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Comprehensive Study of Vapor Pressures and Enthalpies of Vaporization of Cyclohexyl Esters

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Vapor pressures and standard molar enthalpies of vaporization $\Delta_l^g H_m^\circ$ were determined for five cyclohexyl esters: cyclohexyl formate, cyclohexyl acetate, cyclohexyl propanoate, cyclohexyl butyrate, and cyclohexyl valerate. The data were obtained from the temperature dependence of the vapor pressure measured by the Knudsen and the transpiration methods. Additionally, the standard molar enthalpies of vaporization $\Delta_l^g H_m^\circ$ of the same cyclohexyl esters were measured calorimetrically. An analysis of the results obtained from three independent methods has allowed us to improve the determination of the enthalpies of vaporization by the Knudsen effusion method.

Introduction

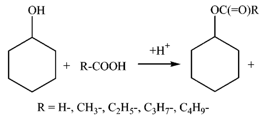
Cyclohexyl esters are usually formed as byproducts in manufacturing of caprolactam from benzene. Hence, the study of their vapor pressures and vaporization enthalpies is very important for the optimization of the separation technologies. The vapor pressure of cyclohexyl acetate (CHA) has been studied only in the temperature range (369 to 445) K.[1] For the other esters, the data on vapor pressure and enthalpies of vaporization are not available.

There are several well-established techniques for the determination of vapor pressures, among them the classical integral effusion mass loss Knudsen-cell method for determination of vapor pressures, which is, however, a demanding and time-consuming method. But at the same time, this technique has some apparent benefits in comparison with other techniques, such as the static or torsion-effusion methods.[2] Among the most important advantages of the Knudsen method are the precise thermostating of the effusion cell and the reliable measurement of the temperature. That is why this method has been widely used for the investigation of low-volatility compounds with vapor pressures < 1 Pa. During the past decade, measurements of enthalpies of vaporization of organic compounds have been performed in our laboratory using two experimental techniques: the Knudsen-cell method and a calorimetric method. It is a source of disappointment that a comparison of the results obtained from the two methods has revealed that enthalpies of vaporization from the Knudsen method are systematically higher than those measured calorimetrically. For instance, this difference in our previous experiments on alkyl derivatives of urea[2] was close to 4 kJ·mol^{-1}. This study has been conceived and performed in order to understand reasons for such discrepancies.

In this paper we report the results of vapor pressure and vaporization enthalpy measurements for the following cyclohexyl esters: cyclohexyl formate (CHF), cyclohexyl acetate (CHA), cyclohexyl propanoate (CHP), cyclohexyl butyrate (CHB), and cyclohexyl valerate (CHV). An effusion Knudsen apparatus and Calvet type differential calorimeter[3] located at the Belarusian State University were used for the measurements. For a more detailed comparison and understanding of the results, a transpiration apparatus,[4,5] located at the University of Rostock, was also used. A careful analysis of the results obtained from three independent methods has allowed us to elucidate a reason for anomalous deviations of the values of enthalpies of vaporization from the effusion and those from calorimetric experiments and suggests a means to eliminate this effect.

Experimental Section

Materials. The samples of the esters (CHF, CHA, CHP, CHB, and CHV) were synthesized via esterification reaction from cyclohexanol and an appropriate carboxylic acid in the presence of 5 mass % H_2SO_4 as a catalyst:



The molar ratio of reagents carboxylic acid/cyclohexanol was taken to be 3:1 in order to increase the conversion of cyclohexanol. The samples of cyclohexyl esters were purified by vacuum distillation. The purities of all the samples were determined by gas−liquid chromatography. The purities of the samples used for experiments with effusion and calorimetric methods were as follows (in mass fraction): CHF, 0.998; CHA, 0.999; CHP, 0.997; CHB, 0.999; CHV, 0.995. The purities of the samples used for the transpiration method was better than 0.999 mass fraction.

Knudsen Technique. Vapor pressures and enthalpies of vaporization of the cyclohexyl esters have been determined with the help of the Knudsen method.

The schematic diagram of the apparatus used in this study is presented in Figure 1. The stainless steel cylindrical container of 25 mm length and 10 mm internal diameter was used as an effusion cell. The thickness of the walls was 1 mm. While the thermal conductivity of stainless steel

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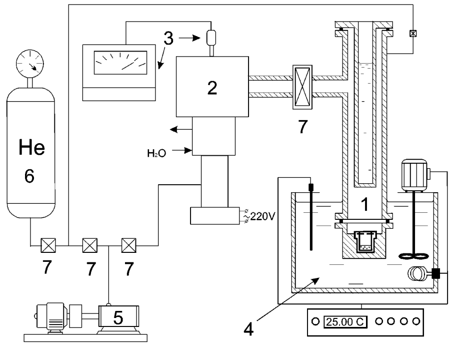

Figure 1. Apparatus for vapor pressure measurements by the Knudsen method: 1, measuring block (effusion cell with a sample, vacuum connection, coldfinger); 2, oil diffusion pump; 3, vacuum gauge; 4, thermostat; 5, rough pump; 6, helium cylinder; 7, bellows gate valves.

