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Vapor Pressures and Vaporization Enthalpies of the *n*-Alkanes from C_{21} to C_{30} at $T = 298.15$ K by Correlation Gas Chromatography

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The temperature dependence of gas chromatographic retention times for *n*-heptadecane to *n*-triacontane is reported. These data are used to evaluate the vaporization enthalpies of these compounds at $T = 298.15$ K, and a protocol is described that provides vapor pressures of these *n*-alkanes from $T = 298.15$ to 575 K. The vapor pressure and vaporization enthalpy results obtained are compared with existing literature data where possible and found to be internally consistent. Sublimation enthalpies for *n*-C_{17} to *n*-C_{30} are calculated by combining vaporization enthalpies with fusion enthalpies and are compared when possible to direct measurements.

Introduction

The *n*-alkanes serve as excellent standards for the measurement of vaporization enthalpies of hydrocarbons.[1,2] Recently, the vaporization enthalpies of the *n*-alkanes reported in the literature were examined and experimental values were selected on the basis of how well their vaporization enthalpies correlated with their enthalpies of transfer from solution to the gas phase as measured by gas chromatography.[3] A plot of the vaporization enthalpies of the *n*-alkanes as a function of the number of carbon atoms is given in Figure 1. The plot is remarkably linear from C_5 to C_{20} but does show some curvature above C_{20}. This curvature was explained on the basis of a systematic error in adjusting the vaporization enthalpies of the *n*-alkanes, C_{21} to C_{28} and C_{30}, found in the literature, from the temperature of measurement to $T = 298.15$ K.[3] Since these *n*-alkanes exhibit very low vapor pressures at ambient temperatures, vapor pressure measurement for most of these materials were conducted at temperatures that required a significant temperature adjustment to $T = 298.15$ K. This temperature adjustment ranged from 9.3 to 51.9 kJ·mol^{-1}.[3] In view of this curvature and our continuing interest in using the larger *n*-alkanes as standards for correlation gas chromatography measurements (c-gc), we have reexamined these values and would like to report the results of our measurements of both vaporization enthalpy and vapor pressure at $T = 298.15$ K. The results of our c-gc experiments of the *n*-alkanes from C_{21} to C_{30} were obtained using a method best described as a stepladder extrapolation. The results of this stepladder approach are tested by comparison of $\Delta_l{}^gH_m(T_m)$ values and vapor pressures obtained by c-gc to those measured by other methods at temperatures where experimental data are available.

Correlation gas chromatography has proven to be quite successful in providing vaporization enthalpies of both liquids and solids. The technique relies on the linear correlation observed between enthalpies of transfer from solution to the vapor, $\Delta_{sln}{}^gH_m$, as measured by gas chromatography and the vaporization enthalpy ($\Delta_l{}^gH_m$) of a series of standards. The vaporization enthalpies of the standards have usually been chosen at $T = 298.15$ K, but the correlation works for other temperatures as well. The linear correlation that is observed between $\Delta_{sln}{}^gH_m$ and $\Delta_l{}^gH_m$ is empirical and can be criticized as lacking a theoretical basis. In this article we would like to provide a simple mathematical basis for the linear correlation observed. The correlation is applied to the evaluation of vapor pressures and enthalpies of vaporization of the *n*-alkanes from C_{21} to C_{30} at $T = 298.15$ K.

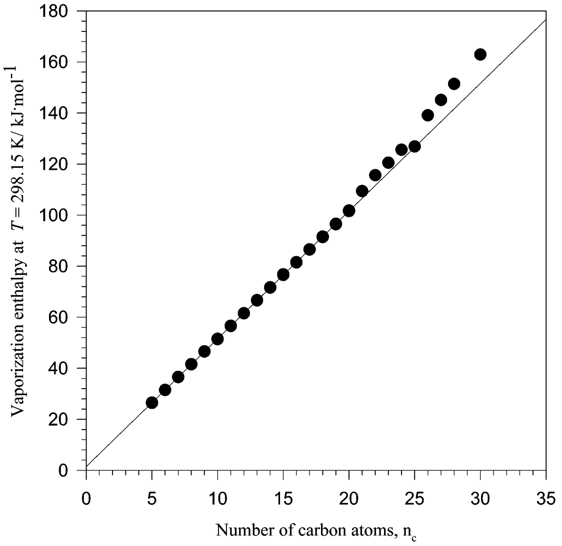

Figure 1. Vaporization enthalpies of the *n*-alkanes; the straight line represents the results obtained by a linear regression analysis of the recommended vaporization enthalpies of *n*-C_5 to C_{20}.[11]

Discussion

Enthalpies of transfer from solution to the vapor, $\Delta_{sln}{}^gH_m$, are measured by gas chromatography by measuring the retention times of a mixture consisting of both standards and target solutes as a function of temperature. The retention times, *t*, are adjusted for the dead volume of the column by measuring the retention time of an unretained solute, usually the solvent. Since the retention time of the unretained solute is governed by the flow rate of the carrier, its retention time as a function of temperature

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behaves differently from those of the other solutes. The viscosity of the carrier gas, usually He in our experiments, increases with temperature. Thus, the retention time of the nonretained reference, t_{nrr}, increases while that for the other solutes decreases with temperature. This observation is useful in ensuring a reliable measurement of the time needed to traverse the column at each temperature. The adjusted retention time, $t_a = t - t_{\mathrm{nrr}}$, measures the amount of time the solute spends on the stationary phase, and this time is inversely proportional to the compound's vapor pressure above the condensed phase. A plot of $\ln(1/t_a)$ versus $1/T$ (K^{-1}) results in a linear plot with a slope equal to $-\Delta^{g}{}_{\mathrm{sln}}H_m(T_m)/R$. This technique has been used by others, notably the work of Fuchs et al.,[4] who pioneered the use of enthalpies of transfer in conjunction with enthalpies of solution to evaluate vaporization enthalpies.

The term $\Delta^{g}{}_{\mathrm{sln}}H_m(T_m)$ can be equated in a thermodynamic cycle to the sum of the vaporization enthalpy measured at $T = T_m$ and the enthalpy of solution or adsorption ($\Delta_{\mathrm{sln}}H_m$) of each solute on the stationary phase of the column as shown below. The sensitivity of the flame ionization detector ensures dilute concentrations of solute, and since the solute dissolves in the stationary phase, the same thermodynamic cycle applies to both solids and liquids.

$$\Delta^{g}{}_{\mathrm{sln}}H_m(T_m) = \Delta^{g}{}_{l}H_m(T_m) + \Delta_{\mathrm{sln}}H_m(T_m) \qquad (1)$$

Peacock and Fuchs measured $\Delta^{g}{}_{\mathrm{sln}}H_m(T_m)$ values of a series of compounds by gas chromatography and adjusted the results for temperature. They combined enthalpies of vaporization and solution in the liquid stationary phase of the column, DC 200, and compared their results to $\Delta^{g}{}_{\mathrm{sln}}H_m(T_m)$ values adjusted for temperature to $T = 298.15$ K. The thermochemical cycle yielded results that were not exactly identical but were very similar and were linearly correlated.[4]

In correlation gas chromatography, $\Delta^{g}{}_{\mathrm{sln}}H_m(T_m)$ values are correlated directly with the vaporization enthalpies of the standards at the temperature of interest, usually at $T = 298.15$ K. Provided the standards are appropriately chosen in relation to each other and to the target solutes, a linear correlation is obtained between $\Delta^{g}{}_{\mathrm{sln}}H_m(T_m)$ and $\Delta^{g}{}_{l}H_m(T_m)$. The correlation equation derived from known vaporization enthalpies is then used to evaluate the vaporization enthalpies of the target solutes.[5] The following narrative describes the origin of this correlation.

