

Measurements of Saturated Vapor Pressure above the Liquid Phase for Isomeric Dichlorobenzenes and 1,2,4-Trichlorobenzene

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Saturated vapor pressures have been measured for liquid 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, and 1,2,4-trichlorobenzene by precision comparative ebulliometry over an approximate pressure range from 6 to 105 kPa. The relative error in pressure is estimated to be less than or equal to $\pm 0.05\%$ of the measured value and the absolute error in temperature is estimated at less than or equal to ± 0.01 K on ITS-90. The results have been represented by the Antoine and Wagner-type equations within experimental uncertainties and compared with the data so far available in the literature. On the basis of the present and previous measurements, vapor pressure equations for the chlorobenzenes covering the entire range of liquid existence have been constructed and discussed.

Introduction

Chlorobenzenes are synthetic products that have been introduced into the environment only by human activities; so far they have not been found to occur in nature. Nevertheless, their industrial use is wide: liquid chlorobenzenes (chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, and 1,2,4-trichlorobenzene) are used as solvents and extractive agents for organic compounds. Chlorobenzene and 1,2,4-trichlorobenzene (and hexachlorobenzene) are used as intermediates in the manufacture of pesticides and herbicides. Furthermore, 1,3-dichlorobenzene and 1,4-dichlorobenzene are used as active components in disinfectants and deodorants.

Chemical waste dump leaching, direct manufacturing effluents, solvent applications, stack effluents from refused-fired steam boilers and power plants are the major sources of chlorobenzenes emissions into the atmosphere. Owing to their low solubility in water and slow rate of biodegradation in water and soil, chlorobenzenes tend to accumulate in fat tissue of living organisms. Since chlorobenzenes have also been widely detected in ambient air, population exposure may generally occur both through oral consumption of contaminated drinking water and food (particularly fish) and through inhalation of contaminated air. Even though the effects of chlorobenzenes on humans have not yet been in all aspects satisfactorily determined, they are known to have narcotic effects as well as to cause harm to the nervous system and internal organs.

To understand the partitioning and fate of chlorobenzenes in the environment, it is necessary to know the values of several types of basic physical–chemical properties in the temperature range from about -30 to 50 °C. Vapor pressure is certainly one of the most important properties needed, the others being solubility in water, Henry's law constant, octanol–water partition coefficient, and enthalpy of vaporization. Despite the fact that vapor

pressures of all chlorobenzenes are quite low at environmentally relevant temperatures, data of high accuracy are still required. Even though some data on vapor pressure are available for each of the chlorobenzenes, they are either of dubious quality or cover only a narrow range of conditions (or both).

This work has been concerned with experimental determination of accurate vapor pressures of all isomeric dichlorobenzenes and of 1,2,4-trichlorobenzene over the range of conventional ebulliometric conditions. In future work, recommended data on vapor pressure and heat of vaporization for all isomeric dichlorobenzenes, trichlorobenzenes, and pentachlorobenzene will be generated by simultaneous correlation of vapor pressures and thermal data using the vapor pressure data measured in this work, data measured by a static method (Poledníček et al., 1996), and data selected from literature.

Experimental Section

Materials. *1,2-Dichlorobenzene* ($C_6H_4Cl_2$). Fluka product of stated purity $>99\%$; original purity determined by GC analysis was 99.58%. The sample was further purified by a duplicate fractional distillation under reduced pressure of about 1.5 kPa in a packed column and dried over molecular sieves type 4A. The final purity determined by GC was 99.98%.

1,3-Dichlorobenzene ($C_6H_4Cl_2$). Aldrich product of stated purity 98%; original purity determined by GC analysis was 99.38%. The sample was further purified and dried as stated above, reaching the final GC purity of 99.55%.

1,4-Dichlorobenzene ($C_6H_4Cl_2$). Aldrich product of stated purity $>99\%$; original purity determined by GC analysis was 99.91%. The sample was further purified by four times repeated zone-refining at ambient temperature between -10 and 5 °C. The final amount of impurities was below the limit of GC detection.

