

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 μm . 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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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 (± 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

Table 2Results from measurements of the vapor pressure p of halogen-substituted fluorobenzenes using the transpiration method.

T^a K	m^b mg	$V_{(N_2)}^c$ dm ³	Gas-flow dm ³ /h	p^d Pa	$(p_{exp}-p_{calc})^e$ Pa	$\Delta_1^g H_m$ kJ mol ⁻¹
2-Chloro-fluorobenzene: $\Delta_1^g H_m (298.15\text{ K}) = (44.0 \pm 0.3) \text{ kJ mol}^{-1}$						
$\ln(p/\text{Pa}) = \frac{263.8 \pm 1.8}{R} - \frac{60902 \pm 516}{R \times (T, \text{K})} - \frac{56.8 \pm 7.4}{R} \ln\left(\frac{T, \text{K}}{298.15}\right)$						
277.5	38.4	2.259	0.847	341.1	3.7	45.14
280.6	20.3	0.953	0.853	419.1	0.4	44.97
280.6	9.5	0.442	0.856	431.2	12.6	44.97
283.5	8.1	0.314	0.856	509.8	0.0	44.80
283.6	14.3	0.554	0.853	504.1	-9.2	44.80
286.4	22.9	0.706	0.847	624.1	6.4	44.64
286.6	7.6	0.243	0.856	617.6	-8.4	44.63
289.5	16.5	0.409	0.847	770.5	15.6	44.46
289.6	8.5	0.214	0.856	774.9	15.2	44.46
292.4	9.9	0.214	0.856	897.4	-9	44.30
295.7	12.2	0.214	0.856	1093.2	-17.1	44.11
298.5	13.4	0.200	0.856	1268.4	-45.1	43.95
301.3	18.3	0.231	0.867	1521.3	-26.8	43.79
304.1	27.7	0.296	0.867	1794.7	-28.6	43.63
307.4	29.5	0.26	0.867	2169.1	-18.3	43.44
310.1	22.8	0.173	0.867	2497.4	-38.3	43.29
313.6	28.5	0.173	0.867	3121.4	64.2	43.09
316.3	36.5	0.195	0.867	3551.5	31.8	42.94
319.2	41.9	0.188	0.867	4225.8	144.3	42.77
3-Chloro-fluorobenzene: $\Delta_1^g H_m (298.15\text{ K}) = (43.0 \pm 0.2) \text{ kJ mol}^{-1}$						
$\ln(p/\text{Pa}) = \frac{263.1 \pm 1.4}{R} - \frac{59851 \pm 429}{R \times (T, \text{K})} - \frac{56.4 \pm 7.3}{R} \ln\left(\frac{T, \text{K}}{298.15}\right)$						
275.8	20.9	0.946	0.860	441.2	11.2	44.30
280.1	21.6	0.736	0.849	582.9	4.9	44.06
283.1	22.3	0.623	0.849	706.1	0.0	43.89
286.0	45.8	1.061	0.849	831.5	-21.3	43.72
