J. Chem. Eng. Data **2007,** *52,* 499−510

Thermochemistry of Chlorobenzenes and Chlorophenols: Ambient Temperature Vapor Pressures and Enthalpies of Phase Transitions

Sergey P. Verevkin* and Vladimir N. Emel'yanenko

Department of Physical Chemistry, University of Rostock, 18051 Rostock, Germany

Andreas Klamt

COSMOlogic GmbH&CoKG, 515 Burscheider Strasse, 51381 Leverkusen, Germany, and Institute of Physical Chemistry, University of Regensburg, 93040 Regensburg, Germany

This work has been undertaken in order to obtain additional data on vapor pressures of chlorobenzene derivatives and to develop the group-additivity values necessary for predicting their vaporization enthalpies at the reference temperature $T = 298.15$ K. Molar enthalpies of sublimation and of vaporization of hexachlorobenzene and of mono-, di-, tri-, and pentachlorophenol were obtained from the temperature dependence of the vapor pressure measured by the transpiration method. Thermochemical investigations of chlorobenzenes and chlorophenols available in the literature were collected and combined with our own experimental results to obtain their reliable standard molar enthalpies of vaporizaton at $T = 298.15$ K. The COSMO-RS procedure has been used for a priori prediction of the vapor pressures and vaporization enthalpies of the whole data set of chlorobenzenes and chlorophenols. The new results help to resolve uncertainties in the available thermochemical data on chlorobenzenes and chlorophenols studied.

Introduction

In order to predict the environmental behavior of organic compounds, knowledge of their chemical and physical properties is required. Vapor pressure is one of the fundamental properties that governs the distribution of organic compounds in the environment. Evaporation from soils and vapor−particle equilibria in the atmosphere depend on vapor pressure. Chlorinated benzenes and phenols are long-lived pollutants frequently found in industrial effluents. Thermochemistry of chlorobenzenes has attracted much attention the past decade,[1−5] and a set of reliable vapor pressures and phase transitions for di- and poly-chlorinated benzenes was recommended recently.[4,5] However, only very few experimental vapor pressures of chlorophenols are known from the literature.[6−10] We report here a systematic determination of the vapor pressures and vaporization enthalpies of a series of mono-, di-, tri-, and pentachlorophenols as well as hexachlorobenzene by using the transpiration method.

Experimental Section

Materials. Samples of chlorophenols were of commercial origin (Aldrich, Fluka). The solid chlorophenols were purified by repeated sublimation in vacuum. The liquid 2-chlorophenol was purified by repeated distillation using a spinning-band column under reduced pressure. The degree of purity was determined 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 $\text{cm}^3 \cdot \text{s}^{-1}$. A capillary column HP-5 (stationary phase cross-linked 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 $T = 333$ K for 180 s followed by a heating rate of 0.167 $\text{K} \cdot \text{s}^{-1}$ to $T = 523$ K. No total impurities (greater than mass fraction 0.003) could be detected in the samples used for the vapor pressure measurements.

Measurements of the Enthalpies of Sublimation and Enthalpies Vaporization Using the Transpiration Method. Vapor pressures, enthalpies of sublimation, and enthalpies of vaporization of the chlorobenzene derivatives (see Table 1) were determined using the transpiration method.[11−12] This method involves the generation of a saturated vapor phase by passing a N_2-stream through the pure compound, which is coated on the inert support. About 0.5 g of the sample was mixed with glass beads and placed in a thermostatted U-tube of length 20 cm and diameter 0.5 cm. A nitrogen stream was passed through the U-tube at constant temperature (± 0.1 K), and the transported amount of material was condensed in a cooled trap. The amount of condensed product was determined by GLC analysis using an external standard (hydrocarbon). The saturation vapor pressure (p_i^{sat}) at each temperature (T_i) was calculated from the amount of product collected within a definite period of time, and the small value of the residual vapor pressure at the temperature of condensation was added. The latter was calculated from a linear correlation between $\ln(p_i^{\text{sat}})$ and T^{-1} obtained by iteration. Assuming that Dalton's law of partial pressures applied to the nitrogen stream saturated with the substance i of interest is valid, values of p_i^{sat} were calculated:

$$p_i^{\text{sat}} = m_i R T_a / V M_i; \quad V = V_{N_2} + V_i; \quad (V_{N_2} \gg V_i) \qquad (1)$$

where $R = 8.314472$ $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; m_i is the mass of transported compound, M_i is the molar mass of the compound, and V_i is its

---

* To whom correspondence should be addressed. E-mail: sergey.verevkin@uni-rostock.de. Phone: +49-381-498-6508. Fax: +49-381-498-6502.

10.1021/je060429r CCC: $37.00

Table 1. Vapor Pressures *p*, Enthalpies of Sublimation $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}$, or Enthalpies of Vaporization $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ Obtained by the Transpiration Method

T^{a}	m^{b}	$V(\mathrm{N_2})^{c}$	flow	p^{d}	$p_{\mathrm{exp}} - p_{\mathrm{calc}}$	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}$ or $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$	T^{a}	m^{b}	$V(\mathrm{N_2})^{c}$	flow	p^{d}	$p_{\mathrm{exp}} - p_{\mathrm{calc}}$	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}$ or $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$
K	mg	dm^3	dm^3·h^{-1}	Pa	Pa	kJ·mol^{-1}	K	mg	dm^3	dm^3·h^{-1}	Pa	Pa	kJ·mol^{-1}
Hexachlorobenzene:[e] $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K) = (96.76 ± 0.49) kJ·mol^{-1}													
$\ln(p/\mathrm{Pa}) = \frac{304.7}{R} - \frac{105968.6}{R(T/\mathrm{K})} - \frac{30.9}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$													
358.0	10.40	62.73	7.21	1.44	0.00	94.91	382.9	10.80	8.29	7.21	11.23	−0.11	94.14
362.9	14.70	59.00	7.21	2.16	−0.05	94.76	389.0	21.40	10.09	7.21	18.36	0.35	93.95
368.9	11.50	26.52	7.20	3.73	0.05	94.57	392.8	14.60	5.29	7.21	23.80	−0.06	93.83
373.1	11.60	19.35	7.21	5.19	−0.02	94.44	397.9	13.00	3.36	7.21	33.41	−1.06	93.68
377.8	11.50	12.84	7.20	7.71	0.11	94.30	402.8	13.60	2.40	7.21	49.01	0.39	93.52
2-Chlorophenol: $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K) = (52.34 ± 0.22) kJ·mol^{-1}													
$\ln(p/\mathrm{Pa}) = \frac{285.8}{R} - \frac{72345.6}{R(T/\mathrm{K})} - \frac{67.1}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$													
288.4	12.02	2.71	2.43	86.3	−0.9	53.00	306.2	10.39	0.648	2.43	308.3	−2.4	51.80
291.3	9.67	1.70	2.43	110.2	1.7	52.80	309.2	9.12	0.466	2.43	376.3	−2.1	51.60
294.3	8.94	1.26	2.43	137.8	2.2	52.60	312.2	8.80	0.365	2.43	463.3	4.5	51.40
297.3	9.52	1.09	2.43	168.1	−0.2	52.40	315.2	8.83	0.304	2.43	557.9	4.2	51.20
300.3	9.30	0.871	2.43	205.9	−2.0	52.20	318.2	7.02	0.203	2.43	664.9	−0.6	51.00
303.3	10.50	0.790	2.43	255.9	0.2	52.00	321.2	5.07	0.122	2.43	799.2	2.6	50.80
3-Chlorophenol: $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K) = (76.87 ± 0.25) kJ·mol^{-1}													
$\ln(p/\mathrm{Pa}) = \frac{303.6}{R} - \frac{84617.1}{R(T/\mathrm{K})} - \frac{26.0}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$													
275.3	1.35	31.99	2.59	0.82	0.01	77.46	291.3	1.38	5.21	2.63	5.09	−0.09	77.04
276.6	1.61	32.75	2.62	0.95	0.00	77.43	294.3	1.99	5.30	2.61	7.21	0.05	76.97
278.3	1.63	27.35	2.60	1.15	−0.02	77.38	297.3	2.03	3.89	2.61	9.99	0.15	76.89
280.3	2.92	37.74	2.59	1.49	0.01	77.33	300.3	1.79	2.58	2.61	13.23	−0.20	76.81
283.2	1.16	10.49	2.61	2.12	0.04	77.26	302.2	1.70	2.00	2.61	16.26	−0.03	76.76
285.2	1.44	10.52	2.63	2.62	0.00	77.20	306.0	1.65	1.32	2.63	23.95	0.14	76.66
288.3	1.45	7.63	2.63	3.66	−0.06	77.12							
3-Chlorophenol: $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K) = (63.52 ± 0.34) kJ·mol^{-1}													
$\ln(p/\mathrm{Pa}) = \frac{302.9}{R} - \frac{84036.8}{R(T/\mathrm{K})} - \frac{68.8}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$													
308.3	2.08	1.36	2.63	29.4	0.2	62.83	323.2	2.59	0.548	2.63	90.5	0.9	61.80
311.1	2.07	1.10	2.63	36.1	−0.3	62.64	326.2	2.55	0.438	2.63	111.6	0.9	61.60
314.2	2.35	0.986	2.63	45.5	−0.7	62.42	329.2	2.50	0.351	2.63	136.6	0.5	61.39
317.2	2.59	0.855	2.63	58.0	0.1	62.22	332.2	2.29	0.263	2.63	166.9	0.3	61.18
320.3	2.59	0.679	2.63	73.0	0.3	62.00	335.2	2.29	0.219	2.63	200.2	−2.8	60.98
4-Chlorophenol: $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K) = (77.13 ± 0.23) kJ·mol^{-1}													
$\ln(p/\mathrm{Pa}) = \frac{297.9}{R} - \frac{84019.4}{R(T/\mathrm{K})} - \frac{23.1}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$													
283.2	1.99	29.04	2.39	1.32	−0.01	77.48	303.2	2.64	4.34	2.39	11.63	0.06	77.02
288.2	0.29	2.35	2.39	2.36	0.01	77.36	306.2	2.71	3.31	2.39	15.71	0.09	76.95
291.2	1.29	7.45	2.39	3.32	0.04	77.29	309.2	3.09	2.85	2.39	20.76	−0.18	76.88
294.2	1.68	7.01	2.39	4.59	0.05	77.22	311.2	2.40	1.81	2.39	25.35	−0.02	76.83
297.2	1.90	5.86	2.39	6.22	−0.02	77.16	313.2	2.64	1.63	2.39	30.92	0.25	76.79
300.2	2.29	5.22	2.39	8.39	−0.14	77.09							
4-Chlorophenol: $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K) = (64.42 ± 0.27) kJ·mol^{-1}													
$\ln(p/\mathrm{Pa}) = \frac{304.8}{R} - \frac{85264.7}{R(T/\mathrm{K})} - \frac{69.9}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$													
318.2	2.11	0.833	2.38	48.5	0.1	63.03	336.2	3.70	0.417	2.38	169.9	−1.4	61.77
321.2	2.10	0.655	2.38	61.5	1.0	62.82	339.2	3.35	0.317	2.38	202.2	−6.0	61.56
324.2	2.34	0.595	2.38	75.4	0.2	62.61	342.2	4.46	0.337	2.38	253.4	1.4	61.35
327.2	2.69	0.555	2.38	92.6	−0.4	62.40	345.2	4.12	0.258	2.38	305.8	1.9	61.14
330.2	2.96	0.496	2.38	114.1	−0.4	62.19	348.2	4.20	0.218	2.38	368.4	3.4	60.93
333.2	2.88	0.397	2.38	138.8	−1.5	61.98	351.2	4.57	0.198	2.38	440.9	4.2	60.72
2,3-Dichlorophenol: $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K) = (76.93 ± 0.37) kJ·mol^{-1}													
$\ln(p/\mathrm{Pa}) = \frac{303.2}{R} - \frac{84294.8}{R(T/\mathrm{K})} - \frac{24.7}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$													
294.3	1.97	3.84	2.65	7.8	−0.1	77.03	312.2	2.82	0.882	2.65	48.2	0.9	76.58
297.3	2.22	3.13	2.65	10.7	0.0	76.95	315.2	2.78	0.662	2.65	63.3	0.7	76.51
300.2	2.65	2.69	2.65	14.9	0.4	76.88	318.1	3.03	0.574	2.65	79.8	−1.9	76.44
303.2	2.52	1.98	2.65	19.2	−0.5	76.81	321.2	3.37	0.471	2.65	108.1	0.1	76.36
306.2	2.73	1.54	2.65	26.7	0.2	76.73	324.3	4.18	0.441	2.65	142.9	1.0	76.29
309.2	3.07	1.32	2.65	35.1	−0.4	76.66	327.3	5.36	0.441	2.65	183.5	−0.4	76.21