1,2,4-Trichlorobenzene ($C_6H_3Cl_3$). Aldrich product of stated purity 98%, original purity 98.65%. The sample was

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Table 1. Vapor Pressure of 1,2-Dichlorobenzene

<i>T</i> /K	<i>P</i> /kPa	eq 1			eq 5		
		ΔT /K	ΔP /kPa	100 $\Delta P/P$	ΔT /K	ΔP /kPa	100 $\Delta P/P$
363.343	5.729	0.014	-0.005	-0.08	0.012	-0.004	-0.07
372.679	8.333	0.000	-0.000	0.00	0.003	-0.002	-0.02
372.680	8.335	0.002	-0.001	-0.01	0.004	-0.002	-0.03
380.150	11.074	-0.007	0.005	0.04	-0.003	0.003	0.02
386.415	13.917	-0.009	0.009	0.06	-0.006	0.006	0.04
391.760	16.800	-0.009	0.011	0.07	-0.007	0.008	0.05
391.760	16.799	-0.010	0.012	0.07	-0.007	0.009	0.05
397.290	20.290	-0.006	0.010	0.05	-0.005	0.008	0.04
403.085	24.569	-0.002	0.003	0.01	-0.002	0.003	0.01
408.697	29.394	0.004	-0.008	-0.03	0.003	-0.005	-0.02
414.174	34.818	0.007	-0.022	-0.06	0.006	-0.016	-0.05
419.442	40.757	0.007	-0.025	-0.06	0.005	-0.016	-0.04
419.444	40.761	0.008	-0.026	-0.06	0.005	-0.017	-0.04
424.807	47.625	0.007	-0.031	-0.07	0.005	-0.020	-0.04
433.252	60.273	0.004	-0.024	-0.04	0.002	-0.011	-0.02
441.334	74.765	0.001	-0.006	-0.01	0.000	0.002	0.00
450.062	93.403	-0.002	0.020	0.02	-0.001	0.010	0.01
451.995	97.970	-0.004	0.043	0.04	-0.003	0.026	0.03
454.783	104.893	-0.006	0.058	0.06	-0.003	0.031	0.03
mean abs. dev		0.006	0.017	0.04	0.006	0.023	0.27
standard dev.		0.007	0.024		0.009	0.054	

further purified and dried as described above for 1,2-dichlorobenzene. The final GC purity was 99.87%.

Owing to relatively large consumption of substances, the Karl Fischer titration method was used to determine the water content only for 1,2,4-trichlorobenzene, the only hygroscopic species among the compounds studied. The water content found was less than 0.01 mass%. It was then assumed that water content in all the remaining compounds was also lower than 0.01 mass%.

Water used as a reference substance for indirect pressure determinations was a sample redistilled upon addition of potassium permanganate in a quartz batch distillation unit.

Apparatus and Procedure. A modified ebulliometer and an apparatus based on comparative ebulliometry have been used for the vapor pressure measurements. Experimental arrangement has been described in detail by Aim (1994a,b), and thus only a brief characterization is given below.

Two very similar ebulliometers essentially of the classical Swietoslawski design have been used. A reference ebulliometer was filled with water as a reference fluid of known vapor pressure and partly enclosed in a box, which shielded it from temperature fluctuations of the surroundings. The measuring ebulliometer (all made of quartz) was filled with about 60 mL of the investigated compound and placed in an air thermostat. Both ebulliometers were connected in parallel via cold traps to the pressure-controlling assembly, whose main parts were two buffer reservoirs (connected in series by pneumatic resistor) and an air-thermostated mercury manostat. The pressure control assembly made it possible to maintain the pressure in the ebulliometric system constant within less than ± 3 Pa at a series of evenly spaced pressure values in the range from 3 to over 100 kPa.

The boiling temperatures (of water and of a compound investigated) in the two ebulliometers at a given pressure were measured simultaneously by two 2850D-type probes of the Hewlett-Packard quartz thermometer (model HP-2801A). Both probes had been repeatedly calibrated against a Leeds & Northrup standard platinum 25 Ω resistance thermometer (model 8163-B) coupled in a four-wire connection with a precision resistance bridge model F17A (Automatic Systems Laboratories, Milton Keynes, U.K.). The resulting overall accuracy in the measured boiling temperatures is estimated to be better than ± 0.01 K within ITS-90 over the whole investigated range.

From the boiling temperature of water, the corresponding equilibrium pressure in the system was calculated at each point by using the accurate vapor pressure equation given by Šifner and Klomfar (1996). The accuracy in pressure determined in this manner is estimated to be better than $\pm 0.05\%$ of the measured pressure value over the entire range studied.

Results and Discussion

Measured vapor pressures of 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, and 1,2,4-trichlorobenzene are presented in Tables 1–4 together with the results of their representation by the Antoine equation. (For the included results on eq 5 see below.)

