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Thermodynamic properties of glycerol: Experimental and theoretical study

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ABSTRACT

Vapor pressures of highly pure glycerol were measured by the static and the transpiration methods in a broad temperature range. The standard molar enthalpy of vaporization of glycerol was derived from the vapor pressure temperature dependencies. Thermodynamic data on glycerol available in the literature were collected, evaluated, and combined with own experimental results. We recommend the set of vaporization and formation enthalpies for glycerol at 298.15 K (in kJ mol^{-1}): $\Delta_f H_m^\circ$ (g) = $-(578.8 \pm 0.6)$, $\Delta_f H_m^\circ$ (l) = $-(669.3 \pm 0.5)$, and $\Delta_l^g H_m^\circ$ = (90.5 ± 0.3) as the reliable benchmark properties for further thermochemical calculations. Quantum-chemical calculations of the gas phase molar enthalpy of formation of glycerol have been performed using the G4 method and results were in agreement with the recommended experimental data. The standard molar entropy of formation and the standard molar Gibbs function of formation of glycerol were estimated.

1. Introduction

Biodiesel is on-going substitute for fossil fuel in the near future. Biodiesel is industrially produced from renewable sources (vegetable oils or animal fats) via reaction with alcohols. In the production of biodiesel, glycerol appears as a by-product, representing ca. 10 wt% of the total output. In the last few years, the world glycerol production has surpassed 2 million metric tons, glycerol coming from the biodiesel industry representing more than two-thirds of the total outcome [1]. Utilization of the glycerol is one of the much researched topic in present times. Chemical feasibility of new strategies to utilize renewable feedstocks into value-added products can be easy assessed by thermodynamic calculations, provided that reliable data are available. Last evaluation of the thermodynamic data for glycerol was published

in 1985 [2] with a focus on properties in the condensed phase. Vapor pressures, vaporization enthalpies, as well as the gas phase thermodynamic properties of glycerol still require a careful evaluation. This contribution complements and extends our previous work on thermodynamics of aliphatic polyols [3–6]. In the focus of current work was an experimental and computational study of glycerol aiming at evaluation of available thermochemical properties. Vapor pressures of glycerol were measured over a broad temperature range by using the static method [7]. Additionally, we apply the transpiration method [8] to measure vapor pressures at temperatures possibly close to the reference temperature T = 298.15 K in order to derive vaporization enthalpy $\Delta_l^g H_m^\circ$ (298.15 K) less affected by temperature adjustment. From our experience, reliable evaluation of the experimental data can be performed, provided that the vapor pressures are independently measured by using at least two different techniques on the same highly pure sample. Consistent own results obtained in different temperature ranges can be used as a basis for analysis of the available literature data. Joint treatment of the available consistent data for each compound of interest yields the evaluated data set, which can be recommended for further thermochemical calculations.

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List of symbols

$C_{p,m}^{\circ}$	Standard molar heat capacity, $J\,K^{-1}\,mol^{-1}$
p_i	Saturated vapor pressure, Pa
p^{o}	Standard pressure = 10^5 Pa
S_m°	Standard molar entropy, $J\,K^{-1}\,mol^{-1}$
θ	Arbitrary chosen reference temperature for data treatment, K
$\Delta_f G_m^{\circ}$	Standard molar Gibbs energy of formation, $kJ\,mol^{-1}$
$\Delta_f H_m^{\circ}$	Standard molar enthalpy of formation, $kJ\,mol^{-1}$
$\Delta_f S_m^{\circ}$	Standard molar entropy of formation, $J\,K^{-1}\,mol^{-1}$
$\Delta_l^g C_{p,m}^{\circ}$	Molar heat capacity difference at the reference temperature, $J\,K^{-1}\,mol^{-1}$
$\Delta_l^g G_m^{\circ}\,(\theta)$	Standard molar Gibbs energy of vaporization at the reference temperature, $kJ\,mol^{-1}$
$\Delta_l^g H_m^{\circ}\,(\theta)$	Standard molar enthalpy of vaporization at the reference temperature, $kJ\,mol^{-1}$
$\Delta_l^g S_m^{\circ}\,(\theta)$	Standard molar entropy of vaporization at the reference temperature

2. Materials and methods

2.1. Materials

A sample of glycerol (IUPAC name 1,2,3-propanetriol) available from Sigma–Aldrich with the purity 99.5% was further purified by fractional distillation with a spinning-band column in vacuum. No impurities (greater than 0.02 mass per cent) could be detected in the samples used for vapor pressure measurements. The degree of purity was determined using a GC with capillary column HP-5 was used with a column length of 30 m, an inside diameter of 0.32 mm, and a film thickness of 0.25 μm. Provenance and purity of the compound prepared for thermochemical study in this work are given in Table 1.

