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# Vaporization Enthalpies at 298.15 K of the *n*-Alkanes from C<sub>21</sub> to C<sub>28</sub> and C<sub>30</sub>

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The vaporization enthalpies of the *n*-alkanes reported previously in the literature are corrected to 298.15 K and compared to vaporization enthalpies obtained from correlation-gas chromatography. The vaporization enthalpies at 298.15 K for C<sub>21</sub>–C<sub>28</sub> and C<sub>30</sub> are critically evaluated, and the accuracy of measurements derived from some recent torsion effusion measurements is questioned. A series of vaporization enthalpies consistent with the gas chromatographic results are obtained which correlate with the number of carbon atoms in the molecule. The following vaporization enthalpies in kJ·mol<sup>-1</sup> at 298.15 K are recommended: heneicosane, 107.3 ± 2.5; docosane, 113.7 ± 0.3; tricosane, 118.5 ± 0.4; tetracosane, 125.6 ± 2.7; pentacosane, 126.9 ± 1.4; hexacosane, 139.1 ± 7.7; heptacosane, 145.6 ± 8; octacosane, 151.4 ± 8.4; triacontane, 162.1 ± 8.0.

## Introduction

There has been considerable interest, both recent and past, in the vapor pressures and enthalpies of vaporization of the *n*-alkanes. Vaporization enthalpies at 298.15 K for the *n*-alkanes with fewer than 21 carbons have been established (Ruzicka and Majer, 1994; Pedley *et al.*, 1986; Majer and Svoboda, 1985). Although a considerable amount of vapor pressure data is available for the *n*-alkanes greater than C<sub>21</sub> and vaporization enthalpies at other temperatures have been reported, vaporization enthalpies at 298.15 K are not available.

We have had an interest in using the *n*-alkanes as standards in evaluating vaporization enthalpies of hydrocarbons by the technique of correlation-gas chromatography (Chickos *et al.*, 1995a). The *n*-alkanes behave ideally as standards, resulting in very good linear relationships when vaporization enthalpies,  $\Delta_{\text{vap}}H_m^\circ(T \text{ or } 298.15 \text{ K})$ , are plotted against enthalpies of transfer from solution to vapor,  $\Delta_{\text{slr}}^\circ H_m$ . The lack of  $\Delta_{\text{vap}}H_m^\circ(298.15 \text{ K})$  data for the larger *n*-alkane compounds has limited the size of the hydrocarbons and related molecules we have been able to study with this technique. In a recent study (Chickos *et al.*, 1995b), the vaporization enthalpies of a collection of large quaternary hydrocarbons have been reported. In the process of collecting the  $\Delta_{\text{vap}}H_m^\circ(T_m)$  data for the larger *n*-alkanes to use as standards, we realized large discrepancies associated with the experimental data. This work is an attempt to identify the most reliable values and the uncertainty associated with each for the series, C<sub>21</sub>–C<sub>30</sub>.

Recently, vaporization enthalpies based on a new series of torsion effusion experiments have been reported (Piacente *et al.*, 1994). These results are in considerable variance with much of the earlier data in the literature. This report by Piacente and co-workers is particularly troublesome since much of the earlier work in this area has also been reported by this laboratory (Piacente and Scardala, 1990; Piacente *et al.*, 1991; Pompilli and Piacente, 1990). The new report apparently corrects for some temperature uncertainties in the apparatus used in their earlier torsion effusion measurements. Of concern to us is the fact that although a good linear correlation between  $\Delta_{\text{vap}}H_m^\circ(298.15 \text{ K})$  and the number of carbon atoms has been observed for the linear alkanes from C<sub>4</sub> to C<sub>17</sub> by Morawetz (1972) and others (Chickos *et al.*, 1981), a discontinuity in the slope is observed at C<sub>20</sub> using the new torsion effusion

data. This leads to a different linear relationship for  $\Delta_{\text{vap}}H_m^\circ(298.15 \text{ K})$  vs carbon number for the *n*-alkanes from C<sub>20</sub> to C<sub>30</sub>. Ruzicka and Majer (1994) have carefully reviewed the vapor pressure literature for the alkanes from C<sub>5</sub> to C<sub>20</sub>. They showed that the measurements of Piacente *et al.*, (1991) for eicosane consistently differed from the results of other workers, suggesting a problem with this data. This paper focuses on the vaporization enthalpies reported for C<sub>21</sub> to C<sub>28</sub> and C<sub>30</sub> by Piacente and Scardala (1990), Piacente *et al.* (1994), and others (Chirico *et al.*, 1989; Grenier-Loustalot *et al.*, 1981; Piacente *et al.*, 1991; Ruzicka and Majer, 1994; Sasse *et al.*, 1988; Stull, 1947; TRC, 1996).

To determine whether the discontinuity in the slope observed at C<sub>20</sub> and continuing through the higher alkanes is real or an artifact of the new measurements, we have collected all of the readily available experimental vapor pressure data on the *n*-alkanes from C<sub>21</sub> to C<sub>28</sub> and computed the vaporization enthalpy,  $\Delta_{\text{vap}}H_m^\circ(T_m)$ , at the mean temperature of the experiments,  $T_m$ . The resulting vaporization enthalpies have been adjusted from the mean temperature of measurement,  $T_m$ , to 298.15 K using the literature procedure (Chickos *et al.*, 1993a,b) described below. The resulting  $\Delta_{\text{vap}}H_m^\circ(298.15 \text{ K})$  data have been critically evaluated using the simple criteria described below. The vaporization enthalpies that satisfied these criteria were then separated into two groups. One consisted of the most recent torsion effusion results of Piacente *et al.* (1994) and the other of the vaporization enthalpies reported by other workers. The former are referred to as P94 and the latter as the other literature values (OLV). Vaporization enthalpies that did not meet the criteria cited below were not considered further. The two groups of vaporization enthalpies were evaluated independently, using the procedure of correlation-gas chromatography.

## Experimental Section

The *n*-alkanes C<sub>15</sub>, C<sub>16</sub>, C<sub>18</sub>, C<sub>20</sub>, C<sub>22</sub>–C<sub>27</sub>, C<sub>28</sub>, and C<sub>30</sub> were obtained from Aldrich Chemical Co. The chemical purities were high, but this is not of concern since chromatography generally separates the minor components. The GC correlation experiments reported in Tables 1–3 were performed on an HP 5890 Series II gas chromatograph run isothermally on a 60 m BD-5 capillary column at a head pressure of 204 kPa using He as the carrier gas

**Table 1. GC Retention Times for a Series of *n*-Alkanes in Seconds**

<i>T</i> /K	473.1	483	492.8	502.8	512.7
carbon tetrachloride	124	125	127	128	129
pentadecane	188	175	165	158	153
hexadecane	221	199	183	171	163
octadecane	330	275	237	211	193
eicosane	558	429	344	286	247
docosane	1045	748	557	432	348
tricosane	1452	1008	727	545	425

**Table 2. GC Retention Times for a Series of *n*-Alkanes in Seconds**

<i>T</i> /K	533.15	543.25	553.35	563.35	573.15
carbon tetrachloride	143	145	147	148	149
eicosane	215	201	192	184	178
docosane	270	242	221	206	196
tricosane	311	271	243	222	208
pentacosane	434	357	305	267	241
hexacosane	524	420	349	299	264
octacosane	795	604	477	389	329

