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Enthalpies of Vaporization of a Homologous Series of *n*-Alkanes Determined from Vapor Pressure Measurements

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Vapor pressures and enthalpies of vaporization of the homologous series of *n*-alkanes C_nH_{2n+2} ($20 < n < 38$ except $n = 29$ and 35) have been determined by the torsion–effusion method. Increments of about 2.7 kJ mol^{-1} of the $\Delta_{vap}H°_T$ for even- and odd-numbered *n*-alkanes and of about 5.3 kJ mol^{-1} of the $\Delta_{sub}H°_{298.15}$ for the even-numbered *n*-alkanes due to the CH_2 increment were found.

Introduction

As part of a research program on the study of the vaporization process of organic compounds (*1–5*), we have determined the enthalpies of vaporization of the homologous series of high molecular weight *n*-alkanes C_nH_{2n+2} ($20 < n < 38$ except $n = 29$ and 35) from the temperature dependence of their vapor pressures measured by the torsion–effusion method.

Redeterminations have been carried out for some of the *n*-alkanes studied previously (*5*) in which the reported thermochemical values were found unreliable. In fact a subsequent analysis of the reported data revealed that the temperature correction evaluated by calibration experiments is not constant but changes slightly with the increase of the furnace temperature. Therefore, the high pressures are referred to temperatures higher than the true ones. For this reason the slopes of the $\log p$ vs $1/T$ equations obtained with these values and the second-law enthalpies of vaporization calculated from these slopes are slightly lower than the correct values.

Some empirical expressions (*6–8*) and some experimental values of the vapor pressures of these compounds are available in the literature: eicosane (*9–13*), heneicosane and pentacosane (*11*), docosane and tetracosane (*9, 11*), hexacosane (*11, 14, 15*), heptacosane (*16*), octacosane (*10, 11*), and dotriacontane (*15, 17*).

A new torsion–effusion assembly accurately calibrated over a large temperature range was used in this work to measure the vapor pressures of the *n*-alkanes.

Experimental Section

The *n*-alkane samples, supplied by Aldrich Chemical Co., Sigma Chemical Co., and Fluka Chemika, present commercial purities ranging from 99.8% to 99%. The small amount of impurities does not represent a practical problem because generally they are attributable to other alkanes of the homologous series that vaporize in the first and last steps of the experiments. For this reason, in all experiments, the first and the last points are not taken in consideration in the calculation of the pressure–temperature equations.

The new torsion–effusion assembly used is shown in Figure 1.

The torsion–effusion method is well known (*18*). The torsion constant of the assembly, $K = p_i/\alpha_i$ (α_i is the measured torsion angle when the vapor pressure of the sample is p_i), was experimentally determined by vaporizing very pure standard substances, such as mercury (*19*), urea (*1*), naphthalene (*20*), and benzoic acid (*21*), having well-known vapor pressures ranging from 10^{-5} to 10^{-2} kPa in different temperature ranges. A conventional aluminum cell having effusion holes 1 mm in diameter and graphited for improving the heating efficiency was used. In the alkane experiments the cell was loaded with small quartz wool flocks impregnated with the melted sample in order to increase the sample surface and to minimize creeping-out effects. The torsion angles were opportunely measured by comparing the alignment of two needles (welded in opposition on the assembly) with an index fixed on a large goniometer. The uncertainty in the α measurements with this assembly is about 3×10^{-3} rad. The sample was heated by a new furnace having a large isothermal zone (~25 cm). For rapid cooling of the system the furnace can be rapidly let down. The temperatures were measured by a calibrated chromel–alumel thermocouple inserted in a second cell equal to the torsion cell and placed beneath it. In order to measure the correct temperature of the sample, a particular procedure was used. By employing a standard compound having its vapor pressure detectable at the melting temperature (urea (*1*), cadmium, and zinc (*19*)), the temperature T_x was calculated by the relation

$$T_x = T_0 + (RT_0^2/\Delta_{sub}H°_T)\ln(\alpha/\alpha°) \qquad (1)$$

where $\Delta_{sub}H°_T$ is the sublimation enthalpy of the used standard, T_0 is its melting point, and α and $\alpha°$ are the torsion angles measured at the temperature T_x and at the melting point, respectively, $\alpha°$ easily measurable during the melting of the zero-variant system. The differences obtained in several experiments between the temperatures calculated by eq 1 and those measured were constant around 2.0 ± 0.5 K in a large temperature range. The experimental temperatures of the sample were corrected with this value. In order to check that the thermodynamic equilibrium condition was obtained within the cell, sublimation enthalpies of pure cadmium (*19*) and benzoic acid (*21*) were determined by second- and third-law treatments of their vapor pressures. Very good agreement (within 0.2%) was found between the $\Delta_{sub}H°_{298.15}$ obtained from both procedures and those selected in the literature. This agreement and the absence of evident temperature trends in the third-law $\Delta_{sub}H°_{298.15}$ values indicated that possible errors in temperature measurements were not large.