The Antoine equation was employed in the form

$$\log(P/\text{kPa}) = A - B/[(T/K) + C] \quad (1)$$

where P and T denote the saturated vapor pressure and temperature, respectively, and A , B , and C are adjustable parameters characteristic of a substance.

The parameters A , B , and C in eq 1 were evaluated from the experimental vapor pressure data by the method of maximum likelihood, see, e.g., Aim (1981a,b), allowing for the fact that both the measured variables are subject to experimental uncertainties. A symmetric maximum likelihood objective function was used in the form

$$S = \sum [(\Delta T_n)^2 (\sigma_{T,n})^{-2} + (\Delta P_n)^2 (\sigma_{P,n})^{-2}] \quad (2)$$

where the index in summation runs over all experimental observations and $\sigma_{T,n}$ and $\sigma_{P,n}$ are estimated standard deviations in measured temperature and pressure for the n th observation, respectively. For all computations with the original data presented in this work, these were assigned values $\sigma_{T,n} = 0.01$ K and $\sigma_{P,n} = 0.0005 P_{\text{expt},n}$ for all observations as a priori estimated from the properties of the experimental setup. The parameters of the correlating eq 1 and the calculated values $T_{\text{calc},n}$ and $P_{\text{calc},n}$ corresponding to each observation were evaluated by minimizing the objective function defined in eq 2 by a robust iterative procedure (using the simplex method in each of the alternating steps).

The resulting parameters of eq 1 obtained for the present vapor pressure data on isomeric dichlorobenzenes and 1,2,4-trichlorobenzene are given in Table 5 along with the

Table 2. Vapor Pressure of 1,3-Dichlorobenzene

<i>T</i> /K	<i>P</i> /kPa	eq 1			eq 5		
		ΔT /K	ΔP /kPa	100 $\Delta P/P$	ΔT /K	ΔP /kPa	100 $\Delta P/P$
357.603	5.731	0.009	-0.003	-0.05	0.010	-0.004	-0.06
366.800	8.343	0.005	-0.002	-0.03	0.010	-0.005	-0.06
374.140	11.076	-0.003	0.002	0.02	0.003	-0.002	-0.02
380.320	13.920	-0.007	0.007	0.05	-0.003	0.002	0.02
385.583	16.799	-0.008	0.010	0.06	-0.005	0.006	0.04
391.042	20.292	-0.007	0.011	0.05	-0.005	0.008	0.04
391.043	20.291	-0.008	0.012	0.06	-0.007	0.009	0.05
396.755	24.569	-0.004	0.008	0.03	-0.004	0.007	0.03
402.291	29.396	0.000	0.001	0.00	-0.001	0.003	0.01
407.685	34.819	0.004	-0.012	-0.03	0.002	-0.006	-0.02
412.865	40.761	0.007	-0.023	-0.06	0.004	-0.015	-0.04
418.143	47.623	0.008	-0.032	-0.07	0.005	-0.020	-0.04
418.143	47.623	0.008	-0.032	-0.07	0.005	-0.020	-0.04
426.451	60.276	0.008	-0.040	-0.07	0.005	-0.026	-0.04
434.409	74.765	0.004	-0.027	-0.04	0.002	-0.017	-0.02
443.009	93.403	0.000	0.004	0.00	0.000	-0.002	0.00
445.197	98.670	-0.003	0.029	0.03	-0.002	0.015	0.02
448.070	105.933	-0.007	0.068	0.06	-0.004	0.044	0.04
448.357	106.716	-0.004	0.045	0.04	-0.002	0.019	0.02
mean abs. dev.		0.005	0.019	0.04	0.007	0.064	0.44
standard dev.		0.007	0.028		0.013	0.179	