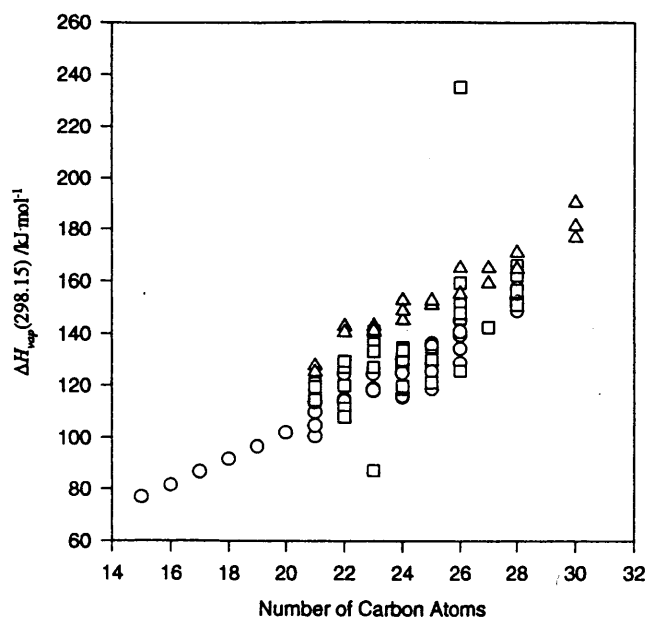
**Table 3. GC Retention Times for a Series of *n*-Alkanes in Seconds**

<i>T</i> /K	512.45	522.35	533.45	542.45	552.35
carbon tetrachloride	130.1	131.3	132.1	133.3	134.3
hexacosane	856.2	636.6	491.1	392.9	326.7
heptacosane	1106	801	601.3	469	380.1
octacosane	1442	1019	745.7	566.1	447.7
triacontane	2488	1685	1178	852.6	646

as described previously (Chickos *et al.*, 1995a,b). The column temperature was monitored independently using a Kluge 51 K/J thermometer. Constant temperature was maintained within  $\pm 0.1$  deg. Carbon tetrachloride was used as the nonretained standard. Corrected retention times,  $t_r$ , were calculated by subtracting the corresponding retention time of carbon tetrachloride from each value at each temperature. Two separate mixtures were prepared because of the large differences in retention times. Each series of experiments were performed twice to ensure reproducibility. The reproducibility of the slopes of the lines obtained in the two runs varied from 0.8 to 1.6% with the largest deviations associated with the smallest slope. The results of only one of the series are reported here.

## Results

The experimental vapor pressure (*p*)–temperature (*T*) data reported in the literature were collected, and vaporization enthalpies were calculated from the slope of the line generated from a linear regression analysis of a  $\ln(p)$  vs.  $1/T$  plot, according to the Clausius–Clapeyron equation. The results,  $\Delta_{\text{vap}}H_m^\circ(T_m)$ , which were obtained from the slope of the line are summarized in column 2 of Table 4. The vaporization enthalpies were calculated using data covering the temperature range shown in column 3, typically 40 K (data rounded to the nearest degree for inclusion in this table). For some compounds, vapor pressure data are available over a larger temperature range. In these instances, because of limitations associated with the heat capacity adjustments to the standard state as discussed below, vapor pressure data closest to the standard state were chosen. The mean temperature of this range,  $T_m$ , is listed in column 4 and is the upper temperature used in eq 2. The correlation coefficient,  $r^2$ , which characterizes the quality of the least squares fit, is listed in column 5. The uncertainty in the vaporization enthalpy was derived from the standard deviation generated from the uncertainty in the slope obtained by the regression analysis. The recommended vaporization enthalpies of pentane to eicosane are also included in Table 4. The vaporization enthalpies of pentane to eicosane have been critically reviewed and



**Figure 1.** Experimental vaporization enthalpies of the *n*-alkanes from dodecane to octacosane as a function of the number of carbon atoms. Circles refer to all literature vaporization enthalpies (298.15 K) except those evaluated from the torsion effusion data of Piacente *et al.* Data derived from torsion effusion measurements are shown in squares (Piacente *et al.* 1994) and triangles (Piacente *et al.* 1991).

their values, with perhaps the exception of eicosane, are not in dispute (Ruzicka and Majer, 1994; Majer and Svoboda 1985; Pedley *et al.*, 1986). The vaporization enthalpies of some of the smaller alkanes have been used as standards to evaluate the reliability of the vaporization enthalpies of the larger *n*-alkanes as discussed below.

Correction of  $\Delta_{\text{vap}}H_m^\circ(T_m)$  to 298.15 K was achieved as reported previously (Chickos *et al.*, 1993a,b) by using the following relationships:

$$\Delta_g^1 C_p(T_m - 298.15 \text{ K})/\text{J}\cdot\text{mol}^{-1} = (10.58 + 0.26C_{\text{pl,est}})(T_m - 298.15) \quad (1)$$

$$\Delta_{\text{vap}}H_m^\circ(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = \Delta_{\text{vap}}H_m^\circ(T_m) + (10.58 + 0.26C_{\text{pl,est}})(T_m - 298.15)/1000 \quad (2)$$

$\Delta_g^1 C_p$  in eq 1 refers to the difference in heat capacities of the liquid and gas phase and  $C_{\text{pl,est}}$  in eqs 1 and 2 refers to the heat capacity of the liquid which was estimated by a group additivity approach. The relationship between  $\Delta_g^1 C_p$  and  $C_{\text{pl,est}}$  in eq 1 was obtained by correlating differences in experimental heat capacities between the liquid and gas phases at 298 K with the heat capacity of 289 organic liquids as estimated by a group additivity approach. Equation 1 was the relationship obtained from this correlation. Heat capacities for both the liquid and gas phases are temperature dependent. Equation 1 is based on the assumption that  $\Delta_g^1 C_p$  will be less sensitive to temperature. This assumption was tested by comparing the predictions of eq 2 to differences observed in experimental vaporization enthalpies measured at temperature *T*, and a reference temperature, usually 298.15 K. Vaporization enthalpies of a total of 126 different compounds were examined. Vaporization enthalpies of these materials were reported over the temperature range 260–370 K. Excluding compounds that form hydrogen bonds (15/126), the standard error associated with eq 2 in these estimations was 490 J·mol<sup>-1</sup>. The fact that the applicability and reliability of eq 2 has not been tested over a larger temperature range is the major factor prompting the use

Table 4. Summary of the Literature Vaporization Enthalpies of the *n*-Alkanes from C<sub>12</sub> to C<sub>30</sub> Exclusive of C<sub>28</sub><sup>a</sup>