288.9	23.6	0.439	0.849	1030.6	5.3	43.56
292.0	23.9	0.368	0.849	1237.1	-5.5	43.39
295.1	21.1	0.269	0.849	1490.6	-8.1	43.21
298.1	23.8	0.255	0.849	1766.9	-21.9	43.04
301.0	29.7	0.269	0.849	2096.3	-17.7	42.88
304.1	31.5	0.241	0.849	2468.6	-48.2	42.70
307.3	38.4	0.245	0.773	2963.3	-36.4	42.52
310.3	38.9	0.206	0.773	3567.8	45.4	42.35
313.3	37.8	0.174	0.773	4106.5	-14.4	42.18
316.5	45.3	0.174	0.773	4927	74.5	42.00
319.5	50.8	0.167	0.773	5736.7	101.0	41.83
4-Chloro-fluorobenzene: $\Delta_1^g H_m (298.15\text{ K}) = (42.8 \pm 0.3) \text{ kJ mol}^{-1}$						
$\ln(p/\text{Pa}) = \frac{264.1 \pm 1.3}{R} - \frac{59681 \pm 387}{R \times (T, \text{K})} - \frac{56.4 \pm 7.3}{R} \ln\left(\frac{T, \text{K}}{298.15}\right)$						
277.6	24.6	0.822	1.027	600.8	5.3	43.97
280.6	25.7	0.685	1.027	742.1	12.4	43.80
283.2	22.9	0.514	1.027	872.9	6.2	43.65
286.2	25.8	0.479	1.027	1057.3	5.0	43.48
289.3	30.9	0.479	1.027	1258.9	-20.6	43.31
292.4	21.0	0.266	0.888	1870.2	-21.5	43.13
295.7	27.3	0.281	0.888	1982.1	-16.3	42.95
296.9	18.0	0.178	0.888	2405.4	-42.4	42.88
299.8	23.9	0.192	0.888	2857.6	11.2	42.72
302.7	26.3	0.178	0.888	2468.6	36.9	42.55
305.7	30.7	0.178	0.888	3284.7	-44.1	42.38
308.4	42.0	0.207	0.888	3854.8	3.5	42.23
311.6	46.4	0.192	0.888	4574.6	15.0	42.05
314.3	45.3	0.163	0.888	5275.6	21.3	41.90
317.6	61.5	0.192	0.888	6058.9	-145.3	41.71
320.4	53.1	0.141	0.888	7146.5	25.8	41.55
323.5	63.3	0.141	0.888	8510.1	244.0	41.38
2-Bromo-fluorobenzene: $\Delta_1^g H_m (298.15\text{ K}) = (47.0 \pm 0.3) \text{ kJ mol}^{-1}$						
$\ln(p/\text{Pa}) = \frac{267.9 \pm 1.6}{R} - \frac{64580 \pm 460}{R \times (T, \text{K})} - \frac{58.9 \pm 7.6}{R} \ln\left(\frac{T, \text{K}}{298.15}\right)$						
278.5	5.4	0.643	1.102	124.7	1.0	48.18
279.4	8.6	0.913	0.898	138.5	6.2	48.13
280.6	5.4	0.551	1.102	142.2	-2.3	48.06
282.3	8.8	0.763	0.898	168.4	4.9	47.96
282.5	5.3	0.478	1.102	160.4	-5.6	47.94
283.4	4.3	0.367	1.102	171.6	-5.5	47.89
284.5	5.9	0.461	1.107	184.3	-7.2	47.83

