Chemical Equilibria in Methanol Synthesis Including the Water–Gas Shift Reaction

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# Chemical Equilibria in Methanol Synthesis Including the Water−Gas Shift Reaction: A Critical Reassessment

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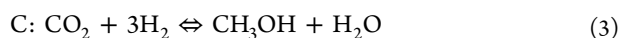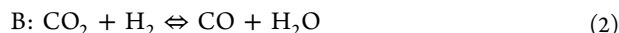
S Supporting Information

ABSTRACT: A large number of experimental equilibrium constants for the reactions involved in methanol synthesis were collected or calculated from several literature sources. Equilibrium relationships were derived from basic thermochemical data and subsequently fitted to the experimental results by adapting only the Gibbs energy of formation values for CH_3OH and CO. Very small changes of these parameters as compared to the original literature values were sufficient to obtain accurate relationships that adequately describe the experimental results.
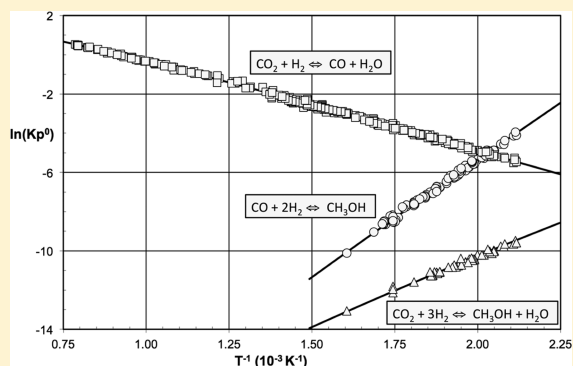
1. INTRODUCTION

Methanol synthesis is a highly important industrial process governed by the following reversible reactions.

$$A: CO + 2H_2 \Leftrightarrow CH_3OH \qquad (1)$$

$$B: CO_2 + H_2 \Leftrightarrow CO + H_2O \qquad (2)$$

$$C: CO_2 + 3H_2 \Leftrightarrow CH_3OH + H_2O \qquad (3)$$

At equilibrium conditions only two of these three reactions suffice to describe the equilibrium composition, provided that accurate equilibrium constants are available. However, a literature survey reveals that no clear picture exists on this important subject especially regarding the methanol formation reactions 1 and 3. To a lesser extent the same applies for the (reverse) water−gas shift reaction 2, but in this case the differences between equilibrium constants are much smaller.

The purpose of this publication is twofold. First we will clarify why these differences between equilibrium constants exist. Second, we will present new relationships for the equilibrium constants of the reactions involved based on experimental information from an extensive literature survey and thorough analysis.

2. THEORY

Ideal gas equilibrium constants can be calculated with the use of the following equations.

$$\ln Kp°(T) = \frac{1}{R}\left[\frac{-\Delta G°(T_{ref})}{T_{ref}} + \int_{T_{ref}}^{T} \frac{\Delta H°(T)}{T^2}\, dT\right] \qquad (4)$$

$$\Delta H°(T) = \Delta H°(T_{ref}) + \int_{T_{ref}}^{T} \Delta c_p°(T)\, dT \qquad (5)$$

When the heat capacities of the components ($c_p°$) are known as fourth-order polynomial functions of temperature, the following relationship for $Kp°$ results.

$$\ln Kp°(T) = \frac{1}{RT}[a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4 \\ + a_6 T^5 + a_7 T \ln T] \qquad (6)$$

Industrial methanol synthesis is carried out at elevated pressures (±100 bar). Therefore, corrections for nonideal gas behavior are necessary. Graaf et al.[1,2] have shown that the Soave−Redlich−Kwong equation of state (SRK-EoS)[3] is suitable for this purpose. Recently van Bennekom et al.[4] have optimized an adapted version of the SRK-EoS as published by Mathias[5] for the methanol synthesis system. Furthermore, we found that a better fit of experimental equilibrium constants results by using the H_2-specific α-function as described by Graboski and Daubert.[6] We have used this optimized and extended SRK-EoS version in our analysis.

Despite the fact that accurate thermochemical information is available nowadays, it turns out that still no consistent information on the chemical equilibria in methanol synthesis exists in the open literature. In order to get a better understanding of this observation we have conducted a sensitivity analysis with respect to the derivation of equilibrium relationships based on eq 6 and thermochemical data from the literature. From this analysis we conclude that the accuracy of the heat capacity data is sufficient

and can not be the cause for the discrepancies. The accuracy of the $\Delta H°(T_{ref})$ and $\Delta G°(T_{ref})$ values however is a decisive factor for obtaining accurate equilibrium constants (as might be expected). Comparing thermochemical data from various sources[7−12] reveals that the $\Delta G°(T_{ref})$ value for CH_3OH shows the greatest variation. Consequently, the greatest uncertainty of the calculated $Kp_1°$ values is caused by this parameter. It turns out that the sensitivity of $Kp_1°$ for the $\Delta G°(T_{ref})$ value for reaction 1 is a factor 4 higher as compared to $\Delta H°(T_{ref})$, taking the different variations of the thermochemical parameters into account. Furthermore, the sensitivity of $Kp_1°$ for the $\Delta G°(T_{ref})$ value for CH_3OH is a factor 3.5 higher relative to CO, again including the observed variations of these parameters.

Haynes et al.[8] present a $\Delta G°(T_{ref})$ value for methanol of −162.298 kJ/mol (T = 298.15 K; p = 1 bar). With this value and in combination with the other thermochemical basic data from the same source an ideal gas equilibrium constant for reaction 1 of 2.07×10^{-3} bar^{-2} is calculated at T = 523.15 K. Further calculations with $\Delta G°(T_{ref})$ values which are 0.5% lower or higher yield equilibrium constants of 2.88×10^{-3} and 1.50×10^{-3} bar^{-2} respectively. This clearly shows the enormous effect of very small changes in the $\Delta G°(T_{ref})$ value for methanol on the calculated equilibrium constants: the difference between the highest and lowest $Kp_1°$ value is almost a factor 2. The 0.5% change of the $\Delta G°(T_{ref})$ value for methanol leads to an average change of 33% of the $Kp_1°$ value.