compound	$\Delta_{\text{vap}}H_m^\circ(T_m)/$ kJ·mol <sup>-1</sup>	TR/K	$T_m/K$	$r^2$	$C_p(l)/$ J·mol <sup>-1</sup> ·K <sup>-1</sup>	$\Delta_f^1C_p(\Delta T)/$ kJ·mol <sup>-1</sup>	$\Delta_{\text{vap}}H_m^\circ(298.15\text{ K})/$ kJ·mol <sup>-1</sup>	EM	S	lit.
pentane							26.4			b
hexane							31.5			b
heptane							36.6			b
octane							41.6			b
nonane							46.6			b
decane							51.4			b
undecane							56.6			b
dodecane							61.5			b
tridecane							66.7			b
tetradecane							71.7			b
pentadecane							76.8			b
hexadecane							81.4			b
heptadecane							86.5			b
octadecane							91.4			b
nonadecane							96.4			b
eicosane							101.8			b
eicosane	110.8 ± 1.9	351–384	368	0.9967	644	12.3 ± 1.0	123.1 ± 2.1	TE	n	c
eicosane	109.3 ± 1.8	347–388	368	0.9969	644	12.3 ± 1.0	121.7 ± 2.0	TE	n	c
heneicosane	89.6 ± 1.1	379–434	407	0.9997	676	20.2 ± 1.6	109.8 ± 1.9	T	u	d
heneicosane	74.4 ± 0.4	412–457	435	0.9648	676	25.4 ± 2.0	100.5 ± 2.1	T	n	d
heneicosane	105.9 ± 2.0	359–398	379	0.9962	676	15 ± 1.2	120.9 ± 2.3	TE	n	d
heneicosane	100.5 ± 1.6	352–393	373	0.9956	676	13.9 ± 1.1	114.4 ± 2.0	TE	n	d
heneicosane	110.1 ± 7.7	329–367	348	0.9713	676	9.3 ± 0.7	119.4 ± 7.8	KE	n	d
heneicosane	74.4 ± 0.4	426–496	461	0.9999	676	30.4 ± 2.4	104.7 ± 2.5	NA	u	e
heneicosane	112.1 ± 0.6	365–400	382	0.9997	676	15.7 ± 1.3	127.7 ± 1.4	TE	n	f
heneicosane	109.6 ± 2.9	366–399	383	0.9937	676	15.7 ± 1.3	125.3 ± 3.2	TE	n	f
heneicosane	92.7 ± 0.8	393–428	411	0.9998	676	21.0 ± 1.7	113.7 ± 1.9	NA	u	g
docosane	92.3 ± 1.4	379–434	407	0.9995	708	21.1 ± 1.6	113.4 ± 2.2	T	u	d
docosane	87.1 ± 3.7	420–461	441	0.9661	708	27.7 ± 2.1	114.8 ± 4.3	T	n	c
docosane	104.5 ± 2.5	358–399	379	0.996	708	15.6 ± 1.2	120.1 ± 2.8	TE	n	c
docosane	111.7 ± 4.5	358–397	378	0.9875	708	15.4 ± 1.2	127.1 ± 4.6	TE	n	c
docosane	96.5 ± 8.9	360–388	374	0.8935	708	14.7 ± 1.1	111.2 ± 9.0	TE	n	c
docosane	112.5 ± 2.3	365–406	386	0.9952	708	17 ± 1.3	129.5 ± 2.6	TE	n	c
docosane	97.2 ± 4.8	341–366	354	0.9878	708	10.8 ± 0.8	108 ± 4.9	KE	n	c
docosane	99.4 ± 0.6	353–393	373	0.9998	708	14.6 ± 1.1	114.0 ± 1.3	EG	u	h
docosane	124.8 ± 0.7	372–410	391	0.9996	708	18.1 ± 1.4	142.9 ± 1.6	TE	n	f
docosane	122.7 ± 3.5	372–408	390	0.9944	708	17.9 ± 1.4	140.6 ± 3.8	TE	n	f
docosane	95.5 ± 0.9	402–438	420	0.9998	708	23.7 ± 1.8	119.2 ± 2.0	NA	u	g
tricosane	87.4 ± 4.4	426–471	448	0.9657	740	30.5 ± 2.3	117.9 ± 4.9	T	n	c
tricosane	86.2 ± 4.0	438–480	459	0.9831	740	32.7 ± 2.4	118.9 ± 4.7	T	u	c
tricosane	117.4 ± 3.9	370–412	391	0.9914	740	18.8 ± 1.4	136.2 ± 4.1	TE	n	c
tricosane	108.4 ± 2.0	369–411	390	0.9968	740	18.6 ± 1.4	127.1 ± 2.4	TE	n	c
tricosane	114.5 ± 1.9	369–413	391	0.9972	740	18.9 ± 1.4	133.4 ± 2.4	TE	n	c
tricosane	75 ± 7.8	348–368	358	0.9582	740	12.1 ± 0.9	87.1 ± 7.9	KE	n	c
tricosane	79.5 ± 0.4	443–515	489	0.9999	740	38.7 ± 2.9	118.2 ± 2.9	NA	u	e
tricosane	123 ± 1.1	378–416	397	0.9991	740	20 ± 1.5	143.1 ± 1.9	TE	n	f
tricosane	122.7 ± 1.2	370–409	389	0.9989	740	18.3 ± 1.4	141 ± 1.8	TE	n	f
tricosane	122.4 ± 2.2	374–409	392	0.9964	740	18.9 ± 1.4	141.3 ± 2.6	TE	n	f
tricosane	98.1 ± 7.2	411–477	429	0.9999	740	26.5 ± 2.0	124.6 ± 2.1	NA	u	g
tetracosane	104.5 ± 12.5	379–434	407	0.9724	772	22.9 ± 1.6	127.4 ± 12.6	T	u	d
tetracosane	82.2 ± 8.7	501–523	512	0.9183	772	45.2 ± 3.2	127.4 ± 9.2	T	n	c
tetracosane	83.8 ± 0.7	457–529	493	0.9999	772	41.1 ± 2.9	124.9 ± 3.0	NA	u	e
tetracosane	96.9 ± 4.8	383–421	402	0.9737	772	21.8 ± 1.6	118.8 ± 5.0	TE	n	c
tetracosane	111 ± 7.4	397–425	411	0.9615	772	23.8 ± 1.7	134.8 ± 7.6	TE	n	c
tetracosane	99.1 ± 1.6	376–416	396	0.9968	772	20.7 ± 1.5	119.8 ± 2.1	TE	n	c
tetracosane	104.5 ± 2.2	400–438	419	0.9945	772	25.5 ± 1.8	130 ± 2.8	TE	n	c
tetracosane	119.1 ± 6.4	343–393	368	0.9913	772	14.7 ± 1.0	133.8 ± 6.5	KE	n	c
tetracosane	82.5 ± 4.1	451–487	455	0.9735	772	33 ± 2.3	115.5 ± 4.7	T	u	i
tetracosane	92.6 ± 2.6	461–497	479	0.9924	772	38.1 ± 2.7	130.7 ± 3.7	T	u	i
tetracosane	81.3 ± 8.6	457–469	463	0.9576	772	34.8 ± 2.5	116.1 ± 8.9	T	n	i
tetracosane	109.4 ± 0.9	374–413	393	0.9997	772	20.1 ± 1.4	129.5 ± 1.7	EG	u	h
tetracosane	123.8 ± 2.0	388–413	401	0.9985	772	21.6 ± 1.5	145.4 ± 2.5	TE	n	f
tetracosane	129.3 ± 1.2	387–417	410	0.9992	772	23.6 ± 1.7	152.9 ± 2.1	TE	n	f
tetracosane	126.3 ± 1.0	386–425	406	0.999	772	22.7 ± 1.6	148.9 ± 1.9	TE	n	f
tetracosane	100.2 ± 1.1	419–456	437	0.9998	772	29.4 ± 2.1	129.6 ± 2.3	NA	u	g
pentacosane	104.6 ± 1.0	379–434	407	0.9998	804	23.8 ± 1.6	128.4 ± 1.9	T	u	d
pentacosane	86.5 ± 5.3	461–491	476	0.9818	804	39 ± 2.7	125.5 ± 5.9	T	u	i
pentacosane	71.7 ± 6.1	495–531	513	0.9394	804	47.1 ± 3.2	118.8 ± 6.9	T	n	c
pentacosane	104.2 ± 2.6	403–444	424	0.9923	804	27.6 ± 1.9	131.8 ± 3.2	TE	n	c
pentacosane	104.8 ± 6.5	400–432	416	0.9351	804	25.8 ± 1.8	130.6 ± 6.7	TE	n	c
pentacosane	93.7 ± 5.3	413–435	424	0.9659	804	27.5 ± 1.9	121.2 ± 5.6	TE	n	c
pentacosane	113.4 ± 6.6	356–394	375	0.9899	804	16.9 ± 1.2	130.2 ± 6.7	KE	n	c
pentacosane	96.2 ± 6.2	465–498	482	0.9637	804	40.2 ± 2.8	136.5 ± 6.8	T	n	i
pentacosane	125.1 ± 1.3	402–434	418	0.999	804	26.3 ± 7.6	151.4 ± 7.7	TE	n	f
pentacosane	126 ± 1.3	397–428	413	0.999	804	25.1 ± 7.6	151.1 ± 7.7	TE	n	f
pentacosane	127.6 ± 1.6	398–428	413	0.9985	804	25.2 ± 7.6	152.8 ± 7.7	TE	n	f
pentacosane	103.1 ± 1.1	427–464	445	0.9998	804	32.3 ± 2.2	135.4 ± 2.5	NA	u	g
hexacosane	109.7 ± 1.1	380–434	407	0.9998	835	24.7 ± 1.6	134.4 ± 1.9	T	u	d

