

# EQUILIBRIUM THERMODYNAMIC ANALYSIS OF LIQUID-PHASE ETHYL TERT-BUTYL ETHER (ETBE) SYNTHESIS

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Keywords: Reaction equilibrium, equilibrium constant, ethyl tert-butyl ether (ETBE)

## INTRODUCTION

There are two forces driving the increasing usage of oxygenates (alcohols and ethers) in gasoline. First, lead compounds, long used for octane improvement in gasoline, have now been phased out by the EPA. The second reason is the Clean Air Act Amendments (CAAA) bill of 1990, which has two programs involving the use of oxygenates: 1) *Oxygenated Gasoline Program* that requires the use of gasoline containing a minimum of 2.7 wt. % oxygen in 44 cities during the four winter months as a strategy to reduce CO emissions; and 2) *Reformulated Gasoline Program* for the nine worst ozone non-attainment areas, beginning Jan 1, 1995, that will require gasoline reformulation to lower toxic and ozone generating pollutants (VOC emissions), but containing at least 2 wt. % oxygen.

The main competing oxygenates at present, are ethanol and methyl tertiary butyl ether (MTBE, or 2-methoxy 2-methyl propane). MTBE is now the second largest volume organic chemical, only behind ethylene, produced in the U.S. (Reisch, 1994). This is remarkable since its commercial production began barely two decades ago. Although MTBE is currently the industry standard, it has been proposed (Lucht, 1993) that ethanol and other renewable additives make up to 30% of the oxygenate market. This proposal is aimed primarily at reducing dependence on the finite fossil fuel resources. Furthermore, it would alleviate concerns about the buildup of carbon dioxide in the atmosphere, the major "greenhouse" gas. As a result, ethyl tertiary butyl ether (ETBE, or 2-ethoxy 2-methyl propane), derived from renewable ethanol and isobutylene, has emerged as a promising new oxygenate. ETBE also has a somewhat lower blending Reid vapor pressure as well as a higher octane number than MTBE.

The commercial production of ETBE, by the equilibrium limited exothermic reaction of ethanol and isobutylene over an acid ion exchange catalyst, has recently begun (Oxy-Fuel News, 1992). In spite of its anticipated industrial importance, reliable information on the thermodynamics of the liquid-phase formation of ETBE is virtually non-existent in the open literature. Iborra et al. (1989) proposed an expression for the equilibrium constant for the ETBE reaction in the gas phase. However, since commercially the reaction occurs in the liquid phase, it is the thermodynamics of the liquid-phase reaction that is of the principal interest. Vila et al. (1993) have recently reported an expression for the liquid-phase ETBE equilibrium constant; however, the constants of integration in it were used as fitted parameters. Consequently, a careful thermodynamic analysis is warranted, and is provided here along with experimental data over a range of temperatures of practical interest. Alternate thermodynamic pathways are considered by Jensen and Datta (1994).

## THERMODYNAMIC EQUILIBRIUM CONSTANT

The equilibrium constant for the non-ideal liquid-phase reaction,  $\sum_{j=1}^n \nu_j A_j = 0$ , among the species  $A_j$  is

$$K(\ell) \equiv \prod_{j=1}^n a_{j\ell}^{\nu_j} = \left( \prod_{j=1}^n \gamma_{j\ell}^{\nu_j} \right) \left( \prod_{j=1}^n x_{j\ell}^{\nu_j} \right) \equiv K_\gamma K_x \quad (1)$$