Table 1. (Continued)

T^a	m^b	$V(N_2)^c$	flow	p^d	$p_{exp} - p_{calc}$	$\Delta_{cr}^{g}H_m$ or $\Delta_{l}^{g}H_m$	T^a	m^b	$V(N_2)^c$	flow	p^d	$p_{exp} - p_{calc}$	$\Delta_{cr}^{g}H_m$ or $\Delta_{l}^{g}H_m$
K	mg	dm^3	$dm^3 \cdot h^{-1}$	Pa	Pa	$kJ \cdot mol^{-1}$	K	mg	dm^3	$dm^3 \cdot h^{-1}$	Pa	Pa	$kJ \cdot mol^{-1}$
2,3-Dichlorophenol: $\Delta_{l}^{g}H_m$ (298.15 K) = (57.34 ± 0.20) $kJ \cdot mol^{-1}$													
$\ln(p/\mathrm{Pa}) = \frac{292.4}{R} - \frac{79130.2}{R(T/\mathrm{K})} - \frac{73.1}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$													
331.2	9.78	0.603	2.65	244.9	0.4	54.92	346.2	10.07	0.265	2.65	574.5	−0.7	53.83
334.3	10.33	0.529	2.65	294.6	0.6	54.70	349.2	9.73	0.221	2.65	666.2	−9.1	53.61
337.2	9.23	0.397	2.65	350.8	2.7	54.48	352.1	11.52	0.221	2.65	788.1	2.1	53.40
340.3	9.06	0.331	2.65	413.2	−2.2	54.26	355.2	14.19	0.232	2.65	924.7	3.3	53.17
343.2	8.55	0.265	2.65	487.4	−0.9	54.05	358.2	15.76	0.221	2.65	1078.3	7.3	52.95
2,4-Dichlorophenol: $\Delta_{cr}^{g}H_m$ (298.15 K) = (77.96 ± 0.30) $kJ \cdot mol^{-1}$													
$\ln(p/\mathrm{Pa}) = \frac{309.5}{R} - \frac{85326.1}{R(T/\mathrm{K})} - \frac{24.7}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$													
278.2	4.49	39.08	2.83	1.75	0.04	78.46	303.3	4.53	2.44	2.82	28.01	0.00	77.84
283.3	7.72	37.53	2.79	3.12	−0.03	78.33	306.3	4.49	1.76	2.82	38.48	0.58	77.76
289.3	4.86	11.75	2.82	6.26	0.00	78.18	309.4	4.86	1.41	2.82	52.08	0.62	77.69
294.4	5.20	7.25	2.79	10.82	−0.18	78.06	312.4	5.65	1.25	2.82	68.48	−0.28	77.61
297.3	3.87	3.99	2.82	14.64	−0.37	77.98	315.2	5.49	0.917	2.82	90.34	0.67	77.54
300.4	5.61	4.18	2.82	20.25	−0.54	77.91							
2,4-Dichlorophenol: $\Delta_{l}^{g}H_m$ (298.15 K) = (58.97 ± 0.42) $kJ \cdot mol^{-1}$													
$\ln(p/\mathrm{Pa}) = \frac{298.0}{R} - \frac{80763.4}{R(T/\mathrm{K})} - \frac{73.1}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$													
317.2	10.29	1.46	2.84	106.1	−0.6	57.58	332.2	14.18	0.756	2.84	283.1	−0.3	56.48
320.3	11.61	1.32	2.84	132.6	0.8	57.35	335.2	13.80	0.614	2.84	339.3	−1.0	56.26
323.2	12.60	1.18	2.84	161.2	1.3	57.14	338.2	12.60	0.473	2.84	402.7	−4.2	56.04
326.1	13.31	1.04	2.84	193.3	0.3	56.93	341.2	10.62	0.331	2.84	484.6	−0.1	55.83
329.2	14.38	0.898	2.84	241.9	6.8	56.70	344.2	7.31	0.189	2.84	583.5	8.3	55.61
2,5-Dichlorophenol: $\Delta_{cr}^{g}H_m$ (298.15 K) = (77.25 ± 0.14) $kJ \cdot mol^{-1}$													
$\ln(p/\mathrm{Pa}) = \frac{305.3}{R} - \frac{84617.0}{R(T/\mathrm{K})} - \frac{24.7}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$													
294.3	2.58	4.39	2.83	8.9	0.1	77.35	312.2	7.98	2.26	2.83	53.2	−0.3	76.91
297.3	3.16	3.91	2.83	12.2	0.1	77.27	315.2	6.42	1.37	2.83	70.8	−0.1	76.83
300.4	3.99	3.58	2.83	16.8	0.1	77.20	318.3	6.64	1.06	2.83	94.4	0.0	76.76
303.3	4.81	3.25	2.83	22.3	−0.1	77.13	321.3	7.07	0.849	2.83	125.7	2.0	76.68
306.3	5.86	2.92	2.83	30.2	0.0	77.05	324.4	7.16	0.660	2.83	163.6	0.9	76.61
309.2	6.85	2.59	2.83	39.9	−0.2	76.98	327.4	6.33	0.448	2.83	213.3	2.2	76.53
2,5-Dichlorophenol: $\Delta_{l}^{g}H_m$ (298.15 K) = (56.69 ± 0.14) $kJ \cdot mol^{-1}$													
$\ln(p/\mathrm{Pa}) = \frac{291.6}{R} - \frac{78487.1}{R(T/\mathrm{K})} - \frac{73.1}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$													
333.3	14.98	0.708	2.83	319.8	0.4	54.13	349.2	16.72	0.330	2.83	764.3	−5.8	52.96
337.2	14.98	0.566	2.83	399.6	−0.5	53.84	352.2	16.76	0.283	2.83	894.0	−5.3	52.74
340.2	14.76	0.472	2.83	472.6	−1.2	53.62	355.2	18.02	0.259	2.83	1048.5	1.8	52.53
343.2	15.50	0.425	2.83	551.3	−7.7	53.40	358.1	19.19	0.241	2.83	1204.3	−4.3	52.31
346.2	16.28	0.377	2.83	651.4	−5.8	53.18	361.2	22.36	0.241	2.83	1403.3	−1.7	52.09
2,6-Dichlorophenol: $\Delta_{cr}^{g}H_m$ (298.15 K) = (79.33 ± 0.16) $kJ \cdot mol^{-1}$													
$\ln(p/\mathrm{Pa}) = \frac{307.0}{R} - \frac{86691.6}{R(T/\mathrm{K})} - \frac{24.7}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$													
298.5	2.26	4.668	2.80	7.3	0.0	79.32	316.4	5.13	1.772	2.80	43.7	−0.5	78.88
301.6	3.11	4.690	2.80	10.0	−0.1	79.24	319.4	5.75	1.470	2.80	59.1	0.5	78.80
304.6	2.73	3.010	2.80	13.7	−0.1	79.17	322.4	6.35	1.238	2.80	77.4	0.2	78.73
307.4	4.24	3.500	2.80	18.3	−0.1	79.10	325.4	7.00	1.050	2.80	100.6	−0.6	78.66
310.4	4.70	2.892	2.80	24.5	−0.2	79.03	328.4	6.70	0.770	2.80	131.2	−0.7	78.58
313.4	4.61	2.100	2.80	33.1	0.0	78.95	331.3	6.25	0.560	2.80	168.5	−1.3	78.51
2,6-Dichlorophenol: $\Delta_{l}^{g}H_m$ (298.15 K) = (59.58 ± 0.32) $kJ \cdot mol^{-1}$													
$\ln(p/\mathrm{Pa}) = \frac{296.9}{R} - \frac{81374.5}{R(T/\mathrm{K})} - \frac{73.1}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$													
341.2	16.03	0.703	2.81	344.4	2.1	56.44	356.3	13.27	0.259	2.81	774.5	−14.6	55.33
344.7	15.53	0.562	2.81	417.3	−1.5	56.18	360.3	15.04	0.233	2.81	973.4	2.8	55.04
347.3	15.04	0.469	2.81	483.8	−1.0	55.99	363.3	19.58	0.259	2.81	1143.1	13.8	54.82
350.3	15.14	0.399	2.81	572.7	0.4	55.77	366.3	20.32	0.233	2.81	1314.9	5.0	54.60
353.3	13.56	0.303	2.81	674.5	1.3	55.55	371.4	20.76	0.188	2.81	1664.4	−9.8	54.23

Table 1. (Continued)