For the water−gas shift reaction a similar sensitivity analysis was conducted. Here we investigated the effect of a 0.2% change in the $\Delta G°(T_{ref})$ value for CO, because the other thermochemical data have higher accuracies. Based on the work of Haynes et al.[8] a $Kp_2°$ value of 1.12×10^{-2} at T = 523.15 K results. $\Delta G°(T_{ref})$ values for CO which are either 0.2% lower or higher yield equilibrium constants of 1.25×10^{-2} and 1.00×10^{-2} respectively. Also in this case the sensitivity is very large: the average change in the $Kp_2°$ value is 11% due to a 0.2% change in the $\Delta G°(T_{ref})$ value for CO.

$Kp_1°$ values from some literature relationships are presented in Table 1 together with the results of the sensitivity analysis.

Table 1. $Kp_1°$ Values of Several Authors Including the Sensitivity Results with Regard to $\Delta G°(T_{ref})$ for CH_3OH

source	$Kp_1°$ (200 °C) (bar^{-2})	$Kp_1°$ (250 °C) (bar^{-2})	$Kp_1°$ (300 °C) (bar^{-2})
Haynes et al.[8]	2.22×10^{-2}	2.07×10^{-3}	2.85×10^{-4}
Haynes et al.[8] "plus"[a]	1.60×10^{-2}	1.50×10^{-3}	2.06×10^{-4}
Haynes et al.[8] "minus"[b]	3.08×10^{-2}	2.88×10^{-3}	3.96×10^{-4}
Cherednichenko[13]	2.45×10^{-2}	2.22×10^{-3}	2.98×10^{-4}
Peter[15]	2.06×10^{-2}	1.95×10^{-3}	2.80×10^{-4}
Graaf et al.[1]	1.74×10^{-2}	1.59×10^{-3}	2.22×10^{-4}
Klier et al.[14]	1.67×10^{-2}	1.58×10^{-3}	2.25×10^{-4}

[a]Plus means that a 0.5% higher $\Delta G°(T_{ref})$ value for CH_3OH is applied. [b]Minus means that a 0.5% lower $\Delta G°(T_{ref})$ value for CH_3OH is applied.

It shows that the differences between the various relationships are even smaller than the extremes of the sensitivity analysis. Consequently, it can be concluded that very small differences in the $\Delta G°(T_{ref})$ value for CH_3OH can explain the differences between the various relationships, where the highest $Kp_1°$ values[13] are approximately 40% higher as compared to the lowest values.[14] This is further illustrated by the fact that Graaf et al.[1] have used a $\Delta G°(T_{ref})$ value for CH_3OH of −161.830 kJ mol^{-1} (0.3% higher relative to Haynes et al.[8]), which indeed turns out to be the

main cause for the observed differences in the calculated equilibrium constants.

A similar overview for the water−gas shift reaction is presented in Table 2. Literature $Kp_2°$ values show less variation

Table 2. $Kp_2°$ Values of Several Authors Including the Sensitivity Results with Regard to $\Delta G°(T_{ref})$ for CO

source	$Kp_2°$ (200 °C)	$Kp_2°$ (250 °C)	$Kp_2°$ (300 °C)
Haynes et al.[8]	4.24×10^{-3}	1.12×10^{-2}	2.46×10^{-2}
Haynes et al.[8] "plus"[a]	3.79×10^{-3}	1.00×10^{-2}	2.20×10^{-2}
Haynes et al.[8] "minus"[b]	4.73×10^{-3}	1.25×10^{-2}	2.75×10^{-2}
Newsome[16]	4.78×10^{-3}	1.20×10^{-2}	2.58×10^{-2}
Bissett[17]	4.44×10^{-3}	1.17×10^{-2}	2.58×10^{-2}
Graaf et al.[1]	4.44×10^{-3}	1.17×10^{-2}	2.58×10^{-2}
Singh and Saraf[18]	4.18×10^{-3}	1.10×10^{-2}	2.43×10^{-2}

[a]Plus means that a 0.2% higher $\Delta G°(T_{ref})$ value for CO is applied. [b]Minus means that a 0.2% lower $\Delta G°(T_{ref})$ value for CO is applied.

as compared to the $Kp_1°$ results. Maximum $Kp_2°$ values are approximately 10% higher than the lowest values. However, also in this case the differences can be explained by very small changes in the $\Delta G°(T_{ref})$ value for (in this case) CO.

From this analysis the conclusion seems justified that the differences between literature equilibrium relationships are caused by very small differences in the underlying basic thermochemical data and, most likely, the $\Delta G°(T_{ref})$ values for CH_3OH and CO. The sensitivity for these basic data is very high. This also means that accurate experimental chemical equilibrium data may provide better estimates for these $\Delta G°(T_{ref})$ values.

3. DERIVATION OF CHEMICAL EQUILIBRIUM CONSTANTS FROM EXPERIMENTAL LITERATURE DATA

3.1. Water−Gas Shift Reaction. First we will focus on the water−gas shift reaction, because our investigations showed that in several cases experimental equilibrium data from the literature for reaction 1 (methanol synthesis from CO/H_2) could only be derived under the assumption that the equilibrium constant of the water−gas shift reaction is well-known. Therefore, we first need to establish an accurate $Kp_2°$ relationship that can be used in further analysis.

Literature data on experimental equilibrium data for the water−gas shift reaction can be divided in two categories. The first category consists of experimental results that were obtained with the purpose of obtaining experimental equilibrium data. The second category consists of catalytic activity testing results as a function of temperature or flow rate. In several cases these latter results contain data points at higher temperatures or lower flow rates where chemical equilibrium is closely approached. In Table 3 an overview is presented of literature sources for the first category.

