Thermodynamics of the Sublimation and of the Vaporization of ε-Caprolactam

Dzmitry H. Zaitsau, Yauheni U. Paulechka, Gennady J. Kabo,* and Aleh N. Kolpikau

Chemistry Department, Belarusian State University, Leningradskaya 14, Minsk 220050, Belarus

Vladimir N. Emel'yanenko,[†] Andreas Heintz, and Sergey P. Verevkin*

Institute of Physical Chemistry, University of Rostock, Hermannstrasse 14, 18055 Rostock, Germany

The vapor pressure for crystalline ε-caprolactam (CAS Registry No. 105602) was measured by the Knudsen method in the temperature range (293 to 338) K with a modified effusion cell with enlarged sublimation surface and by the transpiration method between $T = (302 \text{ and } 339)$ K. The latter method was also used to measure the vapor pressures of the liquid phase between $T = (345 \text{ and } 373)$ K. The thermodynamic parameters of sublimation and of vaporization and the standard entropy of caprolactam in the ideal gas state were estimated from the obtained data. Calculations of the thermodynamic properties of caprolactam in the ideal gas state were carried out based on the molecular data and the results obtained by DFT (B3LYP/6-311G*) quantum-mechanical calculations. The experimental and calculated values of the entropy of gaseous caprolactam agree with each other within 0.2 % at 298 K.

Introduction

ε-Caprolactam is widely used for the manufacture of the polymer Capron. The common way to synthesize caprolactam from benzene[1] is accompanied by the production of a vast amount of byproducts and requires too much energy and chemical materials at the stages of cyclohexane oxidation, cyclohexanone oxime isomerization, and caprolactam extraction.

Recently some attempts have been made to develop new ways of synthesis of caprolactam with cyclohexanone oxime isomerization in the gaseous phase[2] or in ionic liquids.[3] A comprehensive study of thermodynamic properties of the substances used in the synthesis is required for further improvements of the production technology.

Previous investigation of the thermodynamic properties of caprolactam in the condensed and in the gaseous states were performed.[4] It was found that the enthalpy of sublimation of caprolactam obtained from effusion measurements is 2.5 kJ·mol⁻¹ higher than the value obtained by calorimetry. Such discrepancy is about 2 times lager than the combined uncertainty of these methods. Our recent findings[5] have revealed that the isotropy failure phenomenon should be taken into account in order to get reliable values of vapor pressure and enthalpy of sublimation from the results of effusion method. For this reason, we decided to repeat vapor pressure measurements on crystalline caprolactam using the effusion method. Additionally, the temperature dependence of the vapor pressure of both crystalline and liquid caprolactam has been studied by using the transpiration method. Results obtained by two different methods have found to be in close agreement. Because the value of $S°(\mathrm{g})$ obtained with the help of the new derived data for p_sat and $\Delta_\mathrm{sub}H$ differs from that published in ref 4, thermodynamic properties of caprolactam have been re-evaluated using methods of statistical thermodynamics.

Experimental Section

For the effusion experiments, an industrial sample of ε-caprolactam (Grodno Azot) with an initial mass fraction purity of 0.999 was used. It was purified by sublimation at $T = 338$ K and $p = 0.3$ kPa. GC purity determination with FID (flame-ionization detector) shows the absence of impurities in the sample. For GC determination, the capillary column of 30 m length and 0.3 mm diameter with stationary phase RTX-1 was used. The temperature program of the GC was $T = 323$ K, followed by a heating rate of 0.1 K·s⁻¹ to $T = 573$ K. Injector and detector were heated to 523 K.

For determination of the vapor pressure using the transpiration method, a solid sample of caprolactam of commercial origin (Aldrich) was purified by repeated sublimation in a vacuum. Examination of the sample using GC showed no discernible amounts of impurities. The sample was analyzed with a Hewlett-Packard gas chromatograph 5890 series II equipped with a flame ionization detector and Hewlett-Packard 3390A integrator. Carrier gas (nitrogen) flow was 12.1 cm³·s⁻¹. Capillary column HP-5 (stationary phase cross-linked 5 % PH ME silicone); column length, inside diameter, and film thickness 25 m × 0.32 mm × 0.25 μm. The temperature program of the GC was $T = 373$ K, followed by a heating rate of 0.167 K·s⁻¹ to $T = 523$ K.

The IR spectrum of caprolactam in the crystalline state (tablets with KBr) in the range of (4000 to 400) cm⁻¹ was recorded on a Specord-IR 15 spectrometer. The Raman spectrum of powder-like caprolactam was recorded by a Ramanor-U 1000 spectrometer with argon laser ($\lambda_\mathrm{B} = 514.5$ nm) in the range of (4000 to 50) cm⁻¹.