Table 4. Continued

compound	$\Delta_{\text{vap}}H_m^{\circ}(T_m)/$ kJ·mol <sup>-1</sup>	TR/K	$T_m$ /K	$r^2$	$C_p(l)/$ J·mol <sup>-1</sup> ·K <sup>-1</sup>	$\Delta_g^1C_p(\Delta T)/$ kJ·mol <sup>-1</sup>	$\Delta_{\text{vap}}H_m^{\circ}(298.15 \text{ K})/$ kJ·mol <sup>-1</sup>	EM	S	lit.
hexacosane	76.9 ± 4.4	506–546	526	0.9356	835	51.9 ± 3.4	128.8 ± 5.6	T	n	c
hexacosane	122.7 ± 15.1	405–443	424	0.9969	835	28.6 ± 1.9	151.3 ± 15.2	TE	n	c
hexacosane	135.4 ± 5.8	391–417	404	0.9767	835	24.1 ± 1.6	159.5 ± 6.0	TE	n	c
hexacosane	117.9 ± 4.9	412–432	422	0.9816	835	28.2 ± 1.9	146.1 ± 5.2	TE	n	c
hexacosane	120.5 ± 3.1	406–431	419	0.9897	835	27.4 ± 1.8	148 ± 3.6	TE	n	c
hexacosane	108.4 ± 4.2	356–392	374	0.9956	835	17.3 ± 1.1	125.7 ± 4.3	KE	n	c
hexacosane	104.9 ± 6.9	461–488	475	0.9626	835	40.2 ± 2.6	145.1 ± 7.4	T	n	i
hexacosane	101.1 ± 6.2	476–508	492	0.9783	835	44.1 ± 2.9	145.2 ± 6.8	T	u	i
hexacosane	99.1 ± 2.9	456–495	475	0.9905	835	40.3 ± 2.7	139.5 ± 3.9	T	u	i
hexacosane	135.5 ± 3.0	420–437	429	0.9938	835	29.7 ± 2.0	165.2 ± 3.6	TE	n	f
hexacosane	129.5 ± 2.3	391–433	412	0.997	835	25.9 ± 1.7	155.5 ± 2.8	TE	n	f
hexacosane	129.5 ± 2.3	392–431	412	0.9969	835	25.8 ± 1.7	155.3 ± 2.9	TE	n	f
hexacosane	206.4 ± 15.1	415–434	424	0.93	835	28.7 ± 1.9	235.1 ± 15.3	TE	n	c
hexacosane	105.5 ± 0.9	435–472	453	0.9998	835	35.3 ± 2.3	140.9 ± 2.5	NA	u	g
heptacosane	122.5 ± 3.9	377–390	384	0.997	867	20.1 ± 1.3	142.6 ± 4.1	KE	n	c
heptacosane	129.8 ± 2.7	408–440	423	0.9957	867	29.5 ± 1.9	159.4 ± 3.3	TE	n	f
heptacosane	135.4 ± 1.4	411–438	424	0.9992	867	29.8 ± 1.9	165.2 ± 2.4	TE	n	f
octacosane	128.9 ± 9.3	398–434	416	0.9948	899	28.8 ± 1.8	157.6 ± 9.4	T	u	d
octacosane	107.9 ± 1.3	453–493	473	0.9996	899	42.8 ± 2.6	150.7 ± 2.9	IP	u	j
octacosane	110.3 ± 1.1	449–487	468	0.9998	899	41.5 ± 2.5	151.8 ± 2.8	NA	u	g
octacosane	98.1 ± 6.1	508–546	527	0.9562	899	56.0 ± 3.4	154.0 ± 7.0	T	n	c
octacosane	114.7 ± 3.0	426–469	448	0.9937	899	36.6 ± 2.2	151.2 ± 3.8	TE	n	c
octacosane	127.8 ± 3.0	447–465	456	0.9951	899	38.5 ± 2.4	166.2 ± 3.8	TE	n	c
octacosane	125.7 ± 7.2	438–458	448	0.9711	899	36.6 ± 2.2	162.3 ± 7.6	TE	n	c
octacosane	139.2 ± 27.7	356–383	370	0.8937	899	17.4 ± 1.1	156.6 ± 27.7	KE	n	c
octacosane	105.4 ± 3.4	473–514	494	0.9926	899	47.7 ± 2.9	153.2 ± 4.5	T	u	i
octacosane	100.9 ± 3.7	474–515	495	0.9896	899	48 ± 2.9	148.9 ± 4.7	T	u	i
octacosane	138.4 ± 1.9	408–456	432	0.9967	899	32.7 ± 2.0	171.1 ± 2.8	TE	n	f
octacosane	132.4 ± 1.1	407–455	431	0.9989	899	32.5 ± 2.0	164.8 ± 2.3	TE	n	f
triacontane	143.4 ± 2.8	422–466	444	0.9984	963	38.0 ± 2.6	181.4 ± 3.8	TE	n	f
triacontane	150.5 ± 1.6	431–472	452	0.9984	963	40.0 ± 2.7	190.6 ± 3.1	TE	n	f
triacontane	140.7 ± 2.6	427–447	437	0.9961	963	36.2 ± 2.5	176.8 ± 3.6	TE	n	f

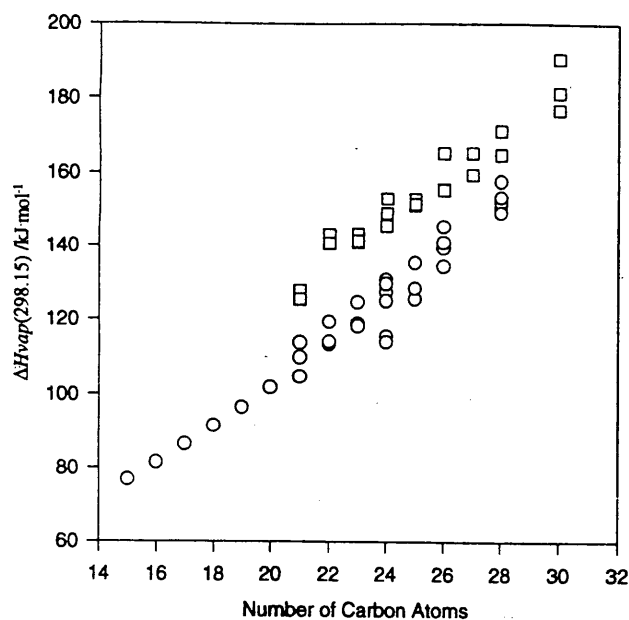
<sup>a</sup> The following summarize the contents of each column: TR, temperature range of the measurements;  $T_m$ , mean temperature;  $r^2$ , square of the correlation coefficient;  $C_p(l)$ , calculated heat capacity of the liquid;  $\Delta T$ ,  $T_m - 298.15 \text{ K}$ ; S, status of each vaporization enthalpy according to the criteria listed in the text (u, used; n, not used in calculating the mean other literature value ( $OLV_{\text{mean}}$ ) as defined in the text); lit., literature reference; EM, experimental methods used to measure vapor pressure including: transpiration (T), vacuum equilibrium still (VES), torsion effusion (TE), Knudsen effusion; (KE), electronic gauge (EG), inclined piston (IP), ebulliometry (E), not available (NA). <sup>b</sup> Ruzicka and Majer, 1994. <sup>c</sup> Piacente *et al.*, 1991. <sup>d</sup> Grenier-Loustalot *et al.*, 1981. <sup>e</sup> Stull, 1947. <sup>f</sup> Piacente *et al.*, 1994. <sup>g</sup> TRC, 1996. <sup>h</sup> Sasse *et al.*, 1988. <sup>i</sup> Piacente and Scardala, 1990. <sup>j</sup> Chirico *et al.*, 1989.