The $Kp_2°$ values were calculated from the experimental gas composition, pressure, and temperature correcting for nonideal gas behavior with the use of the Soave−Redlich−Kwong equation of state[3] as adapted by Mathias[5] using critical constants and acentric factors as presented by Poling et al.[9] Binary interaction parameters were taken from van Bennekom et al.,[4] except for hydrogen-containing binaries. In this case binary interaction parameters were set at zero values, because for H_2 we used the SRK-adaptation as described by Graboski and Daubert.[6] From a preliminary analysis we found that this approach for H_2 results in a better fit of the experimental $Kp°$-data. The H_2-specific

Table 3. Experimental Equilibrium Data for the Water–Gas Shift Reaction (WGS): Literature Overview Category 1 (Equilibrium Experiments)

source	system	T (K)	p (bar)
Emmett and Shultz[19–21]	WGS	723–1273	1.013
Graaf et al.[1,2]	methanol synthesis	472–539	10–73
Kaneko and Oki[22,23]	WGS	648–793	<1.013
Kodama et al.[24]	WGS	623–673	1.013
Kuznetsov et al.[25]	methanol synthesis	523	1.013
Liu et al.[26,27]	methanol synthesis	493–534	40–66
Neumann and Köhler[28]	WGS	568–1264	1.013
Oki and Mezaki[29]	WGS	740–795	<1.013
Sorgato and Angelin[30]	WGS	593–673	21–294

α-function as described by Graboski and Daubert[6] (including effective critical constants) was tested with the experimental PvT-data of Presnall.[31] Presnall accurately measured the molar volume of hydrogen in the temperature range 200–600 °C and at pressures ranging from 100 up to 1800 atm (108 experiments). It turns out that a significant better fit results as compared to the conventional modeling of H_2 (molar volume H_2: AAD = 1.6 and 3.0%, respectively). Critical constants and acentric factors of other components (Ar, He, N_2, CH_4, C_2H_6, C_3H_8 and dimethyl ether) were also taken from Poling et al.[9]

In Figure 1 the resulting (pseudo)experimental $Kp_2°$ values are presented as a function of temperature together with the results as calculated from our sensitivity analysis. Apart from experimental scattering most of the results are well in line with the $Kp_2°$ relationship derived from the work of Haynes et al., 2015.[8] The results of Liu et al.,[26,27] however, show a deviating pattern. Therefore, we decided to analyze the results of Liu et al. in depth.

Liu et al.[26] have described their experimental approach in detail. Experiments were performed with a combination of two isothermal fixed bed reactors in series using a combination of gas flow rate and amount of catalyst which is sufficient to ensure that equilibrium is reached. The reactor exit stream is led to a condensor/separator, where methanol and water are condensed and separated from the exit stream. The composition of the dry exit stream is analyzed with a GC. The composition of the reactor inlet stream is also determined by GC-measurements. The condensed methanol and water stream is not analyzed: the reactor exit mole fractions of methanol and water are calculated from material balances instead. Our analysis revealed that this approach leads to significant deviations of the material balances for carbon, hydrogen and oxygen (by comparing the calculated and the experimental dry gas composition). From a sensitivity analyis we conclude that it is not meaningful to derive both $Kp_1°$ and $Kp_2°$ values from Liu's experimental data. However, we will show later in this paper that for most experiments it is possible to derive fairly accurate $Kp_1°$ values, if the mole fractions for water are calculated from a reliable $Kp_2°$ relationship.

Figure 1 also shows that the results of Neumann and Köhler[28] at higher temperatures are in good agreement with the $Kp_2°$ relationship derived from the work of Haynes et al.[8] At lower temperatures (<425 °C) these data show considerable scattering, mainly because here, according to the authors, the reaction rates are too low to ensure a close approach to equilibrium. Therefore, we will only use the results at higher temperatures.

Table 4 gives an overview of literature sources concerning the second category and the collected $Kp_2°$ values of both categories are presented in Figure 2. For category 2 (WGS) the necessary experimental gas composition data were calculated from reported CO or CO_2 conversion values and the reactor inlet composition by solving the material balances over the reactor. Here, we only used experimental data at or very close to equilibrium. For methanol synthesis results the calculation procedure is more complicated as will be dealt with later in this paper.

Figure 2 shows that the experimental results of category 2 are well in line with the results of category 1, regardless whether the results were obtained from methanol synthesis (higher pressures and system complexity) or the water–gas shift system without methanol formation. Furthermore, the $Kp_2°$ relationship based on the work of Haynes et al.[8] corresponds well with the experimental results. This is confirmed by fitting the $\Delta G_{CO}°(T_{ref})$ value in this relationship to the experimental results by minimizing the SSR value, yielding the following: $\Delta G_{CO}°(T_{ref})$ = −137.218 ± 0.025 kJ/mol (99% confidence level) with AAD = 5.6% based on 351 experimental data points
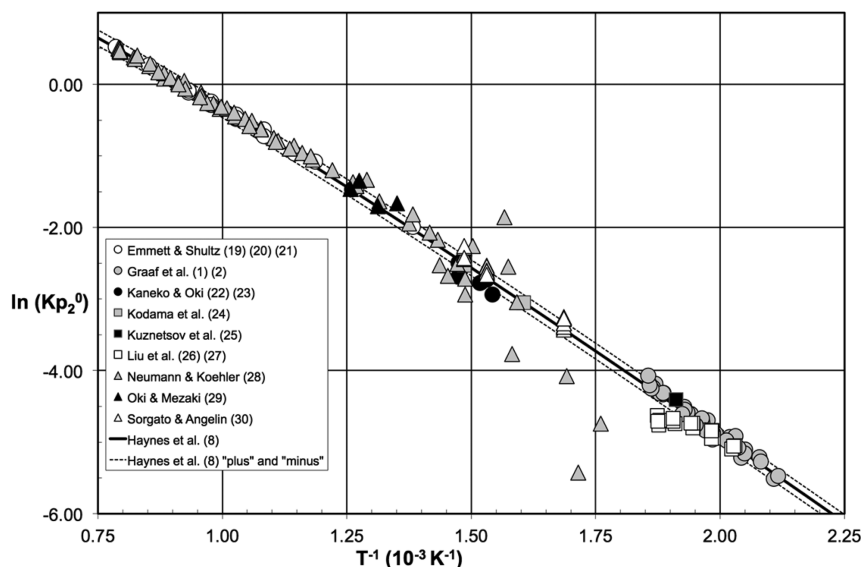
Figure 1. Experimental $Kp_2°$ values (category 1) as a function of temperature.

taken from 42 literature sources. The literature value[8] equals −137.168 kJ/mol. This very small difference (0.03%) is hardly visible in Figure 2 where the fitted curve is presented. The curve based on the work of Haynes et al.[8] lies slightly below the fitted $Kp_2°$ relationship.