T^a	m^b	$V(N_2)^c$	flow	p^d	$p_{exp} - p_{calc}$	$\Delta_{cr}^{g}H_m$ or $\Delta_{l}^{g}H_m$	T^a	m^b	$V(N_2)^c$	flow	p^d	$p_{exp} - p_{calc}$	$\Delta_{cr}^{g}H_m$ or $\Delta_{l}^{g}H_m$
K	mg	dm^3	$dm^3 \cdot h^{-1}$	Pa	Pa	$kJ \cdot mol^{-1}$	K	mg	dm^3	$dm^3 \cdot h^{-1}$	Pa	Pa	$kJ \cdot mol^{-1}$
3,4-Dichlorophenol: $\Delta_{cr}^{g}H_m$ (298.15 K) = (89.79 ± 0.37) $kJ \cdot mol^{-1}$ $\ln(p/Pa) = \frac{322.2}{R} - \frac{97139.7}{R(T/K)} - \frac{24.7}{R}\ln\left(\frac{T/K}{298.15}\right)$													
291.4	0.72	40.13	2.81	0.27	−0.01	89.94	320.4	2.12	3.96	2.83	8.06	0.15	89.23
294.3	0.95	36.07	2.84	0.40	0.00	89.87	323.3	2.07	2.92	2.83	10.69	0.01	89.16
300.3	0.95	16.60	2.83	0.86	0.03	89.72	326.3	2.14	2.19	2.83	14.74	0.25	89.08
303.5	0.89	11.19	2.81	1.21	−0.01	89.64	329.3	2.52	1.91	2.83	19.92	0.37	89.01
306.7	0.60	5.08	2.81	1.77	0.00	89.57	332.3	3.07	1.77	2.83	26.18	−0.03	88.93
309.5	2.10	12.83	2.83	2.47	0.05	89.50	335.3	1.98	0.873	2.83	34.23	−0.73	88.86
314.3	1.38	4.92	2.81	4.23	0.11	89.38	337.3	1.73	0.637	2.83	40.96	−1.26	88.81
317.2	1.60	4.12	2.81	5.87	0.23	89.31							
3,4-Dichlorophenol: $\Delta_{l}^{g}H_m$ (298.15 K) = (70.84 ± 0.15) $kJ \cdot mol^{-1}$ $\ln(p/Pa) = \frac{315.0}{R} - \frac{92633.5}{R(T/K)} - \frac{73.1}{R}\ln\left(\frac{T/K}{298.15}\right)$													
341.3	2.75	0.728	2.91	57.0	−0.4	67.69	356.3	4.22	0.412	2.91	154.4	−1.2	66.59
344.3	2.94	0.631	2.91	70.3	−0.4	67.47	359.2	4.16	0.338	2.91	185.8	−0.6	66.38
347.2	3.16	0.558	2.91	85.4	−0.6	67.26	362.2	4.30	0.291	2.91	223.0	−1.1	66.16
350.3	3.73	0.533	2.91	105.5	−0.2	67.03	365.4	5.20	0.291	2.91	269.6	−1.9	65.93
353.2	3.67	0.437	2.91	127.0	−0.6	66.82	368.4	5.69	0.267	2.91	321.7	−2.2	65.71
2,4,6-Trichlorophenol: $\Delta_{cr}^{g}H_m$ (298.15 K) = (82.26 ± 0.29) $kJ \cdot mol^{-1}$ $\ln(p/Pa) = \frac{306.3}{R} - \frac{90278.2}{R(T/K)} - \frac{26.9}{R}\ln\left(\frac{T/K}{298.15}\right)$													
299.4	1.33	9.84	4.92	1.77	0.02	82.23	320.3	3.44	2.87	4.92	15.00	0.07	81.66
316.8	1.40	1.68	4.92	10.44	−0.20	81.76	323.3	3.38	2.10	5.04	20.13	0.29	81.58
316.8	1.80	2.13	4.92	10.61	−0.03	81.76	326.3	3.56	1.68	5.04	26.45	0.22	81.50
302.3	1.57	8.28	4.92	2.45	0.06	82.15	329.4	3.99	1.43	5.04	34.88	0.08	81.42
305.2	1.59	6.35	4.92	3.19	−0.07	82.07	332.5	4.42	1.22	5.04	45.31	−0.60	81.34
308.3	1.69	4.88	4.92	4.40	−0.11	81.99	335.5	5.35	1.13	5.04	58.82	−0.90	81.25
311.3	1.81	3.85	4.92	5.93	−0.22	81.91	338.2	5.06	0.840	5.04	75.13	−0.22	81.18
314.3	2.07	3.24	4.92	8.05	−0.25	81.82	340.3	5.14	0.714	5.04	89.78	−0.26	81.13
317.3	2.61	2.91	4.92	11.25	0.08	81.74							
2,4,6-Trichlorophenol: $\Delta_{l}^{g}H_m$ (298.15 K) = (67.16 ± 0.27) $kJ \cdot mol^{-1}$ $\ln(p/Pa) = \frac{313.6}{R} - \frac{90597.1}{R(T/K)} - \frac{78.6}{R}\ln\left(\frac{T/K}{298.15}\right)$													
342.8	3.76	0.458	0.90	102.7	2.4	63.66	359.4	4.52	0.203	0.90	278.4	−0.3	62.35
343.2	5.62	0.675	0.89	104.1	1.1	63.63	359.4	4.52	0.203	0.90	278.4	−0.3	62.35
343.8	3.54	0.408	1.63	108.1	1.1	63.58	360.5	4.63	0.193	0.89	299.4	2.4	62.27
345.2	3.57	0.375	0.90	119.1	2.0	63.47	362.5	5.00	0.188	0.90	332.2	−0.8	62.11
346.3	5.65	0.556	0.89	127.1	1.4	63.38	363.2	4.26	0.156	0.89	341.2	−5.3	62.05
347.3	3.56	0.338	0.90	131.7	−2.3	63.30	364.1	5.59	0.190	1.63	366.3	1.8	61.98
348.3	3.45	0.304	0.89	141.9	−0.7	63.22	365.5	2.57	0.083	0.90	387.8	−6.5	61.87
348.9	3.42	0.285	1.63	149.5	1.5	63.18	366.3	4.63	0.141	0.89	409.5	−2.7	61.81
350.4	3.59	0.278	0.90	161.3	−1.3	63.06	368.1	6.04	0.163	1.63	462.3	7.1	61.67
351.4	3.16	0.230	0.89	171.6	−1.3	62.98	368.6	2.79	0.075	0.90	463.0	−4.8	61.63
353.3	3.88	0.255	0.90	189.8	−4.3	62.83	369.4	4.41	0.111	0.89	493.9	5.3	61.57
353.9	3.45	0.217	1.63	197.5	−3.7	62.78	372.4	3.74	0.082	0.89	571.4	−2.7	61.33
354.4	3.75	0.223	0.89	210.2	2.8	62.75	373.2	7.05	0.144	1.63	610.3	11.3	61.27
356.4	4.23	0.233	0.90	226.8	−6.9	62.59	373.2	4.03	0.083	0.90	608.7	9.7	61.27
357.5	3.89	0.193	0.89	251.9	2.5	62.50	375.4	4.04	0.074	0.89	679.4	7.0	61.09
359.0	4.29	0.190	1.63	280.9	8.6	62.38							
Pentachlorophenol:[e] $\Delta_{cr}^{g}H_m$ (298.15 K) = (91.64 ± 0.45) $kJ \cdot mol^{-1}$ $\ln(p/Pa) = \frac{296.8}{R} - \frac{100885.6}{R(T/K)} - \frac{31.0}{R}\ln\left(\frac{T/K}{298.15}\right)$													
348.1	10.4	75.57	7.15	1.27	−0.04	90.09	383.0	15.4	6.56	7.15	21.72	−0.11	89.01
353.1	17.0	76.53	7.15	2.06	0.04	89.94	388.9	13.9	3.93	7.15	32.68	−0.69	88.83
358.0	13.1	39.72	7.45	3.04	−0.04	89.79	393.2	20.9	4.41	7.15	43.74	−1.30	88.70
363.0	14.0	26.82	7.15	4.83	0.18	89.63	397.8	12.2	1.85	4.84	60.45	−1.18	88.56
367.8	11.3	15.38	7.15	6.81	−0.07	89.48	399.8	23.1	2.98	7.15	71.43	0.96	88.49
371.9	21.1	20.03	7.15	9.75	0.25	89.36	403.2	23.5	2.38	7.15	90.99	2.79	88.39
378.1	15.3	9.30	7.15	15.17	−0.03	89.17							

[a] Temperature of saturation. [b] Mass of transferred sample, condensed at $T = 299$ K. [c] Volume of nitrogen, used to transfer mass m of sample. [d] Vapor pressure at temperature T, calculated from m and the residual vapor pressure at the cooling temperature $T = 243$ K. [e] Mass of transferred sample was condensed at $T = 293$ K and was weighted with the accuracy ± 0.0001 g.

volume contribution to the gaseous phase. V_{N_2} is the volume of transporting gas, and T_a is the temperature of the soap bubble meter. The volume of the gas V_{N_2} transferred through the tube was determined from the flow rate and time measurements. The flow rate was maintained constant using a high precision needle valve (Hoke). The accuracy of the volume V_{N_2} measurements from the flow rate was assessed to be (± 0.001 dm^3).

The relation expressing the equilibrium existing between the vapor and the liquid phase of a pure substance is given by

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_l^g H_m}{T\Delta_l^g V_m} \tag{2}$$

where $\Delta_l^g V_m$ is the molar volume difference between the vapor phase and the liquid phase. $\Delta_l^g H_m$ depends on the temperature along the coexisting phase line. The correct expression has already been derived by Kulikov et al.:[11]

$$\frac{\mathrm{d}\Delta_l^g H_m}{\mathrm{d}T} = \Delta_l^g C_p + \left(\Delta_l^g V_m - T\frac{\partial \Delta_l^g V_m}{\partial T}\right)\frac{\Delta_l^g H_m}{T\Delta_l^g V_m} \tag{3}$$

where $\Delta_l^g C_p = C_p^g - C_p^l$ is the difference of the molar heat capacities at constant pressure for the gaseous and liquid phase, respectively. At low pressure the molar volume of the liquid phase may be neglected in comparison with that of the vapor, and in case of non-associating or weakly associating vapors the perfect gas law may be adopted neglecting contributions arising from the second virial coefficient. With $\Delta_l^g V_m \approx RT/p$, one obtains the Clausius−Clapeyron equation:

$$-\frac{R\,\mathrm{d}(\ln(p))}{\mathrm{d}\left(\frac{1}{T}\right)} = \Delta_l^g H_m \tag{4}$$

and eq 3 reduces to

$$\frac{\mathrm{d}\Delta_l^g H_m}{\mathrm{d}T} = \Delta_l^g C_p \tag{5}$$

Provided $\Delta_l^g C_p$ is independent of temperature in the temperature range considered, it follows that

$$\Delta_l^g H_m \cong \Delta_l^g H_{m,T_0} + \Delta_l^g C_p(T - T_0) \tag{6}$$

After substituting eq 6 into eq 4, integration gives

$$R\ln(p) = a + \frac{b}{T} + \Delta_l^g C_p \ln\left(\frac{T}{T_0}\right) \tag{7}$$

where the vaporization enthalpy at the temperature T is given by

$$\Delta_l^g H_m(T) = -b + \Delta_l^g C_p T \tag{8}$$

T_0 appearing in eqs 6 and 7 is an arbitrarily chosen reference temperature.