Table 3. Vapor Pressure of 1,4-Dichlorobenzene

<i>T</i> /K	<i>P</i> /kPa	eq 1			eq 5		
		ΔT /K	ΔP /kPa	100 $\Delta P/P$	ΔT /K	ΔP /kPa	100 $\Delta P/P$
358.289	5.729	0.004	-0.001	-0.02	-0.008	0.003	0.05
367.455	8.334	0.003	-0.002	-0.02	0.003	-0.002	-0.02
374.806	11.074	0.000	0.000	0.00	0.004	-0.003	-0.03
380.986	13.921	-0.003	0.002	0.02	0.003	-0.002	-0.02
386.253	16.800	-0.005	0.006	0.04	0.000	0.001	0.00
391.714	20.290	-0.006	0.008	0.04	-0.002	0.004	0.02
391.718	20.292	-0.006	0.008	0.04	-0.002	0.003	0.02
397.440	24.570	-0.004	0.008	0.03	-0.003	0.005	0.02
402.972	29.388	0.000	0.001	0.00	-0.001	0.001	0.00
408.373	34.809	0.003	-0.009	-0.03	0.002	-0.004	-0.01
413.566	40.752	0.005	-0.017	-0.04	0.002	-0.008	-0.02
418.852	47.615	0.006	-0.026	-0.05	0.003	-0.011	-0.02
427.182	60.269	0.005	-0.025	-0.04	0.001	-0.006	-0.01
427.183	60.271	0.005	-0.026	-0.04	0.001	-0.006	-0.01
435.159	74.759	0.001	-0.007	-0.01	-0.001	0.007	0.01
443.772	93.393	-0.002	0.017	0.02	0.000	0.003	0.00
446.010	98.783	-0.003	0.031	0.03	0.000	0.004	0.00
448.776	105.783	-0.004	0.048	0.04	0.000	0.001	0.00
mean abs. dev.		0.004	0.013	0.03	0.004	0.073	0.20
standard dev.		0.004	0.020		0.006	0.212	

calculated normal boiling temperatures. Tables 1–4 display also the corresponding characteristics of the fit, namely, the deviations

$$\Delta T_n = T_{\text{calc},n} - T_{\text{expt},n} \quad \text{and} \quad \Delta P_n = P_{\text{calc},n} - P_{\text{expt},n}$$

evaluated at the minimum of the objective function. The deviations in percent of pressure are also displayed, since the second term in objective function (eq 2) with $\sigma_{P,n}$ specified as a constant multiple of the n th pressure value just minimizes the percent deviations in pressure. Also given in Tables 1–4 are the mean absolute deviations a_T and a_P given by

$$a_X = \sum |X_{\text{calc},n} - X_{\text{expt},n}|/N, \quad X = T \text{ and } P \quad (3)$$

and the standard deviations s_T and s_P defined by

$$s_X = \left[\sum (X_{\text{calc},n} - X_{\text{expt},n})^2 / (N - M) \right]^{-1/2}, \quad X = T \text{ and } P \quad (4)$$

where M is the number of parameters in the correlating equation ($M = 3$ for eq 1 and $M = 4$ for eq 5) and N is the number of experimental observations. It is seen from the tables that Antoine equation represents the experimental

vapor pressure data of all the four substances within the estimated experimental errors.

To describe a wider range of vapor pressure still based on the present data, we have performed a study on Wagner-type equations including also the recent data (extending to lower pressures) obtained by static method for isomeric dichlorobenzenes by Poledníček et al. (1996). For the required coordinates of the critical points, we have taken the values given by Dreisbach (1955). Slightly superior results were obtained by using the vapor pressure equation of the form

$$\ln(P/P_c) = (T_c/T) (A\tau + B\tau^{1.5} + C\tau^3 + D\tau^5), \quad \tau = 1 - T/T_c \quad (5)$$

where A , B , C , and D are adjustable parameters characteristic of a substance and subscript c denotes the critical properties. In fact, when proper weighting of all individual data points was applied in the above-described parameter estimation procedure, namely, by using the uncertainties of $\sigma_{T,n} = 0.04$ K and $\sigma_{P,n} = 0.006P_{\text{expt},n}$ estimated for observations by Poledníček et al. (1996) and the values given above for the present data, both the data series have been represented simultaneously by eq 5 just within the