Results

The experimental torsion results are reported in Table 1. The $\log p$ vs $1/T$ equations obtained by treating the data for each run by least-squares analysis are given in Table 2. By weighting the slopes and the intercepts of these equations proportionally to the experimental points, the temperature–pressure equations reported in Table 3 were selected. The

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Table 1. Torsion Vapor Pressure of the Studied *n*-Alkanes

compound	run	T/K	p/kPa	run	T/K	p/kPa	run	T/K	p/kPa
$C_{20}H_{42}$	a	351	6.41×10^{-4}	b	347	3.20×10^{-4}			
		353	9.61×10^{-4}		351	4.81×10^{-4}			
		355	1.28×10^{-3}		354	6.41×10^{-4}			
		357	1.52×10^{-3}		356	8.01×10^{-4}			
		359	1.84×10^{-3}		359	1.28×10^{-3}			
		362	2.40×10^{-3}		362	1.60×10^{-3}			
		365	3.36×10^{-3}		365	2.40×10^{-3}			
		367	4.17×10^{-3}		368	3.04×10^{-3}			
		369	4.97×10^{-3}		371	4.17×10^{-3}			
		372	6.57×10^{-3}		374	4.65×10^{-3}			
		375	8.33×10^{-3}		377	6.89×10^{-3}			
		377	1.04×10^{-2}		380	8.65×10^{-3}			
		381	1.51×10^{-2}		386	1.43×10^{-2}			
		384	1.94×10^{-2}		388	1.71×10^{-2}			
$C_{21}H_{44}$	a	365	9.61×10^{-4}	b	366	1.12×10^{-3}			
		369	1.44×10^{-3}		368	1.44×10^{-3}			
		374	2.24×10^{-3}		372	2.24×10^{-3}			
		377	3.04×10^{-3}		375.5	2.88×10^{-3}			
		381	4.33×10^{-3}		379	4.17×10^{-3}			
		383	5.45×10^{-3}		381	4.81×10^{-3}			
		385.5	6.73×10^{-3}		385	6.73×10^{-3}			
		389.5	9.61×10^{-3}		388	8.65×10^{-3}			
		392	1.23×10^{-2}		393	1.41×10^{-2}			
		396	1.70×10^{-2}		396	1.73×10^{-2}			
		399.5	2.31×10^{-2}		399	2.21×10^{-2}			
$C_{22}H_{46}$	a	372	7.21×10^{-4}	b	372	6.41×10^{-4}			
		374	8.81×10^{-4}		376.5	1.12×10^{-3}			
		376	1.12×10^{-3}		381	2.24×10^{-3}			
		379	1.60×10^{-3}		385.5	3.20×10^{-3}			
		382	2.08×10^{-3}		390	4.97×10^{-3}			
		385	2.72×10^{-3}		395.5	8.01×10^{-3}			
		388	3.85×10^{-3}		400.5	1.22×10^{-2}			
		391	5.13×10^{-3}		404	1.67×10^{-2}			
		395	7.37×10^{-3}		408	2.24×10^{-2}			
		398	1.01×10^{-2}						
		401	1.38×10^{-2}						
		404	1.81×10^{-2}						
		407	2.36×10^{-2}						
		410	2.95×10^{-2}						
$C_{23}H_{48}$	a	377.5	6.41×10^{-4}	b	370	3.20×10^{-4}	c	374	5.61×10^{-4}
		381	8.01×10^{-4}		375	6.41×10^{-4}		377	6.41×10^{-4}
		384	1.12×10^{-3}		380	9.61×10^{-4}		379	8.01×10^{-4}
		387	1.60×10^{-3}		383	1.36×10^{-3}		380	1.12×10^{-3}
		390	2.08×10^{-3}		385	1.60×10^{-3}		384	1.44×10^{-3}
		393	2.88×10^{-3}		388	2.08×10^{-3}		387	1.92×10^{-3}
		397	4.01×10^{-3}		391	2.88×10^{-3}		390	2.72×10^{-3}
		400	5.61×10^{-3}		394	3.85×10^{-3}		394	4.01×10^{-3}
		403	7.21×10^{-3}		396.5	5.13×10^{-3}		396	4.97×10^{-3}
		406	9.61×10^{-3}		399.5	6.57×10^{-3}		400	7.05×10^{-3}
		409	1.23×10^{-2}		402	8.17×10^{-3}		404	9.77×10^{-3}
		411.5	1.54×10^{-2}		404.5	1.03×10^{-2}		406.5	1.19×10^{-2}
		416	2.19×10^{-2}		407	1.30×10^{-2}		409	1.46×10^{-2}
					409.5	1.55×10^{-2}			
$C_{24}H_{50}$	a	388	8.01×10^{-4}	b	387	7.21×10^{-4}	c	386	7.21×10^{-4}
		394	1.60×10^{-3}		391	1.12×10^{-3}		387	8.01×10^{-4}
		399	2.40×10^{-3}		394	1.44×10^{-3}		389	8.81×10^{-4}
		402	3.20×10^{-3}		397	2.08×10^{-3}		391	1.12×10^{-3}
		405.5	4.33×10^{-3}		401	2.88×10^{-3}		393	1.44×10^{-3}
		408	5.61×10^{-3}		404	4.17×10^{-3}		395	1.76×10^{-3}
		411.5	7.37×10^{-3}		407	5.29×10^{-3}		398	2.32×10^{-3}
		413	8.49×10^{-3}		410	6.89×10^{-3}		399	2.56×10^{-3}
					412	8.49×10^{-3}		400	2.80×10^{-3}
					414	1.01×10^{-2}		402	3.12×10^{-3}
					417	1.28×10^{-2}		404	4.17×10^{-3}
					429	1.71×10^{-2}		405	4.65×10^{-3}
					423	2.16×10^{-2}		407	5.61×10^{-3}
								410	7.21×10^{-3}
								413	9.29×10^{-3}
								416	1.19×10^{-2}
								418	1.41×10^{-2}
								420	1.70×10^{-2}
								425	2.53×10^{-2}
$C_{25}H_{52}$	a	402	1.92×10^{-3}	b	397	1.28×10^{-3}	c	398	1.28×10^{-3}
		306	2.56×10^{-3}		399	1.44×10^{-3}		400	1.52×10^{-3}
		408	3.02×10^{-3}		403	2.08×10^{-3}		402	1.76×10^{-3}
		411	4.01×10^{-3}		406	2.72×10^{-3}		404	2.08×10^{-3}
		414	5.13×10^{-3}		409	3.52×10^{-3}		406	2.40×10^{-3}
		418	7.53×10^{-3}		412	4.65×10^{-3}		415	5.77×10^{-3}