is less than that of copper or silver, the inert nature of the steel is an advantage in case of possible decomposition of the organic sample during the experiment. The cell was covered with a nickel membrane (thickness 0.050 mm), equipped with a PTFE ring and a copper washer, and was closed by a copper lead screwed onto the cell body. To adjust the temperature of the membrane and avoid its supercooling during effusion, the top of the copper lead had a parabolic shape. Two membranes with different orifices were used. The diameters of the orifices were measured using a horizontal compare circuit IZA-2 with an uncertainty of (±0.0001) mm. Because the orifices were not ideally round, the determination of their diameters was performed by rotation of the membrane with steps of 15°. The average diameters of the orifices measured according to this procedure were (0.1833 ± 0.0004) mm (membrane 1) and (0.4467 ± 0.0005) mm (membrane 2). The area of the orifices was >500 times less than the area of the liquid surface. That is why the vapor in the cell was close to saturation. For the maintenance of a constant temperature in the cell, a homemade thermostat was used. The temperature was maintained constant to within ±0.01 K throughout all experimental runs within a range of (273 to 363) K. In the temperature range from (243 to 273) K, the liquid thermostat filled with antifreeze A-40 M as a thermostating liquid was used. Cool vapor from boiling liquid nitrogen was used as a refrigerant. The pressure of nitrogen was adjusted by variation of the power dissipated in a heater placed in the Dewar. Temperature was maintained within (±0.02) K because of the usually high viscosity of the antifreeze. The temperature in the thermostat was measured with a platinum resistance thermometer. We used an oil diffusion pump having a pumping rate of 10^5 $m^3 \cdot s^{-1}$ in the region of pressures from $(4 \times 10^{-2}$ to $4 \times 10^{-3})$ Pa and a residual pressure of 6.7×10^{-5} Pa, providing an outlet pressure of 10 Pa. To reach this pressure, an additional rough pump was used. Its pumping rate was greater than 5.5×10^{-3} $m^3 \cdot s^{-1}$ for pressures from (0.26 to 101.3) kPa, and the residual pressure was 0.67 Pa. To control the pressure in the pumping system, a thermocouple vacuum gauge PMT-2 was used. The residual pressure (about 10^{-3} Pa) in the system near the effusion cell was measured with the help of an emission gauge. To finish an experiment rapidly, helium gas was supplied at ambient pressure. It was connected to the measuring system by a flexible rubber tube.

Despite the fact that Knudsen procedures are well-established, some additional refinements were suggested in our laboratory. Thus, according to our earlier finding,[4] the exposition time during an experiment has to be corrected with the residual time, which is usually necessary for the system to reach a working pressure of 10^{-3} Pa. In this work, to increase the evacuation rate from the apparatus, the procedure at the beginning of the experiment was changed. The measuring block was pumped by the rough pump for a period of 10 s, and afterward the oil diffusion pump was switched to the block. The time necessary to reach the working pressure in the apparatus was determined in experiments with hexadecane. Since this time was <1 s, it did not impact the results in the experiments that are longer than 1 h. Therefore, the time of the exposition has to be measured from the moment that the rough pump is switched on. At the beginning of the experiment, the integral Knudsen cell with the sample should be thermostated under helium gas at 101.3 kPa. In this work, we studied the rate of evaporation of the sample from the cell during this prearrangement. It was found that the loss of mass during the thermostating depends on the temperature, the parameters of the membrane, the vapor pressure, and the nature of the compound. The appropriate corrections for the mass loss in the each measurement were obtained in individual experiments and presented in Tables 1−5. The vapor pressure is calculated with the equation

$$p_{\mathrm{sat}} = \frac{\Delta m}{k s \tau}\sqrt{\frac{2\pi R T}{M}} \tag{1}$$

where Δm is the loss of mass of a sample during time t/s; M is the molar weight of the vapor; s is the area of an orifice; k is the transmission probability; $R = 8.314\,47$ $J \cdot mol^{-1} \cdot K^{-1}$; and T is temperature. The uncertainty of the technique was estimated to be 5%.

Transpiration Method. Vapor pressures and enthalpies of vaporization of cyclohexyl esters were also determined by using the method of transference in a saturated N_2-stream. The method has been described before[5,6] and has been shown to give results that are in excellent agreement (within 1 to 2%) with those of well-established techniques for determining vapor pressures of pure substances and enthalpies of vaporization from the temperature dependence of the vapor pressure. About 0.5 g of a sample was mixed with glass beads and placed in a thermostated U-tube of length 20 cm and diameter 0.5 cm. A nitrogen stream was passed through the U-tube at constant temperature (±0.1 K), and the transported amount of material was condensed in a cooled trap. The mass of condensed product was determined by GLC analysis using an external standard (hydrocarbons). Assuming the validity of Dalton's law for the saturated nitrogen stream, values of the vapor pressure p_{sat} were calculated from

$$p_{\mathrm{sat}} = m R T_{\mathrm{a}}/V(\mathrm{N_2})M \tag{2}$$

where $R = 8.314\,47$ $J \cdot K^{-1} \cdot mol^{-1}$, m is the mass of transported compound, $V(N_2)$ is the volume of transporting gas, M is the molar mass of the compound, and T_a is the temperature of the soap bubble meter. The volume of the gas $V(N_2)$ transferred through the tube was determined from measurements of flow rate and time. The vapor pressure p_{sat} at each saturation temperature was calculated from the amount of product collected within a definite time period, to which was added the small value of the residual vapor pressure at the temperature of condensation. The latter was calculated from a linear correlation between ln p_{sat} and T^{-1} obtained by iteration.

To calculate the standard molar enthalpy of vaporization at the mean temperature $\langle T \rangle$ of the experimental temperature range, $\Delta_l^g H_m^\circ(T)$, the integrated form of the linear Clausius−Clapeyron equation

$$\ln(p_{sat}/\mathrm{Pa}) = a - b(T/\mathrm{K})^{-1} \tag{3}$$

was applied, where $b = \Delta_l^g H_m^\circ(T)/R$. The errors in the thermodynamic functions were defined as deviations of experimental $\ln p_{sat}$ from the linear correlation.

Calorimetric Method. The third method used in this work to measure enthalpies of vaporization of the cyclohexyl esters is calorimetry. A differential Calvet type microcalorimeter MID-200 was used. The technique was established in this laboratory a few years ago, and the special cell designed for these measurements has been recently improved.[3] In this study the calorimeter was equipped with a more sensitive voltmeter having the measuring range between (10^{-9} and 2) V and relaxation time from (2 to 30) s. The sample was placed in a hermetically sealed cell made of stainless steel and covered with a nickel foil. After preliminary thermostating of the cell, the foil was punctured with a special rod and the thermal flow caused by the evaporation of the sample was recorded. The values of enthalpies of vaporization, $\Delta_l^g H_m^\circ$, were calculated with

$$\Delta_l^g H_m^\circ = K^{-1} M m \int_{\tau=0}^{\tau} \Delta E \, d\tau \tag{4}$$

where m is the vacuum mass of the sample, K is the calorimetric constant of the cell, ΔE is the difference of the potentials of thermocouples, which corresponds to the temperature imbalance between the cell and the thermostat of the calorimeter at the time τ, $\int_{\tau=0} \Delta E \, d\tau$ is the total signal value recorded during the experiment, and M is the molar mass of a compound.