Table 4. Vapor Pressure of 1,2,4-Trichlorobenzene

<i>T</i> /K	<i>P</i> /kPa	eq 1			eq 5		
		$\Delta T/K$	$\Delta P/kPa$	$100\Delta P/P$	$\Delta T/K$	$\Delta P/kPa$	$100\Delta P/P$
391.821	5.728	-0.022	0.008	0.14	-0.021	0.008	0.14
401.533	8.331	0.008	-0.004	-0.05	0.009	-0.005	-0.06
409.378	11.070	0.007	-0.006	-0.05	0.008	-0.006	-0.05
415.963	13.911	0.008	-0.009	-0.06	0.008	-0.009	-0.06
415.969	13.914	0.008	-0.009	-0.06	0.008	-0.009	-0.06
421.590	16.794	0.009	-0.012	-0.07	0.009	-0.011	-0.07
427.439	20.281	0.005	-0.008	-0.04	0.004	-0.006	-0.03
427.458	20.290	0.003	-0.005	-0.03	0.002	-0.004	-0.02
433.591	24.566	0.000	0.000	0.00	-0.001	0.002	0.01
439.536	29.387	-0.003	0.007	0.03	-0.004	0.010	0.04
445.338	34.807	-0.006	0.017	0.05	-0.007	0.021	0.06
450.905	40.745	-0.008	0.028	0.07	-0.008	0.032	0.08
456.574	47.613	-0.008	0.037	0.08	-0.009	0.039	0.08
465.478	60.271	-0.007	0.039	0.07	-0.007	0.039	0.06
465.481	60.264	-0.008	0.049	0.08	-0.008	0.049	0.08
473.976	74.748	-0.004	0.029	0.04	-0.003	0.024	0.03
483.139	93.380	0.003	-0.033	-0.04	0.005	-0.045	-0.05
485.547	98.847	0.006	-0.061	-0.06	0.007	-0.074	-0.08
489.037	107.216	0.009	-0.105	-0.10	0.010	-0.122	-0.11
mean abs. dev.		0.007	0.025	0.06	0.007	0.027	0.06
standard dev.		0.009	0.039		0.009	0.045	

Table 5. Constants in Antoine Equation (Eq 1)

	<i>A</i>	<i>B</i>	<i>C</i>	<i>t_b</i> /°C
1,2-dichlorobenzene	6.151 51	1612.27	-64.447	180.190
1,3-dichlorobenzene	6.161 51	1595.19	-62.398	173.095
1,4-dichlorobenzene	6.130 50	1575.69	-65.007	173.864
1,2,4-trichlorobenzene	6.119 73	1677.35	-78.926	213.492

respective claimed experimental uncertainties with a single set of parameters for each of the three isomeric dichlorobenzenes. For the data measured in this work this is documented in Tables 1–3, where the appropriate deviations for eq 5 are given in the last three columns. However, one should pay attention only to the deviations for single points in this case since the statistics given by eqs 3 and 4 are necessarily somewhat distorted by simultaneous representation of the data set by Poledníček et al. (1996). The evaluated constants of Wagner equation (eq 5) are summarized in Table 6 along with the critical temperature and pressure values used and with the normal boiling points calculated from eq 5. It is seen that the boiling points are in expected agreement with the values of Table 5.

There are no recent dependable vapor pressure data available for 1,2,4-trichlorobenzene extending to pressures below the lower limit of data of the present study. Just to provide a complete set of Wagner-type equations for the chlorobenzenes considered, we have therefore estimated the parameters of eq 5 on the basis of our data only (again by using the critical temperature and pressure from Dreisbach (1955)). The results are correspondingly reported in Tables 4 and 6. An approximate equation extending down to low pressure is given at the end of this section.

To summarize, the Wagner-type equations (eq 5) with constants and criticals of Table 6 describe simultaneously and within estimated experimental uncertainties both the data measured in this work and the data of Poledníček et al. (1996) for dichlorobenzenes over the entire merged ranges, i.e., from 256, 249, 333, and 390 K up to the critical point for 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, and 1,2,4-trichlorobenzene, respectively. These equations are used as the zero baselines in Figures 1–4, wherein the comparisons of the present vapor pressure measurements with literature data for the four chlorobenzenes examined are displayed in the form of percentage deviation plots.

For 1,2-dichlorobenzene, the available literature vapor pressure data sources are the following: data measured

by Fisk and Noyes (1936) by a static method over a narrow temperature interval from 273 to 297 K, data reported in a compilation by Stull (1947), medium-pressure range data measured by using a dynamic method by Dreisbach and Shrader (1949), five points covering the low to atmospheric pressure range given in Dreisbach (1955) monograph (for original data both the mentioned compilations refer to Dow Chemicals Co. files), the measurements repeated by the dynamic method by McDonald et al. (1959), one point reported by Riding et al. (1956), and finally two equations, the "DIPPR equation" as given by Daubert and Danner (1989), based reportedly on Stull's data and some hardly accessible secondary sources of rather old origin, and the "TRC equation" as reported in TRC k-7330 (1989), based mostly on the data by Dreisbach and Shrader (1949) and McDonald et al. (1959) (and a few single data points of lower accuracy).

