



Vapor pressures and standard molar enthalpies, entropies and Gibbs energies of sublimation of two hexachloro herbicides using a TG unit

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ABSTRACT

The vapor pressures above the solid hexachlorobenzene (HCB) and above both the solid and liquid 1,2,3,4,5,6-hexachlorocyclohexane (lindane) were determined in the ranges 332–450 K and 347–429 K, respectively, by measuring the mass loss rates recorded by thermogravimetry under both isothermal and nonisothermal conditions. The results obtained were compared with those taken from literature. From the temperature dependence of vapor pressure derived by the experimental thermogravimetry data the molar enthalpies of sublimation $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(\langle T \rangle)$ were selected for HCB and lindane as well as the molar enthalpy of vaporization $\Delta_{\text{l}}^{\text{g}}H_{\text{m}}^{\circ}(\langle T \rangle)$ for lindane only, at the middle $\langle T \rangle$ of the respective temperature intervals. The melting temperatures and the molar enthalpies of fusion $\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(T_{\text{fus}})$ of lindane were measured by differential scanning calorimetry. Finally, the standard molar enthalpies of sublimation $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K})$ were obtained for both chlorinated compounds at the reference temperature of 298.15 K using the $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(\langle T \rangle)$, $\Delta_{\text{l}}^{\text{g}}H_{\text{m}}^{\circ}(\langle T \rangle)$ and $\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(T_{\text{fus}})$ values, as well as the heat capacity differences between gas and liquid and the heat capacity differences between gas and solid, $\Delta_{\text{l}}^{\text{g}}C_{\text{p,m}}^{\circ}$ and $\Delta_{\text{cr}}^{\text{g}}C_{\text{p,m}}^{\circ}$, respectively, both estimated by applying a group additivity procedure. Therefore, the averages of the standard ($p^{\circ} = 0.1 \text{ MPa}$) molar enthalpies, entropies and Gibbs energies of sublimation at 298.15 K, have been derived:

Compound	$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K}) (\text{kJ mol}^{-1})$	$\Delta_{\text{cr}}^{\text{g}}S_{\text{m}}^{\circ}(298.15 \text{ K}) (\text{J mol}^{-1} \text{ K}^{-1})$	$\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\circ}(298.15 \text{ K}) (\text{kJ mol}^{-1})$
HCB	81 ± 6	114 ± 6	47 ± 6
Lindane	96 ± 9	156 ± 9	50 ± 6

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1. Introduction

Volatilization from soil and vegetation and vapor transport are important processes significantly controlled by vapor pressure, which represents, along with other remarkable quantity like the water solubility and the octanol/water partition coefficient, a fundamental parameter to assess the environmental fate and behaviour of pollutants and contaminants. In the last decades, the determination of vapor pressure for compounds of environmental relevance like pesticides was carried out using mainly Knudsen and torsion effusion as well as gas saturation techniques at temperatures usually much higher than room temperature, because of their typical low volatility. In fact, phase distribution and transport phenomena commonly play a fundamental role in controlling the environmental fate and bioaccumulation of this class of compounds that tends to persist in the

atmosphere for times longer than for more readily degradable substances.

However, comparison of vapor pressures reported in literature on some organochlorine pesticides (i.e., hexachlorobenzene and 1,2,3,4,5,6-hexachlorocyclohexane) measured by different authors in limited ranges of temperature [1–15] revealed very poor agreement among values. Therefore, the aim of this paper, which extends our previous studies on different classes of organic compounds [16–19], is to measure the vapor pressure of solid hexachlorobenzene (HCB) and both the solid and liquid 1,2,3,4,5,6-hexachlorocyclohexane (lindane) using nonisothermal and isothermal thermogravimetry (NITG and ITG, respectively). The molecular structures of the compounds examined are reported in Fig. 1. From the temperature dependence of the vapor pressure so obtained the standard ($p^{\circ} = 0.1 \text{ MPa}$) molar enthalpies of vaporization, $\Delta_{\text{l}}^{\text{g}}H_{\text{m}}^{\circ}(\langle T \rangle)$, were derived at the mean temperature of the experiments, $\langle T \rangle$. Finally, to obtain the standard ($p^{\circ} = 0.1 \text{ MPa}$) molar enthalpies, entropies and Gibbs energies of sublimation at the reference temperature of 298.15 K, the molar enthalpies of fusion were determined by differential scanning calorimetry (DSC),

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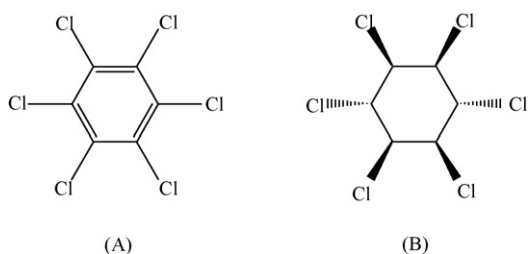


Fig. 1. Molecular structures of the two hexachloro pesticides studied. (A) HCB; (B) lindane.

and the heat capacity differences between gas and liquid as well as the heat capacity differences between gas and solid, $\Delta_1^g C_{p,m}^\circ$ and $\Delta_{cr}^g C_{p,m}^\circ$, respectively, were estimated by applying a group additivity scheme taken from literature [20].