The second equality stems from the definition of activity,  $a_j \equiv \gamma_j x_j$ . Upon relating the activity coefficients,  $\gamma_j$ , to the mole fraction,  $x_j$ , through an appropriate relation, such as the UNIFAC correlation, the equilibrium composition may be determined for a given  $K(\ell)$ . The equilibrium constant, in turn, is related to the thermodynamic properties of the mixture through

$$K(\alpha) = \exp \left\{ -\frac{\Delta G_T^\circ(\alpha)}{RT} \right\} \quad (2)$$

for a reaction occurring in a phase  $\alpha$  at the reaction temperature  $T$ . The standard Gibbs energy change for the reaction

$$\Delta G_T^\circ(\alpha) = \sum_{j=1}^n \nu_j \Delta C_{fT}^\circ(\alpha) \quad (3)$$

where  $\Delta C_{fT}^\circ(\alpha)$  is the Gibbs energy of formation of species  $j$  in the phase  $\alpha$  at the reaction temperature,  $T$ . Alternatively, the standard Gibbs energy change for the reaction may be computed from the standard enthalpy and entropy change for the reaction at the temperature  $T$  by

$$\Delta G_T^\circ(\alpha) = \Delta H_T^\circ(\alpha) - T \Delta S_T^\circ(\alpha) \quad (4)$$

where the change in the standard enthalpy and entropy are determined by equations of the form of eq 3 for the reaction in the  $\alpha$  phase.

Normally the reported data on Gibbs energy and enthalpy of formation are, however, available only at the standard state (ideal gas;  $P^\circ = 1$  bar;  $T^\circ = 298.15$  K), rather than at the reaction conditions of interest (e.g., condensed phase;  $P \neq P^\circ, T \neq T^\circ$ ). While the effect of pressure is usually small,  $\Delta G_T^\circ(\alpha)$  for temperatures and phase other than the standard is obtained as follows. Using an integrated form of the van't Hoff equation the effect of temperature may be accounted for by

$$\frac{\Delta G_T^\circ(\alpha)}{RT} = \frac{\Delta G_{T^\circ}^\circ(\alpha)}{RT^\circ} - \frac{1}{R} \int_{T^\circ}^T \frac{\Delta H_T^\circ(\alpha)}{T^2} dT \quad (5)$$

where the enthalpy of reaction as a function of temperature may be obtained from the Kirchoff equation

$$\Delta H_T^\circ(\alpha) = \Delta H_{T^\circ}^\circ(\alpha) + \int_{T^\circ}^T \Delta C_p^\circ(\alpha) dT \quad (6)$$

where for the reaction

$$\Delta C_p^\circ(\alpha) \equiv \sum_{j=1}^n \nu_j \Delta C_{pj}^\circ(\alpha) \quad (7)$$

The molar heat capacities of species are generally expressed as a polynomial in temperature of the form (Reid et al., 1987)

$$C_{pj}^\circ(\alpha) = a_j(\alpha) + b_j(\alpha)T + c_j(\alpha)T^2 + d_j(\alpha)T^3 \quad (8)$$

Upon using eqs 7 and 8 and carrying out the integration in eq 6, there results

$$\Delta H_T^\circ(\alpha) = I_H(\alpha) + \Delta a(\alpha)T + \frac{\Delta b(\alpha)}{2}T^2 + \frac{\Delta c(\alpha)}{3}T^3 + \frac{\Delta d(\alpha)}{4}T^4 \quad (9)$$

where  $I_H(\alpha)$  is the constant of integration obtainable from Eq 9 by using  $T = T^\circ$  and

$$\begin{aligned} \Delta a(\alpha) &\equiv \sum_{j=1}^n \nu_j a_j(\alpha) ; \Delta b(\alpha) \equiv \sum_{j=1}^n \nu_j b_j(\alpha) \\ \Delta c(\alpha) &\equiv \sum_{j=1}^n \nu_j c_j(\alpha) ; \Delta d(\alpha) \equiv \sum_{j=1}^n \nu_j d_j(\alpha) \end{aligned} \quad (10)$$

The use of eq 9 in eq 5 results in

$$\frac{\Delta G_T^\circ(\alpha)}{RT} = -I_K(\alpha) + \frac{I_H(\alpha)}{RT} - \frac{\Delta a(\alpha)}{R} \ln T - \frac{\Delta b(\alpha)}{2R} T - \frac{\Delta c(\alpha)}{6R} T^2 - \frac{\Delta d(\alpha)}{12R} T^3 \quad (11)$$

where  $I_K(\alpha)$  is the constant of integration that can be obtained from Eq 9 by using  $T = T^\circ$ . Finally, using eq 11 in eq 2 gives

$$\ln K(\alpha) = I_K(\alpha) - \frac{I_H(\alpha)}{RT} + \frac{\Delta a(\alpha)}{R} \ln T + \frac{\Delta b(\alpha)}{2R} T + \frac{\Delta c(\alpha)}{6R} T^2 + \frac{\Delta d(\alpha)}{12R} T^3 \quad (12)$$

