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Benchmark thermodynamic properties of 1,3-propanediol: Comprehensive experimental and theoretical study

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ABSTRACT

Thermochemical properties of 1,3-propanediol are in disarray. A new standard ($p° = 0.1$ MPa) molar enthalpy of formation at the temperature $T = 298.15$ K of the liquid 1,3-propanediol was measured using combustion calorimetry. A new molar enthalpy of vaporisation of 1,3-propanediol was derived from the vapour pressure temperature dependence measured by the transpiration method. Thermodynamic data on 1,3-propanediol available in the literature were collected, evaluated, and combined with own experimental results. This collection together with the new experimental results reported here has helped to resolve contradictions in the available enthalpies of formation data and to recommend the set of vaporisation and formation enthalpies for 1,3-propanediol at $T = 298.15$ K (in kJ · mol^{-1}): $\Delta_f H_m°$ (g) = −(410.6 ± 2.2), $\Delta_f H_m°$ (l) = −(481.8 ± 2.2), and $\Delta_l^g H_m°$ = (71.2 ± 0.2) as the reliable benchmark properties for further thermochemical calculations. Quantum-chemical calculations of the gas phase molar enthalpy of formation of 1,3-propanediol have been performed using the G3MP2 method and results were in excellent agreement with the recommended experimental values. The standard molar entropy of formation and the standard molar Gibbs function of formation have been calculated.

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1. Introduction

The manufacturing of renewably-sourced platform chemicals and polymers is an active area of interest [1]. Large scale fermentation of glycerol [2] or glucose [3] to form 1,3-propanediol is an attractive way for valorisation of renewable feed stocks since 1,3-propanediol is a valuable precursor for production high value polymers and intermediates [3]. New strategies to utilise renewable feedstock into value-added products are important for the future competitiveness of the chemical industry. Chemical feasibility of new strategies has to be assessed using thermodynamic calculations. Reliability of the prediction is crucially dependent on the quality of experimental data involved in the calculations. Surprisingly, the available thermochemical values for alkanediols are in disarray [4]. The standard molar enthalpy of formation, $\Delta_f H_m°$, of 1,3-propanediol in the liquid state reported in the literature [5–7] from combustion calorimetry measurements show spread over 15 kJ · mol^{-1}. New additional experiments with 1,3-propanediol

are intending to resolve contradictions among available data. This contribution complements and extends our previous work on thermodynamics of aliphatic diols by our group [4,8,9]. The aim of this study is an experimental and computational study of 1,3-propanediol in order to evaluate available thermochemical properties.

2. Materials and methods

2.1. Materials

A sample of 1,3-propanediol available from Alfa Aesar with mass fraction purity 0.99 was further purified by fractional distillation with a spinning-band column in vacuum. No impurities (greater than 0.02 mass percent) could be detected in the samples used for the combustion experiments and the vapour 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. The standard temperature program of the GC was $T = 333$ K for 180 s followed by a heating rate of 0.167 K · s^{-1} to $T = 523$ K. Provenance and purity of the compound prepared for thermochemical studies in this work are given in table S1 (Supplementary information).

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2.2. Vapour pressure measurements. Transpiration method

Vapour pressures of 1,3-propanediol were determined using the method of transpiration [10] in a saturated nitrogen stream. 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 of 1,3-propanediol was determined by GC analysis using an external standard n-C_9H_{20}. The absolute vapour pressure p_i at each temperature T_i was calculated from the amount of the product collected within a definite period. 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:

$$P_i = m_i \cdot R \cdot T_a / V \cdot M_i; \quad V = V_{N2} + V_i; \quad (V_{N2} \gg V_i), \quad (1)$$

where $R = 8.314462 \, J \cdot K^{-1} \cdot mol^{-1}$; m_i is the mass of the transported compound, M_i is the molar mass of the compound, and V_i; its 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. Experimental results are given in tables 1 and 2.

the 10 mL pycnometer using the syringe of 250 μL nominal volume and the mixture was analysed by GC with the same reproducibility.

