Measurement of the Vapor Pressure of Several Low-Volatility Organochlorine Chemicals at Low Temperatures with a Gas Saturation Method

Frank Wania, Wan-Ying Shiu, and Donald Mackay*

Department of Chemical Engineering and Applied Chemistry, University of Toronto,
Toronto, Ontario, Canada M5S 1A4

The vapor pressures of hexachlorobenzene, γ-hexachlorocyclohexane, *p,p'*-DDT, i.e., 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane, 4-monochlorobiphenyl, 4,4'-dichlorobiphenyl, 2,3,4,5-tetrachlorobiphenyl, and 2,2',4,4',6,6'-hexachlorobiphenyl were measured in the temperature range -30 to +40 °C with a gas saturation technique. Coefficients describing the temperature dependence of these vapor pressures are reported. Enthalpies of sublimation derived from these data show no significant temperature dependence in the temperature range investigated.

Introduction

Vapor pressures are indispensable for the assessment of the environmental fate and behavior of environmental contaminants. Volatilization from soil and vegetation is largely controlled by the compound's vapor pressure. The diffusive gas exchange of a substance between the air and the water phase is controlled by Henry's law constant, a parameter closely related to, and derivable from, vapor pressure. Adsorption to airborne particles and consequently the rate of wet and dry deposition processes from the atmosphere are largely controlled by a compound's vapor pressure.

Most determinations of the vapor pressure of environmental contaminants have been at or above room temperature, because the vapor pressures of important groups of contaminants such as many organochlorine compounds or polycyclic aromatic compounds are quite low and easier to determine at higher temperatures. Further, until recently the study of the environmental behavior of pollutants has focused primarily on the temperate regions, where these chemicals are primarily produced and used.

There is an increasing need to obtain accurate physical-chemical property data of contaminants at subzero temperatures. Many of the contaminants of temperate regions are also found in the colder regions of the globe, and the dependence of volatility on temperature may explain how these compounds are transported to these regions (*1*). Extrapolations of measurements at higher temperatures may not accurately predict values at the temperatures encountered in the environment at high altitudes and latitudes.

The saturation column technique has been widely employed to measure low vapor pressures. General descriptions are given by Thomson (*2*) and Spencer and Cliath (*3*). Westcott et al. (*4*) and Burkhard et al. (*5*) reported the use of solid sorbent traps to collect the saturated vapor. These were eluted with solvent and then analyzed by gas chromatography (GC). The direct transfer of the trapped material onto a GC column by thermal desorption was described by Rordorf et al. (*6*). Similarly, Hales et al. (*7*) collected saturated vapor on a packed GC column and subsequently heated the GC oven for analysis. These latter methods are capable of measuring very low vapor pressures because the entire amount of sampled vapor is transferred onto the GC and not only an aliquot as in the case of solvent-extracted sorbent traps. A method based on the same principle, but employing solvent elution and HPLC to measure the vapor pressure of polynuclear aromatic hydrocarbons, was reported by Sonnefeld et al. (*8*). Quantification of hydrocarbon vapors can also be accomplished by catalytic combustion in combination with an infrared analyzer to measure the amount of carbon dioxide produced (*9, 10*).

This paper describes a modified saturator column method using thermal desorption and gas chromatography. It is capable of determining vapor pressures at subzero temperatures down to 10^{-6} Pa, although, as is discussed later, certain precautions must be taken at low temperatures. The feasibility and accuracy of the experimental setup and quantification method were confirmed by reproducing literature values of the vapor pressure and the enthalpy of sublimation of naphthalene in the temperature range -30 to 0 °C. The paper reports vapor pressures and enthalpies of sublimation for hexachlorobenzene (HCB), γ-hexachlorocyclohexane (γ-HCH), 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (*p,p'*-DDT), and four isomers of polychlorinated biphenyls (PCBs) at temperatures to -30 °C.

Experimental Section

Chemicals. The following chemicals were used for the vapor pressure determinations: naphthalene (Fisher Scientific), hexachlorobenzene (OAS, BDH Chemicals Ltd.), lindane (lot no. LA-24809, Supelco Inc.), *p,p'*-DDT (97.0%, lot no. 63-45A, ChemService), *p*-monochlorobiphenyl (ICN Pharmaceuticals Inc.), 4,4'-dichlorobiphenyl (98%, Aldrich Co.), 2,3,4,5-tetrachlorobiphenyl (99+%, lot no. A-0949, Ultra Scientific), 2,2',4,4',6,6'-hexachlorobiphenyl (99+%, lot no. D-0322, Ultra Scientific). The chemicals were used as supplied.

Apparatus. A modified version of the gas saturation technique described by Rordorf et al. (*6*) was used, which employs sorbent traps, thermal desorption, and gas chromatography to analyze saturated vapor concentrations in a gas stream. The apparatus consisted of several components as shown in Figure 1: a source of purified and dried gas equilibrated at the experimental temperature, a column to saturate the gas stream with the chemical, an adsorbent trap to collect the chemical from the gas stream, and a device to measure the volume of gas passed through the system.

The gas source had to be extremely clean and dry to prevent condensation of impurities and water in the saturator column or the sampling trap, thereby interfering with the saturation process or the quantification. Nitrogen gas (Liquid Air Ltd., ultrahigh purity) was pretreated by passing it sequentially

---

* To whom correspondence should be addressed.