## EXPERIMENTAL RESULTS AND DISCUSSION

Experimental results for the thermodynamic equilibrium constant were obtained from the disassociation of ETBE (obtained from Aldrich Chemical, 99% purity) with Amberlyst 15 ion exchange resin as a catalyst, in a 6 cm. stainless steel reactor tube (diameter 1/4"). The catalyst (obtained from Sigma Chemical Co.) was prepared by first washing the resin with distilled water, followed by 0.1 M nitric acid and dried overnight

in a vacuum oven at 110 °C. After filling the stainless steel reactor tube with liquid ETBE, approximately 10 - 20 grains (particle size, 16 - 50 mesh) of Amberlyst 15 were added and the tube was sealed and placed in a temperature controlled water bath. The experiments were performed over the range of temperatures, 20 - 60 °C. The reactor system was allowed to equilibrate for at least 24 hours before sampling, and for substantially longer periods for temperatures under 35° C. At least three liquid samples were taken by a syringe through a septum and analyzed by a Perkin Elmer AutoSystem Gas Chromatograph with helium as the carrier gas (25 ml/min) using a PORAPAK R column (6'x1/8") at an oven temperature of 170 °C. The GC was calibrated for ETBE over a wide range of compositions for accurate analysis, and, consequently, the maximum error in the measurement of its mole fraction was estimated to be ±0.005. Activity coefficients were calculated making use of the UNIFAC method.

Thermochemical data given in Table 1 for the liquid-phase system was obtained from the TRC Thermodynamics Tables (1986). The coefficients for the third order polynomial in temperature, eq 8, were fitted to the experimental data for ethanol and isobutylene taken from Gallant (1968). However, the liquid-phase Gibbs energy of formation for isobutylene was not found in the literature and, therefore, was calculated making use of a form of the Clausius-Claperyon equation.

Table 1. Liquid Phase Thermochemical Data\* and Liquid Phase Heat Capacity Equation Coefficients

Component	Heat Capacity Coefficients of Equation 10				$\Delta G_{ff}^{\circ}$ kJ/mol	$\Delta H_{ff}^{\circ}$ kJ/mol
	a <sub>j</sub>	b <sub>j</sub>	c <sub>j</sub>	d <sub>j</sub>		
Isobutylene	35.44	0.802	-3.124E-3	5.045E-6	60.672 <sup>a</sup>	-37.7
Ethanol	29.01	0.2697	-5.658E-4	2.079E-6	-174.8 <sup>b</sup>	-277.51
ETBE	40.418	0.7532	-1.053E-3	1.8066E-6	-126.8	-357.5 <sup>c</sup>

\* TRC Thermodynamics Tables (1986)

<sup>a</sup> not given in literature, calculated by Clausius-Claperyon equation

<sup>b</sup> from CRC Handbook (1992)

<sup>c</sup> adjusted value

Initially, the literature value of the standard liquid-phase enthalpy of formation of ETBE was taken from the TRC Thermodynamics Tables (1986) as -351.5 kJ/mol, but was subsequently adjusted to -357.5 kJ/mol, or by about 1.7%. Figure 1 shows the liquid-phase thermodynamic equilibrium constant as a function of temperature calculated using liquid-phase thermochemical data (Table 1), with the adjusted and non-adjusted values for the standard enthalpy of formation of ETBE. The expression resulting from the adjusted value is

$$\ln K(l) = 10.387 + \frac{4060.59}{T} - 2.89055 \ln T - 0.0191544 T + 5.28586 \times 10^{-5} T^2 - 5.32977 \times 10^{-8} T^3 \quad (13)$$

As shown in Figure 2, eq 13 agrees quite well with experimental data from not only this work, but also those reported by Vila et al. (1993) and by Françoise and Thyron (1991), and is, consequently, the recommended expression.