Table 2 (Continued)

T^a K	m^b mg	$V_{(N_2)}^c$ dm ³	Gas-flow dm ³ /h	p^d Pa	$(p_{exp} - p_{calc})^e$ Pa	$\Delta_1^g H_m$ kJ mol ⁻¹
285.5	7.7	0.539	0.898	208.1	2.5	47.77
288.7	8.1	0.450	0.900	262.0	5.1	47.58
291.7	10.3	0.480	0.900	311.5	-3.4	47.40
294.5	14.4	0.539	0.898	383.7	4.6	47.24
297.5	9.2	0.285	0.900	463.6	3.2	47.06
300.3	8.2	0.210	0.898	557.8	8.2	46.90
303.5	19.1	0.405	0.900	667.5	-2.2	46.71
306.6	21.2	0.375	0.900	800.0	-7.3	46.52
309.5	17.0	0.255	0.900	944.0	-13.6	46.35
312.6	23.0	0.285	0.900	1140.6	-3.9	46.17
315.4	21.3	0.225	0.900	1338.1	-1.6	46.01
318.6	35.8	0.315	0.900	1609.6	12.2	45.82
321.4	29.2	0.225	0.900	1857.8	1.1	45.65
324.3	31.8	0.210	0.900	2174.2	11.5	45.48
3-Bromo-fluorobenzene: $\Delta_1^g H_m (298.15\text{ K}) = (44.3 \pm 0.3)\text{ kJ mol}^{-1}$ $\ln(p/\text{Pa}) = \frac{261.9 \pm 1.6}{R} - \frac{61760 \pm 473}{R \times (T, \text{K})} - \frac{58.5 \pm 7.6}{R} \ln\left(\frac{T, \text{K}}{298.15}\right)$						
280.8	7.8	0.482	0.877	227.8	-9.8	45.32
283.4	8.4	0.426	0.852	291.2	7.3	45.17
283.7	11.5	0.58	0.849	287.5	-2.2	45.15
284.7	7.8	0.365	0.877	310.9	1.0	45.10
286.6	10.5	0.426	0.852	355.9	3.2	44.98
287.7	10.5	0.395	0.877	371.1	-6.8	44.92
288.7	13.3	0.472	0.859	403.0	-0.2	44.86
289.4	10.5	0.355	0.852	424.5	2.6	44.82
292.5	11.9	0.327	0.852	516.8	1.3	44.64
293.4	11.6	0.301	0.859	547.6	4.1	44.59
295.3	13.1	0.298	0.852	620.2	7.0	44.47
298.4	21.7	0.412	0.852	744.1	6.4	44.29
299.7	13.9	0.243	0.859	810.6	13.6	44.22
301.5	14.6	0.234	0.877	878.4	-7.6	44.11
302.4	14.4	0.215	0.859	948.3	14.6	44.06
305.8	15.9	0.200	0.859	1125.4	-11.8	43.86
308.5	18.6	0.200	0.859	1312.1	-6.4	43.70
311.6	21.9	0.200	0.859	1541.3	-20.4	43.52
314.6	20.3	0.157	0.859	1819.0	-13.5	43.35
317.6	28.2	0.186	0.859	2137.5	-5.0	43.17
4-Bromo-fluorobenzene: $\Delta_1^g H_m (298.15\text{ K}) = (44.0 \pm 0.4)\text{ kJ mol}^{-1}$ $\ln(p/\text{Pa}) = \frac{259.2 \pm 1.9}{R} - \frac{61441 \pm 552}{R \times (T, \text{K})} - \frac{58.4 \pm 7.5}{R} \ln\left(\frac{T, \text{K}}{298.15}\right)$						
278.2	8.7	0.787	0.87	166.2	2.6	45.20
281.3	9.5	0.685	0.87	204.3	1.5	45.02
283.5	9.2	0.568	0.87	238.4	2.9	44.89
284.4	8.0	0.481	0.87	244.6	-5.5	44.84
286.5	7.7	0.393	0.87	285.0	-2.4	44.71
287.3	12.7	0.626	0.87	295.6	-7.2	44.67
289.4	12.1	0.495	0.87	353.2	6.4	44.54
290.2	11.8	0.466	0.87	366.8	1.9	44.50
292.4	8.3	0.291	0.87	408.7	-10.4	44.37
295.4	9.4	0.262	0.87	514.4	10.0	44.19
296.1	11.8	0.320	0.87	528.3	2.1	44.15
298.3	9.2	0.219	0.87	602.8	2.3	44.02
300.1	11.2	0.233	0.87	682.2	14.2	43.92
301.4	9.5	0.189	0.87	713.8	-6.8	43.84
304.4	10.4	0.175	0.87	846.1	-9.9	43.67
307.6	12.2	0.175	0.87	987.4	-36.5	43.48
310.5	13.6	0.160	0.87	1203.5	3.7	43.31
313.4	16.0	0.160	0.87	1409.6	8.6	43.14
316.4	17.3	0.146	0.87	1673.0	34.3	42.97
2-Iodo-fluorobenzene: $\Delta_1^g H_m (298.15\text{ K}) = (51.5 \pm 0.3)\text{ kJ mol}^{-1}$ $\ln(p/\text{Pa}) = \frac{275.1 \pm 1.6}{R} - \frac{70057.5 \pm 480}{R \times (T, \text{K})} - \frac{62.1 \pm 8.1}{R} \ln\left(\frac{T, \text{K}}{298.15}\right)$						
282.8	6.8	1.903	2.855	39.7	-0.3	52.48
285.7	7.2	1.665	2.855	48.3	-1.9	52.30
285.7	7.8	1.761	2.855	49.3	-1.0	52.30
288.7	10.4	1.808	2.855	63.8	0.6	52.11
289.5	9.7	1.602	3.203	68.6	1.5	52.06
292.5	10.0	1.335	3.203	84.3	0.6	51.87
296.4	10.6	1.068	3.203	111.1	0.4	51.63
298.4	10.2	0.889	2.667	126.9	-0.5	51.51
301.4	11.8	0.801	3.203	163.3	6.6	51.32
303.4	11.0	0.667	2.667	181.9	2.6	51.2

Table 2 (Continued)