A somewhat better fit can be obtained if both $\Delta G_{CO}°(T_{ref})$ and $\Delta H_{CO}°(T_{ref})$ are optimized from the experimental data. However, this improvement turns out to be very small and can not be

Table 4. Experimental Equilibrium Data for the WGS: Literature Overview Category 2 (Catalytic Activity Experiments Close to Chemical Equilibrium)

source	system	T (K)	p (bar)
An et al.[32]	methanol synthesis	533−553	40
Brooks et al.[33]	WGS	523−573	1.013
Chen and Yuan[34]	methanol synthesis	473−500	10
Dagle et al.[35]	WGS	534−589	1.013
Galuszka et al.[36]	WGS	723	1.1
Jeong et al.[37,38]	WGS	593, 633	1.013
Jingfa et al.[39]	Methanol synthesis	513	20
Lortie[40]	WGS	923−973	1.013
Mendes[41]	WGS	473−573	1.013−1.2
Panagiotopoulou and Kondarides[42−44]	WGS	613−769	1.013
Potdar et al.[45]	WGS	593	1.013
Reddy et al.[46]	WGS	823	1.013
Reddy et al.[47]	WGS	513−628	1.013
Rosa et al.[48]	WGS	573−603	1.013
Sakurai et al.[49−51]	methanol synthesis	573−623	8, 50.7
Sakurai et al.[52]	WGS	473−674	50.7
Shakeel[53]	WGS	528−573	1.013
Subramanian et al.[54]	WGS	593	1.013
Swartz et al.[55,56]	WGS	589−593	1.013
Tang et al.[57]	WGS	823	1.013
TeGrotenhuis et al.[58]	WGS	494−598	1.013
Tibiletti et al.[59]	WGS	629−714	1.013
Uemiya et al.[60]	WGS	673	1.013
Xue et al.[61]	WGS	676−725	1.013

regarded as significant. Further testing of the fitting results reveals that the residuals are (almost) normally distributed as can be seen in Figure 3, supporting our choice to optimize only $\Delta G_{CO}°(T_{ref})$.

The confidence intervals (±0.025 kJ/mol) show that the optimized $\Delta G_{CO}°(T_{ref})$ value is very accurate. However, it should be realized that these confidence intervals mainly reflect the effects of experimental scattering. On top of this, some systematic uncertainties exist, due to the fact that uncertainties of the other basic thermochemical data have not been taken into account and also because the correction for nonideal gas behavior may contain some systematic error. On an average basis the deviations from ideal-gas behavior turn out to be rather small ($Kp_2°/Kp_2$ values are very close to 1), because most of the experimental data were obtained at low pressures and high temperatures. Maximum deviations for ideal-gas behavior were calculated from the data of Sorgato and Angelin[30] ($Kp_2°/Kp_2$: 0.63−0.97).

We estimate that these two systematic effects might add up to an uncertainty of the estimated $\Delta G_{CO}°(T_{ref})$ value of ±0.1 kJ/mol. Nevertheless it is fair to conclude that the estimated $\Delta G_{CO}°(T_{ref})$ value is still very accurate with an estimated overall uncertainty of less than 0.1%.

The optimized $Kp_2°$ relationship is defined as

$$\ln Kp_2°(T) = \frac{1}{RT}[b_1 + b_2 T + b_3 T^2 + b_4 T^3 + b_5 T^4 + b_6 T^5 + b_7 T \ln T] \tag{7}$$

$b_1 = -3.94121 \times 10^{+4}$; $b_2 = -5.41516 \times 10^{+1}$; $b_3 = -5.5642 \times 10^{-2}$; $b_4 = 2.5760 \times 10^{-5}$; $b_5 = -7.6594 \times 10^{-9}$; $b_6 = 1.0161 \times 10^{-12}$; $b_7 = 1.8429 \times 10^{+1}$.

The only parameter that results from fitting the experimental data is b_2. The other parameters were calculated from the work of Haynes et al.[8] For this purpose the heat capacity data were fitted to fourth-order polynomials ($T = 298−1500$ K). The optimized $Kp_2°$ relationship is based on experiments in a temperature range 472−1273 K and may be regarded as very accurate in this temperature range. However, it seems plausible
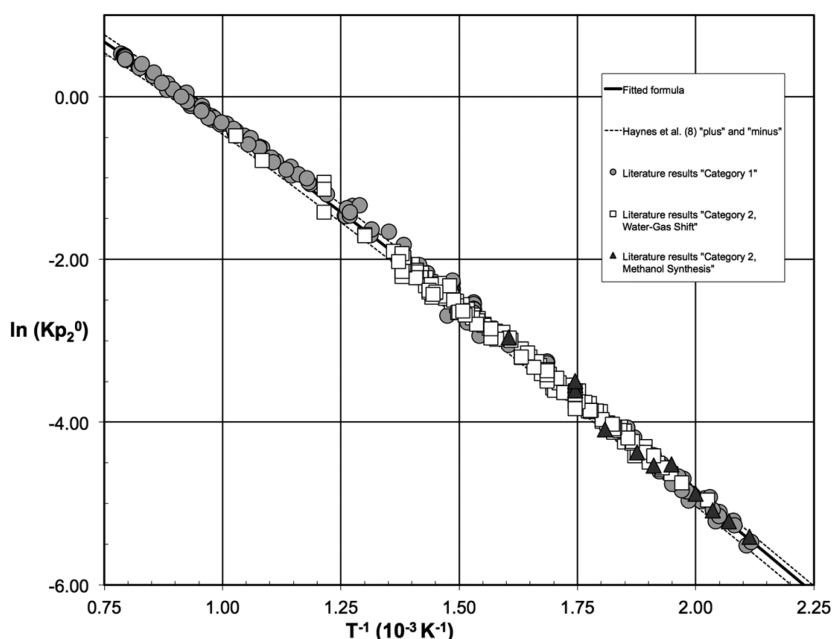