Table 1 (Continued)

compound	run	T/K	p/kPa	run	T/K	p/kPa	run	T/K	p/kPa
$C_{25}H_{52}$	a	420	8.97×10^{-3}	b	415.5	6.41×10^{-3}	c	416	6.73×10^{-3}
		423	1.15×10^{-2}		417.5	7.85×10^{-3}		420	8.97×10^{-3}
		426	1.47×10^{-2}		420	9.61×10^{-3}		421	9.85×10^{-3}
		428	1.79×10^{-2}		423	1.25×10^{-2}		423	1.22×10^{-2}
		432	2.36×10^{-2}		425.5	1.57×10^{-2}		426	1.52×10^{-2}
		434	2.92×10^{-2}		428	1.95×10^{-2}		428	1.84×10^{-2}
$C_{26}H_{54}$	a	420	4.01×10^{-3}	b	391	3.20×10^{-4}	c	392	3.20×10^{-4}
		421	4.49×10^{-3}		394	4.01×10^{-4}		398	4.81×10^{-4}
		422	5.13×10^{-3}		398	4.81×10^{-4}		401	6.41×10^{-4}
		423	5.77×10^{-3}		402	8.01×10^{-4}		404	8.01×10^{-4}
		424	6.41×10^{-3}		405	1.12×10^{-3}		407	1.12×10^{-3}
		425	7.05×10^{-3}		408	1.52×10^{-3}		410	1.60×10^{-3}
		426	7.69×10^{-3}		411	2.08×10^{-3}		413	2.08×10^{-3}
		427	8.33×10^{-3}		415	2.88×10^{-3}		416	2.72×10^{-3}
		428	9.13×10^{-3}		419	4.17×10^{-3}		420	3.85×10^{-3}
		429	9.61×10^{-3}		423	5.77×10^{-3}		425	6.09×10^{-3}
		430	1.09×10^{-2}		430	1.07×10^{-2}		428	7.85×10^{-3}
		431	1.17×10^{-2}		433	1.35×10^{-2}		431	1.04×10^{-2}
		432.5	1.33×10^{-2}						
		435	1.55×10^{-2}						
		437	1.89×10^{-2}						
$C_{27}H_{56}$	a	408	9.33×10^{-4}	b	411	4.87×10^{-4}			
		412	1.20×10^{-3}		414	6.09×10^{-4}			
		415	1.47×10^{-3}		417	8.53×10^{-4}			
		416	1.60×10^{-3}		421	1.22×10^{-3}			
		418	2.13×10^{-3}		423	1.46×10^{-3}			
		420	2.40×10^{-3}		425	1.71×10^{-3}			
		422	2.80×10^{-3}		427	2.07×10^{-3}			
		424	3.33×10^{-3}		431	3.05×10^{-3}			
		429	5.60×10^{-3}		437.5	5.24×10^{-3}			
		433.5	7.86×10^{-3}						
		435.5	9.33×10^{-3}						
		439.5	1.33×10^{-2}						
$C_{28}H_{58}$	a	408	4.01×10^{-4}	b	407	4.01×10^{-4}			
		413	5.61×10^{-4}		409	4.81×10^{-4}			
		416	7.21×10^{-4}		412	5.61×10^{-4}			
		418	8.01×10^{-4}		417	8.81×10^{-4}			
		420	9.61×10^{-4}		419	1.12×10^{-3}			
		422	1.28×10^{-3}		421	1.36×10^{-3}			
		424	1.60×10^{-3}		424	1.68×10^{-3}			
		426	2.08×10^{-3}		427	2.24×10^{-3}			
		429	2.56×10^{-3}		430	2.88×10^{-3}			
		431	3.04×10^{-3}		434	4.17×10^{-3}			
		433	3.76×10^{-3}		437	5.29×10^{-3}			
		435	4.65×10^{-3}		440	6.89×10^{-3}			
		439	6.41×10^{-3}		442	8.01×10^{-3}			
		441	7.53×10^{-3}		446	1.19×10^{-2}			
		443	8.97×10^{-3}		449	1.46×10^{-2}			
		445	1.06×10^{-2}		452	1.84×10^{-2}			
		448	1.35×10^{-2}		455	2.31×10^{-2}			
		453	1.92×10^{-2}						
		456	2.31×10^{-2}						
$C_{30}H_{62}$	a	431	8.01×10^{-4}	b	427	7.21×10^{-4}	c	422	4.81×10^{-4}
		434	1.04×10^{-3}		429	8.81×10^{-4}		429	8.01×10^{-4}
		437	1.52×10^{-3}		431	1.12×10^{-3}		432	9.61×10^{-4}
		439	1.92×10^{-3}		433	1.28×10^{-3}		436	1.44×10^{-3}
		442	2.56×10^{-3}		435	1.60×10^{-3}		439	2.08×10^{-3}
		445	3.20×10^{-3}		437	1.92×10^{-3}		444	3.04×10^{-3}
		448	4.33×10^{-3}		440	2.40×10^{-3}		449	4.49×10^{-3}
		451	5.77×10^{-3}		443	3.04×10^{-3}		452	6.41×10^{-3}
		454	7.05×10^{-3}		446.5	4.17×10^{-3}		454	8.33×10^{-3}
		458	1.03×10^{-2}					459	1.07×10^{-2}
		460	1.22×10^{-2}					463	1.62×10^{-2}
		462	1.43×10^{-2}					465.5	1.94×10^{-2}
		464	1.76×10^{-2}						
		466	1.99×10^{-2}						
		469	2.47×10^{-2}						
		472	3.01×10^{-2}						
		474	3.59×10^{-2}						
		477	4.29×10^{-2}						
		482	5.83×10^{-2}						
		485	7.02×10^{-2}						
		487	8.04×10^{-2}						
$C_{31}H_{64}$	a	439	1.28×10^{-3}	b	433	6.41×10^{-4}			
		442	1.60×10^{-3}		435	8.01×10^{-4}			
		445	2.08×10^{-3}		437	9.61×10^{-4}			