2. Experimental

2.1. Compounds

HCB (CAS no.: 118-74-1) and lindane (CAS no.: 58-89-9) were supplied by Polyscience with a certified purity >0.95 mass fraction, were purified by repeated sublimation under reduced pressure until a final purity >0.99 mole fraction (suitable for vapor pressure measurements) and checked by DSC using a fractional method [21]. High purity samples of reference compounds, benzoic acid (from Fluka), indium and tin (standard samples supplied by Rheometric Scientific), were used as recommended reference compounds [22,23] without further purification.

2.2. Isothermal and nonisothermal thermogravimetry measurements of the vapor pressures

The procedures used in NITG and ITG experiments have been reported in details in a previous paper [19]. The nonisothermal and isothermal TG and DSC measurements were carried out on a Stanton-Redcroft 625 simultaneous TG/DSC connected to a 386 IBM-compatible personal computer. The nonisothermal TG/DSC measurements were performed at a heating rate of 16.7 mK s^{-1} using open aluminum pans having a cross-sectional area of $2.0 \times 10^{-5} \text{ m}^2$, while all the samples were subjected to a pure inert (argon) atmosphere in order to remove the vapor during their vaporization. Calibration of the temperature for both thermogravimetry and DSC apparatuses was carried out by comparing the average onset temperatures of the melting peak derived from four DSC measurements for indium and tin, respectively (429.2, 505.3)K, with those selected from literature [15,16]: (429.75, 505.08)K. As a consequence, the uncertainty associated to temperature was estimated to be $\pm 0.5 \text{ K}$. Calibration of the heat flow rate was performed by comparing the experimental enthalpies of fusion derived from four DSC measurements for indium and tin ($\Delta_{cr}^1 H_{m^\circ}(T_{fus}) = (3.19, 7.20) \text{ kJ mol}^{-1}$) with those selected from the literature: $\Delta_{cr}^1 H_{m^\circ}(T_{fus}) = (3.286, 7.170) \text{ kJ mol}^{-1}$, respectively [23]. On the basis of these results the uncertainty associated to the $\Delta_{fus} H$ value of lindane was estimated to be $\pm 0.9 \text{ kJ mol}^{-1}$.

The vapor pressure p of a compound at a temperature T can be obtained by its mass loss rate ($\Delta m/\Delta t$) determined using TG under both nonisothermal linear heating (NITG) and isothermal (ITG) conditions according to the Langmuir equation [24], which can be conveniently modified in the following form:

$$p = \frac{\Delta m}{\Delta t} \cdot \sqrt{\frac{T}{M}} \cdot \frac{\sqrt{2 \cdot \pi \cdot R}}{S \cdot \alpha'} = \nu \cdot k_{cal} \quad (1)$$

where $\nu = (\Delta m/\Delta t) \cdot (1/S) \cdot (\sqrt{T/M})$ (expressed in $(\text{K mol kg})^{0.5} \text{ s}^{-1} \text{ m}^{-2}$), M is the molar mass of the compound, α' is the vaporization constant, which is equal to unity only for experiments in vacuo [25], S (in m^2) is the surface of the sample considered equal to the area of the bottom of the crucible, R is the gas constant (in $\text{J mol}^{-1} \text{ K}^{-1}$), $k_{cal} = (\sqrt{2 \cdot \pi \cdot R})/\alpha'$ is the calibration constant. Conversion of NITG and ITG experimental mass loss data into vapor pressure values at each selected temperature requires a calibration constant (k_{cal}), whose mean value is obtained by carrying out NITG and ITG experiments on a recommended reference compound (i.e., acetanilide in this paper). Vapor pressures of the reference compound are well known [18] and comparable with those of the compounds studied in the same temperature intervals and under the same condition of the two hexachloro herbicides examined. The consistency of the vapor pressure results above the liquid (melted) substance measured by a thermobalance subjected to isothermal and nonisothermal conditions under a flowing inert gas atmosphere was tested in our previous vaporization studies on pesticides using recommended reference compounds (i.e., benzoic acid [11,26], succinic acid and salicylic acid [11], acetanilide [17] and ferrocene [19]). Vapor pressure measurements above the solid using a more classical weighing torsion effusion technique recently extended above the liquid (molten) using a TG equipment [18,19,27], as well as the extensive use of TG experiments only in deriving vapor pressure data [26,28–31] demonstrated the reliability of TG methods (at least in the pressure range between about 10 and 10^3 Pa). However, in order to verify if vaporization through an inert flowing gas atmosphere could be limited by diffusion, the mass loss rates occurring during the vaporization of a calibrant compound (acetanilide in the present study), calculated from NITG and ITG experiments were compared with the corresponding values predicted using the following equation proposed by Pieterse and Focke [32]:

$$\left(\frac{\Delta m}{\Delta t}\right)_{\text{predicted}} = \left(\frac{M \cdot S}{zRT}\right) \cdot (p_{Lit} \cdot D_{AB}) \quad (2)$$

where z is the diffusion path length, $D_{AB} = k_0 \cdot T^{3/2}$ is the diffusion coefficient in which k_0 is the diffusion constant (calculated using models for gas diffusivity according to procedures reported in literature [33]) and p_{Lit} is the vapor pressure calculated using the Antoine equation whose coefficients were taken from literature [31].