Figure 2. Experimental $Kp_2°$ values (categories 1 and 2) as a function of temperature.
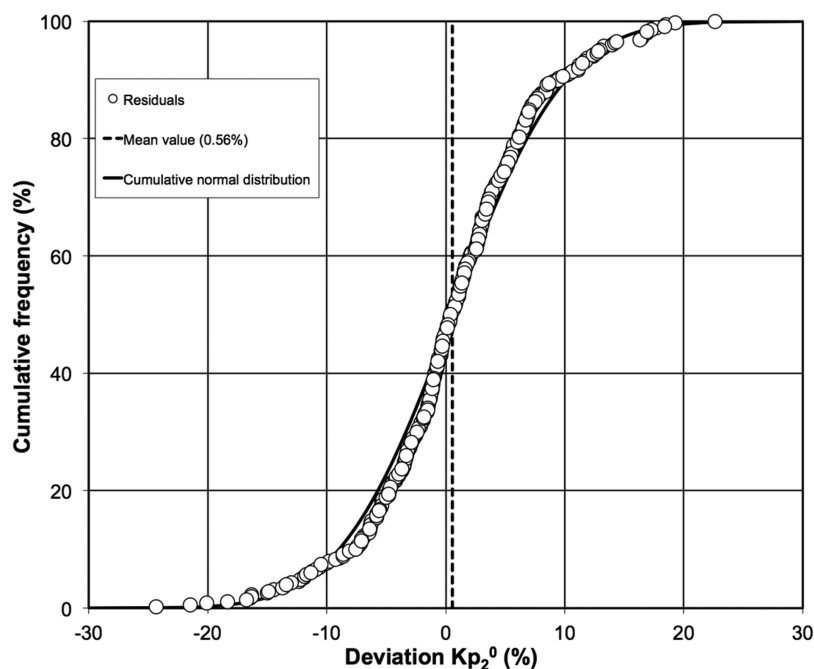
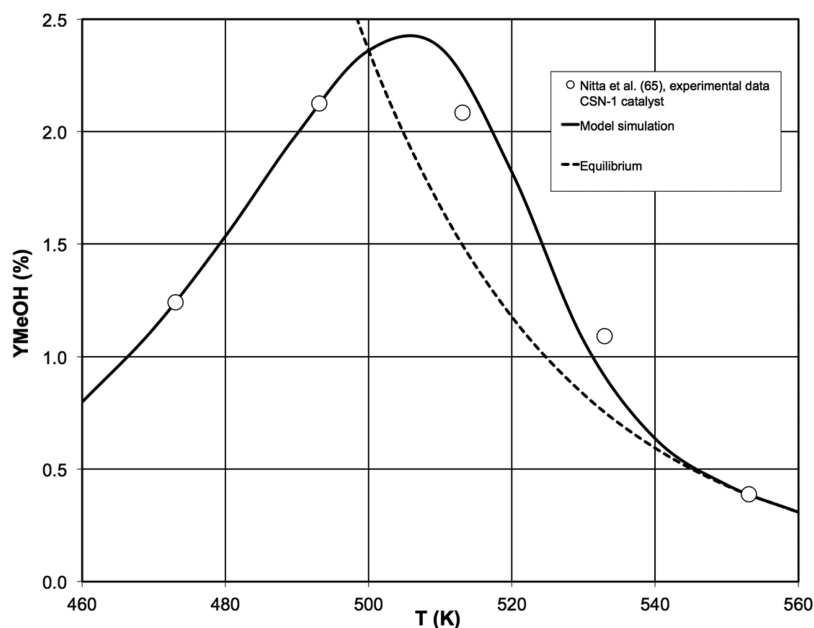**Figure 3.** Cumulative distribution curve of the Kp_2° residuals.

Figure 4. Simulation example: Methanol yield as a function of temperature including optimization of Kp_1° and ACT (correction for catalyst activity). Feed CO_2:H_2 = 1:3; p = 9 bar; F_{in}/W = 5.95 × 10^{-5} mol s^{-1} g^{-1}.

that the formula will also yield acceptable results in the range 298−1500 K.

Equation 7 yields the following results at 200, 250, and 300 °C: 4.33 × 10^{-3}, 1.14 × 10^{-2}, and 2.51 × 10^{-2}. A comparison with the results presented in Table 2 shows that these values lie between those of Haynes et al.[8] and Graaf et al.[1] and Bissett.[17]

3.2. Methanol from CO/H_2 Reaction. A similar approach as described in the previous section was employed to obtain experimental Kp_1° values from the literature. Here, we found that it is much more difficult to find reliable sources. In several cases conversion data were presented as a function of temperature and equilibrium seemed to be reached at higher temperatures at first sight, but analysis showed that this was not true.

We believe that this is mainly caused by the fact that methanol synthesis is a multiple reaction system. To gain a better understanding of this, we made several model simulations for an isothermal methanol synthesis plug flow reactor based on the kinetic model of Graaf et al.[62,63] Modeling details are given in ref 64. Figure 4 shows a typical simulation example where experimental data from Nitta et al.[65] are compared with model calculations.

The experimental data of Nitta et al.[65] obtained at lower temperatures were used to define catalyst activity correction factors (multiplication factors for the kinetic rate expressions). Figure 4 shows that a significant overshoot of the methanol equilibrium yield can take place, caused by the fact that under
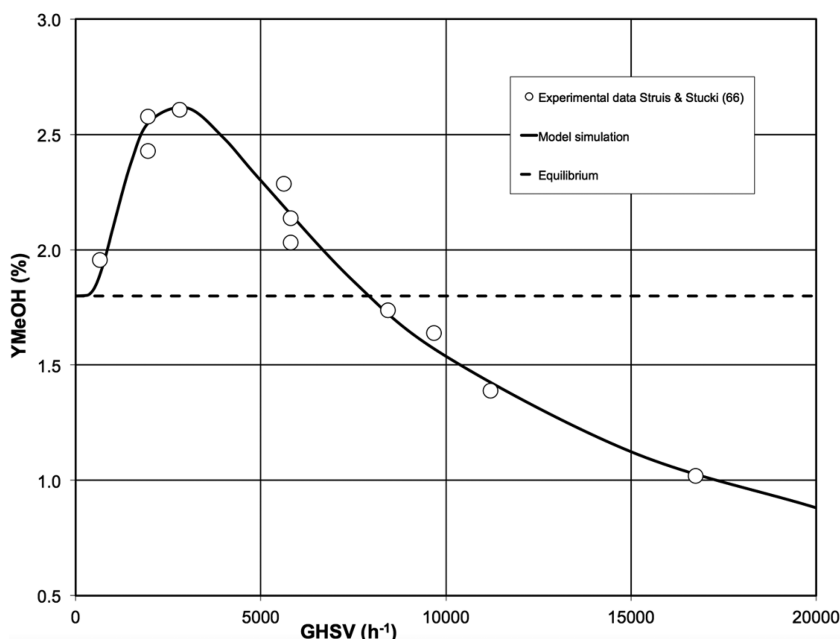
Figure 5. Experimental methanol yields from Struis and Stucki[66] and model simulations including optimization of $Kp_1°$ and ACT for all experiments. T = 473.15 K; p = 4.3 bar; Feed: y_{CO2} = 0.25; y_{H2} = 0.75; AAD = 2.5%.

the investigated operating conditions reaction 3 (methanol from CO_2/H_2) approaches equilibrium faster than the (reverse) water–gas shift reaction and the methanol decomposition to CO/H_2. The equilibrium of reaction 3 alone lies at a higher methanol production level explaining the overshoot behavior. All reactions become faster at higher temperatures (>540 K), causing the reaction system to move to the equilibrium curve. In this specific case the experimental result at 553 K may therefore be regarded as a reliable equilibrium point, contrary to the experimental results at 513 and 533 K.

