Thermodynamic Equilibrium Constants for the Methanol-Dimethyl Ether-Water System

Bang T. Diep*

The Commonwealth Industrial Gases Ltd., Technical Services—Hytec, Wetherill Park, New South Wales 2164, Australia

Mark S. Wainwright

School of Chemical Engineering and Industrial Chemistry, The University of New South Wales, Kensington, New South Wales 2033, Australia

Thermodynamic equilibrium constants of the methanol-dimethyl ether-water system were determined experimentally at temperatures from 498 to 623 K. Equilibrium was established in the dehydration of methanol over a commercial γ-alumina catalyst in a flow reactor maintained at a constant pressure of 200 kPa. The experimental equilibrium conversions obtained in the present investigation were compared with those of the published literature and with estimates from thermochemical data. By use of published thermochemical data together with the experimental data, the enthalpy of formation, $\Delta H_{f,298}$, and free energy of formation, $\Delta G_{f,298}$, of dimethyl ether were calculated to be -180.22 and -109.66 kJ mol^{-1}, respectively.

Introduction

Dimethyl ether (DME) has recently become a popular propellant in the aerosol industry owing to its characteristic properties (*1*) and the belief that fluorocarbons harm the ozone layer. DME also plays an important role in the Mobil methanol to gasoline (MTG) process in which methanol is first catalytically dehydrated to form an equilibrium mixture of DME, water, and methanol, followed by conversion of the equilibrium mixture to hydrocarbons in reactors containing ZSM zeolite catalysts (*2*). This process is currently used to produce synthetic gasoline in New Zealand (*3*).

Methanol is dehydrated on acidic catalysts (*4*) according to

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O \tag{1}$$

This reaction is exothermic and reversible and yields are therefore subject to thermodynamic limitation. Although there have been many kinetic and mechanistic investigations of the reaction over different types of catalysts as reviewed by Chang (*4*), there have been very few studies to determine thermodynamic equilibrium data for this reaction. McKee and Burke (*5*) studied both the forward and reverse reactions over a fixed bed of alumina catalyst at 350 °C. The equilibrium constants calculated for reaction 1 were 3.13 for the forward reaction and 3.25 for the reverse reaction leading to a mean value of 3.19. In the only other reported study (*6*) values of 15.4 and 48.5 were found at 503 and 403 K, respectively. Given (*7*) has used these three values to derive equations for the temperature dependence of the equilibrium constant and free energy for reaction 1.

This paper reports an experimental investigation of the equilibrium of methanol dehydration in the temperature range encountered in industrial reactors. Equilibrium conversions and thermodynamic properties calculated from those data are presented.

Experimental Section

The equilibrium conversions were measured by passing pure methanol vapour over a fixed bed of γ-Al_2O_3 catalyst at flow rates which were sufficiently slow such that there was no measurable increase in conversion with decreased flow rate. The apparatus shown in Figure 1 consisted of packed bed catalytic reactor with an on-line gas chromatograph. The 25 mm o.d. stainless steel reactor and 6 mm o.d. preheater/vaporizer were immersed in a vigorously stirred molten salt bath. The temperature of the catalyst bed was controlled to ±0.5 K by a PI electronic controller and was measured with a 1.5 mm o.d. stainless steel sheathed chromel-alumel thermocouple. The pressure in the reactor was maintained at 200 ± 5 kPa abs by means of a heated needle valve at the exit of the reactor.

Liquid methanol was metered to the preheater/vaporizer by means of an Eldex Model E-120-5-2 HPLC pump. The flow rate of methanol was measured by timing the discharge from a buret used as the methanol reservoir. The preheated methanol vapor passed to the bed of γ-Al_2O_3 catalyst. The catalyst which was obtained from the Norton Co. had a BET surface area of 195 m^2 g^{-1}, a pore volume of 0.59 cm^3 g^{-1}, and a mean pore radius of 61 nm. It was in the form of 1.6 mm diameter × 6 mm extrudates and had a packed density of 0.65 g cm^{-3}. Because of its high surface area and acidity the catalyst was very active for methanol dehydration.