In the thermodynamic cycle outlined by eq 1, all of the enthalpies are referenced to the same temperature. In c-gc, $\Delta^{g}{}_{\mathrm{sln}}H_m(T_m)$ measured at $T = T_m$ is correlated to $\Delta^{g}{}_{l}H_m(298.15\ \mathrm{K})$; the correlation results in the following slope:

$$\text{slope} = \Delta^{g}{}_{\mathrm{sln}}H_m(T_m)/\Delta^{g}{}_{l}H_m(298.15\ \mathrm{K}) \qquad (2)$$

Appropriate substitution of eq 1 into eq 2 results in the following:

$$\text{slope} = [\Delta^{g}{}_{l}H_m(T_m) + \Delta_{\mathrm{sln}}H_m(T_m)]/\Delta^{g}{}_{l}H_m(298.15\ \mathrm{K}) \qquad (3)$$

Vaporization enthalpies of hydrocarbons are known to exhibit excellent group properties. Hydrocarbons can be estimated quite accurately by a variety of simple relationships, including the following:[6]

$$\Delta^{g}{}_{l}H_m(298.15\ \mathrm{K}) = (4.64 \pm 0.13)n_c + (2.93 \pm 0.8); \quad r = 0.965 \qquad (4)$$

In this equation, n_c refers to the number of carbon atoms. This equation takes the general form $mn_c + b$. Although this equation was derived for vaporization enthalpies at $T = 298.15$ K, the temperature selection is arbitrary and it is reasonable to assume that a similar equation of the same type, $m'n_c + b'$, could also be derived for vaporization enthalpies at $T = T_m$, where m' and b' are appropriate constants.[6,7] Vaporization enthalpies at $T = 298.15$ K differ from those at $T = T_m$ by differences in the heat capacities of the liquid and gas phases, and both properties are known to be modeled by group additivity.[8,9] In addition, vaporization enthalpies at both $T = 298.15$ K and $T = T_m$ could be modeled exactly by these equations by simply allowing the intercepts, b and b', to vary. Enthalpies of solution are small in comparison to vaporization enthalpies[10] and also can be modeled by group additivity, $m''n_c + b''$. This modeling can also be exact if b'' is allowed to vary. Substituting these linear functions into eq 3 and combining similar terms results in eq 5, where $m_{\mathrm{sln}} = (m' + m'')$ and $b_{\mathrm{sln}} = (b' + b'')$.

$$\text{slope} = [m_{\mathrm{sln}}n_c + b_{\mathrm{sln}}]/[mn_c + b] \qquad (5)$$

As long as b_{sln} and b are small in comparison to $m_{\mathrm{sln}}n_c$ and mn_c, respectively, the correlation of $\Delta_{\mathrm{sln}}{}^{g}H_m(T_m)$ with $\Delta_{l}{}^{g}H_m(298.15\ \mathrm{K})$ will be linear because the ratio $[m_{\mathrm{sln}}n_c + b_{\mathrm{sln}}]_{\mathrm{tranfer}}/[mn_c + b]_{\mathrm{vap}}$ is a hyperbolic function approaching its asymptote, m_{sln}/m. Similar arguments can also be made for hydrocarbon derivatives containing a single functional group or multiple functional groups provided the number and type of functional groups in the correlation are kept constant. Alternatively, the hydrocarbon portion can be kept constant and the number of identical functional groups varied. In either of these instances, it would be necessary to define n_c differently.

Experimental Section

All *n*-alkanes were purchased from the Aldrich Chemical Co. and were used without any further purification. Each was analyzed by gas chromatography and found to be at least 99 mol % pure. Correlation gas chromatography experiments were performed on an HP 5890A series II gas chromatograph equipped with a split/splitless capillary injection port and a flame ionization detector run at a split ratio of 100/1. Retention times were recorded to three significant figures following the decimal point on a HP 3989A integrator. The instrument was run isothermally using a 30 m SPB-5 capillary column. Helium was used as the carrier gas. At the temperatures of the experiments, the retention time of the solvent, CH_2Cl_2, increased with increasing temperature. This is a consequence of the increase in viscosity of the carrier gas with temperature; it is the criterion used to confirm that the solvent is not being retained on the column. The retention times of the solvent were used to determine the dead volume of the column. Adjusted retention times, t_a, were calculated by subtracting the measured retention time of the solvent from the retention time of each analyte as a function of temperature over a 30 K range. Column temperatures were controlled by the gas chromatograph and were monitored independently by using a Fluke 51 K/J thermometer. Temperature was maintained constant by the gas chromatograph to ±0.1 K.

Results

Experimental retention times are presented in Table 1 for a series of mixtures. A plot of $\ln(1/t_a)$ versus $1/T$ (K^{-1})

Table 1. Retention Times

	retention times, *t*/min, for C_{14} to C_{20}						
	T/K = 434.3	T/K = 439.3	T/K = 444.2	T/K = 449.1	T/K = 454.1	T/K = 459	T/K = 463.8
methylene chloride	1.251	1.215	1.246	1.216	1.222	1.228	1.249
tetradecane	3.039	2.695	2.485	2.29	2.145	2.022	1.942
pentadecane	4.107	3.558	3.205	2.887	2.643	2.451	2.288
hexadecane	5.827	4.933	4.344	3.807	3.409	3.084	2.805
heptadecane	8.329	6.907	5.939	5.097	4.47	3.959	3.54
octadecane	12.283	9.994	8.403	7.065	6.071	5.265	4.624
nonadecane	18.549	14.836	12.2	10.075	8.487	7.219	6.211
eicosane	28.345	22.305	17.935	14.57	12.04	10.076	8.522

	retention times, *t*/min, for C_{17} to C_{23}						
	T/K = 493.8	T/K = 498.9	T/K = 503.8	T/K = 508.9	T/K = 513.9	T/K = 518.9	T/K = 523.9
methylene chloride	1.721	1.747	1.746	1.765	1.779	1.792	1.816
heptadecane	2.974	2.849	2.722	2.624	2.556	2.472	2.435
octadecane	3.477	3.276	3.093	2.941	2.83	2.712	2.645
nonadecane	4.182	3.88	3.61	3.375	3.202	3.035	2.926
eicosane	5.144	4.685	4.295	3.952	3.695	3.459	3.294
heneicosane	6.496	5.826	5.255	4.743	4.368	4.034	3.787
docosane	8.37	7.392	6.56	5.811	5.275	4.799	4.44
tricosane	10.923	9.498	8.295	7.232	6.468	5.798	5.288