of vapor pressure data as close to 298.15 K as possible in this analysis.

The estimated heat capacity of the liquid *n*-alkane and the heat capacity adjustment are listed in columns 6 and 7 of Table 4 for each compound. This correction is not trivial in most cases and accounts for a significant portion of the vaporization enthalpy at 298.15 K. The uncertainty included in the heat capacity correction term was derived from the standard deviation of  $15 \text{ J·mol}^{-1}\text{·K}^{-1}$  associated in estimating experimental values of  $\Delta_g^1C_p(298.15 \text{ K})$  (Chickos *et al.*, 1993a). The vaporization enthalpies at 298.15 K are reported in column 8 and when available, the type of apparatus used to make the vapor pressure measurements is indicated in column 9. Column 10 indicates whether each respective value was used (u) or not used (n) in generating the OLV. The last column in the Table 4 lists the reference to the experimental data.

The experimental vaporization enthalpies of Table 4 when plotted against the number of carbon atoms results in Figure 1. The scatter observed in this figure may be considered normal in view of the experimental difficulties associated with measuring low vapor pressures, the large number of different contributors and techniques used to generate the data, and the significant changes in technology that have occurred over the period of time covered by these reports. One aspect of the results of this figure does cause concern. The most recent measurements, the torsion effusion measurements of the Piacente group (1994), identified by the triangles in the figure, are consistently higher than any of the other data. These latest measurements also place doubt on the earlier torsion effusion

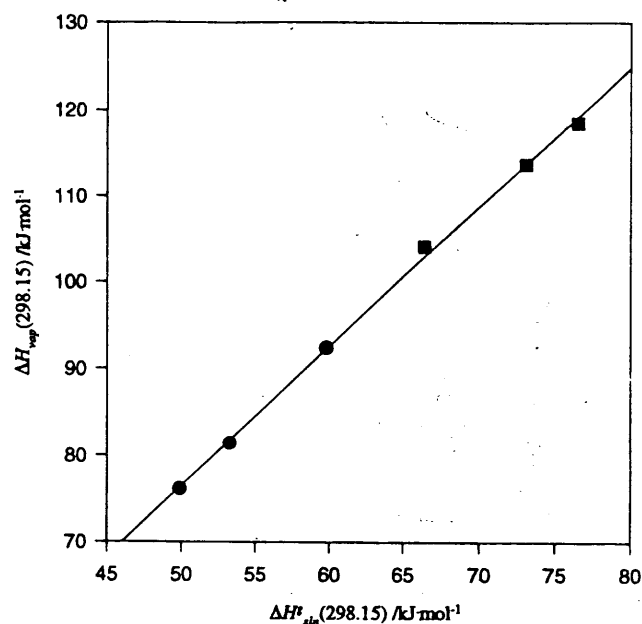
measurements reported by this group, identified in the figure by the squares. In order to try to resolve the ambiguities generated by this new data, we have critically evaluated all the experimental data (squares, triangles, and circles) and have separated surviving data into two groups. One group consists of the new torsion effusion data reported by the Piacente group (squares (1994)). The remaining data were evaluated and either rejected or combined into a second group which we have referred to as the OLV. The criteria used for rejecting data were as follows. Earlier torsion effusion and Knudsen effusion results reported by the Piacente group (both presumably measured on the same apparatus (triangles, Figure 1)) in which difficulties in monitoring the sample temperature were experienced, were not considered any further. The other transpiration data reported by this group were considered along with other literature data, provided the data satisfied the following criterion. Vaporization enthalpies were considered only if the square of the correlation coefficient,  $r^2$  (column 5 of Table 4), characteristic of each plot, exceeded 0.97. While selection of this value is arbitrary, it establishes some lower limit on the precision of the measurements. In fact, plots of  $\ln(p)$  vs  $1/T$  of data characterized by values of  $r^2$  less than 0.97 displayed noticeable scatter or curvature. Column 10 of Table 4 indicates the status of each vaporization enthalpy with regard to whether an individual measurement satisfied this criterion (u, used; n, not used). Data satisfying these criteria were used in evaluating the mean other literature value ( $OLV_m$ ) for each compound.



**Figure 2.** Critically evaluated vaporization enthalpies of the *n*-alkanes at 298.15 K. Squares refer to results derived from P94<sub>m</sub> torsion effusion measurements (Piacente *et al.*, 1994), and circles represent mean literature values (OLV<sub>m</sub>) listed in column 2 of Table 4.

Application of this protocol to the data in Table 4 resulted in Figure 2. The squares refer to the new torsion effusion results of Piacente *et al.* (1994), while the circles refer to the remaining data of Table 4 which satisfied these criteria. These results are summarized in first three columns of Table 5. Column 1 identifies each *n*-alkane; the OLV<sub>m</sub> is included in column 2 and the mean torsion effusion results of Piacente *et al.* (1994), P94<sub>m</sub>, are included as column 3 of the table. The uncertainty in each column refers to the standard deviation of the mean.

We have used the gas chromatographic results of Table 1 and the known vaporization enthalpies of pentadecane, hexadecane, and octadecane to differentiate between these two discordant sets of data listed in columns 2 and 3 of Table 5. It has been shown previously that plots of  $\Delta_{\text{vap}}H_m^\circ(298.15 \text{ K})$  against the "enthalpy of transfer" from solution to the vapor,  $\Delta_{\text{sln}}^s H_m$ , for the *n*-alkanes result in a good linear correlation (Chickos *et al.*, 1995a,b). We have used this anticipated behavior here to differentiate between the two sets of vaporization data listed in Table 5. Enthalpies of transfer,  $\Delta_{\text{sln}}^s H_m$ , have been measured for the series pentadecane, hexadecane, octadecane, eicosane, docosane, and tricosane, by plotting  $\ln(1/t_r)$  vs  $1/T$ . The term  $t_r$  is



**Figure 3.** Vaporization enthalpies of selected *n*-alkanes at 298.15 K plotted against their respective enthalpies of transfer as evaluated from the data in Table 1. Solid circles refer to accepted vaporization enthalpies of C<sub>15</sub>, C<sub>16</sub>, and C<sub>18</sub> at 298.15 K, and the solid squares refer to OLV<sub>m</sub> of C<sub>20</sub>, C<sub>22</sub>, and C<sub>23</sub> as defined in the text. The line was calculated by a least squares fit of the data generated from the solid circles.