The standard ($p^\circ = 0.1 \text{ MPa}$) molar enthalpies of vaporization, $\Delta_1^g H_{m^\circ}(<T>)$, from NITG and ITG experiments, have been derived at the temperature $<T>$ from the slopes of the linear $\ln(p/\text{Pa})$ vs. T^{-1} equations. The relative atomic masses adopted in this study were those recommended by the IUPAC Commission [34].

3. Results and discussion

3.1. Influence of diffusion on mass loss rate and calibration of the thermogravimetry assembly

From the NITG and ITG mass loss rates occurring during the vaporization of pure acetanilide an average value of the diffusion constant k_0 (calculated using models for gas diffusivity according to procedures reported in literature [33]) was found to be equal to $0.85 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \text{ K}^{-3/2}$. Fig. 2 shows a substantial superimposition of both the experimental NITG and ITG mass loss rate values within the uncertainties estimated with those predicted using Eq. (2). Furthermore, from the mass loss rates of acetanilide determined in the temperature interval between 427.2 and 458.2 K using Eq. (2), the logarithmic form of two instrumental constants (a sort of empirical vaporization constants) related the two TG operative methods, $\ln(k_{cal})$, has been reported as a function of temperature in

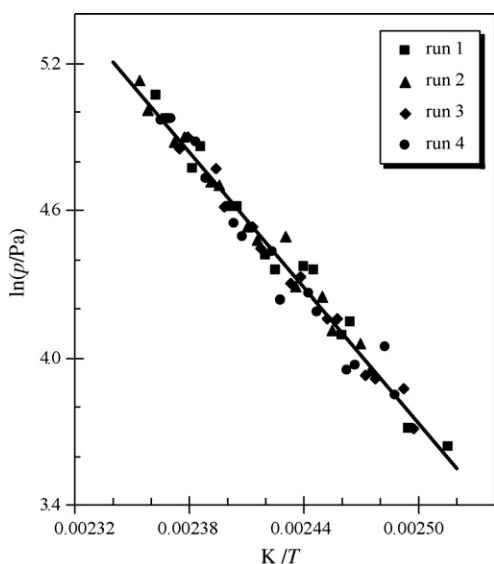


Fig. 2. Vapor pressures derived from the NITG experiments for the solid HCB.

Table 1. A slight increasing trend of $\ln(k_{\text{cal}})$ values is observed with increasing the temperature because of the influence of diffusion, even if the range of values for both methods is very narrow: the dispersion D of all the values around the mean values (12.52 ± 0.04 and 12.53 ± 0.03 for NITG and ITG experiments, respectively) does

not exceed ± 0.05 . Therefore, the mean values can be considered suitable to convert both the NITG and ITG mass loss rate data into vapor pressure values using Eq. (1). It is interesting to note that, despite the fact that vaporization is necessarily diffusion-controlled and k_{cal} can be considered an empirical determination of a mass-transfer coefficient, the average $\ln(k_{\text{cal}})$ values are in excellent agreement with the corresponding average value reported in a previous paper ($\ln(k_{\text{cal}}/\text{kg}^{0.5} \text{ s}^{-1} \text{ m (K mol)}^{-0.5}) = 12.54$) in which benzoic acid was also considered as recommended reference compound [27].

3.2. Vapor pressure measurements and experimental enthalpies and entropies of vaporization

From all the NITG and ITG experiments the derived p/T values were selected above the solid HCB and both solid and liquid lindane using the average k_{cal} found. The results of NITG and ITG experiments were reported in Tables 1 and 2, respectively. Tables 3 and 4 present the detailed parameters of Clausius–Clapeyron equation derived from least-square treatment of all the experimental p/T data and the standard molar enthalpies of sublimation and vaporization at the temperature $\langle T \rangle$ (denoted as $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(\langle T \rangle)$ and $\Delta_{\text{l}}^{\text{g}} H_{\text{m}}^{\circ}(\langle T \rangle)$, respectively) along with the associated errors. By weighing slopes and intercepts proportionally to the experimental points the average molar enthalpies of sublimation and vaporization, substantially equivalent to those obtained by analyzing all the experimental points (global results), were also listed in Tables 3 and 4. In addition, the equilibrium pressure related to

Table 1
Vapor pressures of the examined compounds obtained by NITG experiments.