## CONCLUSIONS

A thermodynamic analysis of the ETBE liquid-phase reaction is done to obtain an expression for the liquid-phase equilibrium constant (eq 13) that agrees well with experimental data. The analysis is based on the thermodynamic data reported in the literature, with the exception of ETBE, for which complete data are not yet available. Consequently, the standard enthalpy of formation of ETBE was adjusted to -357.5 kJ/mol, as compared with a reported value of -351.6 kJ/mol, in order to obtain better agreement with data over a range of temperatures. The liquid-phase equilibrium constant was also calculated using gas-phase thermochemical data, with good results as shown by Jensen and Datta (1994), further supporting the adjusted value for the standard enthalpy of formation of ETBE.

Figure 1. Thermodynamic Equilibrium Constant with Adjusted and Nonadjusted Liquid-Phase Enthalpy of Formation of ETBE

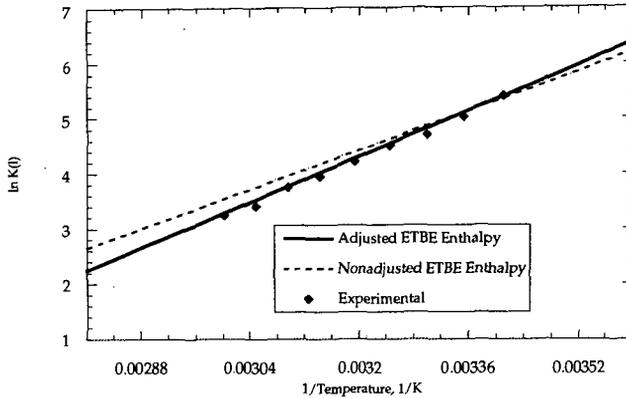
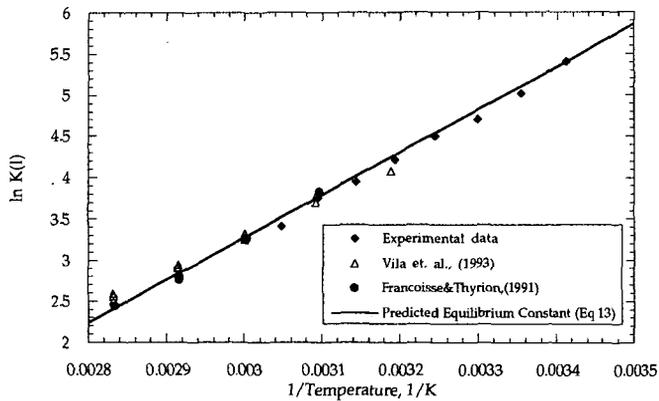


Figure 2. Experimental and Literature Data Compared with the Predicted Liquid-Phase Equilibrium Constant



#### ACKNOWLEDGMENT

The funding provided for this work by the Iowa Corn Promotion Board and the National Renewable Energy Laboratories is gratefully acknowledged.

#### NOMENCLATURE

$a_j, b_j, c_j, d_j$  = coefficients of molar heat capacity expression, eq 10

$a_j$  = activity of species  $j$ ,  $\equiv \gamma_j x_j$

$\hat{C}_{p_j}(\alpha)$  = molar heat capacity of species  $j$  in phase  $\alpha$ , J/mol-K

ETBE = ethyl *tert*-butyl ether

$I_H$  = constant of integration in the Kirchoff equation, eq 11

$I_K$  = constant of integration in v'ant Hoff equation, eq 12

$K(l)$  = liquid-phase thermodynamic equilibrium constant

$K(\alpha)$  = thermodynamic equilibrium constant for phase  $\alpha$

$K_\gamma$  = equilibrium constant in terms of activities, eq 1

$K_x$  = equilibrium constant in terms of mole fractions, eq 1

$l$  = liquid phase

$n$  = total number of species

$P$  = pressure, bar

$P^\circ$  = standard pressure, 1 bar

- $R$  = gas constant, 8.3143 J/mol-K  
 $S_{jT}^{\circ}$  = standard entropy of species  $v$  at the temperature  $T$ , J/mol-K  
 $T$  = temperature, K  
 $T^{\circ}$  = standard temperature, 298.15 K  
 $\bar{V}_j(l)$  = liquid molar volume of species  $j$ , mL/mol  
 VOC = volatile organic compound  
 $x_j$  = mole fraction of species  $j$