Equilibrium overshoot behavior was also reported by Struis and Stucki,[66] who studied methanol synthesis kinetics and derived kinetic parameters based on the kinetic model of Graaf et al.[62,63] Struis and Stucki examined the effect of the gas flow rate and found that equilibrium overshoot occurs at intermediate flow rates. Figure 5 shows their experimental results in combination with our model simulations where the catalyst activity correction value and the $Kp_1°$ value were optimized from the experimental data. The model fit is very good (AAD = 2.5%), allowing for an accurate estimation of the $Kp_1°$ value.

In order to collect reliable equilibrium data we used these kind of model simulations to check whether equilibrium was sufficiently reached and to calculate the $Kp°$ values corresponding with the experimental results. Conversion data at lower temperatures or higher flow rates were used to define catalyst activity corrections for the kinetic model taken from Graaf et al.[62] The kinetic parameters of Graaf et al.[63] and Struis and Stucki[66] were used to check whether the results were consistent, i.e. not significantly dependent on the choice of the kinetic parameters.

In some cases literature data contained information for both methanol and water formation. From these sources (already mentioned in Tables 3 and 4) both $Kp_1°$ and $Kp_2°$ values can be obtained, provided that the experimental accuracy and numerical sensitivity are sufficient. In several literature sources only methanol formation results are presented. When $Kp_2°$ values could not be derived from the experimental data, we used the optimized $Kp_2°$ relationship as presented in the previous section

Table 5. Experimental Equilibrium Data for the Methanol from CO/H_2 Reaction: Literature Overview

source	$Kp_1°/Kp_1°$ and $Kp_2°$	T (K)	p (bar)
An et al.[32]	$Kp_1°$ and $Kp_2°$	533−553	40
Bill[67]	$Kp_1°$	510−575	20
Chen and Yuan[34]	$Kp_1°$ and $Kp_2°$	473−500	10
Graaf et al.[1,2]	$Kp_1°$ and $Kp_2°$	472−539	10−73
Hilmen et al.[68]	$Kp_1°$ (CO/H_2 feed)	560−593	45
Jingfa et al.[39]	$Kp_1°$ and $Kp_2°$	513	20
Kuznetsov et al.[25]	$Kp_1°$ and (partly) $Kp_2°$	523, 575	1.013
Liu et al.[26,a]	$Kp_1°$	493−525	40−66
Nitta et al.[65]	$Kp_1°$	553	9
Omata et al.[69]	$Kp_1°$	513	20
Sakurai et al.[49−51]	$Kp_1°$ and $Kp_2°$	523−623	8, 50.7
Struis and Stucki[66]	$Kp_1°$	473	4.3
Sun et al.[70]	$Kp_1°$	533−553	20
van Bennekom et al.[71,72]	$Kp_1°$	493−543	80−200
Yin[73]	$Kp_1°$	533−553	30−46
Zhang et al.[74]	$Kp_1°$	533	20

[a]See explanation in section 3.1.

in the simulation model. Table 5 gives an overview of the literature sources that we have used for our $Kp_1°$ analysis.

Several older literature results (around 1930) were analyzed as well, but here we concluded that the scattering of these experimental data is too large to derive accurate $Kp_1°$ values from these sources. A similar conclusion was reported by Graaf et al.[1] and Kuznetsov et al.[25]

For the results of van Bennekom et al.[71,72] and Liu et al.,[26] we concluded that the experimental accuracies are not sufficient to retrieve reliable $Kp_1°$ and $Kp_2°$ values. $Kp_1°$ values, however, could be determined with reasonable accuracy for those experiments where the average deviation of the material balances (C, H, and O) did not exceed 5%. In the case of van Bennekom's results the $Kp_1°$ values were determined for each experiment as the average value corresponding with the experimental C and H conversion data. In the case of Liu's
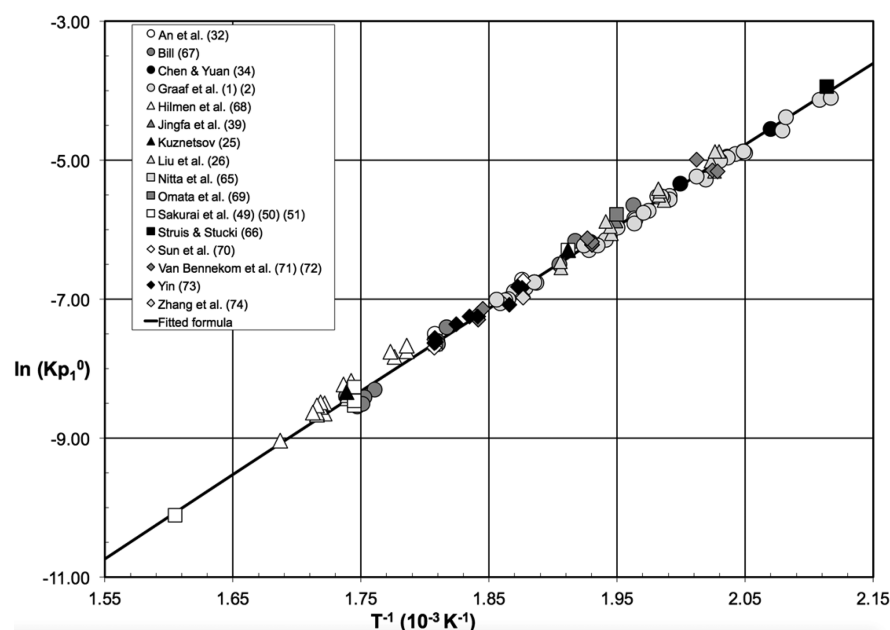
Figure 6. Experimental $Kp_1{}^\circ$ values and the optimized $Kp_1{}^\circ$ relationship as a function of temperature.
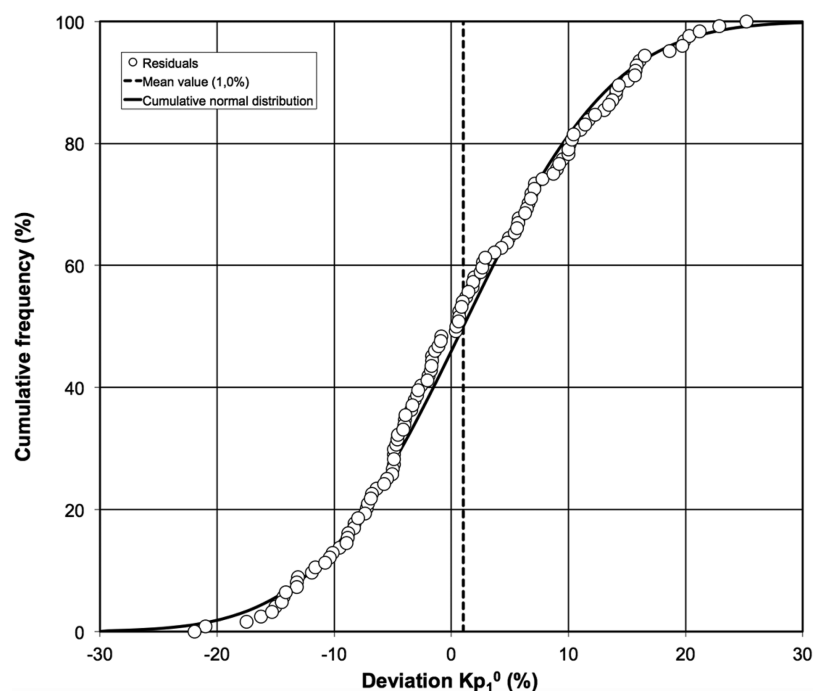