Run 1		Run 2		Run 3		Run 4		Run 5		Run 6	
T/K	p/Pa	T/K	p/Pa	T/K	p/Pa	T/K	p/Pa	T/K	p/Pa	T/K	p/Pa
HCB (cr)											
397.5	38	404.1	52	400.4	41	402.0	47				
400.8	41	404.9	58	401.2	48	402.8	57				
405.8	63	407.4	61	403.6	50	405.3	53				
406.5	60	408.2	70	404.5	51	406.1	52				
409.0	78	410.6	73	407.0	64	408.6	66				
409.8	79	411.4	89	407.8	64	409.4	71				
412.3	78	414.0	88	410.2	76	411.9	69				
413.2	83	414.9	93	411.0	74	412.7	84				
415.7	101	417.4	110	413.6	85	415.3	89				
416.5	101	418.2	112	414.4	93	416.1	94				
419.1	129	420.7	134	417.0	101	418.6	113				
419.9	118	421.5	131	417.8	118	419.5	131				
422.3	144	424.0	149	420.3	134	421.9	144				
423.2	159	424.8	169	421.1	128	422.8	143				
		425.7	173	423.6	146	424.4	152				
Lindane (cr)											
377.5	24										
378.3	26										
379.1	27										
379.9	28										
380.7	30										
381.5	32										
382.4	34										
383.2	37										
384.0	38										
384.8	41										
Lindane (l)											
387.0	49	387.6	46	387.9	46	388.2	46	388.6	43	386.4	44
392.1	65	393.2	60	394.1	67	395.0	70	395.9	79	390.8	51
397.6	74	398.5	77	402.0	95	400.2	88	401.0	100	396.7	85
402.8	106	403.6	104	404.4	125	405.3	131	406.1	139	401.9	109
407.7	153	408.5	142	409.3	158	410.2	148	411.0	174	406.9	119
412.6	177	413.4	174	414.3	192	415.1	202	415.9	195	411.8	168
417.6	229	418.4	235	419.3	261	420.1	257	421.0	254	416.8	211
422.7	286	423.6	306	424.5	301	425.4	331	426.4	366	421.8	267
428.7	416	426.8	342	428.6	367					427.5	405

Table 2
Vapor pressures of the examined compounds obtained by ITG experiments.

Run 1		Run 2		Run 3		Run 4	
T/K	p/Pa	T/K	p/Pa	T/K	p/Pa	T/K	p/Pa
HCB (cr)							
364.5	4	359.7	2	362.5	3	360.2	3
365.5	4	361.6	3	364.4	3	367.4	5
370.3	5	363.6	4	365.4	4	368.0	5
371.5	6	369.5	5	371.5	5	374.1	7
378.2	8	371.0	6	377.1	8	378.1	8
381.4	12	381.4	11	384.4	14	382.3	12
386.2	15	383.1	12	385.8	15	382.4	11
393.3	24	388.5	16	392.7	21	386.6	13
400.6	38	396.7	26	399.6	31	396.3	26
412.3	66	404.4	43	408.3	57	403.2	44
Lindane (cr)							
347.1	2	349.8	2	349.9	2		
351.9	3	352.0	3	354.4	3		
355.0	3	356.2	4	356.4	4		
357.8	4	359.3	5	361.5	5		
363.2	6	364.0	6	364.9	8		
367.2	8	368.1	10	371.1	12		
372.9	12	374.3	17	376.2	17		
377.4	23	379.3	23	380.7	29		
381.8	28	384.0	37				
Lindane (l)							
387.4	45	390.5	53				
389.2	49	392.1	60				
389.9	55	393.5	70				
393.6	65	398.9	86				
396.6	80	399.0	93				
398.7	88	399.9	93				
400.3	95	401.7	103				
403.7	114	403.7	111				
406.5	122	406.9	133				

this temperature, $p(<T>)$, and the entropies of vaporization at equilibrium conditions ($\Delta_i^g S_m(<T>, p(T=<T>))$) were also given in Tables 3 and 4. The plots of the $\ln p=f(1/T)$ of all the data derived by both the NITG and ITG experiments were given in Figs. 2 and 3 and Figs. 4 and 5, respectively.

The vapor pressures obtained in this work for HCB and lindane were compared with those reported in literature in previous papers and books both in Table 5 and in Figs. 6–7, respectively [1–15]. Furthermore, to the best of my knowledge, only one literature value was found for lindane, in the molten state [5]. As it can be seen, the sets of literature values are often determined in limited range of temperature and the agreement among them is poor and the dispersion of values for both compounds is significant. The exper-

imental vapor pressures determined in the present investigation satisfactorily agree with the values reported in Refs. [12,15] for solid HCB. A good agreement was found between experimental data concerning solid lindane with data referred to Refs. [10,14], and between experimental data related to liquid lindane and those obtained by Ref. [5]. The vapor pressure of HCB calculated at 298.15 (slightly outside the experimental temperature range) is only one order of magnitude higher than those calculated by literature data (except that obtained by Ref. [4]), while for lindane this value agrees well with the most reasonable ones calculated using the results of Refs. [8,10,14].