T^a K	m^b mg	$V_{(N_2)}^c$ dm ³	Gas-flow dm ³ /h	p^d Pa	$(p_{exp}-p_{calc})^e$ Pa	$\Delta_1^g H_m$ kJ mol ⁻¹
306.4	9.7	0.48	1.151	223.8	5.2	51.01
308.4	16.1	0.711	2.667	250.0	1.1	50.89
311.3	12.2	0.465	1.117	293.9	-5.4	50.71
313.4	21.2	0.711	2.667	328.9	-12.4	50.58
316.4	10.5	0.279	1.117	420.1	10.0	50.39
317.5	11.4	0.288	1.151	434.8	-3.4	50.32
318.4	11.9	0.282	1.127	468.6	6.2	50.27
321.4	14.1	0.279	1.117	563.8	11.8	50.08
323.5	15.8	0.282	1.127	621.6	-1.7	49.95
326.5	18.7	0.282	1.127	736.4	-2.7	49.76
327.5	19.9	0.288	1.151	761.6	-20.1	49.70
328.6	20.9	0.282	1.127	821.7	-9.2	49.63
3-Iodo-fluorobenzene: $\Delta_1^g H_m$ (298.15 K) = (48.6 ± 0.3) kJ mol ⁻¹						
$\ln(p/\text{Pa}) = \frac{266.6 \pm 2.0}{R} - \frac{66900 \pm 597}{R \times (T, \text{K})} - \frac{61.5 \pm 8.0}{R} \ln\left(\frac{T, \text{K}}{298.15}\right)$						
275.2	7.5	2.700	5.400	32.6	2.0	49.96
280.4	10.2	2.475	4.950	47.4	1.5	49.64
283.4	8.6	1.733	4.95	57.1	-0.3	49.46
283.8	3.2	0.620	1.239	58.0	-1.1	49.43
284.9	1.7	0.309	1.235	62.5	-1.7	49.37
286.8	2.0	0.309	1.235	74.6	0.9	49.25
288.2	9.8	1.361	4.95	82.0	0.6	49.16
288.7	2.3	0.309	1.235	86.1	1.8	49.13
288.7	4.4	0.620	1.239	80.2	-4.2	49.13
290.7	2.7	0.309	1.235	98.6	1.5	49.01
292.6	3.1	0.309	1.235	112.2	1.5	48.89
293.2	13.5	1.320	4.95	115.4	0.0	48.86
293.6	3.2	0.310	1.239	113.7	-4.8	48.83
296.7	4.0	0.310	1.239	143.6	-2.4	48.64
297.6	13.2	0.984	2.512	151.3	-3.7	48.59
297.6	4.1	0.310	1.239	148.1	-6.9	48.59
300.6	5.2	0.310	1.239	184	-4.6	48.40
302.5	5.8	0.310	1.239	208.5	-4.5	48.28
305.6	7.1	0.310	1.239	256	-2.7	48.09
307.5	7.9	0.310	1.239	284.9	-5.8	47.98
307.6	24.8	0.942	2.512	293.2	0.8	47.97
307.6	9.8	0.365	1.46	302.6	10.2	47.97
310.6	8.2	0.253	1.011	364	13.5	47.79
310.6	9.6	0.310	1.239	346.4	-4.1	47.79
312.5	13.4	0.365	1.46	409.4	17.2	47.67
312.5	10.7	0.310	1.239	387.3	-4.8	47.67
315.6	12.9	0.310	1.239	464.2	-5.2	47.48
315.7	11.0	0.253	1.011	483.6	11.5	47.47
317.6	14.3	0.310	1.239	516	-10.0	47.36
317.7	12.3	0.253	1.011	542.7	13.7	47.35
319.6	16.6	0.310	1.239	596.8	8.4	47.23
4-Iodo-fluorobenzene: $\Delta_1^g H_m$ (298.15 K) = (49.6 ± 0.3) kJ mol ⁻¹						
$\ln(p/\text{Pa}) = \frac{269.9 \pm 1.5}{R} - \frac{67852 \pm 436}{R \times (T, \text{K})} - \frac{61.5 \pm 8.0}{R} \ln\left(\frac{T, \text{K}}{298.15}\right)$						
276.5	3.7	1.283	1.75	32.9	0.01	50.85
279.7	2.9	0.783	1.74	42.19	-0.16	50.65
283.9	2.3	0.435	1.74	59.18	0.78	50.40
283.9	2.7	0.525	1.05	58.6	0.19	50.40
286.5	2.9	0.464	1.74	71.44	0.56	50.24
289.4	2.7	0.353	1.06	85.32	-2.2	50.06
289.4	2.7	0.357	1.07	86.15	-1.38	50.06
293.3	1.8	0.177	1.06	116.33	0.97	49.82
298.1	3.1	0.212	1.06	163.81	3.67	49.52
303.0	1.8	0.089	1.07	219.81	-1.23	49.22
308.1	2.9	0.107	1.07	301.52	-3.64	48.91
312.9	3.3	0.089	1.07	412.14	3.47	48.61
317.9	4.4	0.089	1.07	546.97	-0.86	48.30

^a Saturation temperature ($u(T)=0.1$ K).

^b Mass of transferred sample m condensed at $T=243$ K.