0021-9568/94/1739-0572$04.50/0

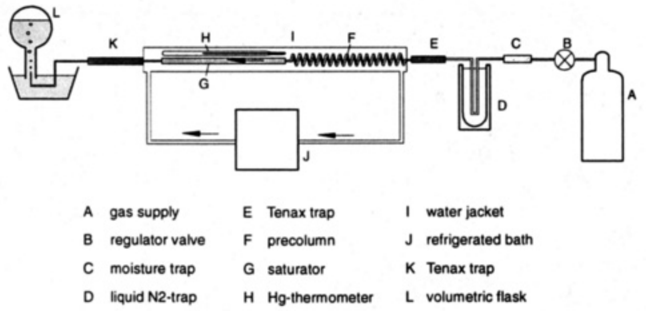

Figure 1. Schematic diagram of the experimental apparatus for measuring very low vapor pressures with the saturator column technique.

through a glass moisture trap (Chromatographic Specialities Ltd. Model GMT 100-2), a coil immersed into liquid nitrogen, and a small tube filled with the sorbent Tenax TA (Chromatographic Specialities, 35/60 mesh). The gas stream was then thermally equilibrated by passing it through a stainless steel coil (200-cm length, 0.317-cm diameter), which was kept at the same temperature as the directly attached saturator column. All connections were made with stainless steel Swagelock fittings.

The saturator column was a 0.635-cm-diameter by 50-cm-long stainless steel column filled with glass beads, which had been coated by mixing a solution of approximately 40 mg of the analyte in hexane with the required amount of glass beads (Chromatographic Specialities, mesh 20/30). After removing the solvent under constant stirring by evaporation at room temperature, the mixture was transferred into the saturator column and the ends were plugged with glass wool. Before use, all the tubing, the glass beads, and the glass wool were rinsed repeatedly with various solvents and baked overnight at 250 °C to remove impurities.

The design of the tubing connecting the saturator column with the sampling trap proved to be of critical importance for satisfactory operation at low temperatures. The interior surface of this tubing must not act as a source or sink of chemical into the gas stream; i.e., there should be no possibility for either premature vapor condensation or desorption of previously condensed chemical into the gas stream. This is essential, when measuring very low vapor concentrations, because the amount of chemical absorbed to the walls of the transfer tubing is potentially much larger than the amount of chemical sampled with the gas stream. This problem was addressed by making the transfer tubing an extension of the saturator column. This requires that all surfaces which come into contact with the saturated gas stream are kept at the experimental temperature and are allowed to equilibrate with the gas stream. This was accomplished by attaching 20 cm of a 0.159-cm-diameter stainless steel tube directly into the brass tee, which served both to deliver refrigerant to the water jacket and to hold the sampling tube collecting the vapor. The possibility of adsorption was further minimized by putting a Teflon coating on the solder which kept the transfer tubing in its place. The details of this construction are shown in Figure 2. The vapor was trapped on the solid sorbent Tenax in a 0.6-cm glass tube of 11.5-cm length. The volume which had passed through the system was measured by collecting the gas in an inverted volumetric flask filled with water.

The precolumn, saturator column, and transfer tubing to the trap were maintained at the experimental temperature by a HPLC column water jacket (Alltech Associates) filled with poly(dimethylsiloxane) (Dow Corning Corp., Syltherm XLT). This heat transfer fluid was cooled in a refrigerated circulating bath (Neslab Endocal LT-50DD). The water jacket and the transfer tubing to the temperature bath were heavily insulated. The temperature was measured with a high-precision mercury thermometer totally immersed into the water jacket and the mercury bulb placed close to the entrance to the saturator column. It was additionally monitored with a thermocouple attached to the end of the precolumn. The temperature could thus be controlled to ±0.1 K. The accuracy of the mercury thermometer was confirmed by measuring the freezing point of water.

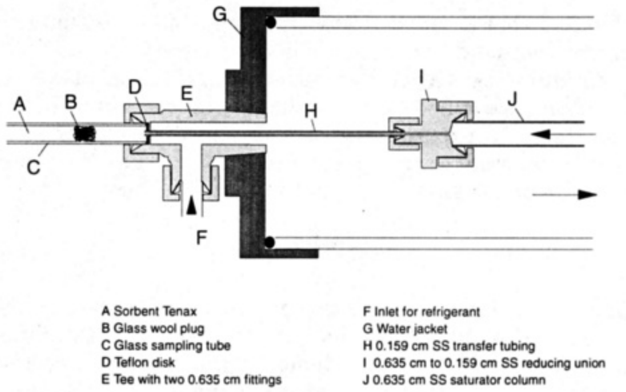

Figure 2. Details of the experimental equipment showing the connection between the saturator column and the sorbent sampling tube.

Procedure. The system was allowed to equilibrate with a flowing gas stream for several days before the first measurement. Another equilibration period of approximately 1 day was employed after each change of temperature. A measurement was started by replacing a dummy sampling tube with a conditioned, clean tube. The volume of gas sampled ranged from 10 mL to 40 L, depending on the vapor pressure, the temperature, and the sensitivity of the detector for the sampled chemical. A measurement was stopped by taking the tube out of the gas stream again. The duration of the measurement, ranging from 1/2 min to 3 days, was measured and the average flow rate calculated.

