



Thermodynamic properties of glycerol: Experimental and theoretical study



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ARTICLE INFO

Article history:

Received 4 December 2014

Received in revised form 25 March 2015

Accepted 25 March 2015

Available online 28 March 2015

Keywords:

Glycerol

Vapor pressure measurements

Enthalpy of vaporization

Enthalpy of formation

Quantum-chemical calculations

Thermodynamic properties

Entropy

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}): $\Delta_f H_m^\circ(\text{g}) = -(578.8 \pm 0.6)$, $\Delta_f H_m^\circ(\text{l}) = -(669.3 \pm 0.5)$, and $\Delta_f^\circ H_m^\circ = (90.5 \pm 0.3)$ 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.

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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 easily 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 $T = 298.15 \text{ K}$ in order to derive vaporization enthalpy $\Delta_f^\circ H_m^\circ(298.15 \text{ K})$ 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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