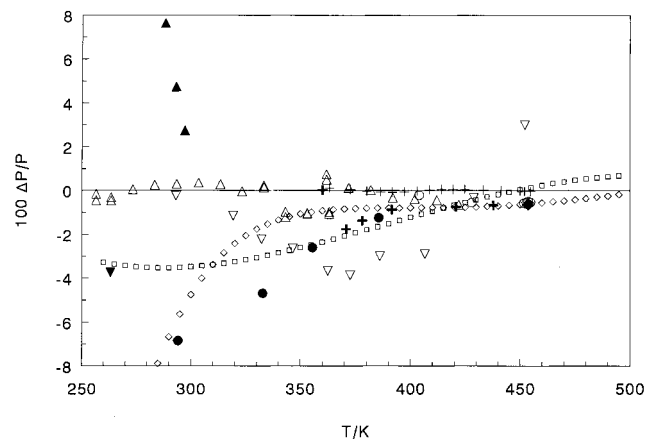
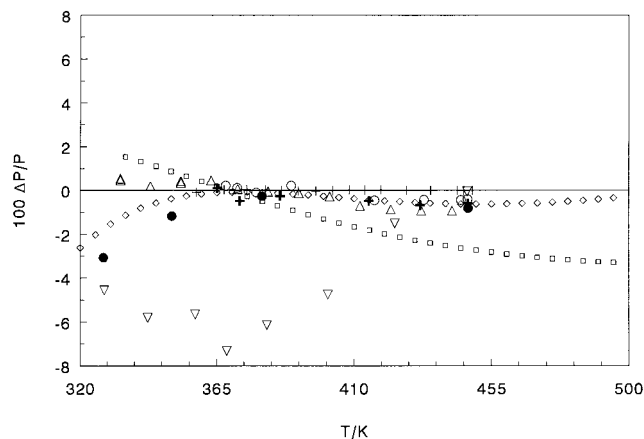
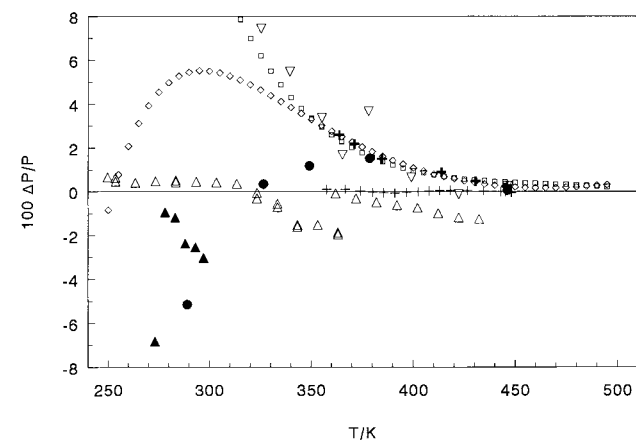
The overall situation for 1,2-dichlorobenzene is clearly seen in Figure 1. Good agreement with our correlation is observed for most of the data considered, with only few exceptions: the data by Fisk and Noyes largely disagree with the underlying data of Poledníček et al. (in fact the difference amounts to more than 13% at the lowest temperature of 273.15 K), and the data given by Stull exhibit quite a large scatter. The DIPPR equation then seems to be based on the data of Stull perhaps along with the one point given by Riding et al., which results in its 4% deviations in the low-temperature region. The TRC equation follows the data by Dreisbach (1955) at low pressures.

Some remarks of more general validity for the four chlorobenzenes can be made as follows: (i) somewhat surprisingly the data by Dreisbach, Stull, and McDonald et al., even though they come from the same laboratory and/or refer to the same origin (Dow Chemicals Co.), are not in mutual agreement, (ii) the most often cited and referred to data given by Stull (1947) exhibit largest scatter and deviations from the data that we would recommend as a result of the present study, and (iii) the data presented by Dreisbach (1955) for the two lowest pressure points (1 and 10 Torr) are obviously a result of extrapolation overestimating the boiling temperature at a given pressure.

