



Benchmark thermodynamic properties of alkanediamines: Experimental and theoretical study



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ABSTRACT

Vapor pressures of (*dl*)-1,2-propanediamine and 2-methyl-1,2-propanediamine were measured using the transpiration method. Molar enthalpies of vaporization were derived from the vapor pressure temperature dependence. Thermodynamic data on alkanediamines available in the literature were collected and treated uniformly. Consistency of the experimental data set for alkanediamines was evaluated with group-contribution and quantum-chemical methods.

The standard molar entropy of formation and the standard molar Gibbs function of formation have been calculated. Vaporization and formation enthalpies of alkanediamines of benchmark quality are recommended for practical thermochemical calculations and validation of empirical and theoretical methods.

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1. Introduction

Quantum chemical methods have become indispensable research tools in chemistry and materials science. They offer the real promise of being able to complement experiment as a means to uncovering and exploring new chemistry [1]. Experimentalists rely increasingly on these methods to interpret and validate their findings. Demonstration of agreement between the independent experimental and computed results can provide strong validation for both results and to establish thermochemical data of benchmark quality. In the context of our experimental and computational studies of N-containing compounds [2–6] we have found that standard molar enthalpies of formation $\Delta_f H_m^\circ$ (g, $T = 298.15$ K) for 1,2-propanediamine, 1,2-butanediamine, and 2-methyl-1,2-propanediamine (see figure 1) calculated by using high-level G3MP2 calculations were systematically less negative in comparison to experimental values [7,8]. At a first glance, the experimental data in reference [8] were of seemingly impeccable quality. However, a more detailed analysis of primary vapor pressures reported in reference [8] have revealed some shortcomings in data treatment, leading to systematically erroneous vaporization

enthalpies and, as a consequence, erroneous $\Delta_f H_m^\circ$ (g, $T = 298.15$ K) values as reported in the modern databases. In order to ascertain the available experimental data we have performed additional vapor pressure studies of (*dl*)-1,2-propanediamine and methyl-1,2-propanediamine by using the transpiration method. The aim of this work was the experimental and computational study of the alkanediamines presented in figure 1 in order to evaluate available thermochemical properties and to recommend a dataset of benchmark quality, capable for validation of quantum-chemical methods.

2. Materials and methods

2.1. Materials

Samples of (*dl*)-1,2-propanediamine and 2-methyl-1,2-propanediamine were of commercial origin. They were further purified by fractional distillation with a spinning-band column in vacuum. No impurities (greater than 0.001 mass fraction) could be detected in the samples used for the vapor pressure measurements. The degree of purity was determined using a GC on a HP-5 capillary column, column length of 30 m, inside diameter of 0.32 mm, and film thickness of 0.25 μm . Provenance and purity of compounds prepared for vapor pressure measurements are given in table S1.

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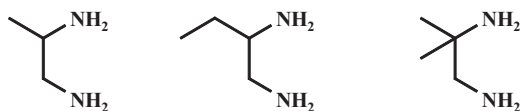


FIGURE 1. Alkanediamines studied in this work: 1,2-propanediamine [CAS 78-90-0]; 1,2-butanediamine [CAS 4426-48-6]; 2-methyl-1,2-propanediamine [CAS 811-93-8].

2.2. Transpiration method

Vapor pressures of 1,2-propanediamine and 2-methyl-1,2-propanediamine were measured using the transpiration method [9,10]. About 0.5 g of a 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 the external standard n -C₉H₂₀. The absolute vapor 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 the following equations:

$$p_i = m_i \cdot R \cdot T_a / V \cdot M_i; \quad V = V_{N_2} + V_i; \quad (V_{N_2} \gg V_i), \quad (1)$$

where $R = 8.314462 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; 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_{N_2} 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_{N_2} was determined from the flow rate and the time measurement.

It is well known that diamines are very reactive compounds and some precautions for the stabilization of diamines was required. For this purpose we have washed the glass beads used in transpiration experiments with 0.1 N NaOH in order to suppress the possible acidity of the glass surface. After careful drying of beads in oven at 110 °C they were used for loading with the sample into the saturator. Such a treatment was helpful to obtain stable and reproducible results with alkanediamines.

Temperature dependence of vapor pressures p_i measured for 1,2-propanediamine and 2-methyl-1,2-propanediamine were fit with the following equation [9]:

$$R \cdot \ln p_i = a + \frac{b}{T} + \Delta_1^{\circ} C_{p,m}^{\circ} \cdot \ln \left(\frac{T}{T_0} \right), \quad (2)$$

where a and b are adjustable parameters and $\Delta_1^{\circ} C_{p,m}^{\circ}$ is difference between isobaric molar heat capacities of the gas, $C_{p,m}^{\circ}(\text{g})$, and the liquid, $C_{p,m}^{\circ}(\text{l})$. Value T_0 appearing in equation (2) is an arbitrarily chosen reference temperature (which has been chosen to be $T = 298.15$ K) and R is the molar gas constant.