defined in the Experimental Section. A plot of  $\ln(1/t_r)$  vs  $1/T$  (K<sup>-1</sup>) for each alkane in Table 1 results in a straight line. Using the retention times for octadecane in Table 1 as an example, this plot results in the following equation:

$$\ln(t_{\text{octadecane}} - t_{\text{carbon tetrachloride}}) = -(7193 \pm 55)(1/T) + (9.88 \pm 0.007) \quad (r^2 = 0.9998) \quad (3)$$

The slopes of these lines (all  $r^2 > 0.9997$ ) when multiplied by the gas constant,  $R$ , afford  $\Delta_{\text{sln}}^s H_m$ . The values of  $\Delta_{\text{sln}}^s H_m$  resulting from the data in Table 1 are listed in column 4 of Table 5. Figures 3 and 4 show the results of plotting the vaporization enthalpies of pentadecane, hexadecane, and octadecane (solid circles) and the OLV<sub>m</sub> of eicosane, docosane, and tricosane (column 2) or  $\Delta_{\text{vap}}H_m^\circ(298.15 \text{ K})$  from the P94<sub>m</sub> torsion effusion measurements (column 3), against  $\Delta_{\text{sln}}^s H_m$  (column 4, Table 5), respectively. The lines drawn in the two figures are those obtained by least squares treatment of the vaporization enthalpies of pentadecane, hexadecane, and octadecane (solid circles). Combining all the data from pentadecane

**Table 5.** Summary of the Mean  $\Delta_{\text{vap}}H_m^\circ(298.15 \text{ K})$  from the Literature, Those from the Torsion Effusion Measurements of Piacente *et al.* (1994), and Those Calculated from  $\Delta_{\text{sln}}^s H_m$  in kJ·mol<sup>-1</sup>

	$\Delta_{\text{vap}}H_m^\circ(298.15 \text{ K})$		$\Delta_{\text{sln}}^s H_m$			$\Delta_{\text{vap}}H_m^\circ(298.15 \text{ K})$			
	OLV <sub>m</sub>	P94 <sub>m</sub>	from Table 1	from Table 2	from Table 3	from eq 4	from eq 5	from eq 6	from eq 7
pentadecane	76.8		49.9			75.8 ± 2.7	72.8 ± 14		
hexadecane	81.4		53.3			81.4 ± 2.8	82.2 ± 15		
heptadecane	86.5								
octadecane	91.4		59.8			92.2 ± 3.1	100.0 ± 17		
nonadecane	96.4								
eicosane	101.8	122.4 ± 0.7	66.4	59.2		103.3 ± 3.4	118.2 ± 18	101.9 ± 5.9	
heneicosane	109.4 ± 2.6	126.5 ± 1.2							
docosane	115.6 ± 1.9	141.7 ± 1.1	73.1	65.0		114.5 ± 3.7	136.7 ± 20	114.2 ± 6.5	
tricosane	120.5 ± 2.0	141.8 ± 1.2	76.5	68.0		120.2 ± 3.9	145.9 ± 21	120.5 ± 6.8	
tetracosane	126.2 ± 2.3	149.1 ± 1.3							
pentacosane	129.8 ± 2.9	151.8 ± 1.0		73.9				133.0 ± 7.3	
hexacosane	140.0 ± 2.2	158.6 ± 6		76.8	78.3			139.1 ± 7.6	
heptacosane		162.3 ± 2.9			81.3				146 ± 8
octacosane	152.4 ± 1.5	168 ± 8.3		82.6	84.4			151.4 ± 8.2	
triacontane		182.9 ± 4.1			90.2				164 ± 8

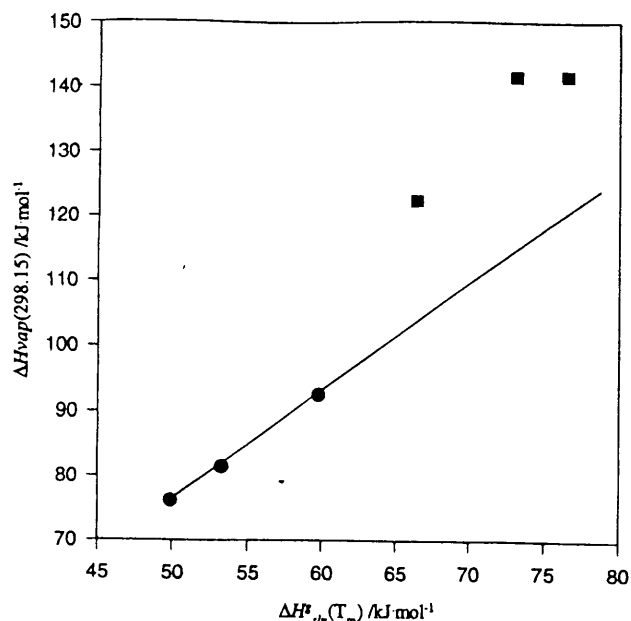


Figure 4. Vaporization enthalpies of selected *n*-alkanes at 298.15 K plotted against their respective enthalpies of transfer as evaluated from the data in Table 1. Solid circles refer to accepted vaporization enthalpies of C<sub>15</sub>, C<sub>16</sub>, and C<sub>18</sub> at 298.15 K, and the solid squares refer to mean torsion effusion results (Piacente *et al.*, 1994) of C<sub>20</sub>, C<sub>22</sub>, and C<sub>23</sub>. The line was calculated by a least squares fit of the data generated from the solid circles.

to tricosane for both plots results in the following two equations:

$$\Delta_{\text{vap}}H_m^{\circ}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.67 \pm 0.049)\Delta_{\text{sln}}^{\circ}H_m - (7.55 \pm 1.2) \quad (r^2 = 0.9966) \quad (4)$$

$$\Delta_{\text{vap}}H_m^{\circ}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (2.74 \pm 0.26)\Delta_{\text{sln}}^{\circ}H_m - (63.7 \pm 6.1) \quad (r^2 = 0.966) \quad (5)$$

An examination of the two plots and the parameters associated with eqs 4 and 5 allows a clear distinction between the two sets of data. The results of Figure 3 and its associated equation, eq 4, give a better correlation and

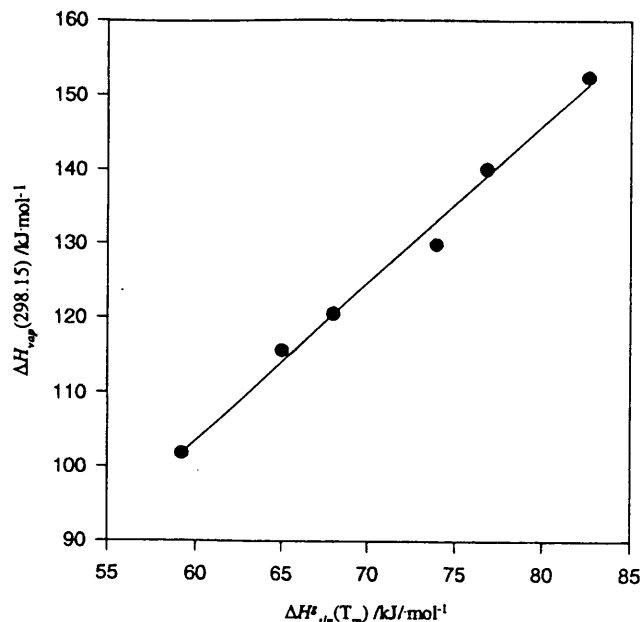


Figure 5. Mean vaporization enthalpies of C<sub>20</sub>, C<sub>22</sub>, C<sub>23</sub>, C<sub>25</sub>, C<sub>26</sub>, and C<sub>28</sub> plotted against their respective enthalpies of transfer as evaluated from the data in Table 2. The line passing through the data was calculated by the method of least squares.

fit to the data. The values of  $\Delta_{\text{vap}}H_m^{\circ}(298.15 \text{ K})$  calculated from eqs 4 and 5 are summarized in columns 7 and 8 of Table 5. We conclude from these plots that the correlation-GC results do not support the discontinuity at C<sub>20</sub> suggested by the P94<sub>m</sub> torsion effusion data.