The vapor pressures (p_sat) of ε-caprolactam in the temperature range of (293 to 338) K were determined by the integral Knudsen effusion method. The detailed description of the

* Corresponding authors. Contact G.J.K. for results from the Knudsen method and thermodynamic calculations (fax: +375-17-2003916; e-mail: kabo@bsu.by). Contact S.P.V. for results from the transpiration method (e-mail: sergey.verevkin@uni-rostock.de).
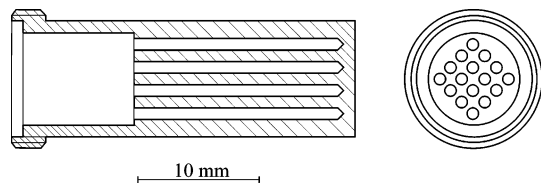† On leave from the Mogilev State University of Food Stuff.

Figure 1. Scheme of the modified cell for the effusion measurements of saturated vapor pressures of solid samples. Left panel is the sectional view. Right panel is the view from above.

apparatus and technique was given earlier.[5] During the effusion measurements, it is crucial to provide a sufficient thermal contact between the sample (solid or liquid) and the internal surface of the Knudsen cell. To improve the thermal contact, a new effusion cell enabling an enlarged contact between the surface of the solid sample and the walls of the cell was used (Figure 1). The cylindrical container of 27 mm length and 10 mm i.d. was made of stainless steel. Sixteen canals (1 mm diameter and 17 mm length) were drilled in the base of the cell. Before the measurements, a thin layer of the substance was spread all over the inner walls of the cell and then pressed against them. Thus, the sublimation surface (this term is used by analogy with the term "evaporation surface") was nearly equal to the inner surface area of the cell. Capillary effects were found to have a negligible influence on the vapor pressure. The cell construction and the loading procedure made it possible to get a 10-fold increase in the sublimation surface in comparison with our previous chamber-type effusion cell.[5] The efficiency of the modified cell for the vapor pressure determination was described earlier.[6] Using benzoic acid, it was shown that the higher values of the vapor pressure were obtained with the modified effusion cell when compared to the hollow cylinder cell. The combined uncertainty of the vapor pressure determination by the Knudsen method was estimated to be ± 5 %.

In the effusion measurements, nickel membranes with the following parameters were used: thickness $l = (50 \pm 1)$ μm and average orifice diameter $d = (0.1833 \pm 0.0004)$ mm; $l = (84 \pm 1)$ μm and $d = (0.4467 \pm 0.0005)$ mm; $l = (50 \pm 1)$ μm and $d = (0.8370 \pm 0.0005)$ mm.

The vapor pressures were calculated using the following equation:

$$p = \frac{\Delta m}{k S_{\text{orif}} \tau} \sqrt{\frac{2\pi RT}{M}} \qquad (1)$$

where p is vapor pressure inside the effusion cell; Δm is mass loss of the sample during the exposition time τ in a vacuum; S_{orif} is the cross-section area of the orifice; T is the temperature of the heat carrier in the thermostat; M is the molar mass of the compound in the vapor phase; $R = 8.31447$ J·mol^{-1}·K^{-1}; and k is the transmission probability coefficient.

The coefficient k was determined according to Wahlbeck's theory.[7] This theory considers the failure of isotropy of a gas near the orifice inside the effusion cell for Knudsen numbers < 10. In terms of this theory, the transmission probability ($k = k_{\text{W}}$) depends on the membrane parameters l and d as well as on the mean free path of molecules (λ), the latter being calculated from the expression:

$$\lambda = \frac{k_{\text{B}} T}{\pi \sigma^2 p \sqrt{2}} \qquad (2)$$

where k_{B} is the Boltzmann's constant; σ is the effective diameter of the molecule (the so-called collision diameter). The effective diameter of caprolactam ($\sigma = 0.578$ nm) was calculated from

Table 1. Saturated Vapor Pressure (p_{sat}) over Crystalline Caprolactam ($M = 0.11316$ kg·mol^{-1}, $\sigma = 0.578$ nm, $R = 8.31447$ J·K^{-1}·mol^{-1}, $\alpha\gamma = 0.0066$) Determined by the Knudsen Method