The calorimeter was calibrated by experiments with a standard reference sample of benzoic acid K-1 (VNIIM, St. Petersburg), as well as with carefully purified samples of naphthalene, *n*-decane, and twice distilled water. The uncertainty of measurements of the enthalpies of vaporization was estimated to be within (±0.5)%.

Since the average temperatures of the measurements deviate from T = 298.15 K, the observed values of the enthalpies of vaporization were adjusted to this reference temperature with the help of the equation

$$\{\Delta_l^g H_m^\circ(\langle T\rangle) - \Delta_l^g H_m^\circ(298.15\ \mathrm{K})\}/\mathrm{kJ \cdot mol^{-1}} = -\Delta C_p\{(\langle T\rangle/\mathrm{K}) - 298.15\} \tag{5}$$

With these corrections (the uncertainty of the correlation was not taken into account) and the measured values of $\Delta_l^g H_m^\circ(T)$, the standard enthalpies of vaporization at T = 298.15 K were calculated. Values of ΔC_p were evaluated on the basis of the experimental molar heat capacities of the liquid[8] $C_p(l)$ and gas[9] $C_p(g)$ to be −69, −76, −74, −74, and −73 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ for CHF, CHA, CHP, CHB, and CHV, respectively. The heat capacity of liquid CHP was measured by adiabatic calorimetry as described earlier.[8]

Results and Discussion

Vapor pressures of the cyclohexyl esters measured by the Knudsen method are presented in Tables 1−5. The effective values of the vapor pressures in these tables were calculated with eq 1 using the transmission probability as proposed by Clausing[10]

$$k = \frac{1}{1 + l/d} \tag{6}$$

where l is the membrane thickness and d is the diameter of the orifice. For the used membranes the Clausing coefficients were 0.7857 (membrane 1) and 0.8993 (membrane 2). The parameters of the linear fit $\ln P$ versus T^{-1} (eq 3) are presented in Table 6. Enthalpies of vaporization, $\Delta_l^g H_m^\circ$, of the cyclohexyl esters measured calorimetrically are listed in Tables 7−11. The calorimetric constants were measured before each series of measurements and are given in Tables 7−11.

Table 1. Vapor Pressures of CHF from the Effusion Method[a]

T/K	τ/s[b]	$10^6\Delta m$/kg[c]	p^*_{sat}/Pa[d]	Kn[e]	k[f]	p_{sat}/Pa
273.18	3600	18.13[g]	81.1	0.19	1.0349	61.7
273.17	3600	17.97[g]	80.4	0.19	1.0344	61.2
273.16	3600	17.38[g]	77.7	0.20	1.0328	59.2
273.15	3600	16.70[g]	74.7	0.21	1.0308	57.0
271.24	3600	15.59[g]	69.5	0.22	1.0275	53.2
268.44	3600	11.80[g]	52.3	0.28	1.0122	40.7
265.94	7260	18.74[g]	41.0	0.35	0.9974	32.4
263.64	7260	15.96[g]	34.8	0.41	0.9868	27.7
263.13	5411	10.58[g]	30.9	0.46	0.9786	24.9
258.50	10800	13.65[g]	19.8	0.68	0.9471	16.5
258.09	7200	8.40[g]	18.3	0.73	0.9412	15.3
253.47	18000	13.74[g]	11.8	1.07	0.9112	10.2
253.02	10800	7.61[g]	10.9	1.15	0.9057	9.49
248.25	3600	10.75[h]	6.74	0.78	1.0857	5.59
243.01	5400	9.15[h]	3.79	1.30	1.0349	3.29
242.71	5400	10.29[h]	4.26	1.17	1.0451	3.66

[a] The thermostating mass loss, Δm_1, is 0 in each case. [b] Exposition time. [c] Experiment mass loss. [d] Effective values according to Clausing. [e] Knudsen number. [f] Transmission probability. [g] Membrane 1. [h] Membrane 2; σ = 6.28 Å.

Table 2. Vapor Pressures of CHA from the Effusion Method[a]

T/K	τ/s	$10^6\Delta m$/kg	$10^6\Delta m_1$/kg	p^*_{sat}/Pa	Kn	k	p_{sat}/Pa
283.67	3820	18.69	0.04	76.0	0.19	1.0339	57.9
283.67	3600	17.46	0.04	75.4	0.20	1.0335	57.4
283.67	3600	17.65	0.04	76.2	0.19	1.0335	58.0
278.73	5400	17.19	0.03	49.1	0.29	1.0111	38.2
273.12	7200	13.33	0	28.3	0.47	0.9755	22.8
268.51	10800	13.07	0	18.3	0.70	0.9448	15.3
263.50	18000	13.39	0	11.2	1.08	0.9101	9.66
258.42	25200	11.17	0	6.59	1.73	0.8773	5.91
253.47	27480	7.35	0	3.94	2.76	0.8512	3.64

[a] Measured with membrane 1; σ = 6.54 Å.

Table 3. Vapor Pressures of CHP from the Effusion Method[a]

T/K	τ/s	$10^6\Delta m$/kg	p^*_{sat}/Pa	Kn	k	p_{sat}/Pa
293.55	6780	27.60[b]	61.5	0.23	1.0252	47.3
293.56	7200	29.18[b]	61.3	0.23	1.0250	47.1
293.57	3600	14.75[b]	61.9	0.23	1.0256	47.5
289.63	5400	16.10[b]	44.8	0.3	1.0076	35.0
287.63	5400	13.08[b]	36.2	0.37	0.9944	28.7
278.71	14400	15.22[b]	15.6	0.78	0.9353	13.1
273.19	18000	11.27[b]	9.13	1.26	0.8990	8.00
263.63	7200	12.31[c]	3.60	1.33	0.9077	3.13
253.48	10800	6.21[c]	1.19	3.45	0.8438	1.11

[a] The thermostating mass loss, Δm_1, is 0 in each case. [b] Membrane 1. [c] Membrane 2; σ = 6.79 Å.