Although the reaction is only mildly exothermic and the vigorously stirred salt bath provided high cooling rates, it was essential to ensure that the equilibrium conversions were measured under isothermal conditions. This was achieved by using a large, undiluted catalyst bed (10 g and 7.65 cm deep) and sufficiently low methanol flow rates (LHSV's are given in Table I) so that equilibrium conversions were approached near the reactor inlet. In this way most of the heat generation and removal occurred near the bed entrance. Measurements with the thermocouple located at various axial positions over the last 3 cm of bed revealed that the reaction was maintained isothermal to ±0.5 K in that region.

The effluent from the reactor passed through an electrically heated (ca. 150 °C) 3.2 mm stainless steel tube to the needle valve and then to a Valco 6-port gas sampling valve which was maintained at 150 °C in an air oven. The sample valve was used to inject 1 cm^3 of product stream into a Gow Mac Series 550 gas chromatograph equipped with a thermal conductivity detector. Peak areas were measured with a Spectra Physics System I computing integrator. The chromatographic separation of water, methanol, and DME was effected on a 1 m × 3.2 mm o.d. stainless steel column packed with 50 wt % Porapak P and 50 wt % Carbosphere. The column was operated isothermally at 150 °C with a helium carrier gas flow of 50 cm^3 min^{-1}. The conversion of methanol was calculated from the areas of the peaks for methanol and DME by using their relative responses. The relative molar response of DME was determined by injecting pure methanol vapor and pure DME with the injection valve (1 cm^3 loop, 150 °C, and 101 kPa abs). The response of DME relative to methanol was calculated from the ratio of the peak areas. The relative response of water compared to methanol was determined by using gravimetric mix-

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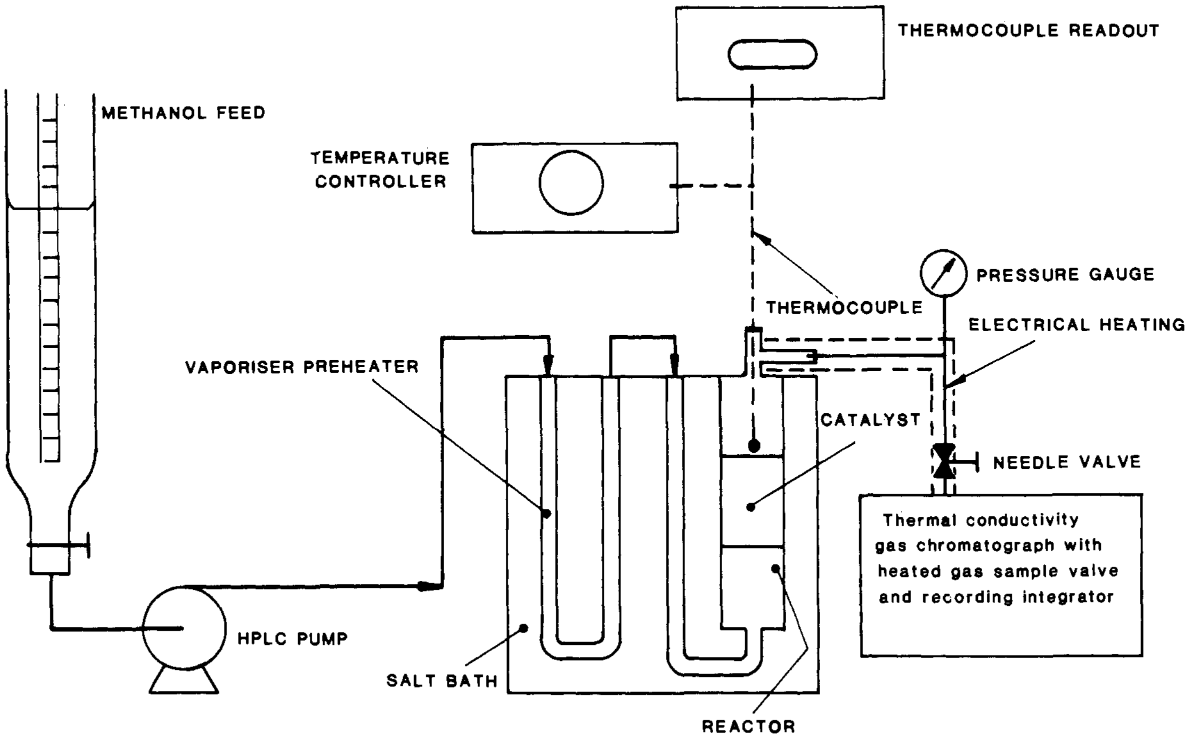

Figure 1. Schematic diagram of experimental apparatus used to measure catalytic dehydration of methanol.

tures of water in methanol. The linearity of the detector was established by injecting liquid samples of pure methanol.