Equation 7 was adjusted to the experimental p, T data using the adjustable parameters a and b, and the molar enthalpies of vaporization $\Delta_l^g H_m$ (T) have been calculated using eq 8. The results together with the parameters a and b are listed in Tables 1 and 2. The reference temperature T_0 = 298.15 K has been chosen. Values of $\Delta_l^g C_p$ (or $\Delta_{cr}^g C_p$) have been derived from the experimental[13,14] isobaric molar heat capacities of liquid (C_p^l) or solid (C_p^{cr}) chlorophenols according to a procedure developed by Chickos and Acree[15,16] (see Table 3). In order to assess the uncertainty of the vaporization enthalpy, the experimental data were approximated with the linear equation $\ln(p_i^{sat}) = f(T^{-1})$ using the method of least-squares. The uncertainty in the enthalpy of vaporization was assumed to be identical with the as average deviation of experimental $\ln(p_i^{sat})$ values from this linear correlation. We have checked experimental and calculation procedure with measurements of vapor pressures of *n*-alcohols.[11] It turned out that vapor pressures derived from the transpiration method were reliable within (1 to 3) % and their accuracy was governed by reproducibility of the GC analysis.

Results and Discussion

Vapor Pressures. Studies of vapor pressure of the hexachlorobenzene has been a popular endeavor due to importance of this compound for the environmental chemistry.[17−21] Transpiration method has been used several times[19−21] to obtain vapor pressures at the ambient temperatures; however, agreement of the available data is very poor (see Figure 1). At temperatures near 298.15 K, the data are more or less in agreement. The disagreement is at temperatures considerably higher and lower than room (ambient) temperatures. The disagreement of vapor pressures is especially drastic at elevated temperatures.[17,18] Our new results for hexachlorobenzene are in acceptable agreement with those measured by a Rodebush gauge.[18] The direct comparison of our results measured in the T range (358 to 403) K with those data measured at the ambient temperatures[19−21] is hardly possible; however, the general trend of the results measured by transpiration method seems to be in agreement (see Figure 1) except for several experimental points above 243 K reported by Wania et al.[21]

Vapor pressures of 2-chlorophenol were measured by Gabaldon et al.[7] in the temperature range (337 to 447) K using the dynamic recirculating still. The comparison of the vapor pressures reported by these authors with our results is presented in Figure 2. In spite of the fact that the temperature ranges are different, both sets of the experimental data are consistent according to the plot in the Figure 2.

Mokbel et al.[8] reported vapor pressures of 2,4- and 2,6-dichlorobenzenes using a static method. Our $p-T$ results for both these isomers, measured in the temperature range above melting points, are in close agreement to those reported by Mokbel et al.[8] (see Figures 3 and 4). However, the vapor pressures of the solid 2,4-dichlorophenol measured in this work are substantially lower than those from Mokbel et al.[8] One of the plausible explanations for this discrepancy could be the insufficient purity of their sample, which was used as the purchased sample (99.4 %, tested by HPLC) without further purification.

Enthalpies of Sublimation and Enthalpies of Vaporization. Values of enthalpies of vaporization $\Delta_l^g H_m$ or sublimation $\Delta_{cr}^g H_m$ at the reference temperature 298.15 K are very important in order to obtain gaseous enthalpies of formation $\Delta_f H_m^\circ$ (g) of organic compounds, provided that their enthalpies of formation in condensed phase $\Delta_f H_m^\circ$ (l or cr) are known. A summary of enthalpies of phase transitions $\Delta_l^g H_m$ and $\Delta_{cr}^g H_m$ of chlorobenzene derivatives available from the literature is presented in Table 2. We treated original experimental results available from the literature[7−10,17−21] using eqs 7 and 8 and calculated $\Delta_l^g H_m$ (298.15 K) or $\Delta_{cr}^g H_m$ (298.15 K) for the sake of comparison with our results. The comprehensive compilations by Stull[17] and by Stephenson and Malanowski[22] contain vapor pressure data for some chlorobenzene derivatives over a wide

Table 2. Compilation of Data on Enthalpies of Sublimation $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}$ or Vaporization $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ of Hexachlorobenzene and Chlorophenols[a]

	techniques	T range K	T_{average} K	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ or $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}$ observed at T_{average} kJ·mol^{-1}	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ or $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}$ extrapolated to T=298 K[b] kJ·mol^{-1}	ref
hexachlorobenzene (cr)	NA	387−492	440	62.0	66.3	17
	Rodebush gage	369−397	383	91.2 ± 8.2	94.4 ± 8.2	18
	transpiration	288−318	303	101.0 ± 0.1	101.2 ± 0.1	19
	transpiration	258−313	286	105.7 ± 5.5	105.3 ± 5.5	20
	transpiration	243−303	273	74.2 ± 1.7	73.3 ± 1.7	21
	calorimetry	338	338	89.6 ± 0.2	90.8 ± 0.2	5
	transpiration	358−403		94.2 ± 0.5	**96.8 ± 0.5**	this work
hexachlorobenzene (l)					**81.2**[c]	this work
2-chlorophenol (l)	NA	333−449	391	46.2	52.4	22
	NA	354−448	401	43.9	50.8	22
	NA	285−448	367	43.3	47.1	
	ebulliometry	337−447	392	44.6 ± 0.2	51.0 ± 0.2	7
	transpiration	288−321	305	51.9 ± 0.2	**52.3 ± 0.2**	this work
3-chlorophenol (cr)	quartz thread			53.1 ± 1.3	53.2 ± 1.3	35
	NA	252−293	273	60.9	60.2	22
	drop calorimetry				69.4 ± 1.8	6
	transpiration	275−306	291	77.1 ± 0.3	**76.9 ± 0.3**	this work
3-chlorophenol (l)	NA	317−487	402	49.6	56.5	17
	transpiration	308−335	322	61.9 ± 0.3	**63.5 ± 0.3**	this work
4-chlorophenol (cr)	quartz thread			51.9 ± 1.3	51.9 ± 1.3	35
	drop calorimetry				69.5 ± 1.6	6
	transpiration	283−313	298	77.1 ± 0.2	**77.1 ± 0.2**	this work
4-chlorophenol (l)	NA	323−493	408	59.3	67.0	17
	transpiration	318−351	335	61.9 ± 0.3	**64.4 ± 0.3**	this work
2,3-dichlorophenol (cr)	drop calorimetry				71.7 ± 2.2	6
	transpiration	294−327	311	76.6 ± 0.4	**76.9 ± 0.4**	this work
2,3-dichlorophenol (l)	transpiration	331−358	345	54.0 ± 0.2	**57.3 ± 0.2**	this work
2,4-dichlorophenol (cr)	static	274−314	294	67.5 ± 1.0	67.4 ± 1.0	8
	drop calorimetry				70.1 ± 1.1	6
	transpiration	278−315	297	78.0 ± 0.3	**78.0 ± 0.3**	this work
2,4-dichlorophenol (l)	NA	391−474	433	49.2	58.9	22
	NA	326−483	405	55.4	62.4	17
	static	323−443	383	52.3 ± 0.3	58.1 ± 0.3	8
	transpiration	317−344	331	56.6 ± 0.4	**59.0 ± 0.4**	this work
2,5-dichlorophenol (cr)	drop calorimetry				73.6 ± 2.1	6
	transpiration	294−327	311	76.9 ± 0.1	**77.3 ± 0.1**	this work
2,5-dichlorophenol (l)	transpiration	333−361	347	53.1 ± 0.1	**56.7 ± 0.1**	this work
2,6-dichlorophenol (cr)	drop calorimetry				75.8 ± 1.0	6
	transpiration	298−331	315	78.9 ± 0.2	**79.3 ± 0.2**	this work
2,6-dichlorophenol (l)	NA	333−493	413	56.4	63.7	22
	NA	353−493	423	53.8	62.1	22
	static	343−457	400	51.6 ± 0.5	58.5 ± 0.5	8
	transpiration	341−371	356	55.4 ± 0.3	**59.6 ± 0.3**	this work
3,4-dichlorophenol (cr)	drop calorimetry				81.3 ± 2.3	6
	transpiration	291−337	314	89.4 ± 0.4	**89.8 ± 0.4**	this work
3,4-dichlorophenol (l)	transpiration	341−368	355	66.7 ± 0.2	**70.8 ± 0.2**	this work
3,5-dichlorophenol (cr)	drop calorimetry				82.8 ± 1.1	6
	NA	273−295	284	71.9	71.5	22
					89.3 [d]	this work
3,5-dichlorophenol (l)					70.9 [e]	this work
2,4,6-trichlorophenol (cr)	static	304−334	319	81.7 ± 0.8	82.2 ± 0.8	8
	transpiration	299−340	320	81.5 ± 0.3	**82.3 ± 0.3**	this work
2,4,6-trichlorophenol (l)	NA	350−519	435	59.0	68.9	17
	static	344−463	404	58.2 ± 0.4	66.1 ± 0.4	8
	transpiration	343−375	359	62.5 ± 0.3	**67.2 ± 0.3**	this work
2,4,5-trichlorophenol (l)	NA	345−525	435	55.4	65.2	17
					65.1 [e]	this work
pentachlorophenol (cr)	NA				67.4 ± 2.1	25,26
	NA	319−393	356	81.9 ± 6.9	83.7 ± 6.9	9
	static	373−453	413	76.6	80.1	10
	transpiration	348−403	376	89.3 ± 0.4	**91.6 ± 0.4**	this work
pentachlorophenol (l)	NA	465−582	524	70.1	89.9	17
	NA	474−507	491	65.5	82.8 ± 0.9	9
	NA	463−507	485	68.5	85.8	22
					85.0[c]	this work

[a] $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ refers to liquids and $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}$ refers to crystals (values taken for the group-additivity calculations are in bold). [b] The observed value at T_{average} was extrapolated to 298.15 K using "Chickos correction" (see text). [c] Derived as the difference of $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}$ from this table and $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}$ (298.15 K) from Table 4. [d] Derived as the sum $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}$ (298.15 K) from Table 4 and $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ from this table. [e] Calculated using group-additivity procedure presented in the Table 4.