Figure 7. Cumulative distribution curve of the $Kp_1{}^\circ$ residuals.

results, the exit mole fraction of H_2O was calculated with the use of eq 7 and subsequently the exit mole fraction of CH_3OH was calculated from the total (molar) material balance over the reactor. The reactor exit mole fractions of the dry gas components (CO, CO_2, H_2, CH_4, and N_2) were calculated from the N_2 material balance (N_2 being an inert component). Following this approach 14 fairly accurate $Kp_1{}^\circ$ values (from a total number of 20 experiments) could be derived from Liu's results.

In Figure 6 the results are presented in combination with the optimized $Kp_1{}^\circ$ relationship. The $\Delta G^\circ(T_{ref})$ value for CO as determined in the previous section was used in these calculations. Here $\Delta G_{CH3OH}{}^\circ(T_{ref})$ was determined by minimizing

the SSR value, yielding -161.751 ± 0.065 kJ/mol (99% confidence level). The literature value[8] equals -162.298 kJ/mol (deviation = 0.3%).

The confidence intervals (± 0.065 kJ/mol) show that the optimized $\Delta G_{CH3OH}{}^\circ(T_{ref})$ value is of high accuracy. However, also in this case the effects of systematic uncertainties have to be taken into account as explained in section 3.1. Furthermore, the uncertainty of the estimated $\Delta G_{CO}{}^\circ(T_{ref})$ value should be added as well. We estimate that these effects add up to an uncertainty of the estimated $\Delta G_{CH3OH}{}^\circ(T_{ref})$ value of ± 0.2 kJ/mol ($\approx 0.1\%$).

The resulting AAD of the $Kp_1{}^\circ$ values equals 8.2% based on 125 experimental data points taken from 20 literature sources. Also in this case we found that optimizing both $\Delta G_{CH3OH}{}^\circ(T_{ref})$
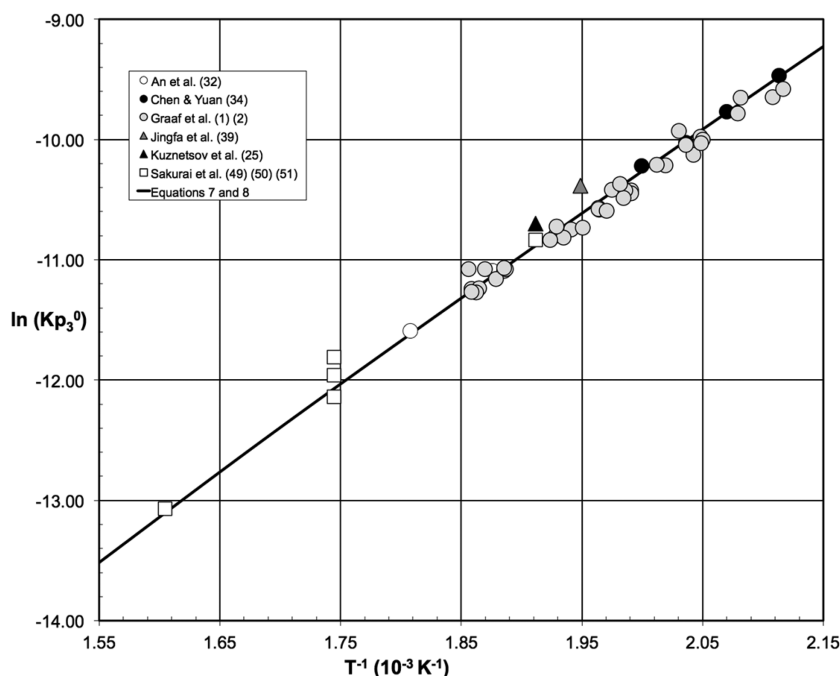
Figure 8. Experimental $Kp_3°$ values and the $Kp_3°$ relationship based on eqs 7 and 8 as a function of temperature.

and $\Delta H_{CH3OH}°(T_{ref})$ does not result in a significant improvement. Figure 7 shows that the residuals sufficiently follow a normal distribution, although the mean value lies slightly above 0 (1.0%). This small deviation is primarily caused by the larger level of experimental scattering at higher temperatures.

