

A Sublimation Study of Lindane

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The vapor pressure of lindane was measured by torsion and Knudsen-effusion methods over the temperature range 310 K to 384 K. The following temperature–pressure equation was obtained: $\log(p/\text{kPa}) = 11.23 \pm 0.50 - (4832 \pm 150)(\text{K}/T)$. From the vapor pressure data, the second-law sublimation enthalpy of this compound, $\Delta_{\text{sub}}H^\circ(298 \text{ K}) = (92 \pm 4) \text{ kJ}\cdot\text{mol}^{-1}$, was derived. The results were compared with literature values.

Introduction

A exhaustive review of previous studies on the sublimation of lindane (γ -1,2,3,4,5,6-hexachlorocyclohexane) and on its vapor pressures as obtained by different techniques (Knudsen, transpiration, pressure balance, gas chromatographic) has been reported in a recent work by Boehncke et al. (1996). The vapor pressure sets were measured in small temperature ranges, and some of those data represent only single values at room temperature. Inspection of reported data reveals that agreement between various reports is poor (see Figure 1) and that further investigations are needed. Therefore we have measured the vapor pressure of lindane again by torsion-effusion and by Knudsen-effusion mass loss methods in order to determine its sublimation enthalpy. The results obtained are reported in the present work.

Experimental Section

The commercial sample of lindane used in this study (99% pure) was supplied by SIGMA Chemical Co., St. Louis, MO. The torsion vapor pressure of this compound was measured by the torsion-effusion method by using two apparatuses of different sensitivity (mainly owing to the different lengths of their tungsten torsion wires). Both have been described in previous work (Piacente et al., 1991, 1994). The two apparatuses have been combined with two conventional graphite torsion cells having effusion holes with very different areas (cell T,1 and T,2 with holes 1.9 and ~ 0.30 mm in diameter, respectively). In both assemblies, the sample temperatures were measured indirectly using a calibrated iron-constantan Rh thermocouple inserted into a fixed blank cell placed close below the torsion cell containing the sample. The true temperatures were evaluated by correcting the measured values. The correction was determined using a procedure described previously (Piacente et al., 1994) and is based on the zero variance of the system at the melting point of a compound. In this work very pure cadmium, having at the melting point (594 K) its vapor pressure detectable with our assembly, was used. In principle, a check of the reliability of the temperature values can be made by measuring the second-law sublimation enthalpy associated with the vaporization process of a substance from the slope of the $\log \alpha$ vs $1/T$ line, where α is the torsion angle of the assembly measured at different temperatures (T) during the vapor-