The vapor pressures and enthalpies of vaporization of the cyclohexyl esters measured in this work by the transpiration method are shown in Table 12. The transpiration method has been used in previous work[11] to derive enthal-

Table 4. Vapor Pressures of CHB from the Effusion Method[a]

T / K	τ / s	$10^6\Delta m$ / kg	p^*_{sat} / Pa	Kn	k	p_{sat} / Pa
310.41	3600	21.49	88.9	0.16	1.0442	67.0
305.24	3800	15.06	58.5	0.23	1.0247	45.0
305.23	3600	14.16	58.1	0.24	1.0243	44.6
305.21	3600	14.25	58.5	0.23	1.0247	44.9
300.19	7200	18.97	38.6	0.34	1.0008	30.4
295.19	7200	12.05	24.3	0.51	0.9697	19.7
290.33	9000	9.82	15.7	0.76	0.9386	13.2
287.95	12600	11.07	12.6	0.90	0.9230	10.8
285.40	12600	9.04	10.2	1.10	0.9090	8.87
282.90	16200	8.73	7.66	1.44	0.8902	6.77
273.17	32400	6.86	2.96	3.40	0.8420	2.77

[a] Measured with membrane 1; $\sigma = 7.02$ Å. The thermostating mass loss, Δm_1, is 0 in each case.

Table 5. Vapor Pressures of CHV from the Effusion Method

T / K	τ / s	$10^6\Delta m$ / kg	$10^6\Delta m_1$ / kg	p^*_{sat} / Pa	Kn	k	p_{sat} / Pa
318.24	3600	13.97[a]	0.15	56.2	0.20	1.0333	42.8
318.18	3600	14.08[a]	0.15	56.1	0.24	1.0227	43.2
318.18	3600	13.97[a]	0.15	56.2	0.24	1.0333	42.8
313.26	5400	14.03[a]	0.14	37.4	0.35	1.0085	28.8
308.35	7210	12.26[a]	0.04	24.3	0.51	0.9730	19.6
303.34	12600	14.21[a]	0.02	16.0	0.74	0.9415	13.3
298.34	18000	12.45[a]	0	9.71	1.15	0.9057	8.44
293.49	14425	46.97[b]	0	6.67	0.71	1.0958	5.47
288.55	5400	11.11[b]	0	4.18	1.10	1.0532	3.57
283.54	11100	13.82[b]	0	2.51	1.69	1.0121	2.23
273.16	21600	8.97[b]	0	0.821	4.68	0.9496	0.777

[a] Membrane 1. [b] Membrane 2; $\sigma = 7.23$ Å.

Table 6. Parameters of the Linear Approximation ln P versus T^{-1}

	Knudsen method		transpiration method	
compd	a	b	a	b
CHF	27.2 ± 0.6	6306 ± 145		
CHA	27.3 ± 0.2	6599 ± 65	26.2 ± 0.3	6321 ± 96
CHP	27.7 ± 0.2	6991 ± 55	26.1 ± 0.2	6570 ± 47
CHB	27.6 ± 0.2	7252 ± 67	26.9 ± 0.3	7060 ± 90
CHV	28.1 ± 0.4	7729 ± 46	26.7 ± 0.3	7382 ± 83

Table 7. Results from Calorimetric Measurements of Enthalpies of Vaporization of CHF[a]

	m / g	T / K	$\int_{\tau=0}^{\tau}\Delta E\,\mathrm{d}\tau$ / mV·s	cell	ΔH / J	$\Delta_l^g H_m^\circ$ / kJ·mol^{-1}
1	0.057 81	303.01	4139.41	A	22.07	48.94
2	0.065 00	302.68	4650.89	A	24.80	48.85
3	0.068 30	303.60	5090.60	B	26.00	48.74
4	0.063 41	304.52	4742.38	B	24.22	48.90
5	0.061 20	303.62	4536.17	B	23.17	48.47
6	0.048 19	303.69	3613.40	B	18.46	49.03

[a] $K_A = 187.52$ mV·s·J^{-1}; $K_B = 195.78$ mV·s·J^{-1}; $\langle\Delta_l^g H_m^\circ(303.52\ \mathrm{K})\rangle = (48.82 \pm 0.21)$ kJ·mol^{-1}.

Table 8. Results from Calorimetric Measurements of Enthalpies of Vaporization of CHA[a]

	m / g	T / K	$\int_{\tau=0}^{\tau}\Delta E\,\mathrm{d}\tau$ / mV·s	cell	ΔH / J	$\Delta_l^g H_m^\circ$ / kJ·mol^{-1}
1	0.064 80	300.19	5159.14	A	23.83	52.29
2	0.072 41	300.36	5774.79	A	26.67	52.38
3	0.060 14	300.46	4799.37	A	22.17	52.41
4	0.064 11	300.17	4843.82	B	23.50	52.12
5	0.069 50	300.30	5255.41	B	25.50	52.17
6	0.063 52	300.40	4786.16	B	23.22	51.98
7	0.067 83	299.45	5370.35	A	24.80	52.00
8	0.071 36	299.51	5374.68	B	26.07	51.96

[a] $K_A = 216.51$ mV·s·J^{-1}; $K_B = 206.13$ mV·s·J^{-1}; $\langle\Delta_l^g H_m^\circ(300.11\ \mathrm{K})\rangle = (52.16 \pm 0.15)$ kJ·mol^{-1}.

Table 9. Results from Calorimetric Measurements of Enthalpies of Vaporization of CHP[a]

	m / g	T / K	$\int_{\tau=0}^{\tau}\Delta E\,\mathrm{d}\tau$ / mV·s	cell	ΔH / J	$\Delta_l^g H_m^\circ$ / kJ·mol^{-1}
1	0.128 09	300.24	8472.84	A	45.73	55.77
2	0.128 64	299.95	8508.29	A	45.92	55.76
3	0.137 10	301.42	9050.31	A	48.84	55.66
4	0.127 77	300.24	8555.26	B	45.64	55.80
5	0.124 25	299.96	8312.65	B	44.34	55.76
6	0.128 94	301.46	8609.12	B	45.93	55.64

[a] $K_A = 185.29$ mV·s·J^{-1}; $K_B = 187.46$ mV·s·J^{-1}; $\langle\Delta_l^g H_m^\circ(300.55\ \mathrm{K})\rangle = (55.73 \pm 0.07)$ kJ·mol^{-1}.