For the methanol synthesis data the deviations from ideal-gas behavior are larger as compared to the water−gas shift results. Here, $Kp_1°/Kp_1$ values roughly equal 0.9 on an average basis and maximum deviations are calculated for the high-pressure results of van Bennekom et al.[71,72] ($Kp_1°/Kp_1$: 0.11−0.84). Without the H_2-specific α-function as described by Graboski and Daubert[6] the AAD of the $Kp_1°$ fit turns out to be higher (9%), supporting the application of the H_2-specific α-function.

The optimized $Kp_1°$ relationship is defined as

$$\ln Kp_1°(T) = \frac{1}{RT}[a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4 + a_6 T^5 + a_7 T \ln T] \tag{8}$$

$a_1 = 7.44140 \times 10^{+4}$; $a_2 = 1.89260 \times 10^{+2}$; $a_3 = 3.2443 \times 10^{-2}$; $a_4 = 7.0432 \times 10^{-6}$; $a_5 = -5.6053 \times 10^{-9}$; $a_6 = 1.0344 \times 10^{-12}$; $a_7 = -6.4364 \times 10^{+1}$.

Here a_2 is the only parameter that results from fitting the experimental data. The other parameters were calculated from the work of Haynes et al.[8] The optimized $Kp_1°$ relationship is at least valid in the experimental temperature range (472−623 K).

Equation 8 yields the following results at 200, 250, and 300 °C: 1.77×10^{-2}, 1.66×10^{-3}, and 2.28×10^{-4} bar^{-2}. Compared with the results presented in Table 2 these $Kp_1°$ results are slightly higher than the values from Graaf et al.[1] and Klier et al.[14] and approximately 25% lower as compared to the work of Haynes et al.[8]

3.3. Methanol from CO_2/H_2 Reaction. Although it is not necessary to repeat the previous analysis for this reaction (because $Kp_3°$ is already defined by $Kp_3° = Kp_1°Kp_2°$), a comparison between experimental $Kp_3°$ values and calculations

based on eqs 7 and 8 provides an additional check regarding the consistency of the results. For this consistency check we only use experimental data from which both $Kp_1°$ and $Kp_2°$ values were derived (see Table 5). The comparison is presented in Figure 8 and shows that the experimental $Kp_3°$ values correspond well with $Kp_3°$ calculated from eqs 7 and 8. The comparison is based on 51 experimental data points taken from 9 literature sources and the AAD equals 7.6%.

4. CONCLUSIONS

Equilibrium constants for the methanol from CO/H_2 reaction calculated from literature relationships show a considerable variation of ±40% (difference between the highest and lowest values). To a lesser extent (±10%) this also holds for the water−gas shift reaction. Based on a sensitivity analysis we conclude that very small differences in the underlying basic thermochemical data, especially the Gibbs energy of formation for CH_3OH and CO, can explain these differences.

From an extensive literature survey we have collected and calculated experimental equilibrium constants for the reactions involved in methanol synthesis. Corrections for nonideal gas behavior were made with the Soave−Redlich−Kwong equation of state[3] as adapted by Mathias,[5] optimized for the methanol synthesis system by van Bennekom et al.[4] and extended with the SRK-adaptation for H_2 as described by Graboski and Daubert.[6] The resulting (pseudo)experimental ideal-gas equilibrium constants can be described very well with relationships derived from literature basic thermochemical data, where only the Gibbs energy of formation values for CH_3OH and CO were fitted to the experimental results, because these basic data obtain the greatest uncertainty. As expected from the sensitivity analysis, very small changes in these parameters were sufficient to obtain a good fit.

The resulting equilibrium relationship for the water−gas shift reaction is based on 351 experimental data points collected from 42 literature sources. The average deviation (AAD) equals

5.6% and the relationship is at least valid in the experimental temperature range 472−1273 K.

The resulting equilibrium relationship for the methanol from CO/H_2 reaction is based on 125 experimental data points in the temperature range 472−623 K which were derived from 20 literature sources. The average deviation (AAD) equals 8.2%.

Since these equilibrium relationships are based on an extensive set of experimental data points derived from a large number of literature sources, it is fair to conclude that these relationships may be regarded as highly accurate. This is further supported by the fact that differences between experimental and calculated equilibrium constants are (almost) normally distributed.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.6b00815.

Overview of the collected Kp_1° and Kp_2° values. Experimental equilibrium composition data as measured by Graaf et al.[1,2] Recalculated equilibrium composition data of Liu et al.[26] Details of reactor simulations for methanol synthesis experimental results. Thermochemical basic data and derivation of the Kp° relationship (PDF)

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Notes

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■ NOMENCLATURE

Abbreviations

AAD = average absolute deviation (%)
SRK-EoS = Soave−Redlich−Kwong equation of state
SSR = Sum of squares of relative residuals:
$$\left(\text{SSR} = \frac{1}{N} \sum_{i=1}^{N} \left(\frac{Kp_{\text{exp}}^\circ - Kp_{\text{calc}}^\circ}{Kp_{\text{exp}}^\circ} \right)^2 \right)$$

List of Symbols

$a_1 - a_6$ = constants in Kp° equation
ACT = activity correction (multiplication) factor for the kinetic rate equations
$b_1 - b_6$ = constants in Kp° equation
GHSV = gas hourly space velocity, $m_{\text{gas}}^3 \, m_{\text{cat}}^{-3} \, h^{-1}$
F = molar flow rate, mol s^{-1}
Kp = equilibrium constant based on partial pressures
N = number of experiments
p = total pressure bar
R = gas constant, J mol^{-1} K^{-1}
T = temperature, K or °C
ν = molar volume, m^3 mol^{-1}

W = amount of catalyst, g
y = mole fraction
YMeOH = yield of CH_3OH = $100 \times F_{CH_3OH,\text{out}}/(F_{CO,\text{in}} + F_{CO_2,\text{in}})$
Δc_p = isobaric heat capacity change, J mol^{-1} K^{-1}
ΔH = enthalpy change (of formation), J mol^{-1}
ΔG = Gibbs energy change (of formation), J mol^{-1}

Superscripts

0 = indicates standard pressure (1 bar) and ideal gas conditions

Subscripts

calc = calculated
cat = catalyst
exp = experimental
f = of formation
gas = gas
i, j = indicates component or experiment number
in = reactor inlet
out = reactor outlet
ref = reference
1 = methanol from CO/H_2 reaction
2 = water−gas shift reaction
3 = methanol from CO_2/H_2 reaction

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