Vaporization enthalpies at temperature T were derived from the temperature dependence of vapor pressures using equation (3):

$$\Delta_1^{\circ} H_m^{\circ}(T) = -b + \Delta_1^{\circ} C_{p,m}^{\circ} \cdot T. \quad (3)$$

Vaporization entropies at temperature T were also derived from the temperature dependence of vapor pressures using equation (4):

$$\Delta_1^{\circ} S_m^{\circ}(T) = \Delta_1^{\circ} H_m^{\circ}(T) / T + R \ln(p_i / p^{\circ}). \quad (4)$$

Experimental absolute vapor pressures measured by the transpiration method, coefficients a and b of equation (2), as well as values of $\Delta_1^{\circ} H_m^{\circ}(T)$ and $\Delta_1^{\circ} S_m^{\circ}(T)$ are given in table 1. The procedure

for calculation of the combined uncertainties of the vaporization enthalpy was described elsewhere [11]. It includes uncertainties from the transpiration experimental conditions, uncertainties in vapor pressure, and uncertainties in the temperature adjustment to $T = 298.15$ K.

3. Results and discussion

3.1. Vapor pressures and vaporization enthalpies

Vaporization enthalpies for 1,2-propanediamine $\Delta_1^{\circ} H_m^{\circ}(T = 298.15 \text{ K}) = (44.1 \pm 0.2) \text{ kJ} \cdot \text{mol}^{-1}$, for 1,2-butanediamine $\Delta_1^{\circ} H_m^{\circ}(T = 298.15 \text{ K}) = 46.9 \text{ kJ} \cdot \text{mol}^{-1}$ (without specification of precision), and for 2-methyl-1,2-propanediamine $\Delta_1^{\circ} H_m^{\circ}(T = 298.15 \text{ K}) = (43.6 \pm 0.2) \text{ kJ} \cdot \text{mol}^{-1}$ were reported by Messerly *et al.* [8]. These values were included in the DIPPR Database [12] as well as in calculations of gaseous enthalpies of formation, which were also included in the databases and thermochemical compilations [13]. The disagreement between these experimental and our quantum chemical values for $\Delta_1^{\circ} H_m^{\circ}(\text{g}, T = 298.15 \text{ K})$ mentioned in the introduction attracted our attention to the experimental details reported in reference [8]. It has turned out that their vaporization enthalpies $\Delta_1^{\circ} H_m^{\circ}(T = 298.15 \text{ K})$ were derived "from the Clapeyron equation with values of the second virial coefficient chosen by rather inexact methods" [8]. Any further details on the vapor pressure data treatment were absent and we treated the available in the paper primary p - T data by using equations (2) and (3). To our concern, we derived significantly different vaporization enthalpies for the following alkanediamines: 1,2-propanediamine $\Delta_1^{\circ} H_m^{\circ}(T = 298.15 \text{ K}) = (46.1 \pm 0.2) \text{ kJ} \cdot \text{mol}^{-1}$, 1,2-butanediamine $\Delta_1^{\circ} H_m^{\circ}(T = 298.15 \text{ K}) = (48.9 \pm 0.3) \text{ kJ} \cdot \text{mol}^{-1}$, and 2-methyl-1,2-propanediamine $\Delta_1^{\circ} H_m^{\circ}(T = 298.15 \text{ K}) = (45.8 \pm 0.3) \text{ kJ} \cdot \text{mol}^{-1}$ (see table 2). The degree of confusion increased after treatment of the p - T data set for 1,2-ethanediamine (CAS 107-15-3) available from the same paper. Indeed, the value $\Delta_1^{\circ} H_m^{\circ}(T = 298.15 \text{ K}) = (45.7 \pm 0.1) \text{ kJ} \cdot \text{mol}^{-1}$ published by Messerly *et al.* [8] was indistinguishable from $\Delta_1^{\circ} H_m^{\circ}(T = 298.15 \text{ K}) = (45.6 \pm 0.3) \text{ kJ} \cdot \text{mol}^{-1}$, calculated from the data according to equation (3). Moreover, both vaporization enthalpies of 1,2-ethanediamine, derived indirectly from the vapor pressure temperature dependencies were in good agreement with the value $\Delta_1^{\circ} H_m^{\circ}(T = 298.15 \text{ K}) = (45.0 \pm 0.1) \text{ kJ} \cdot \text{mol}^{-1}$, measured directly by calorimetry [14]. Thus, the consistency of the data treatment for 1,2-ethanediamine, in contrast to the inconsistency of results for the other alkanediamines from the same paper have motivated the additional experimental studies of 1,2-propanediamine and 2-methyl-1,2-propanediamine (unfortunately the sample of 1,2-butanediamine was commercially not available) by using the transpiration method in this work.

Our experimental vapor pressures for 1,2-propanediamine (see table 1) compare favorably with vapor pressures previously studied at low temperatures by using the inclined piston method [8] (see figure 2). Whereas our transpiration measurements have been already completed, a careful study of 1,2-propanediamine by using the static method was published [15]. As can be seen from figure 2, all available (new and old) vapor pressures of 1,2-propanediamine now agree very well. All the data (see table S2) were regressed together using equation (1) to develop a correlation accurately describing vapor pressures for this compound over a broad temperature range (242 to 346) K:

1,2-propanediamine :

$$\ln(p/\text{Pa}) = \frac{282.04}{R} - \frac{66004.70}{R \cdot (T/\text{K})} - \frac{66.70}{R} \ln \left(\frac{T/\text{K}}{298.15} \right). \quad (5)$$

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