As a means of testing how well the OLV<sub>mean</sub> for some of the higher alkanes correlate with  $\Delta_{\text{sln}}^{\circ}H_m$ , we have also calculated  $\Delta_{\text{sln}}^{\circ}H_m$  for the series of *n*-alkanes C<sub>20</sub>, C<sub>22</sub>, C<sub>23</sub>, C<sub>25</sub>, C<sub>26</sub>, and C<sub>28</sub> from the retention time data in Table 2.  $\Delta_{\text{sln}}^{\circ}H_m$  values were evaluated as before by plotting  $\ln(1/t_r)$  vs  $1/T$  (all  $r^2 > 0.9998$ ) and multiplying the slope of the line by the gas constant. The results of plotting the OLV<sub>m</sub> of these alkanes against the corresponding  $\Delta_{\text{sln}}^{\circ}H_m$  are shown in Figure 5. The line drawn in this figure was generated by consideration of all the data points and is characterized by the following parameters:

Table 6. Comparison of Recommended  $\Delta_{\text{vap}}H_m^{\circ}(298.15 \text{ K})$  Values to the Values Estimated by Equations 5 and 9 for the *n*-Alkanes in  $\text{kJ}\cdot\text{mol}^{-1}$

compound	$\Delta_{\text{vap}}H_m^{\circ}(298.15 \text{ K})$					
	OLV <sub>m</sub>	from eq 9	recommended value	from eq 8	from eq 10	from eq 11
pentane	26.4	26.5	26.4	23.8	2	26.4
hexane	31.5	31.5	31.5	29.2	31.5	31.1
heptane	36.6	36.5	36.6	34.7	36.4	35.8
octane	41.6	41.5	41.6	40.1	41.4	40.5
nonane	46.6	46.5	46.6	45.5	46.4	45.1
decane	51.4	51.5	51.4	50.9	51.4	49.8
undecane	56.6	56.5	56.6	56.4	56.3	54.5
dodecane	61.5	61.5	61.5	61.8	61.3	59.2
tridecane	66.7	66.5	66.7	67.3	66.3	63.9
tetradecane	71.7	71.6	71.7	72.7	71.3	68.6
pentadecane	76.8	76.6	76.8	78.1	76.2	73.3
hexadecane	81.4	81.6	81.4	83.5	81.2	77.9
heptadecane	86.5	86.6	86.5	88.9	86.2	82.6
octadecane	91.4	91.6	91.4	94.4	91.2	87.3
nonadecane	96.4	96.6	96.4	99.8	96.1	92
eicosane	101.8	101.6	101.8	105.2	101.1	96.7
heneicosane	109.4 ± 2.6	106.6	109.4 ± 2.6	110.6	106.1	101.4
docosane	115.6 ± 1.9	111.6	115.6 ± 1.9	116	111.1	106.1
tricosane	120.5 ± 2.0	116.6	120.5 ± 2.0	121.5	116	110.8
tetracosane	126.2 ± 2.3	121.6	125.6 ± 2.7	126.9	121	115.4
pentacosane	129.8 ± 2.9	126.6	126.9 ± 1.4	132.3	126	120.1
hexacosane	140.0 ± 2.2	131.6	139.1 ± 7.7	137.8	131	124.8
heptacosane		136.6	145.1 ± 8.0	143.2	136	129.5
octacosane	152.4 ± 2.9	141.6	151.4 ± 8.4	148.6	140.9	134.2
triacontane		151.6	162.9 ± 8.0	159.5	150.9	143.6

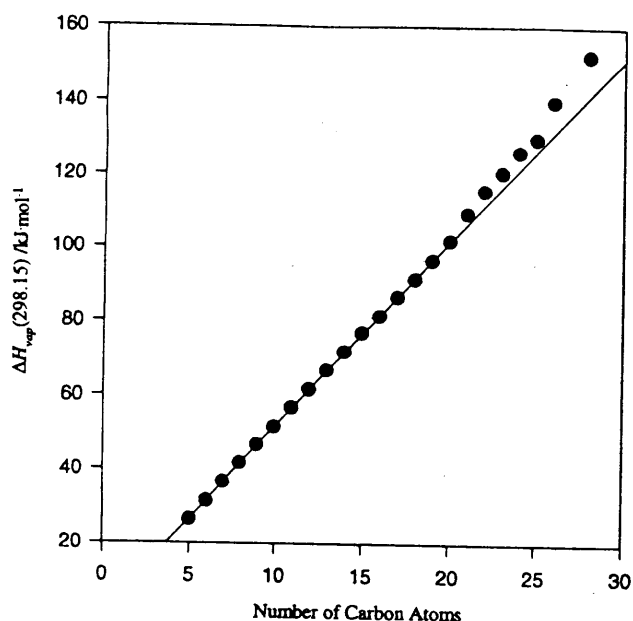


Figure 6. Recommended vaporization enthalpies of the *n*-alkanes at 298.15 K from pentane to triacontane exclusive of C<sub>29</sub> as a function of the number of carbon atoms. The line passing through the data was derived from the vaporization enthalpies of pentane through eicosane by the method of least squares and extrapolated to the larger alkanes.

$$\Delta_{\text{vap}}H_m^\circ(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (2.12 \pm 0.1)\Delta_{\text{sln}}^\circ H_m - (23.4 \pm 1.9) \quad (r^2 = 0.9913) \quad (6)$$

The vaporization enthalpies calculated from this equation are summarized in column 8 of Table 5. A good correlation is obtained although more caution should be exercised here, as is discussed below.

Vaporization enthalpies for C<sub>27</sub> and C<sub>30</sub> have previously been measured by Piacente *et al.* (1991, 1994). However since these measurements were obtained on the same apparatus as those that have been questioned, we decided to measure these by correlation gas-chromatography. Retention time measurements are reported in Table 3 for C<sub>26</sub>, C<sub>27</sub>, C<sub>28</sub>, and C<sub>30</sub>. Enthalpies of transfer were obtained as before and are listed in column 6 of Table 5. Using the values for C<sub>26</sub> and C<sub>28</sub> obtained from previous correlation-GC measurements as standards, the vaporization enthalpies listed in the last column of Table 5 were obtained from a plot of  $\Delta_{\text{vap}}H_m^\circ(298.15 \text{ K})$  vs  $\Delta_{\text{sln}}^\circ H_m$  of the standards. The vaporization enthalpies were calculated from the following equation and the uncertainties listed in this column were estimated.

$$\Delta_{\text{vap}}H_m^\circ(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (2.01)\Delta_{\text{sln}}^\circ H_m - (18.1) \quad (7)$$

The correlation obtained by plotting the mean of  $\Delta_{\text{vap}}H_m^\circ$  (298.15 K) against the number of carbon atoms is shown in Figure 6. A good linear relationship is observed for all the *n*-alkanes from C<sub>5</sub> to C<sub>30</sub> exclusive of C<sub>29</sub>. The equation of the line fitted to all the data by a least squares analysis is given by

$$\Delta_{\text{vap}}H_m^\circ(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (5.43 \pm 0.06)n_c - (3.3 \pm 2.3) \quad (r^2 = 0.9969) \quad (8)$$

The predictions of eq 8 are given in column 5 of Table 6. A closer inspection of the data, however, reveals some curvature in the line beginning at approximately C<sub>20</sub>. This slight curvature is illustrated in Figure 6 by the line drawn through the data. This line was obtained from a linear least squares treatment of the vaporization data from pentane to eicosane followed by extrapolation. The equation of this line is given by

$$\Delta_{\text{vap}}H_m^\circ(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (5.0 \pm 0.007)n_c - 1.49 \pm 0.14 \quad (r^2 = 0.9999) \quad (9)$$

and the predictions of eq 9 are given in column 3 of Table 6.