At a first sight, the experimental vapor pressures above the liquid lindane seem to be reasonable, even if no literature values were

Table 3
Experimental results and average values obtained by the nonisothermal (NITG) and isothermal (ITG) measurements for the solid HCB.

Method	N	<T> K	$\ln(p/\text{Pa})=a-b/T$		$p(T=<T>)$ Pa	$\Delta_{cr}^g H_m^\circ(<T>)^a$ kJ mol ⁻¹	$\Delta_{cr}^g S_m^\circ(<T>, p(T=<T>))$ JK ⁻¹ mol ⁻¹
			a	b/K			
NITG	14	410	26.74 ± 0.96	9197 ± 394		76 ± 5	
	15	415	26.68 ± 0.74	9176 ± 307		76 ± 5	
	15	412	26.73 ± 0.67	9203 ± 277		77 ± 4	
	15	413	26.65 ± 1.21	9175 ± 502		76 ± 6	
Average results	59	411	26.70 ± 0.90	9188 ± 370	77	76 ± 5	126 ± 4
Global results	59	411	26.73 ± 0.44	9198 ± 183	77	76 ± 4	126 ± 2
ITG	10	388	26.72 ± 0.50	9270 ± 192		77 ± 4	
	10	382	26.35 ± 0.32	9141 ± 120		76 ± 4	
	10	386	26.48 ± 0.43	9188 ± 163		76 ± 4	
	10	382	26.44 ± 0.80	9180 ± 302		76 ± 4	
Average results	40	386	26.50 ± 0.51	9195 ± 194	15	76 ± 4	124 ± 3
Global results	40	386	26.54 ± 0.25	9209 ± 93	15	77 ± 2	125 ± 2

^a $\Delta_{cr}^g H_m^\circ(<T>)=b \cdot R$, where $R=8.314472 \text{ J mol}^{-1} \text{ K}^{-1}$.

^b $\Delta_{cr}^g S_m^\circ(<T>, p(T=<T>))=(a-\ln p^\circ) \cdot R$, where $p^\circ=0.1 \text{ MPa}$.

Table 4

Experimental results and average values obtained by the nonisothermal (NITG) and isothermal (ITG) measurements for the liquid lindane.

Method	N	<T> K	ln(p/Pa) = a - b/T		p(T = <T>) Pa	$\Delta_{cr,l}^{\circ}H_m^{\circ}(<T>)^a$ kJ mol ⁻¹	$\Delta_{cr,l}^{\circ}S_m^{\circ}(<T>, p(T = <T>))^b$ JK ⁻¹ mol ⁻¹
			a	b/K			
Lindane (cr)							
NITG	10	381	30.95 ± 0.74	10484 ± 283	31	87 ± 3	161 ± 4
ITG	9	364	30.20 ± 1.48	10287 ± 539		86 ± 5	
	9	367	31.78 ± 1.10	10849 ± 400		90 ± 4	
	9	365	32.46 ± 1.12	11110 ± 408		92 ± 4	
Average results	27	366	31.44 ± 1.24	10734 ± 451	8	89 ± 5	166 ± 7
Global results	27	366	31.41 ± 0.71	10723 ± 257	8	89 ± 3	165 ± 4
Lindane (l)							
NITG	9	408	25.74 ± 0.70	8475 ± 283		70 ± 3	
	9	407	26.29 ± 0.37	8727 ± 152		73 ± 2	
	9	408	25.84 ± 0.60	8528 ± 243		71 ± 3	
	8	407	26.31 ± 0.54	8721 ± 219		73 ± 3	
	8	408	26.44 ± 1.02	8770 ± 417		73 ± 4	
	9	407	26.14 ± 0.84	8649 ± 340		72 ± 4	
Average results	52	408	26.18 ± 0.69	8664 ± 282	134	72 ± 3	121 ± 3
Global results	52	408	26.15 ± 0.27	8653 ± 111	133	72 ± 2	122 ± 1
ITG	9	393	25.76 ± 0.79	8496 ± 311		71 ± 4	
	9	395	25.88 ± 0.98	8535 ± 390		71 ± 4	
Average results	18	394	25.82 ± 0.88	8515 ± 351	83	71 ± 4	119 ± 4
Global results	18	394	25.90 ± 0.57	8547 ± 228	83	71 ± 3	119 ± 3

^a $\Delta_{cr,l}^{\circ}H_m^{\circ}(<T>) = b \cdot R$, where $R = 8.314472 \text{ J mol}^{-1} \text{ K}^{-1}$.^b $\Delta_{cr,l}^{\circ}S_m^{\circ}(<T>, p(T = <T>)) = (a - \ln p^{\circ}) \cdot R$, where $p^{\circ} = 0.1 \text{ MPa}$.

found in literature for comparison, but further calculations still have to be done.