	retention times, *t*/min, for C_{19} to C_{25}						
	T/K = 524.05	T/K = 529	T/K = 534.1	T/K = 539.25	T/K = 544.25	T/K = 549.25	T/K = 553.25
methylene chloride	1.822	1.82	1.847	1.858	1.888	1.935	1.981
nonadecane	2.912	2.785	2.698	2.621	2.579	2.565	2.565
eicosane	3.271	3.096	2.965	2.856	2.785	2.75	2.733
heneicosane	3.77	3.52	3.327	3.17	3.06	2.993	2.95
docosane	4.421	4.072	3.797	3.577	3.412	3.303	3.225
tricosane	5.262	4.78	4.397	4.09	3.856	3.69	3.567
tetracosane	6.365	5.701	5.174	4.751	4.425	4.182	4.001
pentacosane	7.79	6.887	6.167	5.588	5.139	4.8	4.543

	retention times, *t*/min, for C_{21} to C_{27}						
	T/K = 508.7	T/K = 513.8	T/K = 518.9	T/K = 523.9	T/K = 528.9	T/K = 534	T/K = 539
methylene chloride	1.162	1.155	1.141	1.119	1.127	1.115	1.115
heneicosane	3.201	2.898	2.595	2.379	2.188	2.04	1.919
docosane	3.972	3.54	3.12	2.827	2.551	2.344	2.174
tricosane	4.917	4.319	3.76	3.354	2.987	2.708	2.483
tetracosane	6.258	5.412	4.645	4.088	3.581	3.201	2.9
pentacosane	7.92	6.734	5.735	4.962	4.297	3.791	3.395
hexacosane	10.197	8.514	7.192	6.132	5.244	4.574	4.04
heptacosane	13.07	10.71	9.055	7.573	6.425	5.555	4.843

	retention times, *t*/min, for C_{23} to C_{30}						
	T/K = 528.9	T/K = 533.9	T/K = 539	T/K = 544.1	T/K = 549.1	T/K = 554.1	T/K = 559
methylene chloride	1.516	1.49	1.455	1.48	1.416	1.451	1.483
tricosane	4.027	3.611	3.235	2.979	2.726	2.605	2.53
tetracosane	4.817	4.254	3.762	3.42	3.092	2.929	2.812
pentacosane	5.818	5.064	4.422	3.972	3.548	3.327	3.158
hexacosane	7.105	6.1	5.264	4.67	4.121	3.82	3.586
heptacosane	8.795	7.455	6.349	5.565	4.852	4.447	4.126
octacosane	11.099	9.277	7.802	6.753	5.82	5.254	4.83
nonacosane	14.068	11.609	9.649	8.255	7.04	6.264	5.706
tricontane	17.922	14.64	12.041	10.183	8.594	7.547	6.81

resulted in linear plots whose slopes and intercepts are provided in Table 2. The first mixture in Table 3 lists the enthalpies of transfer from solution to the gas phase measured for the series tetradecane to eicosane (column 2) along with recommended vaporization enthalpies (column 3).[11] As can be seen from column 4, the vaporization enthalpy obtained from the correlation equation, given at the bottom of the series in Table 3, is in excellent agreement with the experimental values. Under C_{17} to C_{23} in Table 3, heptadecane through eicosane were used to evaluate the vaporization enthalpies of henicosane, docosane, and tricosane. Once these vaporization enthalpy values were evaluated, they were then used as needed in subsequent mixtures to evaluate the vaporization enthalpies of the remaining *n*-alkanes. Similarly, the vaporization enthalpies of tetracosane and pentacosane, evaluated in Table 3 under C_{19} to C_{25}, were used as knowns in the remaining mixtures in Table 3. The vaporization enthalpies of the *n*-alkanes heneicosane through tricosane at $T = 298.15$ K were evaluated in this fashion. Uncertainties reported in vaporization enthalpies were calculated from the uncertainty associated with the slope of the line obtained in each correlation.

Figure 2 provides some idea of the quality of the correlations represented by the data in Table 3. Experimental data for comparison of the results reported in Table 3 at $T = 298.15$ K are not available for the C_{21} to C_{30} *n*-alkanes without substantial temperature adjustments. Figure 3 illustrates the vaporization enthalpies of the *n*-alkanes from pentane through tricosane as a function of

Table 2. Equations for the Temperature Dependence of $\ln(1/t_a)$[a]

	$\Delta_{sln}{}^{g}H_m/R$	intercept	r^2
	C_{14} to C_{20} at $T_m = 449$ K		
tetradecane	−6393.8 ± 95	14.161 ± 0.01	0.9989
pentadecane	−6787.9 ± 73	14.597 ± 0.01	0.9994
hexadecane	−7251.5 ± 62	15.190 ± 0.01	0.9996
heptadecane	−7612.6 ± 65	15.587 ± 0.01	0.9996
octadecane	−8014.8 ± 71	16.070 ± 0.01	0.9996
nonadecane	−8457.4 ± 74	16.640 ± 0.01	0.9996
eicosane	−8919.6 ± 85	17.257 ± 0.01	0.9995
	C_{17} to C_{23} at $T_m = 508.8$ K		
heptadecane	−6108.2 ± 78.2	12.148 ± 0.008	0.9992
octadecane	−6489.9 ± 63.8	12.584 ± 0.006	0.9995
nonadecane	−6901.0 ± 58.7	13.077 ± 0.006	0.9996
eicosane	−7270.0 ± 60.5	13.496 ± 0.006	0.9996
heneicosane	−7670.9 ± 65.3	13.974 ± 0.006	0.9996
docosane	−8064.5 ± 71.6	14.439 ± 0.007	0.9996
tricosane	−8451.1 ± 73.9	14.897 ± 0.008	0.9996
	C_{19} to C_{25} at $T_m = 538.7$ K		
nonadecane	−6165.3 ± 125.9	11.692 ± 0.01	0.9979
eicosane	−6483.0 ± 127.6	12.013 ± 0.01	0.9980
heneicosane	−6888.5 ± 127.9	12.487 ± 0.01	0.9983
docosane	−7256.5 ± 121.1	12.906 ± 0.01	0.9986
tricosane	−7619.9 ± 116.3	13.318 ± 0.01	0.9988
tetracosane	−7972.5 ± 112.6	13.713 ± 0.01	0.9990
pentacosane	−8320.7 ± 111.6	14.105 ± 0.01	0.9991
	C_{21} to C_{27} at $T_m = 523.8$ K		
heneicosane	−8494.5 ± 115.7	15.987 ± 0.01	0.9991
docosane	−8898.7 ± 106	16.459 ± 0.01	0.9993
tricosane	−9211.7 ± 98.3	16.784 ± 0.01	0.9994
tetracosane	−9573.1 ± 102.1	17.190 ± 0.01	0.9994
pentacosane	−9903.7 ± 95.7	17.560 ± 0.01	0.9995
hexacosane	−10250.6 ± 92.9	17.954 ± 0.01	0.9996
heptacosane	−10522.2 ± 106.3	18.216 ± 0.01	0.9995
	C_{23} to C_{30} at $T_m = 544$ K		
tricosane	−8729.1 ± 288.3	15.607 ± 0.03	0.9946
tetracosane	−9050.3 ± 285.3	15.942 ± 0.03	0.9951
pentacosane	−9362.2 ± 280.4	16.268 ± 0.03	0.9955
hexacosane	−9691.1 ± 273.3	16.628 ± 0.02	0.996
heptacosane	−10035.9 ± 271.9	17.016 ± 0.02	0.9963
octacosane	−10423.3 ± 273.1	17.474 ± 0.02	0.9966
nonacosane	−10792.9 ± 274.5	17.904 ± 0.02	0.9968
triacontane	−11150 ± 271.3	18.311 ± 0.02	0.997

[a] $\ln(1/t_a) = \Delta_{sln}{}^{g}H_m/R$ + intercept.

the number of carbon atoms. The line in the figure was drawn using the values of the *n*-alkanes from *n*-pentane through to *n*-eicosane; it represents the results of a linear regression analysis. As is illustrated by Figure 3, the correlation through to C_{30} remains quite linear in comparison to Figure 1. A further evaluation of the quality of the data generated for *n*-C_{21} to *n*-C_{30} is provided below.