The literature data sources found for 1,3-dichlorobenzene represent just a subset of the references given above for 1,2-dichlorobenzene, namely, they involve Fisk and Noyes (1936), Dreisbach and Shrader (1949), Stull (1947), Dreisbach (1955), and the DIPPR equation by Daubert and

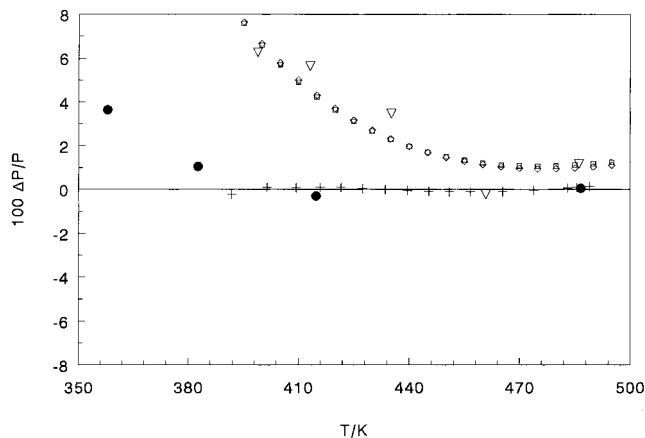
Table 6. Constants in Wagner-type Equation (Eq 5)

	T_b/K	P_b/MPa	A	B	C	D	$t_b/^\circ C$
1,2-DiCB	697.25	4.106	-7.033 04	0.877 004	-2.783 66	-1.732 26	180.201
1,3-DiCB	683.95	3.881	-6.604 65	0.082 970	-2.127 57	-2.153 27	173.104
1,4-DiCB	684.75	3.906	-7.423 05	1.926 47	-4.936 00	1.061 69	173.880
1,2,4-TCB	734.95	3.986	-7.398 23	0.816 681	-1.850 06	-4.800 65	213.499

**Figure 1.** Percent in pressure deviation graph for the vapor pressure of 1,2-dichlorobenzene with zero line representing eq 5 with parameters of Table 6: +, this work; Δ , Poledníček et al.; \blacktriangle , Fisk and Noyes; ∇ , Stull; +, Dreisbach and Shrader; \bullet , Dreisbach; \blacktriangledown , Riding et al.; \circ , McDonald et al.; \square , DIPPR; \diamond , TRC.**Figure 3.** Percent in pressure deviation graph for the vapor pressure of 1,4-dichlorobenzene with zero line representing eq 5 with parameters of Table 6: +, this work; Δ , Poledníček et al.; ∇ , Stull; +, Dreisbach and Shrader; \bullet , Dreisbach; \circ , McDonald et al.; \square , DIPPR; \diamond , TRC.**Figure 2.** Percent in pressure deviation graph for the vapor pressure of 1,3-dichlorobenzene with zero line representing eq 5 with parameters of Table 6: +, this work; Δ , Poledníček et al.; \blacktriangle , Fisk and Noyes; ∇ , Stull; +, Dreisbach and Shrader; \bullet , Dreisbach; \square , DIPPR; \diamond , TRC.

Danner (1989). All the relevant comments correspondingly apply here. Apart from certain scatter and minor disagreement of the data of Poledníček et al. with the present measurements, largest deviations in Figure 2 are again observed for the data of Fisk and Noyes and those of Stull. Nevertheless, most of the data sets converge to a common value for the normal boiling point.

For 1,4-dichlorobenzene no other than the above data sources have been found, the most recent direct measurements being those reported by Mc Donald et al. (1959). As it is seen in Figure 3, both this data set and the results of Dreisbach and Shrader (1949) agree very well with the present work, whereas deviations between our data and those given by Stull are large again. Strange enough, the DIPPR equation neither goes through the Stull's data points (on which it is presumably based) nor does it provide a correct normal boiling temperature; Daubert and Danner (1989) themselves give 447.21 K while the equation yields

**Figure 4.** Percent in pressure deviation graph for the vapor pressure of 1,2,4-trichlorobenzene with zero line representing eq 5 with parameters of Table 6: +, this work; ∇ , Stull; \bullet , Dreisbach; \square , DIPPR; \diamond , TRC.

448.13 K. The TRC equation agrees very well with the present data.

Besides the compilations of Stull, Dreisbach, and DIPPR, the only literature mentions on vapor pressure of 1,2,4-trichlorobenzene provide the papers by Sears and Hopke (1949), reporting only a two-constant equation for the temperature range 17 to 25 $^\circ C$, and Kohler and Rott (1954), giving an (approximate) data point of 0.04 kPa at 20 $^\circ C$. Sticking to the $\pm 8\%$ band, the deviation plot for 1,2,4-trichlorobenzene covering the range studied in this work is displayed in Figure 4, showing good agreement of the present data with the three higher pressure points of Dreisbach, while the DIPPR equation increasingly deviates at lower pressures (as based on Stull's data) and so does in a coinciding manner the TRC equation.