Finally, at the reference temperature of 298.15 K the standard molar enthalpies of sublimation $\Delta_{cr}^{\circ}H_m^{\circ}(298.15 \text{ K})$ can be determined directly from the standard molar enthalpies of sublimation $\Delta_{cr}^{\circ}H_m^{\circ}(<T>)$ using the following equation:

$$\Delta_{cr}^{\circ}H_m^{\circ}(298.15 \text{ K}) = \Delta_{cr}^{\circ}H_m^{\circ}(<T>) + \Delta_{cr}^{\circ}C_{p,m}^{\circ}(T_{\text{fus}} - 298.15) \quad (3)$$

where the heat capacity differences of both solid and gaseous phases at constant pressure is calculated via the following equation:

$$\Delta_{cr}^{\circ}C_{p,m}^{\circ} = -[0.75 + 0.15C_{p,m}^{\circ}(\text{cr})_{\text{estd}}(298.15 \text{ K})] \quad (4)$$

where the value of $C_{p,m}^{\circ}(\text{cr})_{\text{estd}}(298.15 \text{ K})$ is estimated using a group additivity approach proposed by Chickos et al. [20]. For lindane only the standard molar enthalpies of sublimation $\Delta_{cr}^{\circ}H_m^{\circ}(298.15 \text{ K})$ were determined also by the sum of the corre-

Table 5

Comparison of temperature dependence of the vapor pressures of solid HCB and solid and liquid lindane determined in this study and those taken from literature and sublimation vapor pressures calculated at 298.15 K.

Compounds	Method [Ref.]	ΔT range K	ln(p/Pa) = a - b/T		p(298.15 K) mPa
			a ^a	b/K ^a	
HCB (cr)	Transpiration [1]	253–303	23.59 ± 0.82	8920 ± 222	1.8
	Gas saturation [2]	284–321	32.32 ± 0.19	11373 ± 66	3.0
	Knudsen [3]	293–333	32.69 ± 0.04	11695 ± 13	1.5
	Not mentioned [4]	387–558	22.96 ± 0.22	6942 ± 286	724
	Gas saturation [6]	288–318	34.32 ± 1.08	12046 ± 327	2.3
	Generator column [7]	258–313	36.50 ± 2.37	12704 ± 669	2.2
	Vapor Pressure Balance [11]	283–323	31.74 ± 0.08	11302 ± 24	2.1
	Rodebush manometer [12]	369–397	31.19 ± 0.22	11059 ± 82	2.7
	Not mentioned [14]	387–502	24.14	7453	8.0
	Transpiration [15]	358–403	32.02 ± 0.15	11331 ± 57	2.5
	This work ^b	364–423	26.62 ± 0.52	9197 ± 210	15
	Lindane (cr)	Transpiration [1]	243–303	39.12 ± 0.23	12816 ± 104
Knudsen [8]		292–326	34.53 ± 0.21	11754 ± 72	7.5
Gas saturation [9]		293–313	31.19	12178	0.06
Torsion and Knudsen [10]		310–384	32.77 ± 1.15	11128 ± 345	10
Torsion [13]		333–363	40.67	13880	2.8
Not mentioned [14]		313–363	35.20	11934	8.0
This work ^b		347–385	31.27 ± 0.90	10647 ± 330	12
Lindane (l)	GC (retention data) [5]	386–427 ^c	25.67	8474	
	This work ^b	386–427	26.01 ± 0.61	8595 ± 243	

^a Regression parameters are recalculated from experimental vapor pressure–temperature data taken from literature, while associated errors are standard deviations.^b Regression parameters determined in this study are mean of values determined from NITG and ITG experiments.^c This experimental temperature range was selected for comparison purpose because the actual range was not available.

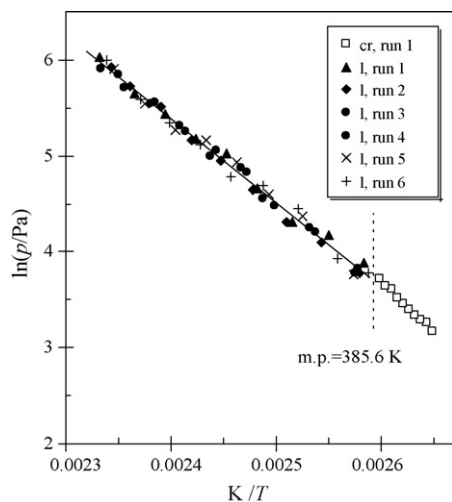


Fig. 3. Vapor pressures derived from the NITG experiments for the solid (cr) and liquid (l) lindane.