One of the advantages of using correlation gas chromatography to evaluate vaporization enthalpies is that the choice of reference temperature is arbitrary. Consequently, it is possible to use the retention time data provided in Table 1 to evaluate vaporization enthalpies of the *n*-alkanes at any temperature where experimental data for the standards are available. However, before testing the equations provided in Table 2 for accuracy in evaluating vaporization enthalpies at other temperatures, we would like to demonstrate the usefulness of these equations in providing vapor pressure data as well.

The use of the correlation equations in providing vapor pressure data has been briefly described previously.[4] These equations relate the temperature dependence of the vapor pressure of the solute ($1/t_a$) above the stationary phase of the column over a narrow temperature range. Although these equations would not be expected to be accurate in predicting vapor pressures by themselves, when used with

Table 3. Vaporization Enthalpies (in kJ·mol^{-1}) of the *n*-Alkanes

C_{14} to C_{20}

		$\Delta_l{}^{g}H_m$(298.15 K)	
	$\Delta_{sln}{}^{g}H_m$(449 K)	lit.	calc
tetradecane	53.2	71.7	71.8 ± 1.0
pentadecane	56.4	76.8	76.5 ± 1.0
hexadecane	60.3	81.4	82 ± 1.1
heptadecane	63.3	86.5	86.3 ± 1.2
octadecane	66.6	91.4	91.1 ± 1.3
nonadecane	70.3	96.4	96.4 ± 1.4
eicosane	74.2	101.8	101.9 ± 1.4

$$\Delta_l{}^{g}H_m(298.15\ \text{K}) = (1.436 \pm 0.019)\Delta_{sln}{}^{g}H_m(T_m) - (4.54 \pm 0.35);\ r^2 = 0.9991$$

C_{17} to C_{23}

		$\Delta_l{}^{g}H_m$(298.15 K)	
	$\Delta_{sln}{}^{g}H_m$(508.5 K)	lit.	calc
heptadecane	50.8	86.5	86.4 ± 2.0
octadecane	54.0	91.4	91.4 ± 2.2
nonadecane	57.4	96.4	96.7 ± 2.3
eicosane	60.4	101.8	101.6 ± 2.4
heneicosane	63.8		106.8 ± 2.5
docosane	67.0		111.9 ± 2.7
tricosane	70.3		117.0 ± 2.8

$$\Delta_l{}^{g}H_m(298.15\ \text{K}) = (1.57 \pm 0.04)\Delta_{sln}{}^{g}H_m(T_m) - (6.66 \pm 0.30);\ r^2 = 0.9985$$

C_{19} to C_{25}

		$\Delta_l{}^{g}H_m$(298.15 K)	
	$\Delta_{sln}{}^{g}H_m$(538.7 K)	lit.	calc
nonadecane	51.3	96.4	96.8 ± 2.2
eicosane	53.9	101.8	101.2 ± 2.3
heneicosane	57.2	106.8	106.8 ± 2.5
docosane	60.3	111.9	112.0 ± 2.5
tricosane	63.3	117.0	117.0 ± 2.7
tetracosane	66.3		121.9 ± 2.8
pentacosane	69.2		126.8 ± 2.9

$$\Delta_l{}^{g}H_m(298.15\ \text{K}) = (1.67 \pm 0.042)\Delta_{sln}{}^{g}H_m(T_m) - (11.04 \pm 0.41);\ r^2 = 0.9981$$

C_{21} to C_{27}

		$\Delta_l{}^{g}H_m$(298.15 K)	
	$\Delta_{sln}{}^{g}H_m$(523.8 K)	lit.	calc
heneicosane	70.6	106.3	106.5 ± 2.7
docosane	74.0	111.9	112.4 ± 2.8
tricosane	76.6	117.0	116.8 ± 2.9
tetracosane	79.6	121.9	122.0 ± 3.0
pentacosane	82.3	126.8	126.7 ± 3.1
hexacosane	85.2		131.7 ± 3.2
heptacosane	87.5		135.6 ± 3.3

$$\Delta_l{}^{g}H_m(298.15\ \text{K}) = (1.721 \pm 0.038)\Delta_{sln}{}^{g}H_m(T_m) - (15.02 \pm 0.34);\ r^2 = 0.9985$$

C_{23} to C_{30}

		$\Delta_l{}^{g}H_m$(298.15 K)	
	$\Delta_{sln}{}^{g}H_m$(544 K)	lit.	calc
tricosane	72.6	117.0	117.3 ± 4.1
tetracosane	75.2	121.9	121.9 ± 4.3
pentacosane	77.8	126.8	127.2 ± 4.4
hexacosane	80.6	131.7	131.2 ± 4.6
heptacosane	83.4	135.6	136.1 ± 4.8
octacosane	86.7		141.9 ± 4.9
nonacosane	89.7		147.1 ± 5.1
triacontane	92.7		152.3 ± 5.3

$$\Delta_l{}^{g}H_m(298.15\ \text{K}) = (1.738 \pm 0.057)\Delta_{sln}{}^{g}H_m(T_m) - (-8.82 \pm 0.49);\ r^2 = 0.9968$$

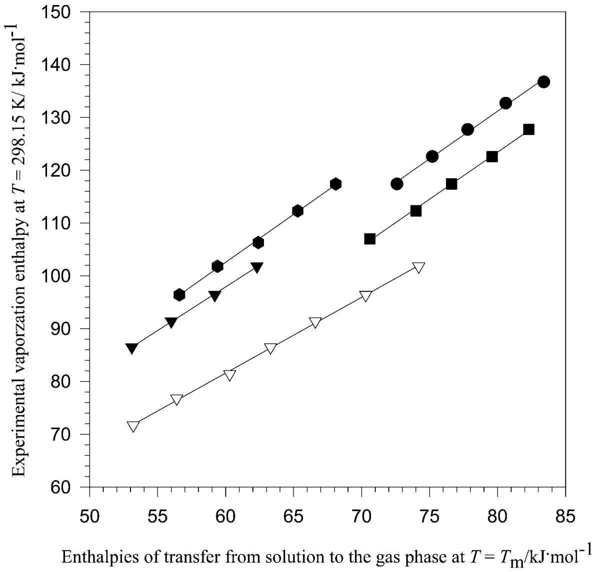

Figure 2. Correlations obtained by plotting vaporization enthalpy at T =298.15 K against the enthalpy of transfer measured at the mean temperature indicated: triangles, n-C_{14} to C_{20} (449 K); solid triangles, n-C_{17} to C_{23} (508.8 K); hexagons, n-C_{19} to C_{25} (538.7 K); squares, n-C_{21} to C_{27} (523.8 K); circles, n-C_{23} to C_{30} (544 K).