Analytical Technique. The amount of chemical trapped on the Tenax trap was analyzed with gas chromatography. The chemicals were thermally desorbed with a thermal tube desorber (Envirochem Inc. Model 850) and transferred directly onto the capillary column of a gas chromatograph. The thermal desorber was controlled by a temperature controller (Envirochem Inc. Model 851) programmed to heat the sorbent tube with the maximum possible ramp speed to 300 °C, which was held for 5 min. The valve compartment and the transfer line between the desorbing unit and GC column were heated to approximately 285 °C. The gas chromatograph was a Hewlett-Packard 5890 with flame ionization detection (for naphthalene) or a ^{63}Ni electron capture detector (for the organochlorines), and peak areas were determined by a Hewlett-Packard Integrator 3392A. The column was a J&W Scientific Durabond-17, 30 m long with a film thickness of 0.25 μm. Helium (FID) and argon/methane (ECD) were employed as the carrier gas (ultrahigh purity, Liquid Air Inc.).

Calibration was done by injecting 50 μL of the solutions with variable concentrations of the analyte in hexane onto a clean sorbent tube filled with Tenax. At the same time a constant amount of internal standard in the hexane solution was injected. The solvent was purged by the carrier gas in the thermal desorption unit for 10 min at room temperature. The internal standard was also injected on the sampling tubes after sampling and before desorption. The ratios between the peak areas of the analyte and internal standard were used for the quantification of the samples. The use of the internal standard thus eliminated any errors caused by fluctuations of the thermal desorption or the GC analysis.

Calculating Vapor Pressure. Using Dalton's law and the ideal gas law, and assuming that the vapor pressure of the analyte at the experimental temperatures (<10 Pa) is very small compared to atmospheric presssure (10^5 Pa), the vapor pressure of the analyte p_s can be calculated from

$$p_s = nRT_s/V_G \qquad (1)$$

where n is the moles of analyte vaporized, R is the gas constant (8.314 J·(K·mol)$^{-1}$), T_s is the temperature of the saturator column, and V_G is the volume of the inert gas at the temperature and the total pressure in the saturator column.

To obtain V_G, the measured gas volume V_M was corrected for the temperature and pressure change between the saturator column and volumetric flask, because V_M is measured at room temperature and atmospheric pressure. The pressure in the saturator column was measured at different flow rates by attaching a water-filled U-manometer between the saturator and trap. With the flow rates used the pressure is generally only a few centimeters of water higher than atmospheric pressure. The pressure correction was therefore considered negligible. V_M was also corrected for the volume of the water vapor, which was generated when the sampling gas stream was bubbled through the water in the volumetric flask. This was done by employing Dalton's law and the vapor pressure of water at room temperature.

The temperature dependence of the vapor pressure of a solid p_s can be described by the Clapeyron equation:

$$\frac{dp_s}{dT} = \frac{\Delta_{sub}H}{T\Delta V} \qquad (2)$$

where T is the absolute temperature, $\Delta_{sub}H$ is the enthalpy of sublimation, and ΔV is the volume change upon sublimation. Assuming that (1) the ideal gas law is applicable, (2) the volume of the solid is negligible compared to the volume of the gas, and (3) $\Delta_{sub}H$ is independent of temperature, eq 2 can be integrated to yield

$$\log p_s = A - B/T \qquad (3)$$

where A and B are constants, B being $\Delta_{sub}H(2.303R)^{-1}$.

Results

Verification of the Method with Naphthalene. To verify that the procedure yielded accurate vapor pressures of low-volatility compounds at low temperature, the vapor pressure of naphthalene was determined. Because of the large number and the generally good agreement of experimental naphthalene vapor pressures, this compound has been recommended by IUPAC as a reference material for the determination of the enthalpy of sublimation (*11*) and vapor pressure (*12*) of low-volatility compounds.

Several measurements of naphthalene vapor pressure at 0 °C were performed at five different flow rates ranging from 1.5 to 20 cm^3·min^{-1} to determine if the measured vapor pressure depends upon flow rate, i.e., whether vapor saturation is indeed established in the saturator column. As illustrated in Figure 3 there is obviously no significant dependence of vapor pressure upon the flow rate up to 20 cm^3·min^{-1}, indicating saturated conditions in this range of flow rates. Assuming the volume of the generator column to be approximately 10 cm^3, this implies that a residence time of only 30 s in the generator column is sufficient to achieve equilibrium. This is in accordance with the findings from Sonnefeld et al. (*8*) for anthracene at 25 °C.

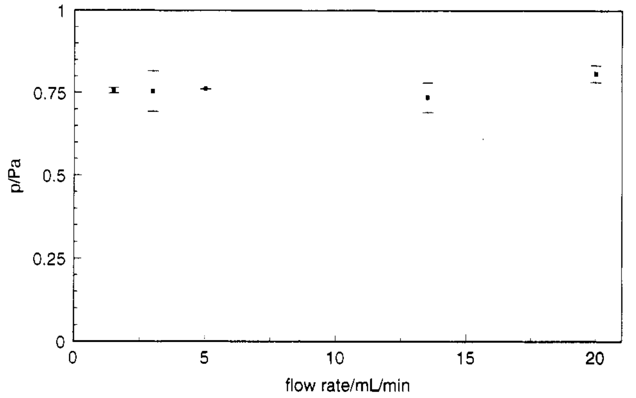

Figure 3. Dependence of the measured vapor pressure of naphthalene at 0 °C on the gas flow rate through the saturator column. The means of triplicate measurements and the respective standard deviations are shown.