T	τ	Δm	d_{orifice}			p^c	$p_{\text{sat}}{}^d$
K	s	mg	mm	$k_{\text{W}}{}^a$	Kn^b	Pa	Pa
293.43	21600	3.95	0.8370	0.9657	12.4	0.127	0.153
298.39	21600	7.15	0.8370	0.9811	7.0	0.228	0.275
303.32	16320	9.41	0.8370	1.0033	4.2	0.391	0.474
308.31	10800	10.87	0.8370	1.0354	2.5	0.667	0.813
308.38	21600	6.37	0.4467	0.8708	7.9	0.815	0.858
313.22	21600	10.74	0.4467	0.8863	4.8	1.36	1.43
318.09	14463	11.97	0.4467	0.9078	3.0	2.23	2.35
322.98	9000	12.77	0.4467	0.9381	1.8	3.72	3.93
323.06	21600	4.60	0.1833	0.8302	4.4	3.76	3.79
327.93	7200	16.97	0.4467	0.9738	1.1	6.00	6.36
328.00	21600	7.52	0.1833	0.8498	2.8	6.04	6.10
332.89	7203	4.23	0.1833	0.8772	1.7	9.95	10.0
332.93	3600	14.44	0.4467	1.0162	0.7	9.86	10.5
337.82	5400	5.02	0.1833	0.9064	1.1	15.4	15.5

^{a} Transmission probability factor calculated according to Wahlbeck's theory.[5] ^{b} Kn is the Knudsen number, the ratio of the mean free path and the orifice diameter. ^{c} Corrected according to the isotropy failure theory[5] using eq 2. ^{d} Corrected with respect to the isotropy failure theory[5] and the condensation coefficient.

the contact-reentrant volume of the molecule. The contract-reentrant volume was calculated using the Tinker 4.0 package[8] according to the geometry of the molecule obtained from quantum-mechanical calculations and using the van der Waals radii of atoms from ref 9. Besides the isotropy failure, the under-saturation of the vapors may occur during the effusion process[10] in the case of condensation coefficient of the sample α < 1. Equation 1 is used for the description of the effusion process through a small orifice. For the free sublimation process from the surface process, one should use Langmuir's equation:[10]

$$(p_{\text{sat}} - p) = \frac{\Delta m}{\alpha\gamma S_{\text{samp}} \tau} \sqrt{\frac{2\pi RT}{M}} \qquad (3)$$

where ($p_{\text{sat}} - p$) is the deviation of the vapor pressure inside the cell from the equilibrium value (undersaturation); $\alpha\gamma$ is the product of the condensation coefficient (Langmuir) and the coefficient characterizing the roughness of sample surface (the determination of each of these values separately is impossible); S_{samp} is the geometric surface area of the sample.

Since the combined process proceeds under steady conditions, the mass flow from the surface and the mass flow through the orifice are equal. In these conditions, the following equation can be derived:

$$(p_{\text{sat}} - p)\alpha\gamma S_{\text{samp}} = p k_{\text{W}} S_{\text{orif}} \qquad (4)$$

To calculate the saturated vapor pressure, one should use eq 4 in the following form:

$$p_{\text{sat}} = p \frac{\alpha\gamma S_{\text{samp}} + k_{\text{W}} S_{\text{orif}}}{\alpha\gamma S_{\text{samp}}} \qquad (5)$$

To obtain the p_{sat} value, the determination of vapor pressures was carried out with the use of three membranes with different geometrical parameters presented in Table 1. The values of $\alpha\gamma$, A, and B were estimated by a least-squares fitting of the function $\sum_i (p_{\text{exp},i}(\alpha\gamma,T) - A + B/T_i)^2$ where A and B are the coefficients of the Clausius–Clapeyron equation $\ln(p) = A - B/T$ presented in the first line of Table 3, the $\alpha\gamma$ product is given in the header of Table 1. In many cases, the corrections for isotropy failure and undersaturation can counterbalance each other. Therefore,

Table 2. Saturated Vapor Pressure (p_{sat}) over Crystalline and Liquid Caprolactam ($M = 0.11316$ kg·mol^{-1}, $R = 8.31447$ J·K^{-1}·mol^{-1}) Determined by the Transpiration Method

T^a	m^b	$V_{(N2)}^c$	p^d	T^a	m^b	$V_{(N2)}^c$	p^d
K	mg	dm^3	Pa	K	mg	dm^3	Pa
		Crystalline Sample					
302.3	0.92	47.29	0.43	323.9	0.68	3.52	4.27
305.4	1.27	42.43	0.66	326.3	0.97	3.79	5.68
306.2	1.39	43.97	0.70	328.3	0.70	2.32	6.68
309.2	0.95	22.94	0.93	330.2	0.90	2.47	8.01
312.2	0.69	12.10	1.27	333.2	0.96	1.98	10.64
314.7	1.00	12.63	1.75	336.3	0.91	1.41	14.22
316.7	0.62	6.56	2.10	337.4	1.50	1.93	17.27
321.1	0.65	4.38	3.27	339.0	1.00	1.20	18.33
321.3	1.33	8.07	3.65				
		Liquid Sample					
345.2	1.32	0.911	31.9	360.2	1.91	0.473	89.0
345.8	1.11	0.765	32.2	362.1	1.57	0.348	99.2
347.8	1.27	0.756	37.6	363.1	1.50	0.321	103.0
350.9	1.28	0.616	45.7	364.9	1.88	0.348	118.9
353.9	1.23	0.488	56.4	366.3	1.90	0.323	129.4
355.4	1.19	0.429	61.2	369.7	2.33	0.321	160.0
357.0	1.24	0.390	71.0	372.2	2.74	0.323	186.6
359.1	1.20	0.348	75.8				