The methanol used in this work was of ChromAr HPLC grade from Mallinckrodt Co. and had a purity of 99.9% and a water content of less than 0.02%. The DME was obtained from Matheson Gas Products and had a minimum purity of 99.5%.

Calculations

The molar responses for DME and water relative to methanol were found from

$$\mathrm{RMRE} = A^{c}_{DME}/A^{c}_{MeOH} = 1.305$$

$$\mathrm{RMRW} = A^{c}_{H_2O}/A^{c}_{MeOH} = 0.636$$

The number of moles of water and DME produced by reaction 1 are equal and so the conversion of methanol can be calculated from

$$X = \frac{n_{H_2O} + n_{DME}}{n_{H_2O} + n_{DME} + n_{MeOH}} = \frac{2n_{DME}}{2n_{DME} + n_{MeOH}} = \frac{2n_{H_2O}}{2n_{H_2O} + n_{MeOH}} \quad (2)$$

Since the response of DME is more than two times that of water, the conversion was calculated by using

$$X = \frac{1}{1 + \dfrac{n_{MeOH}}{2n_{DME}}} = \frac{1}{1 + \dfrac{\mathrm{RMRE}}{2}\dfrac{A_{MeOH}}{A_{DME}}} \quad (3)$$

The following equation was used as a cross check on the results obtained

$$X = \frac{1}{1 + \dfrac{n_{MeOH}}{2n_{H_2O}}} = \frac{1}{1 + \dfrac{\mathrm{RMRW}}{2}\dfrac{A_{MeOH}}{A_{H_2O}}} \quad (4)$$

The equilibrium constant, K_p, for reaction 1 was calculated as

$$K_p = \frac{X_e^2}{4(1 - X_e)^2} \quad (5)$$

where X_e is the equilibrium conversion of methanol. The free energy of reaction was then calculated by using

$$\Delta G_R = -RT \ln K_p \quad (6)$$

Results and Discussion

The experimental equilibrium conversions obtained in the temperature range 498–623 K are summarized in Table I. The values of X_e at all temperatures have a relative standard deviation of less than 0.7%, indicating that equilibrium has been achieved and the data are of high accuracy.

The equilibrium constant, K_p, and the free energy, ΔG_R, for the reaction calculated at each temperature by using eq 5 and 6 are presented in Table II.

If the heat of reaction is assumed to be constant over the temperature range, the temperature dependence of the equilibrium constant, K_p, can be found by using the integrated form of the van't Hoff equation:

$$\ln K_p = \frac{\Delta H_R}{RT} + C \quad (7)$$

When the K_p values in Table II were fitted to this model the following equation was obtained:

$$\ln K_p = \frac{2051.7}{T} - 1.5587 \quad (8)$$

and

$$\Delta H_R\ (498\text{–}623\ \mathrm{K}) = -17.058\ \mathrm{kJ\ mol^{-1}} \quad (9)$$

The correlation coefficient for eq 8 was 0.998.

If, however, the variation of the heat of reaction with temperature is taken into account, a more general temperature dependence of K_p is given by

$$\frac{d \ln K_p}{dT} = \frac{\Delta H_0}{RT^2} + \frac{1}{RT^2}\int_0^T \Delta C_p\, dT \quad (10)$$

The heat capacity data for DME, methanol, and water from Stull et al. (8) were expressed in the form $C_p = a + bT + cT^2$ and were substituted into the integrated form of eq 10 to yield the

Table I. Experimental Equilibrium Conversions for the Dehydration of Methanol to Dimethyl Ether over γ-Al_2O_3 Catalyst at Temperatures from 498 to 623 K at 200 kPa

T, K	498	523	548	573	598	623
LHSV,[a] cm^3 g catalyst^{-1} h^{-1}	<0.04	0.08–0.24	1.03–3.5	1.49–6.08	2.03–12.3	3.12–15.1
X_e	0.885	0.872	0.857	0.846	0.844	0.825
	0.876	0.871	0.858	0.848	0.839	0.827
	0.874	0.862	0.852	0.842	0.836	0.828
		0.864	0.856	0.846	0.833	0.830
		0.876		0.841	0.831	0.823
		0.862		0.841	0.832	0.820
				0.842	0.839	0.823
				0.847	0.841	0.828
						0.829
						0.836
std dev	0.006	0.006	0.003	0.003	0.005	0.004
RSD,[b] %	0.667	0.685	0.307	0.344	0.555	0.542
X_e	0.878	0.868	0.856	0.844	0.837	0.827

[a] Liquid hourly space velocity defined as cm^3 of liquid methanol per gram of catalyst per hour. [b] Relative standard deviation defined as the ratio between standard deviation and the average equilibrium conversions.