sponding standard molar enthalpies of vaporization $\Delta_1^g H_m^\circ(<T>)$ and the enthalpy of fusion $\Delta_{cr}^l H_m^\circ$ determined by DSC:

$$\Delta_{cr}^g H_m^\circ(298.15 \text{ K}) = \Delta_1^g H_m^\circ(<T>) + \Delta_{cr}^l H_m^\circ + \Delta_{cr}^g C_{p,m}^\circ(T_{fus} - 298.15) + \Delta_1^g C_{p,m}^\circ(<T> - T_{fus}) \quad (5)$$

where the heat capacity differences of both liquid and gaseous phases at constant pressure using Eq. (6), where the value of $C_{p,m}^\circ(l)_{\text{estd}}$ (298.15 K) is estimated using a group additivity approach proposed by Chickos et al. [20]:

$$\Delta_1^g C_{p,m}^\circ = -[10.58 + 0.26C_{p,m}^\circ(l)_{\text{estd}}(298.15 \text{ K})] \quad (6)$$

The heat capacities were found to be $C_{p,m}^\circ(\text{cr})_{\text{estd}} = (267.6 \text{ and } 319.8) \text{ J mol}^{-1} \text{ K}^{-1}$ for solid HCB and lindane, respectively, while $C_{p,m}^\circ(l)_{\text{estd}} = 340.2 \text{ J mol}^{-1} \text{ K}^{-1}$ for liquid lindane. All the $\Delta_{cr}^g H_m^\circ(298.15 \text{ K})$ values determined in this study from both NITG and ITG experiments were listed in Table 6.

The consistency of experimental vapor pressure data reported here was established by considering the good agreement between

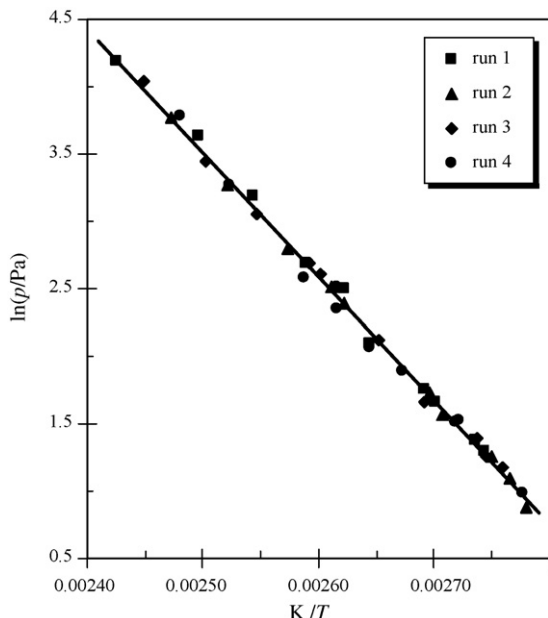


Fig. 4. Vapor pressures derived from the ITG experiments for the solid HCB.

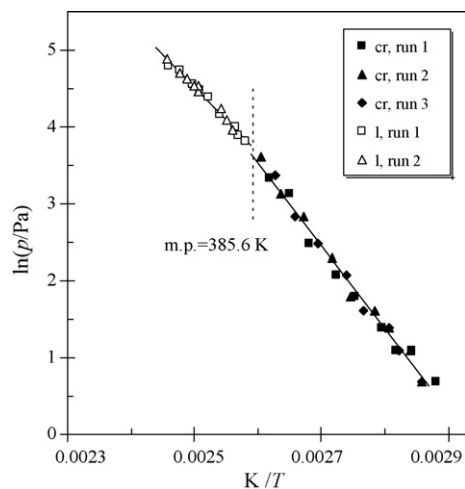


Fig. 5. Vapor pressures derived from the ITG experiments for the solid (cr) and liquid (l) lindane.

the standard molar enthalpy of fusion determined by DSC (adjusted at 298.15 K using the difference of heat capacities of solid and liquid), with that obtained from the difference of the mean values of the standard molar sublimation and vaporization enthalpies at 298.15 K: $\Delta_{cr}^l H_m^\circ(298.15 \text{ K}) = (20.3 \text{ and } 19.3) \text{ kJ mol}^{-1}$, respectively.

The standard ($p^\circ = 0.1 \text{ MPa}$) molar entropies of sublimation adjusted at 298.15 K ($\Delta_{cr}^g S_m^\circ(298.15 \text{ K})$), have been obtained from the NITG and ITG data using the following equations for experiments carried out above the solid and liquid, respectively:

$$\Delta_{cr}^g S_m^\circ(298.15 \text{ K}) = \Delta_{cr}^g S_m^\circ[<T>, p(<T>)] + \Delta_{cr}^g C_{p,m}^\circ \ln(298.15 \text{ K} / <T>) \quad (7)$$

and:

$$\Delta_{cr}^g S_m^\circ(298.15 \text{ K}) = \Delta_1^g S_m^\circ[<T>, p(<T>)] + \Delta_{cr}^l S_m^\circ + \Delta_{cr}^g C_{p,m}^\circ \ln(298.15 \text{ K} / T_{fus}) + \Delta_1^g C_{p,m}^\circ \ln(T_{fus} / <T>) \quad (8)$$