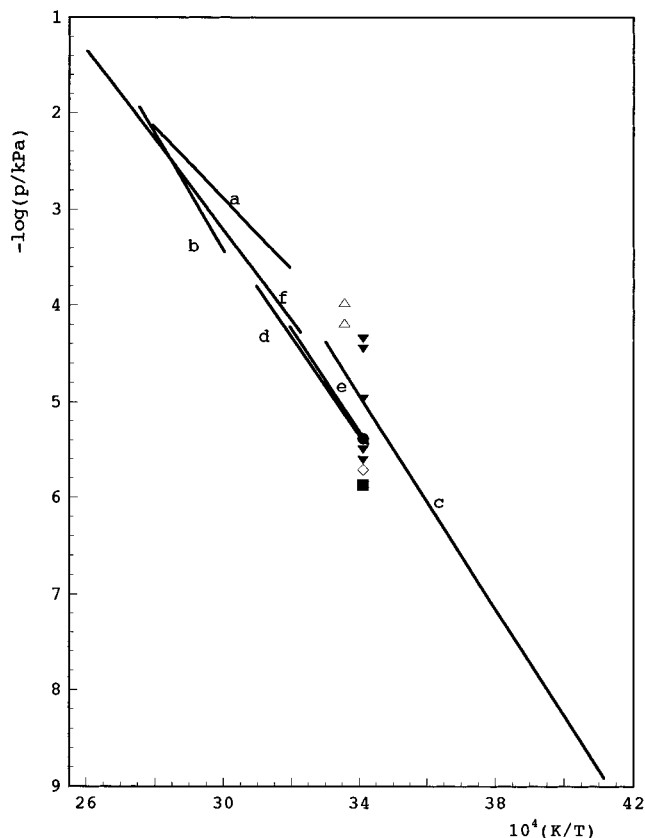


Figure 1. Vapor pressures of lindane: (a) Hinckley et al. (1990); (b) Balson (1947); (c) Wania et al. (1994); (d) Boehncke et al. (1996); (e) Spencer and Cliath (1970); (f) this work; (Δ) Bidleman (1984); (∇) Kim (1985); (\diamond) Eichler (1983); (\bullet) Atkins and Eggleton (1971); (\blacksquare) Gückel et al. (1982).

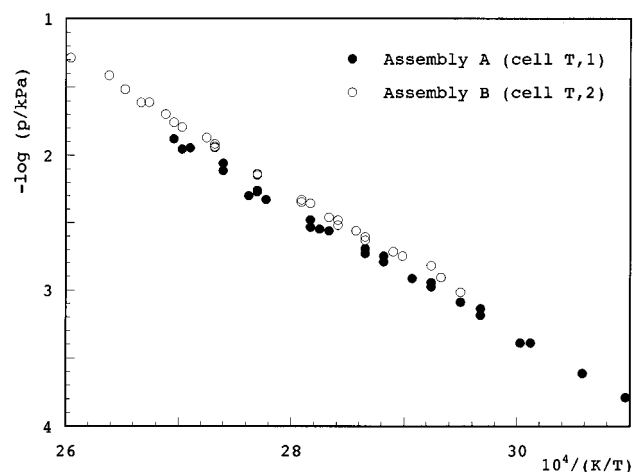
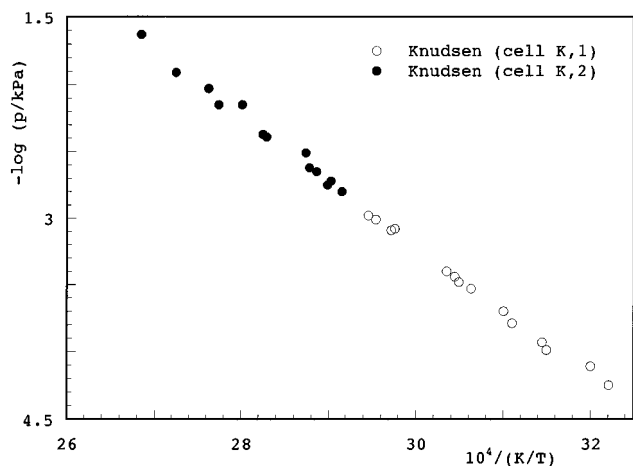
ization. A systematic error in the measured temperatures, especially measuring low values, influences the sublimation enthalpy value calculated in this way. In this work a check was made measuring the sublimation enthalpies of benzoic acid and urea. The enthalpy values so determined agree within 1–2 $\text{kJ}\cdot\text{mol}^{-1}$ with those selected from the literature [$\Delta_{\text{sub}}H^\circ(298 \text{ K}) = 90.5$ and $93.5 \text{ kJ}\cdot\text{mol}^{-1}$ for benzoic acid (Colomina et al., 1982) and urea (Ferro et al., 1987) respectively] so that we believe that the uncertainty associated with the temperatures of the sample should be about ± 1 K.