^c Volume of nitrogen ($u(V)=0.005$ dm³) used to transfer m ($u(m)=0.0001$ g) of the sample.

^d Vapor pressure at temperature T , calculated from the m and the residual vapor pressure at $T=243$ K.

^e The combined standard uncertainty of vapor pressures measurements estimated to be within $u(p)/p=(2-3)\%$, taking into account uncertainties of all variables involved in Eq. (1).

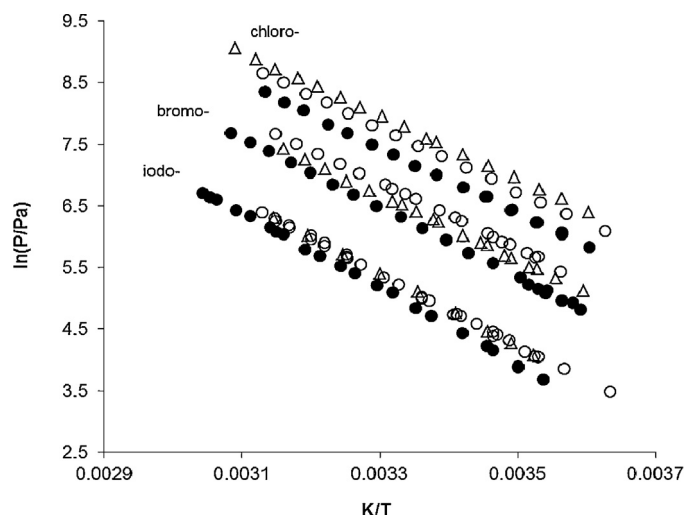


Fig. 1. Temperature dependences of experimental vapor pressures of halogen-substituted fluorobenzenes: ● – are *ortho* substituted benzenes; ○ – are *meta* substituted benzenes; △ – are *para* substituted benzenes.

A very consistent set of vaporization enthalpies measured directly by calorimetry [9] and indirectly [10,11] (from vapor pressure temperature dependence) was found for difluorobenzenes (see Table 4). Enthalpies of vaporization $\Delta_1^g H_m$ (298.15 K) for this series are close, but distinguishable for *ortho*-, *meta*- and *para*-isomers. However, the $\Delta_1^g H_m$ (298.15 K)-values for *ortho*-difluorobenzene are about 1–1.5 kJ mol⁻¹ higher. Similar trends are observed for all three another series of halogen-substituted fluorobenzenes. Surprisingly, independently on the size of halogen, all three *ortho*-isomers show $\Delta_1^g H_m$ (298.15 K) values, always by 1–1.5 kJ mol⁻¹ higher even in the case of the bulky *I*-substituent.

3.3. Evaluation of vaporization enthalpies $\Delta_1^g H_m$ (298.15 K) of halogen-fluorobenzenes

New experimental data have to be always tested for consistency with other data available in the literature. Structure-property analysis is a valuable tool for the data evaluation. For example, vaporization enthalpies $\Delta_1^g H_m$ (298.15 K) exhibit a good linear function of the number of carbon atoms in the chain of the homologous series of *n*-alkanes [12] or *n*-alkyl-nitriles [13]. Linear correlations of $\Delta_1^g H_m$ (298.15 K) of the geminal substituted azides [14] or aromatic ethers [15] with the data for similar structured molecules can be also used to evaluate the experimental data.

Correlations of vaporization enthalpies with the gas-chromatographic parameters such as Kovat's index [16] have been used to assess consistency of vaporization enthalpies measured for halogen-substituted benzenes [1,2] successfully. In this work we correlated vaporization enthalpies of halogen substituted fluorobenzenes as follows.

3.3.1. Correlation of vaporization enthalpies $\Delta_1^g H_m$ (298.15 K) of halogen-substituted benzenes with Kovat's indices

Kovat's index, J_x , is a unique characteristic of a compound measurable by gas-liquid chromatography. Correlation of Kovat's indices with the enthalpies of vaporization is helpful to reveal structure-property relations within series of parent compounds. For example, Kovat's indices on SE-30 reported [17] for isomers 1,2-difluorobenzene ($J_x = 681$) and 1,4-difluorobenzene ($J_x = 661$) suppose that enthalpy of vaporization of the 1,2-isomer is somewhat higher than for 1,4-isomer. This expectation is fulfilled by comparison of the averaged experimental $\Delta_1^g H_m$ (298.15 K) for these isomers given in Table 5. Similar observation was valid for 2-bromo-fluorobenzene ($J_x = 934$, $\Delta_1^g H_m = 47.0$ kJ mol⁻¹) and 4-bromo-fluorobenzenes ($J_x = 908$, $\Delta_1^g H_m = 44.0$ kJ mol⁻¹)

We collected Kovat's indices for some halogen-substituted benzenes in Table 5. The following linear empirical equation for the enthalpy of vaporization has been obtained:

Table 3
Compilation of data on molar heat capacities (in J mol⁻¹ K⁻¹) at 298.15 K of halogen-fluorobenzenes.

