



# 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.

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## 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,  $\Delta_1^{\text{g}}H_m$ , 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  $12.1 \text{ cm}^3 \text{ s}^{-1}$ . 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  $\mu\text{m}$ . The standard temperature program of the GC was  $T = 333.15$  K for 180 s followed by a heating rate of  $0.167 \text{ K s}^{-1}$  to  $T = 523.15$  K. No impurities (greater than mass fraction 0.002) could

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## Nomenclature

### List of symbols

$\Delta_1^g H_m$	Molar enthalpy of vaporization
$T_a$	Ambient temperature
$p_i$	Vapor pressure
$C_{p,m}(\text{liq})$	Molar heat capacity of liquid at constant pressure
$C_{p,m}(\text{g})$	Molar heat capacity of gas at constant pressure
$\Delta_1^g C_p$	Difference of the molar heat capacities at constant pressure

be detected in the samples used for the thermochemical measurements.

### 2.2. Vapor pressure measurements

Well established transpiration method [3,4] was used for measurements of absolute vapor pressures of halogen–fluorobenzenes. 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 ( $\pm 0.1$  K), and the transported material was collected in a cold trap. The amount of condensed sample was determined by GC analysis using an appropriate external standard ( $n\text{-C}_n\text{H}_{2n+2}$ ). The absolute vapor pressure  $p_i$  at each temperature  $T_i$  was calculated from the amount of the product collected within a definite period of time. 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:

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

where  $R = 8.314462 \text{ J K}^{-1} \text{ mol}^{-1}$ ;  $m_i$  is the mass of the transported compound,  $M_i$  is the molar mass of the compound, and  $V_i$  is its 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. Since the amount of substance determination was done by GC, the recovered vapor did not contain any decomposition products.

## 3. Results and discussion

### 3.1. Vapor pressures

Vapor pressures of halogen–fluorobenzenes measured at different temperatures were fitted with the following equation [3]:

$$R \times \ln p_i = a + \frac{b}{T} + \Delta_1^g C_p \times \ln \left[ \frac{T}{T_0} \right] \quad (2),$$

where  $a$  and  $b$  are adjustable parameters, and  $\Delta_1^g C_p$  is the difference of the isobaric molar heat capacities of the gaseous  $C_{p,m}(\text{g})$  and the liquid phases,  $C_{p,m}(\text{liq})$ , respectively.  $T_0$  appearing in Eq. (2) is an arbitrarily chosen reference temperature (which has been chosen to be 298.15 K). A rigorous evaluation of uncertainties of the transpiration method was published elsewhere [2]. It has been established that vapor pressures derived from the transpiration were comparable with available high-precision data within (1–3) % in agreement with our estimations. Experimental vapor pressures measured in this work are given in Table 2.

Temperature dependences of absolute vapor pressures of halogen-substituted fluorobenzenes are presented in Fig. 1. As can be seen on this plot, for all four series *ortho*-isomers exhibit the lowest vapor pressure in comparison to *meta*- and *para*-isomers. The latter isomers have very close pressures, but the order of magnitudes is not regular. For difluoro and Br substitution vapor pressures of *meta*-isomers are slightly higher than those for *para*-isomers. For Cl- and I-substituted fluorobenzenes vapor pressures of *para*-isomers are somewhat higher than those for *meta*-isomers.

### 3.2. Vaporization enthalpies

Vaporization enthalpy at temperature  $T$  was indirectly derived from the temperature dependence of vapor pressures using Eq. (3):

$$\Delta_1^g H_m(T) = -b + \Delta_1^g C_p \times T \quad (3)$$

Values of isobaric heat capacities and their differences  $\Delta_1^g C_p$  are given in Table 3. If available, we used experimental values of  $C_{p,m}(\text{l})$ . The missing heat capacities were estimated by a group-contribution method developed by Chickos et al. [5]. Values of  $C_{p,m}(\text{g})$  were calculated by quantum-chemical method. Experimental results on vaporization enthalpies for halogen–fluorobenzenes and parameters  $a$  and  $b$  are listed in Table 2.

Procedure for calculation of the combined uncertainties of the vaporization enthalpy was described elsewhere [2]. They include uncertainties from the transpiration experimental conditions, uncertainties of vapor pressure, and uncertainties from temperature adjustment to  $T = 298.15$  K.

The compilation of vaporization enthalpies for halogen–fluorobenzenes is presented in Table 4. Temperature dependencies of vapor pressures of Cl-, Br- and I-substituted fluorobenzenes have been reported for the first time. We also collected the literature for difluorobenzenes and systematically treated the experimental data using Eqs. (2) and (3) and with  $\Delta_1^g C_p$  values listed in Table 3 and calculated  $\Delta_1^g H_m$  (298.15 K) for the sake of comparison with our results as well as for the evaluation of the data aiming the recommendation of vaporization enthalpies  $\Delta_1^g H_m$  (298.15 K) for further thermochemical calculations.

**Table 1**  
Provenance and purity of the materials.

Material	CAS RN	Origin	Final GC purity (mass fraction)
2-Chloro-fluorobenzene	348-51-6	Sigma–Aldrich, 99%	0.999
3-Chloro-fluorobenzene	625-98-9	Alfa Aesar, 99%	0.999
4-Chloro-fluorobenzene	352-33-0	Sigma–Aldrich, 99%	0.999
2-Bromo-fluorobenzene	1072-85-1	Acros, 99%	0.999
3-Bromo-fluorobenzene	1073-06-9	Acros, 99%	0.999
4-Bromo-fluorobenzene	460-00-4	Alfa Aesar, 98%	0.998
2-Iodo-fluorobenzene	348-52-7	Acros, 99%	0.999
3-Iodo-fluorobenzene	1121-86-4	Acros, 99%	0.999
4-Iodo-fluorobenzene	352-34-1	Alfa Aesar, 98%	0.999

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