o = 298.15$ K

Substance	$S(P_r, T_o)$, J/mol K
CO ₂ gas	185.32
H ₂ gas	102.32
CH ₄ gas	157.91
H ₂ O gas	160.46

Further, the entropy value of the studied gaseous substance at pressure P_r and temperature T_r was calculated, as follows:

$$S(P_r, T_r) = S(P_r, T_o) + \int_{T_o}^{T_r} C_p/T dT \dots\dots\dots(14)$$

where C_p is the specific heat capacity of the gas, which depends on temperature according to eq. (11) and (12).

The calculation results of TDF using equations (10), and (14) are shown in Table 4.

Table 4 Values of TDF at $T_r= 673.15$ K and $P_r= 3$ MPa

Substance	$\Delta_r H(P_r, T_r)$, kJ/mol	$S(P_r, T_r)$, J/mol K
CO ₂ gas	-376.91	220.79
H ₂ gas	10.92	119.01
CH ₄ gas	-57.42	173.93
H ₂ O gas	-228.58	189.05

Using these TDF, the enthalpy, entropy, and Gibbs potential of the Sabatier reaction at high temperature and pressure were obtained (Table 5).

Table 5 TDF of the reaction (1) at $T_r=673.15$ K and $P_r=3$ MPa

TDF	Values
$\Delta_r H(P_r, T_r)$, kJ/mol	-181.35
$\Delta_r S(P_r, T_r)$, J/mol K	-144.80
$\Delta_r G(P_r, T_r)$, kJ/mol	-83.88

The results showed that the Sabatier reaction is highly exothermic at increased temperature and pressure, while reaction entropy is negative. In addition, the Gibbs potential under these conditions is strongly negative. Thus, the process of methane synthesis from carbon dioxide and hydrogen at elevated temperature $T_r= 673.15$ K and pressure $P_r=3$ MPa is energetically and thermodynamically favorable. Calculations also showed that heating a compressed initial gas mixture from T_o to T_r requires the expenditure of 61.1 kJ/mol of thermal energy, which is 3 times less than that released by the exothermic Sabatier reaction.

Using the Van 't Hoff equation, it was found that the equilibrium constant of the reaction K_{eq} is 3.24×10^6 . This great value of the equilibrium constant confirms that under real conditions the reaction (1) is strongly shifted to the right and leads to the formation of methane with a high yield.

The Sabatier process continues to be improved. New designs of CO₂ hydrogenation reactors with an improved heat exchange have been proposed [2, 8, 12]. In addition, more efficient catalytic systems and the removal of resulting water vapor allow for optimization of reaction conditions and enhance methane yield [2, 5, 12, 13]. The thermal energy of the Sabatier process can be utilized for the heating of the initial gas mixture and for the electrolysis of water to produce hydrogen [14]. Moreover, constructions are being developed that combine a CO₂ hydrogenation reactor with a fuel combustion boiler [2], electrolyzer [2, 14], or electrochemical cell [6, 7].

The carbon dioxide needed for the Sabatier reaction can be extracted from the air, or flue gas using liquefaction, freezing, and sorption technologies or a combination thereof. The resulting purified CO₂ is quite cheap with a commercial price of less than \$0.2 per kg. Unlike CO₂, the cost of electrolytic hydrogen is high, at least \$6-8 per kg. Therefore, to scale up and widely use the Sabatier process cheaper methods of hydrogen production need to be developed.

A promising method for producing cheap hydrogen could be the catalytic steam gasification of renewable biomass or charcoal based on it [15-18].

3. Conclusions

Thermodynamic analysis of the Sabatier reaction was performed. It was shown that the standard Gibbs potential of this reaction is negative. Despite this, under standard conditions ($T_o = 298.15$ K, $P_o = 0.1$ MPa) the methane synthesis does not occur due to kinetic limitations. The further thermodynamic analysis of the Sabatier reaction was carried out for the real reaction conditions, a temperature $T_r = 673.15$ K and a pressure $P_r = 3$ MPa. The calculations showed that under these real conditions, the Sabatier reaction has exothermic enthalpy $\Delta_rH = -181$ kJ/mol, and negative Gibbs potential $\Delta_rG = -84$ kJ/mol. Thus, the methane synthesis from carbon dioxide and hydrogen at elevated temperature T_r and pressure P_r is energetically and thermodynamically favorable. In addition, the equilibrium constant of this reaction K_{eq} is 3.24×10^6 . This great value of the K_{eq} indicates that under real conditions the Sabatier reaction is strongly shifted to the methane synthesis.

Compliance with ethical standards

Disclosure of conflict of interest

The author of this paper declares that there is no conflict of interest.

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