Compound	$C_{p,m}(\text{liq})$	$C_{p,m}(\text{g})^a$	$\Delta_1^g C_p$	Ref.
1,2-Di-fluorobenzene	159.0	104.66	54.3	[6]
1,3-Di-fluorobenzene	159.1	104.67	54.4	[7]
1,4-Di-fluorobenzene	157.5	104.73	52.8	[8]
2-Chloro-fluorobenzene	164.8	108.04	56.8	
3-Chloro-fluorobenzene	164.8	108.45	56.4	
4-Chloro-fluorobenzene	164.8	108.45	56.4	
2-Bromo-fluorobenzene	168.6	109.72	58.9	
3-Bromo-fluorobenzene	168.6	110.14	58.5	
4-Bromo-fluorobenzene	168.6	110.19	58.4	
2-Iodo-fluorobenzene	173.1	110.96 ^b	62.1	
3-Iodo-fluorobenzene	173.1	111.60 ^b	61.5	
4-Iodo-fluorobenzene	173.1	111.62 ^b	61.5	

^a Calculated using G4.

^b Calculated using b3lyp/6-311G(d,p).

Table 4
Compilation of data on enthalpies of vaporization, $\Delta_1^g H_m$, of the halogen substituted benzenes.

Compounds	Method ^a	T-range	$\Delta_1^g H_m$ at T_{av}	$\Delta_1^g H_m$ at 298.15 K ^b	Ref.
1,2-Difluoro-benzene	C	367.1	32.21	36.2 ± 0.7	[9]
	E	304.3–403.4	34.5	36.2 ± 0.4	[8]
				37.2 ± 0.3	[6]
1,3-Difluoro-benzene	C	355.7	31.1	36.8 ± 0.2^c	Average
				34.2 ± 0.7	[9]
				34.5 ± 0.5	[10]
1,4-Difluoro-benzene	E	311.3–391.5		34.7 ± 0.4	[8]
				35.7 ± 0.3	[11]
	C	362	31.8	35.1 ± 0.2^c	Average
2-Chloro-fluorobenzene				35.1 ± 0.7	[9]
				35.7 ± 0.5	[10]
				35.6 ± 0.4	[8]
3-Chloro-fluorobenzene	E	300.4–397.7		36.5 ± 0.3	[11]
				36.0 ± 0.2^c	Average
	T	277.5–319.2	44.0 ± 0.2	44.0 ± 0.3	This work
4-Chloro-fluorobenzene				(39.2 ± 3.0)	[20]
	T	275.8–319.5	43.1 ± 0.2	43.0 ± 0.3	This work
2-Bromo-fluorobenzene	T	277.6–323.5	42.7 ± 0.2	42.8 ± 0.3	This work
3-Bromo-fluorobenzene	T	278.5–324.3	47.0 ± 0.2	47.0 ± 0.3	This work
4-Bromo-fluorobenzene	T	280.8–317.6	44.0 ± 0.2	44.3 ± 0.3	This work
2-Iodo-fluorobenzene	T	278.2–316.4	44.1 ± 0.3	44.0 ± 0.4	This work
3-Iodo-fluorobenzene	T	282.8–328.6	50.8 ± 0.24	51.5 ± 0.3	This work
4-Iodo-fluorobenzene	T	275.2–319.6	48.5 ± 0.23	48.6 ± 0.3	This work
Fluorobenzene				49.5 ± 0.3	This work
Chlorobenzene				35.01 ± 0.30	
Bromobenzene				41.76 ± 0.30	
Iodobenzene				44.29 ± 0.10	
				48.86 ± 0.48	

^a Methods: C, calorimetry; E, ebulliometry; T, transpiration method.

^b Uncertainties of vaporization enthalpies are expressed in this table as standard deviations $u_{\text{final}}(\Delta_1^g H_m)$ (see text). Real uncertainties of literature data were evaluated in this work. Value in brackets was not taken into account.