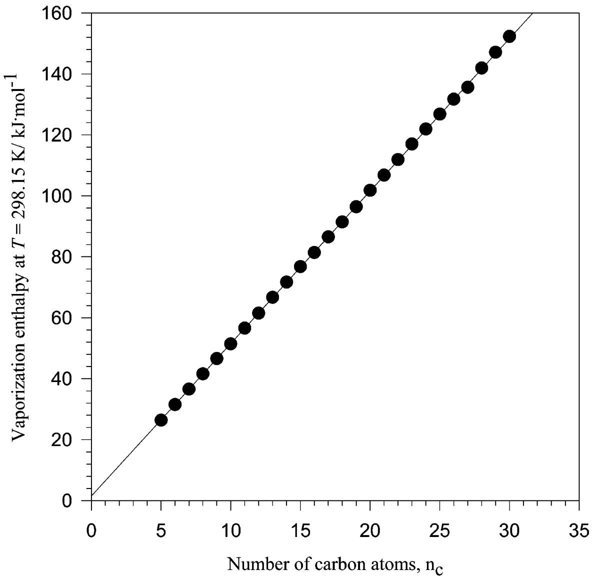

Figure 3. Vaporization enthalpies of n-C_5 to C_{30} as a function of the number of carbon atoms using the data from this study; the straight line represents the results obtained by a linear regression analysis of the recommended vaporization enthalpies of n-C_5 to C_{20}.[11]

a series of standards with known vapor pressures at the temperature of interest, the results obtained through a process of correlation are quite satisfactory. This is illustrated in Figure 4 by the results obtained for n-C_{14} to n-C_{20}. In this instance, the equations in Table 2 have been used to provide $\ln(1/t_a)$ data at $T = 298.15$ K by extrapolation from $T_m = 449$ K. Correlation of the extrapolated $\ln(1/t_a)$ values with experimental vapor pressure data calculated from the Cox equation, eq 6,[11,12] results in the linear relationship illustrated by Figure 4. The reference pressure in the Cox equation, p_0 (101.325 kPa), refers to the vapor pressure at the normal boiling point, T_b. The T_b and A terms in eq 6 for the n-alkanes in question are given in Table 4.

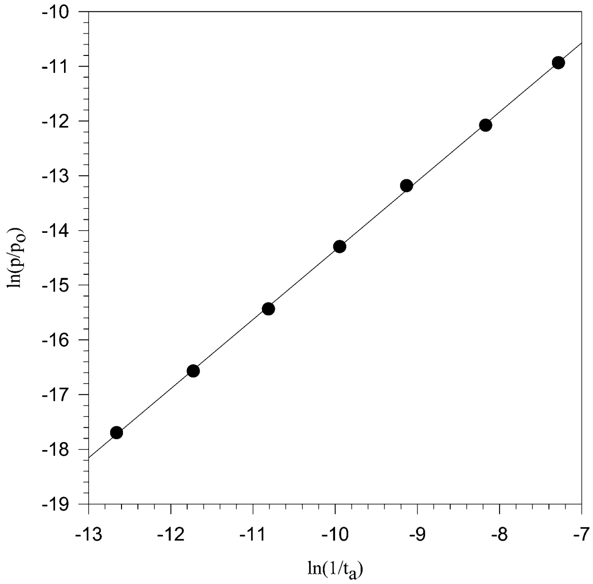

Figure 4. Correlation observed between $\ln(1/t_a)$ calculated by extrapolation to 298.15 K using the equations given in Table 2A and $\ln(p/p_0)$ at 298.15 K calculated from the Cox equation for n-C_{14} to n-C_{20}. The term p_0 represents the vapor pressure (101.325 kPa) at the reference temperature, T_b, the normal boiling point of the n-alkane; the equation of the line obtained by a linear regression is given by $\ln(p/p_0) = (1.26 \pm 0.01)\ \ln(1/t_a) - (1.718 \pm 0.048)$; $r^2 = 0.9997$.

Table 4. Parameters of the Cox Equation Used in the Calculations[a]

	T_b	A_0	10^3A_1	10^6A_2
tetradecane	526.691	3.136 24	−2.063 853	1.541 51
pentadecane	543.797	3.167 74	−2.062 348	1.487 26
hexadecane	559.978	3.182 71	−2.002 545	1.384 48
heptadecane	575.375	3.218 26	−2.04	1.38
octadecane	590.023	3.247 41	−2.048 039	1.362 45
nonadecane	603.989	3.276 26	−2.06	1.35
eicosane	617.415	3.311 81	−2.102 218	1.348 78
octacosane[b]	705	3.413 04	−1.889 4	1.045 75

[a] All data are from ref 11 unless otherwise noted. [b] Reference 12.

$$\ln(p/p_0) = (1 - T_b/T)\exp(A_0 + A_1T + A_2T^2) \qquad (6)$$

The linearity observed between $\ln(p/p_0)$ and $\ln(1/t_a)$ for n-C_{14} through C_{20} suggests a mechanism by which vapor pressure data for the larger n-alkanes can be obtained. Using experimental $\ln(p/p_0)$ data at $T = 298.15$ K (calculated from the Cox equation) and extrapolated $\ln(1/t_a)$ values for n-C_{17} to n-C_{23} (using the appropriate equations given in Table 2 at $T = 298.15$ K), values of $\ln(p/p_0)$ for n-C_{21} to n-C_{23} can be obtained by correlation (the top $\ln(p/p_0)_{calc}$ column in Table 5). The $\ln(p/p_0)$ terms for n-C_{21} to n-C_{23} can then be used as needed with other $\ln(p/p_0)$ values and appropriate $\ln(1/t_a)$ values to derived $\ln(p/p_0)$ values for other n-alkanes. For example, using the calculated $\ln(p/p_0)$ values for n-C_{21} to n-C_{23} (top of Table 5, column 4), the corresponding experimental values for n-C_{19} and n-C_{20}, and $\ln(1/t_a)$ values calculated from the appropriate correlation equations (Table 2, C_{19} to C_{25}), $\ln(p/p_0)$ values for n-C_{24} and n-C_{25} can be calculated (see the top of Table 5, last column). Once a value of $\ln(p/p_0)$ was evaluated, it was used in subsequent correlations with appropriate $\ln(1/t_a)$ values to provide $\ln(p/p_0)$ values for the remaining n-alkanes. This is the protocol that was followed in Table 5.