^{a} Temperature of saturation. N2 gas flow (1.5 to 4.5) dm^3·h^{-1}. ^{b} Mass of transferred sample. Condensed at $T = 243$ K. ^{c} Volume of nitrogen used to transfer the mass m of sample. ^{d} Vapor pressure at temperature T, calculated from m and from the residual vapor pressure at $T = 243$ K.

the neglect of these two corrections may give the results close to those of other methods of vapor pressure determination.
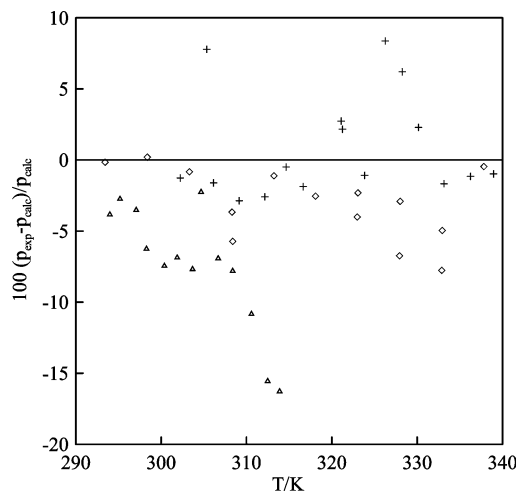
Vapor pressures over crystalline and liquid caprolactam were additionally determined by using the method of transference in a saturated N$_2$-stream. The method was described before[11,12] and gave results that were in excellent agreement with other established techniques for determining vapor pressures of pure substances and enthalpies of vaporization from the temperature dependence of the vapor pressure. About 0.5 g of the 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 ($\pm$ 0.1 K), and the transported amount of material was condensed in a cooled trap. The mass of condensed product was determined by GC analysis using an external standard (hydrocarbons). Assuming that Dalton's law of partial pressures of ideal gaseous mixtures applied to the saturated nitrogen stream was valid, values of the vapor pressure p were calculated according to

$$p = mRT_a/V(N_2)M \tag{6}$$

where $R = 8.31447$ J·K^{-1}·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 the flow rate and time measurements. The vapor pressure p at each saturation temperature was calculated from the mass of sample collected within a definite time period according to eq 6.

Figure 2. Deviation of the experimental vapor pressure data for crystalline caprolactam from the values predicted by eq 7: +, transpiration method data; ◇, effusion method data; △, data from ref 13.

Results

The results of the vapor pressure determination by the Knudsen and transpiration methods are listed in Tables 1 and 2, respectively. The transpiration method results for crystalline caprolactam are (2 to 6) % higher than those obtained by the Knudsen method, but the deviation lies within the combined uncertainty of these two methods (Figure 2). The parameters of the Clausius−Clapeyron equation obtained with the separate treatment of the results obtained from both experimental methods are shown in Table 3.

The vapor pressures of crystalline caprolactam were determined earlier by Aihara[13] and the vapor pressures of the liquid phase were determined by several authors[14−19] (Figure 3). The results reported by Aihara[13] agree well with the those of the present investigation for temperatures below 300 K; however, at higher temperatures the deviations of those results from the presently obtained ones increase up to 15 %.

An analysis of the vapor pressure results for liquid caprolactam was performed by Steele et al.[14] Therefore, a regression analysis using the vapor pressures obtained in this work and the ones reported by other authors[14,19] together with the enthalpies of sublimation[4] from calorimetry for caprolactam was performed. The experimental data used for liquid caprolactam were limited by the temperature 552 K because caprolactam began to decompose above this temperature, as observed by Steele et al.[14]

The Clarke and Glew equation was used for the approximation:[20]

$$\ln(p_{sat}/p°) = A/\theta + B[(1/\theta) - (1/T)] + C[(\theta/T) - 1 + \ln(T/\theta)] + D[(\theta/2)][(T/\theta) - (\theta/T) - 2\ln(T/\theta)]] \tag{7}$$

where θ is the reference temperature and $p°$ is the reference pressure ($p° = 1$ Pa). For vapor pressures below 100 Pa, the

Table 3. Parameters of the Clausius−Clapeyron and of Clarke and Glew Equations for the Temperature Dependence of both Crystalline and Liquid Vapor Pressures of ε-Caprolactam