Table 10. Results from Calorimetric Measurements of Enthalpies of Vaporization of CHB[a]

	m / g	T / K	$\int_{\tau=0}^{\tau}\Delta E\,\mathrm{d}\tau$ / mV·s	cell	ΔH / J	$\Delta_l^g H_m^\circ$ / kJ·mol^{-1}
1	0.073 73	315.67	5259.75	A	25.51	58.82
2	0.057 63	315.04	4106.73	A	19.91	58.76
3	0.077 30	315.64	5517.89	A	26.76	58.86
4	0.072 52	315.80	5161.33	B	24.89	58.35
5	0.056 67	315.28	4055.81	B	19.56	58.68
6	0.080 70	315.98	5789.16	B	27.92	58.82

[a] $K_A = 206.22$ mV·s·J^{-1}; $K_B = 207.38$ mV·s·J^{-1}; $\langle\Delta_l^g H_m^\circ(315.57\ \mathrm{K})\rangle = (58.72 \pm 0.20)$ kJ·mol^{-1}.

Table 11. Results from Calorimetric Measurements of Enthalpies of Vaporization of CHV[a]

	m / g	T / K	$\int_{\tau=0}^{\tau}\Delta E\,\mathrm{d}\tau$ / mV·s	cell	ΔH / J	$\Delta_l^g H_m^\circ$ / kJ·mol^{-1}
1	0.096 59	299.15	6206.06	A	33.37	63.66
2	0.075 71	299.71	4856.42	A	26.11	63.56
3	0.076 10	299.18	4873.74	A	26.21	63.46
4	0.072 46	299.76	4701.80	B	24.98	63.53
5	0.079 62	299.18	5180.29	B	27.52	63.70
6	0.077 02	300.28	5009.12	B	26.61	63.68

[a] $K_A = 185.98$ mV·s·J^{-1}; $K_B = 188.22$ mV·s·J^{-1}; $\langle\Delta_l^g H_m^\circ(299.54\ \mathrm{K})\rangle = (63.60 \pm 0.10)$ kJ·mol^{-1}.

pies of vaporization for cyclohexyl acetate and butyrate in the laboratory at the University of Freiburg. To validate those results, we extended the temperature range as well as the saturation conditions of the transpiration experiments with these cyclic esters. The N_2 gas flow range in each experiment was changed in several steps from (0.22 to 0.69) cm^3·s^{-1} in order to check for the saturation of the gas stream with the transported compound. No impact of the gas flow rate was detected within the investigated range. The results obtained in this work were consistent with the results for the vapor pressure measurements published earlier.[11] Thus, Table 12 presents the results of the joint treatment of both data sets of vapor pressures for cyclohexyl acetate and butyrate.

A summary of the enthalpies of vaporization obtained by different methods is presented in Table 13. Inspection of Table 13 reveals that enthalpies of vaporization, $\Delta_l^g H_m^\circ$(298.15 K), directly measured using calorimetry are very consistent with those obtained from vapor pressure measurements by the transpiration method. However, it is also clear that enthalpies of vaporization of the cyclohexyl esters derived from the Knudsen method are consis-

Table 12. Results for the Vapor Pressure p and $\Delta_l^g H_m^\circ$ Obtained by the Transpiration Method

