



# Thermodynamic properties of cyclohexanamines: Experimental and theoretical study



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## ABSTRACT

Vapor pressures of cyclohexanamine, *N*-methyl-cyclohexanamine, *N,N*-dimethyl-cyclohexanamine, and *N*-cyclohexyl-cyclohexanamine were measured using the transpiration method. Molar enthalpies of vaporization of cyclohexanamine derivatives were derived from vapor pressure temperature dependences. Thermodynamic data on cyclohexanamine derivatives available in the literature were collected and treated uniformly. Consistency of the experimental data was proved with a group-contribution method and quantum-chemical calculations. Evaluated vaporization and formation enthalpies of cyclohexanamine derivatives were recommended for practical thermochemical calculations.

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## 1. Introduction

Cyclohexanamines and their derivatives are finding applications as insecticides, plasticizers, corrosion inhibitors, rubber chemicals, dyestuffs, emulsifying agents, dry-cleaning soaps, acid gas absorbents, and for a variety of miscellaneous uses [1–2]. Thermochemical data for cyclohexanamine derivatives are scarce and inconsistent [1–11]. Very precise molar enthalpy of vaporization of cyclohexanamine  $\Delta_f^g H_m$  (298.15 K) =  $(42.8 \pm 0.1)$  kJ mol<sup>-1</sup> [5] reported from the direct calorimetric measurements was in disagreement with the most indirect determinations of vaporization enthalpy from vapor pressure temperature dependences (Table 1). The calorimetric value from Ref. [5] was selected by Steele [1] to derive a gas phase standard molar enthalpy of formation  $\Delta_f H_m^\circ$  (g, 298.15 K) in combination with his  $\Delta_f H_m^\circ$  (l, 298.15 K) =  $-(147.7 \pm 1.3)$  kJ mol<sup>-1</sup> measured by combustion calorimetry. These formation and vaporization enthalpies were captured by the DIPPR-database [12] and broadly used for industrial calculations. Few years later, the liquid phase enthalpies of formation of five cyclic amines, including cyclohexanamine (with  $\Delta_f H_m^\circ$  (l, 298.15 K) =  $-(141.5 \pm 1.6)$  kJ mol<sup>-1</sup>) were reported by an experienced lab [11]. The

difference between formation enthalpies of 6 kJ mol<sup>-1</sup> for cyclohexanamine (Table 2) is unacceptably large even for technical calculations. Both results require an evaluation. Moreover, such a disagreement also render uncertain other cyclic amines: *N*-methyl-cyclohexanamine, *N,N*-dimethyl-cyclohexanamine, and *N*-cyclohexyl-cyclohexanamine, reported in the same work [11]. Thus, reliability of these experimental values has to be proved. Vaporization enthalpies required for calculation of  $\Delta_f H_m^\circ$  (g, 298.15 K) for the latter species are also absent in the literature. This contribution complements and extends previous work on thermodynamics of aliphatic amines by our group [13–15]. The aim of this study was an experimental and computational study of cyclohexanamine derivatives presented in Fig. 1 in order to evaluate available thermochemical properties.

## 2. Materials and methods

### 2.1. Materials

Samples of cyclohexanamine derivatives were available from Sigma–Aldrich with the purity 99%. 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 equipped with FID. A capillary column HP-5 was used with a

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