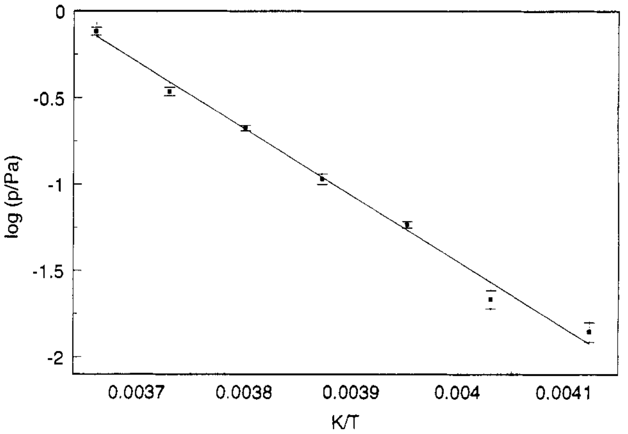

Figure 4. Relationship between log p and $1/T$ for naphthalene. The mean values for each measured temperature, the respective standard deviations, and the linear regression curve are given.

Table 1. Mean and Standard Deviation of Vapor Pressure Measurements of Naphthalene

t/°C	n	p/Pa	t/°C	n	p/Pa
0.0	14	0.7634 ± 0.0389	−20.1	7	0.0586 ± 0.0027
−5.0	7	0.3447 ± 0.0194	−25.0	7	0.0217 ± 0.0026
−10.0	13	0.2122 ± 0.0078	−30.6	7	0.0140 ± 0.0018
−14.9	5	0.1077 ± 0.0075			

The vapor pressure of naphthalene was determined at seven temperatures within the temperature range 0 to −30 °C. The flow rates were maintained in the range in which saturation of the gas stream is assured. Table 1 lists the means and standard deviations of these measurements. Figure 4 shows the plot of the logarithm of the vapor pressure as a function of the inverse absolute temperature. Linear regression gave the intercept and slope of eq 3. Various reported measurements of the vapor pressure of solid naphthalene, regressed as A and B coefficients in Table 2, show excellent agreement, as has been illustrated by a graphical residual analysis by Ambrose et al. (*20*). Our data compare well with previous determinations, particularly with those in the same temperature range. From the value of B an enthalpy of sublimation $\Delta_{sub}H$ of 73.7 kJ·mol^{-1} was estimated for naphthalene in the experimental temperature range. This is in excellent agreement with literature values. De Kruif (*13*) reports a value of 74.4 kJ·mol^{-1} for a temperature of 267.88 K. IUPAC (*11*) recommends a value of 72.5 kJ·mol^{-1} for the enthalpy of sublimation of naphthalene at 298 K. The absolute vapor pressure at 0 °C calculated from the regression

Table 2. Coefficients in the Regression Equation $\log(p/\mathrm{Pa}) = A - B/(T/\mathrm{K})$ for Solid Naphthalene As Reported in the Literature or As Calculated from Reported Vapor Pressure Results, and Vapor Pressures at 0 °C Obtained from These Equations

A	B	n	t/°C	$p_{0°\mathrm{C}}$/Pa	ref
13.95	3851	60	−30.6 to 0	0.710	this work
13.83	3817	9	−53.15 to +80.28	0.718	9
13.81	3809	10	−28.96 to −17.35	0.733	19
14.11	3886	?	−20 to 0	0.765	13
13.70	3773	22	−9.54 to +69.91	0.778	20
14.01	3862	8	−1.69 to +11.48	0.743	21
13.59	3742	66	1.29–80.42		22
13.51	3719	6	7.15–31.85		10
13.67	3767	11	8.1–20.7		23
14.30	3960	12	14.15–32.1		8
13.83	3799	9	9–23.91		24
12.69	3476	?	10–50		25
12.61	3422	?	19–35		26
13.83	3810	6	28.9–79.0		27
13.46	3695	13	40.33–80.33		28

equation agrees well with those of other researchers as shown in Table 2.

Vapor Pressures of Organochlorine Compounds. Tables 3 and 4 give the results of the vapor pressure measurements of organochlorinated compounds. Also listed is the number of replicate measurements (n) at each temperature, which was at least 5. The lowest temperature employed depended on the vapor pressure of the chemical and the sensitivity of the ECD detector for that particular chemical. The standard deviations are generally around or below 10% of the mean value. The flow rates were less than 20 mL/min.

The logarithm of the vapor pressure was regressed by linear least squares as a function of reciprocal temperature using all the data and not just the mean values. Table 5 lists the regression coefficients A and B, as well as the enthalpy of sublimation calculated from the slope of the regression curves. The measured value for the vapor pressure of HCB at −30 °C was not used in the regression, because it is suspected as being less accurate than the other data at higher temperatures.