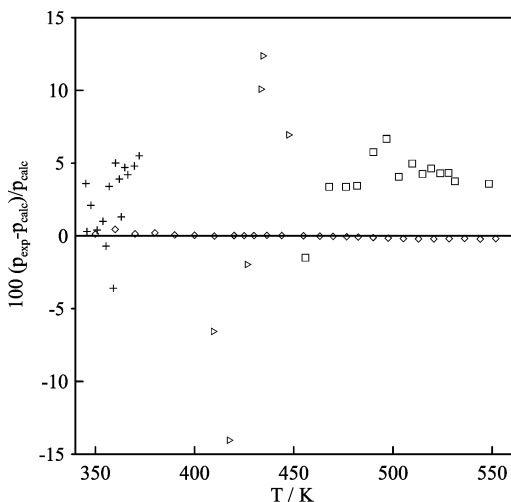| method (phase)	A	B	C	D	temp range	equation type
			Experimental Data Treatment			
Knudsen	33.46 ± 0.30	10372 ± 96			293−338 K	$\ln(p/Pa) = A - B/T$
transpiration	33.76 ± 0.25	10451 ± 80			302−339 K	
			Vapor Pressure Data Regression Parameters			
crystal	349 ± 4	10448 ± 66	−3.476		293−342.31K	Clarke and Glew[20]
liquid	3761.1 ± 0.1	5299 ± 126	−18.9 ± 0.6	0.0113 ± 0.0006	342.31−552K	

Figure 3. Deviation of the experimental vapor pressure data for liquid caprolactam from the values predicted by eq 7: +, transpiration method data; ◇, data from ref 14; □, data from ref 19; open triangle pointing right, data from ref 18. The data from refs 15−17 are not presented because of their enormous deviation from the most reliable results.

coefficients *A*, *B*, *C*, and *D* correspond to $-\Delta^{g}_{cond} G^{\circ}_{m}(\theta)/R$, $\Delta^{g}_{cond} H^{\circ}_{m}(\theta)/R$, $\Delta^{g}_{cond} C^{\circ}_{p,m}(\theta)/R$, and $((d[\Delta^{g}_{cond} C^{\circ}_{p,m}(\theta)])/dT)/R$, respectively.

For higher pressures, the determination of the thermodynamic parameters is complicated by the influence of the different compressibility factors of gas and liquid.

The average temperatures of the measurements $\theta = 320$ K, for crystal phase measurements, and $\theta = 442$ K, for liquid-phase measurements, were chosen as reference temperatures. The statistical weight for the data was chosen so that the deviation between the experimental and calculated values did not exceed the uncertainty of the experimental determination. The extra requirement of $p_{sat}(cr, T_{tr}) = p_{sat}(liq, T_{tr})$ with the statistical weight corresponding to the error of temperature determination of 0.1 K was introduced. For crystalline caprolactam only the *A* and *B* coefficients of eq 7 were estimated. The third coefficient (*C*) is the difference between the calculated value of heat capacity of caprolactam in the ideal gas state and the experimental one for the crystal[4] at 320 K divided by *R*. The heat capacity difference is -28.9 J·K^{-1}·mol^{-1}. The vapor pressure data for liquid caprolactam were approximated by eq 7 using all four parameters. The results are summarized in Table 3. The deviation of the experimental values from the calculated ones is presented in Figures 2 and 3.

The entropy of sublimation for caprolactam $\Delta^{g}_{cr} S^{\circ}_{m}$ (298.15K) = (186.9 ± 1.6) J·K^{-1}·mol^{-1} was calculated on the basis of the results of the joint regression of thermodynamic parameters of sublimation process (Table 3, line 3). This value and the entropy of crystalline caprolactam S°_{m} (298.15K, cr) = (173.2 ± 0.5) J·K^{-1}·mol^{-1} obtained by adiabatic calorimetry[4] were used for the calculation of the entropy of caprolactam in the ideal gas state: S°_{m} (298.15K, ideal gas) = (360.1 ± 1.7) J·K^{-1}·mol^{-1}.

'chair'