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Table 1. Torsion Vapor Pressure of Lindane

Assembly A (Cell T,1)							
run 1		run 2		run 3		run 4	
<i>T</i> /K	$-\log(p/\text{kPa})$	<i>T</i> /K	$-\log(p/\text{kPa})$	<i>T</i> /K	$-\log(p/\text{kPa})$	<i>T</i> /K	$-\log(p/\text{kPa})$
323.0	3.79	332.0	3.39	333.0	3.39	339.0	3.09
327.0	3.61	337.0	3.14	339.0	3.09	344.0	2.91
332.0	3.39	342.0	2.98	344.0	2.91	349.0	2.69
337.0	3.19	347.0	2.79	349.0	2.73	354.0	2.55
342.0	2.94	355.0	2.48	355.0	2.53	360.0	2.33
347.0	2.75	361.0	2.26	362.0	2.30	365.0	2.11
353.0	2.56	365.0	2.06	371.0	1.88	369.0	1.94
361.0	2.27						
370.0	1.95						

Assembly B (Cell T,2)							
run 5		run 6		run 7		run 8	
<i>T</i> /K	$-\log(p/\text{kPa})$	<i>T</i> /K	$-\log(p/\text{kPa})$	<i>T</i> /K	$-\log(p/\text{kPa})$	<i>T</i> /K	$-\log(p/\text{kPa})$
346.0	2.71	339.0	3.02	341.0	2.91	353.0	2.36
349.0	2.61	342.0	2.82	345.0	2.75	356.0	2.25
352.0	2.48	349.0	2.63	350.0	2.56	361.0	2.04
356.0	2.33	352.0	2.52	355.0	2.36	366.0	1.82
361.0	2.14	356.0	2.33	361.0	2.15	370.0	1.69
366.0	1.94	361.0	2.14	367.0	1.87	375.0	1.51
371.0	1.76	366.0	1.94	374.0	1.61	379.0	1.31
		372.0	1.70	377.0	1.51	384.0	1.18

**Figure 2.** Experimental vapor pressure values of lindane measured by the torsion method.**Figure 3.** Experimental vapor pressure values of lindane measured by the Knudsen method.

The Knudsen vapor pressures were measured by using a low-temperature assembly substantially identical to that described in previous work (Pelino et al., 1980), except for the difference in the oil used in the thermostat. Errors in

Table 2. Knudsen Vapor Pressures of Lindane (Estimated Error in *T*, ± 0.5 K, in Δm , ± 0.1 mg, and in *t*, ± 2 min)

<i>T</i> /K	$\Delta m/\text{mg}$	<i>t</i> /min	$-\log(p/\text{kPa})$
Cell, K,1			
310.5	16.11	7035	4.25
312.5	13.64	4245	4.11
317.5	11.11	2685	3.99
318.0	17.92	3735	3.93
321.5	8.73	1340	3.79
322.5	11.55	1423	3.70
326.5	11.47	975	3.53
328.0	12.42	945	3.48
328.5	18.95	1290	3.44
329.5	16.57	1060	3.40
336.0	33.06	1005	3.08
336.5	3.90	120	3.09
338.5	5.26	137	3.01
339.5	3.47	85	2.98
Cell, K,2			
343.0	10.67	575	2.80
344.5	22.31	985	2.72
345.0	4.30	205	2.75
346.5	7.00	265	2.65
347.5	9.55	338	2.62
348.0	39.89	990	2.51
353.5	45.19	945	2.39
354.0	8.44	170	2.37
357.0	11.79	145	2.15
360.5	14.85	145	2.15
362.0	20.96	155	2.03
367.0	19.39	110	1.91
372.5	23.98	70	1.63

the temperature measurements are considered to be negligible using this assembly. Two graphite cells with different effusion areas (cell K,1 and K,2 with hole 0.8 and ~ 0.4 mm in diameter, respectively) were used. The instrumental constants necessary to convert both the torsion and Knudsen experimental values to pressures were determined by vaporizing pure substances having known vapor pressures. In this work substances having vapor pressures comparable with those of lindane such as benzoic acid (Colomina et al., 1982), urea (Fezzo et al., 1987), and mercury (Hultgren et al., 1973) were used as standards. The instrumental constants of each cell obtained were often checked between the various vaporization