Table 5. Calculation of ln(p/p_0) at T = 298.15 K for the n-Alkanes C_{21} to C_{30} by Correlation with the ln(p/p_0) Values of n-C_{17} to n-C_{20} Generated from the Cox Equation[11]

C_{21} to C_{25}

	$\ln(1/t_a)^a$	$\ln(p/p_0)_{expt}{}^b$	$\ln(p/p_0)_{calc}{}^c$	$\ln(1/t_a)^d$	$\ln(p/p_0)_{calc}$	$\ln(p/p_0)_{calc}{}^e$
heptadecane	−8.34	−14.30	−14.2			
octadecane	−9.18	−15.43	−15.4			
nonadecane	−10.07	−16.57	−16.60	−8.99	-16.57^b	−16.61
eicosane	−10.89	−17.70	−17.68	−9.73	-17.70^b	−17.64
heneicosane	−11.75		−18.84	−10.61	-18.84^c	−18.84
docosane	−12.61		−19.97	−11.43	-19.97^c	−19.98
tricosane	−13.45		−21.09	−12.24	-21.09^c	−21.09
tetracosane				−13.03		−22.17
pentacosane				−13.80		−23.24

$$\ln(p/p_0)_{calc} = (1.329 \pm 0.012)\ \ln(1/t_a) - (3.216 \pm 0.024);\ r^2 = 0.9998 \quad (7)$$
$$\ln(p/p_0)_{calc} = (1.377 \pm 0.017)\ \ln(1/t_a) - (4.233 \pm 0.043);\ r^2 = 0.9995 \quad (8)$$

C_{26} to C_{30}

	$\ln(1/t_a)^f$	$\ln(p/p_0)$	$\ln(p/p_0)_{calc}{}^g$	$\ln(1/t_a)^h$	$\ln(p/p_0)_{calc}$	$\ln(p/p_0)_{calc}{}^i$
heneicosane	−12.50	-18.84^c	−18.80			
docosane	−13.39	-19.97^c	−20.04			
tricosane	−14.11	-21.09^c	−21.06	−13.67	-21.09^c	−21.13
tetracosane	−14.92	-22.17^e	−22.19	−14.41	-22.17^e	−22.18
pentacosane	−15.66	-23.24^e	−23.23	−15.13	-23.24^e	−23.19
hexacosane	−16.43		−24.31	−15.88	-24.31^g	−24.23
heptacosane	−17.08		−25.22	−16.64	-25.22^g	−25.31
octacosane				−17.49		−26.49
nonacosane				−18.30		−27.63
tricontane				−19.09		−28.74

$$\ln(p/p_0)_{calc} = (1.405 \pm 0.020)\ \ln(1/t_a) - (1.230 \pm 0.050);\ r^2 = 0.9994 \quad (9)$$
$$\ln(p/p_0)_{calc} = (1.404 \pm 0.034)\ \ln(1/t_a) - (1.944 \pm 0.080);\ r^2 = 0.9982 \quad (10)$$

[a] Calculated at T = 298.15 K using the equations in Table 2 for C_{17} to C_{23}. [b] Calculated at T = 298.15 K using the parameters of the Cox equation given in Table 4. [c] Calculated using eq 7 generated from the data in columns 2 and 3 (under C_{21} to C_{25}). [d] Calculated at T = 298.15 K using the equations in Table 2 for C_{19} to C_{25}. [e] Calculated using eq 8 generated from the data in columns 5 and 6 (under C_{21} to C_{25}). [f] Calculated at T = 298.15 K using the equations in Table 2 for C_{21} to C_{27}. [g] Calculated using eq 9 generated from the data in columns 2 and 3 (under C_{26} to C_{30}). [h] Calculated at T = 298.15 K using the equations in Table 2 for C_{23} to C_{30}. [i] Calculated using eq 10 generated from the data in columns 5 and 6 (under C_{26} to C_{30}).

The calculated ln($1/t_a$) terms in Table 5 have footnotes to identify which equations in Table 2 were used in their generation. The $\ln(p/p_0)_{calc}$ values are also footnoted to identify their origins; eqs 7−10 were used to generate calculated values.

The use of such an extrapolation is risky, since any errors inherent in the first correlation can be amplified in subsequent ones. Consequently, both the vaporization enthalpy and the vapor pressure results obtained as described above need independent confirmation. The linear behavior of vaporization enthalpy as a function of the number of carbon atoms from n-C_5 to n-C_{30} has already been mentioned, suggesting that the vaporization enthalpies obtained for n-C_{21} to n-C_{30} at T = 298.15 K are consistent with previous measurements made on the smaller homologues. Experimental vaporization enthalpies and vapor pressures for n-C_{21} to n-C_{30} at T = 298.15 K are not available for comparison, at least without significant temperature adjustments. However, reliable values are available at elevated temperatures. As noted above, the equations in Table 2 can be used for correlations at any temperature. The range of temperatures for which the Cox equation is applicable for the n-alkanes C_{17} to C_{20} is from T = 298.15 K to the boiling point of heptadecane, T = 575 K.[11] Chirico et al.[12] and Morgan and Kobayashi[13] have reported high precision data for octacosane within this temperature range. Since both the vaporization enthalpy and vapor pressure of octacosane are evaluated last in the series of correlations described in Table 5, it seemed that these experimental data would provide a good test of the quality of the data generated by the equations in Table 2. Using the vapor pressures of n-C_{17} to n-C_{20} generated from the parameters of the Cox equation, Table 4, the equations in Table 2, and the stepladder approach just described for obtaining ln(p/p_0) at T = 298.15 K for n-C_{21} to n-C_{30}, vapor pressures at a series of different temperatures were calculated. These are listed in Table 6 along with the experimental vapor pressures reported by Chirico et al.[12] from T = 453 to T = 483 K and by Morgan and Kobayashi[13] from T = 483.1 to T = 588.1 K. Chirico et al. provide parameters of the Cox equation for octacosane which are listed in Table 4. The Cox equation extrapolates with reasonable precision over a 50−70 K range. The use of this equation to calculate the vapor pressure of octacosane at T = 298.15 K exceeds the range of its applicability. Nevertheless, the value calculated at this temperature for octacosane is compared in Table 6 to the results obtained in this study; the two values compare favorably. The

Table 6. Comparison of the Vapor Pressure and Vaporization Enthalpy of Octacosane Obtained by Correlation Gas Chromatography with Literature Values

T/K	ln(p/p_0) from $\ln(1/t_a)^a$	$\ln(p/p_0)^b$	$\ln(p/p_0)^c$
298.15	−26.49	−25.88	-26.52^d
453.15	−8.92	−8.88	-8.91^d
463.15	−8.30	−8.27	-8.28^d
483.1	−7.16	−7.14	-7.12^e
518.1	−5.45		-5.43^e
553.1	−4.04		-4.01^e
588.1	−2.86		-2.83^e
$\Delta_l{}^gH_m$(468.15 K)/kJ·mol^{-1}	106.7^a	105.6^b	107.2^d

[a] This work. [b] From ref 12. [c] From ref 13. [d] "Conformal" fit to the Wagner equation. [e] Experimental values.