(b) The volume of the carrier gas V_{N2}. For the transpiration experiments with duration over few hours the value of V_{N2} was directly measured by Honeywell S&C – HAFBLF0200-C2AX5 digital flow rate sensor with uncertainty at the level of 2.5%. For the shorter experiments, the carrier gas flow rate was measured with the HP Agilent soap film flow meter (-model 0101-0113). The value of V_{N2} was calculated from the gas-flow and time measurements with uncertainty of 1%.

(c) The temperature of saturator was kept constant within (±0.2 K) using a circulating thermostat. The temperature was measured using a calibrated Pt-100 thermometer with resolution of $T = 0.2$ K.

(d) The ambient temperature T_a of the volume V_{N2} measurements was measured using the calibrated Pt-100 with uncertainty ±0.2 K.

(e) The atmospheric pressure was measured using a digital pressure indicator with uncertainty ±2 hPa absolute.

Uncertainties resulting from correlations are reported as standard deviations (u). Uncertainties associated with combined results were evaluated as follows:

$u(p)/p =$

$(0.0001/0.05) = 0.0040 \cdot 100 = 0.20\%$	mass of the reference sample
$(0.0001/0.03) = 0.0067 \cdot 100 = 0.67\%$	mass of the sample under study
$(0.01/5) + (0.01/10) = 0.0030 \cdot 100 = 0.30\%$	volumes of calibrated pycnometers
$(0.25/200) + (0.1/100) = 0.0022 \cdot 100 = 0.22\%$	volume of the standard solution
$(0.02/2) + (0.02/2) = 0.02 \cdot 100 = 2.0\%$	GC injections (calibration + determination)
$(0.01/2) = 0.005 \cdot 100 = 0.5\%$	volume of transporting gas
$(0.2/323) + (0.2/298) = 0.00129 \cdot 100 = 0.13\%$	T − measurements (saturator + ambient)
$(2/1000) = 0.002 \cdot 100 = 0.20\%$	ambient atmospheric pressure
$u(p)/p = (u_1^2 + u_2^2 + \cdots)^{0.5} \cdot 100 = \mathbf{2.1\%}$	combined uncertainties.

2.3. Uncertainties of vapour pressure measurements

The experimental quantities measured to obtain the vapour pressures and enthalpies of vaporisation are as follows:

(a) The mass, m_i, of compound collected in the cold trap. This amount was determined by GC analysis using an external standard. This GC procedure consists of two steps: calibration of the FID using two reference solutions and injecting of the mixture of the transported sample with the well-defined amount of the standard solution. For the first step, about 0.03 g of sample was weighed in 5 mL calibrated pycnometer, and about 0.05 g of the standard compound (hydrocarbon n-C_nH_{2n+2}) was weighed in 10 mL calibrated pycnometer. We used KERN ACJ 220-4 m balances with the resolution of ±0.0001 g. Both pycnometers were filled with acetonitrile with uncertainty ±0.01 mL. Mixtures for the FID calibration were prepared using the Hamilton syringes of the Gastight 1700 series with (100 and 250) μl volume. Calibration mixtures were analysed by GC with the repeatability within (1 to 2)%. For the mass determination the cold trap was charged with 200 μL of the standard solution from

It has turned out that accuracy of vapour pressures measured by transpiration method governed mostly by the reproducibility of the GC analysis as well as by the volume V_{N2} determination.

The standard uncertainties (u) of the measured vapour pressures have been calculated to be:

$$u(p/Pa) = 0.025 + 0.025(p/Pa) \text{ for } p > 5 \text{ to } 1000 \text{ Pa,}$$

$$u(p/Pa) = 0.005 + 0.025(p/Pa) \text{ for } p < 5 \text{ Pa.}$$

To validate system operation, the vapour pressure of naphthalene was determined at $p = (1 \text{ to } 500)$ Pa experimental vapour pressure of naphthalene obtained using this procedure agreed with the results reported in the literature [11] to within (0.6 to 2.5)%. For validation of our uncertainty estimations we measured vapour pressures for series of n-alkanols [10] where reliable values at $p = (0.1 \text{ to } 1000)$ Pa from different methods were available. It has turned out that vapour pressures of n-alkanols derived from the transpiration method were comparable with available high-precision results generally within (1 to 3)% in agreement with our estimations.