Table II. Equilibrium Constants and Free Energies for Methanol Dehydration to Dimethyl Ether

T, K	498	523	548	573	598	623
K_p	12.948	10.810	8.834	7.318	6.592	5.713
$\Delta G°_R$, kJ mol^{-1}	-10.604	-10.351	-9.926	-9.482	-9.376	-9.027

more correct expression for the temperature dependence of K_p:

$$\ln K_p = 2835.2/T + 1.675 \ln T - 2.39 \times 10^{-4}T - 0.21 \times 10^{-6}T^2 - 13.360 \qquad (11)$$

Several relationships describing the temperature dependence of the equilibrium constant for the dehydration of methanol have appeared in the literature. Given (*7*) has used the two equilibrium constants measured by Gajendragad et al. (*6*) and the single value calculated by McKee and Burke (*5*) to derive the relationship:

$$\ln K_p = 7300/RT - 4.8 \qquad (12)$$

Hayashi and Moffat (*9*) used thermodynamic properties at 25 °C (*10*) and heat capacity data at higher temperatures (*11–13*) to develop the following expression:

$$\ln K_p = 3440/T - 1.67 \ln T + 2.39 \times 10^{-4}T + 0.055 \times 10^{-6}T^2 + 5.496 \qquad (13)$$

The equilibrium conversion values calculated by using K_p values obtained from eq 8, 11, 12, and 13 are compared with the experimental values obtained in this study in Table III. The results in Table III show that eq 8 and 11 accurately represent the experimental equilibrium data. Furthermore, the conversions obtained in this study are higher than those calculated by using K_p values derived from relationships published (*7*, *9*).

Although the free energies and enthalpies of formation of methanol and water have been extensively reported in the literature, the values for dimethyl ether have been reported in only a few investigations. For this reason the equilibrium data for the methanol–dimethyl ether–water system obtained in this investigation have, along with published values of $\Delta G_{f,298}$ and $\Delta H_{f,298}$ for methanol and water, been used to calculate the corresponding values for dimethyl ether.

From eq 8 and 6 the free energy of reaction at 298 K was found to be $\Delta G_{R,298} = -13.20$ kJ mol^{-1}. The standard free energy of formation of dimethyl ether was then calculated by using

$$\Delta G_{f,298}(\text{DME}) = \Delta G_{r,298} + 2\Delta G_{f,298}(\text{MeOH}) - \Delta G_{f,298}(\text{H}_2\text{O}) \qquad (14)$$

Table III. Comparison of Equilibrium Conversions Obtained in This Study with Values Calculated by Using Published Relationships

	equilibrium conversion				
	this study			ref 7,	ref 9,
temp, K	expt	eq 8	eq 11	eq 15	eq 16
498	0.878	0.878	0.878	0.879	0.855
523	0.868	0.867	0.867	0.859	0.828
548	0.856	0.856	0.856	0.838	0.800
573	0.844	0.846	0.846	0.817	0.771
598	0.837	0.836	0.836	0.797	0.742
623	0.828	0.826	0.827	0.776	0.712

Table IV. Comparison of Free Energies and Enthalpies of Formation of DME Calculated in This Study with Published Values

	ref			
	8	*15*	*16*	this work
$\Delta G_f°_{298}$(DME), kJ mol^{-1}	-112.94	-109.04	-112.68	-109.61
$\Delta H_f°_{298}$(DME), kJ mol^{-1}	-184.07	-180.18	-184.07	-180.19[a]
				-182.52[b]

[a] Calculated from eq *15*. [b] Calculated from eq *16*.