In an attempt to extend the validity of the vapor pressure equation for 1,2,4-trichlorobenzene downward, we have also estimated parameters of eq 5 on simultaneous basis of the data determined in this work together with eight points

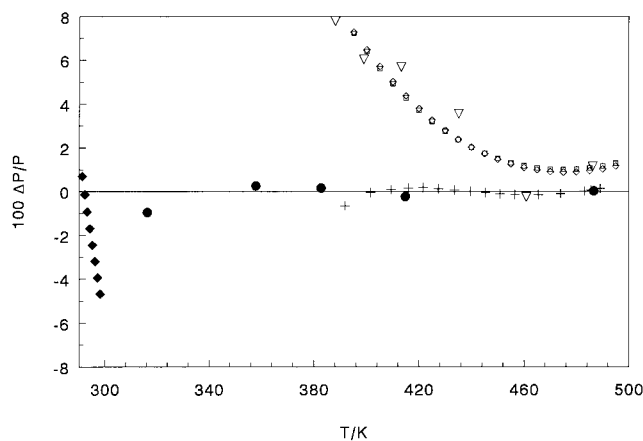


Figure 5. Percent in pressure deviation graph for the vapor pressure of 1,2,4-trichlorobenzene with zero line representing eq 5 with the critical properties of Table 6 and parameters $A = -9.030\ 38$, $B = 4.843\ 01$, $C = -9.249\ 32$, and $D = 5.697\ 31$: +, this work; ∇ , Stull; \blacklozenge , Sears and Hopke; \bullet , Dreisbach; \square , DIPPR; \diamond , TRC.

generated from the equation reported by Sears and Hopke and with the data given by Dreisbach and by Stull (on assigning our data 20 times higher statistical weight than the others). The resulting Wagner-type equation (eq 5 with the critical temperature and pressure taken from Table 6 and parameter estimates of $A = -9.030\ 38$, $B = 4.843\ 01$, $C = -9.249\ 32$, and $D = 5.697\ 31$) still represents our data almost within experimental errors (with mean absolute deviations of 12 mK and 0.09% of pressure). Figure 5, in which this equation is used as the zero baseline, shows that also the data given by Dreisbach are followed quite well and that the equation reasonably reaches the low-temperature points generated from the equation of Sears and Hopke. Assuming that the data of Sears and Hopke are not completely wrong (despite their erroneous slope), the Wagner-type equation (eq 5) with constants given in this paragraph may serve as a tentative tool for estimating the vapor pressure of 1,2,4-trichlorobenzene down to its melting point of 17 °C (290.15 K). We note in passing that the low-pressure data of Stull deviate increasingly up to by more than 30% at 311 K and that the datum point of Kohler and Rott at 293 K lies over 40% above the zero baseline of Figure 5. Accurate low-temperature vapor pressure measurements on liquid 1,2,4-trichlorobenzene are clearly needed.

Conclusions

Saturated vapor pressures of liquid 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, and 1,2,4-trichlorobenzene have been determined by precision comparative ebulliometry over approximate pressure range from 6 to 105 kPa with the relative error in pressure of 0.05% of the measured value and absolute error in temperature of 0.01 K on ITS-90. The results obtained have been represented by the Antoine equation within experimental uncertainty. The same holds also for the Wagner-type equation used to represent simultaneously the present data for dichlorobenzenes together with the data by Poledníček et al. (1996) extending to lower temperature region. As a result, reliable vapor pressure equations are given for liquid 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, and 1,2,4-trichlorobenzene covering the respective ranges from 256, 249, 333, and 390 K up to slightly above the normal boiling point (and interpolating up to the critical point at the same time). At present only a tentative and

approximate extension to lower vapor pressures is possible for 1,2,4-trichlorobenzene as reliable data at low temperatures are yet to be determined. These will be measured and used along with thermal data in a further study focusing on the low vapor pressure region of the entire family of chlorinated benzenes. Work along these lines is in progress.

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Supporting Information Available:

Full original printout tables documenting the estimation of the parameters of the Wagner equation listed in Table 6, as based on the combined sets of the present and Poledníček et al. data for dichlorobenzenes and on the present data for 1,2,4-trichlorobenzene (6 pages). Ordering and accessing information is given on any current masthead page.

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