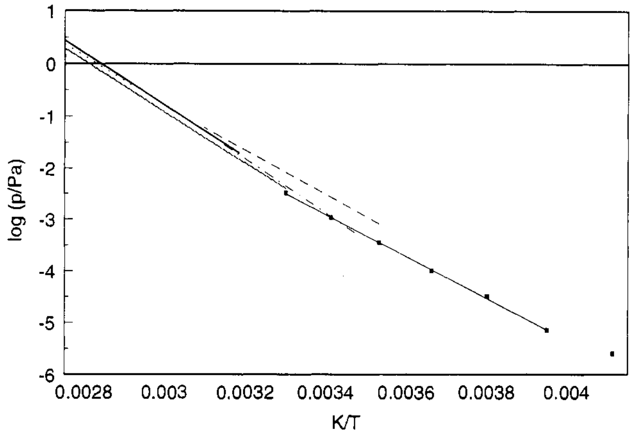

Figure 5. log p to $1/T$ relationship for hexachlorobenzene: (■) this work, (- - -) ref 29, (—) ref 6, (– – –) saturator technique, ref 30, (jagged line) balance technique, ref 30, (- - -) ref 14.

The mean values of log p at each temperature as a function of $1/T$ are plotted in Figures 5–10. The graphs include the calculated linear regression curve. The log p vs $1/T$ relationship is linear in this range of low temperatures. Only the data for 2,2′,4,4′,6,6′-hexachlorobiphenyl suggest that the enthalpy of sublimation may be increasing with lower temperatures.

Comparison with Previous Measurements at Higher Temperature. For comparison, log p to $1/T$ relationships

Table 3. Mean and Standard Deviation of Vapor Pressure Measurements of Hexachlorobenzene (HCB), γ-Hexachlorocyclohexane (γ-HCH), and *p,p′*-DDT

	HCB		γ-HCH		*p,p′*-DDT	
t/°C	n	p/Pa	n	p/Pa	n	p/Pa
+40					13	$(3.846 \pm 0.455) \times 10^{-4}$
+30	6	$(3.276 \pm 0.383) \times 10^{-3}$	11	$(4.192 \pm 0.282) \times 10^{-2}$	12	$(8.180 \pm 0.377) \times 10^{-5}$
+20	13	$(1.092 \pm 0.123) \times 10^{-3}$	9	$(9.395 \pm 0.899) \times 10^{-3}$	6	$(1.715 \pm 0.134) \times 10^{-5}$
+10	9	$(3.556 \pm 0.374) \times 10^{-4}$	11	$(2.209 \pm 0.151) \times 10^{-3}$	6	$(2.531 \pm 0.230) \times 10^{-6}$
0	12	$(1.030 \pm 0.174) \times 10^{-4}$	21	$(4.489 \pm 0.432) \times 10^{-4}$	3	$(5.003 \pm 0.167) \times 10^{-7}$
−10	5	$(3.229 \pm 0.171) \times 10^{-5}$	10	$(8.435 \pm 0.783) \times 10^{-5}$		
−20	5	$(7.257 \pm 0.829) \times 10^{-6}$	12	$(7.353 \pm 0.762) \times 10^{-6}$		
−30	11	$(2.567 \pm 0.294) \times 10^{-6}$	6	$(1.701 \pm 0.599) \times 10^{-6}$		

Table 4. Mean and Standard Deviation of Vapor Pressure Measurements of 4-Monochlorobiphenyl, 4,4′-dichlorobiphenyl, 2,3,4,5-Tetraclorobiphenyl, and 2,2′,4,4′,6,6′-Hexachlorobiphenyl

	4-monoCB		4,4′-diCB		2,3,4,5-tetraCB		2,2′,4,4′,6,6′-hexaCB	
t/°C	n	p/Pa	n	p/Pa	n	p/Pa	n	p/Pa
+30	5	0.2233 ± 0.0223	11	$(4.475 \pm 0.217) \times 10^{-3}$			13	$(7.789 \pm 0.883) \times 10^{-4}$
+20	10	$(6.771 \pm 0.832) \times 10^{-2}$	10	$(1.197 \pm 0.062) \times 10^{-3}$	16	$(1.854 \pm 0.334) \times 10^{-4}$	11	$(3.250 \pm 0.326) \times 10^{-4}$
+10	21	$(1.883 \pm 0.347) \times 10^{-2}$	13	$(4.159 \pm 0.334) \times 10^{-4}$	11	$(6.163 \pm 0.732) \times 10^{-5}$	14	$(8.039 \pm 0.725) \times 10^{-5}$
0	9	$(4.889 \pm 0.321) \times 10^{-3}$	7	$(8.303 \pm 0.495) \times 10^{-5}$	8	$(1.439 \pm 0.092) \times 10^{-5}$	6	$(1.185 \pm 0.134) \times 10^{-5}$
−10	7	$(1.297 \pm 0.054) \times 10^{-3}$	6	$(1.206 \pm 0.116) \times 10^{-5}$	5	$(3.817 \pm 0.425) \times 10^{-6}$	8	$(1.634 \pm 0.603) \times 10^{-6}$
−20	5	$(2.446 \pm 0.149) \times 10^{-4}$			6	$(5.298 \pm 0.632) \times 10^{-7}$		