2.2. Vapor pressure measurements

2.2.1. Static method

In this work we used the self-made experimental setup [7]. The cylindrical cell with the internal volume of 20 cm³ was kept at a constant temperature within ±0.02 K. The uncertainty of absolute temperature determination was ±0.05 K over the working temperature interval of the system of (253–463) K. The sample cell was connected to a high temperature capacitance manometers (MKS Instruments, Inc.) with the working range of $(0.1–10^5)$ Pa with the uncertainty of $\pm 5 \times 10^{-3}\,p$ as stated by the manufacturer. The temperature of tubing connections between the measuring cell and pressure gauges was kept higher by 30–50 K than those in the sample cell in order to avoid condensation of sample vapors in the tubing system. The detailed description of the experimental apparatus, procedure, and uncertainty analysis, is given in Ref. [7]. The experimental setup and the measuring technique were tested measuring benzoic acid, naphthalene, ferrocene, and

Table 1
Provenance and purity of the material.

Material	Glycerol
CASRN	56-81-5
Origin	Sigma–Aldrich, 99.5%
Method of purification	fractional distillation
GC purity (mass fraction)	0.999

benzophenone as reference compounds [7]. Absence of a possible decomposition during the experiment was checked by GC-analysis of the sample after completing the experiment.

2.2.2. Transpiration method

Vapor pressures of glycerol were independently measured using the transpiration method [9]. About 0.5 g of the sample was mixed with small glass beads and placed in a thermostatted U-shaped saturator. A well defined nitrogen stream was passed through the saturator at a constant temperature (±0.1 K), and the transported material was collected in a cold trap. The amount of condensed sample was determined by GC analysis using an external standard n-undecane. The absolute vapor pressure p_i at each temperature T_i was calculated from the amount of the product collected within a definite period of time. Assuming validity of the Dalton's law applied to the nitrogen stream saturated with the substance i, values of p_i were calculated with equation:

$$p_i = \frac{m_i R T_a}{V M_i}; \quad V = V_{N2} + V_i; (V_{N2} \gg V_i) \tag{1}$$

where $R = 8.314462\,J\cdot K^{-1}\,mol^{-1}$; m_i is the mass of the transported compound, M_i is the molar mass of the compound, and V_i, is volume contribution to the gaseous phase. V_{N2} is the volume of the carrier gas and T_a is the temperature of the soap bubble meter used for measurement of the gas flow. The volume of the carrier gas V_{N2} was determined from the flow rate and the time measurement.

3. Results and discussion

3.1. Vapor pressures from the static method

Vapor pressures of glycerol measured by the static method in the broad temperature range 304–436 K were fitted to the Clarke and Glew [10] equation:

$$R \times \ln\left(\frac{p}{p^0}\right) = -\frac{\Delta_l^g G_m^{\circ}(\theta)}{\theta} + \Delta_l^g H_m^{\circ}(\theta)\left(\frac{1}{\theta} - \frac{1}{T}\right)$$
$$+ \Delta_l^g C_{p,m}^{\circ}(\theta)\left[\frac{\theta}{T} - 1 + \ln\left(\frac{T}{\theta}\right)\right], \tag{2}$$

where p is the vapor pressure at the temperature T, p^0 is an arbitrary reference pressure ($p^0 = 10^5$ Pa in this work), θ is an arbitrary reference temperature (in this work we use $\theta = 298.15$ K or θ was an average temperature of the experimental range), R is the molar gas constant, $\Delta_l^g G_m^{\circ}\,(\theta)$ is the difference in the standard molar Gibbs energy between the gaseous and the liquid phases at the selected reference temperature, $\Delta_l^g H_m^{\circ}(\theta)$ is the difference in the standard molar enthalpy between the gas and the liquid phases, and $\Delta_l^g C_{p,m}^{\circ}\,(\theta)$ is the difference in the molar heat capacity at constant pressure between the gaseous and the liquid phase. An advantage of the Clarke and Glew equation is that the fitting coefficients are directly related to the thermodynamic functions of vaporization. Experimental vapor pressures for glycerol measured by using the static method are listed in Table 2. The following thermodynamic functions of vaporization were derived:

$\Delta_l^g G_m^{\circ}$ (298.15 K) = (38.00 ± 0.01) kJ mol^{-1}, $\Delta_l^g H_m^{\circ}$ (298.15 K) = (90.5 ± 0.2) kJ mol^{-1}, and $\Delta_l^g C_{p,m}^{\circ}$ (298.15 K) = −(95.5 ± 0.5) J K^{-1} mol^{-1}.

3.2. Vapor pressure and vaporization enthalpies from the transpiration method

Vapor pressures p_i measured by the transpiration method were measured in the shorter temperature range in comparison to the