Table 3. Compilation of Data on Heat Capacities at 298.15 K of Chlorophenols and Hexachlorobenzene

	C_p^{cr} J·mol^{-1}·K^{-1}	C_p^{l} J·mol^{-1}·K^{-1}	$-\Delta_{cr}^{g}C_p$ J·mol^{-1}·K^{-1}	$-\Delta_{l}^{g}C_p$ J·mol^{-1}·K^{-1}
2-chlorophenol		217.5[a]		67.1
3-chlorophenol	168.6[a]	224.1[a]	26.0	68.8
4-chlorophenol	148.8[a]	228.3[a]	23.1	69.9
dichlorophenol	160.0	240.3	24.7	73.1
trichlorophenol	174.5	261.8	26.9	78.6
tetrachlorophenol	189.0	283.3	31.0	84.2
pentachlorophenol	202.0[b]		31.0	
hexachlorobenzene	201.3[b]		30.9	

[a] Data from ref 13. [b] Data from ref 14.

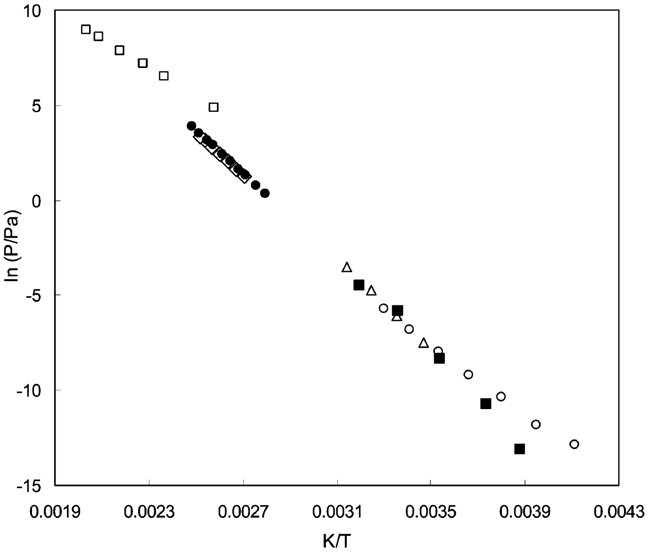


Figure 1. Plot of vapor pressure against reciprocal temperature for the solid hexachlorobenzene: ○, ref 21; □, ref 17; ◇, ref 18; ■, ref 20; △, ref 19; ●, this work.

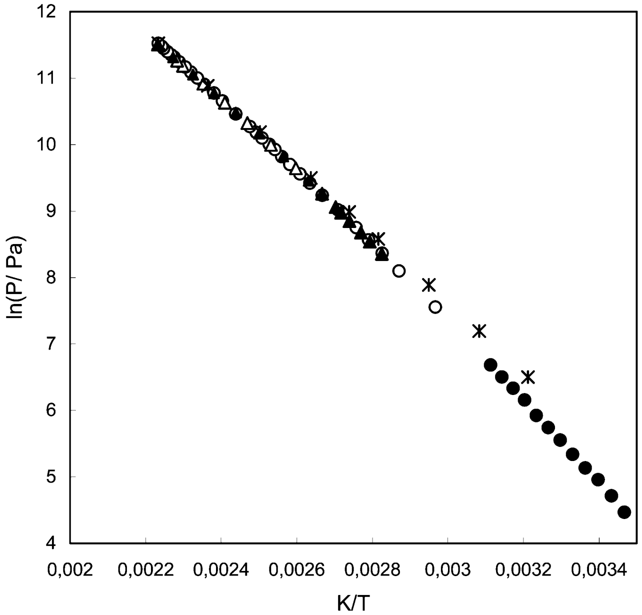


Figure 2. Plot of vapor pressure against reciprocal temperature for the liquid 2-chlorophenol: ○, ref 7; △, ref 22; ▲, ref 22; ∗, ref 24, ●, this work.

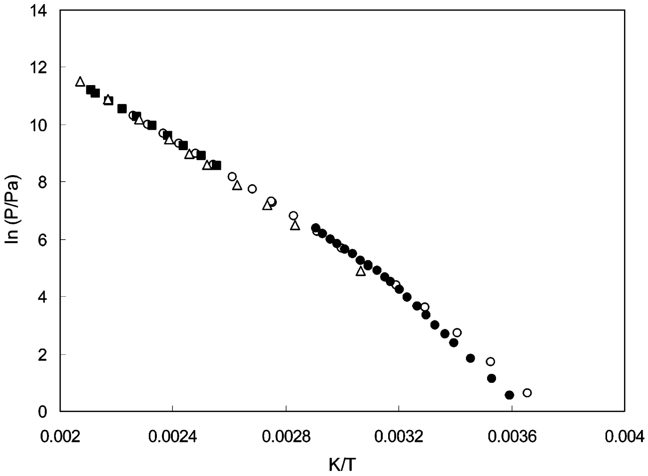


Figure 3. Plot of vapor pressure against reciprocal temperature for the solid and liquid 2,4-dichlorophenol: ○, ref 8; △, ref 17; ■, ref 22; ●, this work.

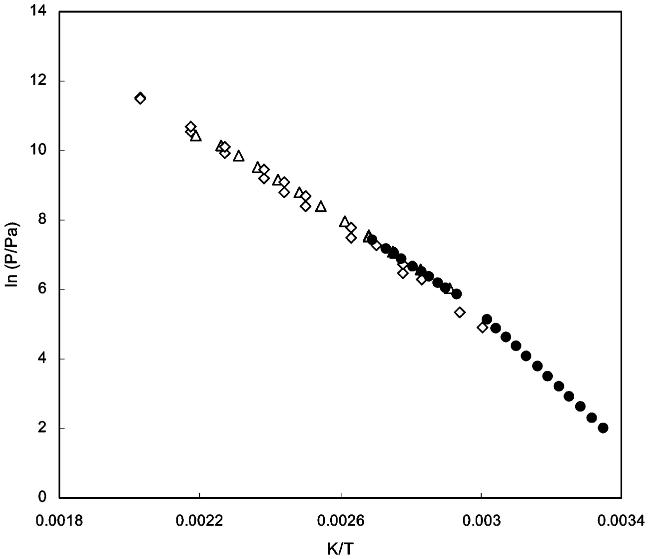


Figure 4. Plot of vapor pressure against reciprocal temperature for the solid and liquid 2,6-dichlorophenol: △, ref 8; ○, ref 22; ●, this work.

range of temperature. The origin of the data presented there is unclear; methods of measurements are unknown as well as are errors of measurements and purities of compounds. In spite of this fact, we also treated the results from Stull[17] and Stephenson and Malanowski[22] using eqs 7 and 8 and calculated $\Delta_l^g H_m$ (298.15 K) for the sake of comparison with our results. However, the agreement or disagreement with other data in each case should be questionable[23] due to inadequate information in compilations.[17,22]

Results reported in the literature for enthalpy of sublimation $\Delta_{cr}^{g}H_m$ (298.15 K) of hexachlorobenzene scatter dramatically in the range (66 to 105) kJ·mol^{-1} (see Table 2). Our result (96.8 ± 0.5) kJ·mol^{-1} meets the average of the all available values and also is in the close agreement with those from the Rodebush gage.[18]

Values of $\Delta_l^g H_m$ (298.15 K) derived from vapor pressure measurements for 2-chlorophenol (ebulliometry),[7] 2,4-dichlorophenol (static),[8] and 2,6-dichlorophenol (static)[8] are in acceptable agreement with our results obtained by the transpiration method (see Table 2).

Values of the standard enthalpies of sublimation $\Delta_{cr}^{g}H_m$ (364 K) of 2.3-, 2.4-, 2.5-, 2.6-, 3.4-, and 3.5-dichlorophenol as well as 3- and 4-chlorophenol have been measured by Ribeiro da Silva et al.[6] by the drop microcalorimetric method with accuracy (1 to 2) kJ·mol.$^{-1}$ From these experimental results at 364 K, they calculated values of the standard enthalpies of sublimation

Table 4. Comparison of Enthalpies of Fusion Measured by DSC with Those Calculated as the Difference $\Delta_{cr}^{l}H_m = \Delta_{cr}^{g}H_m - \Delta_{l}^{g}H_m$ at $T = 298$ K from Transpiration

compound	$\Delta_{cr}^{g}H_m$ at 298.15 K kJ·mol^{-1}	$\Delta_{l}^{g}H_m$^{a} at 298 K kJ·mol^{-1}	$\Delta_{cr}^{l}H_m$^{b} at T_{fus} kJ·mol^{-1}	$\Delta_{cr}^{l}H_m$^{c} at 298 K kJ·mol^{-1}	$\Delta_{cr}^{l}H_m$^{d} at 298 K kJ·mol^{-1}	Δ^{e} kJ·mol^{-1}
	1	2	5	6	7	8
3-chlorophenol	76.9 ± 0.3	63.5 ± 0.3	14.9/305.8[27]	14.3	13.4	0.9
			13.6/304.2[13]	13.6		0.2
4-chlorophenol	77.1 ± 0.2	64.4 ± 0.3	14.1/316.0[27]	14.1	12.7	1.4
			13.8/315.7[13]	12.9		0.2
2,3-dichlorophenol	76.9 ± 0.4	57.3 ± 0.2	21.4/330.0[27]	19.8	19.6	0.2
2,4-dichlorophenol	78.0 ± 0.3	59.0 ± 0.4	20.1/318.0[27]	19.1	19.0	0.1
2,5-dichlorophenol	77.3 ± 0.1	56.7 ± 0.1	22.4/331.0[27]	20.8	20.6	0.2
2,6-dichlorophenol	79.3 ± 0.2	59.6 ± 0.3	22.1/340.0[27]	20.1	19.7	0.4
3,4-dichlorophenol	89.8 ± 0.4	70.8 ± 0.2	20.9/341.0[27]	18.9	19.0	−0.1
3,5-dichlorophenol			20.5/341.0[27]	18.4		
pentachlorophenol	91.6 ± 0.4		17.2/463.0[28]	6.6[f]		
			15.4/463.0[29]			
hexachlorobenzene	96.8 ± 0.5		25.2/502.0[5]	15.6		

[a] Results from this work (see Table 1). [b] The enthalpy of fusion $\Delta_{cr}^{l}H_m$ measured by DSC. [c] The enthalpy of fusion $\Delta_{cr}^{l}H_m$ measured by DSC and extrapolated to 298.15 K (see text). [d] The enthalpy of fusion $\Delta_{cr}^{l}H_m$, calculated as the difference $\Delta_{cr}^{g}H_m - \Delta_{l}^{g}H_m$ from Table 1. [e] The difference between columns 6 and 7. [f] Derived from the average of values reported in refs 28 and 29.