Table 7. Comparison of the Vapor Pressures and Vaporization Enthalpies (in kJ·mol^{-1}) of Several *n*-Alkanes at Various Temperatures

	T/K	$\ln(p/p_0)$ from $\ln(1/t_a)^a$	$\ln(p/p_0)^b$	$\ln(p/p_0)^c$	$\ln(p/p_0)^d$	$\ln(p/p_0)^e$	$\Delta_l^gH_m(T)^a$	$\Delta_l^gH_m(T)$
docosane	463	−5.6		−5.5			85.8	85.2^c
docosane	417.8	−8.1				−8.0	92.6	92.7^e
docosane	417.8	−8.1			−8.0		92.6	91.7^d
tetracosane	463	−6.5		−6.5			93.1	93.3^c
tetracosane	417.8	−9.2				−9.0	100.2	121.4^e
tetracosane	417.8	−9.2			−9.2		100.2	102.2^d
hexacosane	417.8	−10.3				−10.3	108.6	109.2^e
octacosane	417.8	−11.5	−11.4				116.7	114.3^b
octacosane	417.8	−11.5		−11.4			116.7	116.6^c
octacosane	417.8	−11.5				−11.5	116.7	128.9^e

[a] This work. [b] Reference 12. [c] "Conformal" fits to the Wagner equation.[13] [d] Reference 16. [e] Reference 17.

experimental measurements on octacosane by Morgan and Kobayashi are at higher temperatures.[13] Their data were also fit to a form of the Wagner vapor pressure equation. Results of their "conformal fit" are included as the fourth column of the table at temperatures $T = 453$ and 463.15 K, and experimental values are provided from $T = 483.1$ to $T = 553$ K. The "conformal" fit of both vapor pressure and vaporization enthalpy at the lower temperatures is in good agreement with the results of this work; this work also compares well with their experimental data. The vapor pressures reported in Table 6 also allow a determination of the vaporization enthalpy of octacosane at $T = 468.15$ K using the different approaches. The last entry in the table compares values; they appear to be in very good agreement.

As noted above, vaporization enthalpies and vapor pressures are available for all the *n*-alkanes examined in this study at temperatures above $T = 298.15$ K. As a further test of the use of the equations in Table 2, we have examined both vapor pressure and vaporization enthalpy of a selected number of *n*-alkanes. As noted by Lemmon and Goodwin[14] and others,[3] vapor pressures and vaporization enthalpies reported by Piacente and co-workers[15] are not generally consistent with values from other sources; these data as well as data reported prior to 1980 were not included in this comparison.

Table 7 lists the vapor pressures and vaporization enthalpies calculated using the equations in Table 2 for some other *n*-alkanes using the same protocol. The results from these calculations are compared to experimental values from the literature.[16,17] The literature vapor pressures and vaporization enthalpies listed in Table 7 were either calculated from vapor pressures derived from the Cox,[13] Wagner,[17] or Antoine equations or used directly as reported. The agreement with literature values is generally very good. The vaporization enthalpies calculated from the temperature dependence of vapor pressure are listed in the last two columns. Column 7 lists the values obtained in this study while the last column reports literature values. Most of the values compare quite favorably. Two of the three vaporization enthalpies calculated from the limited data reported by Grenier-Loustalot et al.[17] appear out of line with other literature values and the results obtained in this work.

Subcooled liquid vapor pressures of a number of *n*-alkanes between n-C_{16} and n-C_{30} at $T = 298.15$ K have been cited by Goss and Schwarzenbach[18] using data from Daubert and Danner.[19] The vapor pressure data in Table 8, reported as ln(p/Pa), include vapor pressures obtained in this study, data from Daubert and Danner,[19] recommended data from Ruzicka and Majer,[11] and extrapolated data from the Cox equation reported by Chirico et al.[12] Values reported by Morgan and Kobayashi[13] are their "conformal" fits. A comparison of the results obtained from this study using the recommended data of Ruzicka and Majer[11] for n-C_{17} to n-C_{20} with those from Goss and Schwarzenbach[18,19] is quite good for most compounds.

Table 8. Comparison of Absolute Vapor Pressures of C_{16} to C_{18}, C_{20} to C_{22}, and C_{25} to C_{30} Reported in This Study with Other Literature Values at $T = 298.15$ K

	ln(p/Pa) this work	ln(p/Pa)^a	ln(p/Pa)^b	ln(p/Pa)^c	ln(p/Pa)^d
hexadecane	−1.66	−1.68	−1.66		
heptadecane	−2.77	−3.52	−2.77		
octadecane	−3.91	−3.59	−3.91		
eicosane	−6.17	−5.8	−6.17	−6.17	
heneicosane	−7.31	−7.1			
docosane	−8.45	−8.27			−8.53
tetracosane	−10.65	−10.32			−10.7
pentacosane	−11.72	−11.35			
hexacosane	−12.78	−12.2			
heptacosane	−13.70	−13.38			
octacosane	−14.96	−15.38		−14.36	−15.0
nonacosane	−16.10	−16.22			
triacontane	−17.22	−18.58			

[a] References 18 and 19. [b] Reference 11. [c] Reference 12 by extrapolation of the Cox equation. [d] "Conformal" fits to the Wagner equation, ref 13].

Of all the n-C_{17} to n-C_{20} alkanes used as standards, heptadecane is the alkane that exhibits the smallest temperature range for which recommended vapor pressures are available;[11] the range extends from $T = 298.15$ K to $T = 575.4$ K. Using the equations in Table 2 and the vapor pressures calculated from the Cox equations for n-C_{17} to n-C_{20}, vapor pressures for n-C_{21} to n-C_{30} were calculated over 30 K intervals from $T = 298.15$ K to $T = 575$ K using the stepladder approach described above. The plots of $\ln(p/p_0)$ versus $1/T$ for these *n*-alkanes are illustrated in Figure 5. The curves were fitted to a third-order polynomial, eq 11, whose coefficients are provided in Table 9; T in eq 11 refers to the absolute temperature.

$$\ln(p/p_0) = AT^{-3} + BT^{-2} + CT^{-1} + D \qquad (11)$$

The quality of the fit using eq 11 is quite good. The largest fractional error between the vapor pressures calculated using the equations in Table 2 and those in Table 8 was obtained for triacontane. The fractional error ranged from 0.011 at $T = 298.15$ K to 0.003 at $T = 568$ K. The fractional errors associated with the remaining *n*-alkanes were considerably smaller. These equations can now be used to calculate the vapor pressures of n-C_{21} to n-C_{30} and at any temperature between $T = 298.15$ K and $T = 575$ K.

Subcooled liquid vapor pressures and vaporization enthalpies are useful thermodynamic properties. Subcooled

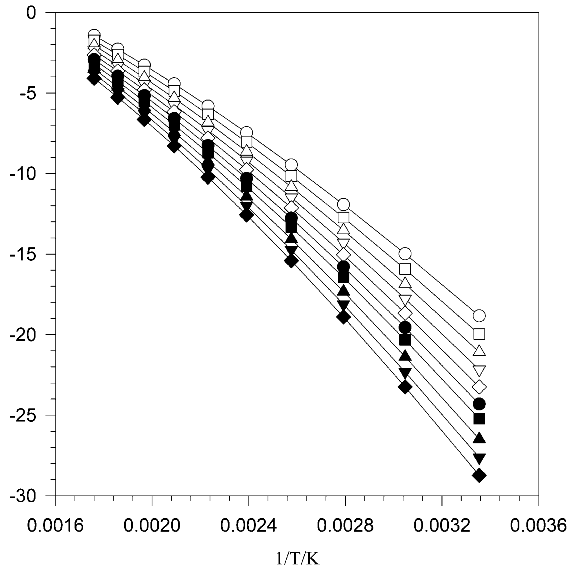

Figure 5. Plot of $\ln(p/p_0)$ versus $1/T$ for the *n*-alkanes: (from top to bottom) ○, n-heneicosane; □, docosane; △, *n*-tricosane; ▽, tetracosane; ◇, pentacosane; ●, hexacosane; ■, heptacosane; ▲, octacosane; ▼, nonacosane; ◆, triacontane.