Table 3. Temperature Dependence of the Vapor Pressure of Solid Lindane by Torsion and Knudsen Methods

method	assembly [cell]	run	no. of points	$\Delta T/K$	$\log(p/\text{kPa}) = A - B/(K/T)$	
					A^a	B^a
torsion	A[T,1]	1	9	323.0 to 370.0	10.68 ± 0.15	4670 ± 52
		2	7	332.0 to 365.0	10.89 ± 0.33	4740 ± 114
		3	7	333.0 to 371.0	10.76 ± 0.44	4708 ± 154
		4	7	339.0 to 369.0	10.83 ± 0.34	4727 ± 122
torsion	B[T,2]	5	7	346.0 to 371.0	11.55 ± 0.10	4939 ± 37
		6	8	339.0 to 372.0	11.49 ± 0.44	4915 ± 154
		7	8	341.0 to 377.0	11.81 ± 0.20	5025 ± 73
		8	8	353.0 to 384.0	12.33 ± 0.24	5223 ± 89
Knudsen	[K,1]	9	14	310.5 to 339.5	10.89 ± 0.29	4706 ± 95
Knudsen	[K,2]	10	13	343.0 to 377.0	11.46 ± 0.50	4889 ± 175

^a The quoted errors are standard deviations.

Table 4. Temperature Dependence of the Vapor Pressures of Lindane and Its Sublimation Enthalpy

author	method	$\Delta T/K$	$\log(p/\text{Pa}) = A - B/(K/T)$		$p(298.15)/10^{-6}$ (kPa)	$\Delta_{\text{sub}}H^{\circ}(T) \cong$ $\Delta_{\text{sub}}H^{\circ}(298 \text{ K})$ (kJ·mol ⁻¹)
			A	B		
Balson (1947)	torsion	333 to 363	17.66	6027	2.79	115
Spenser and Cliath (1970)	transpiration	293 to 313	15.69	5294	8.58	101
Atkins and Eggleton (1971)	transpiration				4.13 ^a	
Gückel et al. (1982)	Knudsen				1.34 ^a	
Eichler (1983)	balance				1.90 ^a	
Bidleman (1984)	gas-chromat.				108, 66	
Kim (1985)	gas-chromat.				44, 35, 11, 3, 2 ^{a,b}	
Hinckley et al. (1990)	gas-chromat.	313 to 358	11.16	3684	63.80	70.5
Wania et al. (1994)	transpiration	243 to 303	17.01 ± 0.23	5572 ± 104	20.96 ± 0.89	107 ± 2
Boehncke et al. (1996)	Knudsen	293 to 323	15.01 ± 0.21	5110 ± 72	7.50 ± 0.14	98 ± 2
this work	torsion and Knudsen	310 to 384	14.23 ± 0.50	4832 ± 150	10.4	92.5 ± 4

^a Reported by the authors at 293.15 K. ^b Approximated values as evaluated from the points reported in Figure 1 of Boehncke's work (1996).

runs of lindane. The results were reproducible within 5% of their average value. The error associated with the absolute pressure value due to this uncertainty is fairly negligible resulting in a displacement in the $\log(p/\text{kPa})$ values of about ± 0.08 . The influence of the effusion hole area on the pressure measured by torsion effusion was evaluated by coupling the cell T,1, with the larger effusion holes, to the less sensitive torsion apparatus (A) and the cell T,2, with the smaller effusion holes, to the torsion assembly (B) of higher sensitivity. In this way the vapor pressures of lindane were measured over comparable temperature ranges employing cells having different effusion holes. The results plotted in Figure 2 as $\log p$ vs $1/T$ show a small shift of the results obtained using the different cells, but this shift is comparable with the uncertainty associated with the torsion measurements so that we consider that the obtained vapor pressure data are not dependent on the effusion holes area. No pressures were measured at temperatures lower than 320 K because the thermostat cannot be accurately controlled below this temperature.