Table 5. Regression Parameters for $\log(p/\mathrm{PA}) = A - B/(T/\mathrm{K})$ and Enthalpies of Sublimation Calculated from the Measured Vapor Pressure Data

compound	n	A	B	r^2	t/°C	$\Delta_{\mathrm{sub}}H$/(kJ·mol^{-1})
naphthalene	60	13.95 ± 0.06	3851 ± 51	0.990	−30.6 to 0.0	73.7 ± 1.0
HCB	50	10.83 ± 0.06	4044 ± 41	0.995	−20.0 to +30.0	77.4 ± 0.8
γ-HCH	80	16.99 ± 0.10	5566 ± 45	0.995	−30.0 to +30.0	106.6 ± 0.9
p,p′-DDT	40	16.62 ± 0.05	6276 ± 52	0.997	0.0 to +40.0	120.2 ± 1.0
4-monoCB	57	14.15 ± 0.06	4493 ± 47	0.994	−19.9 to +30.0	86.0 ± 0.9
4,4′-diCB	47	14.10 ± 0.08	4977 ± 69	0.991	−10.0 to +30.0	95.3 ± 1.3
2,3,4,5-tetraCB	46	12.10 ± 0.08	4632 ± 64	0.992	−20.0 to +20.0	88.7 ± 1.2
2,2′,4,4′,6,6′-hexaCB	52	14.84 ± 0.15	5399 ± 120	0.976	−10.0 to +30.0	103.4 ± 2.3

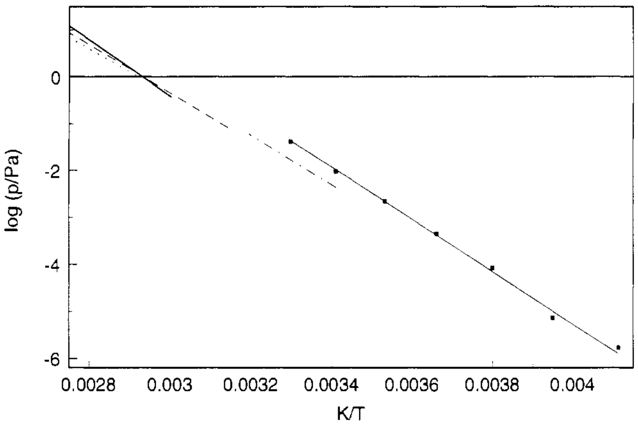

Figure 6. log p to $1/T$ relationship for lindane: (■) this work, (– – –) ref 17, (—) ref 31, (- - -) ref 14.

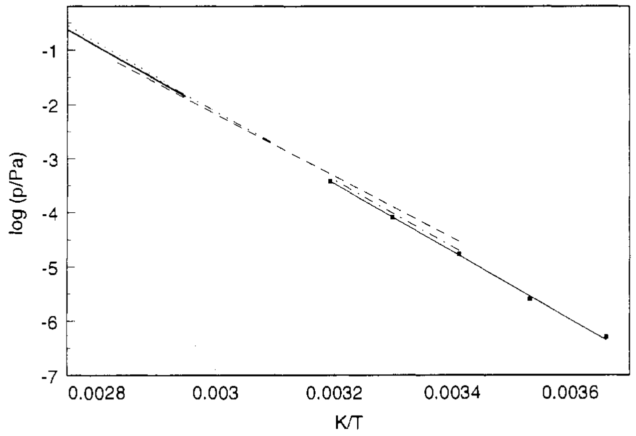

Figure 7. log p to $1/T$ relationship for p,p'-DDT: (■) this work, (- - -) ref 32, (—) ref 31, (- - - -) ref 33, (– – –) ref 34, (- - -) ref 14.

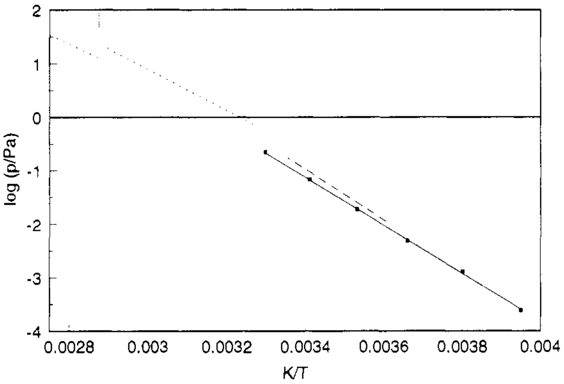

Figure 8. log p to $1/T$ relationship for 4-monochlorobiphenyl: (■) this work, (– – –) ref 5, (- - -) ref 35.

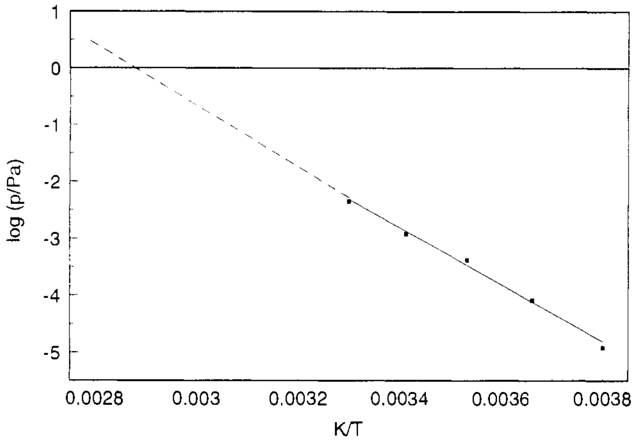

Figure 9. log p to $1/T$ relationship for 4,4′-dichlorobiphenyl: (■) this work, (– – –) ref 36.

