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Vaporization enthalpies of a series of the halogen-substituted fluorobenzenes

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ABSTRACT

Vapor pressures of 2-, 3-, and 4-halogen-substituted fluorobenzenes (halogen = Cl, Br, and I) were measured by the transpiration method. Molar standard enthalpies of vaporization were calculated from temperature dependences of vapor pressures. New enthalpies of vaporization at 298 K and those available from literature were tested for consistency by correlation gas-chromatography and evaluated by group-additivity method. Contributions to vaporization due to mutual interactions of halogens on the benzene ring were derived and recommended for prediction vaporization enthalpies of halogen-substituted aromatics.

1. Introduction

Halogen and polyhalogen aromatics are of an environmental concern. Spread and fate of pollutants are predictable, provided that sufficient amount of thermodynamic data is available. This work continues our systematic studies of halogen–benzenes. Experimental thermochemistry of halogen-substituted methylbenzenes has been arranged recently [1,2]. This paper presents new vapor pressure data for nine halogen-substituted fluorobenzenes with Cl, Br, and I in *ortho, meta-,* and *para*-position on the benzene ring. Molar standard enthalpies of vaporization, $\Delta_1^g H_m$, at the reference temperature $T = 298.15$ K for these compounds were derived from vapor pressure temperature dependences. Thermochemical data of halogen–fluorobenzenes available in the literature were collected and treated uniformly in order to derive their enthalpies of vaporization for comparison. Apart from the mere publication of new experimental results, in this paper we tested the recovered thermochemical data for internal consistency by using correlation gas-chromatography and additivity rules. The evaluated values of vaporization enthalpies at 298.15 K were used to develop a group-additivity procedure for halogen-substituted benzenes.

2. Experimental

2.1. Materials

Origin of samples and initial purity are given in Table 1. Prior to experiments the samples were purified by repeated vacuum fractional distillation with the Teflon spinning-band column under reduced pressure. The final degree of sample purity was determined by using a Hewlett Packard gas chromatograph 5890 Series II equipped with a flame ionization detector and a Hewlett Packard 3390A integrator. The carrier gas (nitrogen) flow was 12.1 $cm^3 s^{-1}$. A capillary column HP-5 (stationary phase crosslinked 5% phenyl methyl silicone) was used with a column length of 30 m, an inside diameter of 0.32 mm, and a film thickness of 0.25 mm. The standard temperature program of the GC was $T = 333.15$ K for 180 s followed by a heating rate of 0.167 K s^{-1} to $T = 523.15$ K. No impurities (greater than mass fraction 0.002) could

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