at the reference temperature of 298.15 K, $\Delta_{cr}^{g}H_m$ (298.15 K), using constant contribution 10.15 kJ·mol^{-1} estimated by the group-additivity method using values from Stull et al.[24] However, values for $\Delta_{cr}^{g}H_m$ (298.15 K) of mono- and dichlorophenols reported by Ribeiro da Silva et al.[6] are (3 to 8) kJ·mol^{-1} lower than our results presented in the Table 2, and this discrepancy exceed the boundaries of the experimental uncertainties of both methods. A possible reason for such discordance might be the simplified extrapolation procedure used by Ribeiro da Silva et al.[6]

Having significant discrepancy with the results from Ribeiro da Silva et al.,[6] we need additional arguments to support reliability of our own experimental measurements. The difference $\Delta_{cr}^{g}H_m - \Delta_{l}^{g}H_m = \Delta_{cr}^{l}H_m$ defines the enthalpy of fusion, $\Delta_{cr}^{l}H_m$. A valuable test of consistency of the experimental data on sublimation and vaporization enthalpies measured in this work provides a comparison with a set of experimental values of enthalpies of fusion of the solid chlorophenols measured by DSC (see Table 4). Indeed, in this work, the solid chlorophenols were investigated by the method of transference in both ranges above and below the temperature of fusion, and the values $\Delta_{cr}^{g}H_m$ (298.15 K) and $\Delta_{l}^{g}H_m$ (298.15 K) were derived (see Tables 1 and 2). For each compound studied, comparison (see Table 4) of the enthalpy of fusion $\Delta_{cr}^{l}H_m^{\circ}$, calculated as the difference $\Delta_{cr}^{g}H_m - \Delta_{l}^{g}H_m$ (both values referred to $T = 298.15$ K) from Table 1, and the enthalpy of fusion $\Delta_{cr}^{l}H_m$ measured by DSC (and adjusted to $T = 298.15$ K, see below) demonstrate discrepancies only on the level of 1 kJ·mol^{-1} and are acceptable within the boundaries of the experimental uncertainties of the methods used. Thus, the sets of vaporization and sublimation enthalpies of mono- and dichlorophenols given in Table 1 have been successfully proven for the internal consistency.

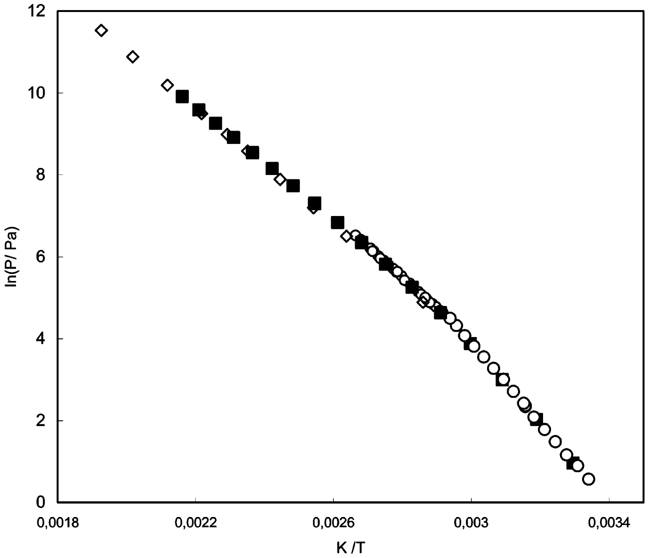


Figure 5. Plot of vapor pressure against reciprocal temperature for the solid and liquid 2,4,6-trichlorophenol: ■, ref 8; ◇, ref 17; ○, this work.

The experimental enthalpies of fusion $\Delta_{cr}^{l}H_m$ are referred to the melting temperature and are recorded in Table 4. Because of the deviations from $T = 298.15$, these observed values of the enthalpies of fusion of chlorophenols had to be corrected to this reference temperature. The corrections were estimated with help of the correction:[15,16]

$$\{\Delta_{cr}^{l}H_m\,(T_{fus}/\mathrm{K}) - \Delta_{cr}^{l}H_m\,(298.15\ \mathrm{K})\}/(\mathrm{J{\cdot}mol^{-1}}) = \{(0.75 + 0.15C_p^{cr})[(T_{fus}/\mathrm{K}) - 298.15]\} - \{(10.58 + 0.26C_p^{l})\,[(T_{fus}/\mathrm{K}) - 298.15]\} \quad (9)$$

where value of $\Delta_{cr}^{l}C_p$ has been derived from the isobaric molar heat capacities of the liquid chloro-benzene derivatives, C_p^{l}, and isobaric molar heat capacities of the solid substances, C_p^{cr} (see Table 3). With these corrections and the measured values of $\Delta_{cr}^{l}H_m$ (T_{fus}) the standard molar enthalpies of fusion at $T = 298.15$ K, $\Delta_{cr}^{l}H_m$ (298.15 K), were calculated (Table 4).

From the series of the trichlorophenols, only vapor pressures of 2,4,6-trichlorophenol has been measured by use of static method[8] (results listed in the compilation[22] for of 2,4,5-trichlorophenol are of ill-defined quality). Our results are in acceptable agreement with those from the static method within the boundaries of the experimental uncertainties (see Table 2 and the Figure 5).

Surprisingly, only one value of the enthalpy of sublimation of the penta-chloro-phenol is reported in the literature:[25,26] $\Delta_{cr}^{g}H_m$ (298.15 K) = (67.4 ± 2.1) kJ·mol^{-1} cited as the unpublished result by Stull.[26] This value is apparently too low if compared with the enthalpy of sublimation of pentachlorobenzene[4] or hexachlorobenzene (Table 1). Some available data on vapor pressures of pentachlorophenol (see Figure 6) provide the value of the enthalpy of sublimation on the level of 80 kJ·mol^{-1}, but these values do not resolve the contradiction due

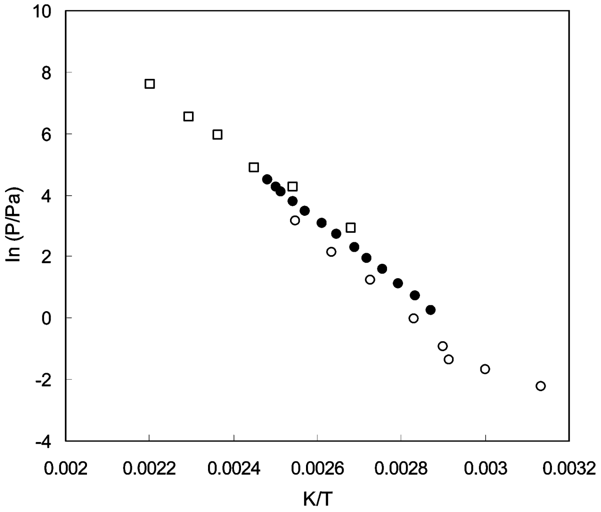


Figure 6. Plot of vapor pressure against reciprocal temperature for the solid pentachlorophenol: ○, ref 9; □, ref 10; ●, this work.

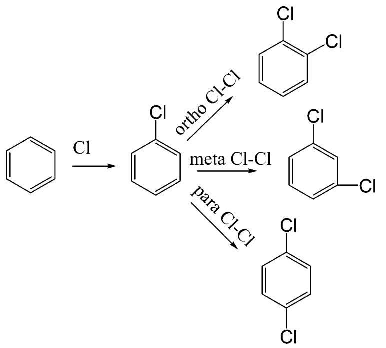
to very large experimental uncertainties of the data reported by McDonald et al.[9] Our vapor pressure measurements are in agreement with those reported by Carswell and Nason[10] (see Figure 6) but only in the upper temperature range of their measurements. However, the value of $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K) = (91.6 ± 0.4) kJ·mol^{-1}, derived in this work (Tables 1 and 2) is substantially higher than all others reported in the literature. Thus, it is necessary to validate this result. For this purpose, the procedure that has been used above (comparison vaporization and sublimation enthalpies via fusion enthalpy) to test the consistency of the experimental data on mono- and dichlorophenols has been modified now for pentachlorophenol. Using the difference $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}} - \Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}$ the enthalpy of vaporization of pentachloropnenol $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K) = 85.0 kJ·mol^{-1} has been estimated in this work (Table 2). This value is in acceptable agreement with other available results (see Table 2) taking into account a long way of extrapolation of all enthalpies involved in comparison. Thus, the set of sublimation, vaporization, and fusion enthalpies of pentachlorophenol given in Table 4 is internally consistent.

Vapor pressures and phase transitions for di- and polychlorinated benzenes have recently been critically evaluated by Rohac et al.,[5] and a set of reliable $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K) was recommended. Together with the experimental results on $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K) selected (marked in bold) for mono- and poly-chlorophenols listed in the Table 2, we have now obtained the extended set of enthalpies of vaporization of the chlorobenzene derivatives (see Table 5).

Additive Calculations of Enthalpies of Vaporization. A simple way to establish consistency of the experimental results on vaporization enthalpies of the chlorobenzene derivatives presented in the Table 5 is to check whether they obey additivity rules. Indeed, traditional prediction methods based on constants related to the effective atoms (like Benson method[32] or Domalski and Hearing[33] method) or effective bonds (like Tatevski method[34]) are well-established and provide the possibility to check the input data for internal consistency. For any well-established calculation scheme, one of the best flags to possible experimental errors is a large discrepancy between experimental and calculated values—especially if other, closely related compounds show no such discrepancy.

In our previous work,[37] we applied an incremental scheme to the alkylurea derivatives which consists of the determination of increments for substitution of H atoms by CH_3 groups in the standard series starting with urea itself. This procedure has been shown to provide consistent results for enthalpies of formation in the solid state as well as for enthalpies of sublimation of alkylureas.[37] Data set of chlorinated benzene or phenol derivatives collected in the Table 5 presents a similar subsequent substitution of H atoms by Cl atoms in the series of benzene or phenol derivatives. Hence, we decided to apply the incremental scheme to the chlorinated benzene derivatives as well.