The uncertainties associated to the values of $\Delta_{cr}^g S_m^\circ(298.15 \text{ K})$ were obtained taking into account the uncertainties assigned to

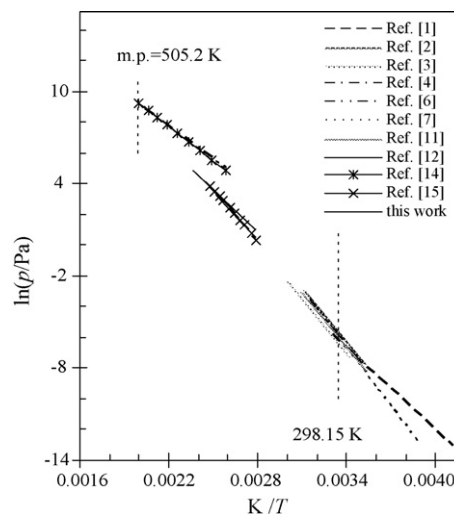


Fig. 6. Comparison of the experimental temperature dependence of vapor pressure for solid HCB with those taken from literature.

Table 6

The standard ($p^\circ = 0.1$ MPa) molar enthalpies of sublimation, along with entropies and Gibbs energies of sublimation adjusted at $T = 298.15$ K.^a

Compounds	Technique	$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^\circ(298.15 \text{ K})$ (kJ mol ⁻¹)	$\Delta_{\text{cr}}^{\text{g}}S_{\text{m}}^\circ(298.15 \text{ K})$ (J mol ⁻¹ K ⁻¹)	$\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^\circ(298.15 \text{ K})$ (kJ mol ⁻¹)
HCB	NITG	81 ± 5	113 ± 6	47 ± 5
	ITG	80 ± 7	114 ± 4	46 ± 5
lindane	NITG	97 ± 9	155 ± 9	51 ± 6
	ITG	96 ± 9	156 ± 9	49 ± 6

^a Correction of the mentioned thermodynamic quantities to 298.15 K was performed using the following values: $\Delta_{\text{cr}}^{\text{g}}C_{p,m}^\circ = (-42.3$ and $-48.7)$ J mol⁻¹ K⁻¹ for solid HCB and lindane, respectively while $\Delta_{\text{l}}^{\text{g}}C_{p,m}^\circ = -99.0$ J mol⁻¹ K⁻¹ for liquid lindane.

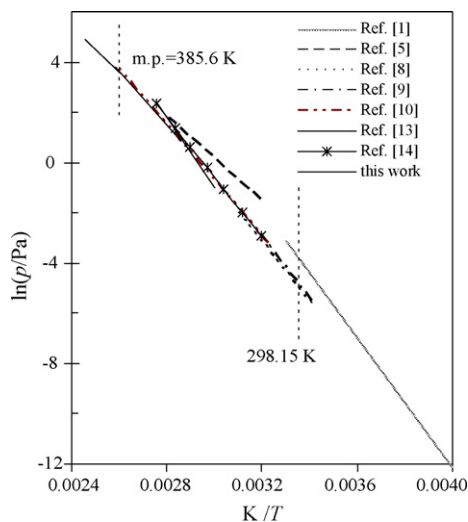


Fig. 7. Comparison of the experimental temperature dependence of vapor pressure for solid and liquid lindane with those taken from literature.

the values of $\Delta_{\text{l}}^{\text{g}}S_{\text{m}}^\circ[<T>, p(<T>)]$, those of $\Delta_{\text{cr}}^{\text{g}}C_{p,m}^\circ$ and $\Delta_{\text{l}}^{\text{g}}C_{p,m}^\circ$ along with those of $\ln p(<T>)$ derived from the standard deviations of the regression parameters of the Clausius–Clapeyron equation given in Tables 3 and 4. The $\Delta_{\text{cr}}^{\text{g}}S_{\text{m}}^\circ(298.15 \text{ K})$ values derived from both the NITG and ITG experiments were also given in Table 6 and substantially agree with each other within the associated uncertainties assigned to the standard molar entropies of sublimation at 298.15 K.

Finally, the standard ($p^\circ = 0.1$ MPa) molar Gibbs energies at 298.15 K ($\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^\circ(298.15 \text{ K})$) have been calculated using the following equation:

$$\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^\circ(298.15 \text{ K}) / (\text{kJ mol}^{-1}) = \Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^\circ(298.15 \text{ K}) - 298.15 \Delta_{\text{cr}}^{\text{g}}S_{\text{m}}^\circ(298.15 \text{ K}) \quad (9)$$

and the resulted values are reported in Table 6.

In spite of the significant lower standard molar enthalpies and entropies of sublimation of HCB with respect to those of lindane at 298.15 K, only very small differences are observed between the mean values of the standard molar Gibbs energies of sublimation (3 kJ mol⁻¹) and the sublimation vapor pressures (3 mPa, Table 5), resulted in only a slight difference in their volatility.

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