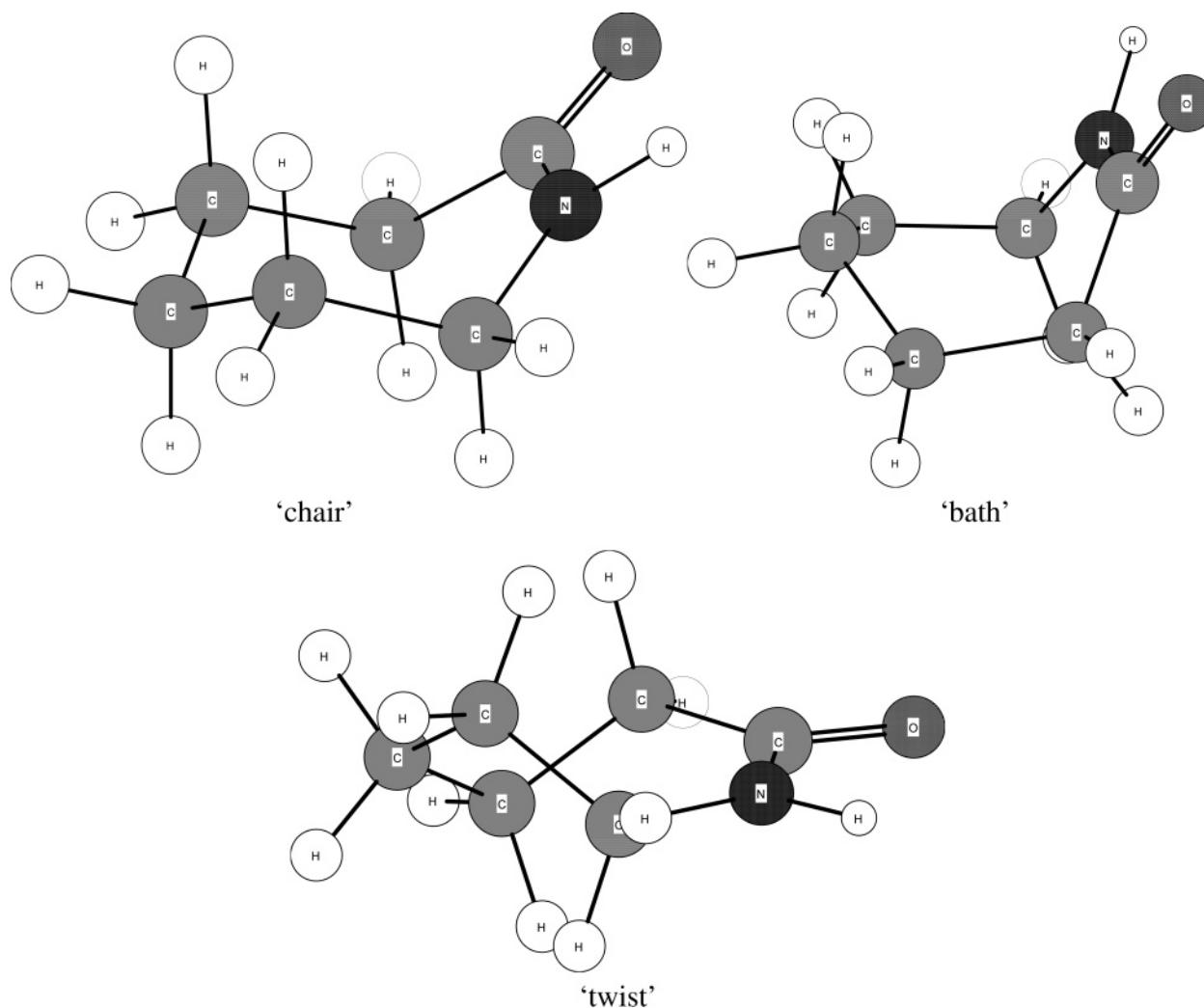'bath'

'twist'

Figure 4. Conformers of ϵ-caprolactam.

Table 4. Product of the Principal Moments of Inertia and the Differences in Thermodynamic Properties of the Conformers of ε-Caprolactam

conformer	$10^{134}\,\mathrm{kg^3 \cdot m^6}$ $I_A I_B I_C$	$\Delta E^\circ_{tot,0}$ $\mathrm{kJ \cdot mol^{-1}}$	ΔH°_0 $\mathrm{kJ \cdot mol^{-1}}$	ΔH°_{298} $\mathrm{kJ \cdot mol^{-1}}$	ΔG°_{298} $\mathrm{kJ \cdot mol^{-1}}$
chair	7.804	0	0	0	0
twist	7.684	15.7	16.2	16.3	15.7
boat	6.895	15.4	16.3	16.3	15.7

Theory

The caprolactam molecule is conformationally non-rigid. Therefore, it is necessary to estimate the number of the conformers of caprolactam and their relative energies in order to perform adequate calculations by statistical thermodynamics.

The search of the conformers of caprolactam was carried out in terms of the density functional theory at the B3LYP/6-311G* level.[21,22] It was found that this molecule has three conformers (Figure 4) each existing in *R*- and *S*-configurations. The 'chair' conformer is about 15 kJ·mol⁻¹ lower in energy than the 'twist' and the 'bath' conformers (Table 4). The relatively high energies of the latter conformers when compared to 'chair' were confirmed in previous works,[23,24] where the presence of only one conformer in CCl₄ solution at $T < 300$ K was found by the NMR method.

On the basis of the present calculations, the C−N(H)−C(=O)−C fragment was found to remain plane in all the conformers. So, the conformers of caprolactam are analogous to those of cycloheptene but not to those of cycloheptanone as was stated in ref 4.