^c Average value calculated using the uncertainty as the weighting factor.

$$\Delta_1^g H_m(298.15\text{K}) / (\text{kJ mol}^{-1}) = 8.48 + 0.0404 \times J_x$$

with ($R^2 = 0.991$) (4)

where J_x is the Kovat's index of a substituted benzene on the SE-30 stationary phase and R^2 is the correlation coefficient. This linear relationship can be considered as a proof of internal consistency of our new experimental results for vaporization enthalpies. Moreover, this relationship can be used to assess enthalpies of vaporization of the parent substituted benzenes provided that their Kovat's indices are known.

3.3.2. Estimation of $\Delta_1^g H_m(298.15\text{K})$ of halogen-substituted benzenes by group contribution method

Another possibility to prove internal consistency of new vaporization enthalpies is to use the group-additivity procedure developed in our previous work [1,2]. In short, the difference between vaporization enthalpies of fluorobenzene and benzene provides the increment $\Delta H(H \rightarrow F)$ for substitution of H atom on the benzene ring by F substituent. Introduction of the second fluorine atom into the benzene ring requires few additional increments *ortho*(F–F), *para*(F–F), and *meta*(F–F), taking into account the mutual interactions of substituents on the benzene

Table 5
Compilation of Kovat's indices of methylbenzenes and halogen-benzenes measured on a non-polar SE-30 column with a temperature program starting from 313 K for 4 min and a heating rate of 10K/min to 473 K.^a

Compound	J_x	$\Delta_1^g H_m$ (298.15 K) kJ mol ⁻¹ , exp.	$\Delta_1^g H_m$ (298.15 K) kJ mol ⁻¹ , Eq. (4)	Δ
1	2	3	4	5
Fluorobenzene	664	35.0	35.3	-0.3
Chlorobenzene	839	41.8	42.4	-0.6
1-Fluoro-3-methylbenzene	774	39.0	39.7	-0.7
1,2-Difluorobenzene	681	36.8	36.0	0.8
1,4-Difluorobenzene	666	36.0	35.4	0.6
4-Chloro-fluorobenzene	827	42.3	41.9	0.4
2-Bromo-fluorobenzene	934	47.0	46.2	0.8
4-Bromo-fluorobenzene	901	44.0	44.9	-0.9
1-Iodo-2-fluorobenzene	1053	51.5	51.0	0.5
1,2-Dichlorobenzene	1001	48.8	48.9	-0.1
1,3-Dichlorobenzene	995	47.7	48.7	-1.0
1,4-Dichlorobenzene	994	47.6	48.6	-1.0
1,3,5-Trichlorobenzene	1146	55.6	54.8	0.8
1,2,4-Trichlorobenzene	1160	55.3	55.3	0.0
1,2,3-Trichlorobenzene	1214	57.6	57.5	0.1

^a Data for J_x from Ref. [17].

Table 6Parameters for the calculation of enthalpies of vaporization $\Delta_1^g H_m(298.15\text{ K})$ of halogen-substituted benzenes.

Group contribution	Value, kJ mol^{-1}
Benzene	33.9 [19]
$\Delta H(\text{H} \rightarrow \text{F})$	0.8 [1]
$\Delta H(\text{H} \rightarrow \text{Cl})$	7.9 [1]
$\Delta H(\text{H} \rightarrow \text{Br})$	10.4 [2]
$\Delta H(\text{H} \rightarrow \text{I})$	14.9 [2]
<i>ortho</i> F- <i>Hal</i>	1.5
<i>meta</i> F-(F or Cl)	0.0
<i>meta</i> F-(Br or I)	-1.0
<i>para</i> F-(F or Cl)	0.4
<i>para</i> F-(Br or I)	-0.5

ring. The following general formula for calculation of vaporization enthalpy of polyhalogen-substituted benzenes at 298.15 K can be suggested (e.g., for polyfluorobenzene):

$$\Delta_1^g H_m(\text{polyfluorobenzene}) = \Delta_1^g H_m(\text{B}) + n_a \times \Delta H(\text{H} \rightarrow \text{F}) + n_b \times \textit{ortho}(\text{F} - \text{F}) + n_c \times \textit{para}(\text{F} - \text{F}) + n_d \times \textit{meta}(\text{F} - \text{F}) \quad (5)$$