Vaporization enthalpies appear to be a good linear function of the number of carbon atoms from the range C<sub>5</sub>–C<sub>20</sub>. It is quite possible that over a larger range, some curvature might be observed in this relationship. An alternative, and in our opinion, a more probable source of this curvature is the presence of a small systematic error in OLV<sub>m</sub> that increases with carbon number. One likely source of this error is the large contribution of the heat capacity term ( $\Delta_g^1 C_p(\Delta T)$ ). Any systematic error inherent in this contribution is likely to be largest at the end of the scale where both  $\Delta_g^1 C_p$  and  $\Delta T$  are at their largest values. Examining the average heat capacity adjustment,  $\langle C_p T_m \rangle$ , used for each compound (column 7 of Table 4) in the correlation resulted in the following (reported in kJ·mol<sup>-1</sup>; the uncertainty is the standard deviation associated with each adjustment and is included to illustrate the numerical spread of the correction associated with each compound): heneicosane, (23.8 ± 4.6); docosane, (19.8 ± 3.8); tricosane, (32.6 ± 5.0); pentacosane, (31.7 ± 6.2); hexacosane, (36.1 ± 7.3); octacosane, (41.8 ± 7.0). The average heat capacity adjustment fluctuates for the series heneicosane to pentacosane but is largest for hexacosane and octacosane. Deviations of the OLV<sub>m</sub> from the values calculated from eq 9 (Table 6, columns 2 and 3, respectively) are small for most compounds (within two standard deviations of the precision) but become significantly larger for hexacosane and octacosane (more than three standard deviations). In view of this fact, we recommend using the vaporization enthalpies for hexacosane and octacosane obtained by correlation-gas chromatography. The vaporization enthal-

Table 7. Phase Transition Enthalpies for the Solid *n*-Alkanes in kJ·mol<sup>-1</sup>

compound	$\Delta_{\text{vap}}H_m^\circ(298.15 \text{ K})$	$\Delta_{\text{fus}}H_m^\circ(T_{\text{fus}}) + \Delta_{\text{trans}}H_m^\circ(>298.15 \text{ K})$	$\Delta_{\text{sub}}H_m^\circ(298.15 \text{ K})$
octadecane	91.4	61.2 ± 0.5 (5)	152.6
nonadecane	96.4	45.7 ± 1.8 (3)	142.1
eicosane	101.8	68.7 ± 2.3 (6)	170.5
heneicosane	109.4 ± 2.6	62.8 ± 0.5 (2)	172.2
docosane	115.6 ± 1.9	77.2 ± 0.9 (6)	192.8
tricosane	120.5 ± 2.0	75.4 ± 1.5 (3)	195.9
tetracosane	125.6 ± 2.7	84.7 ± 1.8 (6)	210.3
pentacosane	126.9 ± 1.4	82.1 ± 2.0 (4)	209.0
hexacosane	139.1 ± 7.7	93.4 ± 0.9 (7)	232.5
heptacosane	145.1 ± 8.0	89.4 (1)	234.5
octacosane	151.4 ± 8.4	99.4 ± 1.5 (4)	250.8
triacontane	162.9 ± 8.0	105.8 ± 0.7 (2)	268.7



pies of these two compounds obtained by correlation-gas chromatography are nearly identical with the  $OLV_m$ , but the precision associated with these measurements is more likely in line with the probable uncertainties in these numbers. Similar errors are also proposed for the vaporization enthalpies of heptacosane and triacontane which have been derived from the vaporization enthalpies of hexacosane and octacosane.

The vaporization enthalpies at 298.15 K recommended for the linear  $n$ -alkanes from  $C_5$  to  $C_{28}$  and  $C_{30}$  are given in the fourth column of Table 6. All except the last four entries are from either the recommended values reported by Ruzicka and Majer (1994) or the mean of the other literature values ( $OLV_m$ ) corrected to 298.15 K. Also included in Table 6 are predictions by the equation derived previously by Morawetz (1972) for the  $n$ -alkanes:

$$\Delta_{vap}H_m^\circ(298.15\text{ K})/\text{kJ}\cdot\text{mol}^{-1} = 4.97n_c + 1.61 \quad (10)$$

and a more general equation reported by Chickos *et al.* (1981) to estimate the vaporization enthalpies of hydrocarbons of any structure:

$$\Delta_{vap}H_m^\circ(298.15\text{ K})/\text{kJ}\cdot\text{mol}^{-1} = 4.69\bar{n} + 1.3n_Q + 3.0 \quad (11)$$

The term  $n_c$  in eq 10 refers to the number of carbon atoms, while the terms  $\bar{n}$  and  $n_Q$  in eq 11 refer to the number of nonquaternary and quaternary carbons, respectively. The predictions of both equations are included in the last two columns of Table 6. In estimating the vaporization enthalpy of the  $n$ -alkanes, the standard deviations between the predictions of eq 8–11 and the recommended values in  $\text{kJ}\cdot\text{mol}^{-1}$  are 2.2, 3.8, 3.9, and 5.8, respectively. Agreement is poorest for eq 11 but still quite good considering its simplicity and broader range of applicability.

Starting with octadecane, the larger  $n$ -alkanes are all solids at room temperature. The  $\Delta_{vap}H_m^\circ(298.15\text{ K})$  values listed in Table 6 are those calculated with the aid of eq 2 for the supercooled isotropic liquid. Table 7 summarizes both vaporization and fusion enthalpies for these solids,  $\Delta_{fus}H_m^\circ(T_{fus})$ , and their sum, eq 12, which is usually a very good approximation of their sublimation enthalpy. The fusion enthalpies are from Domalski and Hearing (1996) and are averages of the values reported in the compendium. Also incorporated in the fusion enthalpies in Table 6 are those solid–solid phase changes occurring above 298.15 K,  $\Delta_{trans}H_m^\circ(>298.15\text{ K})$ . The number in parentheses in column 3 is the number of entries available for each compound. Uncertainties are the standard deviation of the mean.

$$\Delta_{sub}H_m^\circ(298.15\text{ K}) \approx \Delta_{vap}H_m^\circ(298.15\text{ K}) + \Delta_{fus}H_m^\circ(T_{fus}) + \Delta_{trans}H_m^\circ(>298.15\text{ K}) \quad (12)$$

In summary, the vaporization enthalpies of the  $n$ -alkanes from  $C_{21}$  to  $C_{30}$  exclusive of  $C_{29}$  have been corrected to 298.15 K and the vaporization enthalpies have been found to correlate with the number of carbon atoms. The vaporization enthalpies of the  $n$ -alkanes from  $C_5$  to  $C_{30}$

appear to be a linear function of the number of carbons as described previously. The recent torsion effusion measurements of Piacente and Scardala (1990) and Piacente *et al.* (1994) reported for  $C_{21}$ – $C_{30}$  are not particularly compatible with earlier vaporization enthalpies and the correlation-gas chromatographic results. The accuracy of the results reported for  $C_{31}$ – $C_{38}$  by these workers is similarly subject to question.

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