T^a / K	m^b / mg	$V(N_2)^c$ / dm^3	$p_{sat}{}^d$ / Pa	$(p_{exp}-p_{calc})$ / Pa	T^a / K	m^b / mg	$V(N_2)^c$ / dm^3	$p_{sat}{}^d$ / Pa	$(p_{exp}-p_{calc})$ / Pa
CHA; $\Delta_l^g H_m^\circ$(294.05 K) = (52.56 ± 0.80) kJ·mol^{-1} $\ln(p_{sat}/\mathrm{Pa}) = 26.2275 - 6321.532/(T/\mathrm{K})$									
274.1	1.67	1.26	23.1	−0.5	294.3	1.68	0.261	112.1	−3.2
276.1	1.71	1.09	27.3	−0.7	297.4	1.86	0.228	141.7	−2.5
278.4	3.23	1.67	33.8	0.0	298.2	5.75	0.634	158.0	5.3
280.1	1.69	0.750	39.3	0.5	300.4	1.64	0.163	175.5	−2.9
282.2	1.70	0.652	45.3	−0.6	303.1	6.60	0.516	222.9	7.7
283.2	3.76	1.27	51.7	2.1	306.5	2.41	0.163	257.9	−13.2
285.2	2.58	0.783	57.5	−0.6	308.2	6.85	0.384	310.8	7.0
288.2	4.74	1.10	75.1	1.9	309.6	3.54	0.196	315.5	−17.8
291.3	1.73	0.326	92.4	0.0	313.2	7.75	0.316	427.3	5.8
293.1	6.56	1.03	110.5	4.9	318.2	5.56	0.166	583.6	4.8
CHP; $\Delta_l^g H_m^\circ$(293.92 K) = (54.62 ± 0.39) kJ·mol^{-1} $\ln(p_{sat}/\mathrm{Pa}) = 26.075 - 6569.545/(T/\mathrm{K})$									
274.7	0.78	1.47	8.44	−0.2	290.9	0.87	0.412	33.6	0.8
276.7	0.78	1.19	10.4	0.1	301.0	0.78	0.178	69.6	−0.4
278.7	0.77	1.01	12.1	−0.1	292.9	0.87	0.356	38.7	0.4
280.7	0.82	0.898	14.6	0.1	303.0	0.74	0.145	80.7	−0.2
282.8	0.85	0.786	17.2	0.0	294.9	0.80	0.289	44.1	−0.5
284.8	0.81	0.645	19.8	−0.4	305.1	0.99	0.167	94.5	0.6
286.8	0.79	0.512	24.5	0.7	307.1	1.06	0.156	108.1	0.1
288.8	0.86	0.490	27.8	0.0	309.1	0.86	0.111	122.6	−1.4
297.0	0.88	0.267	52.0	−0.2	311.2	1.01	0.112	142.8	−0.4
299.0	1.02	0.267	60.6	0.1	313.2	1.16	0.112	163.5	−0.4
CHB; $\Delta_l^g H_m^\circ$(294.35 K) = (58.70 ± 0.74) kJ·mol^{-1} $\ln(p_{sat}/\mathrm{Pa}) = 26.850 - 7059.958/(T/\mathrm{K})$									
278.0	0.63	2.13	4.31	0.03	296.3	1.15	0.808	20.7	0.1
280.0	1.47	4.11	5.21	0.08	298.2	1.49	0.893	24.3	0.4
282.1	1.87	4.39	6.19	0.00	299.3	0.95	0.527	26.2	0.1
282.1	0.92	2.14	6.21	0.02	302.4	0.92	0.404	33.1	−0.1
284.1	0.94	1.84	7.43	0.04	303.1	2.72	1.10	36.0	0.9
287.2	1.09	1.63	9.68	0.02	305.4	0.79	0.281	40.8	−1.0
288.1	0.97	1.42	9.98	−0.45	308.2	2.20	0.622	51.5	−0.1
290.2	1.21	1.37	12.8	0.4	308.5	0.95	0.264	52.2	−0.5
293.1	1.30	1.26	15.0	−0.8	313.2	2.58	0.495	75.9	1.5
293.2	1.48	1.33	16.1	0.1					
CHV; $\Delta_l^g H_m^\circ$(312.10 K) = (61.38 ± 0.69) kJ·mol^{-1} $\ln(p_{sat}/\mathrm{Pa}) = 26.740 - 7381.731/(T/\mathrm{K})$									
293.2	1.69	4.79	4.74	−0.04	312.2	1.98	1.24	21.3	−0.8
293.2	0.66	1.89	4.70	−0.08	314.2	2.02	1.08	25.0	−0.7
293.2	1.81	4.98	4.87	0.09	315.2	2.40	1.22	26.4	−1.3
296.2	1.75	3.72	6.30	0.13	317.2	1.91	0.812	31.5	−0.6
297.2	1.61	3.25	6.66	−0.05	319.2	2.23	0.785	38.0	0.9
299.2	1.84	2.98	8.28	0.36	320.2	2.12	0.704	40.3	0.4
300.2	1.79	2.71	8.87	0.28	321.2	1.66	0.514	43.3	0.4
302.2	1.86	2.43	10.2	0.1	323.2	2.14	0.595	48.2	−1.2
303.2	1.83	2.19	11.2	0.2	323.2	2.14	0.595	48.2	−1.2
305.2	1.84	1.89	13.0	0.2	326.2	2.07	0.460	60.1	−0.9
306.2	1.96	1.84	14.3	0.4	326.2	2.07	0.460	60.1	−0.9
308.2	1.92	1.62	15.8	−0.4	329.2	1.90	0.325	78.3	3.3
308.2	1.87	1.62	15.4	−0.8	329.2	1.90	0.325	78.3	3.3
308.2	1.95	1.65	15.8	−0.5	332.2	1.89	0.271	93.6	1.8
309.2	2.60	1.95	17.9	0.3	332.2	1.89	0.271	93.6	1.8
311.2	2.15	1.43	20.0	−0.5					

[a] Temperature of saturation. N_2 gas flow 0.22−0.69 cm^3·s^{-1}. [b] Mass of transferred sample condensed at $T = 243$ K. [c] Volume of nitrogen used to transfer mass m of sample. [d] Vapor pressure at temperature T calculated from m and the residual vapor pressure at $T = 243$ K.

tently higher than those from calorimetry and transpiration.

The most probable reason for this disagreement is a violation of isotropy for the gas that is close to the effusion orifice.[12] The equation for the orifice transmission probability k was derived according to the theoretical analysis:[12]

$$k = 2(C + DA) + G\left(1 + \frac{B/3 - AD}{0.5 - C}\right) \qquad (7)$$

where A is a function that describes the violation of isotropy of a gas from the vacuum opening. This value is calculated with

$$A = \frac{1}{\lambda}\int_l^\infty \left(1 - \frac{L}{(L^2 + r^2)^{1/2}}\right) \exp\left(-\frac{L}{\lambda}\right) \mathrm{d}L \qquad (8)$$

where l is the membrane thickness, λ is the length of the free path of a molecule, and r is the radius of the orifice.

B is also a function that describes the violation of isotropy of a gas, but from the side of the sample. This value is calculated from an equation that is similar to eq 8 with the lower integration limit equal to zero.

Table 13. Comparison of the Results from Knudsen, Transpiration, and Calorimetric Determinations of Enthalpies of Vaporization of Cyclohexyl Esters

compd	source[b]	$\langle T\rangle$ K	$\Delta_l^g H°(\langle T\rangle)$ kJ·mol^{-1}	$\Delta_l^g H°$ [a] kJ·mol^{-1}	$\langle\Delta_l^g S°\rangle$[a] J·K^{-1}·mol^{-1}
CHF	eme	257.95	54.92 ± 1.3	52.03 ± 1.3	
	cme	257.95	52.43 ± 1.2	49.54 ± 1.2	
	tr				
	cal	303.52	48.82 ± 0.21	49.27 ± 0.21	
	aw			49.28 ± 0.21	120.0 ± 5.0
CHA	eme	268.57	58.79 ± 0.51	56.47 ± 0.51	
	cme	268.57	54.87 ± 0.54	52.55 ± 0.54	
	tr	294.1	52.56 ± 0.80	52.25 ± 0.80	
	cal	300.11	52.16 ± 0.15	52.32 ± 0.15	
	aw			52.33 ± 0.14	122.5 ± 1.4
CHP	eme	273.53	61.12 ± 0.84	59.40 ± 0.84	
	cme	273.53	58.13 ± 0.45	56.41 ± 0.45	
	tr	293.9	54.62 ± 0.39	54.32 ± 0.39	
	cal	300.55	55.73 ± 0.07	55.90 ± 0.07	
	aw			55.86 ± 0.07	124.5 ± 1.2
CHB	eme	291.80	64.57 ± 0.60	64.11 ± 0.60	
	cme	291.80	60.30 ± 0.56	59.84 ± 0.56	
	tr	294.4	58.70 ± 0.74	58.42 ± 0.74	
	cal	315.57	58.72 ± 0.20	60.13 ± 0.20	
	aw			60.00 ± 0.19	130.5 ± 1.4
CHV	eme	293.21	67.52 ± 0.82	67.17 ± 0.82	
	cme	293.21	64.27 ± 0.38	63.92 ± 0.38	
	tr	312.1	61.38 ± 0.69	62.38 ± 0.69	
	cal	299.54	63.60 ± 0.10	63.72 ± 0.10	
	aw			63.71 ± 0.10	132.2 ± 2.0