The values $\Delta G_{f,298}$ (MeOH) = -162.51 kJ mol^{-1} and $\Delta G_{f,298}$ (H_2O) = -228.61 kJ mol^{-1} obtained from Stull et al. (*8*) were substituted into eq 9 to give $\Delta G_{f,298}$(DME) = -109.61 kJ mol^{-1}. This is in close agreement with the published values presented for comparison in Table IV.

If the value of the heat of reaction at 298 K is calculated from the temperature dependence expression for the heat of reaction it is possible to estimate the heat of formation of dimethyl ether and compare the value with literature values.

When $\Delta H_0 = -23\,573$ J mol^{-1} from eq 11 and the ΔC_p values are used, the expression for the heat of reaction as a function of temperature is given by

$$\Delta H_{R,T} = -23573 + 13.924T - 1.988 \times 10^{-3}T^2 - 3.487 \times 10^{-6}T^3 \qquad (15)$$

The value of $\Delta H_{R,298}$ calculated from eq 15 is -19.69 kJ mol^{-1}.

Another method of calculating $\Delta H_{R,298}$ uses the free energy function $(G°_T - H°_{298})/T$ in the relation

$$(\Delta H_{R,298})/T = -RT \ln K_p + T\Delta[(G°_T - H°_{298})/T] \qquad (16)$$

When the $(G°_T - H°_{298})/T$ values for DME, water, and methanol tabulated in Stull et al. (*8*) and the experimental K_p data were substituted into eq 16, the value of $\Delta H_{R,298}$ was found to be −22.02 kJ mol^{-1}.

The enthalpy of formation for DME in its standard state at 298 K was calculated from

$$\Delta H_{R,298}(\mathrm{DME}) = \Delta H_{R,298} + 2\Delta H_{f,298}(\mathrm{MeOH}) - \Delta H_{f,298}(\mathrm{H_2O}) \qquad (17)$$

where the values $\Delta H_{f,298}(\mathrm{MeOH}) = -201.17$ kJ mol^{-1} and $\Delta H_{f,298}(\mathrm{H_2O}) = -241.84$ kJ mol^{-1} were obtained from Stull et al. (*8*). The values of $\Delta H_{R,298}$ obtained from eq 15 and 16 yield estimates of $\Delta H_{f,298}(\mathrm{DME})$ of −180.19 and −182.52 kJ mol^{-1}, respectively. These values are in close agreement with the value of −184.07 kJ mol^{-1} calculated by Pilcher et al. (*14*) using the standard heat of combustion which they measured using flame calorimetry.

The values of $\Delta H_{f,298}(\mathrm{DME})$ are compared with data from standard thermodynamic sources in Table IV. The close agreement between the values is to be expected since the heat of reaction is low compared to the value for $2\Delta H_{f,298}(\mathrm{MeOH}) - \Delta H_{f,298}(\mathrm{H_2O})$.

Conclusions

The equilibrium constants for the dehydration of methanol to produce dimethyl ether have been determined over the temperature range encountered in industrial reactors. The temperature dependence relationship for the equilibrium constant will be found useful in kinetic modelling of the catalytic dehydration reaction and for reactor and plant design applications.

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Glossary

A	peak area count of sample
A^c	normalized peak area count of calibration standard
C_p	heat capacity, J mol^{-1} K^{-1}
$(G^\circ_T - H^\circ_{298})/T$	free energy function, kJ mol^{-1}
K_p	equilibrium constant for reaction 1
n	number of moles
R	gas constant, 8.31432 J mol^{-1} K^{-1}
RMRE	molar response of DME relative to methanol
RMRW	molar response of water relative to methanol
T	temperature, K
X	conversion of methanol for reaction 1
X_e	equilibrium conversion of methanol for reaction 1
ΔG_R	free energy of reaction, kJ mol^{-1}
$\Delta G_{f,T}$	free energy of formation at temperature T, kJ mol^{-1}
ΔH_R	average heat of reaction, kJ mol^{-1}
$\Delta H_{R,T}$	heat of reaction at temperature T, kJ mol^{-1}
$\Delta H_{f,T}$	enthalpy of formation at temperature T, kJ mol^{-1}
ΔH_0	constant in eq 10, J mol^{-1}

Subscripts

DME	dimethyl ether (CH_3OCH_3)
H_2O	water
MeOH	methanol (CH_3OH)

Registry No. CH_3OH, 67-56-1; CH_3OCH_3, 115-10-6; Al_2O_3, 1344-28-1.

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