Results

The vapor pressures measured in the present work by torsion and Knudsen methods are reported in Figures 2 and 3 and in Tables 1 and 2. The least-squares treatment of the data obtained in each run gives the temperature-pressure equations reported in Table 3. The slight inconsistencies among these equations are probably due to small systematic errors in the experimental data obtained in different runs and/or to expectable failure of the least-squares treatment when applied to a few number of points. From these equations, by weighing their slopes and intercepts proportionally to the number of the experimental points, the following equations were obtained from the different torsion and Knudsen assemblies:

$$\text{assembly A (cell T,1) } \log(p/\text{kPa}) = 10.78 \pm 0.30 - (4709 \pm 100)(K/T) \quad (1)$$

$$\text{assembly B (cell T,2) } \log(p/\text{kPa}) = 11.79 \pm 0.25 - (5025 \pm 90)(K/T) \quad (2)$$

$$\text{Knudsen (cell K,1) } \log(p/\text{kPa}) = 10.89 \pm 0.29 - (4706 \pm 95)(K/T) \quad (3)$$

$$\text{Knudsen (cell K,2) } \log(p/\text{kPa}) = 11.46 \pm 0.50 - (4889 \pm 175)(K/T) \quad (4)$$

The uncertainties were estimated. From these equations, the final equation

$$\log(p/\text{kPa}) = 11.23 \pm 0.50 - (4832 \pm 150)(K/T) \quad (5)$$

representative of the vapor pressure of lindane in the temperature range 310 K to 384 K, was selected by giving the same weight to the torsion and Knudsen results. The stated errors are overestimated.

Because of the absolute pressures measured by both methods and cells with different effusion hole area can be considered to be substantially in agreement among themselves, all the points have been treated together by the least-squares method. The obtained equation [$\log(p/\text{kPa}) = 11.22 \pm 0.17 - (4830 \pm 58)(K/T)$], where the errors are standard deviations] is practically identical to the selected eq 5. This equation is drawn in Figure 1 and reported in Table 4 together with the literature data. Our results are in good agreement with the absolute vapor pressures reported by Spenser and Cliath (1970) and by Boehncke et al. (1996). The vapor pressure evaluated at 298 K by our selected equation, $p = 1.04 \times 10^{-5}$ kPa, falls in the middle of the values reported in the literature (see Table 4).

From the slope of eq 5, the second-law sublimation enthalpy, $\Delta_{\text{sub}}H^\circ(350 \text{ K}) = (92.4 \pm 3) \text{ kJ}\cdot\text{mol}^{-1}$, was derived. Considering that the temperatures at which the vapor pressures were measured are very close to 298 K, this value can be considered standard with a risen error of $4 \text{ kJ}\cdot\text{mol}^{-1}$. This value is lower than those determined by other authors (Table 4) except for the lowest value found by Hinckley et al. (1990), $\Delta_{\text{sub}}H^\circ(298 \text{ K}) = 70 \text{ kJ}\cdot\text{mol}^{-1}$.

Conclusion

Equation 5 gives the best fit of the temperature dependence of the total vapor pressures of lindane measured by two different methods. This equation is reported in Figure 1 and Table 4 for comparison with those found in the literature. The derived second-law sublimation enthalpy of this compound, $\Delta_{\text{sub}}H^\circ(350) \cong \Delta_{\text{sub}}H^\circ(298 \text{ K}) = 92 \pm 4 \text{ kJ}\cdot\text{mol}^{-1}$, is lower than those reported by other authors. Considering that (i) the second-law sublimation enthalpy values of the reference substances used in the calibration experiments agree very well with those selected in the literature (therefore no large errors in the temperature measurements should be made), (ii) there is substantial agreement of our vapor pressures measured by different methods, assemblies, and effusion cells (so that large errors in the absolute vapor pressure data should be excluded), and finally (iii) there is a large number of points and a large temperature range covered in the our experiments, we believe that the selected sublimation enthalpy derived from our vapor pressure data should be more reliable than those previously reported.