Table 1 (Continued)

compound	run	T/K	p/kPa	run	T/K	p/kPa	run	T/K	p/kPa
$C_{31}H_{64}$	a	447	2.56×10^{-3}	b	441	1.52×10^{-3}			
		450	3.36×10^{-3}		444	1.92×10^{-3}			
		452	4.17×10^{-3}		449	3.04×10^{-3}			
		454	4.97×10^{-3}		453	4.17×10^{-3}			
		456	5.61×10^{-3}		455	4.81×10^{-3}			
		458	6.57×10^{-3}		459	6.89×10^{-3}			
		460	7.69×10^{-3}		462	8.65×10^{-3}			
		462	8.97×10^{-3}		465	1.09×10^{-2}			
		464	1.09×10^{-2}		470	1.60×10^{-2}			
		466	1.30×10^{-2}		474	2.08×10^{-2}			
		468	1.47×10^{-2}						
		470	1.68×10^{-2}						
		472	1.87×10^{-2}						
$C_{32}H_{66}$	a	437	8.01×10^{-4}	b	442	1.12×10^{-3}	c	441	9.61×10^{-4}
		442	1.12×10^{-3}		445	1.28×10^{-3}		443	1.28×10^{-3}
		445	1.44×10^{-3}		448	1.76×10^{-3}		446	1.60×10^{-3}
		447	1.70×10^{-3}		451	2.56×10^{-3}		449	2.08×10^{-3}
		450	2.24×10^{-3}		454	3.20×10^{-3}		452	2.72×10^{-3}
		452	2.88×10^{-3}		458	4.49×10^{-3}		456	3.68×10^{-3}
		456	4.01×10^{-3}		460.5	5.45×10^{-3}		459	4.81×10^{-3}
		461	6.09×10^{-3}		466	8.33×10^{-3}		462	6.25×10^{-3}
		465	8.01×10^{-3}		468.5	1.01×10^{-2}		464.5	7.69×10^{-3}
		470	1.30×10^{-2}		471	1.22×10^{-2}		466.5	9.45×10^{-3}
					473.5	1.54×10^{-2}		470	1.30×10^{-2}
					476	1.86×10^{-2}		474	1.68×10^{-2}
								477	2.10×10^{-2}
$C_{33}H_{68}$	a	435	3.20×10^{-4}	b	440	5.45×10^{-4}			
		440	4.81×10^{-4}		443	6.41×10^{-4}			
		447	9.61×10^{-4}		447	1.04×10^{-3}			
		451	1.28×10^{-3}		451	1.44×10^{-3}			
		456	1.92×10^{-3}		456	2.08×10^{-3}			
		461	3.04×10^{-3}		460	2.88×10^{-3}			
		466	4.81×10^{-3}		463	4.01×10^{-3}			
		372	7.69×10^{-3}		466	4.97×10^{-3}			
		477	1.19×10^{-2}		469	6.25×10^{-3}			
		482	1.76×10^{-2}		473	8.49×10^{-3}			
					480	1.47×10^{-2}			
$C_{34}H_{70}$	a	449	6.41×10^{-4}	b	446	4.81×10^{-4}			
		451	8.01×10^{-4}		449	6.41×10^{-4}			
		453	9.61×10^{-4}		457	1.36×10^{-3}			
		455	1.12×10^{-3}		459	1.60×10^{-3}			
		457	1.36×10^{-3}		461	1.92×10^{-3}			
		459	1.60×10^{-3}		464	2.48×10^{-3}			
		461	1.92×10^{-3}		469	3.85×10^{-3}			
		463	2.24×10^{-3}		473	5.29×10^{-3}			
		467	3.04×10^{-3}						
		469	3.68×10^{-3}						
		472	4.65×10^{-3}						
		475	6.09×10^{-3}						
		478	7.37×10^{-3}						
		481	9.45×10^{-3}						
		484	1.20×10^{-2}						
		487	1.55×10^{-2}						
		490	1.92×10^{-2}						
		493	2.42×10^{-2}						
		497	3.14×10^{-2}						
$C_{36}H_{74}$	a	466	9.61×10^{-4}	b	452	3.20×10^{-4}			
		271	1.44×10^{-3}		455	4.81×10^{-4}			
		474	1.92×10^{-3}		460	6.41×10^{-4}			
		480	3.36×10^{-3}		463	8.65×10^{-4}			
		483	4.17×10^{-3}		465	9.61×10^{-4}			
		486	5.77×10^{-3}		468	1.28×10^{-3}			
		488	6.57×10^{-3}		472	1.76×10^{-3}			
		490.5	8.01×10^{-3}		476	2.24×10^{-3}			
		493	9.77×10^{-3}		480	3.36×10^{-3}			
		496	1.20×10^{-2}		483	4.33×10^{-3}			
		499	1.52×10^{-2}		487	5.77×10^{-3}			
		501	1.75×10^{-2}		492	8.97×10^{-3}			
		503	2.11×10^{-2}		495	1.19×10^{-2}			
		507	2.71×10^{-2}		498	1.52×10^{-2}			
		510	3.27×10^{-2}		502	2.07×10^{-2}			
		513	4.01×10^{-2}		507	3.03×10^{-2}			
					510	3.72×10^{-2}			
					513	4.42×10^{-2}			
					516	5.16×10^{-2}			
$C_{37}H_{76}$	a	471	9.61×10^{-4}	b	475	1.60×10^{-3}	c	473	1.28×10^{-3}
		474	1.28×10^{-3}		477	1.84×10^{-3}		474	1.44×10^{-3}