#### Greek letters

- $\alpha$  = phase ( $g$  or  $l$ )  
 $\gamma_j$  = activity coefficient of species  $j$   
 $\Delta G_{ff}^{\circ}(\alpha)$  = standard Gibbs energy of formation of species  $j$  in phase  $\alpha$  at temperature  $T$ , kJ/mol  
 $\Delta G_r^{\circ}(\alpha)$  = standard Gibbs energy change for reaction in phase  $\alpha$  at temperature  $T$ , eq 3, kJ/mol  
 $\Delta H_{ff}^{\circ}(\alpha)$  = standard enthalpy of formation of species  $j$  in phase  $\alpha$  at temperature  $T$ , kJ/mol  
 $\Delta H_r^{\circ}(\alpha)$  = standard enthalpy change for reaction in phase  $\alpha$  at temperature  $T$ , eq 5, kJ/mol  
 $\Delta S_T^{\circ}$  = standard entropy change for reaction at temperature  $T$ , J/mol-K  
 $\nu_j$  = stoichiometric coefficient of species  $j$  in reaction

#### Subscripts

- $e$  = at equilibrium  
 $f$  = of formation  
 $j$  = of species  $j$   
 $T$  = at temperature  $T$   
 $T^{\circ}$  = at standard temperature

#### Superscripts

- $^{\circ}$  = at standard state (1 bar; also ideal gas for gas phase)

#### LITERATURE CITED

- CRC *Handbook of Chemistry and Physics*, Lide, D. Ed., CRC: Boca Raton, 73rd Edition, 1992.  
 Françoise, O.; Thyron, F. C. Kinetics and Mechanism of Ethyl tert-Butyl Ether Liquid-phase Synthesis. *Chem. Eng. Process.* **1991**, *30*, 141-149.  
 Gallant, R. *Physical Properties of Hydrocarbons*, Gulf Publishing: Houston, Volume 1, 1968.  
 Iborra, M.; Izquierdo, J.; Tejero, J. F.; Cunill F. Equilibrium Constant for Ethyl tert-Butyl Ether Vapor-Phase Synthesis. *J. Chem. Eng. Data.* **1989**, *34*, 1-5.  
 Jensen, K.; Datta, R. Equilibrium Thermodynamic Analysis of the Liquid-Phase Ethyl tert-Butyl Ether (ETBE) Reaction. *Ind. Eng. Chem. Res.* Submitted **1994**.  
 Lucht, G. Ethanol Approval Creates Hugh Sighing Sound, *Iowa Farmer Today*, Dec. 25, 1993, (10), 1-2.  
*Oxy-Fuel News*. ARCO Chemical, Coastal to Produce ETBE in Texas. Vol IV, No. 22, Sept. 7, **1992**, 1.  
 Reid, R.; Prausnitz, J.; Poling, B. *The Properties of Gases & Liquids*, McGraw-Hill: New York, Fourth Edition, 1987.  
 Reisch, M. Top 50 Chemicals Production Rose Modestly Last Year, *C&EN* **1994**, April 11, 12-15.  
 TRC *Thermodynamics Tables, Hydrocarbons and Nonhydrocarbons*, Thermodynamics Research Center, Texas A&M University, 1986.  
 Vila, M.; Cunill, F.; Izquierdo, J. F.; Tejero, J.; Iborra, M. Equilibrium Constants For Ethyl tert-Butyl Ether Liquid-Phase Synthesis. *Chem. Eng. Comm.* **1993**, *124*, 223-232.