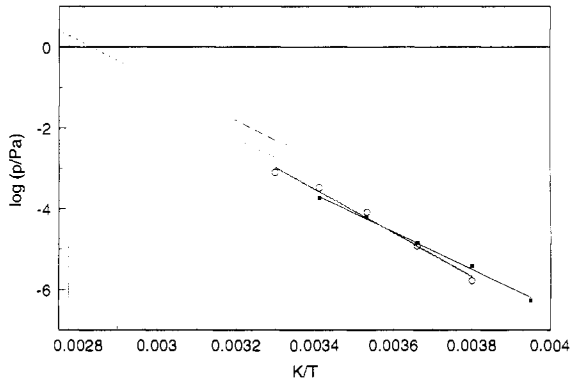

Figure 10. log p to $1/T$ relationship for selected PCB isomers: (■) 2,3,4,5-tetrachlorobiphenyl (this work), (○) 2,2′,4,4′,6,6′-hexachlorobiphenyl (this work), (– – –) 2,2′,5,5′-tetrachlorobiphenyl (ref 4), (- - -) 2,2′,5,5′-tetrachlorobiphenyl (ref 14), (- · -) 2,2′,4,5,5′-pentachlorobiphenyl (ref 4), (···) 2,2′,4,5,5′-pentachlorobiphenyl (ref 14).

for the chemicals, which have been reported in the literature, are included in the graphs. Hinckley et al. (*14*) used a GC retention time method, which is believed to yield the vapor pressure of the subcooled liquid. To permit comparison, these data were converted to estimated solid-phase vapor pressures at temperatures below the melting point using the expression

$$\log p_s = \log p_l - \Delta_{fus}S(T_m/T - 1)/(2.303R) \qquad (4)$$

and entropies of fusion $\Delta_{fus}S$ and melting point temperatures T_m listed in Miller et al. (*15*), Hinckley et al. (*14*), and Shiu and Mackay (*16*).

The figures show that this work extends the data to temperatures substantially beyond the lowest temperatures measured previously. The agreement between our measurements and previously reported ones at higher temperatures is good for 4-monochlorobiphenyl, 4,4′-dichlorobiphenyl, and p,p'-DDT. The slope of the log p to $1/T$ relationship for γ-HCH is close to that reported by Spencer and Cliath (*17*), but the vapor pressures are slightly higher. Our data for HCB suggest a smaller slope than that of previous measurements at higher temperature. There have been no previous measurements of the vapor pressures of 2,3,4,5-tetrachlorobiphenyl and 2,2′,4,4′,6,6′-hexachlorobiphenyl. We therefore included data for the vapor pressures of 2,2′,5,5′-tetrachlorobiphenyl and 2,2′,4,5,5′-pentachlorobiphenyl reported by Burkhardt et al. (*5*) and Hinckley et al. (*14*). Compared to these measurements, 2,3,4,5-tetrachlorobiphenyl has a very low vapor pressure. Its vapor pressure is in the same range as that for the hexachlorinated isomer. This unusually low vapor pressure may be a result of the very asymmetric chlorination pattern with all four chlorine atoms attached to the same aromatic ring, although this is not reflected in a particularly high melting point.

Environmental Implications. The data obtained for HCB, γ-HCH, p,p'-DDT, and four PCB isomers suggest that the enthalpy of sublimation of these chemicals is virtually independent of temperature in the temperature range investigated. This is equivalent to suggesting that the enthalpy of vaporization $\Delta_{vap}H$ changes little in this range. Additional evidence for this assertion can be obtained from the consideration of the likely change in $\Delta_{vap}H$ as a function of temperature as estimated by the Watson equation (*18*). These chemicals have estimated critical temperatures in the range of 450–800 °C; thus, the low temperatures of +30 to −30 °C correspond to reduced temperatures in the range 0.23–0.42. The Watson equation suggests a change in $\Delta_{vap}H$ of less than 5% in this range which may be difficult to determine as a significant change in the slope of log p vs $1/T$. We conclude that for the purposes of assessing environmental fate in colder regions of the global environment it may be sufficient to measure vapor pressures in the range 0–50 °C and extrapolate to lower temperatures, possibly including an estimated variation in $\Delta_{vap}H$ as a function of reduced temperature.

Conclusion

The gas saturation method described here can be used to determine very low vapor pressures (i.e., down to 10^{-6} Pa) at low temperatures. These results suggest that for environmental contaminants of the type discussed here it may be possible to estimate vapor pressures with sufficient accuracy at low temperatures, i.e., down to −30 °C, by extrapolation of data obtained in the range 0–30 °C.

Acknowledgment

The authors would like to acknowledge the assistance of H. Hung, T. Harner, and D. Tam during some of the experiments.