The products of the principal moments of inertia ($I_A I_B I_C$) for the conformers are shown in Table 4. The $I_A I_B I_C$ value for the 'chair' conformer is about 8 % higher than that estimated in ref 4 on the basis of the results of the crystallographic study.[25] The $I_A I_B I_C$ values calculated here quantum-mechanically using the PC GAMESS 6.4 package[26] were used for statistical thermodynamics calculations.

The complete set of fundamentals for the 'chair' conformer was determined using the results of quantum-mechanical calculations (B3LYP/6-311G*), IR, and Raman spectra for crystalline caprolactam and IR spectrum for vapor state[27] and for solution in CCl₄.[28] The correspondence between the experimental and the calculated values of fundamentals was found with the use of calculated and observed intensities of the absorption Raman and IR bands. While compiling the complete set of the fundamentals, the experimental values of the frequencies of normal modes were favored (Table 5).

Vibrational frequencies calculated quantum-mechanically are usually higher than the experimental ones. To find the vibrational frequencies invisible in the experimental spectra and to correct the calculated spectra for the 'bath' and the 'twist' conformers, the values of scaling factors $\chi = \varpi_{exp}/\varpi_{calc}$ were estimated. The following equations were used:

$$\chi = (1.084 \pm 0.030) - (1.3 \pm 0.8) \cdot 10^{-4} (\varpi_{calc}/\mathrm{cm}^{-1}) \quad (8)$$

for the range (70 to 500) cm⁻¹ according to experimental Raman spectra for crystalline caprolactam;

$$\chi = (1.002 \pm 0.017) - (2.0 \pm 1.4) \cdot 10^{-5} (\varpi_{calc}/\mathrm{cm}^{-1}) \quad (9)$$

for (500 to 1800) cm⁻¹ interval using the IR spectrum of gaseous caprolactam. The scaling factor was (0.959 ± 0.004) for higher frequencies.

The procedure of statistical thermodynamic calculations of the thermodynamic properties in the ideal gas state is described

Table 5. Experimental and Calculated (B3LYP/6-311G*) Fundamentals (in cm⁻¹) for Chair Conformer of the Caprolactam

Raman	IR	IR gas[27]	scaled calculated frequencies	chosen
79			79	79
			169	169
			241	241
324			324	324
346			342	346
399			395	399
485	488		490	490
			497	490
	503	502	521	502
585	580	574	590	580
702	689	694	696	694
748			730	748
	818	806	805	806
844			838	838
865	863	874	864	874
	887		888	887
956	959	958	953	958
	978		975	978
1019	1010	1014	1009	1014
1088	1082	1082	1068	1082
			1081	1082
1124	1119	1122	1117	1122
			1163	1165
1200	1192	1194	1201	1194
	1233	1230	1235	1230
1256	1252	1262	1264	1262
1290	1285		1293	1290
	1310	1310	1313	1310
	1328		1339	1328
1367	1358	1358	1357	1358
			1362	1358
			1369	1358
		1394	1387	1394
1430	1432	1438	1440	1438
			1449	1438
1454	1460	1450	1451	1450
			1460	1450
1488	1479	1466	1470	1466
			1473	1466
	1650	1714	1705	1714
	2852	2866	2883	2866
			2886	2866
		2874	2890	2874
			2893	2874
2899			2907	2900
2932	2926		2923	2932
		2942	2931	2942
2970			2939	2970
		2978	2955	2978
			2996	2996
3084	3073	3446	3441	3446

Table 6. Thermodynamic Properties of ε-Caprolactam in the Ideal Gas State ($M = 0.11316\,\mathrm{kg \cdot mol^{-1}}$, $p^\circ = 10^5\,\mathrm{Pa}$)

T K	$\Delta^T_0 S^\circ_m$ $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$C^\circ_{p,m}$ $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$\Delta^T_0 H^\circ_m/T$ $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	Φ°_m $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$\Delta_f H^\circ_m$ $\mathrm{J \cdot mol^{-1}}$	$\Delta_f G^\circ_m$ $\mathrm{J \cdot mol^{-1}}$
100	267.8	54.6	41.6	226.2	−218.1	−172.2
200	316.1	90.0	56.6	259.4	−230.6	−121.4
298.15	359.6	132.3	74.4	285.3	−241.9	−65.4
400	405.1	179.1	95.1	310.0	−251.5	−3.5
500	449.6	220.3	116.1	333.5	−258.5	59.3
600	492.9	254.5	136.5	356.5	−263.4	123.4
700	534.3	282.3	155.4	378.9	−266.4	188.1
800	573.5	305.0	172.7	400.8	−268.0	253.5
900	610.6	323.9	188.5	422.1	−268.4	318.3
1000	645.5	339.8	202.8	442.7	−267.8	383.6

in detail elsewhere.[29] The thermodynamic properties of ε-caprolactam were calculated in the ideal gas state over the interval (100 to 1000) K (Table 6). The entropy of ε-caprolactam in the ideal gas state at $T = 298.15$ K calculated by statistical thermodynamics agrees with the experimental results within 0.2

%, which was essentially below the combined uncertainty of both types of determinations.