Table 1 (Continued)

compound	run	T/K	p/kPa	run	T/K	p/kPa	run	T/K	p/kPa
$C_{37}H_{76}$	a	476	1.60×10^{-3}	b	480	2.32×10^{-3}	c	478	1.76×10^{-3}
		478	1.76×10^{-3}		483.5	3.28×10^{-3}		481	2.24×10^{-3}
		481	2.24×10^{-3}		488	4.57×10^{-3}		484	2.72×10^{-3}
		485	3.52×10^{-3}		491	5.69×10^{-3}		487	3.68×10^{-3}
		487	4.01×10^{-3}		493	6.49×10^{-3}		490	4.49×10^{-3}
		490	4.81×10^{-3}		496	8.09×10^{-3}		493	5.77×10^{-3}
		493	6.09×10^{-3}		500	1.09×10^{-2}		496	7.37×10^{-3}
		495	7.21×10^{-3}		503	1.35×10^{-2}		499	9.45×10^{-3}
		497	8.17×10^{-3}					502	1.20×10^{-2}
		499	9.93×10^{-3}					505	1.49×10^{-2}
		501	1.12×10^{-2}					508	1.84×10^{-2}
		505	1.51×10^{-2}					511	2.23×10^{-2}
		507	1.70×10^{-2}						
		510	2.08×10^{-2}						
$C_{38}H_{78}$	a	471	6.41×10^{-4}	b	471	6.41×10^{-4}	c	474	8.81×10^{-4}
		475	9.61×10^{-4}		473	8.01×10^{-4}		476	1.04×10^{-3}
		478	1.28×10^{-3}		476	9.61×10^{-4}		479	1.44×10^{-3}
		482	1.76×10^{-3}		478	1.28×10^{-3}		481	1.68×10^{-3}
		485	2.08×10^{-3}		480	1.60×10^{-3}		486	2.40×10^{-3}
		487	2.56×10^{-3}		482	1.92×10^{-3}		487	2.72×10^{-3}
		490.5	3.20×10^{-3}		485	2.24×10^{-3}		490	3.52×10^{-3}
		493	3.85×10^{-3}		489	2.88×10^{-3}		494	4.65×10^{-3}
		495	4.49×10^{-3}		493	4.33×10^{-3}		497	5.93×10^{-3}
		500	6.73×10^{-3}		496	5.29×10^{-3}		500	7.21×10^{-3}
		503	8.81×10^{-3}		499	6.89×10^{-3}			
		506	1.15×10^{-2}		502	8.33×10^{-3}			
		511	1.67×10^{-2}		505	1.09×10^{-2}			
					508	1.35×10^{-2}			
					511	1.63×10^{-2}			