where $\Delta_1^g H_m(\text{B})$ is vaporization enthalpy of benzene; $\Delta H(\text{H} \rightarrow \text{F})$ is an increment of $\text{H} \rightarrow \text{F}$ substitutions on the benzene ring. The mutual interactions of the F atoms were taken into account through the three types of corrections in *ortho*-, *para*-, and *meta*-position on the benzene ring. n_a , n_b , n_c , n_d are the quantities of the corresponding increments and interactions. Similar approach is valid [1,2,18] for any kind of poly-substitution of the benzene ring (e.g., $\Delta H(\text{H} \rightarrow \text{Hal})$ for $\text{Hal} = \text{F}, \text{Cl}, \text{Br}$ and I in this work). Such a simple substitution pattern could be also applied to the toluene, xylenes, or poly-methyl benzenes using the increment $\Delta H(\text{H} \rightarrow \text{CH}_3)$ for methyl substituent and the appropriately modified Eq. (5) with the pairwise interactions parameters specific for methyl group, e.g., *ortho*($\text{CH}_3 - \text{CH}_3$), *para*($\text{CH}_3 - \text{CH}_3$), and *meta*($\text{CH}_3 - \text{CH}_3$) as it has been described earlier [1,2].

We used the experimental enthalpies $\Delta_1^g H_m(298.15\text{ K})$ of benzene (33.92 ± 0.06) kJ mol^{-1} , [19], and halogen benzenes (Table 4) in order to derive increments $\Delta H(\text{H} \rightarrow \text{Hal})$. We used new vaporization enthalpies of halogen-substituted fluorobenzenes in order to derive parameters for mutual interactions of substituents on the benzene ring (see Table 6).

Parameters required for estimation of vaporization enthalpies of halogen-substituted benzenes are listed in Table 6, column 1. It has turned out, that contributions to $\Delta_1^g H_m(298.15\text{ K})$ from interactions of the F with the *Hal*-substituent were as follows: *ortho*-interactions (in kJ mol^{-1}) $\text{F} (1.3) < \text{Cl} (1.4) < \text{Br} (1.9) = \text{I} (1.9)$. For all *meta*- and *para*-interactions of the F with the *Hal*-substituent very small contributions mostly less than 1 kJ mol^{-1} were observed. For the sake of simplicity we decided to reduce the

number of parameters required for prediction vaporization enthalpies of halogen-substituted benzenes. Considering uncertainties of the parameters derived in Table 5 at the level of 0.5 kJ mol^{-1} we have averaged the mutual interactions and some of them neglected for the sake of brevity.

Comparison of the experimental and estimated vaporization enthalpies (see Table 7) has revealed that the average deviation of experimental and calculated vaporization enthalpies on the level of 0.5 kJ mol^{-1} are quite comparable with the experimental uncertainties of the most entries in Table 1. Following, the enthalpies of vaporization of the mono- and dihalogen-substituted benzenes can be predicted with acceptable accuracy using the reduced Eq. (5) with only basic increments $\Delta H(\text{H} \rightarrow \text{Hal})$ and with few additional increments responsible for the mutual (*Hal-Hal*) interactions.

4. Conclusion

Experimental vapor pressures and vaporization enthalpies of the series of nine halogen-substituted fluorobenzenes have been taken as a basis for evaluation of new and available in the literature data. We used the correlation GC method to establish consistency of the experimental data. The simple group-contribution procedure was developed for calculation enthalpies of vaporization of halogen-substituted benzenes which also proved the internal consistency of our experimental data. Parameters of this procedure should be transferable for prediction of vaporization enthalpies of halogenated polyaromatic compounds, dibenzodioxins or dibenzofurans.

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Table 7Comparison of experimental vaporization enthalpies, $\Delta_1^g H_m(298.15\text{ K})$, and those estimated using the group additivity (all values are in kJ mol^{-1}).

Compound	$\Delta_1^g H_m$ exp.	$\Delta_1^g H_m$ Eq. (5)	Exp.-calc.
1,2-Difluorobenzene	36.8	37.0	-0.2
1,3-difluorobenzene	35.1	35.5	-0.4
1,4-Difluorobenzene	36.0	35.9	0.1
2-Chloro-fluorobenzene	44.0	44.1	-0.1
3-Chloro-fluorobenzene	43.0	42.6	0.4
4-Chloro-fluorobenzene	42.8	43.0	-0.2
2-Bromo-fluorobenzene	47.0	46.6	0.4
3-Bromo-fluorobenzene	44.3	44.1	0.2
4-Bromo-fluorobenzene	44.0	44.6	-0.6
2-Iodo-fluorobenzene	51.5	51.1	0.4
3-Iodo-fluorobenzene	48.6	48.6	0.0
4-Iodo-fluorobenzene	49.5	49.1	0.4

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