[a] At 298.15 K. [b] eme, effective mass effusion; cme, corrected mass effusion; tr, transpiration; cal, calorimetry; aw, average weighed.

Coefficients C and D depend on the orifice parameters (radius r and membrane thickness l) and are calculated from

$$C = \int_0^{\pi/2} \cos(x)\sin(x) R(P)\,\mathrm{d}x \tag{9}$$

$$D = \int_0^{\pi/2} \cos^2(x)\sin(x) R(P)\,\mathrm{d}x \tag{10}$$

G is the contribution to the gas flow of molecules, that leave the orifice only after collisions with walls of the cell

$$G = \int_0^f 2\cos(x)\sin(x)\left(\frac{2}{\pi}\alpha(\arcsin(P) + P\sqrt{1-P^2}) + \frac{4}{3\pi}(1-2\alpha)\frac{(1-(\sqrt{1-P^2})^3)}{3}\right)\mathrm{d}x + \int_f^{\pi/2} 2\cos(x)\sin(x)\left(\alpha + \frac{4(1-2\alpha)}{2\pi P}\right)\mathrm{d}x \tag{11}$$

where $R(P)$ is a function which takes into account scaling down of the area of an orifice at the angle θ because the membrane thickness differs from zero. It is calculated from

$$R(P) = \frac{2}{\pi}(\arccos(P) - P\sqrt{1-P^2}) \quad \text{for} \quad P \le 1 \tag{12}$$

$$R(P) = 0 \quad \text{for} \quad P > 1$$

The p value can be obtained from

$$P = \frac{l\tan(x)}{d} \tag{13}$$

where l is the membrane thickness and d is the diameter of an orifice.

Parameter α in eq 11 characterizes the membrane itself and is calculated according to the Clausing[9] theory

$$\alpha = \frac{\sqrt{l^2 + 4r^2} - l}{2r + \dfrac{4r^2}{\sqrt{l^2 + 4r^2}}} \tag{14}$$

The values of C, D, and G depend only on the parameters of the membrane. They can be calculated for each membrane and then used as constants. An iterative procedure was applied for correction of the vapor pressures. The experimental value of the effective vapor pressure was used as an initial approximation.

Let us consider as an example the point at temperature 273.16 K for CHF. The total mass loss was 0.01738 g. The exposition time was 3600 s. The parameters of the membrane used were $d = 1.833 \times 10^{-4}$ m and $l = 5 \times 10^{-5}$ m. The integrals were evaluated with the Mathematica 4.1 package to be $C = 0.291\,664$, $D = 0.226\,791$, and $G = 0.203\,919$, the Clausing transmission probability k was 0.7857. The following steps were performed.

1. The effective vapor pressure was calculated (without taking into account the violation of isotropy of a gas).

$$p^*_{\mathrm{sat}} = \frac{1.738 \times 10^{-5}}{(0.7857159)(3.1416)(9.165 \times 10^{-5})^2(3600)} \times \sqrt{\frac{(2)(3.1416)(8.31447)(273.16)}{0.128}} = 77.72\ \text{Pa} \tag{15}$$

2. The value of p^* was used to calculate the mean free path of a CHF molecule

$$\lambda = \frac{kT}{\sqrt{2}\pi\sigma^2 p_{\mathrm{sat}}} \tag{16}$$

where σ is the effective molecular diameter (collision diameter). This parameter was calculated from

$$\sigma = \sqrt[3]{\frac{3V}{4\pi}} \tag{17}$$

V is the volume of the molecule calculated from its geometry with the help of the force field calculation method MM3.[13] The diameter of the molecule was calculated from its van der Waals volume, assuming that a molecule has a spherical form. For CHF, σ was estimated to be 6.277 Å (6.277×10^{-10} m). Inserting this value in eq 16 gave

$$\lambda = \frac{(1.38 \times 10^{-23})(273.16)}{\sqrt{2}(3.1416)(6.277 \times 10^{-10})^2(77.72)} = 2.77 \times 10^{-5}\ \text{m} \tag{18}$$

3. The value of λ was used for calculation of the integrals A and B in eq 8. After the integration, the values $A = 0.5020$ and $B = 0.742\,827$ were obtained. The transmission probability k was then calculated with eq 7

$$k = 2[0.291664 + (0.226791)(0.4239)] + 0.203919\left(1 + \frac{\dfrac{0.742827}{3} - (0.4239)(0.226791)}{0.5 - 0.291664}\right) \tag{19}$$

$$k = 1.14586 \tag{20}$$

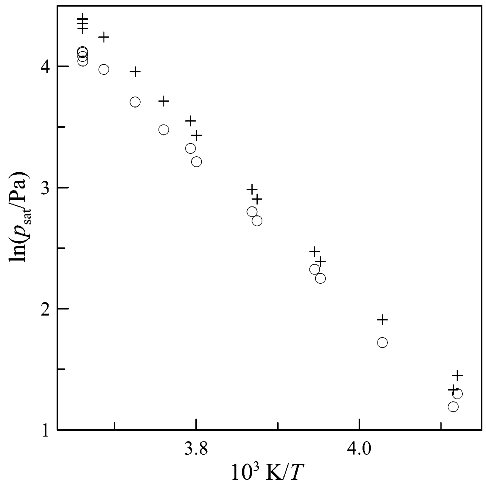

Figure 2. Temperature dependence of vapor pressures of CHF: +, effective values of p^*_{sat} obtained by the Knudsen method; ○, corrected values of p_{sat} obtained by the Knudsen method.