Table 2. Temperature–Vapor Pressure Equations of the Studied *n*-Alkanes

compound	run	no. of points	ΔT/K	$\log(p/\mathrm{kPa}) = A - B/(T/\mathrm{K})$	
				A	B
$C_{20}H_{42}$	a	14	351–384	13.37 ± 0.26	5785 ± 97
	b	14	347–388	12.96 ± 0.25	5709 ± 92
$C_{21}H_{44}$	a	11	365–399.5	13.04 ± 0.12	5866 ± 47
	b	11	366–399	12.50 ± 0.17	5649 ± 64
$C_{22}H_{46}$	a	14	372–410	14.37 ± 0.10	6516 ± 37
	b	9	372–408	14.04 ± 0.49	6388 ± 191
$C_{23}H_{48}$	a	13	377.5–416	13.80 ± 0.15	6428 ± 59
	b	14	370–409.5	13.84 ± 0.16	6404 ± 61
	c	13	374–409	13.86 ± 0.27	6412 ± 105
$C_{24}H_{50}$	a	8	388–413	13.57 ± 0.26	6459 ± 106
	b	13	387–423	14.25 ± 0.12	6726 ± 49
	c	19	386–425	13.92 ± 0.13	6591 ± 0.51
$C_{25}H_{52}$	a	12	402–434	13.40 ± 0.15	6489 ± 64
	b	12	397–428	13.64 ± 0.16	6579 ± 67
	c	12	398–428	13.82 ± 0.19	6662 ± 81
$C_{26}H_{54}$	a	15	420–437	14.50 ± 0.36	7084 ± 153
	b	12	391–433	13.75 ± 0.29	6765 ± 119
	c	12	392–431	13.65 ± 0.29	6748 ± 120
$C_{27}H_{56}$	[a]		401–441	12.48 ± 0.40	6103 ± 150
	a	12	408–439.5	13.54 ± 0.34	6787 ± 143
	b	9	411–437.5	13.94 ± 0.18	7095 ± 76
$C_{28}H_{58}$	a	19	408–456	14.24 ± 0.23	7226 ± 100
	b	17	407–455	13.55 ± 0.13	6912 ± 58
$C_{29}H_{60}$	[a]		423–456.5	13.84 ± 0.40	7161 ± 150
$C_{30}H_{62}$	a	21	431–487	14.39 ± 0.20	7513 ± 93
	b	9	427–446.5	14.07 ± 0.32	7342 ± 141
	c	12	422–465.5	14.37 ± 0.33	7490 ± 140
$C_{31}H_{64}$	a	16	439–472	14.20 ± 0.17	7506 ± 78
	b	13	433–474	14.28 ± 0.18	7554 ± 83
$C_{32}H_{66}$	a	10	437–470	14.41 ± 0.33	7671 ± 149
	b	12	442–476	14.33 ± 0.24	7648 ± 110
	c	13	441–477	14.59 ± 0.16	7757 ± 75
$C_{33}H_{68}$	a	10	435–482	14.41 ± 0.16	7797 ± 72
	b	11	440–480	14.06 ± 0.20	7630 ± 92
$C_{34}H_{70}$	a	19	449–497	14.24 ± 0.06	7823 ± 27
	b	8	446–473	14.96 ± 0.09	8148 ± 41
$C_{36}H_{74}$	a	16	466–513	14.85 ± 0.16	8321 ± 79
	b	19	452–516	14.52 ± 0.15	8149 ± 74
$C_{37}H_{76}$	a	16	471–510	14.42 ± 0.18	8203 ± 88
	b	10	475–503	13.91 ± 0.17	7936 ± 82
	c	14	473–511	14.08 ± 0.22	8039 ± 109
$C_{38}H_{78}$	a	13	471–511	14.45 ± 0.23	8302 ± 113
	b	15	471–511	14.61 ± 0.23	8373 ± 114
	c	10	474–500	14.53 ± 0.25	8330 ± 119

[a] Results of the previous work (*4*).

Table 3. Selected Temperature–Vapor Pressure Equations and Enthalpies of Vaporization of the Studied *n*-Alkanes

compound	T/K	$\log(p/\mathrm{kPa}) = A - B/(T/\mathrm{K})$		$\Delta_{\mathrm{vap}}H^{\circ}{}_{T}/(\mathrm{kJ\ mol^{-1}})$
		A	B	
$C_{20}H_{42}$	367	13.16 ± 0.25	5747 ± 100	110 ± 2
$C_{21}H_{44}$	382	12.77 ± 0.20	5757 ± 100	110 ± 2
$C_{22}H_{46}$	391	14.24 ± 0.20	6466 ± 100	124 ± 2
$C_{23}H_{48}$	393	13.83 ± 0.10	6414 ± 50	123 ± 1
$C_{24}H_{50}$	405	13.96 ± 0.30	6608 ± 100	126 ± 2
$C_{25}H_{52}$	415	13.62 ± 0.20	6577 ± 50	126 ± 1
$C_{26}H_{54}$	414	14.01 ± 0.30	6882 ± 50	132 ± 1
$C_{27}H_{56}$	423	13.71 ± 0.40	6919 ± 200	132 ± 4
$C_{28}H_{58}$	431	13.91 ± 0.20	7078 ± 150	135 ± 3
$C_{29}H_{60}$[a]	440	13.84 ± 0.40	7161 ± 150	137 ± 3
$C_{30}H_{62}$	454	14.31 ± 0.20	7470 ± 100	143 ± 2
$C_{31}H_{64}$	450	14.43 ± 0.20	7614 ± 100	146 ± 2
$C_{32}H_{66}$	456	14.45 ± 0.25	7695 ± 50	147 ± 1
$C_{33}H_{68}$	458	14.23 ± 0.20	7710 ± 50	148 ± 1
$C_{34}H_{70}$	471	14.45 ± 0.10	7921 ± 100	152 ± 2
$C_{36}H_{74}$	484	14.67 ± 0.20	8228 ± 100	157 ± 2
$C_{37}H_{76}$	491	14.17 ± 0.20	8079 ± 100	155 ± 2
$C_{38}H_{78}$	491	14.53 ± 0.20	8337 ± 50	160 ± 1

[a] Results of the previous work (*4*).

reported errors are estimated considering the uncertainties in the α measurements and the standard deviation of the calibration constant value. These equations are plotted in Figure 2. From their slopes the molar vaporization enthalpies $\Delta_{\mathrm{vap}}H^{\circ}{}_{\mathrm{T}}$ at the midpoint temperatures of the studied *n*-alkanes were calculated and reported in Table 3. Considering that the midpoint temperatures to which the vaporization enthalpies are referred (350–490 K) are very near 298.15 K, these values were considered as standard and plotted in Figure 3 as a function of the carbon number (n_{C}), with the $\Delta_{\mathrm{vap}}H^{\circ}{}_{298.15}$ of the homologous series of *n*-alkanes from C_{12} to C_{20} determined by Morawetz (*23*). Even if by increasing the value of n_{c} the line of our enthalpies of vaporization exhibits a very slight curvature, due to the different temperatures at which the $\Delta_{\mathrm{vap}}H^{\circ}{}_{\mathrm{T}}$ are referred, their values can be represented by two essentially parallel straight lines for even- and