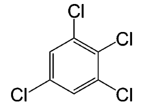
In the substitution procedure, benzene or phenol are used as a reference compound to produce chloro derivatives by subsequent substitution of Cl atoms for H. For instance, the sequence of substitution yielding a chloro substituted benzene is of the form:



The formula for the vaporization enthalpy calculations of chlorobenzenes (ClB) at 298.15 K is

$$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}(\mathrm{ClB}) = \Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}(\mathrm{B}) + n_{\mathrm{a}}\Delta\mathrm{H}(\mathrm{H}{\rightarrow}\mathrm{Cl}) + n_{\mathrm{b}}(\text{ortho Cl}-\text{Cl}) + n_{\mathrm{c}}(\text{para Cl}-\text{Cl}) + n_{\mathrm{d}}(\text{meta Cl}-\text{Cl})$$

where $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ (B) is enthalpy of vaporization of benzene; ΔH(H→Cl) is an increment of H→Cl substitutions on the benzene ring. The mutual influence of the introduced Cl atoms was 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}, and n_{d} are the quantities of the corresponding increments and correction. For example, for the 1,2,3,5-tetrachlorobenzene the calculation formula is



Benzene + 4 ΔH (H→Cl) + 2 ortho Cl-Cl +
+ 3 meta Cl-Cl + 1 para Cl-Cl

The formula for the calculations of vaporization enthalpy of chlorophenols (ClPh) at 298.15 K requires extension:

$$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}(\mathrm{ClPh}) = \Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}(\mathrm{B}) + n_{\mathrm{a}}\Delta H(\mathrm{H}{\rightarrow}\mathrm{Cl}) + n_{\mathrm{b}}(\text{ortho Cl}-\text{Cl}) + n_{\mathrm{c}}(\text{para Cl}-\text{Cl}) + n_{\mathrm{d}}(\text{meta Cl}-\text{Cl}) + \Delta H(\mathrm{H}{\rightarrow}\mathrm{OH}) + n_{\mathrm{e}}(\text{ortho OH}-\text{Cl})_{\mathrm{HB}} + n_{\mathrm{f}}(\text{ortho OH}-\text{Cl})_{\mathrm{non-HB}} + n_{\mathrm{g}}(\text{para OH}-\text{Cl}) + n_{\mathrm{h}}(\text{meta OH}-\text{Cl})$$

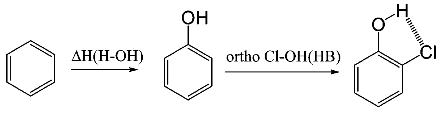
where ΔH(H→OH) is an increment of H→OH substitutions on the benzene ring. The mutual interactions of the introduced Cl atoms with the OH-group were taken into account through the three types of additional corrections in ortho-, para-, and meta-position on the benzene ring. n_{e}, n_{f}, n_{g}, and n_{h} are the quantities of the corresponding additional corrections.

Table 5. Group-Additivity and COSMO-RS Procedures for Calculation of the Enthalpies of Vaporization $\Delta_l^g H_m$ of Chlorinated Benzenes and Phenols at 298.15 K in kJ mol^{-1}

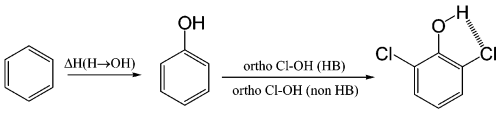
compound	exp	calcd (Σ_{increm} from Table 6)	Δ^{add} = exp − calcd	calcd COSMO-RS	$\Delta^{\text{COSMO-RS}}$ = exp − calcd
benzene	33.60[a]			34.79	−1.19
chlorobenzene	41.00[a]			43.20	−2.20
1,2-dichlorobenzene	48.82[b]	49.06	−0.24	49.81	−0.99
1,3-dichlorobenzene	47.68[b]	48.24	−0.56	50.00	−2.32
1,4-dichlorobenzene	47.60[b]	47.99	−0.39	50.29	−2.69
1,2,3-trichlorobenzene	57.55[b]	56.96	0.59	55.67	1.88
1,2,4-trichlorobenzene	55.30[b]	55.88	−0.58	55.90	−0.60
1,3,5-trichlorobenzene	55.56[b]	55.31	0.25	55.92	−0.36
1,2,3,4-tetrachlorobenzene	62.70[c]	64.44	−1.74	61.22	1.48
1,2,4,5-tetrachlorobenzene	63.04[c]	63.37	−0.33	61.60	1.44
1,2,4,6-tetrachlorobenzene	62.30[c]	63.62	−1.32	61.28	1.02
pentachlorobenzene	70.14[b]	71.76	−1.62	66.34	3.80
hexachlorobenzene	81.20	79.75	1.45	70.81	10.39
phenol	57.80[d]			61.88	−4.08
2-chlorophenol	52.34	51.18	1.16	53.53	−1.19
3-chlorophenol	63.52	64.45	−0.93	64.81	−1.29
4-chlorophenol	64.42	65.04	−0.62	68.08	−3.66
2,3-dichlorophenol	57.34	58.49	−1.15	58.43	−1.09
2,4-dichlorophenol	58.97	58.26	0.71	59.81	−0.84
2,5-dichlorophenol	56.69	57.41	−0.72	59.24	−2.55
2,6-dichlorophenol	59.58	60.99	−1.41	60.86	−1.28
3,4-dichlorophenol	70.84	72.35	−1.51	71.84	−1.00
2,4,6-trichlorophenol	67.16	67.90	−0.74	66.31	0.85
pentachlorophenol	85.00	82.85	2.15	74.51	10.49

[a] Data from ref 30. [b] Data from ref 4. [c] Enthalpy of vaporization calculated using $\Delta_{cr}^g H_m$ (298.15 K) from ref 36 and $\Delta_{cr}^l H_m$ (T_{fus}) reported in ref 5. Values $\Delta_{cr}^l H_m$ (298.15 K) have been adjusted to the reference temperature using the procedure of Chickos and Acree.[15,16] [d] Enthalpy of vaporization calculated as the difference $\Delta_{cr}^g H_m$ (298.15 K) = (68.7 ± 1.0) kJ·mol^{-1}and $\Delta_{cr}^l H_m$ (T_{fus}) = 11.55 kJ·mol^{-1} from ref 31. The value $\Delta_{cr}^l H_m$ (298.15 K) = 10.90 kJ·mol^{-1} has been adjusted to the reference temperature using the procedure of Chickos and Acree.[15,16]

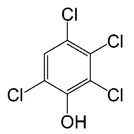
We considered two different additional corrections for the interaction of the C*l*-atom and the OH-group in ortho-position on the benzene ring. The first one, (ortho OH−Cl)$_{\text{HB}}$, is specific for the 1,2-substitution, where formation of a favorable intramolecular interaction between the hydroxyl-hydrogen and the chlorine bond was possible:



Because the OH-group can only make such interaction with one of its neighbors, a second neighboring chlorine as in the 2,6-dichlorophenol is taken into account by a different correction (ortho OH−Cl)$_{\text{non-HB}}$:



For example, for the 2,4,5,6-tetrachlorophenol the calculation formula is



Benzene + 1OH + 4 Cl + 1 ortho Cl-OH(non HB) + 1 ortho Cl-OH(HB) +
+ 1 meta Cl-OH + 1 para Cl-OH + 2 ortho Cl-Cl + 3 meta Cl-Cl + 1 para Cl-Cl

The matrix of the parameters involved in calculation of the vaporization enthalpies of chlorinated benzene derivatives is presented in the Supporting Information. The method of the polyfunctional least-squares was used to evaluate the additive parameters, which are presented in the Table 6. Comparison of the experimental and calculated values is performed in the Table 5. As can be seen from this table, the average deviation of experimental and calculated vaporization enthalpies does not exceeds 0.7 kJ·mol^{-1}. Even the tetra-, penta- and hexachloro-substituted benzenes and phenol fit in this simple group-additivity procedure with deviations at the level of (1 to 2) kJ·mol^{-1}, which are comparable with the experimental uncertainties of vaporization enthalpies of these compounds. Hence, even the simple group-additivity scheme applied in this work do not reveal any outlier in the data set of $\Delta_l^g H_m$ (298.15 K) for mono- and poly-chlorophenols and poly-chlorobenzene derivatives (Table 5). These data could be recommended as the consistent set for the interpretation of enthalpies of formation in the gaseous phase, which will be performed in the forthcoming work.

Table 6. Parameters for the Calculation of Enthalpies of Vaporization $\Delta_l^g H_m$ of Chlorobenzenes and Chlorophenols at 298.15 K

group contribution	value/kJ·mol^{-1}
benzene	33.6
ΔH(H→Cl)	7.4
ΔH(H→OH)	24.2
ortho Cl−Cl	0.66
meta Cl−Cl	−0.41
para Cl−Cl	−0.16
ortho Cl−OH (HB)	−14.02
ortho Cl−OH (non-HB)	2.57
meta Cl−OH	−0.16
para Cl−OH	−0.75

Prediction of the Vapor Pressures and Vaporization Enthalpies of the Chlorobenzenes and Chlorophenols Using COSMO-RS. Although the previously explained group-additivity scheme apparently proves the internal consistency of our experimental data, an independent, theoretical method is desired that allows us to perform a thermodynamic consistency test of measured in this work vaporization enthalpies. Therefore, we also compared the experimental data for the $\Delta_l^g H_m$ (298.15 K) collected in Table 5 with estimations performed using the quantum chemically based COSMO-RS method,[38−41] which is able to predict a wide range of liquid−liquid and vapor−liquid equilibrium data just from the respective quantum chemical calculations for the solutes and solvents without any need for parameter fitting for the special compounds. Obviously, the agreement with experiment to be expected from such calculations is worse than that to be expected by additive data fitting to the special class of compounds under consideration, but the COSMO-RS is unbiased with respect to the available set of experimental data. The COSMO*therm* implementation of COSMO-RS was used, and the latest optimum quality COSMO-RS parametrization[42] BP-TZVP-C21-01.05 was employed. The underlying quantum chemical DFT/COSMO calculations for the compounds considered in this data set mostly have already been available in the COSMO*base* database.[43] Only for two compounds new calculations have been performed using the highly efficient TURBOMOLE program package.[44] The results of the COSMOtherm predictions are shown in Table 5 together with the experimental data and with the group-additivity results. Large deviations of 10 kJ·mol^{-1} to the enthalpies of vaporization are observed only for hexachlorobenzene and for pentachlorophenol. The reason for these deviations is not obvious, but may have to do with deficiencies of the COSMO-RS method in the description of Cl−Cl contacts. These are much more frequent in these highly chlorinated species than in less chlorinated compounds, because usually chlorine atoms try to avoid contacts with each other. At the same time, the COSMO-RS predictions of vaporization enthalpy of the chlorobenzenes and chlorophenols are reasonably close to the experimental values with deviations mostly less than 2 kJ·mol^{-1}(see Table 5). As an example, the big difference between 2-chlorophenol and 3-chlorophenol arising from the intramolecular hydroxyl chlorine interaction in 2-chlorophenol is remarkably well-described. Altogether we conclude that the experimental results on $\Delta_l^g H_m$ (298.15 K) collected in the Table 5 have been proved once more for the internal consistency by using the purely theoretical COSMO-RS method.

