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Thermodynamic properties of S-(−)-nicotine

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ABSTRACT

In this work, a reliable and reciprocal set of thermodynamic properties of nicotine has been formed using the experimental and theoretical methods. The values of the enthalpies of combustion and formation of the substance in liquid state have been measured using combustion calorimetry. The temperature dependence of the vapor pressure of nicotine within the low temperature interval 289–373 K has been obtained via transpiration method along with calculation the value of enthalpy of vaporization. The analysis of the substance vapor pressure measurements available in the published sources has been performed, the set of nicotine vapor pressure values in the wide temperature interval has been formed. The enthalpy of formation in the gas state of the substance was determined using the experimental data. Quantum chemical calculation reaffirmed its reliability. The method of statistical thermodynamics has been used to calculate the values of thermodynamic functions of the compound in the ideal gas state within the interval 298.15–1500 K.

1. Introduction

Nicotine is an alkaloid of the pyridine series. It is found mainly in the leaves and stems of tobacco, which in turn is used in the production of cigarettes and cigars [1]. Smoking is a complex thermochemical process where the knowledge of physico-chemical and transport properties of the main component of tobacco, nicotine, is necessary to enable its description and modeling. These properties, in addition to others, include vapor pressure in a wide temperature range and the values of the thermodynamic properties (enthalpies of formation, enthalpies of phase transitions, absolute entropy and free Gibbs energy).

Nicotine is an optically active compound having two enantiomeric forms. The naturally occurring form of nicotine: S-(−)-nicotine is levorotatory. The dextrorotatory form, R-(+)-nicotine, is physiologically less active than S-(−)-nicotine. The observations show that S-(−)-nicotine exhibits more toxic properties than R-(+)-nicotine [2].

The analysis of published data shows that thermodynamic properties of S-(−)-nicotine have not been fully studied. The enthalpy of combustion and formation of the liquid substance were measured only once in 1899 in Berthelot [3]. The vapor pressures of the substance have been measured many times [4–10] and are in satisfactory agreement with each other. However, prevailing majority of measurements was performed at temperatures higher than 373.15 K and the enthalpies of vaporization of the substance referenced to the temperature 298.15 K vary significantly. For instance, ref. [10] contains the compilation of the collected and analyzed measurements of the temperature dependences of nicotine vapor pressures available in the literature [4–9]. The obtained enthalpies of vaporization at 298.15 K based on these values fall within the interval 61.8 ÷ 68.5 kJ·mol^{-1} [10]. The heat capacity and entropy of the compound have not been measured before.

The aim of this study is obtaining a reliable set of thermodynamic properties of S-(−)-nicotine. To reach this goal, the vapor pressure of the substance was measured in close proximity to the temperature 298.15 K by transpiration method. The enthalpy of vaporization was determined. The enthalpy of formation of liquid S-(−)-nicotine was obtained using the highly precise combustion calorimetry. Based on this data, the value of enthalpy of formation in the gaseous state of substance has been derived.

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