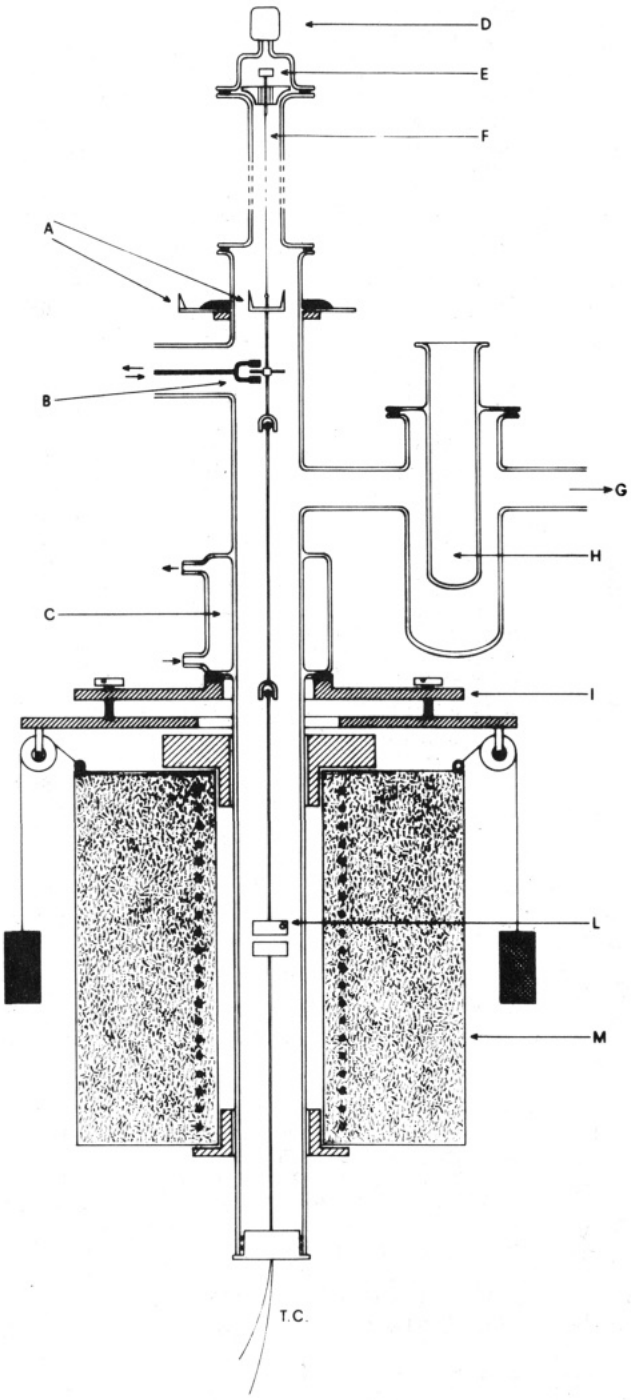

Figure 1. Torsion–effusion assembly: A, assembly for torsion-angle measurement; B, magnetic damping apparatus; C, water cooling; D, Penning gauge; E, height regulator of the torsion equipment; F, torsion wire; G, vacuum system; H, liquid nitrogen trap; I, support and alignment system of the torsion assembly; L, torsion cell; M, furnace; TC, thermocouple.

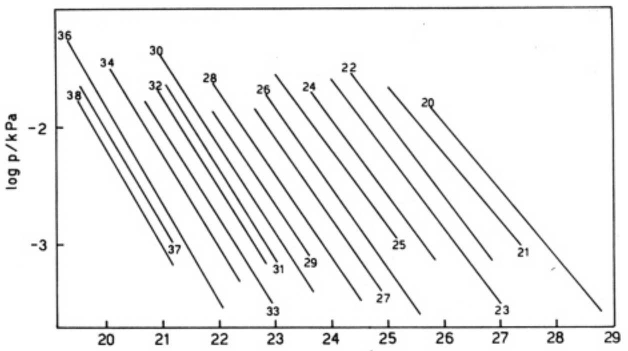

Figure 2. Vapor pressures of n-alkanes. The numbers are the carbon numbers of the n-alkanes. The line of nonacosane is that found in the previous work (*4*).

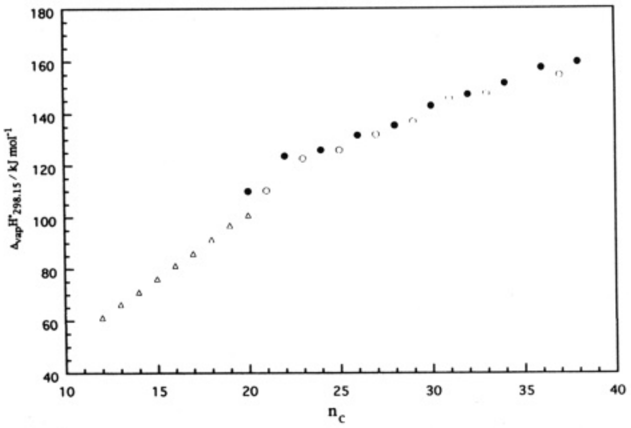

Figure 3. Molar enthalpies of vaporization of n-alkanes: ●, ○, our data (even and odd, respectively); △, Morawetz (*23*).