Table 9. Coefficients for Calculating $\ln(p/p_0)$ for *n*-C_{21} to C_{30} from T = 298.15 K to T = 568 K According to Eq 11

	$10^{-8}A$	$10^{-6}B$	C	D
heneicosane	1.9989	−2.9075	−98.135	6.6591
docosane	2.1713	−3.1176	110.72	6.5353
tricosane	2.3386	−3.322	310.77	6.4198
tetracosane	2.5072	−3.5286	530.15	6.2817
pentacosane	2.6738	−3.7307	741.19	6.1496
hexacosane	2.8244	−3.9193	910.53	6.0704
heptacosane	3.0092	−4.1253	1198.8	5.8109
octacosane	3.1389	−4.312	1279.4	5.8835
nonacosane	3.2871	−4.5043	1431.2	5.8413
triacontane	3.4404	−4.6998	1601.6	5.7696

liquid vapor pressures of polyaromatic hydrocarbons have been used in a wide range of environmental applications;[18−20] the vapor pressures of the *n*-alkanes should serve as excellent standards for their evaluation.[2,5] All the *n*-alkanes C_{21} to C_{30} are solids at T = 298.15 K; the vaporization enthalpies reported in Table 3 represent values for the subcooled liquid state. Sublimation enthalpies for these compounds have not been measured directly. Table 10 lists the values calculated by adding $\Delta_l{}^gH_m$(298.15 K) to fusion enthalpies and any additional phase transitions occurring between T = 298.15 K and $T = T_{fus}$.[21] All of the *n*-alkanes from C_{21} to C_{30} have at least one additional phase transition occurring between T = 298.15 K and $T = T_{fus}$. The sum of these two terms, $\Delta_{tpce}H_m$, was adjusted to T = 298.15 K using the following equation:[22]

$$\Delta_{tpce}H_m(298.15\ \mathrm{K})/\mathrm{kJ{\cdot}mol^{-1}} = \Delta_{cr}{}^{l}H_m(T_{fus}) + \Delta_{cr2}{}^{cr}H_m(T_t) + (0.15C_{p_c} - 0.26C_{p_l} - 9.83)(T_{fus} - 298.15)/1000 \quad (12)$$

The C_{p_l} and C_{p_c} terms in eq 12 represent the heat capacities of the solid and liquid states and were estimated using group values of 34.9 and 36.6 J·mol^{-1}·K^{-1} for each methyl group and 31.9 and 26.9 J·mol^{-1}·K^{-1} for each methylene group, respectively.[23] The sublimation enthalpy calculated for each alkane is listed in the last column of the table. The uncertainty in sublimation enthalpy reported in this column represents the combined uncertainty associated with the vaporization enthalpy and the temperature adjustment. An uncertainty of 15% in the temperature adjustment (±σ) was arbitrarily assigned.

Piacente et al.[15] have also combined vaporization enthalpies with fusion enthalpies for a number of *n*-alkanes, but as noted above, the results of their vaporization enthalpy measurements have been questioned.[14] Of the *n*-alkanes listed in Table 10, sublimation enthalpies for

Table 10. Sublimation Enthalpies Obtained by Combining $\Delta_l{}^gH_m$(298.15 K) with Total Phase Change Fusion Enthalpies Adjusted to T = 298.15 K[a]

	$\Delta_{cr2}{}^{cr}H_m(T_t)$ + $\Delta_{cr}{}^{l}H_m(T_{fus})$[b]	T_{fus}/K	C_{p_l}(298.15 K)	C_{p_c}(298.15 K)	$\Delta_{tpce}H_m$(298.15 K)	$\Delta_l{}^gH_m$(298.15 K)	$\Delta_{cr}{}^gH_m$(298.15 K)
octadecane	61.5	301.3	580.2	503.6	61.2	91.4	152.6[c]
nonadecane	47.4	304	612.1	530.5	46.9	96.4	143.3[c]
eicosane	67.8	308.8	644	557.4	66.8	101.8	168.6[c]
heneicosane	63.18	313.7	675.9	584.3	61.66	106.8	169.1 ± 2.6
docosane	77.35	316.1	707.8	611.2	75.52	111.9	187.7 ± 2.7
tricosane	75.35	320.7	739.7	638.1	73.33	117	190.7 ± 2.8
tetracosane	86.19	324.1	771.6	665	83.32	121.9	205.6 ± 2.8
pentacosane	83.81	326.7	803.5	691.9	80.53	126.8	207.8 ± 2.9
hexacosane	91.7	329.5	835.4	718.8	87.96	131.7	220.2 ± 3.3
heptacosane	87.59	332.1	867.3	638.1	83.4	135.6	219.6 ± 3.4
octacosane	100.08	334.5	899.2	665	95.44	141.9	238.0 ± 5.0
nonacosane	95.82	336.6	931.1	691.9	90.74	147.1	238.6 ± 5.2
triacontane	106.32	338.7	963	718.8	100.8	152.3	253.9 ± 5.3

[a] Heat capacities are in J·mol^{-1}·K^{-1}. Enthalpies are in kJ·mol^{-1}. [b] $T_t \geq$ 298.15 K; see ref 21 for literature values. [c] Literature values: C_{18}, 152.7; C_{19}, 143.6; C_{20}, 170.4 kJ·mol^{-1}; ref 24.

Table 11. List of Symbols and Their Definitions

$\Delta_l{}^gH_m(T_m)$	enthalpy of vaporization at the mean temperature, T_m
$\Delta_{sln}{}^gH_m$	enthalpy of transfer from solution (gc column) to the vapor
$\Delta_{sln}H_m$	enthalpy of solution or adsorption on a gc column
t_a	the time an analyte spends on a gc column
p, p_0	vapor pressure, 101.325 kPa
C_{p_c}, C_{p_l}	heat capacity of the solid, heat capacity of the liquid
n_c	number of carbon atoms
T_{fus}	melting temperature
$\Delta_{cr2}{}^{cr}H_m(T_t)$	solid to solid transition occurring at temperature T_t
$\Delta_{cr}{}^{l}H_m(T_{fus})$	enthalpy of fusion at the melting temperature
$\Delta_{tpce}H_m$(298.15 K)	total phase change enthalpy of the solid from T = 298.15 K to T_{fus} adjusted to T = 298.15 K

n-C_{18} to n-C_{20} have been measured directly; values of 152.7, 143.6, and 170.4 kJ·mol^{-1}, respectively, have been reported.[24] These results can be compared with the values of 152.6, 143.3, and 169.1 kJ·mol^{-1} calculated by adding $\Delta_{tpce}H_m$(298.15 K) to $\Delta_l^gH_m$(298.15 K). The results for n-C_{18} to n-C_{20} are included in Table 10 simply to demonstrate the good agreement that can be obtained when sublimation enthalpies measured directly are compared to the sum of experimental vaporization and fusion/total phase change enthalpies when each enthalpy is adjusted to a common temperature.

Conclusions

A series of equations are reported in Table 2 that describe the temperature dependence of corrected retention time for n-C_{17} to n-C_{30}. These equations have been used with appropriate auxiliary data for the n-alkanes from the literature to provide vapor pressure and vaporization enthalpy data for these n-alkanes as a function of temperature. These equations appear applicable within the temperatures range T = 298.15 K to T = 575 K.

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