Conclusion

Multi-substituted aromatic or polyaromatic molecules, such as chlorinated dioxins and chlorinated furans, are often observed in the effluent streams from combustion or incineration processes. These compounds are thought to be hazardous and toxic and as a consequence are highly undesirable products of incomplete combustion. It would be of significant value to have knowledge of their fundamental thermodynamic properties and to have understanding of the reaction pathways of their formation. In this paper, we have measured vapor pressures and phase transitions of a series of poly-substituted benzenes and phenols. These compounds could serve as a model compounds for chlorinated dioxins and chlorinated furans. We have developed a simple procedure to calculate enthalpies of vaporization of chlorinated benzenes, which proves internal consistency of our experimental data. Many parameters of this procedure should be transferable for prediction of phase transitions of chlorinated dioxins and chlorinated furans, by using dibenzodioxin or dibenzofuran as the starting molecules. The a priori predictions of enthalpies of vaporization with the COSMO-RS method also are in reasonable agreement with the experimental data, although the absolute deviations are considerably larger than for the specially adjusted group additivity method.

Supporting Information Available:

Matrix for calculation of enthalpies of vaporization of chlorbenzenes and chlorophenols at 289.15 K. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Shiu, W-Y.; Ma, K.-C. Temperature dependence of physical−chemical properties of selected chemicals of environmental interest. II. Chlorobenzenes, polychlorinated biphenyls, polychlorinated dibenzo-*p*-dioxins, and dibenzofurans. *J. Phys. Chem. Ref. Data* **2000**, *29*, 387−462.

(2) Polednicek, M.; Guetachew, T.; Jose, J.; Ruzicka, V.; Rohac, V.; Zabransky, M. Vapor pressures and sublimation pressures of dichlorobenzenes (1,2-, 1,3-, and 1,4-), trichlorobenzenes (1,2,3- and 1,3,5,-), and pentachlorobenzene. *ELDATA: Int. Electron. J. Phys-Chem. Data* **1996**, *2*, 41−49.

(3) Rohac, V.; Ruzicka, V.; Ruzicka, K.; Aim, K. Measurements of saturated vapor pressure above the liquid phase for isomeric dichlorobenzenes and 1,2,4-trichlorobenzene. *J. Chem. Eng. Data* **1998**, *43*, 770−775.

(4) Rohac, V.; Ruzicka, V.; Ruzicka, K.; Polednicek, M.; Aim, K.; Jose, J. Recommended vapour and sublimation pressures and related thermal data for chlorobenzenes. *Fluid Phase Equilib.* **1999**, *157*, 121−142.

(5) Sabbah, R.; An, X.-W. Etude thermodynamique des chlorobenzenes. *Thermochim. Acta* **1991**, *179*, 81−88.

(6) Ribeiro Da Silva, M. A. V.; Ferrao, M. L. C. C. H.; Jiye, F. Standard enthalpies of combustion of the six dichlorophenols by rotating-bomb calorimetry. *J. Chem. Thermodyn.* **1994**, *26*, 839- 846.

(7) Gabaldon, C.; Marzal, P.; Monton, J. B. Vapor−liquid equilibria of the 1-butanol + *o*-chlorophenol system. Effects of association in the vapor phase. *J. Chem. Eng. Data* **1995**, *40*, 190−193.

(8) Mokbel, I.; Pauchon, V.; Jose, J. Vapor pressures and sublimation pressures of 2,4-dichlorophenol, 2,6-dichlorophenol, and 2,4,6-trichlorophenol. *ELDATA: Int. Electron. J. Phys-Chem. Data* **1995**, *1*, 53−57.

(9) McDonald, R. A.; Shrader, S. A.; Stull, D. R. Vapor pressures and freezing points of 30 organics, *J. Chem. Eng. Data* **1959**, *4*, 311−313.

(10) Carswell, T. S.; Nason, H. K. Properties and uses of pentachlorophenol. *Ind. Eng. Chem.* **1938**, *30*, 622−626.

(11) Kulikov, D.; Verevkin, S. P, Heintz, A. Enthalpies of vaporization of a series of linear aliphatic alcohols. Experimental measurements and application of the ERAS-model for their prediction. *Fluid Phase Equilib.* **2001**, *192*, 187−207.

(12) Verevkin S. P. Pure component phase changes liquid and gas in experimental thermodynamics. In *Measurement of the Thermodynamic Properties of Multiple Phases*; Weir, R. D., de Loos, Th. W., Eds.; Elsevier: Amsterdam, 2000; Chapter 1, pp 6−30.

(13) Lipovska, M.; Schmidt, H.-G.; Rohac, V.; Ruzicka, V.; Wolf, G.; Zabrinsky, M. Heat capacities of three isomeric chlorobenzenes and of three isomeric chlorophenols. *J. Therm. Anal. Calorim.* **2002**, *68*, 753−766.

(14) Hildenbrand, D. L.; Kramer, W. R.; Stull, D. R. The heat capacities of hexachlorobenzene and pentachlorophenol from 15 to 300 K. *J. Phys. Chem.* **1958**, *62*, 958−959.

(15) Chickos, J. S.; Acree, W. E., Jr. Enthalpies of vaporization of organic and organometallic compounds, 1880−2002. *J. Phys. Chem. Ref. Data* **2003**, *32*, 519−878.

(16) Chickos, J. S.; Acree, W. E. Jr. Enthalpies of sublimation of organic and organometallic compounds, 1910−2001. *J. Phys. Chem. Ref. Data* **2002**, *31*, 537−698.

(17) Stull, D. R. Vapor pressure of pure substances organic compounds. *Ind. Eng. Chem.* **1947**, *39*, 517−540.

(18) Sears, G. W.; Hopke, E. R. Vapor pressures of naphthalene, anthracene and hexachlorobenzene in a low pressure region. *J. Am. Chem. Soc.* **1949**, *71*, 1632−1633.

(19) Farmer, W. J.; Yang, M. S.; Letey, J.; Spencer, W. F. Hexachlorobenzene: Its vapor pressure and vapor phase diffusion in soil. *Soil Sci. Soc. Am. J.* **1980**, *44*, 676−680.

(20) Liu, K.; Dickhut, R. M. Saturation vapor pressures and thermodynamic properties of benzene and selected chlorinated benzenes t environmental temperatures. *Chemosphere* **1994**, *29*, 581−589.

(21) Wania, F.; Shui, W.-Y.; Mackay, D. Measurement of the vapor pressure of several low-volatility organochlorine chemicals at low temperatures with a gas saturation method. *J. Chem. Eng. Data* **1994**, *39*, 572−577.

(22) Stephenson, R. M.; Malanowski, S. *Handbook of the Thermodynamics of Organic Compounds*; Elsevier: New York, 1987.

(23) Emel'yanenko, V. N.; Verevkin, S. P.; Koutek, B.; Doubsky, J. Vapor pressures and enthalpies of vaporization of a series of the linear aliphatic nitriles. *J. Chem. Thermodyn.* **2005**, *37*, 73- 81.

(24) Stull, D. R.; Westrum, E. F.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969.

(25) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970; pp 1−636.

(26) http://webbook.nist.gov/.

(27) Poeti, G.; Fanelli, E.; Braghetti, M. A differential scanning calorimetric study of some phenol derivatives. *J. Therm. Anal.* **1982**, *24*, 273−279.

(28) Plato, C.; Glasgow, A. R., Jr. Differential scanning calorimetry as a general method for determining the purity and heat fusion of high-purity organic chemicals. Application to 95 compounds. *Anal. Chem.* **1969**, *41*, 330−336.

(29) Donnelly, J. R.; Drewes, L. A.; Johnson, R. L.; Munslow, W. D.; Knapp, K. K.; Sovocool, G. W. Purity and heat of fusion data for environmental standards as determind by differential scanning calorimetry. *Thermochim. Acta* **1990**, *167*, 155−187.

(30) Majer, V.; Svoboda, V. *Enthalpies of Vaporization of Organic Compounds*: *A Critical Review and Data Compilation*; Blackwell Scientific Publications: Oxford, 1985; 300 pp.

(31) Verevkin, S. P. Determination of the ortho-, para-, and meta-interactions in secondary-alkylphenols from thermochemical measurements. *Ber. Bunsen-Ges. Phys. Chem.* **1998**, *102*, 1467−1474.

(32) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976.

(33) Domalski, E. S.; Hearing, E. D. Estimation of the thermodynamic properties of C-H-N-O-S- Halogen compounds at 298.15 K. *J. Phys. Chem. Ref. Data* **1993**, *22*, 805−1159.

(34) Yarovoi, S. S. *Methods of Calculations of Physico-Chemical Properties for Hydrocarbons*; Khimia: Moscow, 1978.

(35) Wolf, K. L.; Weghofer, H. Ueber Sublimationswaermen. *Z. Phys. Chem. B* **1938**, *39*, 194−208.

(36) Platonov, V. A.; Simulin, Yu. N.; Rozenberg, M. M. Standard heat of formation of pentachlorobenzene. Calculation of $\Delta H_c°$ (g) and $\Delta E_s°$ (g) of polychlorobenzenes by the Tatevskii method. *Russ. J. Phys. Chem. (Engl. Transl.)* **1985**, *59*, 814−817.

(37) Emel'yanenko, V .N.; Kabo, G. J.; Verevkin, S. P. Measurement and prediction of thermochemical properties. Improved increments for the estimation of enthalpies of sublimation and standard enthalpies of formation of alkyl derivatives of urea. *J. Chem. Eng. Data* **2006**, *51*, 79−87.

(38) Klamt, A. Conductor-like screening model for real solvents: a new approach to the quantitative calculation of solvation phenomena. *J. Phys. Chem.* **1995**, *99*, 2224−2235.

(39) Klamt, A.; Jonas, V.; Bürger, T.; Lohrenz, J. Refinement and parametrization of COSMO-RS. *J. Phys. Chem.* **1998**, *102*, 5074−5085.

(40) Klamt, A.; Eckert, F. COSMO-RS: a novel and efficient method for the a priori prediction of thermophysical data of liquids. *Fluid Phase Equilib.* **2000**, *72*, 43−48.

(41) Klamt, A. *COSMO-RS: From Quantum Chemistry to Fluid Phase Thermodynamics and Drug Design*; Elsevier: Amsterdam, 2005.

(42) *COSMOtherm program, Release C2.1, Revision 01.05*; COSMOlogic GmbH&CoKG: Leverkusen, Germany, 2005.

(43) *COSMObase databse, Release C2.1, Revision 01.05*; COSMOlogic GmbH&CoKG: Leverkusen, Germany, 2005.

(44) *Turbomole, Version 5.8*; Universität Karlsruhe: Karlsruhe, Germany, 2005.

Received for review September 29, 2006. Accepted November 18, 2006. V.E. acknowledges gratefully a research scholarship from the Research Training Group “New Methods for Sustainability in Catalysis and Technique” of German Science Foundation (DFG).

JE060429R