Literature Cited

(1) Wania, F.; Mackay, D. *Ambio* **1993**, *22*, 10.
(2) Thomson, G. W. in *Technique of organic chemistry*, 3rd ed.; Weissberger, A., Ed.; Interscience: New York, 1959; Vol. 1, Part 1, p 401.
(3) Spencer, W. F.; Cliath, M. M. *Residue Rev.* **1983**, *85*, 57.
(4) Westcott, J. R.; Simon, C. G.; Bidleman, T. F. *Environ. Sci. Technol.* **1981**, *15*, 1375.
(5) Burkhard, L. P.; Armstrong, D. E.; Andren, A. W. *J. Chem. Eng. Data* **1984**, *29*, 248.
(6) Rordorf, B. F.; Sarna, L. P.; Webster, G. R. B. *Chemosphere* **1986**, *15*, 2073.
(7) Hales, J. L.; Cogman, R. C.; Frith, W. J. *J. Chem. Thermodyn.* **1981**, *13*, 591.
(8) Sonnefeld, W. J.; Zoller, W. H.; May, W. E. *Anal. Chem.* **1983**, *55*, 275.
(9) Sinke, G. C. *J. Chem. Thermodyn.* **1974**, *6*, 311.
(10) Macknick, A. B.; Prausnitz, J. M. *J. Chem. Eng. Data* **1979**, *24*, 175.
(11) Cox, J. D. *Pure Appl. Chem.* **1974**, *40*, 425.
(12) Ambrose, D. In *Recommended Reference Materials for the Realization of Physicochemical Properties*; Marsh, K. N., Ed.; Blackwell Scientific: Oxford, 1987; p 94.
(13) De Kruif, C. G. *J. Chem. Thermodyn.* **1980**, *12*, 243.
(14) Hinckley, D. A.; Bidleman, T. F.; Foreman, W. T.; Tuschall, J. R. *J. Chem. Eng. Data* **1990**, *35*, 232.
(15) Miller, M. M.; Ghodbane, S.; Wasik, S. P.; Tewari, Y. B.; Martire, D. E. *J. Chem. Eng. Data* **1984**, *29*, 184.
(16) Shiu, W. Y.; Mackay, D. *J. Phys. Chem. Ref. Data* **1986**, *15*, 911.
(17) Spencer, W. F.; Cliath, M. M. *J. Agric. Food Chem.* **1970**, *18*, 529.
(18) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The properties of gases and liquids*, 4th ed.; McGraw-Hill: New York, 1986.
(19) Van Ekeren, P. J.; Jacobs, H. G.; Offringa, J. C. A.; De Kruif, C. G. *J. Chem. Thermodyn.* **1983**, *15*, 409.
(20) Ambrose, D.; Lawrenson, I. J.; Sprake, C. H. S. *J. Chem. Thermodyn.* **1975**, *7*, 1173.
(21) Colomina, M.; Jimenez, P.; Turrion, C. *J. Chem. Thermodyn.* **1982**, *14*, 779.
(22) De Kruif, C. G.; Kuipers, T.; Van Miltenburg, J. C.; Schaake, R. C. F.; Stevens, G. *J. Chem. Thermodyn.* **1981**, *13*, 1081.
(23) Bradley, R. S.; Cleasby, T. G. *J. Chem. Soc. London* **1953**, 1690.
(24) Radchenko, L. G.; Kitaigorodskii, A. I. *Russ. J. Phys. Chem.* **1974**, *48*, 1595.
(25) Karyakin, N. V.; Rabinovich, I. B.; Pakhomov, L. G. *Russ. J. Phys. Chem.* **1968**, *42*, 954.
(26) Sears, G. W.; Hopke, E. R. *J. Am. Chem. Soc.* **1949**, *71*, 1632.
(27) Grayson, B. T.; Fosbraey, L. A. *Pestic. Sci.* **1982**, *13*, 269.
(28) Fowler, L.; Trump, W. N.; Vogler, C. E. *J. Chem. Eng. Data* **1968**, *13*, 209.
(29) Farmer, W. J.; Yang, M. S.; Letey, J.; Spencer, W. F. *Soil Sci. Soc. Am. J.* **1980**, *44*, 676.
(30) OECD. *OECD Guidelines for Testing of Chemicals*; Organisation for Economic Cooperation and Development: Paris, 1981.
(31) Balson, E. W. *Trans. Faraday Soc.* **1947**, *43*, 54.
(32) Spencer, W. F.; Cliath, M. M. *J. Agric. Food Chem.* **1972**, *20*, 645.
(33) Dickinson, W. *Trans. Faraday Soc.* **1956**, *52*, 31.
(34) Rothman, A. M. *J. Agric. Food Chem.* **1980**, *28*, 1225.
(35) Ferro, D.; Piacente, V.; Scardala, P. *Thermochim. Acta* **1983**, *68*, 329.
(36) Smith, N. K.; Gorin, G.; Godd, W. D.; McCullough, J. P. *J. Phys. Chem.* **1964**, *68*, 940.

Received for review December 11, 1993. Accepted March 11, 1994.[⊗] The authors are grateful to the Gottlieb Daimler-und-Carl Benz-Stiftung, Germany, and the Natural Sciences and Engineering Research Council, Canada, for financial support.

[⊗] Abstract published in *Advance ACS Abstracts*, April 15, 1994.