Literature Cited

- Atkins, D. H. F.; Eggleton, A. E. J. Studies of Atmospheric Washout and Deposition of α -BHC, Dieldrin, and *p,p'*-DDT Using Radiolabeled Pesticides. *Proc. Int. At. Energy Agency IAEA-SM* **1971**, 142a/32, 521–533.
- Balson, E. W. Studies in Vapour Pressure Measurements, Part III.—An Effusion Manometer Sensitive to 5×10^{-6} Millimetres of Mercury: Vapour Pressure of DDT and Other Slightly Volatile Substance. *Trans. Faraday Soc.* **1947**, 43, 54–60.
- Bidleman, T. F. Estimation of Vapor Pressures for Nonpolar Organic Compounds by Capillary Gas Chromatography. *Anal. Chem.* **1984**, 56, 2490–2496.
- Boehncke, A.; Martin, K.; Muller, M. G.; Commenga, H. K. The Vapor Pressure of Lindane (γ -1,2,3,4,5,6-Hexachlorocyclohexane)—A Comparison of Knudsen Effusion Measurements with Data from Other Techniques. *J. Chem. Eng. Data* **1996**, 41, 543–545.
- Colomina, M.; Jimenez, P.; Turrion, C. Thermochemical Properties of Benzoic Acid Derivatives. *J. Chem. Thermodyn.* **1982**, 14, 779.
- Eichler, D. *Physikochemische Eigenschaften, Verhalten und Analytik der HCH-isomeren. DFG-Forschungsbericht, Hexachlorcyclohexan als Schadstoff in Lebensmitteln*; Verlag Chemie: Weinheim, 1983.
- Ferro, D.; Barone, G.; Della Gatta, G.; Piacente, V. Vapour Pressures and Sublimation Enthalpies of Urea and Some of its Derivatives. *J. Chem. Thermodyn.* **1987**, 19, 915–923.
- Gükel, W.; Kästel, R.; Lewerenz, J.; Synnatscke, G. A. A Method for Determining the Volatility of Active Ingredients Used in Plant Protection III. The Temperature Relationship Between Vapor Pressure and Evaporation Rate. *Pestic. Sci.* **1982**, 13, 161–168.
- Hinckley, D. A.; Bidleman, T. F.; Foreman, W. T.; Tuschall, J. R. Determination of Vapor Pressures for Nonpolar and Semipolar Organic Compounds from Gas Chromatographic Retention Data. *J. Chem. Eng. Data* **1990**, 35, 232–237.
- Hultgren, R.; Desai, P. D.; Hawkins, D. T.; Gleiserand, M.; Kelley, K. K. *Selected Values of the Thermodynamic Properties of the Elements*; American Society for Metals: Metal Park, OH, 1973.
- Kim, Y. H. Evaluation of a Gas Chromatographic Method for Estimating Vapor Pressures with Organic Pollutants. Dissertation Thesis, University of California, Davis, CA, 1985.
- Pelino, M.; Ferro, D.; Piacente, V. Vapour Pressure of α -Iodonaphthalene. *Thermochim. Acta* **1980**, 41, 297–304.
- Piacente, V.; Pompili, T.; Scardala, P.; Temperature Dependence of the Vaporization Enthalpies of *n*-Alkanes from Vapour-Pressure Measurements. *J. Chem. Thermodyn.* **1991**, 23, 379–396.
- Piacente, V.; Fontana, D.; Scardala, P. Enthalpies of Vaporization of a Homologous Series of *n*-Alkanes Determined from Vapor Pressure Measurements. *J. Chem. Eng. Data* **1994**, 39, 231–237.
- Spencer, W. F.; Cliath, M. M. Vapor Density and Apparent Vapor Pressure of Lindane (γ -BHC). *Agric. Food Chem.* **1970**, 18, 529–530.
- Wania, F.; Siu, W. Y.; Mackay, D. Measurements 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.

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