Table 4. Enthalpies of Vaporization and Standard Molar Enthalpies of Sublimation of Even-Numbered *n*-Alkanes

compound	T/K	$\Delta_{vap}H^\circ_T$/ (kJ mol^{-1})	$T_{fus}{}^b$/K	$\Delta_{fus}H^{\circ\,b}$/ (kJ mol^{-1})	$\Delta_{sub}H^\circ_{298.15}{}^c$/ (kJ mol^{-1})
$C_{12}H_{26}{}^a$	298.15	61.3 ± 0.3			
$C_{14}H_{30}{}^a$	298.15	71.1 ± 0.3			
$C_{16}H_{34}{}^a$	298.15	81.4 ± 0.3			
$C_{18}H_{38}{}^a$	298.15	91.6[e]	301	61.1[f]	152.7 ± 0.8[d]
$C_{20}H_{42}{}^a$	298.15	100.9[e]	309	69.5[f]	170.4 ± 1.2[d]
$C_{20}H_{42}$	367	110 ± 2	309	69.5[f]	179.5 ± 2
$C_{22}H_{46}$	391	124 ± 2	316	48.6[f]	172.6 ± 2
$C_{24}H_{50}$	405	126 ± 2	322	54.9[f]	180.9 ± 2
$C_{26}H_{54}$	414	132 ± 1	329	59.5	191.5 ± 1
$C_{28}H_{58}$	431	135 ± 3	334	64.6	199.6 ± 3
$C_{30}H_{62}$	454	143 ± 2	339	68.8	211.8 ± 2
$C_{32}H_{66}$	456	147 ± 1	343	76.6	223.6 ± 1
$C_{34}H_{70}$	471	152 ± 2	346	80.0	232 ± 2
$C_{36}H_{74}$	484	157 ± 2	349	88.8	245.8 ± 2
$C_{38}H_{78}$	491	160 ± 1	351 ± 1	98 ± 3	258 ± 4

[a] Reference 23. [b] Reference 22. [c] Calculated by summing the $\Delta_{vap}H^\circ_T$ and the $\Delta_{fus}H^\circ$. [d] Experimental value from ref 23. [e] Calculated from $\Delta_{sub}H^\circ_{298.15}$ minus $\Delta_{fus}H^\circ$. [f] Average of different values.

odd-numbered n-alkanes. The equations, obtained by least-squares treatment of the data, are

$$\Delta_{vap}H^\circ_T(\text{even})/(\text{kJ mol}^{-1}) = (63 \pm 4) + (2.62 \pm 0.14)n_C \qquad (2)$$

$$\Delta_{vap}H^\circ_T(\text{odd})/(\text{kJ mol}^{-1}) = (57 \pm 6) + (2.74 \pm 0.22)n_C \qquad (3)$$

Hence, within the associated uncertainties (standard deviations), the increment of the $\Delta_{vap}H^\circ_T$ values due to the CH_2 increment for all the studied n-alkanes is equal to about 2.7 kJ mol^{-1}. This value could be considered an upper limit considering the influence on the slopes of eqs 2 and 3 of the corrections on the $\Delta_{vap}H^\circ_T$ values if they are referred to the same temperature. It is interesting to note that the experimental $\Delta_{vap}H^\circ_{298.15}$ values found by Morawetz (*23*) lie on a line having a slope decidedly higher, with the break at around docosane. No obvious experimental errors can justify the found behavior.

Since the enthalpies of fusion of the even-numbered n-alkanes are available (*22*) (except for octatriacontane of which a value of about 98 ± 3 kJ mol^{-1} was found from a

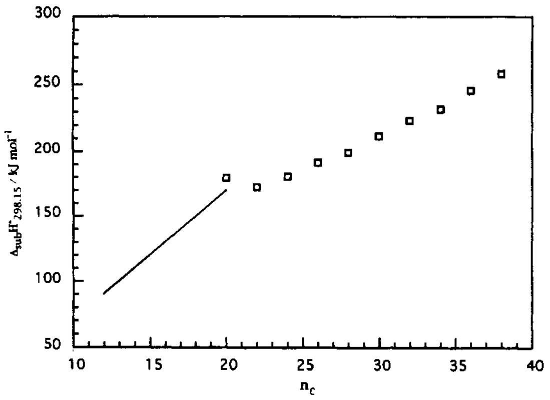

Figure 4. Standard enthalpies of sublimation of even-numbered *n*-alkanes: —, Morawetz (*23*); □, our data.

calorimetric determination carried in our laboratory), we have evaluated their molar enthalpies of sublimation at 298.15 K by summing the heats of fusion at the $\Delta_{vap}H°_T$. The obtained values, reported in Table 4 as a function of n_C, can be represented by the equation

$$\Delta_{sub}H°_{298.15}/(\text{kJ mol}^{-1}) = (52.5 \pm 3.7) + (5.3 \pm 0.1)\cdot n_C \quad (4)$$

This equation was determined not considering the value for eicosane (179.5 kJ mol^{-1}), which is probably too high also for the too high heat of fusion value selected from the literature (69.5 kJ mol^{-1}) (*24–26*). The dependence of $\Delta_{sub}H°_{298.15}$ on n_C leads to an increment of this parameter for the CH_2 increment of about 5.3 kJ mol^{-1}, a value lower than those (8.7 and 8.9 kJ mol^{-1}) derivable from two linear expressions reported by Morawetz (*23*): $\Delta_{sub}H°_{298.15}/(\text{kcal mol}^{-1}) = -1.031 + 2.082n_C$ and $-2.05 + 2.14n_C$, both obtained from the enthalpies of vaporization treated in two different ways.

From Figure 4, in which are reported the $\Delta_{sub}H°_{298.15}$ of Morawetz (*23*) and those from our study, it can be concluded that also in this case the behavior of the dependence of the enthalpies of sublimation on n_C is similar to that found for the enthalpies vaporization, with a break of the slope at about $n_C = 20$.

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