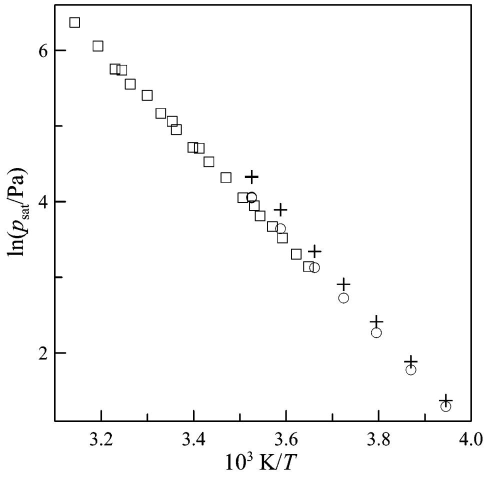

Figure 3. Temperature dependence of vapor pressures of CHA: +, effective values of p^*_{sat} obtained by the Knudsen method; ○, corrected values of p_{sat} obtained by the Knudsen method; □, results from the transpiration method.

4. The corrected value of the vapor pressure was calculated using the above transmission probability k

$$p^*_{sat} = \frac{1.738 \times 10^{-5}}{(1.14586)(3.1416)(9.165 \times 10^{-5})^2(3600)} \times \sqrt{\frac{2(3.1416)(8.31447)(273.16)}{0.128}} = 53.29 \text{ Pa} \quad (21)$$

Then, this value of vapor pressure was used in step 2 to compute the mean free path of the molecule and the coefficient of transmission probability. The iterative procedure was stopped when the values of the pressure in consecutive iterations differed by less than 0.001%. The transmission probabilities are shown in Tables 1−5. Now, as shown in Figures 2−6, the values of vapor pressures obtained from the Knudsen method that were corrected by the aforementioned procedure are in satisfactory agreement with the data obtained by the transpiration method. For CHA, CHP, and CHB the results of both methods agree within the common uncertainty of both methods when the ratio (known as the Knudsen number) of the mean free path of the molecule to the orifice diameter is >0.5, which can be considered as the lower threshold of the proposed effusion technique. For CHV the Knudsen data are (7 to 20)% higher than those from the transpiration method.

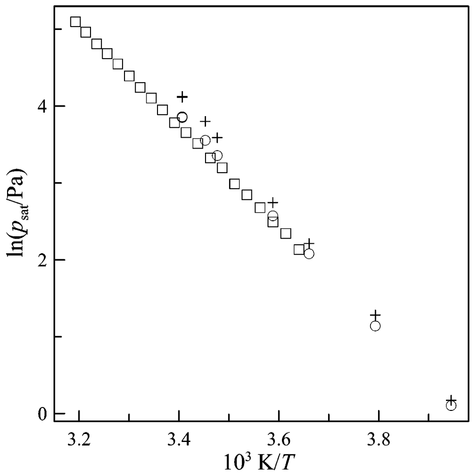

Figure 4. Temperature dependence of vapor pressures of CHP: +, effective values of p^*_{sat} obtained by the Knudsen method; ○, corrected values of p_{sat} obtained by the Knudsen method; □, results from the transpiration method.

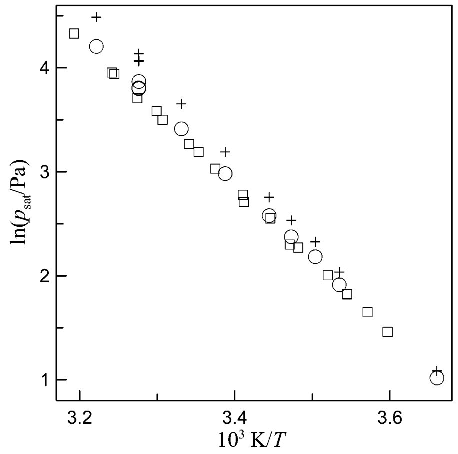

Figure 5. Temperature dependence of vapor pressures of CHB: +, effective values of p^*_{sat} obtained by the Knudsen method; ○, corrected values of p_{sat} obtained by the Knudsen method; □, results from the transpiration method.

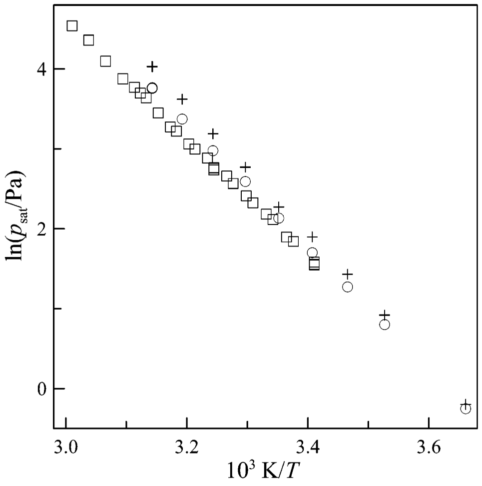

Figure 6. Temperature dependence of vapor pressures of CHV: +, effective values of p^*_{sat} obtained by the Knudsen method; ○, corrected values of p_{sat} obtained by the Knudsen method; □, results from the transpiration method.

The corrected values of vapor pressure from the Knudsen method were fitted by eq 3, and the coefficients *a* and *b* are given in Table 6. These coefficients were used to calculate the values of enthalpies and standard entropies of vaporization of the cyclohexyl esters. A good agreement of the enthalpies of vaporization obtained by three different methods is shown in Table 13, and this fact confirms the reliability of the experimental and calculation procedures applied in this work.

As one can see from these results, the failure of isotropy plays a significant role in the calculation of the vapor pressure from effusion rate data. This phenomenon must be considered[12] when the Knudsen number is <10. The proposed computational procedure allows us to extend the effusion method to the Knudsen number (0.45 to 0.50).

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