The value of $\Delta_f H°$(cr, 298.15 K) = −(329.4 ± 1.7) kJ·mol^{-1} derived from bomb calorimetry experiments[4] and $\Delta_{sub}H°$(298.15 K) = (87.5 ± 0.6) kJ·mol^{-1} derived from regression of the data determined in the present work (Table 3, Clarke and Glew equation) were used to calculate the enthalpy of formation of caprolactam in the gaseous state $\Delta_f H°$(g, 298.15 K) = −(241.9 ± 1.8) kJ·mol^{-1}.

Literature Cited

(1) Carma, A.; Garcia, H. *Chem. Rev.* **2003**, *103*, 4307−4365.
(2) Shuangfeng, Y.; Boqing, X. *Cuihua Xuebao* **2002**, *23* (6), 507−512.
(3) Ren, R. X.; Zueva, L. D.; Ou, W. *Tetrahedron Lett.* **2001**, *42*, 8441−8443.
(4) Kabo, G. J.; Kozyro, A. A.; Krouk, V. S.; Yursha, I. A.; Simirsky, V. V.; Gogolinsky V. I. *J. Chem. Thermodyn.* **1992**, *24*, 1−13.
(5) Zaitsau, D. H.; Verevkin, S. P.; Paulechka, Y. U.;Kabo, G. J.; Sevruk, V. M. *J. Chem. Eng. Data* **2003**, *48*, 1393−1400.
(6) Bazyleva, A. B.; Kabo, G. J.; Paulechka Y. U.; Zaitsau, Dz. H.; Blokhin, A. V.; Sevruk, V. M. The thermodynamic properties of 1-bromoadamantane in the gaseous state. *Thermochim. Acta* **2005**, *436*, 56−67.
(7) Wahlbeck, P. G. *J. Chem. Phys.* **1971**, *55*, 1709−1715.
(8) Pappu, R. V.; Hart, R. K.; Ponder, J. W. *J. Phys. Chem. B* **1998**, *102*, 9725−9742.
(9) Askadsky, A. A.; Matveev, Y. I. *The Chemical Structure and Physical Properties of Polymers;* Khimia: Moscow, 1983 (in Russian).
(10) Masherpa, G. *Rev. Chim. Miner.* **1966**, *3*, 153−184.
(11) Verevkin, S. P. *J. Chem. Eng. Data* **2000**, *45*, 946−952.
(12) Kulikov, D.; Verevkin, S. P.; Heintz, A. *J. Chem. Eng. Data* **2001**, *46*, 1593−1600.
(13) Aihara, A. *Bull. Chem. Soc. Japn.* **1960**, *33*, 1188−1194.
(14) Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A. *J. Chem. Eng. Data* **2002**, *47*, 689−699.
(15) Danov, S. M.; Shinyaeva, V. S. *Zh. Fiz. Khim.* **1965**, *39*, 486-489
(16) Moravek, J. *Chem. Prumysl.* **1957**, *7*, 49−51.
(17) Skorokhodova, V. L.; Kogan, V. B. *Zh. Prikl. Khim.* **1973**, *3*, 698.
(18) Vlasov, I. M.; Gubanova, O. K.; Kvasha, V. B. *Khim. Volokna* **1983**, *1*, 18.
(19) Daubert, T. E.; Jalowka, J. W.; Goren, V. *AIChE Symp. Ser.* **1987**, *No. 256*, 128−156.
(20) Clarke, E. C. W.; Glew, D. N. *Trans. Faraday Soc.* **1966**, *62*, 539−547.
(21) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.
(22) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785−789.
(23) Borgen, G.; Rise, F. *Magn. Reson. Chem.* **1993**, *31*, 51−53.
(24) Schneider, B.; Doskocilova, D.; Schmidt, P.; et al. *J. Mol. Struct.* **1976**, *35*, 161−174.
(25) Winkler, F. K.; Dunitz, J. D. *Acta Crystallogr. B* **1975**, *31*, 268.
(26) Granovsky, A. A. http://classic.chem.msu.su/gran/gamess/index.html.
(27) http://webbook.nist.gov/cgi/cbook.cgi?ID=C105602&Units=SI&Mask=80.
(28) http://www.aist.go.jp/RIODB/SDBS/menu-e.html.
(29) Frenkel, M. L.; Kabo, G. J.; Marsh, K. N.; Roganov, G. N.; Wilhoit, R. C. *Thermodynamics of Organic Compounds in the Gas State*; TRC Data Series; TRC: College Station, TX, 1994.